

We thank the three reviewers for their thoughtful comments. The manuscript has been revised accordingly. In particular, we have substantially rewritten the sections on PMF data analysis and solution diagnostics (Section 2.2.2), interpretation of the droplet accumulation mode observed in the sulfate size distributions (Section 3.1.2), interpretation of OA factors and discussions on their sources and processes (Section 3.2), and discussions on the change of OA mass with respect to CO (Section 3.3). Our point-by-point responses to each reviewer's comments, which are repeated in italic, are given below.

## Reviewer #1

*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.*

[Response No. 1]: We disagree with the reviewer's criticisms about our results. Our detailed responses are given below.

### *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.*

[Response No. 2]: It is true that the time series of HOA usually correlates with CO and BC – the tracer species for primary emissions from fuel combustion – in urban locations, where primary emissions are intense and the HOA concentrations are substantially higher than the level observed in this study. The weak correlations found during the present field campaign were mainly due to the noisy HOA, CO and BC data as a result of weak primary emission influences at T1. For the same reason, the correlation between CO and BC was low during this study as well. Similar observation was reported at a rural site impacted by urban outflow where the correlations between HOA, BC, and CO appeared weak because of noisy data (Zhang et al., 2007). There were also spikes in the time series of HOA, CO and BC, probably due to very narrow plumes (e.g., from sporadic passing cars) that were not captured by all instruments simultaneously. The HR-ToF-AMS, BC and CO instruments used separate, although very closely located, sampling inlets during this study.

As shown in Fig. 11h in the revised manuscript (Fig. 9f in the original), despite noisiness, the time series of HOA, CO, and BC do show similar trends. Indeed, the coefficients of determination ( $r^2$ ) are higher for data averaged for 1 hour interval because of improved signal-to-noise ratios:  $r^2 = 0.32$  (with 1-hour data) vs. 0.16 (for original data) for the correlation between HOA and BC, and  $r^2 = 0.23$  vs. 0.05 for the correlation between HOA and CO. More importantly, the diurnal patterns of HOA, CO and BC are very similar: they all exhibit small increases between 6:00-7:00 and 21:00-22:00. In addition, the average ratio of HOA/CO

(after subtracting a background of 80 ppb) was determined at  $\sim 5 \mu\text{g}/\text{m}^3/\text{ppm}$ , very close to the HOA to CO emission ratios observed in urban plumes (Zhang et al., 2005). For these reasons, as well as the fact that the HOA mass spectrum of this study is very similar to the mass spectra of HOA observed in various urban locations and those of primary particles from vehicle emissions, we believe that the HOA factor determined for this study is valid and representative of POA from combustion sources. In addition, since biomass burning was found negligible during this study, the HOA sources were most likely transport related. We have revised the manuscript to make these points clear.

*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  $\text{CO}_2^+$ , 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  $\text{CO}_2^+$  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?*

[Response No. 3]: There is no basis for assuming that O/C ratio should always correlate with f44. The mass spectrum of an organic aerosol is composed of hundreds of ions that contain carbon and oxygen and the molecular O/C ratio is calculated by summing ion contributions across the whole mass spectrum (Aiken et al., 2007). f44 indicates the contribution of just one ion –  $\text{CO}_2^+$ . As pointed out in a previous study by Chhabra et al. (2010), the formulation reported in Aiken et al. (2008) is unable to predict O/C satisfactorily if fragments other than m/z 44 contribute substantially to overall O/C of the aerosols. And this is what happened in the present case –  $\text{CHO}^+$  and ions from the  $\text{C}_x\text{H}_y^+$  family have very different contributions in the two OOA factors and considerably influence the O/C ratios of these two factors. These points are explained in the revised manuscript.

We have carefully and thoroughly evaluated our PMF analysis results and concluded that the 3-factor solution presented in the paper describes best the sources and processes of organics at the T1 site. Detailed diagnostics were performed on the PMF results and a summary of the results is given in the supplementary Fig. S5 (Fig. S3 in the original manuscript). The Pearson's r for describing the linear relationship between the two OOA factors is 0.79 for the mass spectra and 0.77 for the time series (i.e.,  $r^2 = 0.59$  and  $0.62$ , respectively). These values are not that high and don't necessarily indicate close similarities. Nevertheless, in evaluation of the similarities between two different factors, one should not only focus on the correlation coefficients, but one should also check carefully differences between their mass spectral patterns, ion compositions, and the temporal variations of these factors during different periods. A closer look at the mass spectra of the two OOA factors (i.e., LO-OOA and MO-OOA) indicates that they are quite different, in terms of 1) the O/C ratio (0.42 vs. 0.54), 2) the signal ratio of m/z 43 to m/z 44 (0.47 vs. 1.12), 3) the contribution of ions from the  $\text{C}_x\text{H}_y^+$  family (48% vs. 35%), and 4) the abundance of the  $\text{CHO}^+$  ion (m/z 29) in the mass spectrum (1.0% vs. 7.6%). There are more discussions on other distinct mass spectral features of the PMF OA factors in the manuscript. These results suggest that the bulk chemical compositions

of LO-OOA and MO-OOA were different. The temporal variation patterns of LO-OOA and MO-OOA are also significantly different. More importantly, LO-OOA correlated strongly with ozone (a secondary gaseous specie formed from photochemical processes) during daytime. LO-OOA also showed similar diurnal patterns sulfate and particle number concentrations, indicating its association with transport of urban plumes. In contrast, MO-OOA did not correlate with ozone at all. It instead correlated well with methacrolein (MACR) and methyl vinyl ketone (MVK), which are the first generation oxidation products of isoprene. The diurnal profile of MO-OOA was relatively flat with two small increases in the early afternoon and at night (Fig. 11i in the revised manuscript). The daytime increase is consistent with strong midday emission of isoprene coupled with the simultaneous peaking of photochemical oxidants (e.g., OH). The nighttime increase likely corresponded to the nocturnal downslope winds which transport air masses over the Sierra Mountains back to the foothills (Fast et al., 2012). All these results indicate that the OOA factors determined in this study are physically meaningful and representative of different sources and processes of SOA at T1. In addition, as explained in Response No. 2, the HOA factor determined in this study is also valid and physically meaningful. We therefore for believe the validity of the three factor PMF solution.

