Reviewer comments are in **bold**. Author responses are in plain text. Modifications to the manuscript are in *italics*. We appreciate the reviewers' careful reading of the manuscript and their valuable comments that have led to improvements in the manuscript.

Comments from Anonymous Reviewer 1

General comments

This paper presents a detailed evaluation of the hygroscopicity of isoprene-derived secondary organic material condensed onto ammonium sulfate (AS) seed particles. An elaborate hygroscopicity measuring protocol was applied to the aerosol continuously produced in a flow reactor. To obtain deliquescence relative humidity (DRH) and efflorescence relative humidity (ERH) a sophisticated modeling procedure was developed. The manuscript is well and carefully written but readability suffers in some parts from the many abbreviations that are used. This paper is well suited for ACP since phases and phase transitions of mixed organic/inorganic aerosol particles are an important factor influencing aerosol properties. I recommend publication after the following points have been considered for revisions.

1. A concept of experiments section or paragraph at the beginning of the "Results and discussion section" might improve the readability of the detailed evaluation protocols and procedures. This section or paragraph should summarize in words how DRH and ERH as a function of organic volume fraction are derived from the applied measuring and evaluation procedures. A table that lists all the abbreviations might also be helpful.

We appreciate the reviewer's suggestions on ways to improve the readability of the results and discussion section. In response, we added some very helpful overviews (great suggestion!) of how the data were analyzed, followed by the detailed information. The following text is included in the revised manuscript.

Inserted at P. 9915, line 24. "*The drop from unity of the transmission ratio φ for increasing RH is proportional to the fraction of the particle population that has undergone irreversible deliquescence. The curve φ(RH) of Fig. 2a can then be interpreted as DRH(ε) by point-to-point matching of φ(RH) to the cumulative distribution function P(ε) of organic volume fraction of Fig. 2b.*"

Inserted at P. 9917, line 20. "*The hygroscopic response of the number-diameter distribution of a particle population to changes in RH depends on the organic volume fraction distribution p(ε) of that population. For our analysis, the hygroscopic response is modeled (described in detail below), and the model result is compared to the measurement. In this analysis, the value ε above which ammonium sulfate fully dissolves (i.e., final deliquescence) is optimized until the model result converges with the measurement. This optimized value of ε for final deliquescence is associated with the RH value of the measurement.*"

2. The O:C ratio of the organic material is stated as 0.67-0.74 in many parts of the manuscript including the abstract. Only on page 9923, line 6, it is mentioned that it is connected to a measuring uncertainty of +/- 30%. The range of O:C should be extended to include this uncertainty or the uncertainty should be stated together with the numbers.

In the revised manuscript, the uncertainty is stated with the numbers the first time the O:C ratios appear in the text as well as in the abstract. The manuscript is modified as follows:

P. 9904, lines 6-7. "The particle-phase organic material had oxygen-to-carbon ratios of 0.67 to 0.74 *(± 0.20)* for mass concentrations of 20 to 30 $\mu g\ m^{-3}$."

P. 9922, lines 21-24. "For example, the isoprene SOM presented herein had oxygen-to-carbon (O:C) ratios ranging from 0.67 - 0.74 *(± 0.20)*, whereas the α-pinene and β-caryophyllene SOM had lower O:C ratios of 0.39–0.44 (Smith et al., 2011) and 0.35 (Bertram et al., 2011), respectively."

3. The authors exclude a liquid-liquid phase separation into an organic-rich and AS-rich phase because the low DRH values at high organic volume fractions suggest miscibility. However, a miscibility gap does not need to cover the whole composition range of a phase diagram and might still be present at low organic volume fractions. This should be mentioned in the revised manuscript.

We thank the reviewer for this astute observation. We have carefully investigated the possibility of a miscibility gap in the phase diagram: Transmission ratios for an efflorescence experiment were modeled for the case of no miscibility gap as well as for two different miscibility gap phase spaces at low organic volume fraction ($\varepsilon < \sim 0.5$). These models reveal that, if a miscibility gap were present, the transmission ratio would not decrease smoothly, but would instead exhibit a discontinuous drop when the miscibility phase space intersected the line of ERH(ε). Therefore, while we cannot rule out a gap in miscibility over a small portion of the phase space, it is not detected in our measurements. We have addressed this topic in the manuscript with additional text in the manuscript and supplementary material, as well as prepared a new supplementary figure (Fig. S6) showing the comparisons of the modeled and measured transmission ratio data.

