Response to Reviewers for “Chemistry of new particle growth in mixed urban and biogenic emissions - Insights from CARES”

We thank the two anonymous reviewers for their comments, which have helped us to improve the paper. Our specific responses can be found below, with reviewer comments in black and our responses in blue.

Reviewer #1

This manuscript describes particle microphysical and chemical properties during new particle events (NPEs) that occurred in an urban-influenced forested site in California. The principal finding is that NPEs occurred primarily under urban transport; new particle formation and growth did not occur in the absence of an anthropogenic trigger. This finding is in contrast with the extensive work on new particle formation and growth in the forests of Finland, where no anthropogenic component is required for frequent regional NPEs. In both cases the growth is primarily due to organic composition, yet in the California case NPEs happen only when the urban plume is over the measurement site.

The manuscript is well written and of interest to ACP readers. I have some suggestions to shorten the manuscript a bit; I recommend it be accepted with minor modification.

Suggested Changes (page numbers and line numbers refer to "printer-friendly" version of manuscript):

1) The Experimental section describes the facilities at the urban (T0) site and the forested (T1) site. Nowhere is it explicitly stated that chemical composition was measured only at the T1 site, while size distributions were measured at both. This is a problem because later in the paper the chemical data are introduced without stating clearly that the measurements are from the T1 site, which caused me some confusion at first.

We already mentioned in the section 2.1 (Sampling site and instrumentation) that the AMS data was that of T1 (from page 2049 line 23 to page 2050 line 8), and that the SMPS data were from both T0 and T1 (page 2050, from line 9 to 22). However, in the revised manuscript, we have added a sentence in the Experimental section to further clarify this point.

2) P. 2051, lines 5-12, there is a discussion about thresholds for discriminating "strong" from "weak" NPE cases. There is no mention of the time required for the stated increase – is it 800 particles/cm^3/hr? Why is this inconsistent with the number increase shown in Table 1, where the "strong" and "weak" cases are shown? This needs to be clarified both here and in Table 1.

Indeed, our classification does not take into account the time needed for the increase of the particle concentration. The threshold to consider an event as NPE is an increase by 800 #/cm^3 (not 800 #/cm^3/hr), while the threshold between “weak” and “strong” NPE is an increase by 1500 #/cm^3. In this classification, we consider only particles in the range 12-20 nm (in D_m). We agree with the reviewer that the discussion is confusing, because the classification of “strong” and “weak” events presented in the text does not correspond to the data given in Table 1 (ΔN, expressed in #/cm^3/hr). Therefore, we renamed the two columns “ΔN” in Table 1 as “ΔN/Δt, and we included two new columns corresponding to $\Delta N_{12\text{-}20\ nm}$, which is consistent with the discussion in the text.

3) At several locations in the paper (e.g., p. 2051, line 14), the word "mode" is used in place of "modal diameter" or "number geometric mean diameter". "Mode" means the entire aerosol population in a given size range. Please search and correct throughout the text.

We thank the reviewer for pointing this out. We now use the term “modal diameter” throughout the manuscript.

4) p. 2052, line7, it's not clear that these NPEs occur on a regional scale. They are occurring in the urban center and at a downwind site; does this constitute "regional scale" or "plume scale"?

T0 and T1 are separated by ~40 km. The fact that the SMPS data showed "banana shapes" at both locations suggests that these NPEs occurred on a regional scale.

5) p. 2052, line 16. Are the differences in the growth rates at T0 and T1 statistically significant?

We performed a Student's t-test to check the significance of the mean values of the growth rates. The difference in the mean growth rate at T0 (7.1 ± 2.7 nm h^{-1}) and T1 (6.2 ± 2.5 nm h^{-1}) is indeed not statistically significant (i.e., $p>0.05$). However, it is generally true that the growth rate at T0 is higher than at T1 for individual days. This point is now clarified in the manuscript.

6) p. 2053, line 1. Use "T0" and "T1" consistently instead of "Cool" and "Sacramento".

Done.

7) p. 2053, line 7. A nucleation mode is smaller than 10 nm; you are measuring the Aitken mode.

We corrected this point in the manuscript.

8) p. 2053, line 19. By agglomeration do you mean coagulation? Self-coagulation rates are probably very low; growth in the Aitken mode is vastly dominated by condensation in these circumstances of rapid diameter increase.

We agree that coagulation rates are likely very low during these events. We included it in the manuscript and correct the sentence.

9) Recommend removing Fig. 3, as it shows the same information as in Fig. 2. Do you really need both?

We thank the reviewer for this suggestion, but we think that size distributions shown in Fig. 3 are still useful to visualize more quantitatively the apparition of the Aitken mode at 9:00 (T0) and at 11:00 (T1), and also the difference of particle concentrations at the two sites. Therefore, we prefer to keep this figure in the manuscript.

10) p. 2054, it would be very useful to show the condensation sink term on one of the diurnally averaged plots, like Fig. 4 or Fig. 5. The sink term may play as big a role in determining NPEs as does the source term.

We now include the diurnal patterns of condensational sink in Fig. S4.

