We thank the reviewer for the comments and feel they will improve the manuscript. Below, we respond to the reviewers comments in detail and indicate changes we have made to the manuscript in response to the reviewer's concern. We have included the **reviewer's comment** in bold, our response in blue, and *changes to the text* in italics.

Response to Reviewer 1

1) There are two major peaks in OA, CO, and ozone on 28 June at 16:00 and 17:00 PST (Figure 4). These two peaks appear to be located in the plume transect between T0 and T1, but were ignored in the manuscript. These peaks are not coincident with high m/z 69 and m/z 71 in the bottom time trace of Figure 4. A more-detailed examination of the wind speed data at T0 and T1 as well as the WRF-Chem forecast for CO is needed to rule out that these peaks were not from the aged, morning plume over Sacramento. The wind speed data at T0 and T1 from Zaveri et al. (2012) indicates that the winds were light that day (1-2 m/s). The morning plume was likely transported about 18-36 km in 5 hours with these winds, which puts it approximately where the afternoon plume was observed. However, the WRF-Chem forecast indicates that the Bay Area influenced plume which was centered over the T0 site in the morning is pushed farther east than the eastern-most portion of the flight (Figure 2 BD) and so the air mass sampled is believed to be from fresh (< 1 day) Sacramento and biogenic emissions. The results from the WRF-Chem forecasted CO are also questionable because the measured CO concentrations are much higher than estimated by summing the two CO sources (Figure 2 CD) for that afternoon.

We apologize for the confusion regarding the location and origin of the peaks at 16:00 and 17:00. To improve the clarity of the manuscript, we have added corresponding labels on Figures 3 and 4 and Figures 9 and 10 so that the readers can relate positions along the flight track shown in Figures 3 and 9 to the time traces shown in Figures 4 and 10.

As the reviewer states, the peaks at 16:00 and 17:00 are located on the plume transect between the T0 and T1 site. The observations indicate the plume corresponding to these peaks is chemically similar to the plume found in the morning over Sacramento. As detailed in Section 3.2, Figure 4, there are significant concentrations of isoprene and MVK+MACR found in the morning plume, which reacts away as photochemistry proceeds during the day. Similarly, the peak at 16:00 has MVK+MACR concentrations of ~1.5 ppbv and isoprene concentrations of ~1.2 ppbv. The peak at 17:00 has MVC+MACR concentrations of ~1.3 ppbv and isoprene concentrations of ~1 ppbv. These concentrations are consistent with a minimal isoprene source on this leg and with continued photochemical processing. Therefore, we are confident that the peaks at 16:00 and 17:00 contain fresh emissions. We acknowledge that the concentrations are hard to read from the graph in the manuscript, but felt that retaining the same scale between the morning and afternoon viewgraphs was important.

To address the reviewers request for a discussion of the peaks at 16:00 and 17:00, we have added a new panel to Figure 11 showing org vs. CO plots for 1) the morning plume on June 28th, 2) the biogenic-rich leg over the T1 site (leg f) and 3) the transect between T0 and T1 which contains the 16:00 and 17:00 peaks (leg e). This new figure is now discussed in the text, but it shows that OA formation is less efficient in the 16:00 – 17:00 plume than in the 15:40 and 16:40 plume because it contains much less isoprene. We acknowledge in the manuscript that the background

in the region is indeed influenced by aged air from both the Bay Area and recirculation of Sacramento emissions. However, we feel that this new figure combined with the significant amount of isoprene in the plume at all locations show that there are fresh emissions influencing the region.

Evolution of ΔOA/ΔCO within the mixed anthropogenic/biogenic plume on 28 June is further evaluated in Figure 11, Panel B. In the morning, fresh anthropogenic emissions, including CO, are injected into the plume, while photochemistry and OA production have not yet peaked. As a result, ΔOA/ΔCO in the plume is 21 μg/m^{3}ppmv, much smaller than observed in the afternoon on other days. Also shown in Panel B is a comparison of ΔOA/ΔCO in the leading (area f in Figures 3 and 4) and trailing (area e in Figures 3 and 4) edges of the mixed plume for the afternoon of June 28. The plume in both regions has the same nominal photochemical age and similar concentration of CO. However, the leading edge of the plume has larger concentrations of isoprene (3.75 ppbv on average) than the trailing edge (1.95 ppbv isoprene) because it is located deeper into the foothills where isoprene emissions are larger. As a result, ΔOA/ΔCO is 1.5 times larger in the leading edge of the plume (157 μg/m^{3}ppmv) than in the trailing edge of the plume (107 μg/m^{3}ppmv), again suggesting that fresh isoprene emissions are key in generating OA within the mixed plume.

