Interactive comment on "Analysis of multiple new-particle growth pathways observed at the US DOE Southern Great Plains field site" by Anna L. Hodshire et al.

Anonymous Referee #1

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This article presents an important study of growth pathways of nanoparticles, comparing field measurements with results from process modeling. It is well writing and falls within the scope of the journal. While both modeling uncertainties and lack of some key measurements do not allow for closure, uncertainties and limitations are fully acknowledged and discussed. This discussion of limitations is an important aspect of the article, identifying key unknowns holding back out current understanding of nanoparticle growth and signaling ways forward for future work. I recommend this article for publication in ACP with minor revisions.

Scientific Comments 1. GR methods

Page 12 lines 1-5: There are many methods that can be used to calculate GR from measured size distributions. Why is this method used as opposed to e.g. continuous dDp/dt using the mode diameter or using the leading edge of the banana instead of the mode diameter? An evaluation of how the assumptions in this method chosen compare with the way MABNAG calculates GR would show whether any of the systematic discrepancy between measured and modeled GRS is due to method differences instead of missing species as implicitly assumed in later sections. Part of the consistent under prediction of GR from MABNAG compared to these measurements could be due to systematic differences from the method of GR calculation. MABNAG measures wet diam. Temperature of saturators in CPCs of the SMPSs could mean measuring dry diam. For the compositions observed do you have an estimate of how much this could be affecting the particle diameters and thus GRs?

We have reconsidered our GR methods for this work. We have completed the leading edge method and the mode diameter method for each day, as well as made a linear growth rate based upon visual inspection, all for the D_p range of 10-20 nm. We have made figures showing the results of each method (see below) and have included these figures in the supplementary information. It can be seen from the figures that the leading edge and the D_p-mode methods, although fully automated and thus theoretically better than the visual method, do not perfectly track the growing distribution well. We have added the following text to the discussion on calculating the observed growth rates:

"There is considerable noise in the SMPS data (Figure 1, a-c), especially for May 9 and May 11, due possibly to the hypothesized mixing down of particles and possible inhomogeneities in the air mass. For this reason, we have calculated the growth rate between 10-20 nm for each using three different methods. The first method, referred to here as the leading edge method, is adapted from Lehtipalo et al. (2014) and finds the time at which the binned aerosol distribution between 10-20 nm reaches one half of its maximum $dN/dlogD_p$ for each bin. A linear fit between the bin's median diameter and the associated time determines the growth rate. The second method, referred to here as the D_p-mode method, tracks the change in diameter of the maximum $dN/dlogD_p$ of the aerosol size distribution between 10-20 nm; a linear fit between the diameters and time determines the growth rate. When plotted against the size distribution (see supplement, Figures S1-S3), it is seen that the leading edge and D_p mode method both do not always track the growing size distribution well. For this reason, we have included a third method, which we call the visual method, in which we have made a linear growth rate between 10-20 nm for each day based upon visual inspection of the size distribution (see supplement, Figure S1-S3), using Eq. (3):

$$GR_{obs} = dDp/dt \sim= \Delta Dp/\Delta t \qquad (3)$$

These three methods provides a range of growth rates (Table 3) for the particles between 10-20 nm; the specific results for each day will be discussed in section 3. We do not attempt to provide uncertainty estimates for each method, due to the overall noise in the data. Instead, we present the ranges of calculated growth rates as a possible range of the actual growth rates. May 9 and May 11 tend to have higher growth rates: this could be from the influence of the continued mixing down from nucleation aloft and not actually representative of the growth rates of the particles forming near the surface."

In re the SMPS measurements: the measurements were made at ambient dew point. If the temperature inside the trailer were equal to the ambient temperature, then measurements would have been carried out at ambient relative humidity as well. As an approximation, we have assumed that particle sizes in the SMPSs were equal to particle sizes in ambient air (i.e., water was neither lost nor gained; if particles were wet in the ambient they were equally wet in the DMAs). The temperatures in the trailer should be close to that of the ambient temperatures. We have modified the text to make this more clear, "For all systems, filtered ambient air was used for the DMA sheath air, without adjusting the water vapor partial pressure. Therefore, the relative humidity was close to ambient relative humidity, and particle water content was close to that in the atmosphere."

