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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Mexico City aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0) – Part 2: Analysis of the biomass burning contribution and the modern carbon fraction" *by* A. C. Aiken et al.

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Responses to Anonymous Referee #1

R1.1) In view of the large territory covered by this article I will skip the obligatory opening paragraph that says in some other words what the authors have done. Suffice it to say they have done a lot to quantify impacts of biomass burning at an urban location in Mexico City. By no means are all problems solved but I believe that uncertainties are

better exposed. Grouping data into three 4 to 6 day time periods, two with a large BB influence and one with much lower BB impacts was a productive way of looking at the data. It is not the only way. With the exception of 14C and levoglucosan measurements, the data have time resolution of the order minutes or less. Although clearly outside of the scope of the present article, I for one am interested whether the fast response data give additional insights, beyond that contained here and in Part 1. I recommend that this article be published with minor modifications.

[Resp]: We agree with the reviewer that there is more to learn from the very rich MILAGRO datasets with additional detailed analyses and modeling. We are working towards additional papers where we will explore some of those aspects. However given the extensive amount of material already covered in the present paper, our revisions only aim to improve the clarity of the current manuscript and to deal with the various technical issues raised by both reviewers, while covering the same material as the ACPD version.

R1.2) General Comments. It is interesting that with all of the data taken during MILAGRO there is still a major gap between modern carbon measurements and quantified sources. I agree with the authors that finer time resolution measurements are needed.

[Resp]: We agree that the reconciliation of the non-fossil carbon fraction with source apportionment studies such as ours or Stone et al. (2008) deserves further research. However some confusion was introduced in this topic by Marley et al. (2009) who presented modern carbon fractions which do not account for the bomb radiocarbon, and for which 100% non-fossil carbon would correspond to $\sim$110%-120% modern carbon depending on the mix of non-fossil sources.

Several of the authors of this paper are also close to submitting a separate paper where we further discuss the differences between modern and non-fossil carbon, and use a regional model (MM5/CHIMERE) to quantitatively evaluate the concentrations and fractions of modern and fossil carbon during MILAGRO, and compare to both existing

14C datasets. We defer further discussion of this topic to that upcoming manuscript.

R1.3) Variations in CH3CN are discussed, but in the end its origin and relation to BBOA is still ill-defined. Fig. 14a showing a pronounced diurnal cycle in the ratio of BBOA to CH3CN was a complete surprise to me. Many observation, including ones from Mexico City (Table 2) show that CH3CN is correlated with urban CO. Trash burning is a possibility in Mexico City but less likely in NEAQS?

[Resp]: We are using CH3CN as a tracer for biomass burning, which is consistent with most of the literature on the sources of this species. Urban sources of CH3CN in Mexico City are likely, such as biofuel use, trash burning, perhaps motor vehicles, etc., but they are poorly characterized. We agree that the variations of CH3CN in this dataset are not fully understood and deserve further research beyond what is presented in our paper. Part of the goal of showing the variations in CH3CN and its ratios is to show that indeed the interpretation of CH3CN in Mexico City during MILAGRO is not just as a tracer of forest fires, but that the issue is more complex.

We have added the diurnal cycles of CH3CN during the high and low fire periods to Figure 11(e) to further help the interpretation of the variations of CH3CN. This figure shows that during the low fire period, the level of CH3CH is much lower during the early morning compared to the high-fire period, further supporting the conclusions of the paper.

Trash burning is not believed to be a source in NEAQS as it is illegal in the US, whereas it appears to be common in Mexico, especially in rural areas. See also the reply to R1.4 below.

R1.4) How can the contribution of trash burning to BBOA be assessed? In period F3, there might have been less trash burning because of rain, which I believe is mentioned in the text. There were differences in synoptic flow which may have shifted the location of plumes away from T0.

[Resp]: It is unclear how to quantify the contribution of trash burning to BBOA with the current dataset. However the consistency of the BBOA time series with that of the fire impact factor strongly suggests that the majority of the BBOA is due to forest fires and not trash burning.

