

Interactive comment on “Oxygenated organic functional groups and their sources in single and submicron organic particles in MILAGRO 2006 campaign” by S. Liu et al.

S. Liu et al.

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Reply to comments of Referee #2

The authors thank the referee for the detailed and constructive comments. The issues raised by the reviewer have been carefully considered and clarified in the revised manuscript. Please find below the reviewer's questions in italics; our responses below are not italicized.

General comments

1. More information should be given on the evaluation and justification of the statistical

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analyses solutions. The decision of the number of clusters needs more explanation and validation. Please give reference(s) to the 'Ward-type clustering' (P 4570). In particular, technical details about the PMF analysis should be given. It is important that the authors discuss how the error matrices were computed, whether outliers were identified and how they were treated (downweighted or rejected)? Were the PMF analyses done with the robust mode or nonrobust mode? All of these factors may strongly influence the PMF results.

The reference (Ward, 1963) is added to "Ward-type clustering technique" in the text. The number of clusters should be decided so that the resulting clusters represent distinct types of organic particles for which there are sufficient measurements in the project. Figure 2 is revised - a pie chart is added to each cluster panel showing the average organic functional group fractions of each cluster. The seven clusters in Figure 2 represent different shapes of FTIR spectra and different organic functional group compositions. Using more than seven clusters tends to separate C130 spectra out and result in clusters consisting of only two spectra, which is not representative or statistically significant. A brief description of the justification of number of clusters is added to the text.

More technical details of PMF are added to the method part of the text: "The data matrix was composed of the absorptions of the baselined spectra. Baselining error at each wavenumber (which was calculated from the variability of the baselined field blank spectra) was used to estimate the scaling factor for each data point (Appendices in Russell et al., 2009). The robust mode of PMF was used, and the outliers were down weighted during the fitting procedure (Paatero et al., 2003)."

2. It is stated in this manuscript that the number of factors for PMF was determined based on SVD. Usually, the selection of the best number of factors involves carefully monitoring the behavior of the PMF quality of fit parameter - Q. It will be useful that the authors show plots of the variations of the Q value vs. number of factors.

We applied Fixed Size Moving Window - Evolving Factor Analysis (FSMW - EFA) to the entire data set for the determination of the number of factors. FSMW-EFA is based on SVD, it performs SVD analysis on a subset of spectra contained in a "window" of a fixed size (40 cm^{-1}), which is moved along the spectra (Keller et al., 1992). The results of the analysis on all "windows" were plotted together to show the percentage of data recovery at each wavenumber using different number of factors. We have also examined the fit parameter Q for $N = 3-10$. Using different FPEAKs resulted in similar Q values. Q decreases approximately linearly with increase N for $N = 3, 4, 5$, and 6. When N is larger than 6, Q decreases more slowly and approaches twice the theoretically expected value when the N approaches 10. However, there is no mathematical criterion that determines the "correct" number of factors (including an abrupt decrease in Q with size). The most important question is which gives the most reasonable interpretation of the measurements. Six or more factors could recover nearly 100% of the data set according to FSMW - EFA. Four factors were found to reproduce 98% of the data set and to generate factors that represented sufficient organic mass for interpretation based on this data set. We have also examined the residuals using $N = 4$: on average the residual does not have a pattern, and they are of the same order of magnitude as the errors.

3. This manuscript interprets its PMF results, the mass concentration and source profiles of the factors, with a bit too much certainty. Issues that may introduce large uncertainties to the results, such as rotational ambiguity, factor splitting and mixing, and measurement biases were not adequately discussed. Some basic information about sample collection and handling should be repeated; it is not helpful only cite a manuscript that is still under preparation (Gilardoni et al., 2009). What was the collection frequency and duration of the filter samples? This information is important to the interpretation of the statistical analysis results from this study. Filter-based data typically represent measurements averaged over several hours up to 1-2 days. Low time-resolution could make correlations look larger among compounds that actually

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came from different sources and processes. For example, SOA species produced on a time scale similar to the sample averaging time may show good correlation with the POA species that were emitted together with their VOC precursors. As multivariate receptor models, such as PMF, generally have difficulty to separate two sources that are well correlated, one may end up with factors representing the mixtures of the two. Trying to assign specific sources to such factors will give erroneous results.

Additional details of the sample collection and handling were added to the text: "At SIMAT and Alzomoni, two 12-hour samples or three 8-hour samples were collected along with one 24-hour sample. Samples were collected for 20 min to 1 hour on board NCAR C130 at constant altitudes. A field blank was simultaneously collected with each sample. Samples were stored at temperature below 0 °C after collection before FTIR analysis." Gilardoni et al. (2009) has been posted as part of this special issue since February 2009.