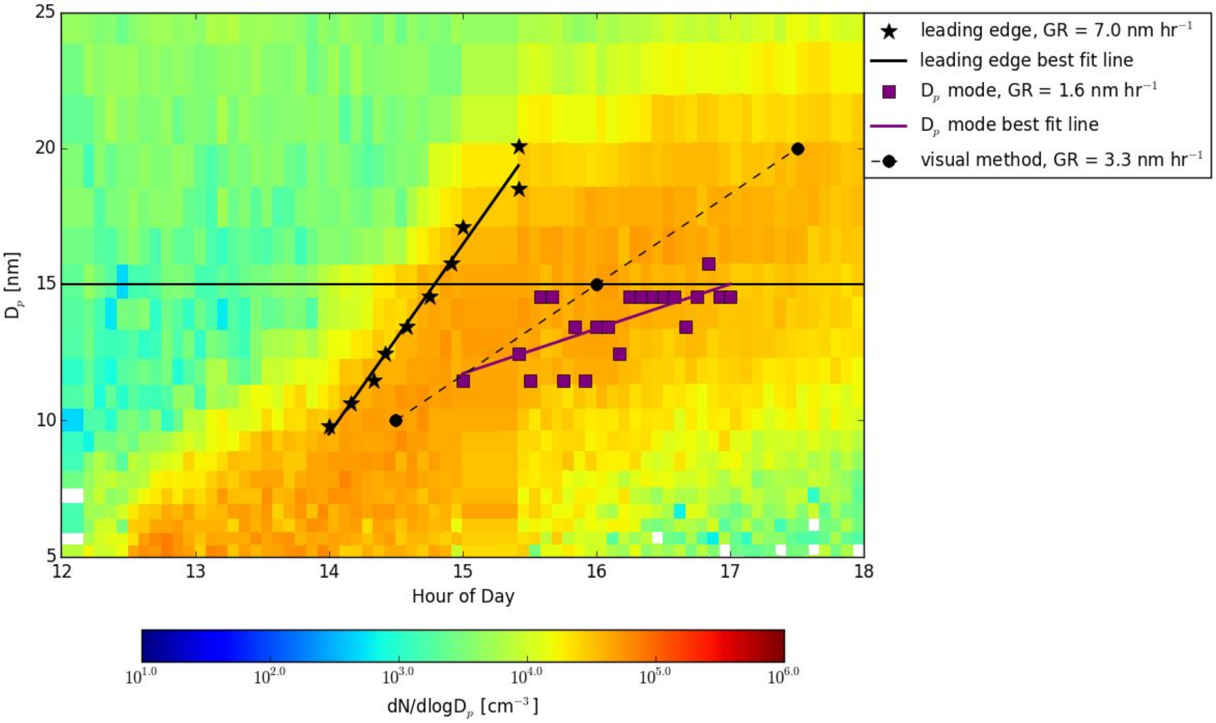

Figure S1. The results of the three growth rate calculations for April 19, 2013. The x-axis represents CDT time. The line at 15 nm D_p is to guide the eye.

