Reply to short comments:

I carefully read this manuscript due to my recent research interests, this is a good paper yet I also have a couple of suggestions, which I hope would be helpful.

We thank Dr. Emerson for the useful suggestions. The answers to the specific questions are listed below.

(1) It is a bit strange to me that, from the title and the abstract, the paper will focus on carboxylic acid formation, yet when reading through the paper, I find a large body of the MS actually reports particle measurements by FTIR and AMS, and their comparison. Only section 4 is for discussion of carboxylic acid formation.

The reviewer is correct in noting that this manuscript reports FTIR and AMS measurements, which provide two proxies for carboxylic acids (molecules), one is acid functional groups (FTIR) and the other is the particulate m/z 44 fragment (AMS). In fact, the title is explicit about the use of such proxies by stating that we are looking at "Carboxylic Acid *Groups*." While it is true that sections 2 and 3 focus on the measured FTIR and AMS quantities since they report the "Sample Collection and Instrumentation" and "Results", respectively, sections 1, 4, and 5 focus on carboxylic acids. To further emphasize this discussion of acids, we have moved some of the detailed methodological discussion of the "PMF factors" to the appendix to make sure a large fraction of the paper describes carboxylic acid group (SOA) formation.

We have also revised the introduction to make this approach more clear:

The second paragraph on Page 7192 (the introduction part) now reads:

"In this work, we compare the contributions of carboxylic acid group and other oxygenated organic groups that can be attributed to photochemical SOA formation in the atmosphere. We use factors identified from the Positive Matrix Factorization (PMF) analyses on the complementary Fourier Transform Infrared (FTIR) spectroscopy and Aerosol Mass Spectrometry (AMS) measurements to separate organic components based on their sources, so that the SOA formation for each source can be considered separately. The oxygenated nature of the fossil fuel combustion factors is used to provide an initial estimate of the total contribution of acid groups to SOA. A second estimate of SOA formation is provided by using a pseudo-Lagrangian framework to identify the fraction of SOA formed in a single day ("Today's SOA"). In addition, we use the size distribution of acid groups to assess the mechanism by which the SOA forms. By comparing the extent to which these three methods are consistent, this study provides both an evaluation of the contribution of acid groups to SOA and an estimate of the timescale, precursors, and oxidants required for SOA formation."

(2) In my opinion, the introduction is not well organized. In the beginning, "The major organic components identified in ambient particles include alkane, carboxylic acid, hydroxyl, amine, and non-acid carbonyl functional groups (Maria et al., 2002; Liu et al., 2009; Russell et al., 2009a)." (here, some other papers can be mentioned, for example, Pietrogrande et al., Environ. Sci. Technol., 2010, 44,4232–4240 on alkanes; Jaoui et al., Anal Chem. 2004, 76(16):4765-78 on carboxylic acids ; Ge et al., Atmos. Environ., 45, 524-546 on amines). Then, the authors talked about alkanes groups, and carboxylic acid groups. Why not other groups? (I understand that is because this paper is going to discuss formation of carboxylic acid groups from alkane groups, yet one or two sentences are clearly needed. In my opinion, this actually can go with later discussion).

We have added the suggested papers to the references, as well as a new Table 4 to explicitly note past ambient measurements of acids as well as text in the introduction and discussion to clarify these important prior studies:

"Carboxylic acids have been frequently observed in atmospheric particles since 1970s (Schuetzle et al., 1975; Cronn et al., 1977; Satsumabayashi et al., 1989; Satsumabayashi et al., 1990; Kawamura and Ikushima, 1993; Rogge et al., 1993). In these measurements, carboxylic acid concentration either correlated to solar radiation or correlated to oxidant concentration (mostly ozone), suggesting they are formed in the atmosphere during photochemical processes. For example, enhanced abundance of ambient carboxylic acids in summer and in the afternoon suggests that carboxylic acids are secondary (Kawamura and Ikushima, 1993; Kawamura and Yasui, 2005). Although primary emission of carboxylic acids from engine exhaust and meat cooking were identified in a few studies (Kawamura and Kaplan, 1987; Rogge et al., 1991), the lack of correlation of carboxylic acids to traffic emission and meat cooking tracers suggest that these primary acid sources may not contribute significantly to carboxylic acid mass."

