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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Investigation of the sources and processing of organic aerosol over the Central Mexican Plateau from aircraft measurements during MILAGRO" *by* P. F. DeCarlo et al.

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Anonymous Referee 1

R1.0) This paper presents a case study analysis of organic aerosol data from an AMS on the C-130 during the MILAGRO intensive. Two flights are analysed, chosen on the basis of one being heavily influenced by biomass burning and one being largely free of it. PMF analysis of the high resolution data is performed and compared with other in situ data sources and regional model outputs in an effort to apportion the

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Interactive Discussion

Discussion Paper

different OA components and explore atmospheric processing. The authors employ what they call 'postprocessing' to reconcile the data from the two flights and quantify the influence of biomass burning on OA components normally ascribed to urban sources. This is an interesting technique, however given than only two flights were used in this paper, it is also intrinsically impossible to validate here (see below) and so some of the conclusions risk being overstated. This paper is generally well written, topical and well within the scope of the MILAGRO special issue and the scientific scope of Atmospheric Chemistry and Physics. I recommend that this be published after the authors consider the following (hopefully minor) comments:

We thank the reviewer for the detailed and thoughtful comments. Our responses below follow each italicized original comment. We have attempted to clarify text which may have been confusing, and address the reviewer's comments in detail.

General Comments

R1.1) The authors give very little discussion of the altitude of measurement. This is important, because if any data collected in the free troposphere or any residual layers were included in the analysis, these would add an additional transition beyond the plume/background interaction model that forms the basis of this analysis (fig 1) and artificially inflate correlation statistics. I would strongly recommend filtering these data from the analysis and if they have already been removed, the authors should state as such.

Although some portions of the flight did occur in free tropospheric air, this is due to complex topography of the plateau and the tendency of the Mexico City plume to detach from the ground and embed itself in the free troposphere. This is the situation shown in Figure SI-2 with the plume/background transition and the CO determination. We have chosen not to remove these points from the analysis, and in-fact discuss this potential problem in section 2.5 of the paper and in Figure SI-3.

R1.2) The "postprocessing" technique is interesting, but given that there are only two

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flights being analysed, there is no way that the validity of this technique can be verified within this work. Unless additional flights can be included in the analysis (which I'm guessing they can't), the authors need to be more upfront about this intrinsic limitation in the discussion. I would also recommend reporting the non-postprocessed values in the conclusions section in addition to those given.

We agree that there are limitations to the postprocessing technique. However post-processing of the solution is necessary to obtain a source apportionment of the OA for this dataset, given the wide range of sources and airmass ages sampled. To our knowledge this is the first aircraft-based OA direct source apportionment study, and it is important to document the possibilities and limitations of the technique. We have modified the text in section 3.5 to clarify this point:

"For a dataset such as the one in RF3, with several strong source types and a large dynamic range of photochemical aging, postprocessing of the PMF results using external information such as source tracers is required. Although the postprocessing technique has limitations which can be explored in other datasets, it is clear that the explicit PMF solution does not adequately report direct source apportionment, and that postprocessing will improve the attribution of OA mass to specific sources."

R1.3) In a more specific case, the analysis performed in 3.5.4 seems a little tenuous. As described, there are many potential confounding issues that are not adequately discounted (the two flights having 'roughly similar' SO4 concentrations is not a particularly compelling argument). In addition, other factors not discussed may include the effect of seed ambiguity in the PMF solutions when comparing the two flights, the effect of aqueous processing or the influence of regional transport from outside of the Mexico City basin. Given the large amount of scatter between LV-OOA and SO4 within the individual flights (as shown on figure 4), this rough calculation of the addition of mass from these processes seems to be a bit of a stretch. Without better justification, I'd be wary about carrying these numbers forward to the conclusions section.

