Reply to Reviewer 2:

This is a very interesting paper that offers a different approach to the problem of separating SOA from other OA sources with a focus on carboxylic acids. It is a complicated analysis of ambient aerosol measurements that combines FTIR and AMS techniques to study increases in OA as a function of change in ozone during transport of aerosols from large source regions. The central hypothesis, based on previous chamber studies, is that the secondary production of condensible carboxylic acids occurs via a two-step process beginning with the oxidation of alkanes by OH followed by the ozonolysis of dihydrofuran. The observations are used to demonstrate the feasibility of this hypothesis as well as estimate the fraction of OA contributed from SOA in this situation. The paper is well written and organized with a few exceptions. Specific comments follow.

We thank the reviewer for the constructive comments. The point-to-point replies to the questions are listed below.

1. The AMS is a great instrument, but it is not a PM1 instrument. All published reports of modelling, laboratory and field measurements indicate that it does not measure 50% of the 1 um geometric diameter particles. The 50% transmission efficiency of the AMS is approximately 0.7 um aerodynamic diameter. If you want to scale your AMS data to some filter-based PM1 measurement(s), then you might call that an estimate of PM1, but the PM1 designation as applied here is unacceptable.

We have changed the designation of “nrPM1” to “PM_{AMS}” and specified in the text that the AMS measured PM is an estimation of PM_1:

Page 7196, line 23: Replace “AMS nrPM” with “which is an estimate of submicron PM and denoted as “PM_{AMS}”.

2. What about the diurnal pattern of sulphate? Assuming no low cloud during the daytime, most sulphate is driven by OH. Based on the AMS, you have almost as much sulphate as OA, and since you estimate that <40% of the OA was secondary you could have a stronger photochemical signal in sulphate than OA. This would help with your discussion on page 7205 as well as with timing of OH reactivity. How fast is the two-step oxidation process, and would you expect to see a slight lag of the acids relative to ozone? It is not possible to tell anything about that from Figure 3.

The average diurnal pattern of sulfate is nearly the same as that of m/z 44, the AMS Combustion factor (revised Fig. 7 shown below), and the carboxylic acid groups. However, there is no correlation of sulfate and carboxylic acid group concentrations (r = 0.1) both for all time-resolved samples and for daily averages. The similarity of the diurnal patterns and the poor correlation of sulfate and carboxylic acid groups suggest that OH radicals contribute to the formation of both components but that the magnitude of the sulfur and combustion emissions that produce the particles are uncorrelated (i.e. from different sources). The magnitude of the average daily sulfate concentration shows more variability than the OM concentrations. Dominguez et al. (2008) found that 44% of the non-sea-salt sulfate in fine particles during a previous study at the same sampling site could be attributed to sulfate from SO_2 emitted by ships. However, ship traffic is likely more variable than the OM emissions associated with the urban and port (trucking) activities.

