

***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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Received and published: 20 April 2010

Responses to Anonymous Referee #2

Aiken and coauthors present part 2 of their analysis of aerosol composition at the T0 supersite in Mexico City during March 2006 as part of the larger MILAGRO campaign. While part I of this analysis (published previously) describes aerosol composition in general, part II (this work) focuses on determining the impact of biomass burning (BB)

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on aerosol at T0. This analysis primarily uses measurements made with a high resolution time of flight aerosol mass spectrometer (AMS) which are interpreted using positive matrix factorization (PMF). New  $^{14}\text{C}$  analysis data of filter samples collected during the same time period, and results from a regional 3-D transport model (WRF/FLEXPART) which includes fire emissions (as estimated from satellite thermal imaging) estimating the impact of regional fires at the T0 site are also included. The results presented are compared with each other and with previous estimates of the impact of fires on Mexico City during the same period. The manuscript is interesting and is recommended for publication in ACP after addressing the following items.

General comments:

R2.0) While (and perhaps because) this manuscript presents and analyzes an immense amount of information, it does suffer in places from a lack of clarity and carefulness in the presentation and analysis. Generally speaking the manuscript could benefit from better organization, streamlining, and distillation of the salient points.

[Resp]: We realize that the paper addresses a large number of topics, which is why we divided each topic into its own sub-section, as detailed in the introduction. We have addressed all specific reviewer suggestions below.

Specific comments:

R2.1) The authors make the argument that regional forest fires contribute a small fraction (2-3%) to the fine PM at T0 as an annual average. Most previous studies generally agree on this point. Even so, there is considerable research which links short-term exposure (hours) to elevated PM to adverse health effects and even death. While the annual contribution of fires to fine PM near the ground in Mexico City may be small, the impact on health may be somewhat more significant due to their higher contribution to short-term 'extreme pollution events'. This point should be added.

[Resp]: we have added the following text to section 4.2 of the paper to address this

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point:

"The impact of forest fire emissions on health in Mexico City is uncertain but may be somewhat larger than the impact on the annual average, due to the influence of plumes with very high particle concentrations."

R2.2) The fire impact factor (FIF) as calculated by WRF/FLEXPART for T0 is shown in Figure 3a. Given the modeling has already been done, it would be useful to readers for the authors to also state the fire impact (FIF) averaged over the populated area of the basin, and discuss any differences from the same quantity at T0.

[Resp]: The question of the relationship between concentrations at T0 and population exposure in the MCMA as a whole as well as in different sub-areas is an interesting one that would probably merit a publication in itself. We have added a new Figure (Fig. S-4 in the revised version) and the following text to the revised paper to briefly address this point:

"FIF's calculated over a 40 km by 40 km square centered on the city look like a smoothed version of the FIF's at T0 discussed here (see Fig. S-4)".

R2.3) The authors show diurnal profiles of acetonitrile (CH<sub>3</sub>CN), levoglucosan equivalent mass (LEM), and FIF, and state that they are consistent with each other. This does not appear to be true. In both cases (12-20 and 14-24) FIF begins to increase at 20:00hrs, but LEM does not appear to begin to increase until ~00:00hrs. FIF, again in both cases has reached its maximum by ~23:00hrs, but LEM and acetonitrile do not reach their maximum until 06:00 hrs. It's not clear that the diurnal profile in LEM and CH<sub>3</sub>CN can ever be matched with FIF by simply by increasing the tail of the smoldering emissions. This needs to be discussed further.

[Resp]: We disagree with the reviewer on this point. The two tracers and the model results are consistent with each other, especially in the fact that they all peak in the early morning. This contrasts with the expectation (expressed by other researchers)

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of maximum fire impacts to T0 in the afternoon when the fires are most intense. The reviewer is taking issue with finer details of the timing of the diurnal profiles, not with the broad features which are indeed consistent. We only implemented a few simple assumptions in the calculation of the FIFs as we were not aiming to obtain a perfect match with the fire tracers, but rather we were investigating if the broad features of the tracers could be reproduced. We already discussed this point in the ACPD version (P25929 L21-23) with the following text: "BBOA and acetonitrile peak even later in the early morning (Aiken et al. 2009), which suggests that smoldering emissions may be active past 24:00 of the day in which the fire count was detected."