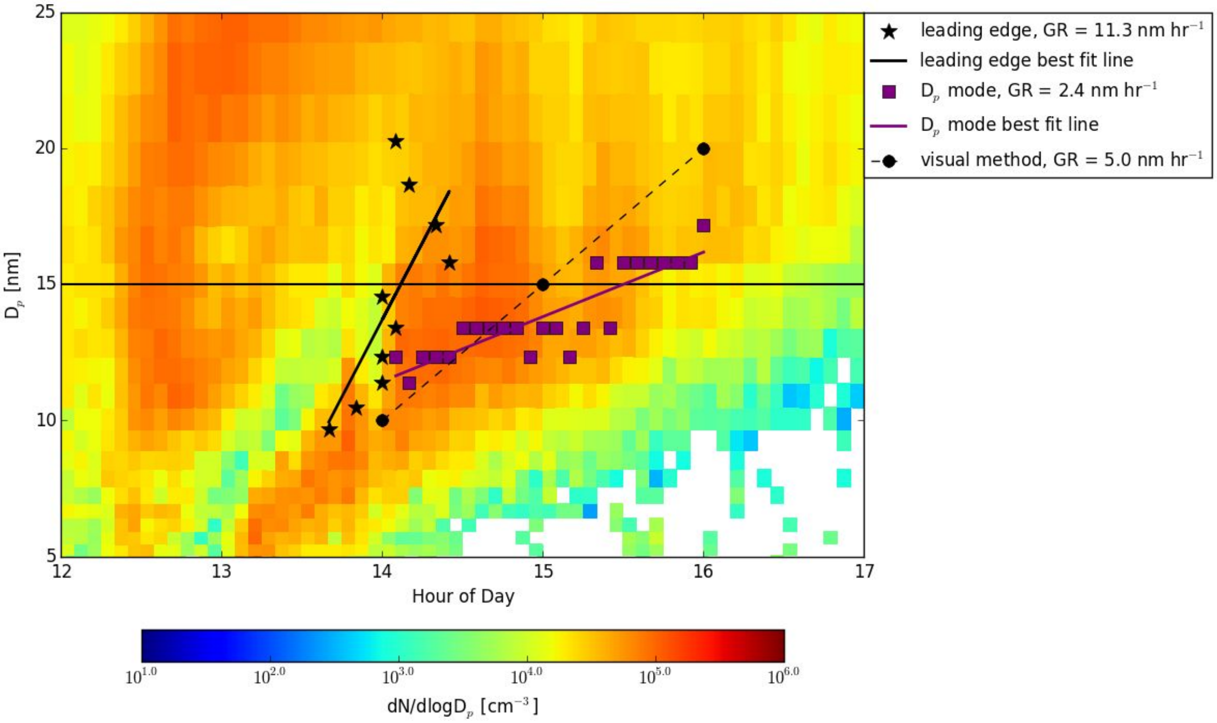

Figure S2. The results of the three growth rate calculations for May 9, 2013. The x-axis represents CDT time. The line at 15 nm D_p is to guide the eye.