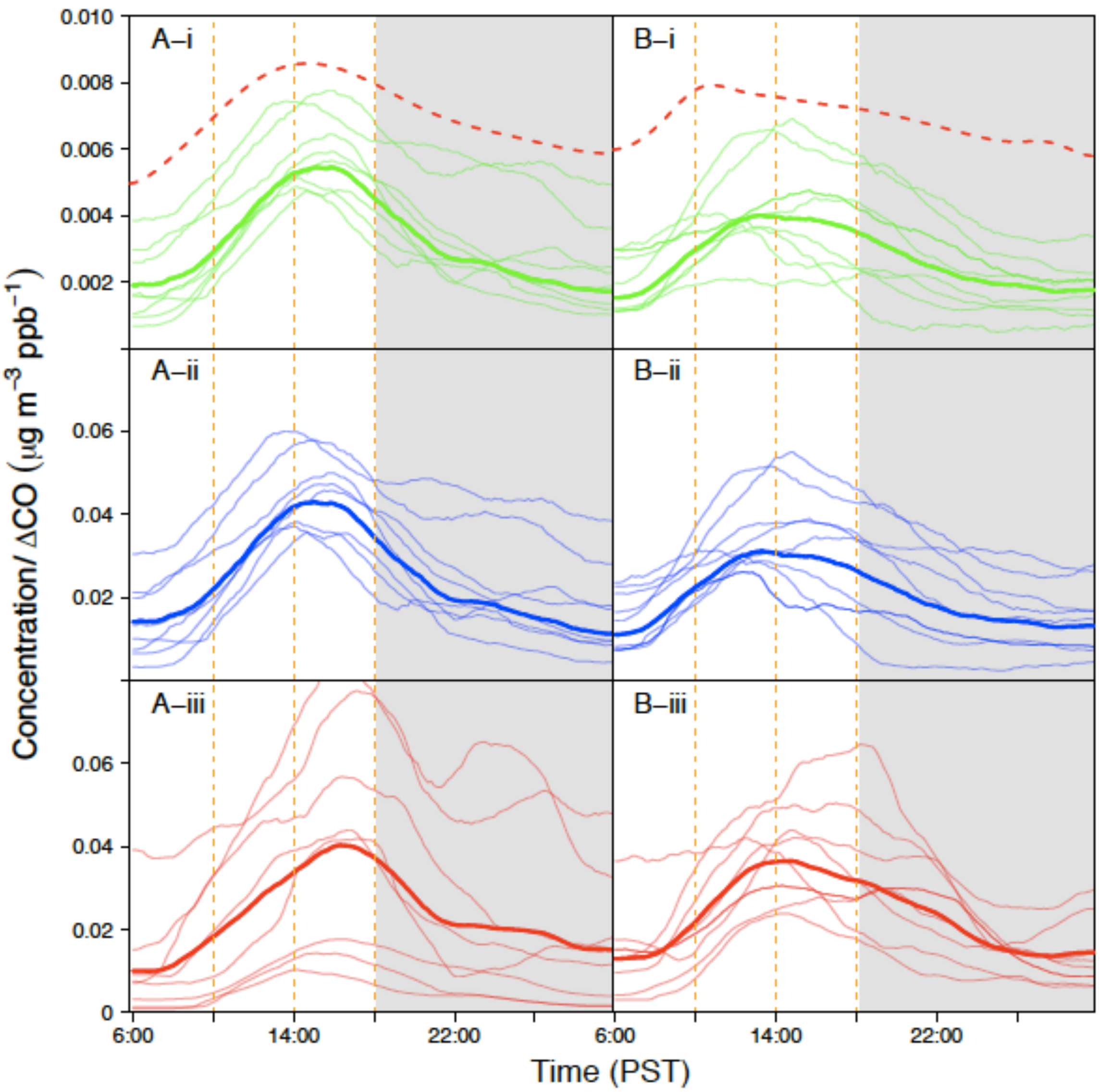
We have added this discussion and the citation of Dominguez et al. (2008) to the text:

"The average diurnal pattern of sulfate is nearly the same as that of m/z 44, the AMS Combustion factor (Fig. 5), and the carboxylic acid groups. However, there is no correlation of sulfate and carboxylic acid group concentrations (r = 0.1) both for all time-resolved samples and for daily averages. The similarity of the diurnal patterns and the poor correlation of sulfate and carboxylic acid groups suggest that OH radicals contribute to the formation of both components but that the magnitude of the sulfur and combustion emissions that produce the particles are uncorrelated (i.e. from different sources). The magnitude of the average daily sulfate concentration shows more variability than the OM concentrations. Dominguez et al. (2008) found that 44% of the non-sea-salt sulfate in fine particles during a previous study at the same sampling site could be attributed to sulfate from SO_2 emitted by ships. However, ship traffic is likely more variable than the OM emissions associated with the urban and port (trucking) activities."