P. 9922, lines 12-15: "By comparison, the implication of the results shown in Fig. 4 is that the SOM produced by photo-oxidation of isoprene is phase miscible with aqueous ammonium sulfate, even to low water activity. *The smooth decrease of the transmission ratio for the efflorescence experiments are also consistent with full miscibility at the water activities of efflorescence and above (cf. Supplementary Material and Fig. S6).*"

Supplementary Material, P. 2:

"***S2. Connection between phase miscibility gap and transmission ratio experiments***
Transmission ratios for efflorescence experiments were modeled to determine whether our data were consistent with a gap in phase miscibility that extended to RH above the curve ERH(ε). For aqueous particles of $d_{m,+1}^{mono}$ *= 90 nm, P(ε) and the parameterized curve ERH(ε) were used to model the transmission ratio response (i.e., as RH is decreased, the drop in transmission ratio at*

any RH is proportional to the fraction of particles in the population that have an ERH ≥ that RH). In Fig. S6, the miscibility gaps investigated (panels a - c) and the corresponding modeled transmission ratios (panels d -f) are shown. Also plotted in panels d – f is the measured transmission ratio. For the case of fully miscible phases (Fig. S6a and d), the modeled drop in transmission ratio is continuous and smoothly decreases with decreasing RH. This transmission ratio response matches the measured data well. For the cases of a miscibility gap (Fig. S6b/e and c/f), tie lines that define the composition of each phase can be drawn between ERH(ε) and the miscibility gap boundary. For decreasing RH, at the point that the miscibility gap boundary and ERH(ε) first intersect, one of the phases in a phase-separated particle is necessarily of a composition that induces particle efflorescence at that RH (i.e., as defined by a tie line). The absence of a discontinuity in the data implies no large miscibility gap is present."

Supplementary Material, P. 11 (caption):

"***Figure S6.*** *The influence of a miscibility gap on transmission ratio experiments. Panels a – c show possible regions of a gap in miscibility (blue hashed area in b and c) and the curve ERH(ε) (dashed black). Panels d – f show the measured (black) and modeled (green) φ associated with each phase diagram case represented to the left. A gap in miscibility causes a discontinuous drop in φ (panels b/e and c/f). The transmission ratio experiment modeled using the assumption of full miscibility agrees with the measurement (panels a/d). Inset in panel a shows P(ε) for* $d_{m,+1}^{mono}$ *= 90 nm.*"

4. The uncertainties connected with the DRH and ERH values extracted from the data are not given in the manuscript. Considering the complex evaluation procedure, uncertainties in the organic volume fraction but also in the DRH and ERH values could be notable. They should be added to Figures 4 and 5 or at least be discussed in the text.

We thank the reviewer for pointing out the need for a discussion of the uncertainty associated with the results presented in this manuscript. The accuracy of the RH sensors is ± 1% RH (as stated by the manufacturer), and the accuracy of the DMA sizing is ± 1 nm, which is regularly confirmed using PSL particles of known diameters. The uncertainty associated with our results is addressed in the revised manuscript by the addition of two explanatory tables in the supplementary material, and the results of our uncertainty analysis also appear in the revised manuscript as gray shading in Figure 4. This shading is omitted from the panels of Figure 5 for clarity.

Addition to Figure 4 caption: "*Gray shaded areas represent the uncertainty in DRH(ε) and ERH(ε) values, taking into account ± 1% uncertainty in RH and ± 1 nm uncertainty in* $d_{m,+1}^{seed}$, $d_{m,+1}^{mono}$, *and* $d_{m,+1}^{filter}$ *(cf. Tables S5 and S6 for a detailed explanation of the uncertainty calculations).*"

Tables added to supplementary material, P. 6-7:

Quantity	*Lower Bound*	*Central Value*	*Upper Bound*
$d_{m,+1}^{seed}$	*+ 1 nm*	*0 nm*	*- 1 nm*
$d_{m,+1}^{mono}$	*- 1 nm*	*0 nm*	*+ 1 nm*
$d_{m,+1}^{filter}$	*+ 1 nm*	*0 nm*	*- 1 nm*
RH_{2}^{nafion}	*- 1 %*	*0 %*	*+ 1 %*
$RH_{1,\beta}^{nafion}$	*- 1 %*	*0 %*	*+ 1 %*

"***Table S4.*** *Combinations of uncertainties in diameter and relative humidity used to determine overall uncertainty in DRH(ε) and ERH(ε) (Fig. 4). The uncertainties of the measurements listed in columns 2 - 4 were applied to the quantities listed in column 1, and the data were subsequently analyzed as described in the main text (cf. Section 3.2) to produce the lower and upper bounds on DRH(ε) and ERH(ε). The ± 1 nm and ± 1% RH uncertainties were combined with sign conventions correlated to maximize the total error in DRH(ε) and ERH(ε) (i.e,. combining opposite signed errors in both* $d_{m,+1}^{mono}$ *and* $d_{m,+1}^{filter}$ *increases the change in the value of* ε_D *determined from number-diameter distribution experiments compared to combining similarly signed errors). Table S5 presents numerical examples of the individual effects of these uncertainties on the obtained values of* ε_D*.* "