FPEAK was restricted to -0.2 to 0.4 since $FPEAK \leq -0.4$ resulted in physically unrealistic spectra (e.g. non-Gaussian spectra) (Russell et al., 2009). Changing FPEAK does not result in significant change of Q value or solution, possibly because the non-negativity constraint was set for > 1500 wavenumbers.

We disagree with the reviewer's assertion that our presentation of the PMF results implies "a bit too much certainty" - in fact the primary reason for including different PMF solutions (all with similar certainty) is to illustrate the quantitative variability of possible solutions - while also showing the qualitative trends in all three solutions. We have revised the text to highlight this issue.

4. The identification of three combustion components seems questionable. What are the physical meanings of these three factors; do they represent different combustion sources? This could be a case of factor splitting, although factor mixing could be involved the same time too. More importantly, the combustion components identified in

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this study could very possibly be 'contaminated' by SOA signals, as discussed in the previous paragraph. Therefore, the high O/C ratios observed for these components should not be taken automatically as the evidence that combustion POA is major contributor of oxygenated species, unless this conclusion is vigorously validated, such as by external data. Overall, the uncertainties of the analyses conducted in this study should be discussed in more depth and the interpretation of the PMF factors, especially their linkage to source types and the subsequently discussions on the functional group composition of different source types, should be done very carefully.

Since SOA and POA are hard to separate in real atmospheric measurements, we have used alternative concepts of "emitted" and "processed" particles (Russell et al., 2009), which are defined in the last paragraph of the introduction. The "emitted" particles are defined as organic components formed directly from the emissions of one source type, and the "processed" particles are defined as organic components formed by multiple source or atmospheric components, which typically have more time for formation in the atmosphere that weakens their correlation to primary metal emissions. Both "emitted" and "processed" particles can contain oxygenated species, with the difference being that the oxygenated species in the "emitted" particles were formed sufficiently fast after emission from the source so that they correlate to tracers of that source; the oxygenated species in the "processed" particles are affected by meteorology or transport or formed slowly so that they do not correlate to tracers of a single source. Table 2 in the manuscript shows the O/C of the "processed" factor is twice as large as the O/C of the combustion factors, but the mass of "processed" factor is much lower, so the mass-weighted O/C contribution of the "processed" factor is lower than the mass-weighted O/C contribution of the combustion factor.

In defining factors as "processed" or "emitted," we had implied a time scale of more than 12 hr to distinguish the oxygenated aerosol. This definition is the consequence of both our low measurement resolution, and the basin-scale mixing which confounds Eulerian measurements. We repeat that we are not distinguishing implicitly or explicitly

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between POA and SOA for the FTIR samples - as this is impossible. We distinguish those that correlate with primary metal emissions (which we intentionally call "emitted" rather than "primary") from those that do not (which we call "(more) processed"). Oxygenated aerosol that forms within 12 hr of emission is considered by this definition "emitted"; but this is not "contamination." We have stated our aim is not to identify POA and SOA, but to identify which organics (oxygenated and otherwise) are co-emitted with specific source types (which we believe has greater regulatory value than SOA) as opposed to those which are formed later or require non-co-emitted reactants or oxidants. We have revised the text to make this more explicit.

In light of the reviewer's comments, the physical meanings of the combustion factors were re-evaluated and simplified. We reviewed PMF solutions both to the combined data set ("combined PMF") and each data set separately ("separate PMF") using three to five factors. By investigating factor chemical compositions, time series, and their possible source regions (using PSCF), similar factors were identified for both "combined PMF" and "separate PMF", indicating similar sources and regional pollution in the MCMA. To simplify the analysis we have

- 1) omitted the 6 factor solution because the 6th factor appeared only on the C130 and was insufficiently sampled for significant PMF results;
- 2) omitted the 5 factor solution because we reevaluated the 5th factor because it resulted in the over-estimation of the measured carbonyl groups and its composition was very similar to Combustion I;
- 3) identified "Combustion I" as biomass burning since the concentration of Combustion I significantly increased during the "fire period" identified at T0 (March 12-14; Aiken et al. (2009)) at 99% confidence level, while the other factors did not show strong correspondence with the fire period. While accounting for a small fraction of OM, this factor was persistent in all runs for all sites and all rotations, indicating its robustness;
- 4) indicated the similarities of the remaining 2-3 factors explicitly by grouping them

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in a two-factor solution consisting of only biomass burning and an indistinct type of urban combustion. All three remaining factors had weak correlations to indistinct and variable sets of elemental markers for combustion from industrial processes, vehicular emissions, and residential activities (e.g. S, Cu, Zn, Se, K, Br, and Fe)(Johnson et al., 2006; Moffet et al., 2008). As a result, a robust separation by source type was not possible.