We do not see a lag of carboxylic acid group concentrations relative to ozone, likely because the time resolution of the FTIR samples that can specifically identify acid groups are 4-12 hours. The AMS m/z 44 and combustion factor show a 1-2 hour time lag relative to the ozone peak for both the "Afternoon High" and the "Noon High" cases. Given the good correlations of carboxylic acid groups to m/z 44 and the AMS Combustion factor (Fig. 8 in the ACPD version of the manuscript), the time lag of carboxylic acid groups is likely 1-2 hours as well. A discussion of the time lag is added to the text:

In the carboxylic acid formation section (section 4.2 in the revised manuscript), add "The peak concentrations of m/z 44 and the AMS combustion factor occurred approximately 1-2 hours later than the peak in O_3 for both the "Afternoon High" and the "Noon High" type days (Fig. 5), indicating the formation is likely within 1-2 hours. Good correlations of carboxylic acid groups to m/z 44 and the AMS combustion factor suggest that carboxylic acid groups likely also lagged O_3 by 1-2 hours (although a direct observation of the lag is not possible given the 4-hour duration of the FTIR daytime samples)."

The diurnal cycle of O_3 is also added to Fig. 7 to facilitate comparisons.



Revised Fig. 7 (Fig. 5 in the revised manuscript): Diurnal cycles of (i) m/z 44, (ii) the AMS combustion factor, and (iii) sulfate for A ("Afternoon High") and B ("Noon High") days. The thinner lines represent daily diurnal cycles and the thicker lines represent the averages. The red dashed lines in A-i and B-i are average diurnal profiles of normalized O_3 mixing ratio for A ("Afternoon High") and B ("Noon High") days. The curves (except for O_3) are smoothed using the "Boxcar Smoothing" method with 30-point averaging to reduce high-frequency noise in the measurements. Shaded areas indicate nighttime periods.

3. Since combustion was the dominant factor (page 7204), I would expect a stronger correlation than r=0.5. To me, this suggests that there are other factor(s) controlling more of the variation in OM from FTIR and AMS than the source. Another possibility is there was a lag, as discussed above. One mechanism that might have significantly influenced the correlation is the sea-breeze. There is really little discussion of the impact of the sea breeze on the main aspects of the paper. There is reference to the impact on the marine component, but we do not

know how the sea breeze may have affected the trajectories and your ability to treat this as a pseudo-Lagrangian scenario. Some discussion of these points is needed.

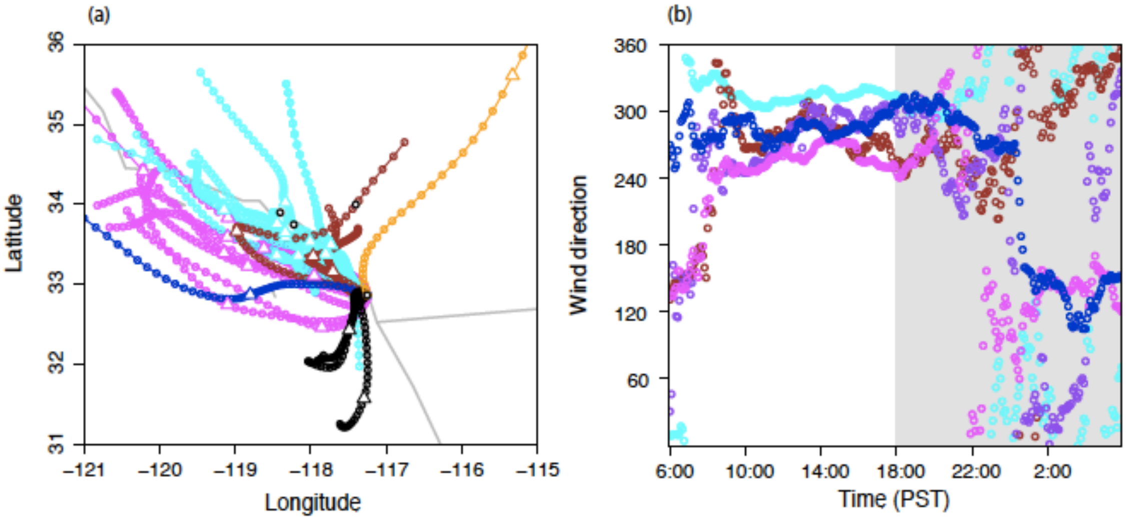
The Reviewer has asked about the result that "The Combustion factors dominated the OM (approximately 60%) from both analyses and the time series correlated to each other with $r = 0.5$ and a slope of 1.2 (FTIR factor OM was 20% higher)." Given the 4 hr resolution of the FTIR, the ~25% uncertainty of each method, the differences in size range and collection efficiency (noted by the Reviewer in item 18), and the inherent differences between spectroscopic and spectrometric methods, the correlation of 0.5 is quite good and suggests a high underlying correspondence. The reviewer is right that this is not as good as the r=0.7 for the biomass burning, which represents a smaller fraction of the OM, but this is likely due to two reasons: (1) while a smaller fraction the BB is more variable on time scales longer than 4 hr, so the FTIR PMF captures more of the variability even though it is a smaller fraction; (2) BB collection efficiency in the AMS appears to be higher (often unity), giving a better match with the FTIR (Hawkins and Russell, 2010).