Source of uncertainty	*DRH(ε) point: (0.80,48%)*	*DRH(ε) point: (0.20,79%)*
+ 1 nm $d_{m,+1}^{seed}$	*- 0.04*	*- 0.01*
- 1 nm $d_{m,+1}^{mono}$	*- 0.09*	*- 0.02*
+ 1 nm $d_{m,+1}^{filter}$	*- 0.12*	*- 0.01*

"***Table S5.*** *Change in* ε_D *determined from number-diameter distribution measurements resulting from uncertainties in diameters. The first column lists the diameter uncertainties that lead to a negative change in* ε_D *. Columns two and three show the decrease in* ε_D *resulting from only the diameter uncertainty listed in the corresponding row of column one (i.e., for row one,* $d_{m,+1}^{seed}$ *was increased by 1 nm while* $d_{m,+1}^{mono}$ *and* $d_{m,+1}^{filter}$ *were not perturbed). The lowest and highest DRH(ε) points of Fig. 4 are shown to highlight the different effects of each type of error: For DRH(0.80) = 48 %, uncertainty in* $d_{m,+1}^{filter}$ *induces the largest error in* ε_D*, while for DRH(0.20) = 79%, the decrease of 1 nm in* $d_{m,+1}^{mono}$ *is the largest source of error.*"

Specific and technical comments

Abstract:
Page 9904, line 4: It should be added that experiments have also been carried out at 60% RH.

The following text is modified in the revised manuscript abstract: “The organic material was produced by isoprene photo-oxidation at 40% *and 60%* relative humidity.”

Page 9904, lines 15-18: The full parameterization does not need to be given in the abstract.

We thank the reviewer for encouraging us to think this through. The parameterizations are concise summaries of the major experimental results presented in this work. Because we aim to make this information as easily accessible to members of the aerosol community as possible, our preference is to retain this information in the abstract.

Introduction:
Page 9905, line 12, multiple phases: is there any example of more than two liquid phases in the context of atmospheric aerosols?

Phase separation within the organic material has been proposed (Bertram et al., 2011) (e.g., in the case of an oxygenated organic material mixed with oily hydrocarbons), but to our knowledge has not been observed in atmospheric particles. Separation into three separate phases has been observed in solutions of water, salt, alcohols, and alkanes, depending on the specific salt, alcohol, or hydrocarbon used (Knickerbocker et al., 1982), and thus may also be possible in atmospheric particles.

Results and discussion:
Page 9920, line 19: shouldn’t it be Figure 3c instead of Figure 3a?

Yes, this correction is made to the revised manuscript.

Page 9921, lines 1-2: It is not clear which points are meant here. They should be marked by a different color in Figs. 4 and 5.

We thank the reviewer for pointing out the need for clarification. The points referred to are changed to circles in Figures 4 and 5 and the text is modified as follows:

P. 9921, lines 1-2. “The results of this protocol appear in Fig. 4 and 5 as the points *(circles)* for ERH > 7%.”

Fig. 4 caption: “Squares show DRH(ε) and ERH(ε) values derived from the type of analysis represented by panels (a)/(b) and (c)/(d) of Fig. 3. *Circles show points derived using the second number-diameter distribution protocol (cf. text).*”

Fig. 5 caption: “Blue lines and *points* reproduce the data set of Fig. 4.”

Conclusions and implications:
Page 9923, lines 24-25. This sentence is confusing. It should be improved or deleted.

We thank the reviewer for pointing out this confusing wording. Our intention was to indicate that a fully solid phase space only exists for pure, crystalline ammonium sulfate, i.e., for $\varepsilon = 0$ at RH less than 80%. We have removed this sentence from the revised manuscript.

Page 9924, lines 10-11. The kinetically driven decrease in ERH on the basis of homogeneous nucleation theory should be explained more explicitly.

P. 9924, lines 10-11: “The decrease in DRH is driven thermodynamically (i.e., the Gibbs-Duhem relation) whereas the decrease in ERH is driven both thermodynamically and kinetically (i.e., *the rate of random molecular associations leading to critical germ formation of crystalline ammonium sulfate is decreased by the presence of dissolved organic molecules*).”

Page 9925, lines 10-13: what is meant by heterogeneous morphology? The solid and/or liquid phases that are meant to occur should be explicitly stated.

We meant “heterogeneous morphology” to indicate that the organic and aqueous ammonium sulfate components are phase separated (in contrast to the use of “homogeneous” morphology indicating that the components are mixed). The revised text avoids these terms and is written in a more straight forward manner:

P. 9925, lines 10-13. “For aqueous ammonium sulfate and terpene-derived SOM, partitioning occurs into *two phases, one of which is organic-rich and other of which is inorganic-rich*. By comparison, for aqueous ammonium sulfate and isoprene-derived SOM, partitioning occurs into *one homogeneously mixed phase of water, ammonium sulfate, and organic material*.”

Appendix A, Hygroscopic growth:
The equation on page 9928 is not numbered. It should be numbered as Eq. A1 and the following equations need to be renumbered.

