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 #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 2×10^{-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 x 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 $J_3 = J_1 \exp\left\{-0.153 \frac{CS}{GR}\right\}$. 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: $\log(J_3) = \log(J_1) - 0.153 \frac{CS}{GR} = n_1 \log[H2SO4] - 0.153 \frac{CS}{GR}$. If we assume that $J_1 \sim J_3$, the associated difference is $0.153 \frac{CS}{GR}$. 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.*

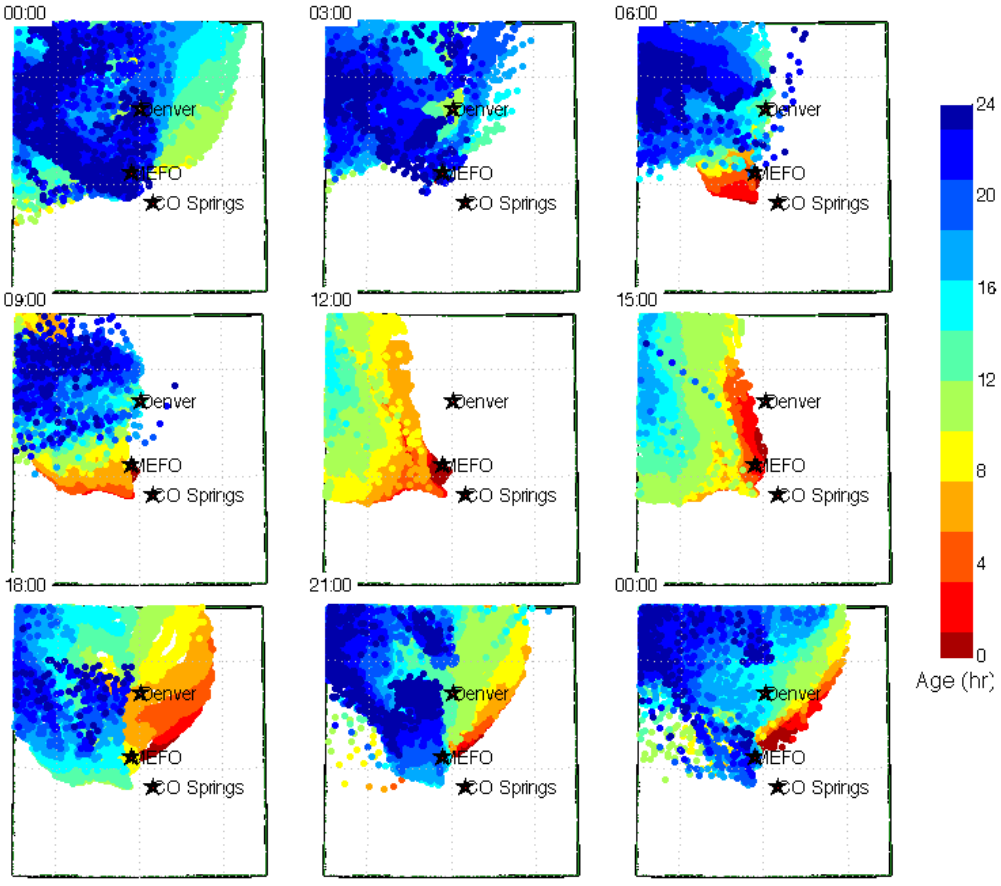
As suggested by the reviewer we used the Flexpart-WRF lagrangian trajectory model to estimate the average time needed for the air mass to be transported to the MEFO site from the nearby anthropogenically influenced areas. During PBE days, the estimated average time for the air mass to be transported 