We also found no discernible difference between the FTIR-AMS combustion factor correlation with and without sea breeze (i.e. the correlation is 0.7 on both onshore and offshore days). The lack of effect of sea breeze on this and more generally on the daytime patterns that we analyzed was surprising; we attribute this to the dominant northerly flow during the daytime. (There is however a strong impact at night, when the wind is quite variable and much more easterly or westerly; for this reason, we have not attempted to analyze the nighttime measurements from a Lagrangian perspective.) However, this effect seems to have been unrelated to the AMS-FTIR differences in the combustion factor, perhaps since the sea breeze did not affect the daytime particle concentrations. While marine OM contributions could affect the interpretation of these data as Lagrangian, there is little evidence of marine OM being sufficiently large or variable to affect this analysis. However, we have explicitly noted this possibility in the text in section 4.2 in the revised manuscript ("SOA identification by pseudo-Lagrangian observations: daytime formation of carboxylic acid groups and oxygenated organic fragments.").

The discussion of the diurnal patterns of the wind directions and the land-sea breeze effects on the chemical concentration was moved from section 3.3 to appendix B so that it will not distract from the main point. The appendix describing the influence of land-sea breeze on chemical concentration is quoted here:

Appendix B

The daytime wind direction was consistent during the study, with winds coming from northwest dominating during the 32 days selected for sample analysis. At night, easterly winds dominated but were more variable (Fig. 1). The average diurnal profiles of wind direction for the “Afternoon High” and the “Noon High” days are shown in Fig. B1. Sea breeze effects on the daytime particle concentrations were not identified. Variability in the concentrations of carboxylic acid groups and alkane groups at night likely result from different sources brought by easterly winds at night. For this reason, the nighttime samples were excluded from the diurnal cycle analysis.



Revised Fig. 1 (a): Averaged 48-h back trajectories for each day (daytime only) representing Los Angeles-Long Beach (cyan; air mass coming from Los Angeles and Long Beach regions), Riverside (brown; air mass originating from Riverside vicinity), Inland (orange; easterly/northeasterly air mass), Tijuana-Ensenada (black; southerly air mass), Mixed coastal (magenta; northerly air mass coming along the coast of California), and Ocean (dark blue; westerly air mass) air mass sectors during the campaign. The triangle in each trajectory indicates 24-h before the air mass arrived at the sampling site. The black circles (from top to bottom) indicate Riverside, Los Angeles, Los Angeles - Long Beach port, and the sampling site; (b) vector-averaged diurnal profile of wind direction (0 degree represents wind coming from north) for the air mass sectors specified in (a). Shaded areas indicate nighttime periods.