FIF based on emissions from 0:00 to 6:00 lead to peak impacts in the bottom 2000 m from 9:00 to 16:00 and in the bottom 500 m from 2:00 to 10:00. From this result, we can see that it would be possible to reproduce the finer details of the CH<sub>3</sub>CN and LEM early morning peaks with a combination of timing adjustments and calculation of surface concentrations. In actual fact, these profiles are campaign averages and this question would be better addressed by looking at the individual episodes and fires and the peaks they cause. This is beyond the scope of the present paper.

R2.4) While the acetonitrile diurnal shape appears very similar to that measured at T1 (de Gouw, et al, 2009), the amplitude appears substantially different (larger by  $\sim 2x$ ). Reasons for this should be discussed.

[Resp]: We have added the following text to the paper to address this point: "Note that while the diurnal profile of CH<sub>3</sub>CN is similar to that measured at T1 by de Gouw et al. (2009), its diurnal amplitude is about 2x larger. The diurnal amplitude of other pollutants such as CO is also much larger at T0 than at T1, due to the stronger influence of urban emissions at the former site, and urban emissions may also explain the higher diurnal amplitude of CH<sub>3</sub>CN at T0. An alternative explanation for this observation is the closer location of T0 to the mountains and thus the forest fires. Given the incomplete understanding of the CH<sub>3</sub>CN sources at T0, we cannot reach a more definitive conclusion based on the data and analysis in this paper."

R2.5) Estimates of ‘urban emissions’ (emissions in the absence of large forest fires) of enhancements in acetonitrile (relative to CO) in Mexico City appear quite consistent between Crouse et al, 2009 (0.24 ppbv ppmv<sup>-1</sup>) and deGouw et al, 2009 (Fig 8b) and similar to those measured previously in a New York city plume (0.25 ppbv ppmv<sup>-1</sup>, de Gouw et al, 2006). It is not stated how this apparent ‘urban’ source of CH<sub>3</sub>CN treated in this analysis? If this has not been included, it needs to be done as it will affect the derived dBBOA/dCH<sub>3</sub>CN.

[Resp]: The reviewer is suggesting to push a quantitative interpretation of CH<sub>3</sub>CN and other tracers as separately arising from wildfires and urban sources. We have attempted this using the CH<sub>3</sub>CN/CO urban ratio estimated by the reviewer. However this ratio may be too high, as the CH<sub>3</sub>CN background appears to be near zero when this ratio is applied, which we know is unrealistic. We could further explore this type of analysis by assuming a series of urban ratios and examining many of our diagnostics and results as a function of those assumed ratios. However this type of analysis quickly becomes a large topic, which is beyond the scope of this paper.

In other words, for the purposes of this paper, we are assuming that the majority of the CH<sub>3</sub>CN is associated with burning activities of different types (wildfires, urban burning), which is supported by the correlation of CH<sub>3</sub>CN with other burning tracers (Fig. 5 & 6). The variations in the ratios observed in e.g. Fig. 14 are then due to mixing of influences from burning sources with different ratios. Attempting to quantitatively separate all of the burning sources in mixed urban air requires more assumptions and introduces more uncertainties, and is beyond the scope of this manuscript.

R2.6) As shown in Fig. 14a dBBOA/dCH<sub>3</sub>CN is highly sensitive to the background level used for CH<sub>3</sub>CN is chosen. It seems the authors have simply picked two CH<sub>3</sub>CN backgrounds to use in this analysis. de Gouw et al, 2009 derive a CH<sub>3</sub>CN background for MC of 250 pptv. It is recommended that ‘effective’ CH<sub>3</sub>CN backgrounds (likely time dependent) relative to BBOA are determined using intercepts from regression after correcting for the ‘urban’ CH<sub>3</sub>CN (point 5 above). Without accounting for these

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two effects, I do not find much quantitative meaning in Fig14b and Fig14C(left) (and associated discussion in the text 4.3.1) and recommend removal.

