Response to the comments of Referee #1

We thank the referee for his/her thorough and constructive comments which help to improve the quality of this article. We have made corresponding revisions throughout the text, not limited to the responses below (particularly for tedious and trivial edits and wording). Here we put together our responses.

[COMMENTS] Calculations using WRF-CHEM are used to determine the perturbations to ozone, POA, SOA, TOA, and BC due to open fires, trash burning, and, in less detail, biofuel use over different spatial domains and time periods. Of particular importance are the ground sites with AMS measurements; T0 having data that covered both simulated episodes, and T1 having data for one episode. The general conclusions are that fires are important, more so for open burning than trash burning and more so for POA than SOA. The fraction of organic aerosol contributed by fires is significantly higher than the fraction contribution to EC.

As the authors acknowledge, results are highly dependent on emission rates. A major concern that I have with the calculations is the justification for an alternative diurnal profile for emissions. The alternative profile is meant to provide a better description of nighttime emissions from smoldering fires. Fire counts are from Modis, which is daytime only. However, the default diurnal cycle is from GOES. Is the implication that the default diurnal cycle is in general, incorrect. Or are nighttime smoldering fires being put into the model to simulate features particular to this time and place where there is observational evidence for such fires. Going one step further, is the observational evidence from visual reports, measured trace gas excursions, or aerosol observations. Fig. 6, shows that the adjusted emission profile makes a large difference on a few days, generally to bring observations and calculations into better agreement. It is difficult to see from the Figure what the integrated effect is.

If the effect of overnight smoldering emissions is due to high concentrations trapped under a low boundary layer, there should be evidence in terms of diurnal cycles. A comparison of simulated and observed diurnal cycles should be provided.

A gauge of whether the emission time dependence is reasonable is part of a larger concern that I have. This is a complicated calculation. Results seem reasonable. But what have I learned, that is not contained in previous studies? Certainly different regions and categories of burning are being considered here. What about processes? Has a convincing argument been made concerning the importance of overnight smoldering emissions? What is the SOA/POA ratio in biomass burning aerosol? This result can be obtained from percent changes in POA, SOA, and TOA (mentioned below). Does the above ratio vary with location? How does this ratio depend on the models chemical mechanism and VOCs that are co-emitted in fires? Are the ratios calculated at varying locations a strong function of plume age?

I believe that additional material on some of the “why” questions (which don’t have to be the ones mentioned above) are needed in this manuscript.

[RESPONSE]: The diurnal profile is indeed a topic in the biomass burning emissions. The fact is that there are an infinite number of possible diurnal profiles and the real diurnal profile is not only unknown, but likely varies from day to day and from fire to fire. We tried a reasonable number of options and ultimately implemented the one that performed best (*profile_2*) in this study. This alternative profile is similar to the one used by Aiken et al. (2010), which was obtained by limiting fires to higher GOES quality data assurance and yielded a better model – measurement agreement for the fire signals during the entire March 2006. The fire onset time in the alternative profile also coincidentally agreed well with aircraft observations in Mexico (Yokelson et al., 2007). This does not imply that we have identified the real profile as explained above. However, our findings do imply that smoldering in the evening may contribute significantly to ground-level impacts in the MCMA. Corresponding statements have been added in the revised paper.

As for the simulation improvement using the alternative profile, we have added a column of statistics in Table 3 for the simulation using the default BB emissions, hoping this can assist for the comparison. We have initially thought of including in the manuscript an episode-averaged diurnal cycle of the BBPOA concentration. However, we found that due to the huge day-to-day variation of the BB signals in the AMS-PMF data in both the magnitude and temporal variability, it did not make sense to have such an averaged diurnal cycle. A larger data sample size over a longer time period could make the averaging physically sound.

To investigate how the POA and SOA evolves in the MCMA outflow, we have included a table (Table 4) to the paper, and following statements have been added: "*Table 4 summarizes the model performance on the OA simulation in term of the POA/TOA ratio at T0 and T1 during the two episodes (the SOA/TOA ratio is not listed, since SOA/TOA = 1 - POA/TOA). It shows that with the BB influence considered, the partition of POA and SOA is well simulated, with SOA being overestimated. It also shows that, from both measurements and simulations, SOA accounts for about 50% of TOA at T0, and increases to 60% at T1, indicating the chemical aging process during the urban plume outflow process. Comparisons of the simulated POA/TOA ratios with and without BB emissions suggest that the major contribution of BB to OA is POA, which is more evident at T1 (the POA/TOA ratio increasing from 0.23 to 0.38), implying that T1 is affected more by BB primary emissions than the aging process in the fire plume.*"

We have added more discussions on the uncertainties and likely underestimations of BB emissions in the article (see our response to Referee #2).