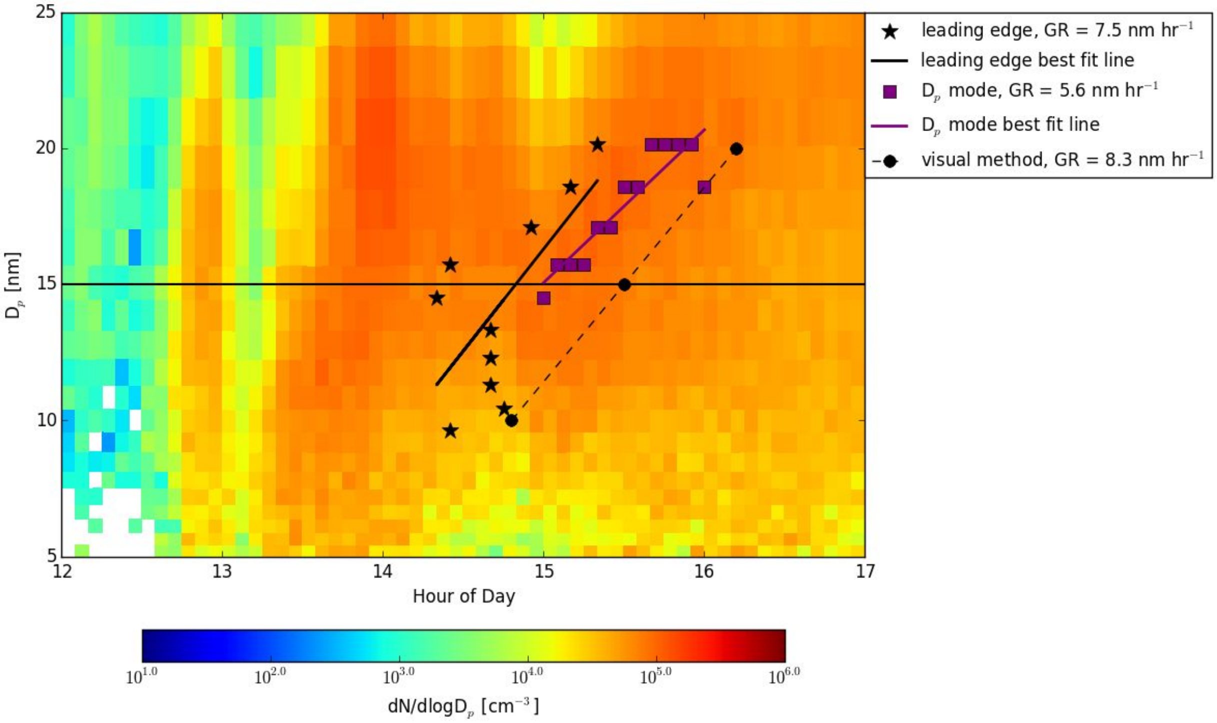

Figure S3. The results of the three growth rate calculations for May 11, 2013. The x-axis represents CDT time. The line at 15 nm D_p is to guide the eye.

2. GR uncertainties

Page 12 paragraph 2: This range of GRs given by the 3 diameter ranges is not a measure of uncertainty, but is presented almost like an uncertainty in the results and evaluation section. Table 3 would be more useful if it showed which GR comes from which diameter range. Is there any trend in how GR varies over the diameter range? A more continuous dDp/dt plotted as a function of Dp would give a clearer view of this and could be usefully compared with how the MABNAG GRs vary with size and an experimental view on whether the reduction of the Kelvin effect with size (line 15) is a significant contributor or not.

See our response to the first half of your first comment under ***Scientific Comments 1. GR methods*** in re the issue of using a range of growth rates; we instead have chosen to present a variety of growth rate methods and their results to show the possible variety in growth rates. Given the variety from just using different methods due to the noise in the SMPS data, we are hesitant to attempt to calculate growth rates at different size ranges, as this will introduce further uncertainties. We do not feel that we can confidently determine any changes in the growth rate from possible Kelvin effects at smaller sizes based on these uncertainties.

Page 15 line 5: 50% MABNAG GR uncertainty from ELVOC concentration uncertainty would lead to a maximum GR of 2.1 nmph, which is still lower than the measured 3nm GR. It needs to be stated clearly that this uncertainty in the ELVOC concentration cannot alone account for the model-measurement discrepancy in this case.

We have added the following to the discussion: “However, even a 50% underprediction of the contribution from ELVOCs to growth would lead to a maximum growth rate of 2.1 nm hr^{-1}, which is on the low end of the growth-rate range that we have calculated from the measurements. Thus, our low bias in growth rate for this day may not be from the ELVOC concentration uncertainties alone.”

Page 15 line 9 and lines 16-19 : If LVOC and SVOC contribute more to growth as the particle size increases we would expect the modeled GR to deviate more from the measured result at larger sizes, especially for the case where organics dominate growth. Is this apparent in the data?

For the three days that are analysed here, getting growth rates much past 20 nm in diameter is tenuous, at best. By the time all three days begin to reach sizes beyond 20 nm in diameter, the amount of noise in the SMPS data increases, making the automated growth rate methods’ results (e.g. the leading edge and D_p-mode methods) more uncertain. Furthermore, none of the days analysed here grow significantly past ~35 nm. April 19 does not grow far enough past 20 nm to confidently get a growth rate even from the visual method. (The strong growth seen until about hour 18 ends at around 22 nm D_p.)

Similarly, the strong growth seen for the 2nd event of May 9 ends at around 20 nm by about hour 15; the SMPS data at higher D_p at later times shows a very similar number concentration across several D_p bins, making it difficult to pick out a possible growth events.