[Resp]: The background values of 100-150 pptv CH<sub>3</sub>CN were chosen based on the lowest levels observed in the PTRMS measurements at T0. They are also consistent with the co-analysis of all the biomass burning tracers in section 3.2.1, where the ACPD version already stated (P25931, L7-9): "The CH<sub>3</sub>CN background when the other tracers are zero (positive Y-intercept) is similar to the tropospheric background of 100-150 pptv within the regression uncertainties."

We also note that the PTRMS used at T1 was a more advanced instrument with a larger quadrupole and thus higher precision than that used at T0, and this may perhaps explain some of the small differences in CH<sub>3</sub>CN backgrounds discussed by the reviewer.

R2.7) Suggest showing separate diurnal profiles of CH<sub>3</sub>CN for F2 and F3 periods so the reader can get a feeling for the differences/similarities in this profile between high and low fire impacts.

[Resp]: We have added the diurnal profiles of CH<sub>3</sub>CN as suggested to Figure 11, which reinforce the conclusions of the paper. We have added the following text to the paper to explain this new graph:

"The CH<sub>3</sub>CN diurnal profiles for the high fire periods are enhanced at night and in the early morning, consistent with the highest BB impacts at T0 during this period. During the afternoon and evening the CH<sub>3</sub>CN levels are similar during all fire periods, again supporting the limited BB impact during this part of the day."

R2.8) The four days (March 21, 22, 26, and 29) on which the 14C filters were collected were not particularly high fire count days according to MODIS fire counts, in fact the fire counts were quite low for all of these days. What fire contribution is inferred if a continuous measure (BBOA or FIF) is scaled to match over the times when the

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filters were collected, and then integrated over the entire period? A direct comparison between AMS BBOA averaged over 14C filter periods would be useful in that it would give a better representation of the variance between these two methods.

[Resp]: Both the CMB and AMS results suggest larger differences between the fire impacts in those days. As discussed in the ACPD paper in reference to Figures 1 & 2, (a) the MODIS fire counts do not capture all fires, (b) the fire counts from the day before also need to be taken into account as they produce smoldering emissions in the evening which affect the city in the next calendar day, and (c) March 21st is discussed explicitly as a day with low fire counts but high fire impact due to a "direct hit" by the plume of a nearby fire (Fig. 2b).

The integrated comparison for the 14C sampling periods that the reviewer is suggesting is already presented in the manuscript, in Fig. 12. During the "high fire" filters, the AMS/CMB BBOA estimates are 14% and 18% of the OA, respectively, while during the "low fire" filters, these estimates are 4% and 7%, respectively.

R2.9) The 14C-bbnf enhancement during the fire period is small (5x smaller than AMS-BBOA, even though the 14C is PM10 samples and AMS is PM1). If this is truly due to mis-apportionment of 14C-bbnf because of an incorrect or uncertain OC/EC ratio, then this seemingly causes an error in the bomb 14C correction. This would in turn cause an over-estimate in modern carbon. The treatment of this should be discussed. The 14-C observations in general are difficult to understand.

[Resp]: This same topic has been discussed in response to comment R1.19, and was already discussed in the ACPD paper on P25940 and 25943. Indeed the enhancement of OA\_bbnf shown in Fig. 13 is surprisingly small, and inconsistent with the enhancements estimated with the other methods. As discussed in response to R1.19, we suspect that sampling statistics, given the small number of filters, are responsible for this inconsistency.

Technical corrections:

R2.10) Throughout manuscript: There exist long paragraphs which contain many ideas. Suggest breaking these apart such that a paragraph contains a single idea which is summarized in the first sentence. This will be very helpful to the reader.

[Resp]: We have reviewed the revised manuscript and broken up several paragraphs according to this suggestion.

R2.11) Throughout manuscript: ppt and ppb and ppm should be written as pptv, ppbv, and ppmv.

[Resp]: changed as suggested.

R2.12) PG 25917 LN 5: Define 'OA'

[Resp]: done

R2.13) PG 25917 LN 10: 'fire impact index' used here and 'fire impact factor (FIF)' used later, make all the same.

[Resp]: We have changed all the occurrences to fire impact factor (FIF).