[COMMENTS] GENERAL QUESTIONS Model results are generally presented as the contribution of a source category (such as biomass burning = open flames + trash burning) to POA, SOA, TOA, and EC, for different time periods and locations. The percent changes in POA, SOA, and TOA combined with the definition of TOA (=POA+SOA) are readily manipulated to give the ratios POA/TOA and SOA/TOA before and after biomass burning emissions have been added to a base case simulation. The relative proportions of POA and SOA are important because they give the reader a sense of the amount of photochemical processing and they provide an additional number that can be compared with observations as seen through the lens of PMF analysis. The paper, as written contains many percent contributions, to the point of confusion for me (but perhaps not for other readers), so I am suggesting that POA/TOA and SOA/TOA be presented only for a subset of the data.

[RESPONSE]: We have included a table (Table 4) to address this topic (see the response above). In addition, the original Tables 4and 5 have been transformed to plots (Figs. 10 and 11) and relevant sentences have been reworded to minimize the confusion.

[COMMENTS] Are ug/m3 at ambient T and P or at STP?

[RESPONSE]: The concentrations expressed at the ambient T and P, which is clarified in the text.

[Ordered list of questions and comments]
Abstract: It is difficult to follow the presentation of percent contributions. I am not sure if MCMA and MCMA plus surrounding areas are being used interchangeably. Rather than cite a string of 4 components and 4 percentages and tie them together with "respectively", I recommend something like this: open fires plus trash burning increase POA by 60%, SOA by 22%, TOA by 33%, and EC by 22%.

The summary section also has multiple lists of percentages in four categories. I recommend a summary Table, without repeating all of the numbers in the text.

It is not obvious that the statement on line 15-16 that SOA formation increased OA by about 10% from open fires and 5% from trash burning is consistent with the values given above. (I did the math, and they are). I would tie these statements together by e.g. Of the 22% increase in SOA (equivalent to a 15% increase in TOA) predicted for biomass and trash burning about 2/3 is from biomass and 1/3 from trash.

[RESPONSE]: For clarity and conciseness, we have reworded relevant sentences and converted the original Tables 4 and 5 to plots (Figs. 10 and 11).

[COMMENTS] page 22896 lines 21-23. Abbreviation TB This is perhaps, obvious. The first sentence uses the term trash burning and the second sentence uses the abbreviation TB. The first sentence should read "trash burning (TB)"

[RESPONSE]: Proper abbreviations are made for TB and others.

[COMMENTS] page 22896 line 22-23. impact of TB on PM2.5 and chloride will be addressed in a companion paper. In the abstract and immediately previous to this sentence you state that this paper covers TB. For clarity, I recommend modifying line 22-23, e.g. Additional analysis of TB impacts on PM2.5 and chloride are presented in a companion paper.

[RESPONSE]: Modified.

[COMMENTS] page 22896, line 26, regarding biofuel. My personal preference would be to replace "we will attempt to provide a first-order" by "we only attempt a first-order"

[RESPONSE]: Modified.

[COMMENTS] Page 22899 line 17 – 24. Do I have this correct? The model contains material not in "conventional calculations" equal to 3.5 times POA not corrected for dilution (additional SVOCs = 2 times conventional POA and co-emitted IVOCs = 1.5 times conventional POA)? The total amount of material (POA+SVOC+IVOC) is 7.5 times POA emissions not corrected for dilution. What is the relation between POA emissions in your calculations and what I am calling "conventional" POA? Some part of the difference between 7.5 and 3.5 is emitted POA in your model. What is the other part? Would that other part also be in a model that did not take into account additional low volatility VOCs? These emissions make a major difference in SOA predictions and it is important for the reader to qualitatively know what they are, without reading cited papers.

[RESPONSE]: Considering the semivolatile property of POA, POA in term of emissions is the "conventional" POA (c-POA) in your definition, e.g. POA = particle-phase POA (p-POA) + SVOCs, and SVOCs = 2 p- POA. IVOCs are 1.5 times of c-POA, which is 4.5 times of p-POA. Therefore the total emissions (p-POA + SVOC +IVOC) = 7.5 p-POA. We have clarified in the text. The emission number for POA in Table 2 is for p-POA.

