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Atmospheric Chemistry and Physics Discussions

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 #3

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This manuscript reported the High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) results from the CARES campaign. The concentrations of organics and various inorganics as well as the size distributions measured by the AMS are presented, indicating that the non-refractory PM1 in the area is dominated by organics. SMPS data showed frequent nucleation events. The authors also performed positive matrix factorization (PMF) analysis and they resolved 3 factors, HOA, MO-OOA, and LO-OOA. It is suggested that MO-OOA is mainly biogenic SOA while the LO-OOA is

associated with urban transport. Based on the change of OA mass with respect to CO, the authors claimed that SOA formation is enhanced when anthropogenic emissions interact with biogenic precursors.

The effect of anthropogenic emissions on biogenic SOA is certainly of interest to the community. However, I have two major concerns: PMF analysis and interpretation of PMF results, as well as the interpretation of deltaOrg/deltaCO slopes in lack of photochemical age data. For the PMF analysis, I do not think that the 3-factor solution is well-justified. The time series and mass spectra of the two OOA factors (as well as each of these factors with other external tracers) are highly correlated. The HOA factor does not have good correlations with primary emission tracers, which does not quite make sense. For the assignment of the two OOA factors (urban vs. biogenic SOA), I do not think we have enough information to infer the origins of OOA based on spectral features alone as for now. It seems to me that the wind direction would be one of the strongest arguments, yet it is not clear that the MO-OOA (biogenic SOA as suggested by the authors) has higher contributions when the wind is coming from the NW/N. For the interpretation of deltaOrg/deltaCO slopes, I think this section is highly speculative given that there is no quantitative data on the photochemical age of the different air masses. The authors should re-write this section to reflect the limitations of their data and avoid over-interpreting the data.

I think this dataset would be of value to literature and eventually help with our understanding of the effects of anthropogenic emissions on biogenic SOA. However, the authors would need to address the above issues before the manuscript can be accepted for publication. Specific comments are listed below.

Specific comments:

1. Page 5610, line 7. If the air masses are mainly from either T0→ T1 transport (dominated by urban SOA) and NW winds (dominated by biogenic SOA as suggested), one would expect very different gas-phase CO2 concentrations in these air masses.

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Did the authors apply a time-dependent CO2 correction to their fragmentation pattern?

2. Page 5611, line 19. In many previous publications on AMS PMF analysis, the m/z 44 peaks were downweighted. Why are these peaks removed in this analysis instead? Did the author confirm that removing these peaks vs. downweighting does not affect their PMF results?

3. Page 5616.

a. Is there any organic interference (CH2O+) at m/z 30?

b. As the authors pointed out, the NO+/NO2+ ratio varies drastically depending on the type of nitrate compound. Based on the previous studies cited by the authors, at most they can say that the observed nitrate is not entirely inorganic, but I do not think that they can make a claim about the relative importance of organic vs. metal nitrate. The way it is written now seems to suggest a more substantial contribution from organonitrate than metal nitrate.

c. How do the authors justify their assumption that NO2+ is being completely generated by ammonium nitrate? Won't organonitrate fragment to give RO and NO2?

d. Shilling et al. (2012) is not included in the reference.

4. Page 5618. I think the discussion on the sulfate droplet mode is highly speculative.

a. I think it would be clearer if the authors discuss the size distribution data in terms of different air masses. They can move Figure 13 to here.

b. While aqueous phase chemistry is important in fog and cloud droplets, the authors did not provide any quantitative data to show that fog and low cloud events are indeed occurring during their sampling periods.

c. The amount of water present in aerosols is orders of magnitudes lower than that in clouds/fog water. Can the authors use their RH data (and/or other relevant measurements) to estimate the amount of aerosol water and justify if aqueous chemistry is

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important in the measured aerosols?

d. If the large droplet mode in sulfate is indeed from aqueous chemistry/oxidation of SO2 from oil refineries in the San Francisco bay, how do the authors explain a similar sulfate droplet mode observed during NW wind period (Fig. 13)?

5. Page 5618, size distribution of m/z 43 and m/z 44. Are the size distributions of m/z 43 and m/z 44 statistically different? The difference as shown in Fig. 5c seems small.

