Review of Analysis of multiple new-particle growth pathways observed at the US DOE Southern Great Plains field site by Hodshire et al.

This article adds to the understanding of particle growth processes in the atmosphere. The article is well written and the topic fits to the scope of the journal. The article gives valuable, yet qualitative information about the growth pathways of nanoparticles, which is derived from both measurement and modelling. I find it especially important that the authors show that the major growth mechanism can vary even at the same site and the same season.

The major weakness of this study is the missing reliable measurement of organic compounds of different volatilities. However, I find that the authors are well aware of the limitations, which are acknowledged appropriately and discussed extensively. Therefore I recommend the article to be published in Atmospheric Physics and Chemistry with minor revisions.

General comments and questions:

-how representative were the 3 discussed cases in light of the whole measurement period? Can you estimate which growth pathway was the most important at this site? What determines the prevailing growth mechanism, the sulfuric acid concentration?

During the campaign, 13 possible new-particle formation events were observed. We selected the 3 events that we did because all of the instruments available were working and the TDCIMS was measuring the sizes of the growing nucleation mode. As our growth hypotheses are based on the particle compositions obtained from the TDCIMS, it was important to have data from the smaller, growing particles. For the 10 events that were not analyzed in the paper, the TDCIMS was measuring at a large (~40 nm) particle size for the event and thus the particle compositions of the growing particles was not captured for the most part. Also, some of these events were not captured by our other instruments due to instrument failure. There were a few events in which the TDCIMS captured particles at the end of the growth event (e.g. when the growing particles reached ~40 nm) but at the larger particle sizes, there is more potential for contamination from the background accumulation-mode aerosols as the TDCIMS tends to take in significantly larger particles than the nominal 40 nm particles at these larger size cuts. With all of these considerations, we do not have the ability to estimate the more important growth pathway(s) for SGP during this campaign.

Regarding what determines the prevailing growth mechanism: We have sulfuric acid measurements for the entire campaign except during occasional periods of instrument failure. We do not currently have ELVOC estimates for the entire campaign, as we obtained the monoterpene emissions data from MEGAN from GEOS-Chem for only the three days considered. Nor do we have any measurements or estimates of higher volatility organics (e.g. LVOCs or SVOCs) that can contribute to growth at larger particle sizes, as has been often brought up in the text. We do see that for the day that showed growth by primarily organics, the ELVOC estimated concentration at the beginning of the event is the highest of the three days and the sulfuric acid concentration at the beginning of the event is the lowest of the three days and that for the ammonium sulfate growth day, the sulfuric acid concentration is the highest out of the three days. Both the organic acid and ELVOC estimated concentrations are higher for the ammonium sulfate day than for the growth by sulfuric-acid/bases/organics, and yet we see significantly more organics for the growth by sulfuric-acid/bases/organics day. It is difficult to draw any conclusions based on only three days as to what determines the prevailing growth mechanism.

-you have particle size distribution measurements from 1.9nm-528nm, yet you report only the growth rate between 10-20nm, why? It would be very interesting to see how the growth rate (and the primary growth mechanism, if you can get that information) changes with particle size

We selected the range 10-20 nm for a few different reasons. We do not see significant growth past ~20 nm for April 19, and we wish to remain consistent in our analysis across the three days. Our analysis of particle composition is somewhat constrained to this smaller size range: our hypotheses of growth mechanisms are based upon the TDCIMS data. During the campaign, the TDCIMS was set to measure at ~40 nm mode diameter when new-particle formation events were not ongoing, and set to measure smaller particle sizes (usually around ~20 nm) when the onset of a new-particle formation event was detected. The smaller size selection was chosen in order to determine what species were in the freshly growing particles. Unfortunately, not all of the events were detected in real-time, and several new-particle formation events occurred without concurrent TDCIMS measurements in the smaller size ranges--these days were not a part of this paper's analyses. Thus we cannot categorically state how the primarily growth mechanism(s) change with particle size, since we do not have TDCIMS data that tracks the growing particles beyond the ~20 nm range for the new-particle formation events.

We have added the following to the text: "We have calculated the observed growth rates between 10-20 nm for each day of our analysis from the SMPS data (Figure 1, a-c). This size range is used since we constrain our analysis of particle composition to the TDCIMS data. During the NPFS campaign, the TDCIMS was set to measure at ~40 nm mode diameter when new-particle formation events were not ongoing. Then, when the onset of a new-particle formation event was detected, the TDCIMS was set to measure smaller particle sizes, around 20 nm mode diameter, in order to determine what species were in the freshly growing particles. Thus, our growth rate calculations represent the size range that the TDCIMS measured in during the events of our analysis."