R2.4) PG 25917 LN 11: Replace 'CH3CN' with 'acetonitrile (CH3CN)'

[Resp]: done

R2.15) PG 25918 LN1-2: '15% higher modern carbon' should also be stated in a form which is directly comparable to AMS BBOA.

[Resp]: We are not sure we understand exactly what the reviewer is suggesting. We do not give a percentage for BBOA only in the abstract. This topic is also discussed in great detail in the 14C section. Since the abstract is already very long, we have decided not to add additional information to it.

R2.16) PG 25918 LN9: Define 'fine' submicron?

[Resp]: Some of the results that we present are PM1 while others are PM2.5. "Fine" is used in the literature to refer to both types of samples, and the fraction of the mass

between PM1 and PM2.5 is small in Mexico City (Salcedo et al., 2006; Querol et al., 2008). Since the details of the size cuts of the different analyses are already discussed in the text and the abstract is already very long, we prefer to not add additional details to the abstract.

R2.17) PG 25918 LN12-17: These sentences are out of place. Either remove from abstract, or insert as a new paragraph above current LN8.

[Resp]: reordered the sentences in the abstract as suggested.

R2.18) PG 25918 LN 25: remove 'formation,'

[Resp]: Done

R2.19) PG 25920 LN1-5: Add actual BB estimates from Moffet and de Gouw.

[Resp]: We have added the BB estimates from the two papers to read:

"Moffet et al. (2008a) report a ~40% contribution of particles containing K to the particle number concentration at the upper end of the accumulation mode at T0. de Gouw et al. (2009) report that the BB impact at the suburban site T1 was not dominant (6-38% of organic carbon, with most days below 20%) and perhaps not dissimilar from previous observations from the same group in the Northeast US."

R2.20) PG 25920 LN5-7: Crouse et. al., estimate 52% OA from BB column average over the smallest box considered for column average, with ~2x greater contribution at 4km (pressure alt) than at surface. This is not exactly what is stated here.

[Resp]: the large majority of the measurements of Crouse et al. were at altitude and not at the surface, and they dominate their estimate of 52%. As shown in Fig. A4 of that paper, the impact at the surface is estimated to be about 1/2 of that aloft. Given the uncertainties in these estimates, we believe that the text in the ACPD version of our paper provides an appropriate summary of the findings of that study.

R2.21) PG 25920 LN24: The bomb radiocarbon correction of +24% for wood does

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not appear to match the number given in Szidat 2009 ( $f_{m,wood} = 1.16$ ). Also, some additional discussion about the assumptions made regarding the age of the trees near Mexico City should be given.

[Resp]: This value is variable depending on the age of the wood. However we have changed the text to 16% for consistency with the cited reference. We have also updated the 14C analyses using +16% instead of +24% which led to small changes (a few percent) in all derived quantities.

R2.22) PG 25932 LN19-24: This statement is imprecise. If levoglucosan is degraded by photooxidation it should decay continuously with a relatively constant rate (with some dependence on dilution of course if the oxidation occurs in the gas phase) until it is gone. Suggest instead the alternative explanation of DeCarlo, et al, 2010) that lev-eq.-mass is a measure of an array of different compounds as opposed to only levoglucosan.

[Resp]: The fact that levog.-eq. mass is much larger than levoglucosan was first reported in Aiken et al. (2009) for this same Mexico City dataset, the Part 1 paper of this series, and not by DeCarlo et al. (2010). This result has recently been confirmed by Lee et al. (submitted, 2010) using data from the FLAME-2 experiment.

Similar to what has been observed in other heterogeneous reactions with mixed particles, levoglucosan or levog.-eq. mass do not appear to decay with a relatively constant rate. Rather, current results suggest a rapid initial decay as the species available to gas-phase radicals are depleted, while the species which may be protected from reaction in the inside of the particle do not react away. See Katrib et al. (J. Phys. Chem. 109, 10910-10919, 2005) for discussion of the possible physical basis of this effect.

R2.23) Section 3.4: This section is not kind to the reader as it is difficult to read and hard to understand. Suggest reworking this more clearly stating the salient points as well as the uncertainties.

[Resp]: We have revised this section, in part by breaking the text into more paragraphs

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with a clearer structure, as also discussed in response to comment R2.10.