Yes, this equation is updated in revised manuscript.

Figure 1:
The writing in this figure is difficult to read even on the screen. The font should be increased.

Figure 1 was resized substantially to fit into the format of ACPD and, when viewed at 100% magnification, we agree with the reviewer that the text is difficult to read. The expectation, however, is that this figure will be a double column (full page) figure in the final manuscript, which resolves the issue of readability.

Figure 2:

The green point in panels a and b of Fig. 2 is difficult to understand: it has P(epsilon) = 0 in panel b but corresponds to a fraction 0.2 of nondeliquesceable particles. Can you clarify this?

We thank the reviewer for pointing out the need for clarification in the interpretation of this figure. In the original text of the manuscript (P. 9915, lines 25+), we state that “Particles deliquescing at the highest RH values, corresponding to the green point of Fig. 2a, have the lowest organic volume fraction, corresponding to the green point of Fig. 2b.” The reason a value of $\varphi = 0.2$ corresponds to a value of $P(\varepsilon) = \sim 0$ is that φ drops from 1 as particles deliquesce, and does not reach 0 unless 100% of the particles deliquesced. The values of φ and $P(\varepsilon)$ for points of correspondence are therefore offset by the fraction of nondeliquesceable particles, which is~0.2 in this case. To further clarify the interpretation of the points in Fig. 2, we make the following modifications in the revised manuscript:

P. 9915, lines 25+: “The data of Fig. 2a plotted for $d_{m,+1}^{mono}$ = 90 nm, show that *the transmission ratio drops from unity to 0.19 as* $RH_{1,\beta}^{nafion}$ *is scanned from 73 to 79%. The interpretation is that particles* deliquescing at the highest RH values, corresponding to the green point of Fig. 2a, have the lowest organic volume fraction, corresponding to the green point of Fig. 2b.”

Figure 2 caption: “Examples of data sets and associated analysis for transmission ratio experiments. **(a)** Transmission ratio φ of the particle population as $RH_{1,\beta}$ *is scanned upward*. These experiments are designed to identify deliquescence transitions. The ratio drops *from unity* as the particles deliquesce. **(b)** Cumulative distribution function of organic volume fraction ε for this particle population. The colored circles of **(a)** and **(b)** show points of correspondence between the φ(RH) and $P(\varepsilon)$ curves *(i.e., the green circle shows that the highest DRH value matches with the lowest value of* ε*)*. The corresponding points of each curve are the basis of the DRH(ε) curves shown in Fig. 4. Panels **(c)** and **(d)** are as described for **(a)** and **(b)** with the difference that $RH_{1,\beta}$ *is scanned downward* in experiments designed to identify efflorescence transitions. The corresponding data points of **(c)** and **(d)** are the basis of the ERH(ε) curves shown in Fig. 4.”

Figure 5:
This Figure would be easier to interpret when the lines and the gray shaded area giving the percentage error in O:C ratio were replaced by lines that directly state the O:C ratio for O:C from 0.7 – 0.9.

We appreciate the input from the reviewer on how to clarify this figure. Labels indicating that the upper edge of the shaded area corresponds to O:C = 0.7 and the lower edge of the shaded area corresponds to O:C = 0.9 have been added to the figure.

If the Bertram et al. (2011) DRH and ERH parameterization is accurate, O:C of the investigated samples should be rather 0.9 than 0.67 – 0.74. Is this discrepancy due to an inaccurate DRH/ERH parameterization or too low O:C ratios of the organic material measured by the AMS?

Imperfect agreement between the parameterization and our data would suggest that O:C is not the sole factor influencing phase transitions (e.g., the specific functional groups of the organic material could be important). The measured O:C of 0.67 – 0.74 have a stated ± 30% error, which puts the upper bound of O:C at 0.96. When the O:C uncertainty is taken into account, our data do fall along the lower edge of the shaded area, in agreement with the parameterization.

Supplementary material:
Caption to Figure S4: Eq. (3A) should be replaced by Eq. (A3).

The equation referred to in this figure caption is Eq. (3a) in the main text. The capitalization has been revised from Eq. (3A) to Eq. (3a) to be consistent with the main text notation. Note: This figure is Figure S5 in the revised manuscript.

Figure S5:
The inset in panel A should also be explained in the figure caption. Shouldn't the y-axis label of the inset read P(epsilon) instead of f(epsilon)?

We thank the reviewer for pointing out the need to further explain the inset in the figure caption. The y-axis is labeled f because the plot is of the fraction of dissolved sulfate, not the cumulative distribution function P. The caption to Figure S5 (Figure S7 in the revised manuscript) is modified to explain the inset as follows:
"These steps are repeated iteratively by refining the assumed dry number-diameter distribution *and inputs to the hygroscopic growth model* until the modeled distribution converges to the implied distribution. *The optimized fraction of dissolved sulfate, which is unity at* $\varepsilon \geq \varepsilon_D$, *that was used to evolve the water-free distribution in panel a to the distribution at 64% RH in panel b is shown in the inset*."

