Review of the manuscript NO. acp-2014-95 entitled: “Modeling ultrafine particle growth at a pine forest site influenced by anthropogenic pollution during BEACHON-RoMBAS 2011”, by Y. Y. Cui et al.

We thank the reviewers for their comments on our paper. To guide the review process we have copied the reviewer comments in *black italics*. Our responses are in regular blue font. We have responded to all the referee comments and made alterations (in **bold text**) to our paper.

Response to Referee #1:

We thank the reviewer for his/her comments and hope we could address them in a satisfactory manner.

Major comments

R1-1) *Abstract: The reviewer cannot understand the definition of Aitken-mode Particle burst Events (APEs). What is the size range of Aitken-mode? It would be better to use the term “nucleation-mode” in the manuscript. Authors need to define the size range of nucleation- and Aitken-modes and to use these two terms separately.*

Response R1-1) As suggested by the reviewer we have updated the manuscript to clarify our naming convention. We have renamed APEs (Aitken-mode Particle Burst Events) into PBEs (small Particle Burst Events) as the measured particles at the site during these events are typically larger than the sizes reported for the freshly nucleated particles in the “nucleation mode” (1-10nm), and are smaller than Aitken-mode particles (10-100nm).

This is now clarified in the manuscript: **“Measurements of ultrafine particles, their precursor gases, and meteorological parameters were performed in a ponderosa pine forest in the Colorado Front Range in July–August 2011, and were analyzed to study processes leading to small Particle Burst Events (PBEs) which were characterized by an increase in the number concentrations of 4-100 nm diameter size particles.”**
“In the current study, we define the term “small Particle Burst Event” (PBE) to describe the appearance and growth of particles that are larger than 4 nm in diameter in contrast with typical nucleation events that include particle diameters as small as 1 nm. Here PBEs refer to both nucleation-mode particles (< 10nm) and Aitken-mode particles (10-100nm).”

The “APE” term was replaced by “PBE” in the entire paper (for details see the version of the manuscript with tracked changes).

R1-2) *Abstract, L20-27: Authors mentioned that the condensation of monoterpene oxidation products onto freshly nucleated particles drive their growth. However, the measurement showed that sub-100 nm particles mainly comprised of sulfate. The interpretation and measurement results are conflict.*

Response R1-2) We agree that this is not clearly explained, and we have clarified it in the new manuscript.

Figure 9 shows measurements of ~20nm (not sub-100nm) particles during PBE days, as well as measurements of submicron (<1 μm) particles during Non-PBE days. These measurements show a larger fraction of sulfate (>60%) in ~20nm particles during PBE days than in submicron particles during Non-PBE days (~40%). From these measurements one cannot conclude if the decreased sulfate fraction in submicron particles is due to the absence of nucleation events, or the partitioning of the organic gases into the aerosol as we are comparing different size ranges. Unfortunately we do not have composition measurements of ~20nm during non-PBE days. Therefore, figure 9a doesn't contradict our sentence in the abstract "*Model results suggest […] that the condensation of monoterpene oxidation products onto freshly nucleated particles contributes to their growth*". It rather supports the fact that there is a lot of organic material in the submicron particles.

We totally agree with the reviewer that the relative fraction of sulfate in ~20 nm particles during PBEs is larger in the measurements than in model predictions (see Figure 9). The possible reason for that difference is that a large fraction of the organic mass may not be identified in the measurements, and the relative importance of organics could be under-predicted compared to sulfate in figure 9a. The other possible reason for this difference between model predictions and measurements is that we are considering different days. Measurements are taken on August 10, whereas the model results are averaged over several PBE days. If we look at the individual days shown in Figure S8, we see that WRF-Chem predicts a higher fraction of sulfate (~40%) on August 10. The robust result from these comparisons (shown in Figure 9b) is the increase in the relative importance of sulfate during PBE days in comparison to non-PBE days in the model simulations.

This is now better explained in the manuscript:
"The plot shows a clear difference in the relative abundance of sulfate during the PBE (~61%) vs. Non-PBE bulk aerosol (~41%). However, this increase in sulfate cannot be attributed to the presence of PBEs, due to the difference in size distributions considered here (20nm vs. submicron)."
"Results for PBEs show a factor of two increase in the relative contribution of sulfate to aerosol mass concentrations relative to Non-PBE days. However, the relative fraction of sulfate in ~20nm particles during PBEs is larger in the measurements than in model predictions. This difference could result from the limitations in the detection of organic species by the TDCIMS instrument leading to an underprediction of the relative fraction of organics compared to sulfate. The fact that we are considering different days could also contribute to this gap i.e. measurements report values for August 10, whereas the model results are averaged over several PBE days. Model predictions for August 10 (Figure S8) show a higher fraction of sulfate (~40%). "

R1-3) *P5622, Figs. 2 and 3: Previous studies showed that the inflow of anthropogenic pollutants can activate the burst of nucleation mode particles in a deciduous forest where* *emission of isoprene is dominant (e.g. Jung et al., 2013). It will be very good addition if isoprene data is available in this study.*

Response R1-3) Isoprene measurements were available during the field campaign and are shown in Ortega et al. (2014). As isoprene is only a small fraction (~10%) of the total biogenic volatile organic compounds (BVOCs) at this location, we have not added a specific plot in the paper, but have cited the published work by Ortega et al. (2014). This is now explained in the revised manuscript: **"Isoprene concentrations were low at the site (Ortega et al., 2014) and are not shown here."**

It should also be noted that we account for the SOA formation from isoprene with a 4% yield as already explained in the original manuscript: **"Simple molar yield calculations are used to form secondary organic aerosols, assuming 15% contribution for α-pinene and limonene and 4% for isoprene (Liu et al. 2012)."**

We also agree with the reviewer that our study complements the previous work performed in the isoprene-dominated environment influenced by anthropogenic pollution. We have added the reference to Jung et al., 2013 in the paper: **"Jung et al. 2013 showed that the inflow of these urban air masses acted as a trigger for the initiation of the burst of nucleation mode particles in an isoprene rich deciduous forest in Northern Japan."**

1. Ortega, J., Turnipseed, A., Guenther, A. B., Karl, T. G., Day, D. A., Gochis, D., Huffman, J. A., Prenni, A. J., Levin, E. J. T., Kreidenweis, S. M., DeMott, P. J., Tobo, Y., Patton, E. G., Hodzic, A., Cui, Y. Y., Harley, P. C., Hornbrook, R. S., Apel, E. C., Monson, R. K., Eller, A. S. D., Greenberg, J. P., Barth, M. C., Campuzano-Jost, P., Palm, B. B., Jimenez, J. L., Aiken, A. C., Dubey, M. K., Geron, C., Offenberg, J., Ryan, M. G., Fornwalt, P. J., Pryor, S. C., Keutsch, F. N., DiGangi, J. P., Chan, A. W. H., Goldstein, A. H., Wolfe, G. M., Kim, S., Kaser, L., Schnitzhofer, R., Hansel, A., Cantrell, C. A., Mauldin, R. L., and Smith, J. N.: Overview of the Manitou Experimental Forest Observatory: site description and selected science results from 2008 to 2013, Atmos. Chem. Phys., 14, 6345-6367, doi:10.5194/acp-14-6345-2014, 2014.