We have limited discussion of other functional groups in order to focus on acids and alkanes, as they represent a large fraction of the aerosol at this location. We have clarified this reasoning by adding a sentence saying that alkane and carboxylic acid groups often account for more than 70% of the OM (below). This focus allows us to give the reader a general view of the state of studies on the topic of acid formation.

Page 7191, line 1, after "Russell et al., 2009a)": add ", among which alkane and carboxylic acid functional groups often account for more than 70% of the OM (Russell et al., 2011)".

(3) "Carboxylic acid groups are generally SOA components…" this is better to have its own paragraph.

We have separated the paragraph on Page 7191 according to the suggestion.

(4) Page 7192: Suddenly, the authors start to talk about SOA. What is the relationship between this and previous paragraphs? And finally, "In this work, organic functional groups are quantified…". Again, it seems like, that the formation of Carboxylic acid is only a minor component of this paper. The authors might need to specify the focus of the paper more clearly, for readers to follow (probably the title needs alteration too). Otherwise it is just confusing.

This paragraph discusses total SOA and the previous paragraph discusses one likely SOA component – carboxylic acid groups. We have revised the introduction as discussed above and added Table 4 (shown below) to compare the SOA fraction to other studies, and the first paragraph on Page 7192 to make this connection:

Page 7192, line 1: replace "Large uncertainty in SOA formation mechanisms makes identification of ambient SOA controversial." with "Despite increasing number of studies on carboxylic acids in recent years, the formation mechanism of carboxylic acids and other SOA components are still poorly understood, making identification of ambient SOA controversial".

We have re-organized the second paragraph on Page 7192 to emphasize the focus of this work as shown above (in the answer to the first question).

Table 4. Comparison of SOA contributions to total OM.

Reference	Total SOA or Hihg O/C Compnent	Recent SOA Contribution	Background SOA	Carboxylic Acid Groups	Identification of SOA
Schuetzle et al., 1975	–	–	–	–	correlation of acids with solar radiation
Cronn et al., 1977	–	–	–	–	correlation of acids with solar radiation
Rogge et al., 1993	–	–	–	–	correlation of acids with solar radiation
Kawamura and Yasui, 2005	–	–	–	–	correlation of acids with solar radiation
Satsumabayashi et al., 1989	–	–	–	–	correlation of acids with ozone
Kawamura and Ikushima, 1993	–	–	–	–	correlation of acids with ozone
Satsumabayashi et al., 1990	–	62–100%	0-38%	30–50%	correlation of acids with ozone
Hildebrandt et al., 2010	nearly 100%	–	–	–	high O/C component
Zhang et al., 2007b	64–95%	–	–	–	high O/C component
Lanz et al., 2007	60–69%	–	–	–	high O/C component
Gilardoni et al., 2007	50%	–	–	31%	high O/C component
Russell et al., 2009a	70%	–	–	31%	high O/C component
Liggo et al., 2010	75–95%	40–50%	35–45%	–	high O/C component and phothchemcial age
This study	60%	15–30%	30–45%	34%	high O/C component and correlation of acids with ozone

(5) I agree with reviewer 1 that the "Aged Combustion factor" should be introduced first, otherwise it is quite strange.

We have moved the "PMF factors" to the Appendix but have discussed their identification briefly before the "Diurnal cycle" section.

(6) It is better to give some detailed PMF analysis results (probably as supplementary materials), for both PMF-FTIR and PMF-AMS. For example ,for

PMF-FTIR analysis, "Two- and three- factor solutions were excluded since only 85% of the OM was reproduced", but later you actually used a 3-factor solution, but resulted from the 6-factor solution, what is the difference, how do they look like respectively, how do the authors recombined 3-factor from a 6-factor solution?

