

Interactive comment on “Submicron particles influenced by mixed biogenic and anthropogenic emissions: high-resolution aerosol mass spectrometry results from the Carbonaceous Aerosols and Radiative Effects Study (CARES)” by A. Setyan et al.

Anonymous Referee #1

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The paper summarizes aerosol composition measurements at the T1 ground site during CARES-2010. The authors have performed PMF analysis and try to determine sources of aerosol at T1 using the PMF results and different gas phase measurements. I see fundamental flaws in the analysis. When the results are reviewed carefully, they don't support the conclusions they authors try to make. Therefore I cannot accept the paper for publication as is.

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Major comments: 1) PMF results are not consistent- both in terms of the 3 factor solution and also in the interpretation of the 3 factors.

a) The HOA factor has a hydrocarbon signature in its mass spectrum, yet it has a very weak correlation with primary emission markers, correlation coefficient with CO <0.1 and with toluene, benzene, BC<0.2?! Even if HOA is related to local traffic, there should be a better correlation with CO and BC! Low concentration of HOA alone cannot explain the low correlation.

b) The two oxygenated factors don't have a consistent f44 and O/C- when the signal at m/z 44 in the mass spec is dominated by CO₂⁺, as is the case for these two oxygenated fragments, the higher the f44 is, the higher the O/C should be. This is certainly not the case here; the calculated O/C from the f44 of this factor, using Aiken et al. parameterization, comes to 0.58, which is 27% higher than what the HR-based O/C estimate is. Previous work has shown that the parameterization for O/C-f44 calculation is very good when f44 is dominated by CO₂⁺ fragment. When one considers the O/C ratio of factor 2 in the 2-factor solution (Figure S4), the parameterization also doesn't work. Therefore I believe there is something wrong with either the HR analysis of the mass spec or the PMF solutions. Also, when considering panel (d) in Figure S3 (as well as Fig. 11 (in terms of factor correlations with external tracers) and Fig. S5 (in terms of spectra correlations between the oxygenated factors)), factor 1 and factor 2 have very similar time series and mass spectra, so how realistic is it to claim a 3-factor solution?

c) c) Authors claim factor 1 (more oxidized OOA) is biogenically influenced. If so, why does it have a higher correlation with BC, toluene and CO₂ than the primary HOA component? Also, if this factor is biogenically influenced, why does it not have a diurnal peak similar to the oxidation products of isoprene (MVK-MACR)?

d) As another support for showing the influence of biogenic emissions on the 'more oxidized OOA', the authors use the f44 vs. f43 space and show that the data from

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the more oxidized OOA factor lies in the space of previous PMF factors from ambient studies with some influence of biogenic emissions. Signals at m/z 44 and 43 are common among anthropogenic and biogenic precursors and cannot be thought of a unique tracer for either of these types of sources. In fact, recent lab and ambient observations show that SOA from crude oil oxidation products also lie exactly in the area that authors suggest is indicative of biogenic-SOA! Also, $C_2H_3O^+$ and $C_3H_6O^+$ signal at m/z 43 and 58 are the dominant ion at these masses in the crude oil SOA, indicating again that such common peaks in the AMS spectra cannot be used to distinguish anthropogenic vs. biogenic influence. All we can say is that there are mildly-oxygenated fragments present in the SOA.

2) I believe interpretation of OA vs. CO is flawed and as is, it cannot be used to conclude what the influence of biogenic-anthropogenic emissions on SOA formation is.

a) Since background OA and CO could be different in different air mass types, in Figure 14 the authors should plot OA vs. CO, before background subtractions, and let the intercept of the fit take care of the background. Consider for example panel (d)-the authors appear to have forced the fit to go through zero, but the pink line doesn't represent the data points! So in such a case, one should not even interpret the value of the slope!

b) Since there are local biogenic emissions around the site, coloring panel (a) in Figure 14 with sum of the biogenic species is not appropriate. What is important is how aged the plumes have been. With warmer temperatures, isoprene emissions go up, but photochemical processing of say anthropogenic precursors is generally higher on warmer days as well. Without separating the influence of photochemical processing, we can't infer what the role of biogenic emissions has been. For calculation of photochemical age or at least to get an idea of how fresh/aged air masses are, authors say they can't use PTR-MS data because they're noisy - consider averaging for longer times to overcome this problem.

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Other comments: 1) The authors keep repeating that the northwesterly flow is biogenically influenced. Looking on the Google map, NW of the site is central valley (so more developed) while north is more forest! Also the wind rose plot in Fig. S8 indicates northerly wind is more common than northwesterly. Again the data do not support the description in the text.

2) The authors indicate that organic and sulfate are externally mixed. I think based on the AMS data, they cannot claim that. Rather, what the data show is that the larger mode particles are more rich in sulfate and the smaller mode particles are more rich in organics. However, at a given size the AMS data cannot distinguish if some particles are only sulfate and some are only organics, and therefore, we cannot conclude that particles are externally mixed. The definition of externally mixed is particles of a give size don't have the same composition. Also, the fact that SO_4 and OA are not correlated well in time (indicated in the abstract) doesn't mean they're externally mixed. That means rather that some air masses had more of a sulfate-source signature while others more of an organic-source signature. Authors should not use the expression of 'externally mixed' particles in this context.

3) Related to the size distribution discussion, the 2nd paragraph in Section 3.1.2 is very speculative. There is no indication of SO_2 or H_2SO_4 mixing ratios in the paper, so we can't tell if condensation of H_2SO_4 was causing the presence of large SO_4 particles or not. Also, as indicated in section 3.1.3, there may be a regional source of sulfate as well, so presence of sulfate in the larger mode may not be solely because of fog-processing.

4) Again, speculation on line 15 of p. 5620 when without much data authors say a lag time of 1-2 hr is needed to detect nucleation particles. Under different conditions, different lag times are needed to detect these particles.

5) Methanol in a forested area is dominantly a primary marker of biogenic emissions, not a secondary marker like acetone, as the authors say (p. 5624). Also compared to

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other OH sources, acetone in these time scales isn't a major source of OH radical.

6) In a few places, authors indicate that the site is 'downwind' of another geographical location. Since wind direction at any location is variable, between two locations, one is downwind of the other only in certain conditions! They should rather say, for example, "T1 is located ** km NE of Sacramento" .

7) Line 16-18 of p. 5622- both OOA are more volatile than sulfate despite a difference in volatility- I find this confusing. Difference in volatility of what and what?

8) I don't think authors can use the comparison to previous work on Δ_{OC}/Δ_{CO} to determine what the age of air masses sampled at T1 site is unless the same types and amount of precursors were present in air masses sampled at T1 and in air masses analyzed by de Gouw et al. or Weber et al. or Sullivan et al., but there's no proof of that here.

9) There are quite a few box and whisker plots, but we don't know what percentiles these plots refer to? 10th, 50th, 90th? Or 25th, 50th, 75th or?

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