The black dashed line in panel B should be explained in the figure caption.

We thank the reviewer for pointing out this omission. The caption to Figure S5 (Figure S7 in revised manuscript) is updated to include an explanation of the dashed line, as follows: "…the modeled distribution *(solid lines, panel b)* is compared to the distribution that is implied by the transfer function of DMA^{mono} (*dashed line*, panel b)."

The measured curve should also be shown in panel B.

The modeled curves shown in panel b are not typically measured because they are used to determine $P(\varepsilon)$ for analysis of transmission ratio. Number-diameter distributions are not measured during a transmission ratio experiment. A measurement of the modeled curve in panel b, which is optimized to agree with the DMA transfer function, would be equivalent to testing whether the particle population selected for the transmission ratio experiment actually was centered at $d_{m,+1}^{mono}$ (or checking the sizing of the DMAs). We regularly confirm the accuracy of the DMA-sizing using polystyrene latex particles.

Comments from Anonymous Reviewer #2

General:

The manuscript describes influence of isoprene photo-oxidation products on deliquescence and efflorescence of ammonium sulphate particles, observed in a laboratory study. In contrast to monoterpene oxidation products isoprene oxidation products have a significant effects on DRH and ERH. This can be important in the atmosphere as the mixed particle will contain water over a larger range of RH compared to ammonium sulphate / monoterpene-SOA particles or pure ammonium sulphate. The experimental procedures applied are sophisticated and as a consequence the analysis and interpretation is complex. The main task was to entangle the different organic loadings distributed over the seed particles. Although the authors clearly take efforts to transport the information in ordered way, the paper was in parts very difficult to read. I attribute that to the large degree of formalization in the description e.g the logical table in the supplement. I would suggest a more descriptive way. However, the results derived are excellent and the conclusions are sound. Overall the paper is acceptable though and it should be published in ACP after the authors have addressed a few minor issues.

General comments:

1. Complex procedure info is often mixed with extra info in brackets is distracting. It would be helpful first to get a straight description of procedures, then details and less important modifications of the previous statements. This regards especially the first paragraph of section 2.2.1 and line 8 – 23 on page 9918.

As suggested by the reviewer, general statements are added to the beginning of section 2.2.1, as well as to the paragraph referred to on page 9918, to aid in the understanding of these sections.

P. 9909, lines 25+.“The transmission ratio experiments directly measured the fraction of the particles in the test population that underwent irreversible diameter changes as a result of RH cycling, such as those associated with deliquescence and efflorescence phase transitions (Rosenoern et al., 2009; Smith et al., 2011). *In overview, the measurement consisted of selecting a specific particle diameter with a differential mobility analyzer (DMA), perturbing the RH of the aerosol, and measuring the number concentration remaining at the original diameter (i.e., using a second DMA and a condensation particle counter (CPC)). A drop in number concentration at the second compared to the first DMA indicated that particles had changed diameter in response to the RH perturbation.*

More specifically, the measurement protocols were as follows. The incoming flow of the TDMA was conditioned to RH^{mono} by use of a Nafion tube (Perma Pure, PD50T-12SS).”

P. 9918, lines 7+:. “S*hifts between the size distributions plotted as gray or black squares in Fig. 3 indicate that at least some particles are not fully deliquesced (i.e., particles of* $\varepsilon < \varepsilon_D(y)$ *are present).* For a single value of *y*, *the specific value of* $\varepsilon_D(y)$ can be determined by scanning ε and observing $N_{3b}(d,y;\varepsilon)$ compared to $N_{3a}(d,y;\varepsilon)$. This statement is explained by the following line of reasoning.”

2. The logical table provided me more difficulties in understanding than it helped. Especially, since the authors switched between RH and epsilon as describing parameters in the final statement in the manuscript.

We thank the reviewer for the input on Table S2. Nevertheless, we feel that the logic table is of interest and use to at least some (but certainly not all) readers of the manuscript. The information presented is fairly specialized, which justifies its placement in the supplementary material.

3. I also had difficulties with the notation “scanning of epsilon” which was never scanned, instead a band width of epsilons contributed to the observations (page 9918, lines 8 or 20).