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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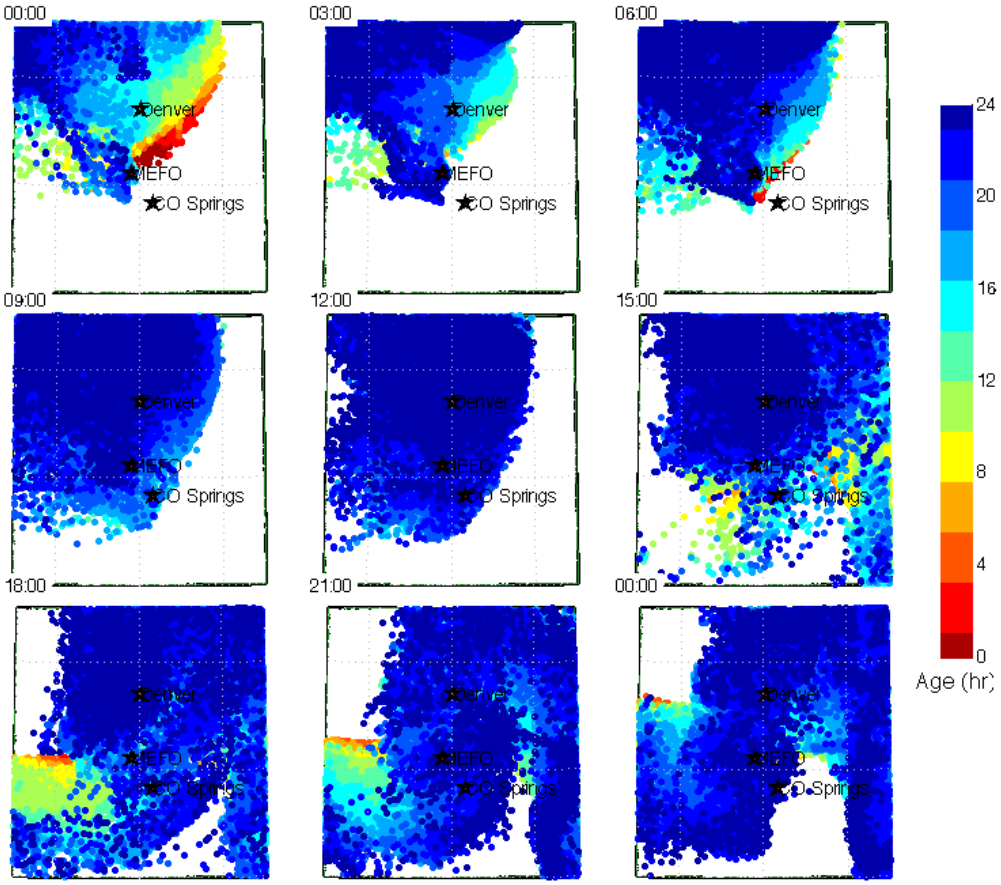
29-Jul-2011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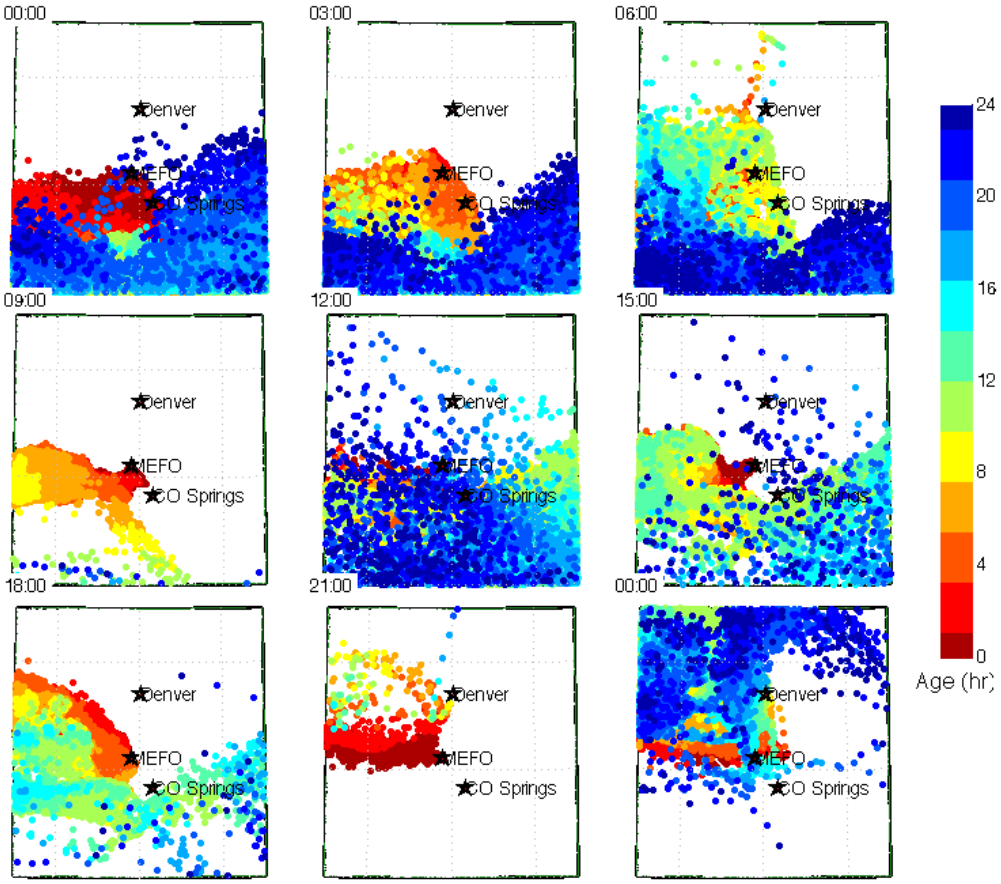
10-Aug-2011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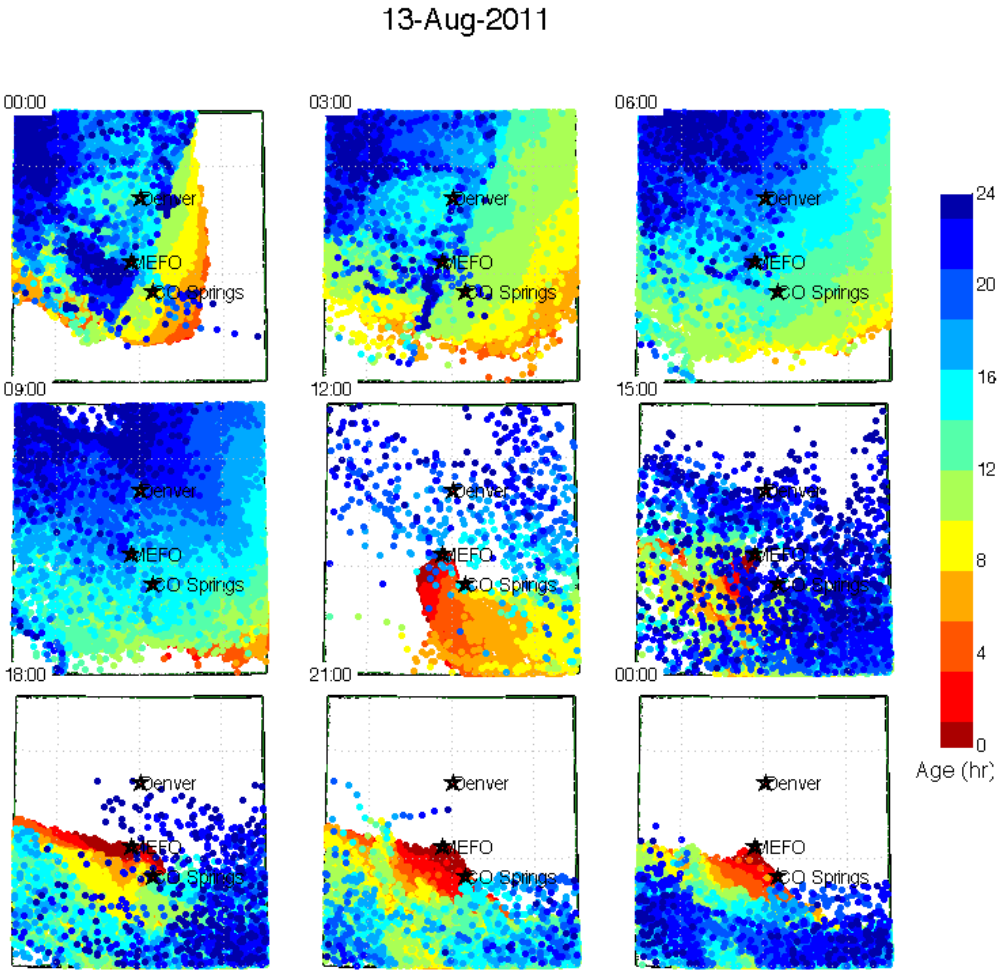

R3-7) *Fonts in Figure 4, 5, 6 are too small.*

Fonts have been made bigger in the revised manuscript.