11) p. 2059, lines 5-8. The compounds you list are not semivolatile and will not partition to the particle phase. They are rather markers of oxidation that are probably correlated with condensable compounds.

We thank the reviewer for pointing this out. The sentence has been modified accordingly.

12) p. 2059 lines 14-18. You haven't shown that the differences in these compounds between NPE days and non-NPE days are significant. The standard deviations certainly overlap. Use "significantly" only when you've done the statistical testing to verify.

Standard deviation indicates the spread of the data points from the mean. Since ambient concentrations vary from time to time, the fact that the (mean ± standard deviation) values for NPE and non-NPE days overlap doesn't necessarily indicate the differences are statistically insignificant. We thus performed Student's t-test and determined the significance of the mean values. Among the anthropogenic species mentioned on p. 2059 lines 14-18, the difference between NPE and non-NPE is significant (i.e., $p<0.05$) for BC, CO, HOA and toluene. NO_x is the only species for which the mean values are not statistically different. We have revised the texts accordingly.

13) p. 2059 line 26 through p. 2060 line 13. This is a long discussion for a very minor issue (RH); can it be shortened to, "there was no evident relationship between measured RH and particle growth rates or the occurrence of NPEs"?

In response to the reviewer's comments, we have shortened this paragraph in the revised manuscript. However, we think that this discussion is important, because previous studies already focused on the influence of RH on nucleation events, and for the moment, the role played by RH on these events is not clear yet.

14) p. 2061 line 24, again, are these growth rate differences really significant?

Based on Student's t-test, the differences in the mean values of the growth rates at T0 and T1 are not statistically significant. We have revised the text accordingly.

15) Figure S5. It would be nice to add a trace of CO to one of these plots so that we can see the urban influence in a non-aerosol tracer. Ozone is good but is secondary and regional, while NO_x gets converted to NO_y and is not a great tracer.

The time series of CO is now included in this graph.

Technical Edits:

1) p. 2058, "NPE events" should just be "NPEs".

We replaced "NPE events" with "NPEs" throughout the manuscript.

2) References, several place names (e.g., Texas, New England) need to be capitalized. Please thoroughly check the references for typos; I have not.

We checked all the references, and corrected the place names.

3) Table 1, column labeled "deltaN" is inconsistent with text describing the "strong"/"weak" classification. Is this a different particle size range than described in the text? Please state what this variable is.

In Table 1, ΔN corresponds to the difference of the particle concentration between the end and the beginning of the growth, normalized to the time, and takes into account all the particles in the range 12-737 nm (for both T0 and T1). We have revised Table 1: 1) rename these two columns to "$\Delta N/\Delta t$" and 2) include two new columns corresponding to "$\Delta N_{12\text{-}20\ nm}$". Our classification of "strong" and "weak" events is based on $\Delta N_{12\text{-}20\ nm}$, thus the discussion in the text and the data in Table 1 are now consistent.

4) Fig. 6 caption, state clearly what the lines+symbols are.

We have clarified in the figure caption that the stacked curves correspond to the % contribution (left axes), while the lines+symbols correspond to the total masses (right axes).

5) Fig. 9 caption. You don't need to define NPE here again. Missing the right-hand column of graphs (d-f)!

We apologize for the wrong figure caption, which refers to a previous version of this graph. We corrected the figure caption.

6) Change "NPG" to "NPE" in this figure.

Done.

7) Supplemental material p. 2, line 22. Define "PToF".

Done.

8) Supplemental material p. 2, line 23. Change "data of ammonium was" to "data of ammonium were".

Done.

9) Figure S1. I have no idea what the various lines, symbols, and bars on this figure mean, or what it's supposed to show. Is this only for those who process AMS data?

We now include a legend on this panel to explain what the various lines mean.

Reviewer #2

This paper discusses aerosol observations during June 2010 at two Californian sites: an urban site in the Sacramento, CA and a rural site about 40 km northeast of Sacramento. The observations focus on the growth of newly formed particles observed on several days at both sites, the connections between the sites and the chemistry of the particles. The new particle growth events are found to be associated with the transport of the aerosol from the urban area towards the rural site. The authors suggest that most of the growth was due to anthropogenic SOA, and there is a link between the growth event and the presence of amines in the particles. The consistency between the AMS mass concentrations and MPSS volume concentrations down to near 30 nm VAD is remarkable (Fig. 8). The presentation is well done. I have a few minor comments for the authors.

Specific comments:

1) I believe that SMPS is a trade mark of TSI, and thus the authors may wish to avoid its generic use here. Why not use MPSS?

We followed the suggestion of the reviewer and used the term "MPSS" throughout the manuscript.

2) Was the AMS lens a standard lens or is it a new design? It is unclear from Setyan et al (2012). What is the reference for its characterization?

The aerodynamic lens of our AMS is a standard lens, described in Zhang et al. (2004). It is now included in the revised paper.

3) Page 2015 – Are all the distributions for which you are estimating the mode diameters log normal?

Yes, the mode diameters are always determined with log normal size distributions. We clarified this point in the manuscript.

