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Interactive comment on “Emissions from biomass burning in the Yucatan” *by* R. Yokelson et al.

R. Yokelson et al.

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Response to comments by Referee #2 on “Emissions from biomass burning in the Yucatan.”

By R. Yokelson and co-authors.

We thank Referee #2 for the comments and they will improve the paper. We describe our general response to the comments of Referee #2 now and will propose specific changes after obtaining additional comments from Referee #1.

In the following text “**R.**” indicates Referee, “**A.**” indicates authors response.

R1. This paper presents a detailed and thorough analysis of emissions of a wide range of trace gas and particulates from fires in the Yucatan peninsula region of Mexico during the MILAGRO study. The study presents a detailed analysis of the emission ratios of a wider range of species than had previously been measured and also provides valuable

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additional information on emissions of previously measured species. An analysis of the development of several trace gases and aerosol components in the plume of a fire as it advects away from the source is discussed. Changes in chemistry and composition are observed, though the changes appear rapid and non linear this not appear to be recognised in the text and the impression is given that changes occur throughout the age of the plume. I see no evidence that this is the case. Regional emission estimates are made and compared with emissions from other major sources in the region. This is a very valuable paper and should certainly be published as it contains a wealth of information. I do, however, have some comments that I would like the authors to address before the paper is accepted for ACP. The AMS Collection efficiency has not been stated nor have the assumptions on which it is based. It would be useful to incorporate details of the formation processes of the species for which emission ratios are discussed where they are known and highlight where they are not rather than just discussing the ratios. This is done for some species but not for all. This will give the reader an understanding of the co-variability and changes in emission ratios that are likely as fuel type and burn condition vary. To what extent is it useful to report emission factors of species that are produced as secondary products via photochemistry in the plume? For example, H2O2 and H2SO4 EF are reported, are the authors suggesting that these are emitted by the fire or formed in the plume? If the latter then what is the value of an EF? I see little evidence for the validity of trend lines and regressions for many of the changes in concentration ratios shown (in particular HCOOH/CO, fig 7a; PM2.5/CO, fig 9a; aerosol component/CO except for possibly NO3/CO, fig 10). Clearly there are marked changes between the measurements made at the point of emission and those in the advected plume and these changes are clearly important. However, thereafter there is much scatter in the data and as far as one can see there is a lack of observable trend in most of the plots. The trend line has been forced by fixing the line at the intercept based on the increased number of observations in the near field of the fire. It is important to recognise that more reliance can be placed on these data (I suggest the variance in the measurement is also shown, see below). I do not see how a trend line can usefully be applied as it implies that the changes are continuously occurring on the timescale of a few hours. One could equally argue that rapid changes take place over the first 15 minutes in many of these ratios but thereafter there is no sign of any further significant changes. The authors comment that OH measurements are a factor of 5-20 times greater in the near field plume than the background but thereafter fall to a factor 2. This supports the hypothesis above that the changes are distinctly nonlinear. The TEM analyses also shows that very significant changes are taking place on time scales of less than 30 minutes. A discussion to reflect this would be useful as it also possibly goes some way to explain other data on regional biomass burning, for example Capes et al. Certainly the data indicate that further work is necessary in this area to understand the apparent non-linearities in the near-field and the authors are right to point this out. The authors comment that there is marked fire to fire variability and that comparing near and far field measurements of different fires can be misleading. This is done by Capes et al., 2008 in west Africa. In the Capes et al paper many different fires are sampled from close to fire sources to several hundred kilometres from the sources. The striking thing about these results is that the ratio of particulate organic matter to CO shows very little variability over such a wide range of space scales. If the fire to fire variability shown in this paper is as large as the authors here suggest then it would be very difficult to se how a relationship such as that observed by Capes et al could ever be observed. It would be good to see a plot of organic mass to CO for the fire impacted air masses across the whole region in a similar way. This would identify whether there was intristically more variability in the Yucatan fires or whether the differences between fires average out between the fires. Capes et al state that many small fires were present across the region and it is possible that the variability between fires was averaged out.

