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.

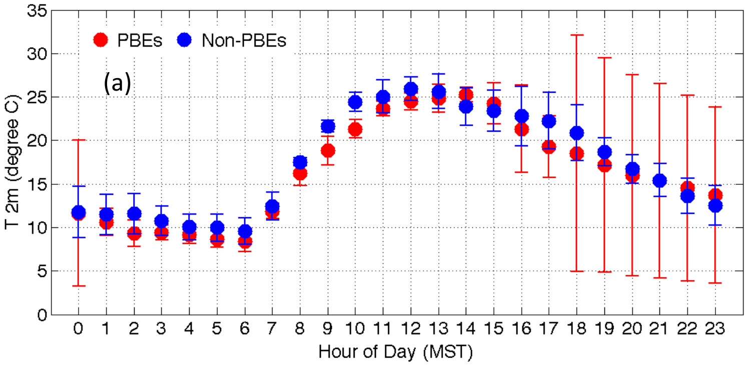
R1-4) *Fig 3: It is better to show one event day as a typical example of APEs so that readers can clearly see diurnal variations of related parameters on APEs.*

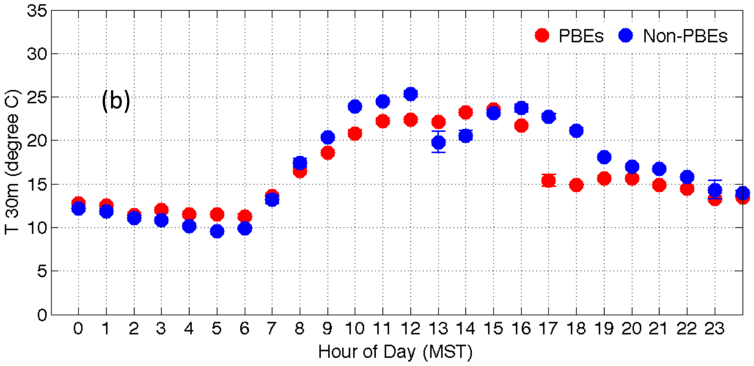
Response R1-4) As suggested by the reviewer we have added one event day (July 28) in Fig. 3 of the revised manuscript. The figure shows the diurnal evolution of the number size distributions on July 28, as well as the wind directions during that day. The following text has also been added to the revised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

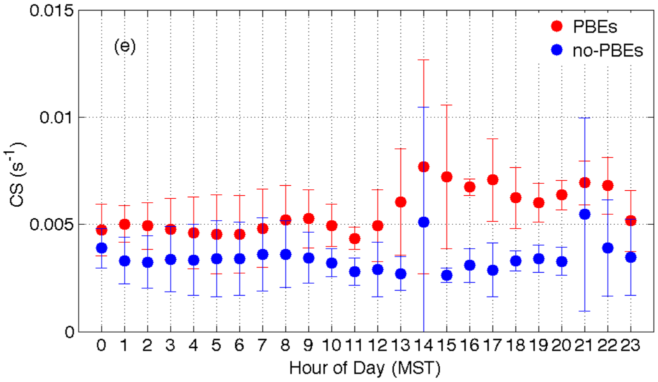
Response R1-6) We agree with the reviewer that the discussion on the role of pre-existing aerosols is of interest for this study. Therefore, we have calculated the condensation sink as described in the manuscript:

"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 $\lambda=6.8\times10^{-8}$ 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 3×10^{-3} to 7×10^{-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. […]"