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We agree with the reviewer that the use of SO4 to postprocess the LV-OOA is not perfect and introduces some additional uncertainty, however, the investigation of other external measurements and tracers did not yield more promising results, and post-processing is necessary to provide estimates of source contributions that are of most interest to the scientific community. As this is a first attempt of postprocessing, we invite other researchers to propose alternative methods for datasets for which post-processing may also be necessary (and the reviewer does not provide an alternative suggestion for this necessary step). For the purposes of this study, we chose SO4 as it is very often observed to correlate with LV-OOA in AMS-PMF datasets (e.g. Lanz 2007, Ulbrich 2009). We felt that the use of the slope information in addition to the correlation coefficient would provide, at minimum, a reasonable constraint for the postprocessing.

R1.4) Given that Crounse et al. informed the postprocessing (e.g. apportioning CO to biomass burning), the comparison in section 3.6 seems a little self-fulfilling. In order for the comparison to be fair, influences of this work should be excluded from the data processing presented here. As a general point, the comparison is not performed very critically in the text; currently, phrases like 'agrees well' are used without any quantitative measure or context as to what would constitute a good agreement.

The reviewer correctly points out that the apportionment of CO from Crounse et al. does inform our own apportionment, however the effect from using this information on our results is very small. Ignoring the CO apportionment and using only the slope change from the HOA to CO regression between RF3 and RF12 yields a 3% reduction in the postprocessed biomass burning factor. The R^2 between the postprocessed BB including the CO apportionment and excluding the apportionment is 0.99. Ultimately the largest change the inclusion of the CO apportionment makes is the fraction of HOA apportioned to fire vs non-fire. When the CO apportionment is excluded the change in the HOA vs CO slope implies that 36% of the HOA is due to fire influence. Including the CO apportionment changes that number to 51%. Since it is well known that wildfires do produce CO, and the apportionment uses the best estimate we have of this influence,

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we feel that this provides the most sound overall source estimate. As in R1.3, this step is needed to provide a best estimate of our source apportionment, and the reviewer does not provide an alternative suggestion on how to carry out this step.

Regarding the discussion of the intercomparison in Figure 9, we do report statistical metrics of comparison between the techniques such as slope, intercept, and R2 in Figure 9e and f. In addition, we have added the following text to the paper:

"Statistics for the comparison given in figure 9 e-f indicate good agreement between the different apportionment methods with R2 larger than 0.8 in both cases and slopes between 0.8 and 1.12 for the urban + non-BB regional OA and fire associated OA respectively."

R1.5) The analysis of seed ambiguity is very interesting and the authors deserve credit for giving a concise account of this as an appendix rather than attempting to bury it in the supplementary material. However, one could suggest that the strong dependence on the seed could be indicative of inappropriate convergence criteria and tweaking this (in conjunction with the error model) might be the more appropriate way of dealing with the issue. The authors' thoughts on this matter would be informative. Also, the ambiguity should also be carried forward and reflected in the numbers shown in the discussion and conclusions sections in some way (see other comments).

We agree with the reviewer that reporting the results obtained with different seeds should be encouraged in PMF publications. Additionally, if seed analysis does not show strong variations in solution (as has been informally reported by some AMS-PMF users), then one could also explore fpeak variations in similar systematic ways, which was also done for this dataset but yielded less variation in solutions, and less plausible solutions.

Recent experimentation (with several other PMF cases) with the final convergence criteria of PMF2 revealed that the solutions change little as long as the convergence criteria are strict enough, as they were in this case. The convergence criteria for the last

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level of iteration in this case was the default value of 0.3 Q units (0.3/(rows * columns - #factors*(rows + columns) Q/Q_{exp} units), whereas the same 0.3 convergence criterion is much looser for typical matrices (100's of rows x 10's of rows, in contrast the dataset used here was 3906 rows by 174 columns).We believe that the differences in the solutions obtained with different seeds do correspond to different local minima in the objective function, and that tightening the convergence criteria would not cause the solution to hop from a local minimum to a global minimum.

We do not agree with the characterization from the reviewer that the differences between the solutions with different seeds (local vs. global minima) are indicative of the uncertainty in the solution, as the differences in the final Q/Q_{exp} are substantial. It would also be not obvious and certainly very laborious to carry out the postprocessing for the solution families with different seeds. We have therefore retained the procedure of working with the set of seed solutions that produce the lower and similar Q/Q_{exp} and the highest total R^2 values.