A1. We note that the bulk of the Referee's comments are concerned with the aging of the Fire #3 plume discussed in section 3.4 and so we address those comments as a group first. An important fundamental thing about the aging plume discussed in section 3.4 is that the aging sequence shown is not a Lagrangian sequence, i.e. it is not documenting progressive changes in a single parcel of air as is explained in the paper. The sequence shown is rather consecutively sampled smoke of increasing age that was produced from initial emissions that varied somewhat at the source. This is a complex data set. Due to changes in the initial emissions, changes in the OH concentration, and changes in the UV intensity as more or less concentrated parts of the plume are accessed by the aircraft, there is not a theoretically sound underlying functional form for the chemical changes observed. In addition, the measurements are intermittent in most cases with different instruments having different frequencies and duty cycles. In particular, the concept of linearity was not rooted in the expected chemistry in this context. We chose the linear fit only as a simple test of whether the entire data set from each instrument suggests that the values at the end of the aging sequence are significantly different from those at the beginning. This specific test is important because we show strong evidence that the initial emissions were likely very similar for the samples probed at the beginning and the end of the sequence. The linear analysis establishes that the values are statistically different within the 95% confidence interval. The significant differences are then clearly important evidence for a net change due mostly to photochemistry. We will summarize this discussion in the revised text with an additional sentence at the point where the fit is introduced. In addition error bars will be added to points on the plots.

On the other hand, we disagree with the statement that there is no evidence that changes occur throughout the aging sequence. That's the whole point of the linear fit, statistically, the average values are quite different for smoke that aged $\sim$1.4 hours. We actually don't have information on the intermediate chemistry for the aged parcels and the non-linear appearance for some graphs could be real or illusory and due to a change in the initial emissions. However, tellingly, a brief glance at the figures confirms that the highest values occur at the end of the sequence for most species. The line also tends to split any scatter present at the end of the sequence. Further, "continued changes" are obvious for ozone, peroxide, PAN, peroxyacetic acid, sulfate, nitrate, and organic aerosol. Also, the potentially more-aged, high level haze layers sampled and

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described in section 3.5 exhibited an even further continuation of the trends started in the Fire #3 plume in most cases. In particular, the ΔOA/ΔCO ratio of 0.17 in the highest aged smoke layer certainly suggests that particle growth may continue at longer time scales. Finally, a reactive mixture subjected to intense tropical sunlight is expected to evolve until it is removed from the atmosphere based on current understanding of general atmospheric chemistry. For instance, with currently accepted values for rates of NO_x oxidation, the chemistry cannot be competed within several hours. Methanol has a lifetime of several days, etc. Thus, no underlying kinetic argument suggests to us that the smoke evolution would be completed during the first half or so of the sequence shown. While, the OH decreased from very high to still well above background, it did not go to zero! The UV levels were actually higher in the aged/diluted plume then nearer the source. Since a factor of 6-10 secondary organic aerosol formation in fossil fuel plumes is now widely accepted, it would be a reasonable first order expectation that a reactive mix of BB emissions might evolve in a similar fashion under similar conditions.

The Capes et al citation will be included in the reference list.

The AMS collection efficiency (the standard value of 0.5) and the justification for it are included in the reference already provided (DeCarlo et al., 2008).

While it is possible that small amounts of H_2O_2 and H_2SO_4 are produced at the source of a fire, it is also possible that these species arose from fast chemistry occurring during the time the plume rose to the altitude of the first samples. We did address this partially for H_2O_2 by mentioning that there was not an obvious altitude dependence in the “enhancement ratio to CO for this species. However, as the Referee points out this point needs to be made more strongly for H_2O_2 and explicitly for H_2SO_4. This will be done in the revised text.