*c) Authors claim factor 1 (more oxidized OOA) is biogenically influenced. If so, why does it have a higher correlation with BC, toluene and CO<sub>2</sub> 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)?*

[Response No. 4]: The correlation coefficients ( $r^2$ ) of MO-OOA vs. BC, toluene and CO<sub>2</sub> are only slightly higher than those of HOA. Higher  $r^2$  do not necessarily indicate stronger correlations. This is because Pearson's  $r$  only indicates the linearity and direction of the relationship between two variables. It does not describe other aspects of the relationship, such as slope, intercept and nonlinearity. The  $r$  value can be quite low for a strong correlation if the relationship is not linear or if its slope and intercept vary. Also, the  $r$  value can be strongly influenced by outliers. To avoid confusions, we have removed the correlation plot (Fig. 11 in the original manuscript).

In terms of the reviewer's question why MO-OOA and MVK-MACR show different diurnal patterns, the reasons is that MACR and MVK are the first generation of oxidation products of isoprene, which undergo further reactions to produce SOA. Thus, the peak of MACR/MVK is earlier than that of the MO-OOA. This observation is confirmed by chamber experiments on isoprene photooxidation, which demonstrated that the production of SOA coincided with the oxidation of the primary oxidation products (MACR+MVK) and that the increase of SOA continued for several hours after MACR/MVK reached maximum (Lee et al., 2006; Holzinger et al., 2007). We have added related discussions in the revised manuscript.

*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 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<sub>2</sub>H<sub>3</sub>O<sup>+</sup> and C<sub>3</sub>H<sub>6</sub>O<sup>+</sup> 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.*

[Response No. 5]: Indeed, signals at  $m/z$  43 (mainly  $C_2H_3O^+$ ) and  $m/z$  44 (mainly  $CO_2^+$ ) are very common in AMS spectra. However, these two ions are chemically different. For example, previous studies indicate that the  $C_2H_3O^+$  ion is commonly associated with aldehydes or ketones (Ng et al., 2011a) and the  $CO_2^+$  ion is usually associated with carboxylic acids (Alfarra, 2004; Takegawa et al., 2007). The f44 vs. f43 plot (i.e., the triangle plot introduced by Ng et al. (2010)) is a practical way of classifying OOA factors identified in different atmospheric environments. In this manuscript, we use the triangle plot to highlight the mass spectral similarities between MO-OOA and previous PMF factors from ambient studies influenced by biogenic emissions. Since the AMS ionizes molecules with 70 eV electrons, the mass spectrum it generates for a mixture (e.g., an OA) should reflect its bulk chemical composition (McLafferty and Turecek, 1993; Canagaratna et al., 2007). The observed mass spectral similarities thus suggest a compositional resemblance between MO-OOA and biogenic SOA.

Given the simplicity of the f44 vs. f43 space, it has limitations and it is not surprising to find exceptions. For example, in addition to SOA from crude oil oxidation products, Chhabra et al. (2011) and Lambe et al. (2011) also found that SOA from diesel fuel, m-xylene and toluene lie on the right side of the triangle, overlapping with those from biogenic precursors and the MO-OOA. However, due to the very low mixing ratios of aromatic VOCs observed at T1, compared to the very high concentration of isoprene, we don't expect to see significant amounts of SOA from these precursors at T1. Moreover, an important support for associating MO-OOA with biogenic SOA comes from its temporal variation profile and the comparisons to several aerosol and gaseous species indicative of different sources and processes. For example, MO-OOA showed very weak correlation with primary emission tracers for anthropogenic sources (e.g., BC, CO, benzene, toluene, and aromatic hydrocarbon derivatives;  $r^2 < 0.2$ ). Yet, it correlated moderately with biogenic VOCs (isoprene and monoterpenes;  $r^2$  of 0.3-0.4) and fairly well with two isoprene oxidation products – methacrolein (MACR) and methyl vinyl ketone (MVK) ( $r^2 = 0.61$ ; Fig. S8a). The covariance between MO-OOA and MACR/MVK was particularly high during several periods in the first three weeks of the study (Fig. 11f in the revised manuscript). Both MO-OOA and MACR/MVK increased during last week of the campaign due to enhanced photochemical processing, but the increase of MACR/MVK was much greater (Fig. 11f), weakening the overall linear relationship between them (Fig. S8a). All these results corroborate the notion that MO-OOA was associated with photochemical processing of biogenic precursors. We have included this discussion in the revised manuscript.

*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!*

[Response No. 6]: Since OA and CO usually correlated poorly during this study, fitting the OA vs. CO data directly is not appropriate. As we mentioned in the text, we determined the background OA and CO based on the averages of the lowest 5% data over the entire study,

which are  $0.3 \mu\text{g}/\text{m}^3$  and 80 ppb, respectively. In response to the reviewer's comments, we used the same method to determine the background OA and CO for each air mass separately. Background OA is the same for the 3 air masses ( $0.3 \mu\text{g}/\text{m}^3$ ) and background CO is quite similar too: 85 (T0→T1 transport), 80 (northwesterly wind periods) and 90 (other periods) ppb respectively. We have updated these in the revised manuscript.

*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.*

[Response No. 7]: We disagree with the Reviewer on the fact that coloring Fig. 14a with the sum of biogenic VOCs would be inappropriate. In fact, it reveals the importance of local emissions of biogenic VOCs in the formation of SOA observed at T1. Moreover, the scatterplot of Fig. 14a clearly shows a rainbow, indicating that the slope of OA vs. CO is influenced by the concentration of biogenic VOCs present at T1 (no matter if these VOCs are local or transported).

We are unable to determine the photochemical age using the PTR-MS toluene and benzene data, even after averaging the data over longer periods. The very low levels of these two species affect the accuracy of their detection, thus the estimation of photochemical age. The toluene and benzene data reported by the PTR/MS, which was equipped with a quadrupole, may contain interferences from other species. A quadrupole MS is unit mass resolution and unable to distinguish isobaric ions that have different compositions. For example, the ion at  $m/z$  79 was attributed to benzene. However, under conditions where the concentration of benzene is low and that of acetic acid is high (as it was the case at the T1 site), the presence of acetic acid can interfere with the measurement of benzene through the formation of the hydrate of protonated acetic acid. The ion at  $m/z$  93 has been attributed to toluene, even if biogenic interferences to the detection of toluene have been reported in the past (de Gouw and Warneke, 2007; Jordan et al., 2009). These interferences are thought to be small for toluene based on similar diurnal patterns for aromatic compounds. However, the presence of compounds interfering with both toluene and benzene introduces a too important uncertainty in the calculation of the toluene/benzene ratio.