2. Jung, J., Miyazaki, Y., and Kawamura, K.: Different characteristics of new particle formation between urban and deciduous forest sites in Northern Japan during the summers of 2010–2011, Atmos. Chem. Phys., 13, 51-68, doi:10.5194/acp-13-51-2013, 2013.

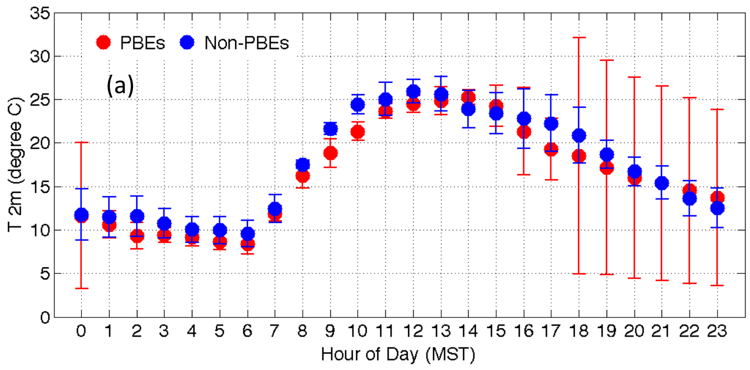
R1-4) *Fig 3: It is better to show one event day as a typical example of APEs so that readers can clearly see diurnal variations of related parameters on APEs.*

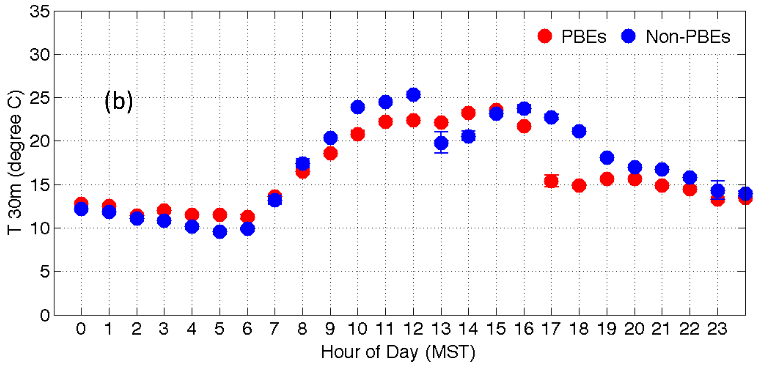
Response R1-4) As suggested by the reviewer we have added one event day (July 28) in Fig. 3 of the revised manuscript. The figure shows the diurnal evolution of the number size distributions on July 28, as well as the wind directions during that day. The following text has also been added to the revised manuscript to discuss the figure:

"A closer look at the diurnal evolution of the number size distribution during the

PBE event of July 28 (Figs 3a,b), shows the typical banana-shaped growth of the number size distributions. The sharp increase in N4- 30nm particles coincides with the shift in wind directions from westerly to northerly, and is followed by an increase in N30-100nm particles."

R1-5) *Fig 3: Ambient temperature is also important for the burst of nucleation mode particles in a forest. Thus, the reviewer suggests adding ambient temperature and comparing them between APEs and Non-APEs periods.*





Response R1-5) As suggested by the reviewer we have added the comparison of the 2m temperatures diurnal profiles between PBE and non-PBE days in the supplementary material (Figure S1). The comparison shows small differences between the two types of events with slightly (1-2 degrees) cooler temperatures during PBE days. We have also compared measurements at other available levels including 7m, 16m, 30m, and 43m (not shown here) and found similar results.

We have also revised the manuscript to read:
"Finally, the comparison of measured ambient 2m temperatures (Figure S1) shows 1-2 degrees cooler temperatures during PBE days."

R1-6) *Fig. 3: It will be good addition if authors can add condensation sink before APEs* *start to occur. Please discuss a role of pre-existing particles on the activation of the burst of nucleation mode particles during APEs and non-APEs periods.*

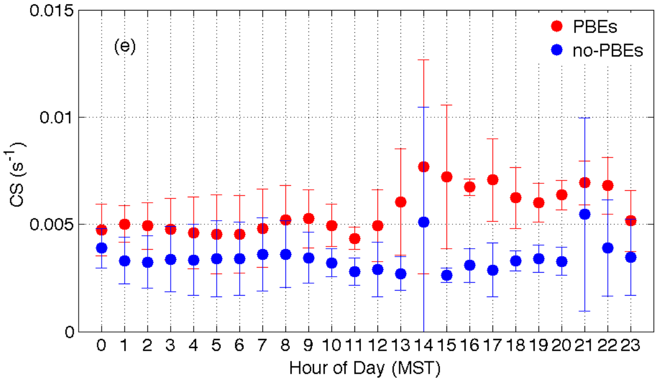
Response R1-6) We agree with the reviewer that the discussion on the role of pre-existing aerosols is of interest for this study. Therefore, we have calculated the condensation sink as described in the manuscript:

"We also calculate the condensation sink (CS, in s^{-1}, Eqn. 1) that is the rate at which the condensable inorganic and organic vapors condense onto pre-existing aerosols.

$$CS = 4\pi D_i \sum_j d_j \beta_m (K_{n_j}, \alpha) N_j \qquad (1)$$

Where D_i is the gas-phase diffusion coefficient of condensable gas *i* ($m^2\ s^{-1}$), N_j is the number concentrations (m^{-3}) of particle *j* with diameter d_j (m), β_m is the transitional correction for the condensational mass flux, and is a function of the Knudsen number K_{nj} ($= 2\lambda/d_j$) and the mass accommodation coefficient α, given by Fuchs & Sutugin (1971), with $\lambda = 6.8\text{x}10^{-8}$ and α =0.1 in this study."

The plot showing the condensation sink for PBE and non-PBE days was added to Figure 4.



This is now discussed in the revised manuscript:

"The condensation sink (CS) values range from $3\text{x}10^{-3}$ to $7\text{x}10^{-3}$ s^{-1} (Figure 4e), and are typical of forest areas (Dal Maso et al., 2002). The PBE days show slightly (~ 1.7 times) higher CS values (Figures 4e and S2) than Non-PBE days before the start of PBEs. During PBE days, the CS values decrease to their minimum around midday, which is generally the PBE onset time, and then progressively increase due to the growth of the ultrafine particles to larger sizes."

R1-7) *Fig. 3: Because SO2 data are available, authors could use the statistical proxy from Mikkonen et al. (2011) or Petäjä et al. (2009) to estimate the sulfuric acid concentration. Petäjä, T., Mauldin, III, R. L., Kosciuch, E., McGrath, J., Nieminen, T., Paasonen, P., Boy, M., Admov, A., Kotiaho, T., and Kulmala, M.: Sulfuric acid and OH concentrations in a boreal forest site, Atmos. Chem. Phys., 9, 7435–7448, 2009. Mikkonen et al.: A statistical proxy for sulphuric acid concentration, Atmos. Chem. Phys., 11, 11319–11334, 2011.*

Response R1-7) To calculate sulfuric acid we need to know not only SO_2 but also OH concentrations. Unfortunately during the considered study period OH measurements were not available. This is now explained in the revised manuscript: "**Sulfuric acid concentrations could not be estimated for this study as OH measurements were not available during the time period considered**."

R1-8) *Sections 4.2, 4.3, and 4.4: It is very difficult to capture the authors' points on comparison study using the model simulation. The reviewer strongly recommends restructuring the sentences so that readers can easily understand the results and interpretations.*

Response R1-8) We have made substantial changes to the revised manuscript in sections 4.2, 4.3 and 4.4 so that the discussion is easier to follow.