The notation of “scanning of epsilon” is a convenient way to develop the logical framework for the interpretation of the number-diameter distribution data, but the reviewer is correct that epsilon was not actually scanned for the data shown in Fig. 3a. The text is modified to make explicit this distinction:

P. 9918, lines 24+: “The particle population of Fig. 3a is characterized by a broad distribution $p(\varepsilon;T)$ (i.e., Fig. 3b) and thus ~~inherently represents a scan~~ a range of ~~low to high~~ ε *contributes to the observations*~~, including to values of ε greater than $\varepsilon_D(40\%)$~~. The black squares compared to the gray squares of Fig. 3a represent the comparison of $N_{3b}(d,y)$ to $N_{3a}(d,y)$. The dependency of relative shifts between $N_{3a}(d,y;\varepsilon)$ and $N_{3b}(d,y;\varepsilon)$ on ε underlies any comparison between the two data sets of Fig. 3a. *The right-shift of* $N_{3b}(d,y)$ *compared to* $N_{3a}(d,y)$ *indicates that particles characterized by* $\varepsilon < \varepsilon_D(40\%)$ *are present in the population.* ~~Even so, these shifts are not~~ *Further interpretation of the shifts* ~~immediately discernible~~ by the unaided eye *is not possible* because their effects are convoluted with the dispersity of $p(\varepsilon;T)$.”

P. 9920, lines 15+: “In the real experiment, the particle population represented in Fig. 3d is characterized by a broad distribution $p(\varepsilon;T)$ ~~and thus inherently represents a scan from high to low ε~~.”

4. I think the authors should comment/exclude the following issues in the manuscript regarding potential artifacts: Are there new particles formed in HEC in absence of ammonium sulphate and isoprene when H_2O_2 is photolyzed? If yes, how much mass is formed and is this of organic nature ?

Is there SOM formed in presence of ammonium sulphate and in absence isoprene when H_2O_2 is photolyzed? If yes, how much mass is condensing on the sulphate seeds and is this of organic nature ?

The procedure for the experiments of this work consisted of allowing the seed particles and the gas phase components to reach steady state in the HEC prior to the initiation of isoprene photo-oxidation by turning on the UV lights. Therefore, we have not done these exact measurements. We are confident, however, that the organic mass concentration is not affected by mentioned artifacts (i.e., organic material not arising from the photo-oxidation of isoprene) for the following reason. Prior to beginning an experiment, the HEC was held at a temperature of 40 °C and continuously flushed with pure air at a rate of 40 lpm with the UV lights on and injection of O_3 (approximately 300 ppb at steady state) for at least 3-4 days. The background concentration of particles exiting the chamber following this process was < 0.1 # cm^{-3}. Any oxidizable organic material in the HEC should react and/or be flushed out of the HEC during this process.

Are there new particles formed when isoprene is oxidized in the presence of ammonium sulphate?

This is an important question, as the presence of nucleated particles would add to the heterogeneity of organic volume fractions in the particle population exiting the HEC and need to be accounted for in the data analysis. Two observations, however, preclude the presence of nucleated particles in the experiments described in this work:

(1) After photo-oxidation is initiated by turning on the UV lights, the number concentration exiting the chamber remains constant whereas nucleation of new particles would cause an increase in number concentration.

(2) A nucleation event in the HEC for unseeded experiments is characterized by continuous particle growth, where a clear mode is seen increasing in diameter. This type of shifting mode was not observed in the steady state seeded experiments. The distribution of particles exiting the chamber was stable over the timescale of each experiment (days).

5. The authors mainly compare the inflow of sulphate particles to the outflow of mixed particles in the manuscript and in Fig. S1. I think, it is necessary to show the comparison of sulphate particles in the outflow of the chamber in absence and presence of isoprene oxidation products.

The intended purpose of Fig. S1 is to show that the seed particle size distribution grows and broadens following condensational growth of the SOM in the chamber and to provide a visual representation of the written descriptions of these distributions in the main text. This is especially important with respect to the distribution of seed particles in the inflow, as the presence of +1 and +2 seed particles must be addressed for accurate interpretation of the measurements.

Nevertheless, in the absence of oxidation products, the shape of the size distribution of ammonium sulfate seed particles in the outflow of the chamber is equivalent to the size distribution in the inflow (size dependent wall losses do not significantly affect the distribution over the narrow range of seed particle diameters). The distributions of sulfate particles in the inflow and outflow of the chamber are measured at the start of every experiment using a TSI SMPS and ensure that no diameter growth occurs before the VOC oxidation is initiated.

In the presence of isoprene oxidation products, the sulfate particles are coated with SOM and thus the sulfate particles in the inflow are distributed over the range of diameters observed in the chamber outflow. The distribution of sulfate seeds within the particles exiting the chamber is a complex topic that manifests itself in the hygroscopic growth and phase transition behavior of these particles, and, as such, we have addressed this topic in detail elsewhere in the original manuscript (cf. Sections 2.1. Particle Generation and 3.1. Particle Populations and

Subpopulations).

Minor remarks / errors:
Page 9904, line 16 : Definition of xi ?