*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.*

[Response No. 8]: Actually, the region on the northwest of the site is not developed. There is only a small town (Auburn, 13000 inhabitants) 8 miles from Cool, while the rest of the region contains forests as well as agricultural fields. The T1 site was influenced by northwesterly winds during only 8 days, out of the 28 days of the study. This is the reason why the wind rose plot of Fig. S8(a) shows only a small frequency of northwesterly wind.

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<sub>4</sub> 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.*

[Response No. 9]: We discussed the mixing states of sulfate and organics on the ground of correlations between mass concentrations and size distribution, which were both poor during this study. However, we agree that strictly speaking that our AMS data cannot directly and unambiguously address the mixing state of the particles. We have removed the statement about aerosol mixing states in the revised manuscript.

3) *Related to the size distribution discussion, the 2<sup>nd</sup> paragraph in Section 3.1.2 is very speculative. There is no indication of SO<sub>2</sub> or H<sub>2</sub>SO<sub>4</sub> mixing ratios in the paper, so we can't tell if condensation of H<sub>2</sub>SO<sub>4</sub> was causing the presence of large SO<sub>4</sub> 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.*

[Response No. 10]: Measurements of SO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> mixing ratios were not available during study. We have two important indications of the presence of sulfate in the droplet mode because of aqueous-phase processing. First of all, we found that sulfate is well correlated to methanesulfonic acid (MSA) or mesylate (a salt of MSA). MSA is known to be mainly produced by the oxidation of dimethyl sulfide emitted from oceanic sources and its formation is enhanced by aqueous phase processing (Barnes et al., 2006). The oil refineries along San Pablo Bay and the Carquinez Straits are the largest SO<sub>2</sub> sources in northern California. We thus deduce that a large fraction of the droplet mode sulfate particles observed during this study likely originated from the San Francisco Bay Area, and where regular morning fogs and low clouds may have promoted aqueous phase reactions. Second, we checked the relative humidity and precipitation data at Oakland North (data from the California Air Resources Board), which is also located on the east coast of the Bay Area, very close to the refineries. The RH at Oakland was frequently close to 100% during the night and in the morning in June 2010 (Fig. S4b and S4c), confirming the frequent presence of fogs and low clouds, thus aqueous-phase processing of aerosol particles, in the region. We now show the relative humidity and precipitation data of Oakland North together with those from T1 in the supplementary material.

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.*

[Response No. 11]: We calculated the lag time based on an average growth rate of ~ 5 nm/hour observed for new particles during this study. This information is now included in the revised manuscript.

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

[Response No. 12]: We thank the Reviewer for pointing out this mistake. Indeed, in forests, methanol is directly emitted by trees. We have corrected this mistake in the revised manuscript. We also removed the part mentioning acetone as 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".*

[Response No. 13]: Indeed, a site can be considered as located "downwind" of another site only if the wind direction is correctly oriented. However, we noticed that it was generally the case for the T1 site during this study. Wind data as well as models confirmed that the wind pattern was as expected: 23 periods of urban transport from Sacramento to Cool have been identified, which corresponds to a very high frequency for a four-week study. Even if the urban transport was not systematic (the wind direction shifted during 8 days, as mentioned in the text), we decided to consider Cool as located "downwind" of Sacramento, in order to stress that the T1 site was regularly influenced by anthropogenic particles and precursors emitted at Sacramento and transported to Cool. We have revised the text to clarify that the site is ~ 40 km northeast of Sacramento, i.e., downwind from T0. The text now reads: "Measurements were conducted at two ground-based sites: one within the Sacramento urban area (denoted T0 to represent the urban emission origin of the project) and one at Cool, CA (denoted T1 to represent a rural receptor site located ~ 40 km northeast of Sacramento, i.e., downwind from T0).

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?*

[Response No. 14]: Our main purpose at here was to explain why we use "more oxidized" (MO-OOA) and "less oxidized" OOA (LO-OOA) in this manuscript, rather than the more commonly used terms of low volatility OOA (LV-OOA) and semivolatile OOA (SV-OOA). The revised text now reads: "For the present study, our preliminary analysis of the thermodenuder data indicates that both OOAs were more volatile than sulfate and that they showed somewhat different volatility profiles. But the differences did not appear statistically significant due to relatively noisy data. We thus use the terms of "more oxidized" (MO-OOA) and "less oxidized" OOA (LO-OOA) in the forthcoming discussions."

8) *I don't think authors can use the comparison to previous work on  $\Delta OC/\Delta CO$  to determine what the age of air masses sampled at T1 site on their inferred volatilities, e.g., LV-OOA (low volatility) and SV-OOA (semi-volatile) (Jimenez et al., 2009).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.*

[Response No. 15]: In the absence of a reliable measurement of the photochemical age at the T1 site ( $NO_x/NO_y$  ratio not available, too much uncertainty in the measurement of toluene and benzene), our purpose of the comparison with previous work on  $\Delta OC/\Delta CO$  was to get an idea on the order of magnitude of the photochemical age in the different air masses. We agree with the reviewer that these comparisons may have issues. For example, the comparison with the

work of Sullivan et al. (2006) and Weber et al. (2007), who measured water soluble OC (WSOC), requires the assumption that  $OC = WSOC$ . Given that we cannot justify this assumption, we have removed the comparison with these two papers in the revised manuscript. We also used an equation reported in de Gouw et al. (2008) based on ambient measurements in the northeastern US in summer to estimate the photochemical age as a function of  $\Delta OC/\Delta CO$ . However, the photochemical age thus calculated is inconsistent with previous studies undertaken at the Blodgett Forest (e.g., Dillon et al., 2002). It is also much longer than the time needed for particles to be transported from T0 to T1 based on model predictions (Fast et al., 2012) or comparisons of observations at T1 and T0, e.g., the time delays between the onset of the new particle growth events and the peaking times of pollutants. Apparently, the relationship derived from the northeastern US does not apply to the Sacramento Valley Air Basin, where the type and concentration of precursors, meteorological conditions, and concentrations of oxidants are vastly different. We have added related discussions in the revised manuscript.

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

[Response No. 16]: All the whiskers correspond to the 10<sup>th</sup> and 90<sup>th</sup> percentile, while the boxes correspond to the 25<sup>th</sup> and 75<sup>th</sup> percentile. The horizontal marks in the boxes are the median, and the colored crosses are the mean. We now include this information in the figure captions where needed.