We have now added appendices to explain in detail that in fact a 6-factor solution was used, but that this solution included 3 factors that correlated in time with the other 3 factors. Here is the detailed description added as Appendix A:

"Appendix A

A1 PMF of the FTIR spectra

The FTIR PMF input matrix consisted of 234 mass-weighted and baselined FTIR spectra. The scaling factors were estimated by baselining errors calculated using the automated algorithm described by Russell et al. (2009a). The robust mode was used and the outliers were downweighted during the fitting procedure. Two to six factors with an FPEAK-range of [0, ±0.2, ±0.4, ±0.6, ±0.8, ±1] were tested. The Q-value versus FPEAK plot showed a "U" shape with the lowest Q values corresponding to FPEAK of -0.2, 0, and 0.2, which resulted in the same factors. The edge-FPEAK values [±0.6, ±0.4, ±0.8, and ±1] resulted in increased Q values, indicating increased residuals associated with the PMF model (Lanz et al., 2007). Because the sensitivity to rotation was negligible for FPEAK=-0.2, 0, and 0.2, FPEAK=0 was selected to represent the solution. Another quantity Q, the sum of squared scaled residuals, can also be used as a mathematical diagnostic of the PMF solutions. Q/Qexp (normalized Q), in which Qexp approximately represents the degree of freedom of the fitted data, is greater than 4 for the two- and three-factor solutions and smaller than 3 for the n>3 solutions (Fig. A1). This decrease of normalized Q indicates that the additional factors in the n>3 solutions explain significantly more variation of the data. Therefore, two- and three-factor solutions were excluded. Correlated factors (r>0.5) with similar compositions were identified in the four-, five-, and six- factor solutions, indicating some factors split into indistinguishable and non-independent components (Ulbrich et al., 2009). The correlated factors in each solution were combined to one factor, resulting in three factors for each of the four-, five-, and six-factor solutions. The combined factors explain the same degree of the OM variability as the individual factors used from the four-, five-, and six-factor solutions, and the combined factor mass is equal to the sum of individual factor masses. The three recombined factors resulting from the six-factor solution were selected because these factors captured events that were associated with trajectories from either known wildfires or from Los Angeles-Long Beach ports. In addition, the factor profiles had similar peak structure (r > 0:8) with the known factors derived from the TEXAQS/GoMACCS 2006 and the Scripps Pier 2008 measurements (Hawkins and Russell, 2010a; Russell et al., 2009a).

The first factor spectrum correlated to the fossil fuel combustion factor profiles of the TEXAQS/GoMACCS (Russell et al., 2009a) and the Scripps Pier 2008 measurements (Hawkins and Russell, 2010a) projects with r of 0.97 and 0.99, respectively, indicating similar organic compositions, likely resulting from similar sources or processes. This factor was characterized by large fractions and co-existence of alkane and carboxylic acid functional groups (51% and 42% of the factor OM, respectively) and was identified as a fossil fuel combustion factor. The concentration of this factor was 3.0 µg m^{-3}, accounting for 62% of the OM on average (Fig. 2c). Hydroxyl and amine functional groups contributed 7% and 1% of the factor OM, respectively. The PSCF image (Fig. A2a) shows the origin of this factor was mainly located at the vicinity of Los Angeles region, which are dominated by fossil fuel combustion emissions. The second factor spectrum correlated to the biomass burning factor profiles identified from the TEXAQS/GoMACCS (Russell et al., 2009a) and the Scripps Pier 2008 measurements (Hawkins and Russell, 2010a) with r = 0.87 and 0.93, respectively. The factor fraction time series (Fig. 2c) showed three high concentration periods: 26 August–2 September, 8–22 August, and 22–27 September, corresponding to the top three fires in acreage that occurred in California: the Station fire (in Los Angeles County), the La Brea fire (in Santa Barbara County), and the Guiberson fire (in Ventura County), respectively (http://www.fire.ca.gov/fire protection/fire protection fire info redbooks 2009.php). The PSCF image (Fig. A2b) indicates that this factor is likely from north of Los Angeles – Santa Barbara County, as well as Baja California regions, consistent with fire events that occurred during the sampling period and fire maps from satellite measurements (Fig. A2c). Based on the similarity of this factor spectrum to previously identified biomass burning factors and the increase in concentration during fire-influenced time periods, this factor was identified as a biomass burning factor. The factor concentration was 0.88 µg m^{-3} on average and accounted for 18% of the OM. Non-acid carbonyl and alkane functional groups dominated this factor, accounting for 44% and 34% of the factor OM, respectively. The factor spectrum of the third factor was comparable (r=0.82) to the spectrum of the polluted marine factor described in the Scripps Pier 2008 measurements (Hawkins and Russell, 2010a). This factor was identified as a marine factor that accounted for 20% of the OM on average and was dominated by hydroxyl functional groups (72%). Alkane, carboxylic acid, and amine functional groups contributed 20%, 4%, and 3% of the OM, respectively. The concentration and composition of the factors are summarized in Table 2.