R1-9) *P5631, L17-20: Authors mentioned that WRF-Chem is not available to simulate new particle formation in a forest site in this study in section 4.2. Thus, how reliable the predicted contribution of nucleation to surface CCN concentrations is in section 4.4?*

Response R1-9) We believe that the reviewer is referring to the Ref-8bins sensitivity simulation. This simulation is based on the WRF-Chem default version, which includes the new particle formation parameterization (Welxer et al. 1994) but is not representing particles smaller than 40nm, which are typically formed by nucleation. We think that it is of great interest to show how the predictions of the default WRF-Chem configuration compare for both number concentrations and CCN to the results of a more sophisticated version of the model developed in this study that can explicitly simulate the growth of nucleated particles in sizes 1-40nm. The default version is the publicly released WRF-Chem setup widely used in the community for various studies including aerosol-cloud interactions (WRF-Chem version 3.5 User's Guide, http://ruc.noaa.gov/wrf/WG11/Users_guide.pdf).

The limitations of the default WRF-Chem simulation (Ref-8bins) in simulating CCN are now more clearly explained in the manuscript:

"The comparison of average diurnal profiles of observed and predicted kappa values during APE and Non-APE days (Figure 6g-6h) shows that the Nucleation-bsoa run improves simulations of hygroscopicity compared to the model default simulation Ref-8bins. In both the Nucleation-bsoa run and measurements, Kappa

values vary from ~0.05 to 0.2 during APE and Non-APE days, and these values are typically a factor of two lower than the default model simulation (Ref-8bins) which doesn't account for the formation of secondary organic aerosols."

Wexler, A. S., F. W. Lurmann, and J. H. Seinfeld (1994), Modeling urban and regional aerosols. I. Model development, Atmos. Environ., 28, 531–546, doi:10.1016/1352-2310(94)90129-5.

Minor comment

R1-10) Abstract, L7: Please define the size range of Aitken mode.

Response R1-10) We have renamed APE events as explained in Response R1-1, and we have defined the size range of Aitken mode particles in the abstract of the revised manuscript as shown bellow:

"[..] and to explicitly simulate the subsequent growth of Aitken particles (10-100 nm in diameter) by condensation of organic and inorganic vapors."

R1-11) Abstract, L10: Ultrafine particles are particles having diameter of smaller than 100 nm. It would be better to express particles having diameter of 4-30 nm as nucleation mode particles?

Response R1-11) thanks, as Response R1-1, R1-10, we decide to use PBEs (small particle burst events) to describe the characteristics of observed 4-100nm particles burst events. Sentences in the revised manuscript read:

"In the current study, we define the term "small Particle Burst Event" (PBE) to describe the appearance and growth of particles that are larger than 4 nm in diameter in contrast with typical nucleation events that include particle diameters as small as 1 nm. Here PBEs refer to both nucleation-mode particles (< 10nm) and Aitken-mode particles (10-100nm)."

R1-12) P5631, L17-20 and P5614, L2: The contribution of nucleation to surface CCN concentration. 67% or 65%, which one is correct?

Response R1-12) We thank the reviewer for catching this error. We have corrected it to 67% in the revised manuscript in the following sentence:

Abstract: "We estimate that nucleation contributes to 67% of surface CCN at 0.5% supersaturation in this pine forest environment. "

Sec 4.4: "Comparing the results of Nucleation-bsoa with Nucleation-off during the two simulating periods, we find that the nucleation explains 67% of near-surface CCN (0.5% SS) concentrations at the MEFO site. […]"

Response to Referee #2:

We thank the reviewer for his/her comments and hope we could respond to them in a satisfactory manner.

Major comment

R2-1) *The scientific approach and applied methods seem valid, and the authors have done a good job in investigating several different aspects that may influence the growth events. However, for a manuscript to be published in ACP it needs to include "substantial new concepts, ideas, methods or data". The authors need to state clearly in the introduction what is novel in their approach compared to the existing literature. The manuscript is reasonably well written in most sections, although some paragraphs need to be more clearly written or require more information.*

We thank the reviewer for recognizing the merits of our study. Following his/her suggestions we have stated more clearly in the introduction what the novelties of our study are compared to previous modeling studies. First, we are investigating the role of anthropogenic pollution on the formation and growth of ultrafine particles in an environment representative of urban-rural interface regions. More and more people live in these areas (e.g. the Colorado Front Range, the Alps), and it is currently unclear how the urban activities are changing the formation patterns of ultrafine aerosols and what the consequences for CCN concentrations are. Ultrafine particle formation events have been rarely investigated in these areas, especially in the terpene-rich forest environments. This is now explained in the manuscript:

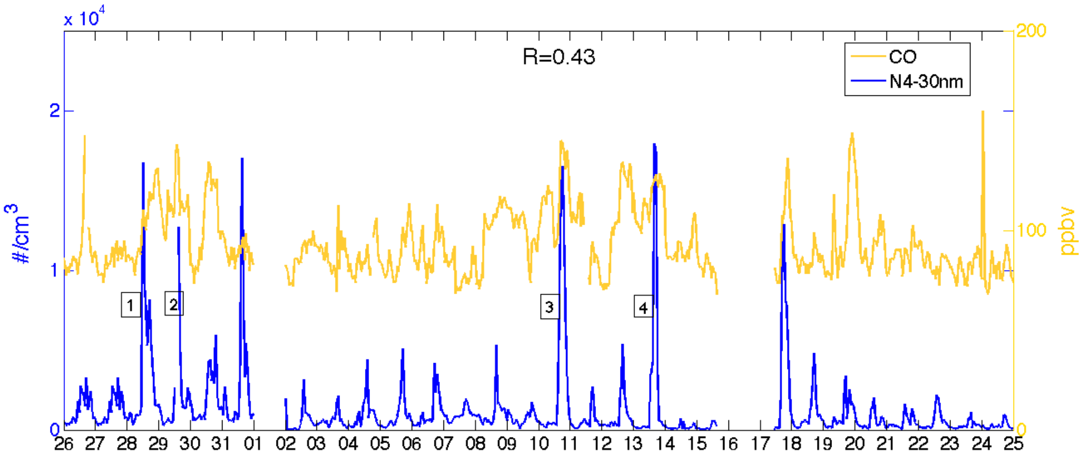
"Understanding how forest environments respond to the inflow of pollutants from the nearby cities is of great scientific interest as more and more people live at the forest-urban interfaces. Jung et al. (2013) showed that the inflow of urban air masses could favor the initiation of the burst of nucleation mode particles in an isoprene-rich deciduous forest in Northern Japan. This study will focus on terpene-rich forests which have been comparatively less studies.. The Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H2O, Organics & Nitrogen (BEACHON, Ortega et al., 2014) field program collected long-term measurement of trace gases, aerosols and meteorological parameters at the Manitou Experimental Forest Observatory (MEFO), which is located within the semi-arid ponderosa pine forest in the Colorado Front Range. The site is representative of an urban-rural interface and provides a unique opportunity to study aerosol formation in a monoterpene-rich environment that is periodically influenced by the inflow of anthropogenic pollution from Denver and Colorado Springs (DiGangi et al. 2012; Fry et al. 2013; Ortega et al. 2014)."