## **Reviewer #2**

### *General comments*

*The manuscript presents HR-ToF-AMS results from the T1 site of the CARES campaign in June 2010. AMS mass spectra, size distributions, time series and PMF analysis are used together with ancillary data to show that SOA formation is enhanced during periods with mixed high anthropogenic and biogenic emissions. While the data set seems to be promising in terms of information content, the analysis shows significant weak points which need to be addressed. I therefore recommend a thorough revision before resubmission of the manuscript, both content- and language-wise.*

### *Main points:*

*1. The interpretation of the size distributions (section 3.1.2) is too speculative and the data seem “over-interpreted”, and references are missing. It cannot be concluded from the data at hand that sulfate and organics were externally mixed. In addition, a “droplet mode” usually refers to wet particles and aqueous phase reactions, can this be confirmed using the data at hand? It is mentioned in the text, but can fog and low clouds in the bay area during the time of the study be confirmed?*

[Response No. 17]: We have removed discussions on the mixing state of organics and sulfate from the revised manuscript. The droplet mode refers to an accumulation mode in particle mass-based size distribution that peaks in the 400 – 1000 nm aerodynamic diameter range. These particles are primarily formed from aqueous-phase reactions in the atmosphere (John et al., 1990; Meng and Seinfeld, 1994). We have downloaded from the website of the California Air Resources Board meteorological data (relative humidity and precipitation) recorded at Oakland North located on the east of the San Francisco Bay, very close to the oil refineries. The RH at Oakland was frequently close to 100% during the night and in the morning in June



2010, confirming the frequent occurrence of fogs and low clouds, thus aqueous-phase processing of aerosol particles, in the region. We have included these discussions in the revised manuscript. The relative humidity and precipitation data at Oakland North as well as at T1 are now shown in the supplementary material.

*2. The PMF solution needs more justification. A discussion of the Figs. S3-S4 should be placed in the main text. Were different SEED values investigated? Why was the solution using  $f_{\text{peak}}=0$  chosen? And how can the 3-factor solution be justified based on the similarity of mass spectra and time series of MO-OOA and LO-OOA. More information should also be given on the PMF input matrices. How many ions were removed, were the isotopes constrained or fitted, were they included in the PMF matrix, what was the mass range, etc.? The high correlation of primary traffic tracers with OOA suggests urban transport as a possible source as opposed to/in addition to local sources.*

[Response No. 18]: We have added more information on the preparation of the PMF input matrices and details about PMF analysis procedures in the revised manuscript. For this study, we took into account of ions up to  $m/z$  100, given that bigger ions had low signal/noise (S/N) ratio. The quantification and identification of bigger ions are less certain as well due to limited mass resolution of the HR-ToF-AMS. Isotopes were systematically constrained in PIKA, but were removed from the data and error matrices, since their presence would have given too much weight to the parent ions in the PMF analysis. We removed ions with S/N ratio  $< 0.2$ , while ions with S/N ratio between 0.2 and 2 were downweighed by a factor of 3, meaning that the error associated to their data was multiplied by 3. We also removed four ions scaled to the  $\text{CO}_2^+$  signal ( $\text{O}^+$ ,  $\text{HO}^+$ ,  $\text{H}_2\text{O}^+$  and  $\text{CO}^+$ ) prior to the PMF analysis, and we reincluded them in the mass spectra of the 3 factors after the analysis. For a given number of factors, the solution with  $f_{\text{peak}}=0$  is always the one which has the lowest  $Q/Q_{\text{exp}}$  value. Based on the mass spectra and the correlations with external tracers, we did not have any justification to choose another  $f_{\text{peak}}$ . We also initiated the PMF algorithm from 10 random starting points (seed values from 0 to 10,  $\delta=1$ ). The different seed values yielded similar solutions to those presented in the paper, which was obtained at seed = 0. In addition, we have extended the section 3.2 and subsequent sub-sections, to provide all the necessary information to justify our choice of the 3-factor solution, and to explain why we think that one of the OOA factors is biogenically-influenced and the other one anthropogenically-influenced. Please also see our Response No. 2 and No. 3 for additional explanations.

*3. The main conclusion of the paper, that SOA formation is enhanced when anthropogenic emissions interact with biogenic precursors, are presented in a confusing and non-consistent manner. This also goes back to the fact that the periods dominated by northwesterly winds and therefore low concentrations for all species (as shown in Fig. S2) are interpreted as dominated by PMF-biogenic-SOA, which a) is not clearly shown and b) depends on the interpretation of the PMF result. The interpretation of the high mass and number concentrations during the afternoon should be made more carefully, especially in terms of urban transport/advection of pollutants and new particle formation (how are these processes related/distinct/dependent, see also comment on PMF).*

[Response No. 19]: We have rewritten section 3.2 and subsequent sub-sections to provide all the necessary information to justify our choice of the 3-factor solution. We also reorganized the texts to streamline the discussions and improve clarity.

*Specific comments*

*The short title reads as “submicron particles influenced by emissions” and should be changed to something more meaningful.*

[Response No. 20]: In response to this comment, we have changed the title to: “Characterization of Submicron Particles Influenced by Mixed Biogenic and Anthropogenic Emissions Using High-Resolution Aerosol Mass Spectrometry: Results from CARES”.

*P. 5608: More details should be given on the sampling inlet, such as diameter, length, and material of the tubing, and/or residence time of particles in the inlet.*

[Response No. 21]: Particles were sampled through a common inlet equipped with a PM<sub>1</sub> impactor at a total flow rate of ~15 l/min (already mentioned in the text). The sampling line was constituted of a total of 14 feet of tubing, including 3 feet of stainless steel tube with an inner diameter of 3/4 inch, 8 feet of copper tube with an inner diameter of 1/4 inch, 2 feet long thermodenuder, and 1 feet long Nafion dryer. We have included this information in the revised manuscript.

*P. 5608, l. 24: The  $D_{va}$  corresponds to the electrical mobility diameter times the particle density assuming sphericity, please correct.*

[Response No. 22]: Corrected

*P. 5608, l. 26: To what stage of the instrument does the pressure value given refer to? The sizing region usually has a pressure of  $10^{-5}$  Torr.*

[Response No. 23]: Indeed, the pressure mentioned in the text ( $10^{-5}$  Torr) refers to the particle sizing region. The pressure in the ionization chamber and in the ion ToF-MS is  $10^{-7}$ - $10^{-8}$  Torr.

*P. 5610, l. 6-9: I would usually recommend regular, short filter measurement intervals (e. g. every week) during a field campaign.*

[Response No. 24]: We thank the reviewer for this suggestion.