It is possible to estimate the growth rate for May 11 using the visual method; we obtain a growth rate of around 3 nm hr^{-1} between 20-30 nm between hours ~16-19. This is slower than the growth rate calculated for May 11 using the visual method between 10-20 nm; that growth rate was found to be 8.3 nm hr^{-1}. (It should be noted that for May 11, we likely have a lot of pre-existing aerosol from the first event in the 20-30 nm bins during this time period, making growth-rate calculations less trustworthy.) Across cases and days, if the aerosol grows past 20 nm, MABNAG predicts a growth rate in the 20-30 nm range that is essentially the same (usually slightly slower but only by a few percent) as what is predicted for the 10-20 nm range. Given our uncertainties in the SMPS data, we cannot estimate whether or not the modelled GRs deviate more from the measured GRs at larger sizes.

Page 15 line 26: What is the uncertainty on the cluster CIMS SA measurement and also for the ammonia and amine concentrations on page 16 line 35?

The uncertainty on the Cluster CIMS SA measurements is given in the SI of Chen et al. (2013). We have added the following to the discussion of the Cluster CIMS: "The detection of sulfuric acid in the CIMS has been quantified and calibrated, and the uncertainties for the concentrations of the monomers and dimers of sulfuric acid are estimated to be factors of 1.5 and 3, respectively (Chen et al., 2012)."

The uncertainty for the data set from the AmPMS for the SGP campaign (ammonia and amine concentrations) is given in the SI of Freshour et al. (2014). We have added the following to the discussion of the AmPMS: "Uncertainties in the AmPMS data for this campaign is discussed further in Freshour et al. (2014) and is estimated to be +150/-60%, overall."

Page 18 lines 27-36: RH uncertainty on MABNAG GR would be more usefully included quantitatively in the discussion of GRs for the separate case. This and the ELVOC concentration uncertainty (put at 50% earlier in the manuscript), the oxalic acid factor 100 uncertainty and perhaps other sources of uncertainty could allow a fuller basis for comparison between model and measurements if they were included quantitatively in the results.

One major difficulty in qualitatively including uncertainties for each day for the different uncertain variables is that we do not know the PDFs of these uncertainties. For instance, is the likelihood of oxalic acid equally distributed between 1x and 100x? Could it in reality be lower than 1x or higher than 100x--and so forth for the other uncertain factors. It is beyond the scope of this paper to attempt to fully map out each uncertain variable in its entirety, and we currently do not have a good enough understanding of the uncertainty spaces of our parameters. Instead, discussing the qualitative uncertainties addresses what limitations we have in this study, without introducing further layers of uncertainty by attempting to quantify each uncertain parameter.

Page 12 lines 5-10: Hypothesis that double nucleation is mixing of nucleation event that occurred higher up + later event lower down seems plausible for May 9th, but May 11th both events show particles growing from the smallest sizes. The plots in fig1. are composite plots from multiple SMPSs – could the larger concentrations at larger sizes on May 11th 1st nucleation event be a compatibility issue between SMPSs (i.e. could the SMPS measuring at larger sizes be measuring with a higher efficiency – perhaps because of unaccounted for diffusion losses in the sampling lines?)

We put a large effort into comparing the responses of the 3 SMPS instruments for the size ranges where they overlap, and it was seen that the SMPS systems are in reasonable agreement for these overlapping size ranges. Thus we are confident that the measurements are reasonably accurate, and that the higher concentrations at larger sizes for the first nucleation event of May 11 are not due to SMPS compatibility issues.

May 11th 2nd nucleation event: condensation/coagulation sink from 1st nucleation event will likely be affecting the GR making it appear smaller than it would be for a single event – some estimation of the size of this effect would be useful as it would further increase the difference between the measured GR and the MABNAG modeled GR

MABNAG does not rely on the condensation sink explicitly to make its predictions. We use the measured gas-phase species to drive MABNAG. The condensation sink from the first event would have affected the measured gas-phase sulfuric acid etc on that day, and thus this condensation sink is implicitly included in the MABNAG simulations.

3. Other

Page 7 paragraph 4: Some discussion on the accuracy of MEGAN2.1 estimations of monoterpine emissions and concentrations and applicability for this site/study is necessary to give confidence in their use.

Guenther et al. (2012) provides an discussion of the various uncertainties related to the MEGAN2.1 model; however, they defer to Lamb et al. (1987) and state that , “the uncertainty estimate of a factor of three can be associated with the annual global emissions” of monoterpenes. However, as far as we are aware, no regional studies have been done to determine what uncertainties should be associated with the SGP region in regards to MEGAN model output. Thus, an uncertainty factor of three for the annual global emissions is the best we have at the moment.