To clarify the WRF-Chem forecasts shown in Figure 2 represent CO above background, with a background of 90 ppbv. Comparison of the WRF-Chem simulated and measured CO for 28 June is shown in Figure 11 of Fast et al. (2012). The model reproduces the measured CO concentrations with reasonable accuracy in the morning, but it is biased low in the afternoon. The measured/modeled CO discrepancy is attributed by Fast et al. (2012) to 1) uncertainties in emission ratios, overprediction of the boundary layer depth by the model, and model underestimation of the background concentrations. WRF-Chem predictions of wind speed and direction were better, so transport patterns are expected to be accurate even if absolute CO concentrations are biased low (Fast et al., 2006).

2) These peaks in OA, CO, and ozone on 28 June at 16:00 and 17:00 PST need to be explained and compared to the peaks on 28 June at about 15:40 and 16:40 PST on the eastern-most portion of the flight that were coincident with biogenic VOCs. Indeed, if the OA data are plotted against the CO data for the 28 June afternoon flight and colored by high/low biogenic VOCs and their first-generation oxidation products, is appears that there is not a trend of higher OA with higher biogenic VOCs.

As the reviewer suggests, we have expanded the discussion of the peaks at 16:00 and 17:00 and compare them to the peaks at 15:40 and 16:40 (new panel Figure 11). There is not a simple correlation of higher ΔOA/ΔCO solely with higher biogenic VOCs, which we illustrate in Figure 11. As we explain in the text, this is due to the fact that the highest VOC concentrations are found in the region to the north of the T1 site which is not impacted by the Sacramento plume. As discussed in Section 3.3 and 3.5, high VOC concentrations in the absence of fresh anthropogenic emissions did not produce higher OA concentrations. The influence of biogenic concentrations on the evolution of the mixed anthropogenic/biogenic plume are shown now shown in Figure 11 B and discussed in the text.

3) As mentioned in the manuscript, the time scale for processing is important for determining the relevance of deltaOA/deltaCO and previous studies have shown that

there is a wide range of deltaOA/deltaCO in the freshest urban air masses (Weber et al., 2007; deGouw et al., 2008). The manuscript further states that a photochemical clock using toluene/benzene ratios was not available for this analysis because their concentrations fell below the detection limit outside of downtown Sacramento. Yet, concentrations for toluene are reported in Figures 4 and 10. So, it is surprising that benzene and toluene were below the detection limits for this dataset and could not be used as a clock. The fact that these are close to or below their detection limits indicates that the air mass sampled on the afternoon of 28 June is mostly older than one day.

We have added the PTR-MS detection limits for benzene and toluene in Section 2 at the reviewer's request. Due to restrictions with the aircraft instrumentation and power, the PTR-MS was shut down every night, breaking the instrument vacuum. As a result, backgrounds and consequently detection limits in the instrument during CARES are higher than when the instrument is operated under normal procedures (i.e., run continuously). As shown in Figures 4 and 10, the toluene concentrations increase above the detection limits of 600 pptv near downtown Sacramento and the I-5 and I-80 corridors on both 12 and 28 June in the morning. Vehicular emissions are the largest source of toluene and the data are consistent with fresh toluene vehicular emissions during the morning rush hour. Unfortunately, benzene concentrations are even lower than toluene concentrations, barely rising above the PTR-MS LOD of 700 pptv even near downtown Sacramento. Since both toluene and benzene concentrations must be above the instrument LOD, we are unable to use the benzene/toluene clock.

We agree that airmass age potentially affects deltaOA/deltaCO measurements and we regret that we do not have measurements that can indicate the photochemical age of the air. However, the presence of isoprene and MACR+MVK in relatively high concentrations near Sacramento when photochemical conditions are favorable for oxidation indicates that significant fresh biogenic emissions have mixed into the airmass. We acknowledge that a high background concentration of CO and OA indicate regional aged urban emissions impact the entire Sacramento and Foothills region. However, OA formation was not observed in the biogenic dominate areas of the flight track despite this aged urban pollution.