R1.6) As regards presentation, I would recommend fewer subheadings be used; many sections are only comprised of single paragraphs, which is frowned on in many journals.

We have retained the subheading structure of the ACPD manuscript as we feel that it facilitates the understanding of the material in the paper, and that this objective should override any small stylistic preferences.

Specific Comments *R1.7) Given that sources and processes of organic aerosol is a common theme of many MILAGRO papers, I recommend the running title is changed to something more specific to this work.*

We gave this suggestion some thought and discussion, but we came to the conclusion that the current title reflects the contents of the paper best. In particular the paper contains the word "aircraft," for which only a handful of organic aerosol papers have been published from MILAGRO.

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R1.8) The fact that this paper presents data from only two flights should be stated in the abstract; currently, it gives the impression that an entire campaign's worth of data was used, whereas in actuality this work is more akin to a case study. Also, as explained below, the '$> 90\%$ anthropogenic' statistic reported is currently unsupportable and should be removed.

The second sentence of the abstract has been edited to read (Bold text indicates the change):

"This study uses the high time resolution measurements **from two research flights** performed onboard the NCAR/NSF C-130 aircraft during the MILAGRO/MIRAGE-Mex field campaign in March 2006 to investigate the sources and chemical processing of the OA in this region."

The second part of the comment is addressed in R1.13 below.

R1.9) P2449: "Traditional" and "recent" are not really sufficient descriptions of the different models; they use fundamentally different approaches (suited to different scientific applications) and as such, they can't be compared on the basis of when they were developed. Better descriptions are warranted.

We have updated this text to: âĂĺ"Rapid and intense secondary OA (SOA) formation (from chemical reactions of gas-phase species) from urban emissions in Mexico City has been reported by several studies. The amount of SOA formed is greatly underpredicted by SOA models which only consider SOA formation from volatile organic compounds (VOCs) (sometimes referred to as "traditional" SOA models, meaning those in use before 2006) (Volkamer et al., 2006; Kleinman et al., 2007; Dzepina et al., 2009; Fast et al., 2009; Hodzic et al., 2009; Tsimpidi et al., 2009; Wood et al., 2010). The amount of SOA observed after a few hours of photochemistry is several-fold the initial POA concentration. This is consistent with results at many other locations (e.g. Hallquist et al., 2009; de Gouw and Jimenez, 2009, and references therein). Models which include SOA formation from semivolatile and intermediate volatility species (S/IVOCs)

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predict much larger amounts of SOA that match or even exceed the observations, although the intensive properties of the SOA (volatility, O/C) are not well predicted and the level of mechanistic understanding remains low (Dzepina et al., 2009; Tsimpidi et al., 2009; Hodzic et al., 2010)."

R.1.10) P2460: The discussion in section 2.5 is mostly redundant and a little self-contradictory in places; if the large correlation is mainly due to plume transactions, then the sources are still effectively 'collocated', only on the scale appropriate to the measurement (i.e. regional rather than local). Generally speaking, much of the caution that must be exercised when interpreting simple correlations is nothing more than sound scientific practice and really doesn't really need covering in as much detail. Specific cases where correlations could be misleading could be dealt with in the discussion.

We agree with the reviewer that section 2.5 is a reminder of sound scientific practice. However, we feel that this is an important reminder for the readers and the scientific community. Few groups work directly with aircraft datasets, and from many discussions about this dataset it has become clear that many researchers are unaware of the subtle points discussed in section 2.5, and interpret correlation as mainly driven by common sources. We did not find any self-contradictions in the text. Given that this is a very short section, we have kept it in the manuscript.

R1.11) P2463: While using the 'LV-OOA' and 'SV-OOA' terminology gives consistency with recently published works, it should be noted that the AMS alone does not measure the volatility of the particulates. As such, the basis for aligning the factors observed here with previous volatility works should be stated.

This was already stated in the ACPD paper, in P2463 L13-16, with the following text: "The naming based on volatility has been recently adopted on the basis of several studies showing a relationship between higher oxygenation and lower volatility (e.g., Lanz et al., 2007; Huffman et al., 2009a; Jimenez et al., 2009; Ulbrich et al., 2009)."

