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Atmospheric
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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.

Anonymous Referee #2

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This manuscript reports a novel study of the functional group composition and the sources of oxygenated organic aerosols observed in the Mexico City metropolitan area. Particle samples were collected from three platforms - urban surface, high altitude, and aircraft - during the MILAGRO 2006 campaign. Organic functional groups and elements of submicron particles were characterized with FTIR and XRF. The abundance of organic functional group in single particles was determined with X-ray spectroscopy. Statistical analyses were performed to identify source groups and atmospheric processes that influenced the aerosol samples. The analyses include correlation tests of time trends, cluster analysis of FTIR spectra, and PMF analysis of FTIR and NEXAFS-STXM spectra. According to PMF analysis, the contributions of different source types to OA mass loading were estimated. This manuscript is logically organized and generally well written. The topic is appropriate for publication in ACP. I recommend the manuscript be accepted for publication following attention to several issues.

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

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.

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 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.

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 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.

Detailed comments:

What’s the statistical significance of PSCF given the relatively small number of samples?

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

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

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

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

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factors will certainly cause a redistribution of the signals. The question is what factors are compared among different solutions? Please clarify.

P 4572, L 3, what volume?

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?

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.

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?

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.

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?

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

Page 4580, give reference to "Turkey’s Honest Significance Difference method"

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.

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 Altzomoni 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.

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.

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

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 4567, 2009.

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