*P. 5610, l. 21-23: Why “adjusted”? And why where the changes proposed in Aiken et al. (Env. Sci. Technol., 2008), not implemented?*

[Response No. 25]: Actually, the fragmentation table available by default in SQUIRREL and PIKA was modified using a standard protocol. We used the term “adjusted” because only a few entries have been modified, mainly to take into account of air interferences and to determine the water fragmentation pattern. We did implement the new calibration factors proposed by Aiken et al. (2008) et al. for scaling four ions ( $O^+$ ,  $HO^+$ ,  $H_2O^+$  and  $CO^+$ ) to the signal of  $CO_2^+$

*P. 5610, l. 25: Cite DeCarlo et al. (Anal. Chem., 2006) and compare to detection limits reported there.*

[Response No. 26]: DeCarlo et al. (2006) report the following detection limits (DLs) for 1-min averaged data in V-mode: 22 (organics), 5.2 (sulfate), 2.9 (nitrate), 38 (ammonium), and 12 (chloride) ng/m<sup>3</sup>. Scaled to 2.5-min (like our dataset) using the following relationship:

$$2.5\text{-min DL} = 1\text{-min DL} \cdot \sqrt{\frac{1}{2.5}}$$

these DLs become 14 (organics), 3.3 (sulfate), 1.8 (nitrate), 24 (ammonium), and 7.6 (chloride) ng/m<sup>3</sup>. Thus, DLs determined during our study are between 2 and 10 times higher than those reported by DeCarlo et al. (2006). We have added this information in the revised manuscript.

*P. 5611, l. 1: I suggest changing “most” to “many” and giving some references.*

[Response No. 27]: Corrected, and four references have been added as examples.

*P. 5611, l. 8-9 and Fig. 2a: Fig 2a. just confirms relative agreement of AMS+BC and SMPS, but not absolute. Since, as seen in Fig. 3, the correlation is nice and the slope is known, why not scale the SMPS volume to “SMPS apparent mass” using the slope in Fig. 3 as a measure for the density and show this comparison in Fig 2a?*

[Response No. 28]: The calculation of the SMPS apparent mass will involve the use of particle density, for which we can derive using the chemical composition data. However, we prefer to show the original SMPS data and infer particle density based on the slope in Fig. 2a. It compares well with the average density determined based on chemical composition.

*P. 5611, l. 13: Add Lanz et al., (Atmos. Chem. Phys., 2007), as reference.*

[Response No. 29]: Reference included

*P. 5613, l. 9-10: Even though you give information on the gas phase instruments here, it should also be given on p. 5608 where they are mentioned for the first time.*

[Response No. 30]: Done as suggested.

*P. 5613, l. 15: repeat again what size of particles you are referring to.*

[Response No. 31]: We do not mention particle size at here. Did the reviewer make a typo with the page or line number?

*P. 5617, l. 3-5: Drawn conclusion not fully clear; rephrase.*

[Response No. 32]: Following a comment from Reviewer #3 on the  $\text{NO}^+/\text{NO}_2^+$  ratio (Specific comments, point 3b), we have modified this section and removed this sentence.

*P. 5619, l. 1-2: Seems to be too much interpretation for this very small difference in the size distributions of Org 43 and Org 44.*

[Response No. 33]: Agree, the size distributions of  $m/z$  43 and  $m/z$  44 are indeed very similar. We have removed this discussion in the revised manuscript.

*P. 5619, l. 9: Is Fig. 6a really necessary? It doesn't add a lot of new information.*

[Response No. 34]: We think that the correlation between organics and sulfate (Fig. 6a) is important and needs to be shown. Organics and sulfate are the two dominant species during this field campaign. The poor correlation between them (Fig. 6a) coupled to their different size distributions (Fig. 5b) is a strong indication that these two species come from different sources and processes. However, the fact that these two species show very similar diurnal patterns (Fig. 7) highlights the strong influence of urban transport on aerosol loading at T1.

*P. 5619, l. 9-10: For this interpretation, more information should be given on the interpretation of the whole time series – why were organics low then? Why was sulfate high? Are clean air masses due to meteorology? Do high organics mean high local organics, or advected organics? Sulfate is usually high during transport from T0 to T1. And there is no linear correlation between organic mass fractions and  $\text{PM}_{10}$ .*

[Response No. 35]: Periods of very low total mass loadings ( $< 1 \mu\text{g}/\text{m}^3$ ) occurred mainly during northwesterly wind periods (Fig. 6d). It was the fraction of sulfate that was high, not sulfate loading. Usually, periods of high concentrations of organics correspond to periods of

transport from T0 to T1, meaning that a large fraction of organics at T1 is advected. As shown in Fig. 5d in the revised manuscript, organic mass fraction correlates positively with PM<sub>1</sub> concentration but the relationship is not linear.

*P. 5619, l. 20: Does Fig. 7 show campaign averages?*

[Response No. 36]: Yes, data recorded during the entire campaign have been used to determine the diurnal patterns of mass concentrations and size distributions shown in Fig. 7.

*P. 5619, l. 26: Show SO<sub>4</sub><sup>-</sup> size distribution for afternoon only.*

[Response No. 37]: The size distributions of sulfate during daytime can be viewed in Fig. 7b (right panel).

*P. 5620, l. 19-20: I don't see that in Fig. 7 ("ultrafine mode"?)*

[Response No. 38]: We have removed the reference to Fig. 7 in this sentence to avoid confusion.

*P. 5621, l. 27: Aren't you seeing a droplet mode, and aren't you mentioning aqueous phase processes earlier? Seems contradictory.*

[Response No. 39]: The discussions at here are not contradictory. We observed a droplet mode for sulfate at T1, based on which we argued that aqueous phase processes likely played important roles in the formation of this droplet mode sulfate. The formation of particulate organics during this study, however, was mainly driven by condensation (see discussions in section 3.1.2).

*P. 5622, l. 25-26: See comment above; this statement is not quantitative. Can you show comparisons, report r values?*

[Response No. 40]: The comparison of the mass spectra of the MO-OOA and LO-OOA vs. those of OOA factors from previous studies, including correlation coefficients, are now included in the supplementary material (Fig. S7).

*P. 5623, l. 2: which OOA factors are you referring to? Unclear.*

[Response No. 41]: We are referring to OOA factors identified during other field campaigns. In order to make this sentence easier to understand, we revised the text and it now reads "the signal of CHO<sup>+</sup> (*m/z* 29) is clearly enhanced in the MO-OOA spectrum compared to that in the average OOA mass spectrum of different field campaigns (Ng et al., 2011b),".