We have added the following to the methods discussion of MEGAN: “For a discussion on the uncertainties associated with emissions from MEGAN2.1, see Guenther et al. (2012). ”

Page 9 paragraph 1: What was the basis for choosing 20 molecules as the initial particle size? How does this choice affect the modeled results?

Choosing 20 molecules of each species as the initial particle size is arbitrary and creates a particle that is ~3 nm in diameter. The choice of molecules in the 3 nm particle has negligible influence on the growth rate and composition in the 10-20 nm size range.

We have added the following to the text: "MABNAG also requires an initial particle size and composition; for simplicity in this study, the initial particle is formed from 20 molecules of each input species, creating a particle approximately 3 nm in diameter. The choice of molecules in forming the initial particle has negligible influence on the growth rate and composition in the 10-20 nm size range."

Page 12 line 5: On what is the assertion that nucleation potentially occurred aloft based?

The assertion that nucleation potentially occurred aloft is based on tethered balloon data that measured particle size distributions that was taken on May 12. We have added further details to the text as follows: "Similar to May 9 and May 11, the SMPS data for May 12 shows what appears to be two nucleation events occurring at the surface where the SMPS collected size distributions. Tethered-balloon flight profiles for May 12 indicate that nucleation potentially occurred aloft. These observations will be described in detail in a manuscript currently in preparation (Craig, et al., 2016, in preparation), but are briefly described here: The balloon payload consisted of two portable condensation particle counters (model 3007, TSI, Inc.) operating at different minimum size-cut points, which allowed the vertically-resolved measurement of 10 to 20 nm diameter particle number concentrations, $N_{10\text{-}20nm}$. On May 12, high concentrations of particles in this size range were detected at 600 m above ground level, exactly coincident with, or slightly prior to, ground-level observations of high concentrations of $N_{10\text{-}20nm}$. We hypothesize the following explanation for the "double" nucleation events observed on May 9, 11, and 12: Nucleation and growth begins to occur aloft in the residual layer. Once the mixed-layer depth grows into the residual layer, these new particles (that may have already grown to ~10 nm) then mix down and are measured at the surface. This hypothesis is supported by the presence of a high concentration of larger particles (D_p = 10-30 nm) that have already undergone growth at the "beginning" of the first event as measured by the SMPS on May 9 and May 11. Then, the second event, which presumably begins near the surface, shows a high concentration of freshly growing particles (3-5 nm, close to the limit of the SMPS detection) before larger particles appear."

Page 16 line 18: GR for ammonium sulfate case shows better model-measurement agreement than for the growth by organics case. SA/amine/organic growth on p17 also shows better agreement. Comment on why this might be?

We expect to do well for an inorganic ammonium-sulfate system, as gas-phase measurements are complete, and the thermodynamic properties and chemical interactions of ammonia/ammonium and sulfuric acid/sulfate are well-known. Growth by organics is much more difficult to constrain especially under this particular modelling framework given the uncertainties discussed throughout the paper (properties, LVOCs/SVOCs etc.). Given these limitations, it is unsurprising that we do not model the growth rates well for the growth by organics case.

We do not necessarily agree that we do much better for the SA/base/organics growth case than we do for the growth by organics case. We appear to do worse in terms of underpredicting growth rates for the SA/base/organics growth case than we do for the organics case. However, we do see a reasonable amount of sulfate and base in the particle phase for many of the sensitivity cases, which once again is likely due to our ability to model inorganic ammonium-sulfate cases well.

Page 17 line 16: The base simulation predicts GR that are way too low compared to measured GR. Therefore the relevance of the composition from this model seems tenuous. In general, different MABNAG simulations have better/worse agreement with the measured GR and also predict different compositions – more could be made of which compositions are more likely to be accurate based on this.

