

***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.***

**Anonymous Referee #2**

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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) 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

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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:

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.

#### Specific comments:

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.

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.

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,

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but LEM does not appear to begin to increase until  $\sim 00:00$ hrs. FIF, again in both cases has reached its maximum by  $\sim 23:00$ hrs, 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.

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.

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.

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 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.

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. 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

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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 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. 9) The 14C-bbnf enhancement during the fire period is small (5x smaller than AMS-BBOA, even through 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.

Technical corrections:

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.

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

PG 25917 LN 5: Define 'OA'

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

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

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

PG 25918 LN9: Define 'fine' submicron?

PG 25918 LN12-17: These sentences are out of place. Either remove from abstract,

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or insert as a new paragraph above current LN8.

PG 25918 LN 25: remove 'formation,'

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

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

PG 25920 LN24: The bomb radiocarbon correction of +24% for wood does not appear to match the number given in Szidat 2009 (fm,wood= 1.16). Also, some additional discussion about the assumptions made regarding the age of the trees near Mexico City should be given.

PG 25932 LN19-24: This statement is imprecise. If levoglucosan is degraded by photo-oxidation 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. 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.

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.

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.

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

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

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.

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

Table 2: Add values from Yokelson, et al, 2007 to this Table (dHCN/dCO and dPM<sub>1</sub>/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.

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?

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).

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 25915, 2009.

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