We disagree with the reviewer's statement that "The fact that these are close to or below their detection limits indicates that the air mass sampled on the afternoon of 28 June is mostly older than one day." Even in the absence of reaction, benzene and toluene concentrations will decrease downwind of the source due to dilution. As seen in Figures 4 and 10, even near downtown Sacramento where sources are strongest, toluene concentrations are small (much smaller than CO) and emissions are confined to well-defined locations near downtown. Given the low toluene concentrations and the fact that benzene:toluene emission ratios are 0.5 - 0.25 in fresh urban air (Baker et al., 2008), it is unsurprising that benzene concentrations are below the instrument LOD. We note that Setyan et al. (2012) report similar limitations in using the benzene/toluene photochemical clock at the T1 site, so the difficulties are not unique to the aircraft instrument (Setyan et al., 2012).

Technical Corrections

1) Section 2 – the detection limits for all measurements should be stated here, esp. since benzene and toluene were reported to be lower.

We have added the detection limits for other species in this section.

The AMS detection limits are approximately 0.3, 0.07, 0.05, and 0.15 μg/m^3 for organics, sulfate, nitrate, and ammonium, respectively though they vary somewhat with the instrument pumpdown time.

Because the PTR-MS was powered down nightly after flights, instrument backgrounds at most masses are higher than normal which also increases the instrument detection limit. Using the method and definitions described by Amann et al., we estimate the PTR-MS limit of quantification for isoprene, MVK+MACR, benzene, toluene, and monoterpenes as 500, 550, 750, 600, and 300 pptv respectively (Amann et al., 2010).

2) P.10, line 28 – probably m/z 43 should be m/z 93 (toluene).

The text is correct as written and references are provided; alkenes, diesel exhaust and pentenes may fragment to produce signal at m/z 43 in the PTR-MS.

3) Figures 5 and 7, along with associated text – should include m/z 93 (toluene).

Toluene concentrations are below the instrument limit of quantification in in all areas except the morning plume on 6/28. Furthermore, the figure includes CO, which is a conserved and much higher S/N tracer for anthropogenic emissions than toluene. Finally, given the small observed toluene concentrations and modest (~10%) SOA yield from toluene, we feel that it is unlikely that toluene contributes significantly to the observed OA formation (Ng et al., 2007).Therefore, we feel adding toluene concentrations to Figures 5 and 7 will not improve the manuscript. We have added some additional text discussing the measured toluene concentrations, but have kept the text to a minimum because of the limited toluene S/N.

Toluene concentrations in this region remain below the PTR-MS detection limit both in the morning and in the afternoon.

Toluene concentrations of up to 1.2 ppbv are observed in the plume, but quickly drop below the PTR-MS detection limit outside the city.

4) P. 17, lines 24-28 – CO also increases (slightly) in the afternoon, so some of the OA could be from anthropogenic sources.

We agree that some of the OA could be from anthropogenic sources. However, measured black carbon concentrations in the Sacramento plume 0.1 - 0.2 ug/m3 were small (Zaveri et al., 2012). Given the relatively small increase in CO, the timing of the increase the anticorrelation between OA and isoprene and its oxidation products, the observed O:C ratios, the small BC concentration, and the T1 site observations, we feel most of the OA is likely produced in the atmosphere from photochemical processes rather than directly emitted. We have amended the text accordingly.

These fresh emissions undoubtedly contain some primary organic aerosol (POA), which will contribute to the increased OA concentrations measured by the AMS. However, given the fact

that the particle O:C did not change, the fact that POA at the T1 site has an O:C of 0.08, much smaller than the observed O:C, the measured black carbon concentrations in the plume (0.1 – 0.2 µg/m³) and the PMF analysis results at T1 site, the POA contribution to observed OA increase likely to be small (<10%) (Setyan et al., 2012;Zaveri et al., 2012).

5) The CO measurements are relatively low (110-150 ppbv) for the anthropogenic dominated air mass (3 June and 12 June in Figure 9). There needs to be an explanation for this (higher wind speeds?).

Wind speeds are much higher on the 3rd and 12th Wind speeds on the 3rd and 12th were as high as 15m/s near the G-1 flight altitude (Fast et al., 2012). In contrast, wind speeds on June 28th were ~2 m/s. As mentioned in Section 3.1 – 3.2 and in Zaveri et al. (2010), recirculation of pollutants also increased the regional backgrounds toward the end of the campaign.

The higher wind speeds on 12 June, which reached as high as 15 m/s at the G-1 altitude, relative to those on 28 June (~2 m/s) contribute to more rapid dispersion of pollutants, lowering their concentrations (Fast et al., 2012;Zaveri et al., 2012).

Response to Reviewer 2.