-can you estimate how accurately was the sulfuric acid concentration measured and how the uncertainties in the total sulfuric acid concentrations affect your conclusions

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., 2013)."

Regarding how the uncertainties of total sulfuric acid concentrations affect our conclusions: consider April 19 as an example. If we assume irreversible condensation (reasonable, given the particle sizes), an accommodation coefficient of 1, and a temperature of ~10 C, the reported sulfuric acid concentration of $2x10^6$ molecules cm^{-3} will lead to a growth rate of ~0.1 nm hr^{-1} by sulfuric acid condensation alone. The concentration of sulfuric acid dimer tends to be at least 2-3 orders of magnitude lower than the concentrations of sulfuric acid monomer throughout the campaign, and often falls beneath the detection limit. Thus, we'll assume that any uncertainty in the dimer concentrations are negligible compared to uncertainties in the monomer concentrations. Under these assumptions, the sulfuric acid could be up to $\sim3x10^6$ molecules cm^{-3}, leading to a growth rate of ~0.12 nm hr^{-1}, a ~20% increase in growth from sulfuric acid alone. We have updated our growth rate calculations (please see our response to your final comment for more details on the growth rates) to include three growth rate methods; for April 19, these three methods yield a possible growth rate range of 1.6-7.7 nm hr^{-1}. So even at the low end of this range, 1.6 nm hr^{-1}, the contribution to growth from sulfuric acid goes from contributing 6.25% to 7.5% towards the total growth rate with a 50% increase in sulfuric acid contribution. This difference is too small when compared to our other uncertainties (including what the actual observed growth rate is) to account for any possible underpredictions in the MABNAG-predicted growth rates.

Similarly, the growth rate for May 9, the day that shows the most growth from sulfuric acid, only has about 0.8 nm hr^{-1} of growth coming from condensation of sulfuric acid, assuming the reported concentration of $\sim2x10^7$ molecules cm^{-3}. A 50% increase in the sulfuric acid concentration to $\sim3x10^7$ molecules cm^{-3} leads to a growth rate of ~1.2 nm hr^{-1}, a 50% increase in the growth rate from sulfuric acid. Thus, the uncertainties in sulfuric acid contribute to smaller uncertainties in growth rates than the other uncertainties discussed in the text.

-based on the text and the showed results it seems that each of the considered days had a predominant growth-mechanism, however, the other compounds also had a minor, but distinct contribution. Therefore, I think it is wrong to say 'growth by organics alone' (as you do in the

abstract) for April 19. I think you need to change the abstract and heading in chapter 3 to say 'Growth primarily by organics' and maybe even add 'with a small contribution from sulfuric acid and ammonia'

We have modified the abstract and heading for chapter 3 to reflect that we see growth primarily from organics.

-the mechanism on May 9: should it be ammonium sulfate or sulfuric acid and ammonia? Maybe also mention the contribution from amines which seems to be non-negligible

We have changed the heading to be Growth by primarily sulfuric acid and ammonia; we indicate in the text of this subsection that amines (and organics) appear to make a small but non-negligible contribution, as well: "A small, but non-trivial, amount of organics and amines are seen in the particle phase as well."

-you claim that on May 11 the mechanism was sulfuric acid/amines/organics, although you say in the text you cannot assess the relative importance of ammonia to amines based on TDCIMS, and also MABNAG predicts both in the particle phase. So why not sulfuric acid, ammonia, amines and organics (or just call it mixed as in the synthesis chapter).

We have changed the abstract and the text to reflect that we see a contribution from bases, instead of only amines.

-there is currently almost no discussion on how the results of this study compare to other recent field and laboratory measurements about nanoparticle growth rates, compositions and proposed growth mechanisms. I suggest the authors could include a short chapter on that before the conclusions section to give an idea how widely representative their results are.

We have added the following brief section:

4. The Southern Great Plains: Comparison to other campaigns

The New Particle Formation Study provided unique insights into new-particle formation events for the region during the spring of 2013, as both gas-phase and particle-phase measurements were taken concurrently in order to assess the species contribution to growth. We see that from three days of the campaign where all instruments were running, three different dominant growth mechanisms are present, from growth by primarily organics to growth by primarily ammonium sulfate to a mixture of growth from organics, sulfuric acid, and bases.