Given this limitation, in order to better understand what this urban combustion factor might include, we have included additional evidence from the site-specific solutions and associated PSCF results. Two types of signatures are revealed: (i) one alcohol/acid/alkane factor associated most strongly with northeastern sources and dust (previously called "Mixed and processed" and "Combustion II"), and (ii) one acid/alkane factor associated more with southwestern sources (previously called "Combustion III"). Because the PSCF footprint of this northeastern combustion factor was similar to that of the "Mixed" factor, and because the correlation to primary elements was not sufficiently low to distinguish this OM as processed (or "secondary"), we determined that there was insufficient evidence for this study to identify it separately. The northeastern combustion factor is associated with elements Fe, Mn, Cu, Zn, and Br that could be emitted from industrial sources in the northeastern MCMA (Johnson et al., 2006; Moffet et al., 2008). The southwestern combustion factor has a source region in and around the city of Toluca, which is the capital of Mexico State and a major industrial city. The four-factor PMF solution has been used to identify three types of source signals (biomass burning, northeast combustion, and southwest combustion) from both the "combined PMF" and the "separate PMF" (at SIMAT and Alzomoni). All three solutions have been shown in the revised manuscript to illustrate both the consistent features and the non-uniqueness of any one PMF solution.

Detailed comments

1. *What's the statistical significance of PSCF given the relatively small number of sam-*

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ples?

The reviewer is correct in implying that the statistical significance of PSCF is limited for this study, given the small number of samples, the short duration of the study, and the influence of the complex terrain on the accuracy of the backtrajectories. Nonetheless, we believe that PSCF is sufficient to provide a useful tool for interpreting the PMF factors that impacted the sample sites and that furthermore there are published precedents for using data sets of this size. One hundred and seven samples were collected at SIMAT site during the campaign; comparable or smaller low-resolution data sets (sampling time for each filter ranged from 24hr to one week) were used in a number of studies (Cheng et al., 2000; Liu et al., 2003; Tsai et al., 2004), which used PSCF to identify possible source locations. One major uncertainty in PSCF analysis is that the trajectories cover limited regions, so there are some grid cells with only a small number of trajectory endpoints. Back trajectory analysis showed that the air masses consistently came from all directions to the sampling sites during MILAGRO campaign. To reduce the uncertainties of large ratios in cells with few trajectories, a cumulative distribution function describing the probable distribution of trajectories in grid cells was formulated. A threshold of 40% of the cumulative distribution was set so that the cells with less than 10 trajectories were not considered in the PSCF calculation. Thus source regions that frequently brought similar components to the sampling site are reflected in the PSCF analysis that is included in the manuscript.

2.P 4569, line 25, as for all acronyms, 'AMS' should be defined when it appears in the text for the first time.

AMS is defined.

3. P 4571, why only 4 FPEAK values were tested? And why wasn't -0.4 tested?

This is discussed above: "FPEAK was restricted to -0.2 to 0.4 since $FPEAK \leq -0.4$

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resulted in physically unrealistic spectra (e.g. non-Gaussian spectra) (Russell et al., 2009). Changing FPEAK does not result in significant change of Q value or solution, possibly because the non-negativity constraint was set for > 1500 wavenumbers."

4.P 4571, in terms of the final selection of 7 clusters, a brief justification of the decision should be given.

A brief justification is added to the text: "Seven clusters were used to best represent distinct types of FTIR spectra of different organic functional group compositions (Fig. 2). Using more than seven clusters resulted in small clusters consisting of only two C130 spectra, which were not representative."

5.It said in the 1st sentence in P 4572: "..., with the largest difference in factor concentrations occurring between the 3-factor results and the 4, 5 and 6-factor results" As the analysis was based on best fit to the measurement data, changing the number of factors will certainly cause a redistribution of the signals. The question is what factors are compared among different solutions? Please clarify.

This argument has been removed given the above discussion of how the factors were simplified.

6. P4572, L 3, what volume?

The sentence is rephrased to reduce confusion: "The factor concentration time series was correlated to metal concentration time series to identify sources most likely associated with each factor."

7.P 4572, last sentence, please explain what is considered as "most representative". Is it based on examining the factor profiles or the correlations with tracer species?