This is an interesting and well-written manuscript that will likely motivate a lot of needed discussion on the role of anthropogenic emissions on biogenic SOA formation. The authors do an incredible job in trying to bridge their aircraft measurements to prior laboratory studies on biogenic SOA formation (particularly those studies on isoprene SOA formation). After carefully reading this manuscript a few times, I have a few questions remaining about the interpretation of the results in relation to the exact chemical mechanism likely producing isoprene SOA in this region. I should note that I agree based on their BVOC measurements that isoprene oxidation likely explains the observed enhancements in OA mass observed when biogenic VOCs mixed with the urban plume.

The authors argue that the enhancements in isoprene SOA might occur due to changes in the VOC:NOx ratio. Although this may be partially true, I think the authors need to be more specific than this. As an aid in describing this chemistry in more detail, I have attached a rough schematic in Figure 1 attached here that outlines what is currently thought to occur in the gas phase to yield isoprene SOA formation. Specifically, I've outlined this according to high-NOx and low-NOx (or NOx-free) regimes. What I would argue is the most important aspect to understand is how the RO2 radicals further react once they are initially formed from isoprene OH-initated oxidation. As this figure shows, understanding the relative ratios of RO2 + HO2 versus RO2 + NO versus RO2+ NO2 are important. Related to this mechanism, does your NOx data indicate whenNO2/NO ratios were at their highest, did you see the most OA formation? In addition to above, a few specific/technical comments outlined below that need to be addressed before publication in Atmospheric Chemistry and

Physics can be considered. As a result of my remaining questions/suggestions, I recommend this manuscript be accepted with major revisions noted.

During the day one would expect the NO to get photochemically converted to NO2. Thus, when isoprene is oxidized in the presence of a higher NO2/NO condition, you will likely have MACR form that then further reacts via the H-abstraction channel from the aldehydic H to yield the acyl peroxy radical that combines with NO2 to form MPAN. Studies by Surratt et al. (2010, PNAS) and Chan et al. (2010, ACP) showed that increasing initial NO2/NO ratios in their photooxidation experiments of isoprene lead to the highest SOA yields likely to the favored formation of MPAN. By favoring MPAN formation, Surratt et al. (2010) and Chan et al. (2010) showed that the OH-initiated oxidation of synthetic MPAN yielded the same types of SOA constituents formed when starting with the photooxidation of isoprene under high-NO2/NO ratios. Before these studies, the work of Kroll et al. (2005, 2006) only examined isoprene SOA formation from the perspective of high-NO or NO-free experiments. Thus, in those initial experiments by Kroll et al. (2005, 2006), they generally found that SOA was at its highest when NO was very low. It was argued in those experiments that RO2 + NO favored the formation of RO radicals that then fragmented into volatile products that would not form SOA from isoprene oxidation. The issue with the low-NO pathway is that aerosol acidity has been demonstrated as a requirement to yield SOA from the reactive uptake of isoprene epoxydiols (IEPOX) (Paulot et al., 2009, Science; Surratt et al., 2010, PNAS; Lin et al., 2012,ES&T). Considering that sulfate aerosol loadings are low during this campaign, which has been demonstrated to provide the necessary surface for reactive uptake of IEPOX, I think the authors have a good case that NOx is playing some role in enhancing isoprene SOA formation.

I wonder if there can be any correlation found between NO2/NO ratios and the OA observed in the field study here? My group has been working further on the high-NOx mechanism to understand how we exactly get SOA from isoprene under these conditions.

In short, it seems that the authors argue correctly that there seems to be some nonlinear NOx-dependent pathway to SOA formation from isoprene. However, based on the new lab studies, we now know that increasing NO2/NO ratios enhance the SOA mass from isoprene under high-NOx regimes.

We thank the reviewer for the comments on the relative reaction rates of RO_2 + HO_2, NO, and NO_2. We agree that the branching of these reaction pathways determines the products that are formed and therefore the SOA yield. We also agree that NO_x appears to have some influence on SOA production during CARES. Similar to the reviewer, we originally concluded in the manuscript that the low-NO_x pathway is unlikely to drive the enhanced SOA formation observed in the mixed biogenic/anthropogenic plume. However, as the reviewer points out, this is an active area of research and determining a detailed chemical SOA production mechanism from field data is extremely difficult. Ultimately, accurately determining the dominant reaction pathways will require a full photochemical model, since OH, HO_2, and RO_2 were not measured in this campaign and all evolve dynamically through the day. We are currently developing a

paper focused on modeling the urban plume evolution episodes described in the present manuscript that will investigate these issues. We feel that describing this modeling effort will require (and deserve) a separate, full publication.