Previous field campaigns have taken place to similarly assess the growth of new-particle formation events in the continental boundary layer. A review paper by Kulmala et al. (2004) and references therein considered over 100 field campaigns, both long-term and intensive, primarily at continental boundary layer sites. Growth rates were found to be mainly within the 1-20 nm hr^{-1} range in the mid-latitudes, and our events are within this range. Furthermore, for campaigns in which growth rates and gas-phase sulfuric acid were measured, it was found that sulfuric acid tended to account for only 10-30% of the observed growth rates (Kulmala et al., 2004); although water and ammonia accounted for some of the remaining growth, organic compounds are thought to comprise the remaining growth. Studies within the past few years have reported growth from either primarily organics (e.g. Smith et al., 2008b; Kuang et al., 2010; Riipinen et al., 2011; Pierce et al., 2012) or inorganic components, primarily sulfate or ammonium sulfate (e.g. Bzdek et al., 2012).

On-line particle-composition measurements of sub-micron aerosols are a relatively new and still-evolving measurement technique. Smith et al. (2004) reported the first such measurements, using the TDCIMS to examine 6-20 nm particles. Another recently developed instrument is the Nano Aerosol Mass Spectrometer (NAMS) (Wang et al., 2006; Wang and Johnston et al., 2006; Pennington and Johnson, 2012), which reports quantitative elemental composition of nanoparticles in the 10-30 nm range. Of the recent studies that have used combined gas-phase measurements with particle-phase measurements (using either the TDCIMS, NAMS, or both) to determine dominant growth mechanisms (e.g. Smith et al., 2008b; Bzdek et al., 2012; Bzdek et al., 2014), this study is, to our knowledge, unique in reporting distinctly different dominant growth pathways for separate yet temporally closely spaced new-particle growth events. However, it is highly unlikely that SGP is truly unique in this regard; instead the findings of this paper point towards the value of investigating more field sites influenced by mixtures of anthropogenic and biogenic emission using similar combinations of gas-phase and particle-phase measurements.

Specific comments:

-your abstract is too long: you could leave out rows 26-30, which is more like introductory material and is indeed repeated in the introduction chapter.

We feel that lines 26-30 briefly supply important motivation for this particular piece in work, in other words, assessing the contribution of growth from these different pathways. As such, we have chosen to leave these sentences in the abstract.

-the four pathways mentioned in the abstract (row 26-29) and introduction (p.3, row 5-9) seem to be missing the interaction between sulfuric acid and bases (which is mentioned elsewhere, though)

We have altered the discussion on sulfuric acid in abstract to read, "condensation of sulfuric acid vapor (and associated bases when available)", and the discussion in the intro to read, "Irreversible condensation of sulfuric acid vapor (produced through gas-phase oxidation of SO_2 by the hydroxyl radical) is known to be a major contributor to growth. The effective equilibrium vapor pressure of sulfuric acid in the presence of tropospheric water vapor is negligible compared to ambient sulfuric acid concentrations (Marti et al., 1997), and sulfuric acid readily condenses to the smallest stable particles, often forming inorganic salts with associated bases when available."

-you could leave out 'analysis of' from the title. It would make it more concise and put emphasis on the fact that you found several different pathways (just a suggestion, though)

Done.

-p. 8, row 5. Please use SI units

Done.

-p. 13, row 10 citation

This was fixed after the pre-ACPD review.

-it should be mentioned in the abstract and table 3 what size range you considered

Done.

-this reviewer found it confusing that you report a range of GRs for each event. Before carefully reading the methods I did not understand where this range came from. Why not give a mean value and then list all the considered size ranges (10-15, 15-20 and 10-20) in table 3, so you also get a feeling of the variation.

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 or 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 that the leading edge and the D_p mode methods, although fully automated and thus theoretically better than the visual method, do not always 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.”

Regarding 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) because 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."