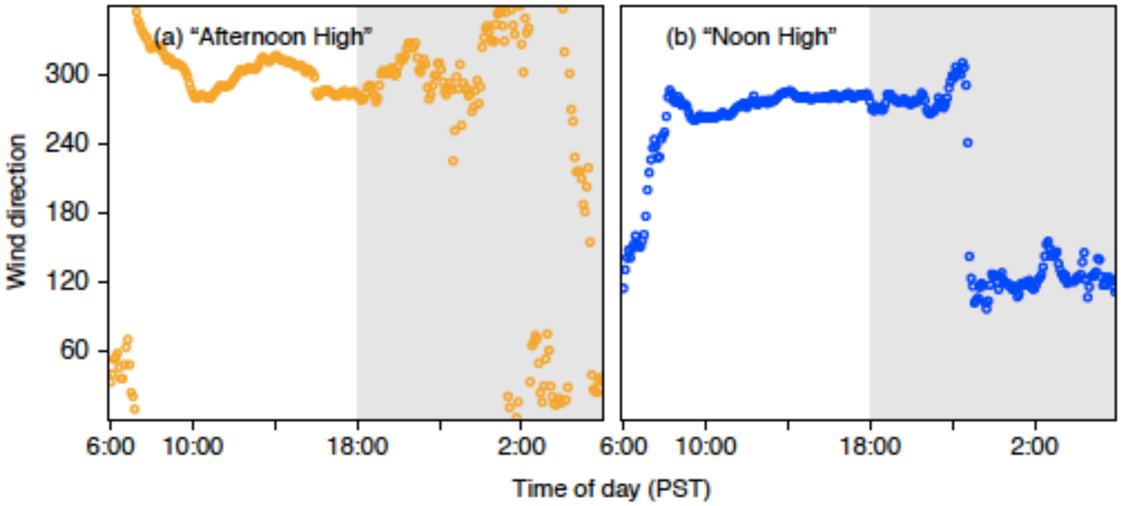


Fig. B1 Vector-averaged diurnal cycles of wind direction (0 degree indicates wind coming from north) for (a) "Afternoon High" and (b) "Noon High" types. Shaded areas indicate nighttime periods.

Minor comments:

4. Additions of CO along the trajectory path, without corresponding additions of OM, will perturb your use of CO as a dilution tracer. See Liggio et al., JGR, 2010 for a discussion of this. Also, Liggio et al. use measurements from a Hi-RES-AMS and a photochemical tracers to estimate about 40% of OA was from SOA approximately one photochemical day downwind of urban emissions. Besides comparing with this, there are references in that paper to other SOA estimations that could be included here.

In the study of Liggio et al., there was a large terrestrial biogenic source of secondary CO, which affected the ability of using CO as an urban tracer. Unlike that study, the biogenic emission in Southern California and offshore is minor; no significant biogenic sources are identified between the source regions (the Los Angeles-Long Beach area) and the sampling site. Therefore, the interpretation of CO as a tracer for urban pollution and its use to account for dilution in a port/urban plume is unlikely to be as complicated as in the Liggio study.

We have compared our results with the results from Liggio et al. (2010) in the new Table 4 and cited related papers in the revised manuscript (section 4.4):

"This "Background SOA" fraction is comparable to the "Background OA" estimated by Liggio et al. (2010) from measurements at Egbert, Ontario (Table 4), while the SOA formed within 24–48 hours in Liggio et al. (2010) (40–50% of the total OM) was higher than "Today's SOA" fraction (15-30% of the total OM estimated from the combustion factors) in this study, indicating that more SOA was formed during the longer time period evaluated by Liggio et al. (2010) or ambient particles at different sites may experience different degrees of oxidation (Ng et al., 2010; Morgan et al., 2010)."