4) Page 2052, line 25 - Page 2053, line 5 – How do your growth rates depend on your somewhat arbitrary definition of "when the growth significantly slows down"? Increased biogenic precursor concentrations could result in larger growth rates. The growth rate in a biogenic environment also depends on the volatility of the condensing material, a point discussed by Riipinen et al (ACP, 2011), Pierce et al (ACP, 2011), Pierce et al (ACP, 2012) and most recently in a Nature publication. These additional points should be mentioned here.

Typically, the growth rate is quite linear during the first 2-3 hours, then it slows down by a factor of ~50% during the following 2-3 hours, and decreases to 0 nm/hr ~8 hours after the start of the observation. One reason for the decrease of the growth rate after a few hours may be due to the fact that when particles grow to a certain diameter, the condensation of additional species onto the surface of these particles will result in a very small increase of their sizes. The reviewer is right to point out that the concentration and volatility of the condensing material may also influence the growth rate. We included this discussion in the manuscript and cited the references.

5) Page 2053-2054 and Figures 2-4 – It is worth pointing out here that the delay between the two sites and the absence of particles smaller than 20 nm compared with T0, suggests that the particle nucleation occurred much near and upwind of T0 and not close to T1. In other words, the banana observed at T1 was likely independent of the emissions in the T1 area and mostly dependent on the emissions near T0 and upwind of T0. That is of course consistent with your general conclusion that the growth was dominated by anthropogenic precursors.

We agree with the reviewer, and this point is mentioned in the manuscript.

6) What about the seemingly independent mode bounded by about 11am and 5 pm and 60-100 nm in Figure 2? Was that common during the NPE days, and how did that mode influence your estimate of the composition of the 40-120 nm particles?

Particles in the range 60-100 nm (in D_m) between 11:00 and 17:00 seem to correspond to particles formed during the previous NPE. This mode was observed very often during nighttime throughout this study, as shown in the diurnal pattern of Fig. 4c. It is a bit difficult to assess the influence of this mode in the particle chemistry in the range 40-120 nm (in D_{va}), because we would need to study the particle chemistry in two different size ranges, e.g. 40-80 nm and 80-120 nm (in D_{va}). Since the PToF data of the AMS species tend to be noisy due to low duty cycle under PToF mode, it will be difficult to obtain useable results without averaging a sufficient number of size bins.

7) Page 2057, lines 12-13 – How were the cases of "dominate biogenic influence" derived?

The periods of biogenic influences were determined with the North American Mesoscale (NAM) model, and given in Fast et al. (2012). The model determined 3 periods (June 10-13, 16-17 and 20-21) during which the wind direction shifted from southwest to north/northwest, due to a trough passing over California. The northwest region of T1 is heavily forested and has a lot of agricultural areas, but without any significant urban areas. The biogenic SOA was more concentrated than the anthropogenic SOA during these 3 periods (Setyan et al., 2012).

8) Page 2057, lines 21-23 and Fig 7c – Despite the highest temperatures from 10 am to 4 pm, a 10% increase in biogenic SOA across that time is sensible compared with previous observations of BSOA (e.g. Slowik et al., 2010; Pierce et al., 2012). The spatial scales of anthropogenic and biogenic emissions are so much different, and your results seem to be an excellent demonstration that the anthropogenic components dominate on smaller scales.

We agree with the reviewer.

9) Section 3.3 and Figure 10 – Was SO_2 measured? Figure 10 appears to need an "(a)" caption.

SO_2 was not measured at T1. The caption of the (a) panel of Fig. 10 is already there (last sentence of the figure caption).

10) Page 2060, lines 6-9 – I am confused by your apparent conclusion in this sentence. Are not sunny days those that would have the solar radiation peak about noon?

During sunny days, the solar radiation peaks at noon and reaches 1000-1200 W/m^2. When the weather is cloudy, the solar radiation usually also peaks at noon, but reaches much lower values.

We modified the sentence in line 8-10, which now reads: "However, in our case, this does not seem to explain the different behavior of RH between NPE and non-NPE days, since the weather was sunny during the entire field campaign."

11) Page 2061, lines 5-15 and page 2062, lines 14-16 – If your results show that biogenic SOA was a small contributor to the growth, what is the basis for saying that growth was promoted by the interaction of urban and biogenic emissions?

T1 is located in a forested region where biogenic influences are always significantly present. As shown in Fig. 10, the average isoprene concentrations were almost identical during NPE and non-NPE days but the first generational products of isoprene oxidation (MACR+MVK) were ~ 20% higher during NPE days. Biogenic SOA, although a smaller contributor to the growth compared to urban transport SOA, its concentration was ~ 50% higher during NPE days than during non-NPE days. In addition, species representative of anthropogenic emissions, including BC, CO, benzene, and toluene, all increased by 30 – 60% during NPE days, indicating the importance of the anthropogenic influence on the occurrence of NPE events. Further, the average concentration of urban transport SOA more than doubled during NPE days. These results together indicate that the growth was promoted by the interaction of urban and biogenic emissions.

References:

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