We are unclear what the Referee means by the “advected” plume. The plume was rising during the measurement sequence. The “apparent” faster “initial change” is likely

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due to mostly to an increased smoldering/flaming ratio at the source when those samples were initially emitted as already described in detail in the text

Adding more details on the formation processes in the plume would normally be an excellent suggestion, but since the paper is already very long we prefer not to commit to lengthening the paper, especially before the other referee comments.

The changes observed by TEM and airborne FTIR analysis were on a different fire and for which the total aging time is approximately equivalent to the beginning of the Fire #3 aging sequence. Not only was the fire different, but we have less ability to probe the possibility that the initial emissions were changing. So those results do support the concept that faster near-field changes are possible, but not the concept that continued changes are unlikely.

There is not enough information in the Capes et al paper regarding the number of plumes sampled or the age of the smoke sampled for us to speculate on how their result could have occurred. Given the high variability in initial emissions they could have happened to sample fresh plumes with high OA/CO values on average and aged plumes that originally had low OA/CO values on average. This could happen if fire characteristics were modified by a rainfall event or just based on time of day. An example of how fire-to-fire variability can lead to conflicting interpretations can be seen in Lefer et al., (1994). Their figure 5 shows the ΔHCOOH/ΔCO for 3 fresh and 2 aged plumes. The variability in the ratios for the fresh plumes is about a factor of two and the variability in the aged plumes is about a factor 3. Clearly, one can envision choosing a subset of the Lefer et al data that could imply either downwind production or loss. Further, the OA/CO ratios obtained in any study depend critically on how the CO background values are selected and we have no information on how those values were selected by Capes et al. There are other plausible explanations for why the Capes et al results differ from ours. One is that the evolution of plumes may vary from fire to fire. Another more subtle reason is as follows. The Sahel features active biomass burning over an ~2500 km E-W distance. The “fresh” smoke samples of Capes et al were obtained in the middle of this region. Those emissions may have been injected into a regional boundary layer composed largely of aged smoke from fires at some distance upwind. In our study, to avoid complications due to dilution by aged regional smoke, the fresh samples had CO concentrations as high as 30 ppm. In the Capes et al study, the "fresh" samples had CO concentrations below 1 ppm. Thus it is feasible that the "fresh" samples of Capes et al had already been partially diluted with aged regional smoke and acquired some of its characteristics. Another possibility is that Capes et al. sampled layers of enhanced CO that were actually aged smoke that was concentrated just below the temporary stable layers that form in Africa below the top of the BL usually before noon. With no firsthand knowledge of their study, these ideas are simply discussion points and not intended as criticisms of the other study.

R2. Page 771, Line 19: The authors state that only a few observations of the chemical evolution of BB smoke have been made. It is also worth citing the measurements of Abel et al., who investigated changes in aerosol properties downwind of fires in southern Africa and Capes et al., who discuss aerosol evolution over the West African Sahel (Capes et al., 2008) at this point.

A2. We will clarify in this sentence that there are only a few studies of the evolution of *individual isolated* BB plumes. The Abel et al. (2003) study did measure an increase in the single scattering albedo within a single aging plume that they attributed to secondary aerosol formation that continued for approximately 5 hours (in good agreement with our discussion above). This is somewhat similar to our finding and will be noted in our section 3.4. The reference will be added to the citations.

R3. Page 773, Lines 9-11: The authors state that - The nephelometer was not available on the 12 March flight so we used the UHSAS particle counting/size data to indirectly determine particle mass. The UHSAS does provide an indirect measure of particle mass but it is hard to see how the assumptions are any more uncertain than those involved in determining mass from the nephelometer, a methodology that also relies on assumptions about the invariance of optical properties and shape.

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A3. The Referee is correct that the UHSAS is not inherently less accurate than the nephelometer. However in our study, the nephelometer was calibrated versus gravimetric data in the lab as explained in the text. Later, a correlation between the UHSAS PV_1 and the nephelometer scattering was noted. In this work the UHSAS data and the equation given were used to infer a scattering value and then subsequently calculate a particle mass. Thus, specifically in this study, the UHSAS-based determination is less direct as it is based on the product of two correlations (each with some uncertainty) rather than a single correlation.