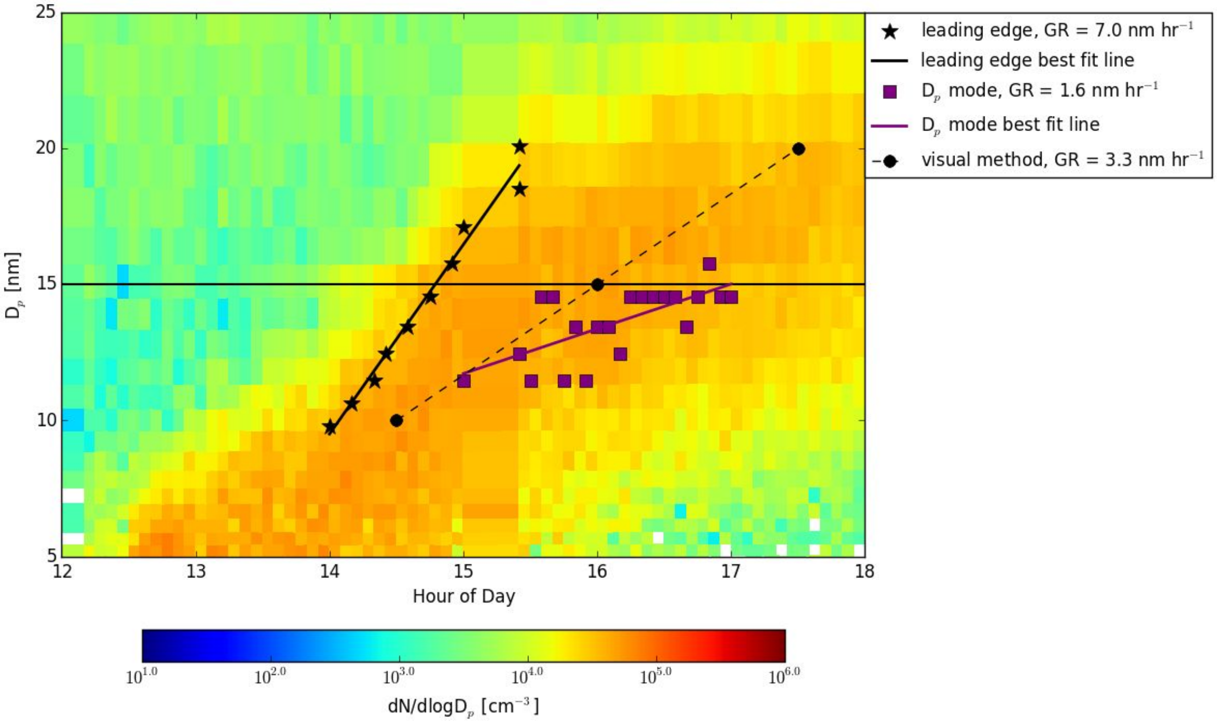

Figure S1. The results of the three growth rate calculations for April 19, 2013. The x-axis represents CDT time. The line at 15 nm D_p is to guide the eye.