We thank the reviewer for pointing out this omission. The symbol χ has been replaced with ε and the revised text is modified as follows: "Parameterizations of the DRH(ε) and ERH(ε) curves were as follows: DRH(ε) = $\sum_i c_{i,d}\varepsilon^i$ valid for $0 \leq \varepsilon \leq 0.86$ and ERH(ε) = $\sum_i c_{i,e}\varepsilon^i$ valid for $0 \leq \varepsilon \leq 0.55$"

Page 9909, line 1 : Why was the SMPS operated at 25% RH?

The aerosol flow exiting the chamber was dried with a diffusion dryer prior to entering the SMPS. This step was taken to minimize the water content of the particles when the polydisperse size distribution was measured by the SMPS.

Page 9911, line 8 : At several instances the authors talk of stepwise changes of d_{mono} and report two diameters. Were these two diameters selected or were the diameters stepwise changed between these limits? See also page 9912, line 26 or Table S1.

In the instances wherein we refer to stepwise changes in diameters, the diameters were changed stepwise between the limits given. We add the following clarifications to the revised text:

P. 9911, line 8: "A series of these deliquescence and efflorescence experiments was carried out in which stepwise changes were made to $d_{m,+1}^{mono}$ between experiments. *The range of* $d_{m,+1}^{mono}$ *values studied was between 75 and 120 nm, implying an associated range of low to high organic volume fractions (specified in greater detail further below).* ~~In this way, a range of organic volume fractions was probed.~~"

Addition to Table S1 caption: "*Numbers enclosed in brackets (e.g., {75,120}) indicate that several values in-between these two numbers were studied.*"

Page 9911, line 21 – page 9912, line 8 :
This is an interesting consideration, but it should go into supplement. The experiments were defacto performed at diff. conditions.

We thank the reviewer for this alert. After reassessing this section, we agree with the reviewer that the discussion of the optimal value of RH^{mono} is more appropriate for the supplementary material, and this paragraph is moved in the revised manuscript (now Section S1).

Page 9912, line : Isn't that a "classical" hygroscopic growth experiment? Why do you call number-diameter distribution experiment ?

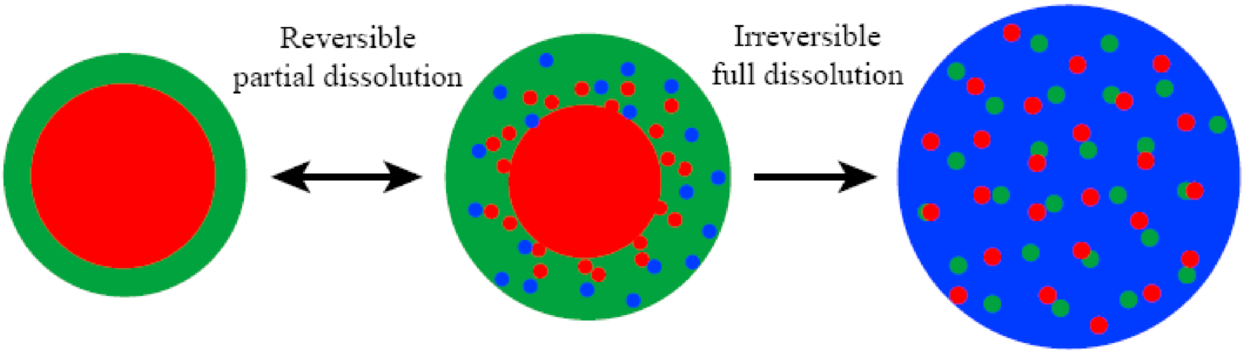
The experimental setup and protocols of section 2.2.2 Number-diameter distribution experiments are similar to HTDMA hygroscopic growth measurements. The term "number-diameter distribution experiment" is used to make explicit the measured quantity (number concentration as a function of diameter). In response to the reviewer's point and in the interest of clarity, the revised manuscript directly states the connection of our measurements to HTDMA measurements. We agree with the reviewer that this update to the text aids in understanding the experimental procedure:

P. 9912, lines 17+. "*The apparatus, when used in number-diameter distribution mode, is similar to a Hygroscopic Tandem Differential Mobility Analyzer (HTDMA)(Duplissy et al., 2009). In overview, the protocol is to size-select quasi-monodisperse particles under dry conditions, expose this aerosol to an elevated RH, and measure the associated number-diameter distribution. Differences between the grown and initial distributions indicate water uptake (or loss).*

A detailed description of the protocol is as follows: A number-diameter distribution $N(d)$ was collected in a single arm for some fixed value of $d_{m,+1}^{mono}$ and a constant RH^{mono} value of 7%, meaning particles classified by DMA^{mono} had minimal water content (Fig.1, rows 3 and 4)."

Page 9915, line 12ff : Here a sketch (in the supplement) would support faster understanding.

We appreciate the reviewers suggestion and add the below figure and caption to the revised supplementary material.



"***Figure S3***. *Illustration of reversible and irreversible fluctuations in diameter with relative humidity. Partially dissolved ammonium sulfate can recrystallize without an activation barrier, whereas fully dissolved ammonium sulfate cannot recrystallize until the efflorescence RH is reached. Key: Red, ammonium sulfate; green, SOM; blue, water*."