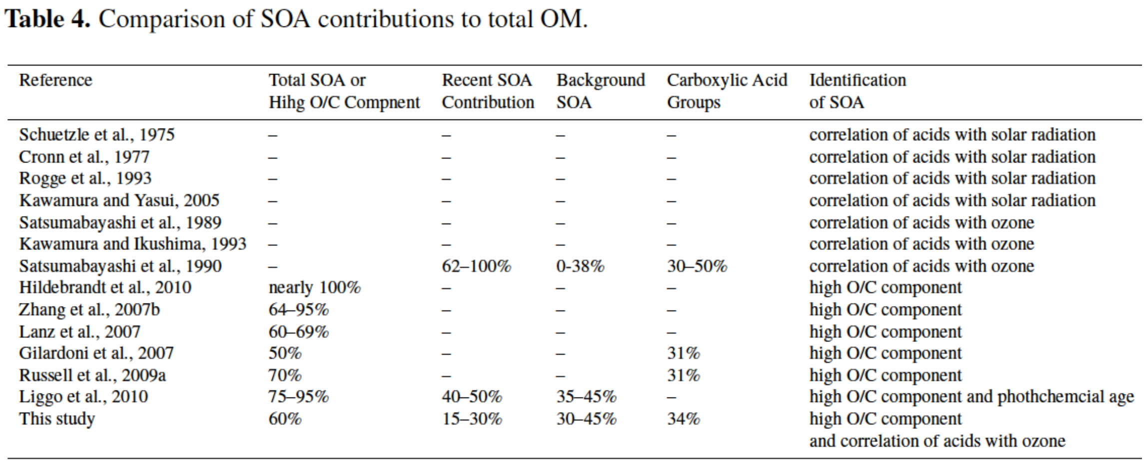


Table 4. Comparison of SOA contributions to total OM.

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. Comment about why the second oxidation step is by ozone rather than OH.

The second step is likely by ozone because it seems to track the timing of the ozone peak on the days studied here; while occasional delayed production from the inferred noontime peak in OH is possible, the correspondence of this delay to the ozone peak suggests that ozone and SOA had related formation pathways at a minimum, if not the more direct relationship of SOA formation by ozone oxidation. We also note that a role for ozone in later-generation SOA production is suggested based on chamber experiments by Russell et al., 2011.

Page 7206, line 11: Replace "with O_3" with "primarily with O_3 since there is little evidence for carboxylic acid formation from OH oxidation (Martin et al., 2002; Russell et al., 2011)".

6. P7190, line 8 – define "tightly correlated".

We have defined this as follows: "This daytime increase in concentration closely tracked the O_3 mixing ratio with a correlation coefficient of 0.7"

7. P7190, line 11 – "derived from" rather than "resulted from"

This is corrected to read "fossil fuel combustion factor derived from the factor analysis".

8. P7191, line 6 – "are found in" rather than "remain in"

This is corrected as suggested.

9. P7191, line 14 – "radiative" rather than "physical"

This is corrected as suggested.

10. P7194, lines 23-25 – The calibration of a TEI 49C does usually does not drift so much that the mixing ratios are that much in error. Some idea of the ozone levels would be useful.

We agree that the calibration is unlikely to affect the project average significantly, but to avoid the potential quantitative interpretation of the graphs, it has been omitted.

11. P7194, line 25 – "are" rather than "were"

This is corrected as suggested.

12. P7195 - first sentence grammar

We have re-written the first paragraph on Page 7195 as follows:

"This section describes the meteorological conditions under which carboxylic acid groups are formed, the composition of organic mass quantified by FTIR, AMS, and STXM-NEXAFS, and the components contributing to organic mass identified from factor analysis. To help to understand the formation mechanism of carboxylic acid groups, the daily variations in organic functional groups, AMS measured components, and O_3 mixing ratio are then compared."

13. Figure 3 and 6 – the print version is very small and difficult to read.

We have reduced and moved the caption to allow a bigger version of this graph in the ACPD format, although the ACP format was likely fine either way.

14. P7195, line 8 – maybe "consistent" rather than "stable". The latter tends to imply something more when discussing temperatures.

This is corrected as suggested.

15. P7195, line 22 – what do you mean by "consistent" number of days?

We have changed "for a consistent number (1-3) of days" to "1-3 consecutive days" to clarify.

16. P7196, line 17 – mass concentration

This is corrected as suggested.

17. P7196, line 20 – a single air mass

This is corrected as suggested.