In addition, our study uses the online-coupled chemistry-transport model at high spatial resolution (4km) to simulate these episodes. The online models are rarely used to study nucleation events, and they have the advantage of simultaneously treating emissions, chemistry and meteorology, and therefore are better suited for predicting the feedbacks between aerosols and clouds than offline models. This has been added to the new manuscript:

“The online WRF-Chem model is particularly well suited for this study as it simultaneously treats biogenic emissions, chemistry and clouds.”

R2-2) *It would be interesting to see the correlations of N4-30 nm with NOx and CO since these are tracers for primary emissions. Furthermore, I think NOx and CO (or at least one of these) should be added to Fig. 3. If NOx or CO is higher during APEs, it is likely that primary aerosol particles contribute to the “inflow of anthropogenic pollutants” and to the APEs.*

We agree that CO and NOx are good tracers of anthropogenic emissions, and high CO is correlated well with N4-30nm during the four PBE events under study here (see figure below). These results are similar to SO2, which we already plotted in Figure 4 and discussed in the paper. As suggested by the reviewer we added the comparison of diurnal profiles of CO between PBE and Non-PBE days to Figure 4. As expected, we find higher values of these variables during PBE days.



However, this doesn’t indicate that the primary emitted aerosols from anthropogenic sources significantly contribute to N4-30nm. These primary aerosols are typically emitted into larger sizes (e.g. 30-40 nm for the traffic emissions, Brines et al. 2014). For instance, in the WRF-Chem model we assume that the primary aerosol emissions follow a lognormal distribution with a median diameter of 50 nm and a standard deviation of 2nm, thus particles with sizes below 30 nm can only be generated by nucleation.

This is now explained in the manuscript: **“CO levels are also higher during PBE days, which confirms that the MEFO site is influenced by the inflow of anthropogenic pollutants. The contribution to N4-30nm of primary particles transported from the Front Range is however expected to be minor as anthropogenic emissions typically occur in larger size ranges (30-40 nm for traffic, Brines et al. 2014).”**

R2-3) *One issue that needs to be discussed more thoughtfully throughout the manuscript is the increase in CCN concentration during the APE events. For instance on page 5624, lines 9-10, the authors write "that nucleated particles had a few hours to grow before arriving at the measurement site". In the Conclusions section, the authors write "SO2 plumes advected from the Colorado Front Range combined with biogenic monoterpenes significantly affect particle number concentrations and CCN during APEs ". It is very unlikely that aerosol particles, containing large amounts of organics, activate at a supersaturation of 0.5% if they are smaller than 50 nm (see e.g. Fig. 1 in Dusek et al. (2006)). Given the observed growth rates of 2.3 nm hr-1, it would take ~22 hours for the particles to reach a diameter of 50 nm. Therefore, the increase in CCN concentration during the afternoons on APE days cannot be associated with the growth of particles that were nucleated only a few hours away. To me it seems that the higher CCN concentrations on APE days are not a result of the APEs themselves but rather a result of higher monoterpene and SO2 concentrations on APE days (Figs. 3a-b) resulting in enhanced growth of pre-existing particles. In Fig. 3e it is clear that concentrations of particles larger than 70 nm are also higher on APE days than on Non-APE days.*

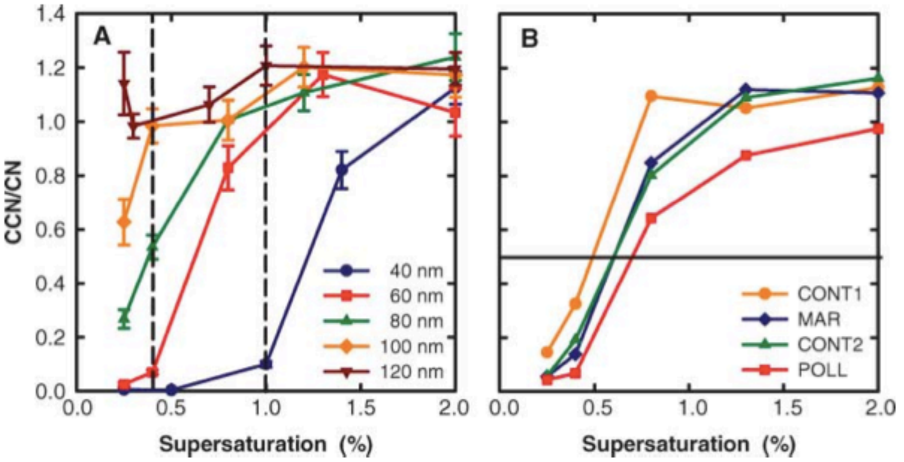


Fig. 1. **(A)** An example of size-resolved 6-hour averaged CCN spectra for particle diameters between 40 and 120 nm. Sixteen individual spectra have been averaged for each diameter. Error bars correspond to 95% confidence intervals of the mean. Vertical lines indicate the *S* values of 0.4 and 1% for which CCN size distributions are derived. CCN/CN ratios that are higher than 1 are due to a small bias in the calibration of the sensing volume, which probably changed slightly during the transport of the instrument to the field site. **(B)** The CCN spectra of particles with d_p = 60 nm are compared for different air mass conditions: CONT1 represents aged industrial pollution, MAR aerosol with Atlantic origin and short transport times over land, CONT2 rural continental aerosol, and POLL urban aerosol after a few hours of aging.

We agree with the reviewer that particles smaller than 50nm are unlikely to activate as CCN at 0.5% SS as shown above (Fig. 1 in Dusek et al. (2006)), and that the increase in CCN at 0.5%SS is not due to local nucleation events, but rather to the growth of pre-existing particles. We have clarified this discussion in the revised manuscript:

“Measured CCN (0.5% SS) number concentrations at the surface are also up to a factor of two higher during afternoon hours on PBE days compared to Non-PBE days (Fig 3d). A sharp increase in CCN is observed in the afternoon, typically three hours after the start of PBEs. It should be noted that only particles larger than ~60nm are likely to activate at 0.5% SS (Dusek et al. 2006). Given the observed growth rates of 2.3 nm hr^{-1} (Table 1), it would take >20 hours for freshly nucleated particles to reach a diameter 60nm. Therefore, the higher CCN concentrations on PBE days are likely the result of the enhanced growth of pre-existing particles.”

From the comparison of our best simulation (Nucleation-bsoa) and the default WRF-Chem configuration (Ref-8bins) which doesn’t account for sub-40nm particles, it appears that sub-40nm particles and their growth to larger sizes (>60nm) that can activate at 0.5% SS significantly contributes to CCN. This was also added to the revised paper:

“The Nucleation-bsoa simulation reproduces more accurately CCN (0.5% SS) concentrations than the Ref-8bins run, especially during PBE days. This difference suggests that sub-40nm particles and their growth to larger sizes (>60nm) that can activate at 0.5% SS significantly contributes to CCN.”

The conclusion was updated to read:

“Considerable differences between PBEs and Non-PBEs indicate that pollution plumes rich in SO2 and primary particles that were advected from the Colorado Front Range combined as well as the enhanced biogenic monoterpenes concentrations significantly affect particle number concentrations and CCN during PBEs.”