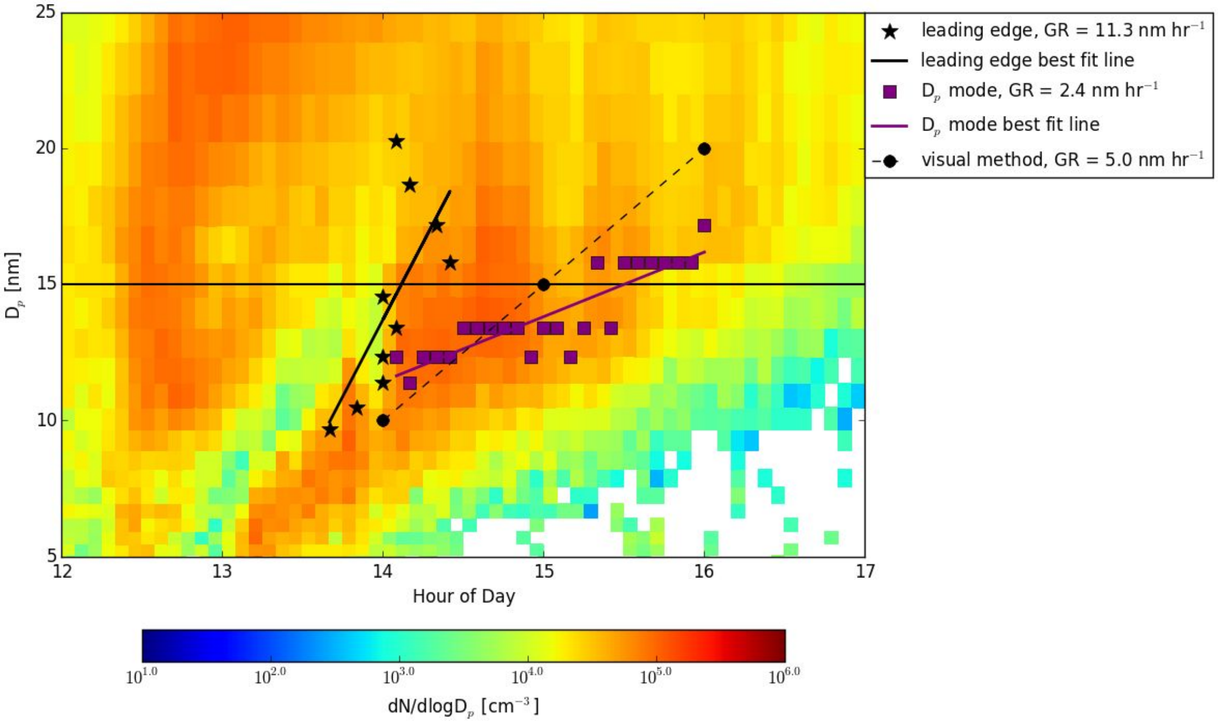

Figure S2. The results of the three growth rate calculations for May 9, 2013. The x-axis represents CDT time. The line at 15 nm D_p is to guide the eye.

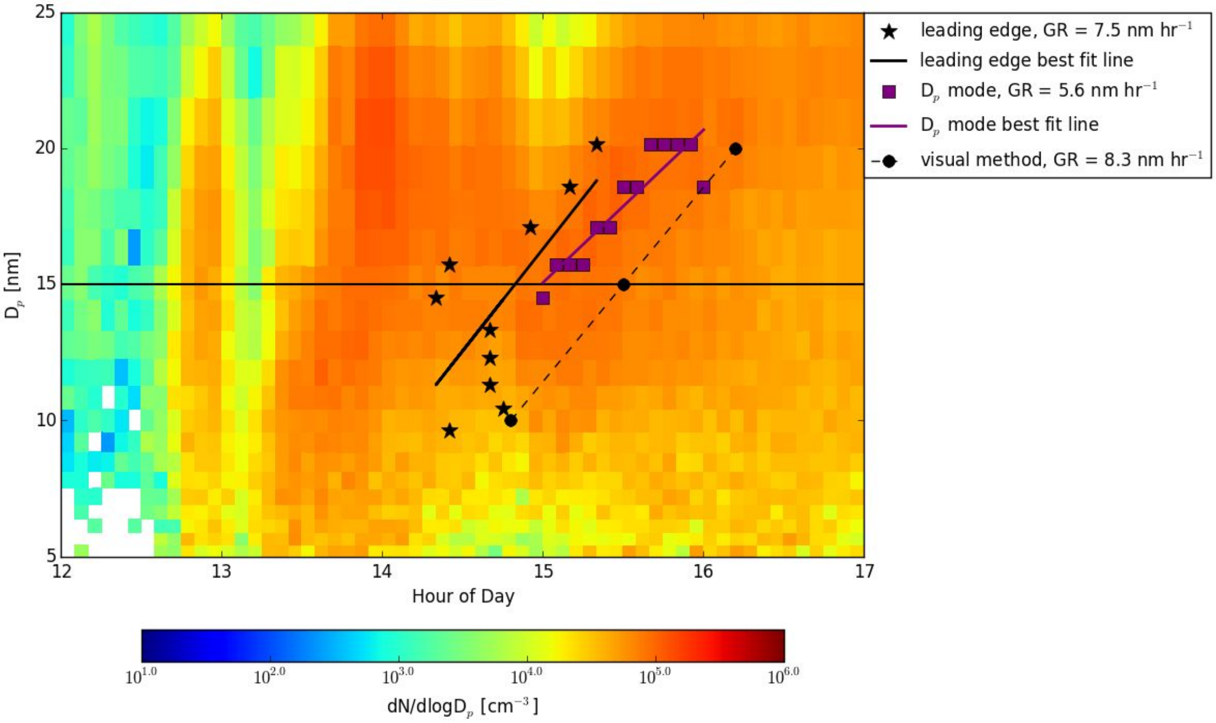

Figure S3. The results of the three growth rate calculations for May 11, 2013. The x-axis represents CDT time. The line at 15 nm D_p is to guide the eye.