R2.24) PG 25940 LN 10-12: what is the precision/accuracy of these measurements? The sampling overlap is not an issue because a direct comparison can (and should) be done (comment 8) for filter collection periods.

[Resp]: This comment has already been addressed in response to comments R2.8 and R2.9.

R2.25) PG 25944 LN 1-5: This is possible. The possibility that BBOA/levoglucosan changes with age should also be stated. Note this change would likely be much more dramatic than the AMS lev-eq-mass change with age, as CMB levoglucosan measurement likely is only levoglucosan, where as other compounds likely contribute to AMS lev-eq-mass.

[Resp]: The first possibility has been added to the paper with the following text:

"This comparison suggests that the ratio used by Stone et al. (2008) may be too low either due to lower source emissions, evaporation, or possibly atmospheric reaction, resulting in an underestimation of the primary BBOA by CMB-OMM."

We suspect that the first two possibilities are more likely than the 3rd, as the majority of the impacts of BBOA at T0 are in the early morning and the smoke has not been photochemically processed at that point.

As discussed in response to point R2.22 above, indeed levog.-eq. mass represents many more species than levoglucosan alone. However the reviewer seems to be assuming that somehow levoglucosan should be more reactive than the other species which produce m/z 60. We are not aware of any evidence to support that point, and it is entirely possible that the reactivity of levoglucosan in the atmosphere is similar or lower than that of other species comprising the levog.-eq. OA mass. In fact the unusually high m/z 60 ion likely arises from a similar molecular subunit with the same chemical functionality in the different species. Thus to a first approximation we would

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assume that the atmospheric reactivity of the other species producing  $m/z$  60 is similar to that of levoglucosan. The results from Hennigan et al. (2009) appear to support this assumption.

R2.26) PG 25944 LN 11: what is referred to with 'PM2.5 sample'?

[Resp]: his text has been changed to "the PM2.5 CMB sample" for clarity.

R2.27) PG 25945 LN 14-15: Qualify this statement with '7-9% of the fine PM at T0. . . .

[Resp]: we have inserted "at T0" in this sentence as suggested by the reviewer.

R2.28) PG 25947 LN 11-12: Text here states 100pptv CH<sub>3</sub>CN background was used in Table 2, while Table 2 caption states 150pptv.

[Resp]: 100 pptv was used in Table 2. Thank you for noticing the error.

R2.29) PG 25950 LN 7: 'g' missing in 'ug am<sup>±</sup>3' units, two places.

[Resp]: Fixed.

R2.30) Table 2: Add values from Yokelson, et al, 2007 to this Table (dHCN/dCO and dPM1/dCO). Add values from Yokelson, et al 2009, (dCH<sub>3</sub>CN/dCO and dHCN/dCO). Add values for 'urban' dCH<sub>3</sub>CN/dCO from Crouse, et al, 2009 and de Gouw et al, 2006.

[Resp]: Done

R2.31) Figure 1: It would be useful if GOES fire count timeline was also shown. Does it make sense to average two days of MODIS counts in comparison with one day of BBOA? What is the mean transport time in the MC region relative to the 60 km circle?

[Resp]: The GOES time series has been added to Figure S1.

The two-day average accounts for the smoldering emissions from the fires detected by MODIS on the previous day. These emissions affect T0 in the early morning of the next day, as discussed in the paper. Thus this assumption is consistent with the transport

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time within the 60 km circle, which is of the order of half a day.

R2.32) Figure 14C(left): A ranges of dBBOA/dCH<sub>3</sub>CN are given in Table 2, but only a single value is listed in Fig. 14C(left) clarification as to what the ranges listed in Table 2 correspond to and which values were used to produce Fig14C is needed. (eg the ratio central values of dBBOA/dCH<sub>3</sub>CN from 'Crouse, et al' and 'this study' (~2.3) is very different from that shown in Fig 14C (~5).

[Resp]: We have added the following text to the caption of Fig. 14 to clarify this point: "The BBOA/delta CH<sub>3</sub>CN values (ug am-3 ppbv-1) used are as follows: This study (6.0), Knighton (3.4), Crouse (37)."

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