In an effort to address the reviewer's question, we have expanded our discussion of the NO_x effect through the manuscript, with more attention paid to the competitive reaction of peroxyradicals with NO and/or NO_2. We have also softened our conclusions on the mechanism, given the discussion and the revisions below. Changes to the manuscript include:

1) In the introduction, we have added text reflecting the reviewer's suggestion to include more discussion about the details of the NOx chemistry.

Under low-NO_x conditions, first-generation isoprene peroxyradicals react primarily with HO_2 to form peroxides which undergo further oxidation to produce isoprene epoxydiols (Surratt et al., 2010;Chan et al., 2010). In the presence of acidic sulfate, these isoprene epoxydiols undergo heterogenous reactions to form organic-sulfate esters (Surratt et al., 2008) and furan diols (Lin et al., 2012) leading efficient SOA formation, especially at low relative humidity (Surratt et al., 2010). Under high-NO_x conditions, first-generation isoprene peroxyradicals react with NO to generate MACR and MVK. In the presence of NO_2, further oxidation of MACR produces peroxyacyl nitrate (MPAN), which undergoes oxidation to form significant SOA (i.e., the MPAN pathway) (Chan et al., 2010).

2) We now include the G-1 measurements of NO, NO_2, NO_2:NO, and bVOC:NOx in figures 4 and 10. In the morning of 6/28, the NO2:NO ratio does not change significantly between the mixed anthropogenic/biogenic plume and areas dominated by fresh biogenics. In the afternoon of 6/28, the NO2:NO ratio is 1.5 – 2x higher in the mixed plume than outside of it. The ratio is slightly higher in the plume during the afternoon flight than in the morning flight as would be expected. We saw significant SOA production during the morning flight while the NO_2:NO ratio does not change significantly as we pass in and out of the mixed plume. We observe further SOA formation in the afternoon and in this case the NO_2:NO ratio does show a significant increase in-plume. Finally, the MPAN pathway generates significant amounts of organic nitrates in the condensed phase. While we can't rule out small contributions of organic nitrates to the OA mass, the data suggests they are not a major fraction of the OA mass. We have made major updates to our discussion of the NOx effect in Section 3.6 to reflect the reviewers suggestions.

When NOx concentrations are low, isoprene derived peroxyradicals react with HO2, eventually generating epoxydiols that, in the presence of sulfate seed aerosol, heterogeneously produce SOA in high yield. with very low vapor pressure are produced from the oxidation of isoprene, particularly in the presence of acidic sulfate aerosol (Surratt et al., 2010;Lin et al., 2012). This mechanism is promising in that it produces very high SOA yields from isoprene while our observations suggest that isoprene is the key biogenic VOC leading to OA formation in this area (Surratt et al., 2010). NO concentrations are highest in the morning 6/28 plume, averaging around 2 ppbv (NOx concentrations range from 10-12 ppbv in-plume) and subsequently decrease to ~200 pptv in the afternoon, suggesting that isoprene-derived epoxydiols may contribute to OA formation in the area. However, NO concentrations outside the plume are also very low while isoprene concentrations are even higher than in the plume yet no significant OA formation was observed (section 3.3). Signal intensity at m/z 82, specifically the C5H6O+ ion,

has been identified as anis an AMS marker for SOA formation from isoprene epoxydiols (Lin et al., 2012;Robinson et al., 2011). Robinson et al. (2011) performed PMF analysis of AMS data collected in a tropical rainforest and identify a factor characterized by strong signal intensity at m/z 82 which they attribute to SOA formation from isoprene. They report that the signal intensity at m/z 82 is 2% of the organic signal (i.e., 82:org) and that 82% of the signal at m/z 82 was from the C5H6O+ ion (i.e., C5H6O+:m/z 82) (Robinson et al., 2011).;Lin et al. (2012) examined heterogeneous SOA formation from isoprene epoxydiols in the presence of acidic sulfate seed and report 82:org of 1-2% and C5H6O+:m/z 82 of 68-95%. We observe relatively small but significant signal intensity at m/z 82 in nearly all mass spectra, regardless of the dominant emission sources. In the mixed anthropogenic/biogenic plume described in Section 3.2, 82:org was 0.6% while C5H6O+:m/z 82 was 63% (Figure 6). Data are very similar for the other mass spectra presented in Figure 6. Therefore, in our data, the C6H10+ ion is a somewhat smaller portion of the signal at m/z 82 than observed by Lin et al. and Robinson et al. and the m/z 82 peak is a somewhat smaller portion of the total organic signal. Additionally, efficient SOA formation from isoprene epoxydiols requires acidic sulfate seed, while the aerosol was largely neutralized during CARES. In light of this evidence, we conclude that isoprene epoxydiol formation may contribute to OA formation during CARES, though it is unlikely to explain our observations of increased OA productions in mixed biogenic/anthropogenic emissions.