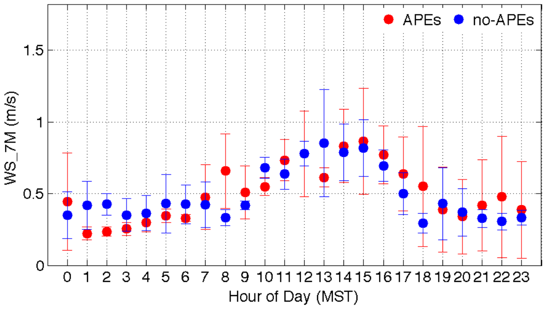
R2-4) *Page 5623, line 28 to page 5624, line 3: This paragraph needs to be more clearly written. On page 5623, line 28 it is written: “Jung et al. (2013) compared APE burst time and particle number size distribution at an urban site and a forest site, and found that late APE burst time and broader particle number size distributions were observed at the forest site than at the urban site. Figure S1 shows similar results for this study.” To me it is not clear how you can observe in Fig. S1 what Jung observed. What time periods are the different size distributions in Fig. S1 averaged over? Do these size distributions represent the beginning of the APE events or the whole events? The following sentence: “These characteristics imply that several hours are needed for urban plumes to reach the site and that new particle formation is happening most likely hours away from the site”. Are these conclusion drawn from Fig. S1?*

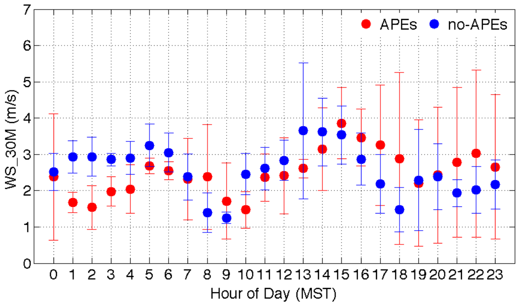
We agree with the reviewer that the comparison with Jung et al., 2013 was misleading, and we have simplified and clarified the manuscript to read:

“The PBEs at the MEFO site typically started around noon and early afternoon (10:20–15:00 MST, Table 1) following a shift in wind directions generally to the east (Fig 5a). This late onset time was reported for other forest sites (Jung et al. 2013).”

"The observed number size distribution during these PBE days (Fig S4) shows a relatively broad distribution similar to previous study performed in an anthropogenically-influenced forest (Jung et al. 2013). Figure S4 also shows the absence of particles smaller than 5nm. Especially in August (Fig. 7a), particles smaller than 10 nm were almost never observed, suggesting that nucleation likely occurred in upwind areas or in the free troposphere, and that freshly nucleated particles grew for several hours before reaching the measurement site."

R2-5) *Page 5622, lines 22-23: "Significantly higher mean values are observed during APE days for both monoterpenes and SO2". The authors link the higher SO2 concentrations to "anthropogenic inflow" and on next page to air masses from industrial sources located in the Colorado Springs area, but what is the reason for the higher monoterpene concentrations when advection is from these areas?*





We checked the wind speed at 2m, 7m, 16m, and 30m, we found during APE days, nighttime wind speeds were lower than non-APE days, which could accumulated more monoterpene during APE days.

Minor comment

R2-6) *Page 5629, lines 22-23: "clear difference in the relative abundance of sulfate during the APE (63%)...". Was this the case also for other APE days than 10 August?*

Unfortunately we didn't have measurements to verify if this was also the case for other APE days.

R2-7) *Page 5617, line 20: What instrument was used to measure the CCN concentrations?*

We added it to the revised manuscript. " **Size resolved CCN measurements made with TSI 3071 DMA followed by DMT CCNC and TSI 3010 CPC (Levin et al. 2012, 2014)**".

R2-8) *Larger fonts are needed in Figs. 5, 6, 7, and 9.*

Thanks, Done.

R2-9) *Page 5630, line 12: should it be 10-6?*

Thanks for catching this error. We have corrected it in the new manuscript.

Response to Referee #3:

We thank the reviewer for his/her comments and hope we could respond to them in a satisfactory manner.

Major comment

R3-1) *Abstract: What is the size range used as Aitken mode in the study? Does it refer to the size range 4 – 40 nm in the manuscript? There is not an exact size range defined for Aitken mode particles, however, particles below 10 nm should not be included as Aitken mode.*

We have removed this confusion from the paper (see Response R1-1). In the revised manuscript, we use the term **small Particle Burst Event" (PBE)** to refer to the 1-100nm diameter particles for the model simulations, and 4-100nm diameter particles for observations which could not detect particles below 4nm. This is now explained as:

"Measurements of ultrafine particles, their precursor gases, and meteorological parameters were performed in a ponderosa pine forest in the Colorado Front Range in July–August 2011, and were analyzed to study processes leading to small Particle Burst Events (PBEs) which were characterized by an increase in the number concentrations of ultrafine 4-30 nm diameter size particles.

In the current study, we define the term "small Particle Burst Event" (PBE) to describe the appearance and growth of particles that are larger than 4 nm in diameter in contrast with typical nucleation events that include particles as small as 1 nm. Here PBEs refer to both nucleation-mode particles (< 10nm) and Aitken-mode particles (10-100nm)."

R3-2) *P5616, Line 5-10: MBO is mentioned here as the dominant VOC emissions at the site. Since previous studies have indicated possible contribution to particle growth by MBO (e.g. Arthur et al. 2009). It would be good to include the contribution from MBO.*

We agree with the reviewer that recent studies identified MBO as a potential contributor to SOA formation. Zhang et al. 2014 showed that epoxides produced from the photooxidation of 2-methyl-3-buten-2-ol (MBO) contributed to SOA formation during BEACHON-RoMBAS with the mass yield of ~4%. The associated formation pathway is still an active area of research and is not included in the current WRF-Chem model.

However, we do include in WRF-Chem the contribution of MBO to SOA formation using a fixed yield of 4%. Indeed, in the CBMz gas-phase mechanism which is used in WRF-Chem, MBO is not treated as an explicit chemical tracer but is lumped with ISOPRENE. Therfore, the 4% yield of ISOPRENE is used to calculate the growth of aerosols from MBO. This is now explained in the manuscript:

"The contribution of MBO to SOA formation is also included with the 4% as suggested by Zhang et al. (2014)."

Zhang et al. (2014): Secondary Organic Aerosol Formation via 2-Methyl-3-buten-2-ol Photooxidation: Evidence of Acid-Catalyzed Reactive Uptake of Epoxides, Environ. Sci. Technol. Lett., 1 (4), pp 242–247.

R3-3) *P5618, Line 25: Does night time boundary layer height of 100 m representative for the site under study? Is there reference to theoretical estimates or observations of the nighttime boundary layer height at the site?*

Large uncertainties exist in the model predictions of the nocturnal boundary height due to the highly stable and stratified atmospheric conditions. In this study, we used a minimum height of 100m based on previous measurements in this same area (Choi et al. 2011) to prevent unrealistically low heights in the model simulations, which can lead to large errors in surface concentrations of pollutants. This is now explained in the manuscript:

"The nighttime minimum planetary boundary layer (PBL) height was set to 100 m in the YSU scheme based on previous studies (Choi et al. 2011) to eliminate overestimating nocturnal concentrations of primary species."

Choi, W., Faloona, I. C., McKay, M., Goldstein, A. H., and Baker, B.: Estimating the atmospheric boundary layer height over sloped, forested terrain from surface spectral analysis during BEARPEX, Atmos. Chem. Phys., 11, 6837-6853, doi:10.5194/acp-11-6837-2011, 2011.