An alternative method to estimate the contribution of trash burning is to use antimony (Sb), which is thought to be a tracer of trash burning (Christian et al., 2010), but which can also have many other sources (brake wear, smelters, etc.). As already show in in Fig S-8, Sb has a similar concentration during the high biomass burning period F2 and the low biomass burning period F3, and only slightly higher concentration during period F1. This may indicate that trash burning did not change significantly between the periods, and thus it could only be a minor source of BBOA. Or it may indicate that Sb is dominated by non-trash burning sources.

These discussions are speculative and thus we have not modified the paper. Some of the authors of this paper are also collaborating with other researchers in a modeling study of trash burning in Mexico City, where we hope to address these issues in a more direct way.

R1.5) Fire period averages of CO are about the same in F1 and F3 (Fig. 9a). Would you draw the conclusion that BB are a minor source of CO? Is there any evidence from the finer time resolution data that BB contributes significantly to CO?

[Resp]: In Part 1, Figure 4, the timeseries of both CO and BBOA are shown. There does not appear to be a dominant correlation between these two species at T0 (R2 = 0.04). The majority of CO does not appear to correlate with the fire impacts, but with the urban (HOA) emissions.

This is consistent with the results of Crounse et al. (2009) based on the C-130 aircraft data, who concluded that the contribution of the forest fires to CO is about $\sim$15% at the surface inside the city during the afternoons. A contribution of this order would be hard to discern on top of the effects of urban CO sources and advection in the current

dataset.

R1.6) Figures 15 e and f are excellent illustrations of the very different pictures obtained from surface and column data. In that regard, I am concerned that the average values presented for fire periods F1, F2, and F3 are heavily weighted towards nighttime values as very high concentrations of primary pollutants are found in a shallow boundary layer. I take it that average values of ratios are obtained by taking the ratio of two averages – which should be explicitly mentioned in the text.

[Resp]: The average values for F1, F2, and F3 are taken over the full 24 hours of the day. For species dominated by primary emissions such as BC or HOA, the early morning is the period with the highest concentrations. For secondary species such as NH4NO3 and OOA, the opposite is true. We note that BBOA and other BB tracers are highest during nighttime hours, so the BB impacts are maximized when averaging the 24 hrs of the day. Also many of our analyses are carried out for the full time series or the diurnal cycles of the species (e.g. Fig 3, 4, 7, 11, 14, 15), precisely so that the effect of the time of the day can be evaluated for the most important tracers.

We are not sure which ratios are being referred to by the reviewer, as most of the ratios we use are shown as diurnal cycles and thus 24-hr averaging is not an issue (e.g. Fig. 11, 14). The ratios in Table 2 are derived from linear regressions.

R1.7) I recommend that more use be made of Tables. For example, the 14C measurements in the present study and by Marley et al; and PMF concentrations and percentages of OA – whatever is of bottom line importance to the conclusion of this article. A Table or Tables should be introduced at the point where the data first appears. All of the numbers are in the text and in Figures. Footnotes or Table entries could cross reference Figures. The problem is that there are so many numbers that by the end of the article it is easy to loose track of where things came from.

[Resp]: We have tried to make clearer some of our conclusions throughougt the paper, including in the abstract (also in response to comment R2.17). We have added some

new information to Table 2 which is central to the conclusions of the paper. The PMF-AMS component concentrations and percentages of OA are already presented in the companion paper (Fig. 10 of Aiken et al., 2009), so we prefer to not repeat them here.

Specific Comments

R1.8) P 25925 Calculation of OCbbnf. An equation would be useful

[Resp]:The following equation has been added to the text:

OCbbnf = ECnf * (OC/EC)bb

R1.9) p 25928, lines 1-5 best estimate of regional influenced OOA background from 8PM to 4 AM. Has it been established that a strong regional influence would be visible within the nocturnal inversion layer? Are wind speeds at night rapid enough to see material from outside the City at T0? What do the models say about nocturnal drainage from mountain-side areas that are burning? This is of particular importance since the fire impacts are calculated to be most pronounced at night. One might expect the nocturnal residual layer to be most effected. Between 10:00 and 12:00 the boundary layer is rapidly incorporating material from the residual layer which, however, would be easily confused with formation of OOA within the boundary layer. Nighttime data from Pico Tres Pardes might be useful.