Thus, our data suggests that the bVOC:NOx ratio plays an important role in regulating OA formation from isoprene in this region and may partially drive our observations of enhanced OA formation in mixed anthropogenic/biogenic plumes. However, the precise mechanism for this enhancement remains unclear. As discussed in the preceding paragraph, our observations suggest that conditions are not favorable for efficient production of SOA from isoprene under low-NOx conditions. Under high-NOx conditions, SOA production is attributed to the formation and subsequent oxidation of MPAN (i.e., the MPAN pathway) (Chan et al., 2010;Surratt et al., 2010). In this case, high ratios of NO2:NO should favor production of MPAN and therefore OA production. In the afternoon of 6/28, the NO2:NO ratio was 1.5 – 2x higher in the mixed plume than outside of it (Figure 4). However, significant OA production was also observed during the morning flight while the NO2:NO ratio does not change significantly as the G-1 passed in and out of the mixed plume. Finally, SOA production via the MPAN pathway generates condensed-phase organic nitrates (Chan et al., 2010;Surratt et al., 2010). While we can't rule out small contributions of organic nitrates to the OA mass, the data suggests they are not a major fraction of the OA mass. Thus, the CARES data suggest NOx plays some role in enhancing SOA formation in the mixed anthropogenic/biogenic plume, though the mechanism remains unclear. A full model simulation is required for determining whether the laboratory measured NOx-dependent isoprene yields effect on yield can fully account for the measured SOA loadings. Further research is also needed to determine whether the relationship between the bVOC:NOx ratio and OA production rates is robust.

3) As a further aid in further investigating possible NOx effects, we plot below organic loading as a function of NO_2:NO for the 6/28 data and color the points by the sum of isoprene, MVK and MACR. As can be seen, there is no clear trend, with both high and low organic loadings found at similar NO_2:NO ratios. Plotting organic loading against the ratio of biogenic VOCs to NO or to NO_2 shows similar trends, with no correlation found. The findings are similar if all the G1 data are plotted together.
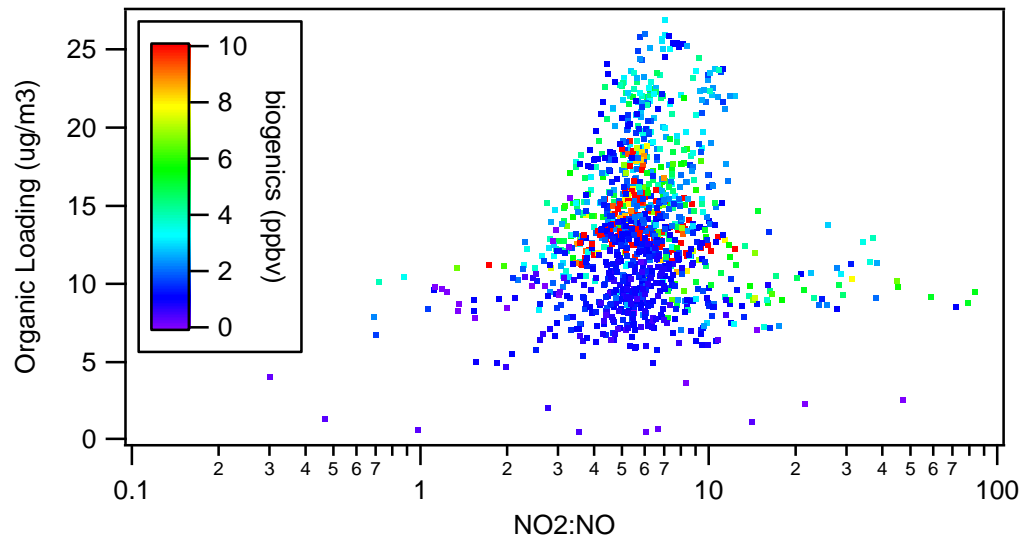
To summarize, our data don't show any strong evidence that the NO_2:NO ratio drives SOA formation and indicate organic nitrates are not a major fraction of the OA. Therefore, while the does not necessarily rule out the dominance of the MPAN pathway, it also does not support it. For the 28 June data, the VOC:NOx ratio remains one indicator of a NOx effect, though we acknowledge it does not explain the mechanism. We believe the modeling study currently in progress will be more informative and help to determine the SOA production mechanism. In light of all of this discussion, we have softened our conclusions in both the abstract and in the conclusions regarding the NOx effect.