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This justification is based on examining the factor profiles. This is addressed in the text: "Two to eight factors were found to reproduce 85-99% of the data set. 4-factor solution with FPEAK set to 0 was found to produce the most representative results by comparing factor spectra with standard reference spectra."

8. *Table 1, for the average values reported, are the data points below detection limits excluded? If so, some of the values could be heavily biased. If not, how were those low S/N data points represented? Please explain.*

In Table 1, elemental concentrations reported were above detection limit for more than 70% of the ambient samples collected. There is no significant change of mass when the below detection limit (DL) values were assigned to DL or DL/2, suggesting the BDL values did not significantly affect the calculated mass. To prevent an artificial high bias by removing BDL points, the reported values are averages of all data points.

9. *Page 4573, it is interesting that this work found the functional group composition of OA was somewhat similar between an urban surface site and a high elevation site, while the C130 samples had the lowest average O/C. The C130 samples also showed the highest mass fraction of alkane functional groups. Was it because more urban plums were sampled on the C130 platform?*

Two sampling issues also contributed this apparent difference. The first was a sampling bias of the aircraft, which flew primarily aloft rather than in the more freshly polluted continental boundary layer (due to flight restrictions in the urban area). As a result, the types of particles sampled on average were "cleaner" than at the two ground sites. Low-level legs in the polluted Mexico City plume were much more comparable to the ground sites (Gillardoni et al., 2009). The second issue was that the lower concentrations of the higher-altitude, cleaner regions resulted in some samples with low signal-to-noise in the COOH region of the spectrum. We estimated the peak

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area of carboxylic acid functional group by scaling the shape of COOH spectrum to the sample spectrum. (The shape of COOH spectrum is retrieved from factor analysis of different online carboxylic acid spectra as described by Russell et al. (2009)). For both of these reasons, the "project average" of the C130 (which sampled a wide geographic and altitude range) cannot be compared directly to the two ground-based platforms.

10. *Page 4574, last sentence, I have trouble understanding why "correlations among organic functional groups and S and K; indicate that "sulfur emissions may also have been oxidized from SO2 to form sulfate during atmospheric processing". Please explain.*

This argument has been removed as the relationship intended was not substantiated by a large enough fraction of the data.

11. *Page 4575, it is said "Concentrations of alcohol and alkane functional groups correlate with each other, but the mass fractions of alcohol and alkane functional groups were anti-correlated." What's the significance of this phenomenon?*

The anti-correlation of alkane and alcohol functional groups indicates that the groups are dominated by different source types or processes. This has been clarified in the text.

12. *Page 4579, line 13, change 'with a rotation of 0'; to 'with a FPEAK of 0'.*

This is corrected.

13. *Page 4580, give reference to "Turkey's Honest Significance Difference method"*

The reference (Lowry, 2008) is added.

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14. *For the discussions on page 4583, "Kleinman, L. I. et al. (2008), The time evolution of aerosol composition over the Mexico City plateau, Atmos. Chem. Phys., 8, 1559-1575" is a relevant reference to cite.*

We thank the reviewer and this reference is cited.

15. *Page 4586, it is said "All of the PMF results suggest that while the processed aerosol has the highest O/C, half of the O/C is associated with the fossil fuel combustion type emissions. This result indicates that the high O/C from Alzomoni is largely the result of direct emissions rather than processing". Again, such conclusion should not be drawn unless the PMF factors derived from this study have been critically evaluated and their interpretation cautiously justified.*

This discussion has been revised to be consistent with the removal of the processed factor.

16. *Fig. 1a - 1c are loaded with information but they are hard to read. The font sizes of some R values are far too small to read. Using symbols of different sizes could be more effective.*

Figures 1a - 1c have been regenerated using correlation maps, and they are condensed into one page.

17. *Fig. 2, define the width and the height of the bars.*

The width and height of the bars have been defined.

18. *Fig. 8 is hard to read. The contrast in surface shading is not high enough and the symbol sizes are too small to see well.*

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The contrast in the surface shading has been improved (the color changes gradually from black to white), and the larger symbols have been used.

Figure captions

Fig. 1. The ratio of Q to the theoretically expected Q as a function of number of factors for four FPEAKs investigated in this study.

Fig. 2. Fraction of data recovery for different number of factors at each wavenumber using FSMW - EFA analysis. Color indicates the percentage of data recovery.

Fig. 3. (a) Air mass back trajectories ending at SIMAT during MILAGRO campaign. (b) Cumulative distribution as a function of trajectory numbers in each grid cell.

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