Text has also been inserted on page 9915, line 17: "*A pictorial representation of partial and full dissolution is illustrated in Fig. S3.*"

Page 9916, line 6 : I don't understand this statement. "Exchanging dependent and independent variables, the line DRH(ε) appears in Fig. 4."

In the notation ε_D(RH), organic volume fraction ε is the dependent variable, while RH is the independent variable. The points of {RH, ε}, however, can be also be expressed as {ε, RH}. Thus, we switch the two variables (dependent and the independent) to obtain DRH(ε), which appears in Fig. 4. The revised text is modified to clarify this statement.

P. 9916, line 6: "*Swapping the* dependent *variable* ε and *the* independent variable *RH,* the line DRH(ε) *is constructed and* appears in Fig. 4."

Page 9917, line 13 : "Extrapolation of the DRH line of Fig. 4 to <15% RH suggests a crossover between cases *b* and *c* at an organic volume fraction close to 1.0." I don't see why Fig 4 is suggesting this.

The reviewer asks a valid question. Technically, if case c is true (particles of $\varepsilon > 0.8$ have a DRH below 15%), case b is also expected to be true (particles of $\varepsilon > 0.8$ have an ERH below 15%). Thus, rather than a crossover between case b and c, the extrapolation actually suggests that case c becomes true at organic volume fraction near 1. Upon reviewing this sentence in the original manuscript, however, we agree with the reviewer that it is confusing and it is removed from the revised version.

Page 9920, line 19 : I think it should read "Fig. 3c".

Yes, this change is made in the revised manuscript.

Page 9922, line 25ff : On oxidation isoprene likely forms small molecules which are highly oxidized compared to the large mono- and sesquiterpenes with less oxidized products. Isoprene products with O/C 0.4 may not even stay in the SOM. Can it be that isoprene oxidation products have stronger effects on ERH than the small molecules applied in Bertram et al. 2011? If so, what do you suggest as a reason? It may well be that C/S and O/C ratio are not sufficient to classify deliquescence and efflorescence behaviour, instead the specific functionalization is of importance.

We agree with the reviewer that O:C and organic:sulfate ratios are not necessarily sufficient to characterize all SOM and that different functional groups can influence the effects of organic material on ERH. Previously observed products of isoprene photo-oxidation, likely to be present in the SOM of this work, include C-5 triols, aldehydes, and ketones (*Surrat et al.*, 2006), while the compounds used in Bertram et al. (2011) in the O:C range of 0.67 - 0.8 are C-5 and C-6 carboxylic acids.

Page 9923, line 12 : I doubt it. Are there indications that Aikens parametrization of retrieval of O/C ratios does not apply to isoprene oxidation products. Your results suggest that O/C of the isoprene oxidation products is larger than determined by AMS.

Disagreement between our data and the prediction of the parameterization would not necessarily suggest that the O:C determined by the AMS is not accurate. Rather, the suggestion is that O:C is not the only factor influencing phase transitions. Nevertheless, the measured O:C ratios of 0.67 – 0.74 have a stated ±30% error, which puts the upper bound of O:C at 0.96. When the O:C uncertainty is taken into account, our data do fall along the lower edge of the shaded area, in agreement with the parameterization.

Page 9934, line 24 : page numbers of reference Smith et al. 2011 are not correct.

Yes, this correction is made in the revised manuscript.

Page 9938, Fig.2 :
Violet point is not at epsilon = 0.6.

We thank the reviewer for this careful observation. The violet point is actually plotted at 0.58. This number is updated in the revised manuscript.

Why do use here the notation "positive" and "negative perturbation". Why not using "increased" and "decreased RH".

To clarify the text and for consistency with the experimental section, the Fig. 2 caption is modified to reflect the description of the RH cycling given in the experimental section (2.2.1 Transmission ratio experiments):

Figure 2 caption: "Panel a shows the transmission ratio φ of the particle population as $RH_{1,\beta}$ *is scanned upward*."
"Panels c and d are as described for panels a and b with the difference that $RH_{1,\beta}$ *is scanned downward* in experiments designed to identify efflorescence transitions."

Page 9940, Fig.3, Caption, line 9 : replace "red lines" by "red dashed line"

The change to "red dashed line" is made in the revised manuscript.

Suppl. Table S1: "For simplicity, adjacent RH values that are equal are condensed to a single RH value in the table." I don't get the point here.

The "adjacent RH values" refers to adjacent components of the TDMA that are maintained at the same RH, as is the case for the first nafion tube and DMA^{mono}, which are both maintained at RH^{mono}. Upon review of Table S1, we recognize that this statement is not needed because the column titles in Table S1 are not explicitly defined as representing each separate component of the TDMA. This statement is removed in the revised manuscript.

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