R1.12) P2463: How much of the difference in HOA/CO ratios could be due to the

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ambiguities in the PMF analysis reported in the appendix?

Systematically for all seed solutions the reported HOA/CO ratio was higher for RF3 than RF12. Excluding the one seed solution with an R2 lower than 0.6 (RF12 family 4) the average ratio of RF3 HOA/CO slope to RF12 HOA/CO slope is 1.93. Only one solution had a ratio lower than 1. The systematically higher ratio in RF3 compared to RF12 across the different seed solutions reinforces the statement that fire influence on this ratio is the likely explanation. We have added the following text to clarify this point:

"All investigated seed solutions (excluding one solution with low HOA to CO correlation) in RF3 have regression slopes systematically higher compared to RF12, indicating this is a general observation for this dataset."

R1.13) P2465: A strong correlation with CO is not adequate to reach the conclusion that the SV-OOA is mainly anthropogenic in origin; biogenic precursors could easily be emitted within the same geographic area as the anthropogenic equivalents. Also, anthropogenic NOx could also be stimulating the formation of biogenic SOA, which would lead to an apparent enhancement within the polluted plume.

The biogenic SOA contribution during MILAGRO has been quantified both experimentally (via specific tracers) and also via modeling, with good agreement between both approaches and a contribution of the order of $1\mu g/m^3$ (Hodzic et al., 2009). Also the large variations of CO over small spatial scales in Central Mexico are indeed dominated by anthropogenic and biomass burning sources, while biogenic sources make a more diffuse contribution that would not produce intense plumes with 400-600 ppbv of CO. Based on all of these pieces of evidence, we believe that our conclusion in this section is correct. To clarify this point, we have added the following sentence to this section:

"Additionally, we can rule out a major contribution of biogenic SOA to SV-OOA for this dataset. Biogenic SOA makes a relatively small background contribution ($1\mu g/m^3$) to the Mexico City region during this period (Hodzic et al., 2009) which is far lower than the SV-OOA levels observed in this dataset, and biogenic CO would also make low

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and slowly varying contributions which could not explain the intense plumes of 400-600 ppbv of CO observed here. ”

R1.14) P2465: I would recommend caution when explaining how atmospheric processes ‘convert’ between the two OOA types; it should be stressed that the two factors represent end points in a continuum of organic composition. The way it currently reads, a reader would be forgiven for thinking that they are two discrete chemical components.

We have changed the word “convert” to “evolve” to better capture the continuum of OA composition observed in the atmosphere.

R1.15) P2475, L5: Many previous studies have shown the contributions of m/z 60 and levoglucosan to vary according to fire type and airmass history, so this conclusion is not new. As a minimum, it would only be fair to cite previous works in the literature. What would be better is if the authors could somehow put numbers to this phenomenon, applicable to this case.

While many ongoing (unpublished) studies have reported a reduction of m/z 60 in BBOA with aging/oxidation in the atmosphere, we are not aware of published papers about ambient studies showing this effect (and unfortunately the reviewer does not provide any references). The variation with fire type (of fuel type) has been the subject of some publications, but it does not seem relevant to our discussion where the main effect is atmospheric aging. We do cite a previous laboratory paper about the possible effect of evaporation. A paper focusing on the reduction of m/z 60 upon photooxidation of woodsmoke in the laboratory has just appeared in GRL (Hennigan et al., GRL). We have modified this text to include that citation and quantify the losses as:

“This loss appears to be initially rapid and of the order of 30% (Fig. 11 inset) and followed by a stabilization. This result is indicative of some loss of the species producing this ion as the plume dilutes and/or is photochemically processed, due to either evaporation or chemical reactions. The possibility of evaporation is supported

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by the results of Huffman et al. (2009a) who showed that the species producing m/z 60 are among the more volatile ones in source and ambient BBOA, based on tandem thermodenuder+HR-ToF-AMS studies. The possibility of chemical reaction is supported by laboratory chamber studies from Hennigan et al. (2010) who show a reduction of m/z 60 of about 30% after several hours of OH exposure."