[Resp]: It has been established with good confidence that there is effective ventilation of the basin on a daily basis (de Foy et al., 2006). This suggests that the basin fills with well-mixed background air in the late afternoon and that consequently night-time concentrations before rush hour would have a sufficient component of regional air for this analysis to hold. After sunset, the winds die down very rapidly and there are weak drainage flows from the surrounding mountains. While these are an additional source of regional air, the main factor of influence is the late afternoon mixing.

We have added the following text to section 4.3.2 of the revised paper to addressing this point and also comment R1.9:

"Note that in this analysis we have neglected the species present above the boundary layer in the morning, as prior studies have found limited pollution in residual layers, especially when compared with the morning emissions. See e.g. Fig. 1 of Herndon et al. (2008)."

References:

de Foy, B., Varela, J. R., Molina, L. T., and Molina, M. J.: Rapid ventilation of the Mexico City basin and regional fate of the urban plume, Atmos. Chem. Phys., 6, 2321-2335, 2006.

S.C. Herndon et al. The Correlation of Secondary Organic Aerosol with Odd Oxygen in a Megacity Outflow. Geophys. Res. Lett., 35, L15804, doi:10.1029/2008GL034058, 2008.

R1.10) p 25928 Fire Impact Factors from FLEXPART. I am concerned that the FLEXPART results are for a column from the surface to 2000m while data that is averaged over periods F1, F2, and F3 will be most affected by high nighttime concentrations in a shallow boundary layer.

[Resp]: When performing the analysis, we tested various heights ranging from the surface 500 m to the entire column. While each choice has its pros and cons, they did not affect the conclusions. We therefore settled on 2000 m as a middle choice. A more detailed analysis of this question would only make sense if we had detailed information of plume rise and vertical mixing.

R1.11) p 25939 line 23 – p 25940, line 5 In the first page OC has important contributions from non-fossil sources, 57 and 43% during the high and low BB periods. On the second page: fossil OC represents 50 and 63% during the high and low BB periods. A stylistic point: In one case numbers are for non-fossil and in the second case for fossil. A substantive point: Numbers are not the same. Is the first statement from Stone et al?

[Resp]: We have removed the second instance of this text as it was repetitious.

Regarding the actual numbers, the first set of numbers was incorrect, while the second set was correct and consistent with Fig. 12. Indeed 51% and 38% of the OC is non-fossil during the high and low fire periods respectively. Thank you for pointing out this mistake.

R1.12) P 25940 Fig. 12b divides OC into WSOC and WIOC. It is difficult to know where to go on graphs to see this (not helped by microscopic size of ACPD PDFs). In this case, the relevant comparison is between slice that is solid purple, and slice with purple lines.

[Resp]: We apologize for the inconsistent colors used in Fig. 12a and 12b. We have changed the colors and patterns to make the distinctions clearer. We have also changed the colors and patterns in Fig. 13 to make them consistent with the revised Fig. 12.

R1.13) p 25941 line 2-5 WSOC and WIOC. What is water soluble is an operational definition.

[Resp]: Yes, and this is explained in Methods Section 2.3 with reference to the previous method papers by Szidat et al. We have added the following text to the revised paper to address this point:

"Although the definition of WSOC is operational, all of these studies measure it under high water/WSOC ratios (high dilution) and thus the results should be approximately comparable."

R1.14) p25942 line 6. reference to Fig. 10 d-f. Fig 10 being in an earlier section, it was not immediately obvious that the authors were going back to the actual 10d-f, rather than presenting something new based on the methods used to construct those figures.

[Resp]:The text was changed to read, "We now perform the same “fire-period analysis” described in section 3.2.2 with the modern carbon data, as shown in Fig. 10d,e,f. "

R1.15) p 25945, line 6-7. “HCN explained 10% of the variance of ammonium nitrate” This is only a minor contribution to BB so my comment has only minor importance. HCN and ammonium nitrate will respond to common meteorological factors determining ventilation. Even without a common source, I am surprised the correlation is so small.