*P. 5623, l. 9-11: That is not only the case for biogenic SOA.*

[Response No. 42]: We thank the Reviewer for pointing this out. We have removed this sentence in the revised manuscript.

*P. 5629, l. 6-7: the assumption that OC = WSOC should be justified*

[Response No. 43]: Given that we cannot justify the assumption that OC = WSOC, we decided to remove the comparison with the two papers reporting the relationship between

$\Delta$ WSOC/ $\Delta$ CO and photochemical age (Sullivan et al., 2006; Weber et al., 2007). Please see our Response No. 15 for other details.

*Figures should be ordered according to their appearance in the text*

[Response No. 44]: Done as suggested

*I suggest moving Figs. 3, 4, 10, and 13 to the Supplement, since they don't add substantially more information*

[Response No. 45]: We thank the Reviewer for this suggestion. However, we decide to keep them in the main paper since each of them provides important information discussed in detail in the main text. For example, Fig. 3 does not only show that AMS and SMPS agreed very well during the entire campaign. The slope of this scatterplot also allows us to infer particle density and the density of organics. Fig. 4 shows that particles are fully neutralized, and that we do not have any acidic particle events. This is an important information on the particle chemistry. Fig. 10 illustrates why LO-OOA has a lower O/C ratio than MO-OOA despite its higher  $f_{44}$  and Org44/Org43 ratio. Indeed, this figure clearly shows that LO-OOA has a higher contribution of ions from the  $C_xH_y^+$  family, which decreases its O/C ratio compared to MO-OOA. It also shows that MO-OOA has a much higher contribution of ions from the  $C_xH_yO_1^+$  family (mainly because of the  $CHO^+$  signal), which increases its O/C ratio. We now merge this figure with Fig. 9 in the original manuscript and it becomes Fig. 11d & 11e in the revised manuscript. Fig. 13 compares the size distributions in the three air masses. Given that in the last section of the paper, we compare the three air masses in terms of chemical composition, size distributions,  $\Delta$ OA/ $\Delta$ CO and VOCs concentrations, we think it is crucial to keep this figure in the main paper.

*Technical corrections*

*P. 5604, l. 13: the ecological balance*

*P. 5604, l. 15: better "consist" than "are constituted"*

*P. 5604, l. 17: better "Analyses" than "However, the analysis"*

*P. 5604, l. 23: better "can also be classified" than "are classified"*

*P. 5605, l. 3-4: Partitioning "into", not "onto"*

*P. 5606, l. 26: Give full name of HR-ToF-AMS since it is mentioned here for the first time (abstract doesn't count). Abbreviation used later (p. 5608, l. 21) is inconsistent, please check*

*P. 5606, l. 28: Inconsistencies in capitalizing "positive matrix factorization" throughout manuscript, please check*

*P. 5608, l. 25: on average*

*P. 5609, l. 25: "allows the determination of the particle diameter Dva"*

[Response No. 46]: All have been corrected.

*P. 5609, l. 7-9: Strange sentence*

[Response No. 47]: The original sentence has been replaced by "The chemical composition of the particles is finally determined by a high resolution time-of-flight mass spectrometer operated alternatively in two modes - "V" and "W"."

*P. 5609, l. 15, 20, 21: better "in V- and W-mode"*

[Response No. 48]: Corrected

*P. 5610, l. 12: “for” Igor*

[Response No. 49]: The sentence has been revised as such “... the standard ToF-AMS analysis toolkits written in Igor Pro 6.2.2.2 (WaveMetrics Inc., Lake Oswego, OR) ...”

*P. 5610, l 12: check throughout manuscript for inconsistencies in giving company information (e. g. name and state or just name, etc.)*

[Response No. 50]: Done as suggested.

*P. 5610, l. 21: “to” instead of “into”*

*P. 5611, l. 23: Better “the PMF solution”*

[Response No. 51]: Corrected

*P. 5612, l. 2: Since it is used here for the first time, say what  $D_m$  is*

[Response No. 52]:  $D_m$  is now defined (mobility diameter) when it is used for the first time.

*P. 5612, l. 15-18: Strange sentence*

[Response No. 53]: We have revised the sentence. It now reads “The data acquisition software applied two corrections to the particle size distribution during the data inversion to take into account the DMA transfer function (Birmili et al., 1997) and the bipolar charge distribution (Wiedensohler, 1988).”

*P. 5612, l. 28: “the” drift tube*

*P. 5613, l 4: an SP2*

*P. 5613, l. 9: concentrations*

*P. 5613, l. 15: “The” spatial distribution*

*P. 5614, l. 11: “in” Fig 2.*

*P. 5615, l. 20: better “of the measured  $\text{NH}_4^+$  concentration vs. the predicted  $\text{NH}_4^+$  concentration assuming. . .”*

*P. 5615, l. 27: “is present” instead of “presents”*

*P. 5616, l. 9: corresponds*

*P. 5616, l. 12: report*

*P. 5616, l. 29: “was present” instead of “presented”*

[Response No. 54]: All have been corrected

*P. 5617, l. 1: “contributed to”*

[Response No. 55]: Actually, “contributed by” is correct in this sentence.

*P. 6717, l. 2: “roughly” instead of “around”*

[Response No. 56]: Corrected.

*P. 5617, l. 24-27: Rephrase*

[Response No. 57]: We forgot the word “of” in this sentence. Corrected.

*P. 5618, l. 25: Really Fig 8a?*

[Response No. 58]: This is correct. Fig. 8a (Fig. 10a in the revised manuscript) shows the average high resolution mass spectrum of organics over the entire campaign. The most abundant signals in this mass spectrum are at  $m/z$  43 and 44. The signal at  $m/z$  28 is also very high, but is scaled to that of  $m/z$  44 ( $\text{CO}^+ = \text{CO}_2^+$ ).

*P. 5620, l. 9: typo (pin)*

*P. 5620, l. 19: spherical particles*

[Response No. 59]: Both have been corrected.

*P. 5620, l. 21-22: strange sentence, rephrase*

[Response No. 60]: We have rephrased the sentence and it now reads “The average increase of the mass concentration of organics ( $\sim 1.1 \mu\text{g m}^{-3}$ ) was  $\sim 6.5$  times higher than that of sulfate ( $\sim 0.17 \mu\text{g m}^{-3}$ ) between 10:00 - 17:00 (Fig. 8), indicating that organics played a more important role in new particle growth than sulfate did.”