A2 PMF of organic fragment concentrations

The input matrix and the error files for PMF of the AMS measurements were prepared using the Igor Pro 5 (Wavemetrics Inc.) codes based on the work of Zhang et al. (2005). Two to six factors with FPEAK-range of [0, ±0.2, ±0.4, ±0.6, ±0.8, ±1] were investigated. The Q-value versus FPEAK plot shows a "U" shape with the lowest Q values corresponding to FPEAK values of -0.2, 0, and 0.2. The factors generated for each rotation were nearly indistinguishable. FPEAK=0 was

selected to represent the solutions. A distinct factor with significant mass was missing when two factors were used. For each of the four-, five-, and six-factor solutions, highly correlated factors (r>0.7) were combined, resulting in three recombined factors, which resembled the three factors generated from the three-factor solution. The normalized Q values for the three-six factor solutions are comparable (differences are within 10%), indicating three factors were likely enough for explaining the variability of the input data matrix. Therefore, the three-factor solution was selected and 98% of the OM was reproduced. The factors were identified by comparing normalized factor spectra with the online AMS reference spectra (Ulbrich et al., 2007, 2009). The first factor spectrum correlated to several LVOOA (low-volatility OOA) and SOA profiles. For example, the factor spectrum correlated to the Pittsburgh OOA factor profile (Zhang et al., 2005; r=0.93 for m/z>44 and r=0.95 for all m/z) and SOA profile from the photooxidation of m-xylene with seed aerosols under RH=55% (Bahreini et al., 2005; r = 0.94 for m/z>44 and r = 0.90 for all m/z). The factor could not be further split into LV-OOA and SV-OOA (semi-volatile OOA) factors as shown in many previous studies (Ng et al., 2010), likely because of the relatively low particle concentration at the sampling site. The diurnal