[Resp]: As discussed in DeCarlo et al. (2008, 2010), this is due to the dominance of forest fires for HCN and of the urban area for NH4NO3, with both sources being strong and not collocated. In the far field, a correlation should develop due to mixing in the regional air, similar to the high correlation observed for HCN and aerosol sulfate for those regional airmasses (see Fig. SI-3 of DeCarlo et al., 2010, http://www.atmos-chem-phys-discuss.net/10/2445/2010/acpd-10-2445-2010-supplement.pdf). However NH4NO3 evaporates in regional air and this process probably reduces the correlation between HCN and NH4NO3 that could be expected in regional air.

R1.16) p 25948 line 18, NR-PM1+BC I suspect that NR was defined previously, but where? Non-refractive? Repetition of definition would be useful.

[Resp]: NR stands for "non-refractory", which is an operational definition for the species that evaporate in a few seconds at 600C, i.e. at the operating conditions of the AMS. This was indeed defined already in P25937 L1. We have changed this text to read "non refractory (NR) PM1 + BC".

R1.17) P 25948 line 18-20 Column abundances. Is the residual layer assumed to have zero aerosol?

[Resp]: This figure represents the column abundances of aerosol for the mixed layer which is in contact with the ground. The concentrations in the residual layer at night are typically much lower than those in the nighttime boundary layer, as discussed in response to comment R1.9 above. We have added the following text to the paper to clarify this issue:

"Note that in this analysis we have neglected the species present above the boundary layer in the morning, as prior studies have found limited pollution in residual layers, especially when compared with the morning emissions (see e.g. Fig. 1 of Herndon et al. (2008))."

R1.18) p 25949, line 24 and other places “an increase of OOA during the low fire periods” This is true but the increase is small and easily explained as natural variability. The more important point, which the authors clearly recognize, is that there is not a large drop in OOA during low fire periods which indicates that the OOA was coming from fires.

[Resp]: We agree that the increase of OOA during the low fire periods is probably coincidental due to changes in dispersion etc. Indeed the major conclusion of our analyses is that OOA does not drop during the low fire periods, in contrast with BBOA and all fire tracers.

R1.19) p 25965 Table 1. Biomass contributions to OC. Why does the 14C analysis indicate the same contribution of 18% for high and low fire periods.

[Resp]: This is the same information as in Fig. 12a. The mass concentration of OCbbnf is higher during the high fire period (2.0 ug m-3) vs. the low fire period (1.5 ug m-3). However indeed the percentage contribution to OC is similar at 13%, since the total concentration of OC is somewhat lower in the low fire period, as shown in e.g. Fig. 13 and Fig. 14. We would expect that the fractional contribution would be lower during the low fire period, and as already discussed on P25940 and 25943, the fact that this is not the case is likely related to the measurement noise given the low number of samples (2 x 24hour periods for each).

R1.20) P 25966 Table 2 and other places in the text. When taking a ratio to CO, what background is subtracted from measured CO?

[Resp]: Many of these ratios are determined from linear regressions, which do not

require the assumption of a background value. For our data we have used a value of 120 ppb per Herndon et al. (2008).

R1.21) p 25969 Fig 3 a and other figures. Are date tic marks at midnight?

[Resp]: Yes, tick marks with a date label are at midnight, as is standard in graphs for which the X-axis is a date. We have added the following text to the caption of Fig. 1 to clarify this point:

"Here and in all subsequent figures, the longer tick marks on the X-axis and a date label correspond to midnight local time."

R1.22) p 25979 and other places. Comparison of 14C measurements with other measurements Are the other measurements averaged over the collection times for the 14C samples or is the averaging done over “fire periods”?

[Resp]: In Fig. 12 the AMS measurements have been averaged over the same periods of the 14C filters, to enable a direct comparison. This was already discussed in the ACPD paper, P25943, L20-22, with the following text: "Figure 13 summarizes the enhancements of carbonaceous aerosol during the high (F1+F2) over the low (F3) fire periods with the three different methods, which are not directly quantitatively comparable as the periods of available data vary with each method."

The following text has been added to the paper for further clarification of this point:

"Fig. 13 uses all available data which overlaps with the high and low fire periods for each of the measurements. The comparison restricted to the 14C periods is already shown in Fig. 12, and as broad a comparison as possible for the MILAGRO period is of interest here."

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