R3-4) *P5620, Section 3.2: Activation nucleation parameterization relates the formation rate of particles at 1nm to sulfuric acid concentration. The author applied this parameterization to introduce particles of 4 – 6 nm. How much uncertainty does this miss-match of particle size introduce to the result?*

At our measurement site, particles smaller than 4.4nm were not observed, therefore we calculated the formation rate needed for the AN parameterization based on measured 4.4nm particles and H_2SO_4 concentrations. The value of $A = 2 \times 10^{-6}\ s^{-1}$ was derived and used to introduce particles into the first model size bin (1-4nm). The used value is consistent with previous studies. E.g. Sihto et al. 2006 reported $A=1.7 \times 10^{-6}\ s^{-1}$, whereas Matsui et al. used the value of $2 \times 10^{-7}\ s^{-1}$ which was a factor of 10 lower in order to offset a factor of 10 model overprediction of H_2SO_4 concentrations in WRF-Chem (so their effective A was equal to $2 \times 10^{-6}\ s^{-1}$).

The associated error is expected to be small at high H_2SO_4 concentrations, which are typical of PBE events. Indeed, Kulmala et al. 2006b showed that formation rates at larger diameters e.g. 3nm can be written as $\mathrm{J_3 = J_1 exp}\left\{-0.153\,\frac{\mathrm{CS}}{\mathrm{GR}}\right\}$. According to Weber et al. (1996) the formation rate of 1nm or 3nm particles can be expressed as a power law dependence of the sulphuric acid concentrations: $J_3 \propto [H_2SO_4]^{n3}$ and $J_1 \propto [H_2SO_4]^{n1}$. By combining the two relationships, one can derive the following equation: $\log(\mathrm{J_3}) = \log(\mathrm{J_1}) - 0.153\,\frac{\mathrm{CS}}{\mathrm{GR}} = \mathrm{n_1}\log[\mathrm{H2SO4}] - 0.153\,\frac{\mathrm{CS}}{\mathrm{GR}}$. If we assume that $J_1 \sim J_3$, the associated difference is $0.153\,\frac{\mathrm{CS}}{\mathrm{GR}}$. If we consider that GR depends on $[H_2SO_4]$, increasing $[H_2SO_4]$ will increase GR. This means that J_3 will approach J_1 at high values of $[H_2SO_4]$ which are typical of PBE events.

This is now explained in the manuscript: **"Here we estimate a representative value of A at out site based on measured H_2SO_4 and number concentrations of ultrafine particles. The H_2SO_4 measurements are available from 9 to 26 August at MEFO and indicate that the average H_2SO_4 concentration is ~ 2 x 10^6 molecules cm^{-3} during the late morning and noon. During the campaign, the smallest particles with diameters of ~ 5nm were detected at the site on July 28, and their number concentrations were used to determine the 5 nm aerosol formation rate (J_{5nm}= ~ 1 cm^{-3} s^{-1} as shown in Table 1). The rate coefficient A of ~2x10^{-6} s^{-1} was derived from those measurements, and is used within WRF-Chem for the AN parameterization to introduce particles into the first model size bin (1-4nm). We assume here that J_{5nm} is a representative value (the lower bound) of formation rate in the model first bin, which is a reasonable assumption at high H_2SO_4 concentrations typically observed during PBE days (Kulmala et al. 2006b). The derived value of A is consistent with previous studies. E.g. Sihto et al. 2006 reported A=1.7x10^{-6} s^{-1}, whereas Matsui et al. 2011 used the value of 2 x 10^{-7} s^{-1} which was a factor of 10 lower in order to offset a factor of 10 model overprediction of H_2SO_4 concentrations in WRF-Chem (so their effective A was equal to 2x10^{-6} s^{-1})."**

1. Kulmala, M., K. E. J. Lehtinen, and A. Laaksonen (2006b), Cluster activa- tion theory as an explanation of the linear dependence between formation rate of 3 nm particles and sulphuric acid concentration, Atmos. Chem. Phys., 6, 787–793, doi:10.5194/acp-6-787-2006.

2. Sihto, S.-L., et al. (2006), Atmospheric sulphuric acid and aerosol forma- tion: Implications from atmospheric measurements for nucleation and early growth mechanisms, Atmos. Chem. Phys., 6, 4079–4091, doi:10.5194/acp-6-4079-2006.

3. Weber, R. J., Marti, J. J., McMurry, P. H., Eisele, F. L., Tanner, D. J., and Jefferson, A.: Measured atmospheric new particle for- mation rates: Implications for nucleation mechanisms, Chemical Engineering Communications, 151, 53–64, 1996.

R3-5) *P5627, Line 27 –29: Figure 7b is the size distribution plot from simulation with AN nucleation and condensation of oxidation products from VOCs. Based on this figure,* *I have difficulty figuring out that the observed ultra fine particles are not due to air mass change. Could you please give more detailed explanation and possibly modify the figure? It appears to me that the airmass change may explain for a significant part of the ultra fine particles observed.*

We agree with the reviewer that the airmass change is likely responsible for the increase in ultrafine particle number concentrations that were observed at the site during August (Figure 7b). In particular, on August 13 the model starts nucleating particles locally but does not grow them. The interpretation of figure 7b was misleading. We agree with the reviewer that the appearance of larger particles in the afternoon (after 5pm MST) is due to the change in the airmass. This is now more clearly explained in the manuscript:

"During August, PBEs were characterized by larger starting diameters (>5nm) suggesting that new-particles formation occurred upwind of the site or above the PBL, and that already somewhat grown particles were transported to the site. During this period, WRF-Chem (the Nucleation-bsoa run) initiated some local nucleation but did not grow these particles beyond 4 nm on August 10, 11 and 14, and not beyond 8 nm on August 12 (Fig. 7b). Model results confirm that the sub-100 nm particles that were both predicted and observed at the site on these days were not locally generated through nucleation. Sensitivity simulations were performed for the PBE day of August 10 to investigate the contribution of the transport of pre-existing particles and of the above-PBL nucleation to predicted sub-100nm particles (Fig S7). In the first sensitivity simulation, the nucleation parameterization was turned off in the model, and the resulting simulation showed very low number concentrations of sub-100nm particles (<500 cm^{-3}, Figure 8d). In the second simulation, the binary nucleation parameterization was used above the PBL and no nucleation was used within the PBL. The results suggest that the above-PBL nucleation explained 90% of the ultrafine particles predicted at the surface on this particular day (Fig S7b). The results from combined Nucleation-bsoa and sensitivity runs suggest that locally formed new particles were not able to grow to detectable sizes, and that free-troposphere nucleated particles could have been mixed downward into the boundary layer and contributed to observed >10nm particles.

On August 13, the model starts nucleating particles locally but does not grow them to larger sizes. Larger particles are however predicted later in the afternoon (after 5pm MST) and are likely due to changes in the airmass. Local wind roses and back-trajectories (Fig S5) both suggest a shift in wind direction from southwest to southeast during that afternoon, which advected polluted air from Colorado Springs to the measurement site as already discussed in section 4.1. This change in the airmass could have brought already nucleated ultrafine particles to the site. As illustrated in Figure 8c (no-nucleation run), the contribution of primary emitted particles to simulated sub-40nm is expected to be negligible as these particles are emitted into the larger size bins (centered at 50nm diameter)."

