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Interactive comment on “Ozone-driven photochemical formation of carboxylic acid groups from alkane groups” by S. Liu et al.

Anonymous Referee #1

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This manuscript describes particulate measurements taken along the coast of Southern California. Much of the discussion focuses on the comparison between the AMS and an FTIR-based method, and the two techniques complement each other nicely.

The authors estimate the contribution of SOA to the total OA observed at the sampling site. I believe that their estimates of the fraction of SOA are too low; this conclusion comes at the detriment of the manuscript. The authors estimate that the OA is about 10-30% SOA. However, it seems that the fraction of SOA may be much higher – at least 30-60%. This dominance of SOA is likely the most important conclusion of the manuscript, as the same SOA fraction is determined by both the AMS and FTIR analyses. The FTIR analysis therefore verifies the large fractions of SOA (measured as OOA) observed at numerous sites in the northern hemisphere with AMS's.

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Overall, the manuscript is poorly written and organized, and at times is difficult to follow. The interesting technical aspects and scientific conclusions are largely obscured by the poor quality of the writing. The underlying data and analysis will be worthy of publication once the writing is improved.

*Page 7191 – The discussion of the importance of “alkane groups” to ambient OA is confusing. I interpret the FTIR-determined alkane groups to indicate aliphatic carbons – those with only C-C and C-H bonds. However, starting in line 26, the authors convolve “alkane groups” with “alkanes” (e.g., Lim and Ziemann, Presto et al). The authors should either be more explicit in their definition of alkane groups or consider using a different term, such as aliphatic groups.

*Page 7195 – The first figure referenced in the text is Fig. 3, followed by Figs 1 and 5. The figures should be referenced in order.

*Page 7196 and Figure 3a – Lines 20-22 of page 7196 note “Only days associated with single air mass sector (32 out of 47 days) were included (Fig. 3a) in the diurnal cycle analysis in order to track the daily changes in compositions caused by chemistry rather than air mixing,” and the caption to Figure 3a says “top green bars indicate samples associated with single air mass sector, which were used for diurnal profile analysis.” I think that the authors are trying to say that the days labeled with the green bar in Figure 3a were days where the sampling site was impacted by air from a single air mass sector, and that there were 32 such days in the 47 days of the study. However, the green bars in Figure 3a clearly cross days represented by different air masses, and in some cases a single day is indicated as being influenced by more than one source region (e.g., August 20-21, August 30-September 1). The explanation both in the text and the figure caption require clarification.

*Page 7197, Section 3.3 – It is not clear why the authors determined the background CO mixing ratio with a plot of OM vs CO, especially considering that the background CO mixing ratio differed for the FTIR and AMS analyses. Why not use the CO measured

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during time periods when the sampling site was impacted by the “Ocean” trajectory in Figure 1 as the background CO? Also, it is not clear that the differences in the intercepts for the FTIR and AMS-determined background CO (80 vs 89 ppb) are insignificant, because the authors do not note average or extreme concentrations of CO measured at the sampling site.

*Page 7198, Line 19 – This is the first reference to Figure 2, and it comes after references to Figures 1, 3, 4, 5, and 6. As a reader I find the disjointed numbering of the figures thoroughly confusing. Also, there is such little discussion of Figure 2 that I am not sure it warrants a place in the manuscript.

*Page 7198, Line 1 to Page 7199, Line 5 – The discussion of the classification of the diurnal profiles is difficult to follow, with four “Types” and two “Classes.” The text seems to describe the thought process that was used to parse the sampling days into types and classes, which may be too much detail. It would be much simpler to state that the days are classified as either “Afternoon high” or “Noon high”, and to describe the minor differences within each class of days.

*Page 7199, Line 6 – I am not familiar with “Aged Combustion Factor,” and I don’t think that the average reader will be either. While the Aged Combustion Factor is described nicely in the subsequent PMF section, it is used both here and in the Abstract with no explanation. This makes the paper difficult to read, and in fact I did not understand large sections of the manuscript until my second reading because, frankly, it is out of order. The PMF classes should be introduced earlier, or not used at all until they are discussed. The description of Figure 7 on page 7199 would not suffer if the authors only discussed the AMS m/z 44.