We do not see one set of assumptions in MABNAG that best captures all three days, and the only cases that had completely unreasonable results were the MAL_LoVP/100ox cases for May 9. Many cases tended to predict similar particle compositions and growth rates with only slight differences from case to case. Given this, the qualitative nature of the TDCIMS data, and that we are not including higher volatility organics (LVOCs and SVOCs) in the model and do not know whether we are accounting for the nitrogen species whose signal often shows up strongly in the TDCIMS, we cannot make definite model-to-observational comparisons and instead present these results as the basis of further research, especially into the areas that we are limited by (i. e. higher volatility organics, etc.).

We have added the following to the discussion for May 11:
“We do note that as MABNAG appears to be underpredicting the growth rates more than for April 19 or May 9 that the MABNAG-predicted particle compositions (Figures 6 and 7) are possibly less representative of the actual particle compositions. However, we reiterate our hypothesis that the underpredictions could be from the nitrogen-containing species that are detected in the TDCIMS but are not accounted for in MABNAG, as well as our uncertainty in ELVOC concentrations and lack of LVOCs, SVOCs, and accretion reactions. Furthermore, this day shows a more variable particle-phase spectrum than April 19 or May 9, as well as a more poorly defined second growth event (Figure 1c), making the observed growth rates difficult to

determine. The TDCIMS particle composition information is only qualitative. Thus, we will not speculate what differences are possible between observed and modelled particle composition.”

We have also added the following sentence to the end of the first paragraph of our synthesis section: “We do not see that one set of assumptions in MABNAG best captures all three days (Figures 3, 5, and 7), and instead present these results as a basis for further research, especially into the contribution of higher-volatility organic species to growth.”

Page 17 line 18: This sentence should include the fact that there are significant additional unknown growth pathways (N, LVOC, SVOC) as well

We do mention the N uncertainty in the previous paragraph, “The TDCIMS negative ion data also indicate the presence of nitrate; as stated previously, we hesitate to attribute significant growth from nitrate due to the unknown sensitivity of the TDCIMS to nitrate.” We have modified the paragraph that page 17/line 18 was in to read, “ Conversely, MABNAG predicts roughly 5-25% of the moles in the particle to be from ELVOCs, with the lowest relative ELVOC contribution seen in MAL_LoVP/100ox cases. Since the TDCIMS shows a variable amount of organics throughout the event, and we do not know the actual individual contributions from ELVOCs and organic acids, nor are we accounting for any higher-volatility neutral organic species (e.g. LVOCs and SVOCs), we cannot conclude which set of organics inputs best captures this day and do not exclude any set of inputs for being unrealistic.”

Technical Comments

Page 9 line 21: SVOC doesn’t seem to be defined here or earlier and should be

Done

Page 7 lines 10-11: “estimated uncertainty in oxalic acid . . . is approximately a factor 100 lower” is unclear. Need a better way of saying the oxalic acid concentrations could be up to 100x larger than measured as done later on page 11

We have modified the text: “Therefore, the estimated systematic uncertainty in the oxalic acid concentration measured via nitrate chemical ionization is approximately up to a factor 100 times lower than reported, indicating that the actual concentration could be up to 100 times higher than observed.”

Page 13 line 16: Reference needed for sulfuric acid concentration of 2e-6 leading to 0.2nmph growth rate

This GR was calculated using the growth rate formula for the kinetic regime,

$$dDp/dt =([H_2SO_4])*(Mw*c*alpha) / (2*rho)$$

Assuming accommodation coefficient alpha = 1; c = sqrt((R*T)/(pi*Mw)); assuming T = 283 K; R = gas constant; Mw = molecular weight of sulfuric acid; $[H_2SO_4]$ = concentration of sulfuric acid; and rho = density of sulfuric acid. This leads to a GR closer to about 0.1 nm hr^{-1}; we have altered the text to reflect that as well as give more information.

The text now reads as follows: “Some notable features of the gas-phase data for April 19 (Figure 2a-b) include relatively low sulfuric-acid concentrations ($\sim 2\times10^6$ cm^{-3}), which should only contribute to growth rates of about 0.08 nm hr^{-1} (assuming kinetic regime growth, an accommodation coefficient of 1, and a temperature of 283 K), or approximately 10% of the observed rates.”