R3-6) *What is the average time for the airmass to move from the anthropogenic* *influential area to the site of study? If the transport time is less than 10 hours, particles formed at the anthropogenic origin would arrive at the site in size range 4 – 40 nm, based on the estimated growth rate as about 3nm/h. A more detailed analysis is needed to differentiate the ultra fine particles due to local nucleation and particles due to airmass change.*

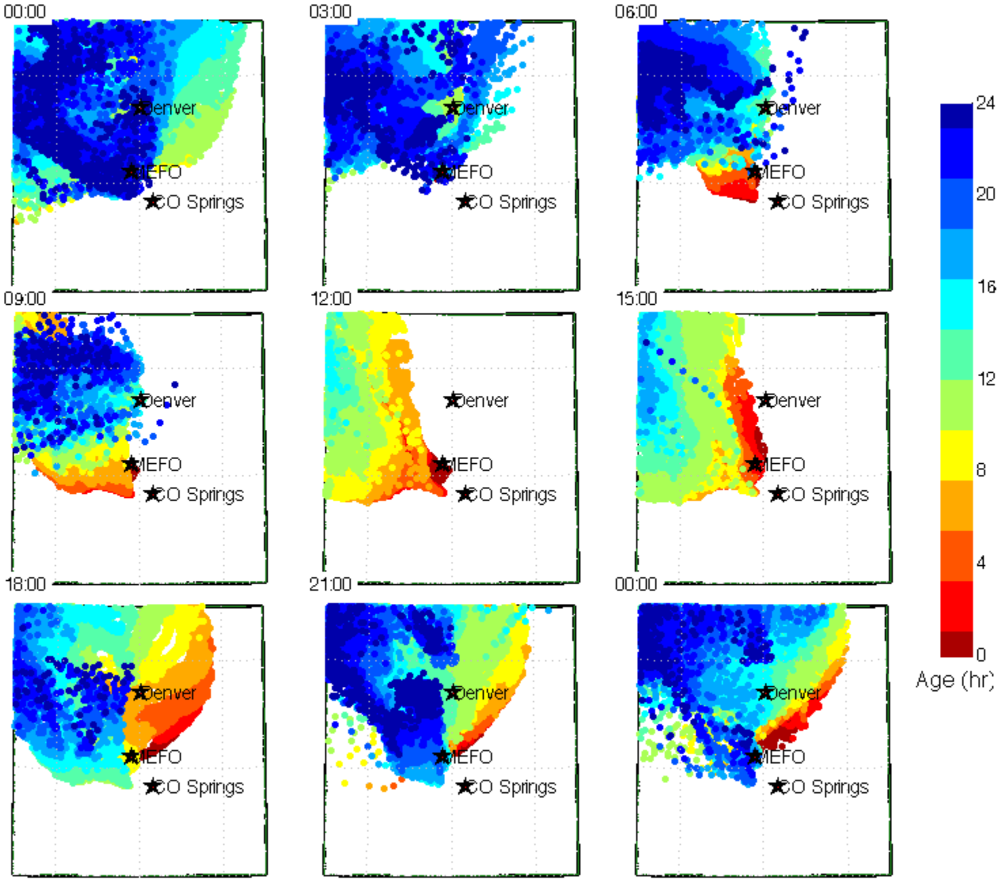
As suggested by the reviewer we used the Flexpart-WRF lagrangian trajectory model to estimate the average time needed for the air mass to be transported to the MEFO site from the nearby anthropogenically influenced areas. During PBE days, the estimated average time for the air mass to be transported from Colorado Springs to MEFO is ~4 hours, and it is 7 hours for the Denver urban area. This information was included in the revised manuscript:

"During PBE days, the estimated average time for the airmass to be transported to MEFO is ~4h for Colorado Springs, and ~7h for the Denver metropolitan area."

Also, this is now explained in the paper: **"Given the estimated transport time, and the estimated growth rates of ~3nm hr^{-1}, particles arriving from Denver would have grown by ~20-30nm during the transportation time to the site, whereas particles arriving from Colorado Springs would have grown by ~15nm. It should be noted that primary emitted particles in the model have sizes of 50nm, and would appear at the MEFO site as 70-80nm particles if they originated in Denver, and as ~ 65nm particles if they originated in Colorado Springs. Therefore their contribution to sub-40nm particles predicted at the site during PBE days is unlikely. Only particles that nucleated over urban areas and that are typically <10nm could contribute to the sub-40nm at MEFO if they were transported to the side. However, nucleation events over urban areas are not very frequent as the condensable gases preferably partition onto existing particles, which are abundant in urban areas. "**

Figures below show the 24 hours back-trajectories for the MEFO site during the four PBE days (28 and 29 July, 10 and 13 August), respectively: (1) For 28 July, back-trajectories mainly show the transport from Denver area with ~8 hours transport time to the MEFO site. Combining with Fig 3 in the manuscript, we consider PBE during that day attribute to both the local nucleation and the transport from the urban area. (2) For 29 July, there is an impact of the transport from urban areas but with relatively long time (average more than 16 hours), which we mainly consider PBE during that day contributed mainly by local nucleation. (3) For 10, 13 August, the airmass change (come from CO Springs area) impacted the MEFO with ~5 hours transport time during the daytime, combining with grow rate (~3nm hr^{-1}) and Fig 8 in the manuscript, we consider the transport from the urban area mainly and significantly contributed PBE during the two days.