*Page 7199, Line 23 – Page 7200, Line 11 – I do not think that the discussion of Figure 9 adds significantly to the manuscript. It should either be expanded or removed.

*Page 7201, Lines 5-10 – The authors should give more explanation to why they combined the 6 factors from the PMF solution into three. As they note in line 5, the three-

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factor solution is not sufficient to describe the variability in the data. How is collapsing the 6-factor solution into three factors better? I assume that the three combined factors were used to facilitate comparison with the 3-factor AMS solution, but perhaps this hides some information from the FTIR PMF solution? I assume that 6 factors were needed to describe the data because there is additional information in the FTIR spectra that is not available in the AMS.

*Section 4.1 -I am not convinced that the strong correlation between carboxylic acid groups and ozone is the smoking gun that the authors suggest. Ozone tends to be highly correlated with OH, and one could consider the periods of high ozone as periods of high photochemical activity, with abundant OH available to participate chemistry. -In the last paragraph on page 7205, which continues to page 7206, the authors state that acid groups are formed from ozone reactions with dihydrofurans (which are produced by isomerization and dehydration in the particle phase). However in the following paragraph, starting on Line 18 of page 7206, the authors further argue that high concentrations of AMS m/z 44 result from condensed phase oxidation. Since AMS m/z 44 is correlated with the FTIR-determined acid groups, aren't these two paragraphs at odds? The first suggests that acids (and therefore AMS m/z 44) form via (1) vapor-phase oxidation with OH, (2) condensed phase processing without oxidation, and (3) vapor-phase oxidation by ozone. All of the oxidation in this scheme occurs in the vapor phase. The second paragraph suggests that AMS m/z 44 (and therefore organic acid groups) form in the condensed phase.

*Section 4.2 – The calculations used to estimate the SOA mass fraction are unclear, but it seems like the authors are severely underestimating the SOA mass fraction. There are several pieces of evidence to consider: (1) The discussion of the PMF factors notes that the AMS Combustion factor is similar to Pittsburgh OOA, which is often considered as a surrogate for ambient SOA. The fraction of m/z 44 in the AMS Combustion factor is 26%, and the fraction of m/z 57 (tracer for fresh emissions) is negligible. One could easily assume that the Combustion factors are pure SOA. (2) The combustion factors

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for the AMS and FTIR are the dominant component of the OA at about 60% of the total mass on average. (3) The average contribution of organic acid groups is 34%. This is likely the lower bound estimate for the SOA mass fraction. As noted in Section 4.1, the organic acids are likely secondary in nature.

Figure 12 seems to suggest that the authors assume that the overnight/background OA is primary. I would argue that this is all or at least mostly aged SOA. Changing the grey portions of the bars in Fig 12 to green would significantly increase the SOA mass fraction.

Based on a rough estimate given the items above, it seems that on average the OA is at least between 34-62% SOA. The real value is likely higher, as the biomass burning factor is aged during transit to the sampling site, and is therefore not purely primary OA.

I think that the most important conclusion from this manuscript is that the FTIR measurements echo the large body of AMS measurements that suggest that SOA is the dominant form of OA in the atmosphere. The authors should state this clearly.

*Table 3 – The values in Table 3 are not clear to me. What is different between the numbers in and out of parenthesis?

Comments on Figures *Figure 3 is too small and therefore hard to read. I had to zoom in significantly to read the details. *Figure 6 is almost impossible to interpret. I think that the green and blue points represent duplicates of the same days, just plotted on different axes for clarity. This is not obvious from the way the axes are labeled – in fact, it looks like there are sets of organic acid measurements for one day, followed by alkane measurements for the next day. The caption mentions “thick” and “thin” rectangles, but it is not obvious that the rectangles have different line thicknesses. *I don’t think that Figure 13 adds to the manuscript, and it could be removed.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 7189, 2011.