[COMMENTS] page 22900 line 13 – 15 regarding alternate emission profile Would it be just as likely for GOES to miss a smoldering fire during the daytime as in the nighttime?

[RESPONSE]: We believe that GOES is more likely to fail to detect nighttime smoldering fires due to lower temperature and higher humidity at night. In addition, it is relatively more frequent for smoldering fires to occur at night than during the day.

[COMMENTS] Page 22901 Section 2.2.3 Trash burning First paragraph is about trash burning. Later paragraphs fold in material on other sources.

[RESPONSE]: The structure of the manuscript has been revised by adding a new section (Section 2.2.4) which summarizes the emissions from different sources and discusses the emission uncertainties and their potential effects in modeling interpretation.

[COMMENTS] page 22902 line 18. 35% uncertainty Unclear whether this refers to PMF method alone or includes accuracy of AMS measurement. My opinion is that 35% is about right for the uncertainty of the measurement. Others may be more optimistic. A reference would shift the blame.

[RESPONSE]: References have been included (Bahreini et al.; Ulbrich et al., 2009).

[COMMENTS] page 22906 line 16 – 18 Lack of correlation between T0 and T1. Image plots show a time lag between polluted air hitting T0 and T1.

[RESPONSE]: A sentence about the time lag has been included.

[COMMENTS] page 22906 line 18 "due to that the" needs rewording.

[RESPONSE]: It has been modified to "due to the fact that…".

[COMMENTS] Page 22907 line 12 "No comparisons at T1 are presented in this study ... limited availability of AMS OA measurements" There is one episode at T1, one third of the AMS data set. This is a lot of data to throw away. Some of it is shown for other purposes.

[RESPONSE]: For the version of AMS-PMF data we had, we did not find any data at T1 before March 14. EC data was from a different source.

[COMMENTS] Page 22907 line 19 – 24 OH recycling, semi-volatile VOCs did not consume OH I don't understand. OH + VOCs don't usually consume OH, but instead are part of a chain reaction. How does the chemistry of intermediate and semi-volatile VOCs differ from other mechanisms.

[RESPONSE]: We believe to date it is unknown what are the oxidation mechanisms for SVOCs and IVOCs. We assume they are analog to the VOC oxidation process in term of OH recycling. We have modified the statements.

[COMMENTS] Page 22908 line 26 – page 22909 line 2 I don't understand how model underestimation of EC at T1 probably contributes to this result.

[RESPONSE]: The underestimate is due to the underestimation in EC emissions. We have modified the sentence: "*…the model underestimation of EC emissions from sources other than the open fires near T1 probably contributes to this result."*

[COMMENTS] Page 22910 line 8 typo replace conductive with convective.

[RESPONSE]: Done

[COMMENTS] Page 22910 line 27 typo replace Table 3 with Table 5a.

[RESPONSE]: Table 5 has been replaced by Fig 11, and text has been modified accordingly.

[COMMENTS] Page 22912 line 12 TB has smaller influence on regional scale Where there TB emission in calculation outside of MCMA. In MCMA they were proportional to population and a few other variables.

[RESPONSE]: Thanks for bring up this information. In fact there were no TB emission estimates outside the MCMA, so the "regional" effect of TB is really not an accurate description. We have made clarifications in the text.t

[COMMENTS] Page 22913 line 2 "PEC emissions" New abbreviation
Page 22915, line 25 typo emissions to another, should be emissions as another

[RESPONSE]: Both are corrected.

[COMMENTS] Page 22917 lines 23-27. There is general agreement between model and observed BBSOA at T0 and T1. Does biofuel SOA get classified with PMF along with SOA from open flames and TB? If so, does this imply that biofuel SOA is small, or that it is within uncertainty of calculation?

[RESPONSE]: To our understanding, AMS-PMF does not separate BBSOA from OOA. We would appreciate if there are AMS-PMF BBSOA data available for further comparisons.

[COMMENTS] Table 1 What are ranges for % contribution?

[RESPONSE]: We tried to obtain the ranges for every study listed, but we can not fabricate a range when the study did not provide the range.

[COMMENTS] Table 4 For those looking for red and green traces in ozone figures, it would be useful to mention that they are so close that red hides green.

[RESPONSE]: You probably meant Fig. 4. Explanations have been added in the figure caption.