*P. 5620, l. 25: observed*

*P. 5620, l. 26: Finnish*

*P. 5620, l. 29: Sierra Nevada foothills*

*P. 5621, l. 24: “than during a field campaign”*

*P. 5622, l. 7: “We performed PMF analysis on”*

[Response No. 61]: All have been corrected.

*P. 5622, l. 11-12: Cite Lanz et al., 2007*

[Response No. 62]: Reference included

*P. 5622, l. 18: Difference “in” volatility*

*P. 5623, l. 16: different levels*

*P. 5623, l. 20: sources and processes*

*P. 5623, l. 28: “the sum”*

*P. 5626, l. 7: tight correlations*

*P. 5626, l. 8: are consistent*

*P. 5626, l. 27: were compared*

*P. 5627, l. 19-22: Remove “frequent” or “frequently”*

*P. 5629, l. 22: We noticed*

*P. 5630, l. 13-14: remove one “average”*

[Response No. 63]: All have been corrected.

**Reviewer #3**

*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 PMI 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  $\Delta\text{Org}/\Delta\text{CO}$  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  $\Delta\text{Org}/\Delta\text{CO}$  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.*

[Response No. 64]: The manuscript has been revised accordingly. In particular, following the Reviewer's comments, we have substantially extended the discussion on the PMF solution diagnostics in order to justify our choice of the 3-factor solution (Section 2.2.2), and rewritten the discussions on the sulfate droplet mode and aqueous-phase processing (Section 3.1.2), interpretation of OA factors and discussions on their correlations vs. tracer compounds (Section 3.2), and discussion on the influence of anthropogenic emissions on biogenic SOA (Section 3.3). All these points are presented in detail in our responses to the specific comments below.

*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 CO<sub>2</sub> concentrations in these air masses. Did the authors apply a time-dependent CO<sub>2</sub> correction to their fragmentation pattern?*

[Response No. 65]: Yes, the gas-phase CO<sub>2</sub> data were used to introduce a time-dependent CO<sub>2</sub> correction in the fragmentation table. This point was very important in the data treatment, since the gas-phase CO<sub>2</sub> showed a strong diurnal pattern (the CO<sub>2</sub> concentration was on average 420 ppm during the night and 390 ppm during the day) and that the gas-phase



CO<sub>2</sub> signal accounted for up to 75% of the total signal of the CO<sub>2</sub><sup>+</sup> fragment during periods of low organics mass loading. We mention this point in the revised manuscript.

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?*

[Response No. 66]: For PMF analysis, removing *m/z* 44-related ions (i.e., CO<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, HO<sup>+</sup>, and O<sup>+</sup>) is equivalent to downweighting the error values for each of these ions and CO<sub>2</sub><sup>+</sup> by multiplying their error values by a factor of  $\sqrt{5}$ .

3. Page 5616.

a. *Is there any organic interference (CH<sub>2</sub>O<sup>+</sup>) at m/z 30?*

[Response No. 67]: Yes, there is an important contribution of organic fragments at *m/z* 30. These fragments (mainly CH<sub>2</sub>O<sup>+</sup>) account for 30% of the total signal at *m/z* 30. High resolution data has been used to modify the fragmentation table in SQUIRREL and to take into account of this contribution of organic fragments at *m/z* 30.

b. *As the authors pointed out, the NO<sup>+</sup>/NO<sub>2</sub><sup>+</sup> 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.*

[Response No. 68]: Indeed, with our data, we cannot determine the relative importance of organic vs. metal nitrate. We have revised related discussions in the manuscript.

c. *How do the authors justify their assumption that NO<sub>2</sub><sup>+</sup> is being completely generated by ammonium nitrate? Won't organonitrate fragment to give RO and NO<sub>2</sub>?*

[Response No. 69]: It is true that significant amount of NO<sub>2</sub><sup>+</sup> could be present in the fragmentation of organonitrates. We have revised related discussions in the manuscript.

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

[Response No. 70]: Actually, that paper is still in preparation. Therefore, we have replace the reference “Shilling et al., 2012” by “Shilling et al., in preparation” in the revised manuscript.

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.*

[Response No. 71]: We discuss the size distribution data in terms of different air masses in Section 3.3 together with the discussions on their differences in chemical composition, ΔOA/ΔCO, and VOCs concentration. We think it makes more sense to keep them in the same section. Moreover, we have revised the discussions on the sulfate droplet mode in order to clarify several points (see our responses to the following comments).

*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.*

[Response No. 72]: Please see our response to Reviewer 1 (Response No. 10) and #2 (Response No. 17) for the details. The relative humidity and precipitation data recorded at Oakland North (data available on the website of the California Air Resources Board) confirm that there were fogs or low clouds in the Bay Area during the night and until the early morning. This time period is consistent with aqueous-phase processing in the early morning before the transport to the T1 site in the afternoon. We have included in the supplementary material (Fig. S4) the relative humidity and precipitation data recorded at Oakland North together with those at the T1 site.

*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 important in the measured aerosols?*

[Response No. 73]: No, we are not able to estimate the amount of aerosol water at T1 because particles were dried with a Nafion dryer prior to the AMS analysis. However, we do not claim that aqueous chemistry occurred locally at the T1 site, given the dry atmospheric conditions during the entire campaign and we only found that aqueous chemistry was important for the present droplet accumulation mode of sulfate. Meteorological data recorded at the Bay Area indicates the presence of fog almost every morning. We think that aqueous chemistry occurred there, before the transport of these particles to the Sacramento Valley.

*d. If the large droplet mode in sulfate is indeed from aqueous chemistry/oxidation of SO<sub>2</sub> 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)?*

[Response No. 74]: The droplet mode of sulfate was still present during northwesterly wind periods, but the concentration was significantly smaller than during the other time periods (Fig. 13b). This may be due to recirculation of air masses in the region.

*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.*

[Response No. 75]: Indeed, the size distributions of m/z 43 and m/z 44 are not so different, we have modified related discussions in the revised manuscript.

*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 SO<sub>2</sub> (line 26, page 5619), or nucleation events (page 5620), or both?*

[Response No. 76]: The increase of sulfate in particles smaller than 300 nm (in  $D_{va}$ ) was due to new particle formation and growth events. However, the formation of new particles and their subsequent growth took place during the day, when SO<sub>2</sub> was transported from the Bay Area to the Sacramento Valley and oxidized by photochemistry. Moreover, SMPS data from the T0 site (not shown in the paper) indicates that new particle growth events were also observed there, suggesting that these events occurred on a regional scale.

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.