R4. Page (P), 776, Line (L) 9: reflect the degree - should be reflects

A4. Changed, thanks.

R5. P783, L9: Andrea should be Andreae

A5. fixed! Thanks.

R6. P786: What are the implications of using acetonitrile as a tracer for BB if the emission ratios are indeed varying by more than a factor of 2.

A6. The uncertainty in the $\Delta CH_3CN/\Delta CO$ ratio for Brazil was about 27% implying at least that much uncertainty in a source apportionment based on this molecule in this region. For the Yucatan fires the uncertainty was not determined.

R7. P786: The emission ratios of HCN from the two aircraft are a factor of 3 different yet the variability within the fires sampled by each aircraft is much less than this difference. Both estimates are a factor of 2 different from that in Brazilian deforestation fires. What is the value in simply averaging two different estimates to get a result closer to that of the Brazilian fires? Are the data from the Twin Otter different for DF and CR fires? What might explain these differences especially as the suggestion from the particulate data is that the two aircraft sampled a similar mix of fires (pg 787 line 16)?

A7. The Twin Otter and C-130 HCN/CO ratios were averaged together simply because that was the simplest way to include all valid measurements, from what were essentially

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two independent studies. The averaging scheme does not impact the results. In fact, weighting each fire equally from the Twin Otter and C-130 gives an ΔHCN/ΔCO ratio of 0.00575 +- 0.00525, which is even closer to the Brazil ratio. In revisiting this analysis, we did notice an error we will fix. The number of ΔHCN/ΔCO determinations for the Twin Otter was given in parentheses as 17. That was actually the total number of fires sampled by the Twin Otter, but the ΔHCN/ΔCO ratio was only measured on 7 of them. The other concerns are already addressed in Table 2 and further along on page 786.

R8. P786, L22-25: To what extent does the temperature of the fire impact on the NOx emission and does this account for some differences or mean that the N content must be considerably higher in the Yucatan than in Brazil?

A8. As background it is worth pointing out a few things. (1) There is actually no such thing as a “fire temperature” although the term is sometimes loosely used in the remote sensing literature to indicate the approximate midpoint of a large range of temperature fields and flaming/smoldering combinations that might characterize a 1 km pixel that would emit the same amount of 4 micron radiation as is measured from said pixel. (2) There is such a thing as a flame temperature. Flame temperatures for all types of fires peak around 1100 C, which is too low to promote thermal NO_x. Thus, we think the differences in NO_x emissions are likely rooted in fuel nitrogen.

R9. P789, L20: This is not true if cloud is present as is the case on several flights. Is the sulfuric acid EF consistent with this finding?

A9. We are discussing the initial emissions at this point and they were not cloud-processed.

R10. P789 and P790: The discussion of organic mass emissions should include the study of Capes et al in the west African Sahel who also used AMS measurements to derive OC:CO. The numbers presented appear to be largely consistent with their estimates though the west African emission ratios appear a little higher.

A10. To keep the paper to a reasonable length, we limited the discussion of BB OM emissions to emissions from tropical forest fires. There are a large number of savanna fire measurements that could be discussed, but it would greatly lengthen the paper.

R11. P794, L25: which of the points are cloud impacted?

A11. The cloud-processed points are given as 1.27-1.47 h on line 6 of page 781.

R12. P794-5: The intercept in some of the regressions (figures 5, 7, 9 and 10) are forced to zero on the grounds that the near field was sampled multiple times and so the authors place greater emphasis on the representative nature of the average of the near field samples than the points obtained in the ageing plume. This is a reasonable thing to do as long as the trends appear linear but is not always the case. Moreover, it would be good to see the variability of the source data possibly expressed using an uncertainty bar that reflects the variation in measurements at source. This would give some idea of the overall variability of the fire at source and allow the reader to interpret the trend data more easily.

A12. The value at the intercept is far better known than at the downwind points and this will be indicated in the revised figure as noted above in the general comments section.