6. Page 5619 and 5620. I found the discussion on the increase of sulfate confusing. Are the authors saying that the increase in sulfate (particles smaller than 300 nm) is from transport (and oxidation) of SO2 (line 26, page 5619), or nucleation events (page 5620), or both?

7. Section 3.2, PMF factors.

a. Why is it that the correlations of CO and BC (primary emissions) with MO-OOA and LO-OOA better than that with HOA (Fig 11)? I do not think this makes sense. The HR-ToF-AMS has very good detection limit, I do not think that the low concentrations can explain such strange correlations.

b. I think the 3-factor solution needs to be further justified. From the Q/Qexp plot (Fig. S3a), I would almost argue that 2-factor solution is enough. Also, the correlations of both the time series and mass spectra (Fig. S3d) of factors 1 and 2 with each other are very high (0.8). They also have similar correlations with external tracers (Fig. 11), which is not surprising if they are highly correlated to start with. It is difficult to see why a 3-factor solution is required. How does the residual (for both time series and mass spectra) change from 2-factor to 3-factor solution? I understand that the authors might not want to include all the details of PMF analysis procedures/justifications in the main text. However, given the significance (urban SOA vs. biogenic SOA) they are trying to give to the two OOA factors, I think it is very important that the authors offer more justifications instead of simply saying that the best solution is chosen based on the

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criteria outlined in Zhang et al. review paper.

c. I do not think that m/z 29 has been shown to be a particular useful tracer for biogenic SOA. Biomass burning OA also has a strong contribution at m/z 29. In fact, other LV-OOA and SV-OOA components observed at other sites (regardless of the sources of the OOA) also showed similar contribution at m/z 29 (Ng et al., 2011, ES&T). At least for now I do not think that there is compelling evidence that m/z 29 is specific to biogenic SOA.

d. The authors wrote that the MO-OOA is highly correlated with MVK and MACR. From Fig 11, it seems that the LO-OOA also has a similar correlation with MVK and MACR. Furthermore, if MO-OOA traces MVK and MACR, why are their diurnal cycles so different (Fig. 9)?

e. In Figure S8, the authors showed that the biogenic SOA is prominent when the wind is from the north, yet throughout the manuscript northwesterly winds is used to infer periods when biogenic SOA is dominant? This needs to be clarified.

f. Page 5625, lines 5-8. Chhabra et al. (2010) has pointed out that the Aiken formulation does not capture the O/C well if fragments other than m/z 44 contribute substantially to overall O/C of the aerosols. This needs to be acknowledged.

g. I think the authors need to caution that the "position" of a PMF factor in the triangle plot does not necessarily correspond to whether a factor is more "biogenic" than others. I do not think that so far we have enough data to draw solid conclusions on this.

h. Robinson et al. (2011) found a new PMF factor with a strong signal at m/z 82 which the authors suggested that it can be from isoprene SOA. The authors should comment on whether such signal is observed in their data, as they mentioned that isoprene is the main biogenic VOC in the area.

8. Section 3.3. Influence of anthropogenic emissions on biogenic SOA. This section is highly speculative. As the authors pointed out, an important parameter is photochemi-

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cal age. Without any quantitative data on this, I think perhaps the authors need to take a step back and avoid over-interpreting their data.

a. It is not clear to me how the authors can simply use the results from Sullivan, Weber, and de Gouw to infer the photochemical age of the air mass observed in this study. This needs to be further explained and justified. For instance, without knowing the photochemical age, it is difficult to tell whether the different slopes in Figure 14 are simply results of differing photochemical age or other effects.

b. In Fig. 14, the slopes in Fig. 14c and 14e are not too different from each other. What does that mean? Obviously the authors are not claiming that "other periods" also have the anthropogenically enhanced biogenic SOA?

c. The inferred photochemical age is much higher than the actual time needed for particles to be transported from T0 to T1. The authors suggested that the particles formed upstream of T0 were already subjected to long photochemical processing. This seems contradictory to their measurements. It is clear from their AMS measurements that the air masses are mildly oxidized (more similar to the SV-OOA observed worldwide). The two OOA factors they resolved also do not have a particularly high O/C. These results do not seem to reflect a highly photochemically aged air mass.

d. Fig 14a axes: need to have "delta".

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 5601, 2012.