[Response No. 77] Please see Response No. 2 for the discussions on the observed low correlation coefficients of HOA towards CO and BC.

b. I think the 3-factor solution needs to be further justified. From the  $Q/Q_{exp}$  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 criteria outlined in Zhang et al. review paper.

[Response No. 78]: The 2-factor solution is unable to separate out HOA and somewhat mix the OOAs (Fig. S6 in the supplementary material). The 3 factor solution is the best solution. Please see Response No. 3 for the details. We have substantially rewritten section 3.2 of the manuscript and have expanded the discussions on our choice of the 3-factor solution in the revised manuscript.

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.

[Response No. 79]: We did not intend to use  $m/z$  29 as an independent evidence for biogenic SOA, we discussed it to point out the consistency in term of mass spectral features. We have revised the text and it now reads: "The O/C ratio and the mass spectrum of MO-OOA are similar to those of biogenic SOA (BSOA) acquired from chamber studies and ambient environments. A few prominent ions measured in BSOA, such as  $C_2H_3O^+$  ( $m/z$  43) and  $C_3H_6O^+$  ( $m/z$  58) (Chen et al., 2009; Kiendler-Scharr et al., 2009; Slowik et al., 2010), are also enhanced in MO-OOA, accounting for 12% and 1.1%, respectively, of the total signal. In addition, the signal of  $CHO^+$  ( $m/z$  29) is clearly enhanced in the MO-OOA spectrum compared to that in the average OOA mass spectrum of different field campaigns (Ng et al., 2011b), but in similar abundance as it is in the spectra of  $\alpha$ -pinene and isoprene SOAs from smog chamber experiments (Alfarra et al., 2006; Shilling et al., 2009; Chhabra et al., 2010), BSOAs from plant chamber experiments (Kiendler-Scharr et al., 2009), and ambient OOAs influenced by biogenic emissions (Chen et al., 2009; Kiendler-Scharr et al., 2009; Slowik et al., 2010). Note that previous studies have reported significant signals at  $m/z$  29 in the spectra of biomass burning particles (Ng et al., 2011b). However, in the absence of signals at  $m/z$  60 ( $C_2H_4O_2^+$ ) and 73 ( $C_3H_5O_2^+$ ), which correspond to the two fragments of levoglucosan usually

used as tracers for biomass burning, the signal at  $m/z$  29 cannot be associated to biomass burning in this study. As shown in Fig. S7, the agreements between the mass spectra of our MO-OOA vs. biogenic SOA identified at Chebogue Point ( $r^2 = 0.95$ ) and from plant chamber experiments ( $r^2 = 0.97$ ; Kiendler-Scharr et al., 2009) are especially high. Since the AMS ionizes molecules with 70 eV electrons, the mass spectrum it generates for an ensemble aerosol should reflect its bulk chemical composition (McLafferty and Turecek, 1993; Canagaratna et al., 2007). The observed mass spectral similarities thus suggest a compositional resemblance between MO-OOA and 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)?*

[Response No. 80]: A close look at the map of the Sacramento Valley indicates that the region between Sacramento and the T1 site is also forested. Therefore, we think that southwesterly winds bring to the T1 site not only anthropogenic precursors emitted at Sacramento, but also biogenic precursors emitted by the forests located between Sacramento and T1. This may explain why the urban transport SOA also some correlation with MACR+MVK as well. However, the time series of LO-OOA and MO-OOA are significantly different, especially after June 20<sup>th</sup>. Most importantly, LO-OOA correlated strongly with ozone during daytime and showed similar diurnal patterns with ozone, sulfate and particle number concentrations that are consistent with transport of urban plumes. MO-OOA, on the other hand, did not correlate with ozone at all. In terms of why the diurnal cycle of MO-OOA is different than that of MVK and MACR, please see our Response No. 4.

*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.*

[Response No. 81]: The T1 site was influenced by northwesterly wind during 8 days, out of the 28 days of the campaign. This is the reason for which the wind rose plot of Fig S8a shows a small frequency of northwesterly wind. Moreover, the “northwesterly wind” periods mentioned by Fast et al. (2012) have been determined using the North American Mesoscale (NAM) modeling system and refer to regional wind patterns over Northern California, while the wind rose plots (Fig. S8) have been plotted using meteorological data recorded directly at the T1 site. This may explain why biogenic SOA is prominent when the local wind is northerly.

*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.*

[Response No. 82]: We have now included this reference in the discussion.

*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.*

[Response No. 83]: We agree. Our main purposes of mapping the PMF factors on the triangle plot are to compare the mass spectra of the OA factors to each other and to OA factors

reported in previous publications (on both ambient observations and chamber experiments). The results are consistent with the association of MO-OOA with biogenic SOA, which was a conclusion we drew also based on the good correlations of MO-OOA with MVK / MACR, the diurnal variation patterns, and the mass spectral features. We have substantially revised section 3.2 to streamline related discussions. We also now point out in the text that “that the “position” of an OOA factor in the triangle plot is not a reliable indicator for its sources.”

*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.*

[Response No. 84]: Our dataset does not show significant signal at  $m/z$  82 in the average OA mass spectrum of this study (Fig. 10a). In addition, neither MO-OOA nor LO-OOA shows enhanced signal at this  $m/z$ .

*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 photochemical 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*

[Response No. 85]: We have substantially revised the manuscript for related discussions and based our discussions primarily on the comparison of  $\Delta\text{OC}/\Delta\text{CO}$  between the three air masses. We have revised discussions on the photochemical age of the air mass observed in this study based on comparisons to previous measurements. Please see Response No. 15 for details.

*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?*

[Response No. 86]: As we explain in the text, “other periods” correspond mainly to nocturnal downslope wind periods, when a part of the pollution which was transported up to the Sierra Nevada Mountains during the day came back to the foothills during the night. The “other periods” were thus also more strongly influenced by anthropogenic emissions. Consistently, we found that the “other periods” were also dominated by the less-oxidized OOA (i.e., urban transport SOA), as shown in Table 1. Related discussions have been made in the manuscript.

*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.*

[Response No. 87]: We agree that the O/C ratios of the two OOAs are not consistent with very long photochemical processing. In addition, the fact that they correlated well respectively with ozone and the two 1<sup>st</sup> generation isoprene oxidation products (methacrolein and methyl vinyl ketone) indicates that SOA was relatively fresh at T1. We have revised the manuscript and clarified these points.

*d. Fig 14a axes: need to have “delta”.*

[Response No. 88]: In Fig. 14a, organics and CO are shown before background subtraction, so the axis labels are correct during revision.

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