In abstract:

After considering several possible anthropogenic/biogenic interaction mechanisms, we conclude that NO_x concentrations play a strong role in enhancing SOA formation from isoprene, though the chemical mechanism for the enhancement remains unclear. If these observations are found to be robust in other seasons and in areas outside of Sacramento, regional and global aerosol modules will need to incorporate more complex representations of NO_x-dependent SOA mechanisms and yields into their algorithms.

In conclusions:

After considering multiple possible anthropogenic/biogenic interaction mechanisms, we conclude that NO_x concentrations play some role in enhancing SOA formation from isoprene, though the chemical mechanism for the enhancement remains unclear. This conclusion is supported by laboratory measurement showing that SOA products and yields from isoprene are a strongly dependent on the gas-phase oxidation pathways, which are complexly dependent on the relative concentrations of NO, NO_2, HO_2, and RO_2 (Kroll et al., 2005;Kroll et al., 2006;Dommen et al., 2006;Chan et al., 2010;Surratt et al., 2010).

I wonder, do the authors have any particle data showing any nucleation events associated with the urban plume mixing with the biogenic emissions?

There is some evidence from CARES that suggests OA and sulfate are important in new particle formation and growth to detectable size (3 – 10 nm depending on instrument), though the G-1 was not equipped to study nucleation. Indeed, the specialized instrumentation required for studying nucleation mode (~1- 10 nm) particle chemical composition were not available either on the ground or in the aircraft.

Setyan et al. (2012) observe frequent new particle formation and growth events at the T1 ground site and find that organics have much higher concentration in the fine particle mode than does sulfate and that the increase of ultrafine mode organics was much faster than that of ultrafine mode sulfate, indicating organics play a more important role in particle growth than sulfate. Zaveri et al. (2012) show that the total number particles correlated primarily with SO_2 concentrations, though the ratio of the number of particles larger than 3 nm to those larger than 10 nm was more strongly associated with high isoprene concentrations (Zaveri et al., 2012). However, SO_2 was regional pollutant in the area and no strong sources were identified in the Sacramento urban plume. In summary, the data thus far suggests that SO_2 and isoprene emissions both play a role in particle formation and growth; however, nucleation events have not been extensively analyzed and the instrumentation required to make definitive conclusions about the role of different emissions on nucleation were not deployed during CARES.

Specific/Technical Comments:

1.) Positive Matrix Factorization (PMF): I'm just curious, why wasn't PMF used for the AMS dataset? I'm assuming this is due to the nature of how the data is collected (i.e.,aircraft measurements). Studies by Slowik et al. (2010, ACP) and Robinson et al. (2010) have showed that a factor could be resolved from the organic fraction that was likely associated to isoprene SOA. Lin et al. (2012, ES&T) showed that these prior studies by Slowik et al. (2010, ACP) and Robinson et al. (2010, ACP) was likely due to reactive uptake of gaseous IEPOX onto pre-existing sulfate aerosols. The unique fragment ion that appeared in the mass spectra associated with these PMF factors was m/z 82. Did the authors confirm that m/z 82 with the same elemental composition was or was not observed in their AMS data set? I ask this since the authors used a HR-TOFMS.

Setyan et al. (2012) performed HR-PMF analysis of AMS data collected at the T1 ground site, which was influenced by both mixed anthropogenic/biogenic emissions and by primarily biogenic emissions (Setyan et al., 2012). They identified a more oxidized OA factor attributed to SOA formation from biogenic emissions and a less oxidized OA factor attributed to anthropogenic emission. They were unable to identify any PMF factor with strong contributions at m/z 82. One possible reason is that the aerosol was nearly completely neutralized at the T1 site and in the G-1 data while SOA formation via the low NOx pathway requires acidic conditions. Given 1) the fact that a m/z 82 dominated factor was not identified in the T1 site data, 2) the similarity between the spectra collected on the G-1 under different conditions (see Figure 6), 3) the more limited S/N in the aircraft data, especially at higher m/z values such as 82, 4) the aerosol observed during flights was nearly completely neutralized, consistent with the ground, and 5) the fact that the aircraft missions were designed to fly through high-SOA plumes at the same time of day and therefore have less natural spectral and temporal variance than the ground data, we decided not to present PMF analysis in this manuscript.