R13. P795, L11-14: The authors state that - The NEMR reached in 1.4 h is as large as the NEMR observed in smoke from Canada that was 8 days old during NEAQS (F. Flocke private communication). This demonstrates the large variability in both initial emissions and photochemical rates that are associated with BB plumes. In what way do near and far field observations demonstrate that there is wide variability from one region to the other. Many of the plumes seen from biomass burning fires from Canada observed during ICARTT and related studies show that there is a marked lack of photochemical processing of fire plumes after long range transport. Could the NEMR have been generated rapidly but then remained unchanged during transport?

A13. We will clarify that the large variability in PAN/CO demonstrates possible variabil-

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ity in either the initial conditions or the processing or both.

R14. P797, L17-26: This discussion is somewhat convoluted and also illustrates my concerns over using trend lines and regressions on this type of data. The authors compare the BC/CO at source and at the end to state that the burn conditions were similar but elsewhere have clearly shown that the burn conditions change in the middle period. Yes there is a change between the source and the most aged part of the plume but there are a number of different factors that affect the data in the middle portion making it difficult to conclude whether the changes are continuous or more rapid and mostly in the near field.

A14. Addressed above

R15. P800, L3-5: It is interesting to speculate why these differences might arise. The extremely high levels of OH in the near source plume in this study are indicative of very fast processing and have the potential for rapid processing to occur. One wonders whether the levels of pollution surrounding the fires studied have any influence as well as the conditions of the burn, for example the background NOx or VOC levels. No OH measurements are available in the BB plumes studied by Capes et al. but in the Sahel there are no other sources of pollution to influence photochemical oxidant levels appreciably. Clearly there are differences and it would be interesting to hear ideas about what these differences might be.

A15. It is interesting to speculate about this, but we prefer not to lengthen the paper at this point. Most likely both the Yucatan and Sahel had a boundary layer that was moderately polluted by regional haze from BB. We summarize this in the paper by agreeing with the Referee's earlier statement that this is a subject worthy of future research.

R16. P800, final paragraph: This discussion also appears to support a rather rapid initial processing of the plume.

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A16. The chloride results could indeed reflect some fast initial chemistry that is “finished” after 20 minutes. However, as noted above, various chemical processes occur on many different time scales so we can’t conclude that all the chemical changes are that rapid.

R17. P802, L10-18: The Capes et al analysis used a similar approach to probe the deltaOA/deltaCO relationship to that discussed here. However, as Capes et al point out, the region is impacted by many small and widely distributed fires and there may well be some averaging associated with such an analysis. Despite this the variability reported in this paper would have been seen in the Capes et al analysis as the approaches are similar. It is unclear at the present time why these differences are present; clearly an understanding of what drives such variability and the rapid changes in chemistry over short time is required as most regional and global models require inputs on spatial and time scales that are of the same order if not larger than the changes observed in this ageing study. This represents a significant challenge.

A17. The challenge for regional-global modeling is well-stated and important. However, we don’t think we can assume what would have been seen in the Capes et al paper as those were different fires, and a different study design, etc. . . .

R18. P807: It is not at all clear to me what section 4.3 adds to the already very long paper. I suggest removal of this section.

A18. Section 4.3 is brief and alerts the reader that much larger impacts can be expected in other NH regions. From a global modeling perspective, BB in Indochina is especially problematic and section 4.3 touches on that.

R19. P808, L5: There are several papers on BB in the Sahelian tropical region in Africa

Haywood et al (2008) and other papers in the same issue.

A19. As indicated above we prefer to confine the discussion to tropical forest fires because a discussion of savanna fires would dramatically increase the paper length.

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R20. P809: Capes et al does not appear in the reference list.

A20. First author error! Thanks! Fixed.

Reference:

Lefer, B. L., Talbot, R. W., Harriss, R. C., et al.: Enhancement of acidic gases in biomass burning impacted air masses over Canada, J. Geophys. Res., 99, 1721-1737, 1994.