Citation: Hennigan, C. J., A. P. Sullivan, J. L. Collett Jr., and A. L. Robinson. Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals. Geophys. Res. Lett., doi:10.1029/2010GL043088.

Technical Comments

R1.16) P2448, L24: It should be mentioned that a more fundamental difference between CMBOMM and AMS multivariate analysis is that the latter uses data from all of the organic mass, rather than a subset.

We have changed this sentence to the following text in order to address this point:

"In the last 5 years SA-OA based on factor analysis of Aerodyne AMS mass spectra has become established as an alternative source apportionment technique. The AMS-based technique is less chemically specific, but has the advantages of (a) very high time resolution, and (b) apportionment based on chemical patterns of the whole OA mass, rather than only based on tracers that contribute minimally to OA mass."

R1.17) P2450, L8: Given the wide variation of OH concentrations in the atmosphere, the concentration relevant for the 'approximately 1 month' statistic should be given.

The text has been modified to the following:

"Carbon monoxide (CO) has a lifetime against oxidation by OH of approximately one month in Mexico based on the measured 24 hour average OH concentrations of $1.6x10^6 molec/cm^3$."

R1.18) P2450, L24: The open, non-agricultural, biomass burning events during MILA-

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GRO were as much grassland fires as forest fires.

We are not sure where this information comes from as no reference is provided. We are aware that grassland fires occurred during MILAGRO. However it is our impression (and also based on works such as Yokelson et al., 2007) that the bulk of the OA emissions from the wildfires during MILAGRO were due to forest fires and not grassland fires. Since the reviewer does not provide any citation that suggests otherwise, we have not changed the text.

R1.19) P2452, L12: Stylistically, the end of the introduction reads more like a conclusions section. Suggest a reword to focus on the hypotheses being tested rather than the findings.

We feel that the last paragraph of the introduction provides an appropriate summary for the paper content, focusing on what was done in this study and mentioning a few key results, and therefore have left the text unchanged.

R1.20) P2452, L19: A citation for the gas phase instrumentation should be specified.

This point was already addressed on the ACPD version (page 2452 line 22) with the following text:

"A more detailed description of the instruments used in this study, the quantification and data analysis techniques, and instrumental intercomparisons can be found in DeCarlo et al. (2008) and Dunlea et al. (2009)."

R1.21) P2453, L6: The ODRPACK95 package used in Igor Pro should probably be referenced.

A reference to this package has been added.

R1.22) P2458: Technically, PMF is an 'algorithm', not a 'model'. Also, it is PMF2 which is being referred to, as a trilinear version (PMF3) exists. Finally, the key constraint is that the solutions are non-negative as opposed to positive (i.e. zeros are allowed).

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We disagree with the reviewer on this point. PMF is a model which can be solved by many algorithms and software packages, while the PMF2 software package implements a particular algorithm to solve the PMF model. For a discussion of the differences between the "model" and "algorithm" terms in this context, see the interactive comment by P. Paatero: Atmos. Chem. Phys. Discuss. 6, S5920–S5926, 2007 (http://www.atmos-chem-phys-discuss.net/6/11681/2006/acpd-6-11681-2006-discussion.html, see item 3 on that comment). Our use of the words "model" and "algorithm" in the present paper is consistent with the definitions of P. Paatero.

It is also clear in this text that we are discussing only the bilinear problem, e.g. in the text "bilinear unmixing model". No mention of higher dimensional models is made in this section and we prefer to keep the text simple to avoid confusion. In reference to the non-negative constraint, a survey of all seed solution time series and mass spectra showed that while quite small values were present all were greater than zero. We have left the text as "positive" for this reason.

R1.23) P2459, L16 (and elsewhere): 1 atm should be specified in SI units.

The text has been changed (at the single occurrence) to 1013.25 hPa or 1 atm.

R1.24) P2460, L3 (and elsewhere): LST should be defined (relative to UTC), as it is not a normal time zone code.

We have added a definition of Local Standard Time (LST) as UTC -6 at the first occurrence (corresponding to P2460 L3 in the ACPD version).

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 2445, 2010.