cycle of this factor showed a significant increase in concentration during the day and decrease in the morning and night (Fig. 5), indicating photochemical origins of this factor. This factor likely represented an aged component formed from processed primary emissions. The factor was identified as an aged combustion factor, which accounted for 61% of the AMS nrOM and was associated with the largest m/z 44 nrOM fraction and m/z 44 to m/z 43 ratio among all factors (Table 2). The second factor profile strongly correlated with the wood burning spectrum (r =0:90 for both m/z>44 for all m/z) identified by Lanz et al. (2007) and the brush fire spectrum (r =0.94 for m/z>44 and r =0.92 for all m/z) described by Bahreini et al. (2005). This factor was identified as a biomass burning factor, accounting for 26% of the nrOM. No correlation was found between the third factor spectrum and the spectra from the AMS database. The factor concentration correlated to none of the concentrations of the AMS-measured inorganic compounds. The factor profile correlated moderately (r =0.5) with the third factor (which was likely influenced by the ocean) from the ICEALOT study (Frossard et al., 2011) and the time series correlated to that of the FTIR marine factor with r =0.5. This factor likely represented a marine factor, which accounted for 13% of the nrOM."
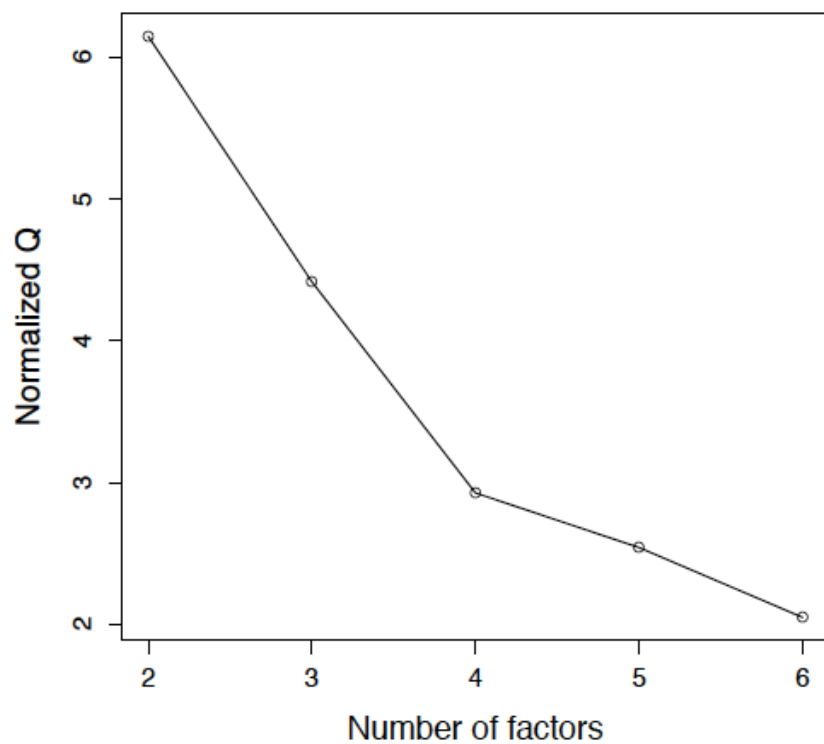
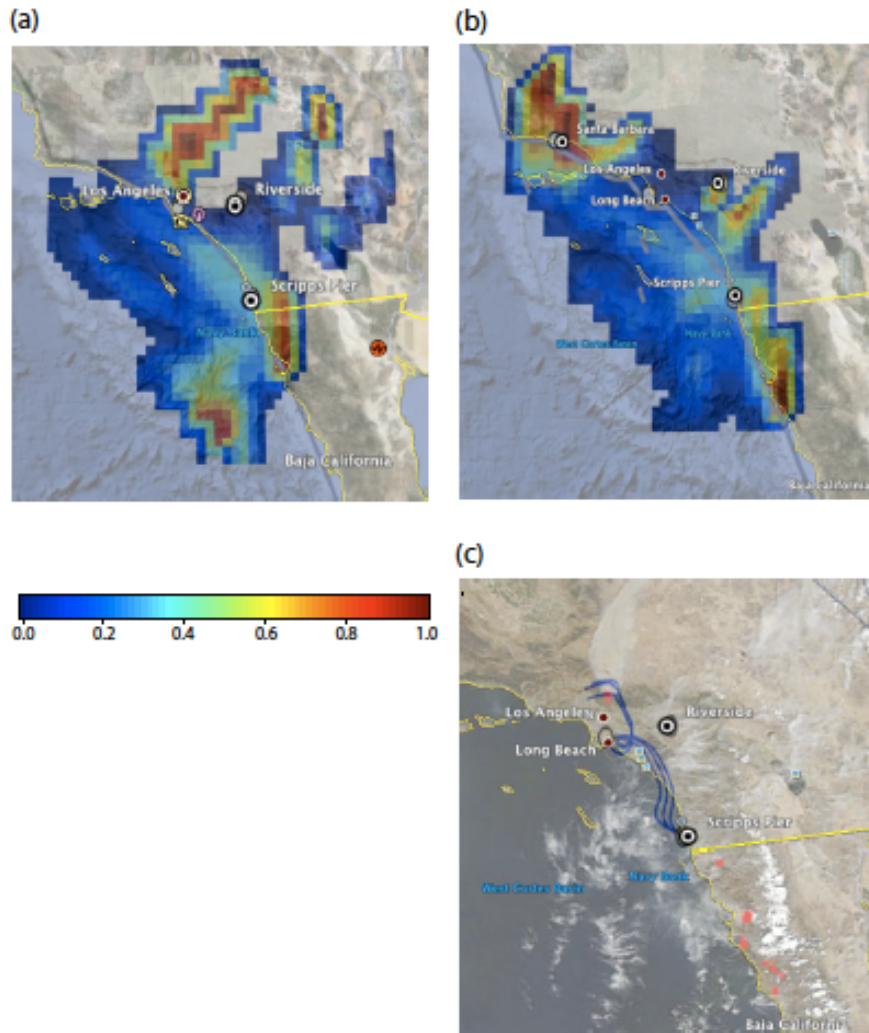Fig. A1 Normalized Q values versus number of factors for the FTIR PMF analysis.

Fig. A2 Potential Source Contribution Function (PSCF) images of (a) the FTIR combustion factor and (b) the FTIR biomass burning factor with warmer colors indicate higher probability. (c) Fire map on 29 August 2009 with red points showing fire spots and blue lines indicating back trajectories ending at the Scripps Pier. The fire image was obtained from NOAA's Aqua satellite.