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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.

Anonymous Referee #2

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Review of "Investigation of the sources and processing of organic aerosol over the Central Mexican Plateau from aircraft measurements during MILAGRO" by DeCarlo et al., for ACP

In order to discern aerosol composition, source attribution and effects of aging, data from two flights of the C130 are analyzed; RF3 (3/10/2008) a flight affected by biomass and RF12 (3/29/2008) a flight less affected. Use is made of PMF analysis of OA measured with a high resolution AMS. Correlations with other aerosol species and gas phase tracers are considered. Most results are normalized to CO in excess of back-

ground in order to account for dilution.

Overall this is an very good paper with much new information and many excellent insights. I have multiple concerns which may be viewed in apart as a statement about just how hard it is to determine mechanistic information from a complicated data set. Please try to address the concerns (General comments 1-6) to the extent that they can be addressed without greatly expanding the scope of the study.

I recommend publication after revisions.

General Comments

1. Sec 2.2.2 CO background I don't know if there is a satisfactory way to determine CO background. 55 or 60 ppb determined for RF3 or the entire C130 data set are, I assume, free tropospheric values. In Fig. S1-2 (a) is the C130 passing into and out of the free troposphere or are the 20 ug/m3 organic plumes actually in the free troposphere? For measurements near Mexico City, higher values appear more appropriate, 90 ppb as used in RF12 up to the 125-130 used in other studies. The choice of background will not matter much in a concentrated urban plume but will make a significant difference in regional sampling. Fig. 4 shows that much of the data set has CO below 200 ppb on RF 12. CO values are hard to see on the RF3 plot, but appear to be even lower. My overall concern is applying somewhat perturbed background levels to air masses that might have zero organic at a higher CO level than used here. Comments?

2. Can anything be said about the contributions of urban biomass burning (trash, cooking, and certain light industries) to BBOA. Yokelson et al (ACP, 2009 or 2010) reported emissions at these "non-traditional" source with implication that they contribute a large (perhaps, unrealistically large) fraction of OA. Also, as deGouw et al have shown in several locations, CH3CN from nominally urban source regions scales with CO (but not nearly as steeply as in open fires). Yet, BBOA on RF12 is close to zero. This null result has implications which should be mentioned.

3. Sec 3.5.1 Ascribing 30% of CO to biomass burning on RF3. This may be correct but in my opinion it is not supported appropriately given the measurements available on the C130. Pick a tracer that is emitted primarily from urban rather than biomass burning sources. Does the ratio of that tracer to CO change between RF3 and RF12? I don't off hand know emission factors relative to CO for fires, but I would consider, benzene, toluene, and NOy. Another consideration is that emissions could have changed between RF3 (Monday) and RF12 (Saturday).

4. Sec 3.5.2 Relation between BBOA and HCN It appear from the scatter plot in Fig. 4 that almost all of the data points have HCN below 1 ppb. Considering just these points, there is a good correlation between BBOA and CO on RF3 with slope (given in text) that is similar to what others have measured. Yet on RF12, there is almost no BBOA associated with 1 ppb HCN. Graphs are very small and hard to read in ACPD and with that caveat in mind, the RF12 time series of HCN has a background of about 500 ppt but I can't see a background on RF3. RF12 does show HCN "plumes" with increases from 500 to 1000 ppt coincident with other aerosol constituents. These features need to be explained.

I presume that the C-130 had a PTR-MS that measured CH3CN. Why is that not also used in identification of biomass burning? Some comments on the relative utility of these two tracers would be useful. CH3CN is the more commonly used tracer, though this certainly reflects instrument availability. Perhaps CH3CN could also supply confirming evidence for the near absence of biomass burning on RF12.

5. Sec 3.5.4 Use of sulfate to apportion LV-OOA to open biomass burning I believe that using the difference in aerosol sulfate between two flights to apportion LV-OOA to biomass burning is more of a what if exercise than a result that follows from the data. I do not see any mechanistic reason why LV-OOA (in the absence of biomass burning) should be related to SO4 with the same proportionality constant on two flights. Locations of OA precursors and SO2 are different. Flight patterns shown in S1-1 are very different for the 2 flights. Perhaps more volcanic emissions were intercepted on

RF3.

6. A2 Variation in the 4 factor solution This section was an eye-opener to me. Figures A1 and A2 are valuable, though in ACPD format most details are lost in A2. The family 3 solutions look very different than the solutions used in the paper that are from family 1. By the objective standards of Q and cumulative R2, the family 1 solution is better but I don't know whether the differences are large enough to be a deciding factor. I am guessing that if a family 3 solution was used in this study, conclusions would be different. Even though the text states "that no solution is uniquely best and the variability within a general solution group should be considered some measure of the uncertainty of the final solution", this is unsettling and raises a number of questions:

1. Is the spread in PMF solution depending on seed typical? Is it the result of sampling a wide range of chemical conditions? 2. Are the differences in r2 and Q really big enough to say that one solution is say 90% more probably correct than another? 3. If not, how is the family 1 solution justified?

If you feel that these questions go beyond the material that belongs in this paper, a response only in the reply to reviewer would be appreciated.

The BBOA to HCN slopes are very different for RF3 and RF12 as noted above. It appears that this feature is robust to the selection of solution.

Specific Comments

7. p2456, line 1-8 Not enough explanation for me to understand what is shown in Fig S1-2 and what it implies about overestimate of volatility.

8. p24599, line 13 and elsewhere. Unit in error matrix is Hz. I guess this is correct and standard cgs usage. It just sounds like an awkward replacement for what I think is counts per second.

9. p2459 line 17-20 Hard to follow. Construction of "joint data set" explained more clearly latter on in paper.

10. p2460 line 11-13. Good point, that is often forgotten. Many other good points that I did not get around to calling out.

11. page 2472, Section 3.6 and Fig. 9 I found the discussion hard to follow. A more explicit description of plots in Fig. 9 would help. i.e. “post processed urban+non-BB regional OA (line 5). What trace should I be looking at? I know that this figure will be more legible in ACP format, but as it is I can’t tell the difference between Crounse Traffic and Crounse Fire

12. page 2473, line 21 What does subscript pp mean? “photochemical processing” is mentioned a few lines above but post processing makes more sense.

13. page 2477, line 8 family types What defines a family type?

14. page 2478, line 3 total R2 Is this equal to 10? 5 regressions times 2 flights?

15. page 2478, line 24 -28. take into account slope of regression when choosing a PMF solution. There implies that you know what the PMF solution should look like. Maybe solutions that are not within physical bounds could be eliminated – or solutions that conflict with some other aspect of data set.

16. Figure 10. What is the relation between points on this graph and points in Fig. 4. The number of data points in Fig. 10 is much less than in Fig. 4. Also, urban CO in Fig. 10 is much lower than total CO in Fig. 4. Adding Fire CO and background to Urban points in Fig. 10 would not change this inequality.

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