In the Lin et al and Robinson et al data, the fragment at m/z 82 was primarily composed of the $C_5H_6O^+$ ion with minor contributions from the $C_6H_{10}^+$ ion. Lin et al report the ion $C_5H_6O^+$ comprises 68-95% of the total signal at m/z 82 and that m/z 82 comprises 1-2% of the total organic signal from synthetic isoprene oxidation products. Robinson et al. report 82% of the m/z 82 signal is $C_5H_6O^+$ and m/z 82 is 2% of the total organic signal.

In the mixed anthropogenic/biogenic plume described in Section 3.2, the $C_6H_{10}^+$ peak was 63% of the m/z 82 signal while the $C_6H_{10}^+$ ion was 31% of the signal at m/z 82 (Figure 6). A minor portion of the signal at m/z 82 was from other fragments. The m/z 82 peak was 0.6% of the total organic signal. Data are very similar for the other mass spectra presented in Figure 6. Therefore, in our data, the $C_6H_{10}^+$ ion is a somewhat smaller portion of the signal at m/z 82 than observed by Lin et al. and Robinson et al. and the m/z 82 peak is a somewhat smaller portion of the total organic signal. Based on these observations and the requirement of acidic sulfate seed for generating SOA from IEPOX, our original conclusions regarding IEPOX-derived SOA, namely that they may contribute to SOA formation, but are unlikely responsible for SOA enhancements in the mixed biogenic/anthropogenic plumes, is reasonable. We have included the details from the discussion above in the manuscript.

Signal intensity at m/z 82, specifically the $C_5H_6O^+$ ion, has been shown to be an AMS marker for SOA formation from isoprene epoxydiols (Lin et al., 2012;Robinson et al., 2011). *Robinson et al. (2011) performed PMF analysis of AMS data collected in a tropical rainforest and identify a factor characterized by strong signal intensity at m/z 82 which they attribute to SOA formation from isoprene. They report that the signal intensity at m/z 82 is 2% of the organic signal (i.e., 82:org) and that 82% of the signal at m/z 82 was from the $C_5H_6O^+$ ion (i.e., $C_5H_6O^+$:m/z 82) (Robinson et al., 2011).Lin et al. (2012) examined heterogeneous SOA formation from isoprene epoxydiols in the presence of acidic sulfate seen and report 82:org of 1-2% and $C_5H_6O^+$:m/z 82 of 68-95%.* We observe relatively small but significant signal intensity at m/z 82 in nearly all mass spectra, regardless of the dominant emission sources. *In the mixed anthropogenic/biogenic plume described in Section 3.2, 82:org was 0.6% while $C_5H_6O^+$:m/z 82 was 63% (Figure 6). Data are very similar for the other mass spectra presented in Figure 6. Therefore, in our data, the $C_6H_{10}^+$ ion is a somewhat smaller portion of the signal at m/z 82 than observed by Lin et al. and Robinson et al. and the m/z 82 peak is a somewhat smaller portion of the total organic signal.*

2.) On p. 26325, line 20, the authors state: "Signal intensity at m/z 82 is an AMS marker for isoprene epoxydiols (Lin et al., 2012; Robinson et al., 2011); we observe relatively small but significant signal intensity at m/z 82 in nearly all mass spectra, regardless of the dominant emission sources. "It would be better to say m/z 82 is a marker for isoprene epoxydiols-derived SOA, instead of IEPOX itself, since IEPOX is the gas phase precursor that would not be measured AMS.

We have made the suggested change and significantly revised this discussion (see above).

Signal intensity at m/z 82 is an AMS marker for *SOA derived* from isoprene epoxydiols…

3.) PTR-MS data: Did they observe ions at m/z 119 or m/z 101? If so, did these correlate or anti-correlate with isoprene, MVK, or MACR signals? These ions might indicate the [M + H]+ ion for gaseous IEPOX (MW 118) or the [M - H2O]+ ion.

Our PTR-MS sampling strategy needed to strike a balance between the number of masses monitored, the signal averaging time at a particular m/z, and the measurement frequency. Unfortunately, we did not sample at m/z 101 or 119 and therefore cannot comment further on the role of gaseous IEPOX.

4.) Abstract, p.26298, line 24: Did the authors mean to say: "A strong, non-linear NOx dependence" It seemed maybe the word NOx was missing here.

The word NO_x was indeed missing from the text and we have corrected the text.

A strong, non-linear NO_x dependence of SOA yield from isoprene is the explanation…

5.) Section 3.2, p. 26310, line 1: Change "show" to the word "shown"

We have made the suggested change.

As *shown* in Figure 1, a buildup of aerosol in the Sacramento area occurred toward the…

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