18. P7197, near end of first full paragraph, you say “This is consistent with the fact that the sulfate-based CE used here was developed for ambient samples associated with relatively high sulfate fractions that were about 40% on average”. Why then did you use that adjustment for the CE? In Figure 4, there is no correlation for points above 4 ug/m3. Which has more uncertainty in its OM concentration, the FTIR or the AMS?

Due to the lack of other independent chemical composition measurements (such as PILS-IC) at the sampling site, which could be used to correct the AMS measurements, the “self correction” based on the AMS measured inorganic components is an independent way to correct the AMS data for comparison to FTIR OM. Another commonly-used method is to use CE=0.5 for all AMS measurements, but the correlation of FTIR and AMS OM is actually higher for the sulfate-based correction than for the constant value. We have revised the text to note this in section 2: “Another commonly used method for CE correction is to use CE = 0.5, when no other simultaneous measurements are available. In this study, the sulfate-based correction resulted in a greater correlation of the FTIR and the AMS OM than using a constant CE of 0.5. Therefore, the sulfate-based method is used in this study.”

The uncertainty of the FTIR OM is typically 20-30% (Russell et al., 2003), and the uncertainty for the AMS OM is approximately 25% (Canagaratna et al., 2007). Therefore, the uncertainties for the two techniques are comparable and both could contribute to the poor correlation for points above 4 $\mu g\ m^{-3}$.

19. P7197, line 23 - "insignificant relative to the ambient variations" or something like that.

This is corrected: Since the difference of the two intercepts is small relative to the ambient variations (which had a standard deviation of 71 ppb), an average value of 85 ppb was used as the background CO mixing ratio for both the FTIR and the AMS measurements.

20. Figure 6 - Why is the ozone variation not shown for the overnight period?

The O_3 mixing ratio was not shown in Fig. 6 because the nighttime variability gave no meaningful average cycle. The average O_3 profile is shown in Fig. 7 in the revised version (shown above).

21. P7204, line 16 – transmission efficiency rather than collection efficiency.

This is corrected as suggested.

22. P7205, line 8 – “tightly” again.

The next sentence explains that the correlation of carboxylic acid groups and O_3 is good. So “tightly” is removed.

23. P7205, lines 10-12 – A correlation of the carboxylic acid groups with odd oxygen (O3+NO2) would be preferable to just ozone, but NO2 measurements were unavailable during this study.

This is corrected: “A correlation of carboxylic acid groups with odd oxygen (O_3 + NO_2) may be stronger than O_3 alone (Herndon et al., 2008), but NO_2 measurements were not available in this study.”

24. P7206, line 23 – The OM peaks about 300-500 nm, but OM/PM1 peaks below 200 nm. Clarify what you are plotting: OM/(total AMS mass) where both terms are for a particular size interval.

This is clarified in the caption of Fig. 11: “The ratios (m/z 44/nrOM and nrOM/PM_{AMS}) were calculated for each size bin then plotted versus particle size.”

25. P7209, line 2 – “are MOSTLY secondary”. Even in your Figure 12, you show a background carboxylic acid level some of which at least can not be ruled out as primary.

We added “mostly” as suggested.

References:

Canagaratna, M.R., Jayne, J.T., Jimenez, J.L., Allan, J.D., Alfarra, M.R., Zhang, Q., Onasch, T.B., Drewnick, F., and Coe, H., Middlebrook, A., Delia, A., Williams, L.R., Trimborn, A.M., Northway, M.J., DeCarlo, P.F., Kolb, C.E., Davidovits, P., and Worsnop, D.R.: Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer, Mass Spectrometry Reviews, 26, 185-222, 2007.

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Russell, L.M.: Aerosol organic-mass-to-organic-carbon ratio measurements, Environ. Sci. Technol., 37, 2982-2987, 2003.

Russell, L.M, Bahadura, R. and Ziemann P.J.: Identifying organic aerosol sources by comparing functional group composition in chamber and atmospheric particles, Proceedings of the National Academy of Sciences, doi/10.1073/pnas.1006461108, 2011.