28-Jul-2011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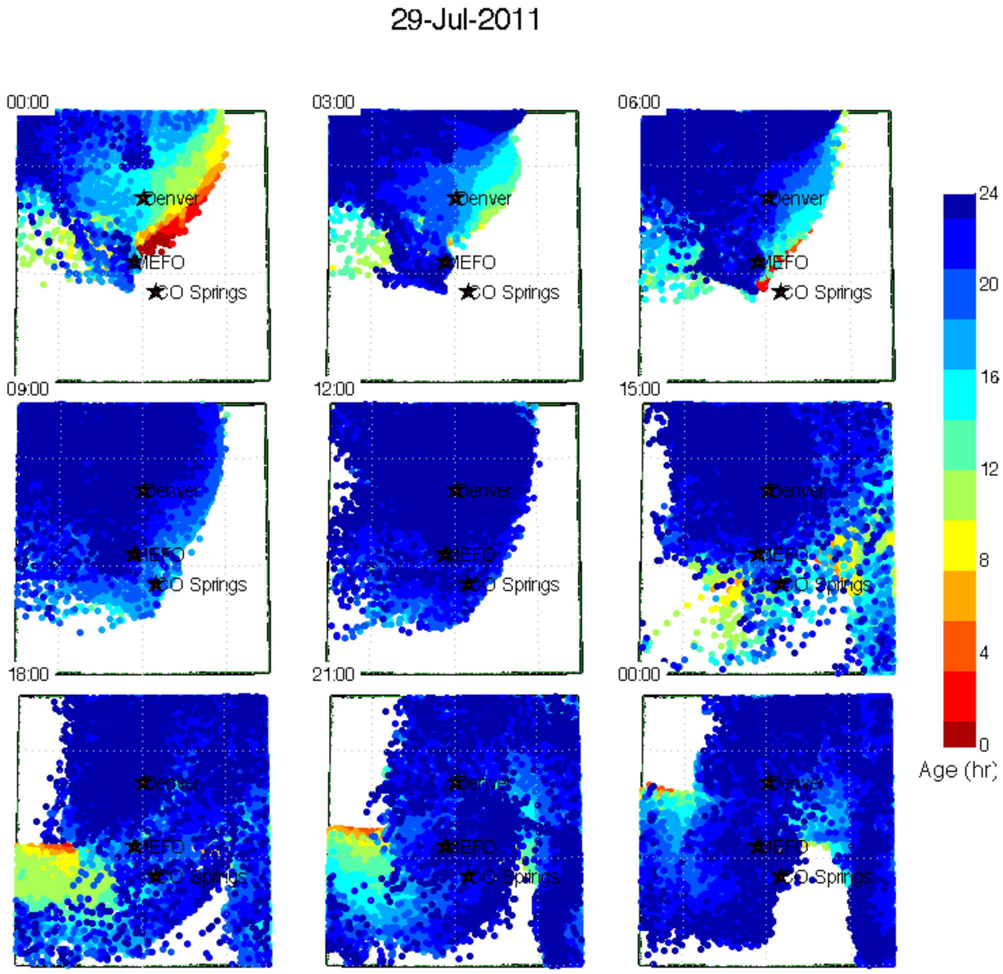
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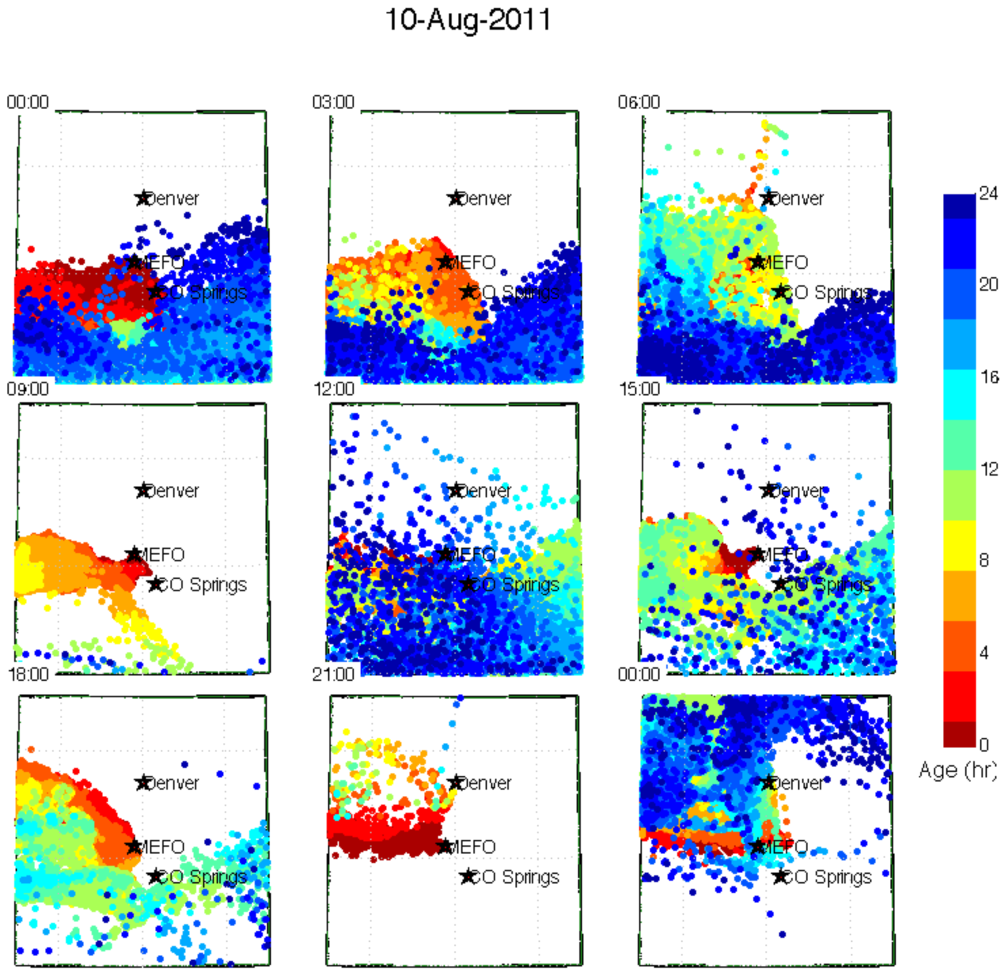
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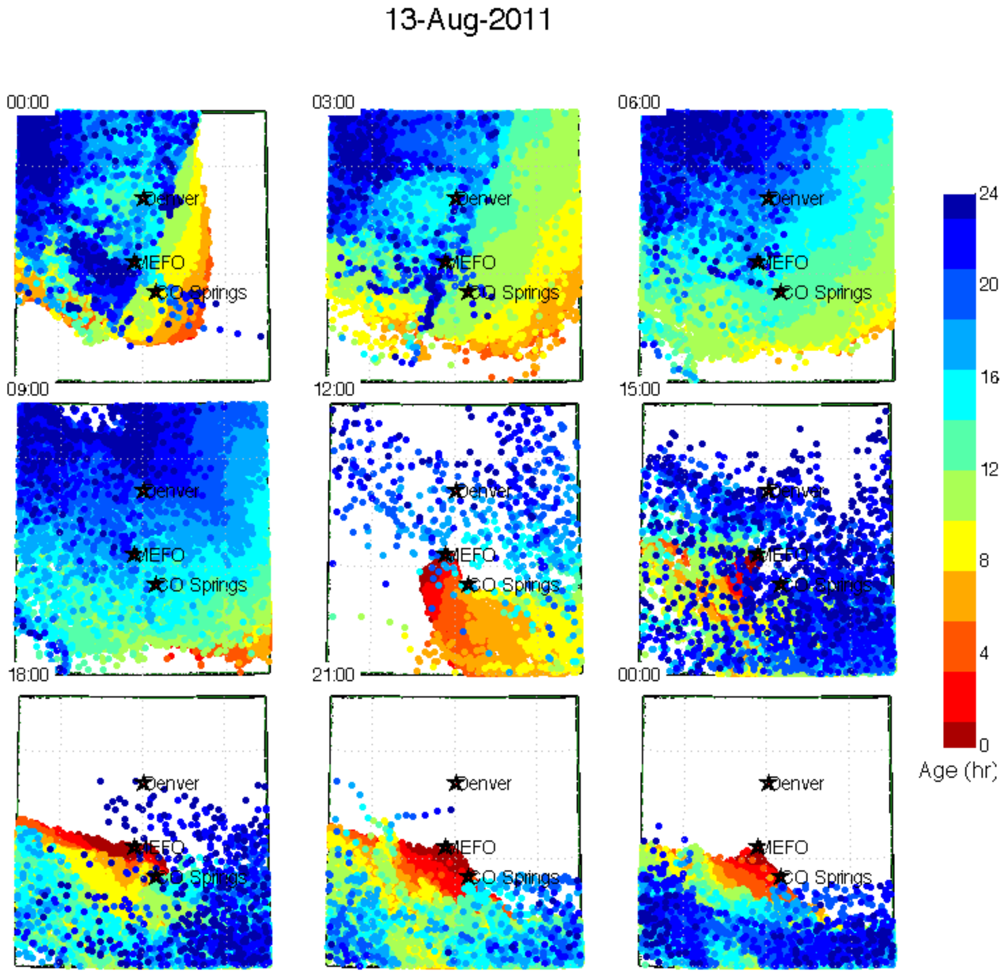

R3-7) *Fonts in Figure 4, 5, 6 are too small.*

Fonts have been made bigger in the revised manuscript.