**Atmospheric
Chemistry
and Physics
Discussions**

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

R. Yokelson et al.

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Final Response to Comments by Referees #1 and #2 on "Emissions from biomass burning in the Yucatan."

By R. Yokelson and co-authors.

Referee #1

"3 fires" has been changed to "three fires" throughout the text and tables. Significantly, Referee #1 has also endorsed the already-published general description of our plan to respond to the extensive comments of Referee #2. The logic behind our response to Referee #2 is found in the interactive discussion as AC S1892. The specific changes in response to condensed versions of Referee #2's comments follow next:

Referee #2

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First we thank Referee #2 for an expert and thorough review of our very long paper. The comments of Referee #2 are sometimes condensed here as they are published twice in full already. Our specific changes in response to those comments follow in full detail. The changes are in some cases based on the detailed arguments presented in ACS1892. In the following text "**R.**" indicates Referee, "**A.**" indicates authors response.

R1. The AMS Collection efficiency has not been stated nor have the assumptions on which it is based.

A1. 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).

R2. 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.

A2. Adding more details on the formation processes in the plume would normally be an excellent suggestion, but since we already need to add important HONO information (vide infra) and the paper is already very long we prefer not to lengthen section 3.4.

R3. 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, H_2O_2 and H_2SO_4 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?

A3. While it is possible that 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 a discernable altitude dependence in the "enhancement ratio to CO for this species with increased altitude." However, as the Referee points out

these issues could be discussed more explicitly for H_2O_2 and H_2SO_4 even though we did not actually report EF for H_2SO_4. This is done in the revised text as follows:

For peroxides: Page 785, lines 9-11

Old text:

"The presence of the peroxide species in the nascent smoke may reflect some fast initial photochemistry (e.g. recombination of peroxy radicals (RO_2, HO_2)), but there is no increase in the peroxide species with altitude in our samples."

New text:

"The presence of the peroxide species in the nascent smoke may partially reflect fast initial photochemistry (e.g. recombination of peroxy radicals (RO_2, HO_2)). There was no increase with altitude in the ratio of peroxide species to CO when comparing the freshest sample of each fire, but we cannot rule out a photochemical contribution to our reported initial emissions since even the freshest smoke (from Fire #2) could have been ~3-10 minutes old and photochemical production of H_2O_2 was observed in the aging plume from Fire #3 (Sect. 3.4)."

For H_2SO_4 and MSA: Page 785, lines 16-19

Old text:

"The NCAR SICIMS detected traces of H_2SO_4 ($\Delta H_2SO_4/\Delta CO$, 5.4×10^{-7} $\pm 5.2 \times 10^{-7}$) and MSA ($\Delta MSA/\Delta CO$ ~$8.4 \times 10^{-8} \pm 1.3 \times 10^{-7}$) in the young fire emissions also for the first time. The initial amount of these species varies greatly probably due to variations in fuel S and plume reactivity."

New text:

"The NCAR SICIMS detected traces of H_2SO_4 ($\Delta H_2SO_4/\Delta CO$, 5.4×10^{-7} $\pm 5.2 \times 10^{-7}$) and MSA ($\Delta MSA/\Delta CO$ ~$8.4 \times 10^{-8} \pm 1.3 \times 10^{-7}$) in the young fire emissions also for the first time. The initial amount of these species varies greatly potentially

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due to differences in fuel S and plume reactivity. To "normalize" for fuel S variation and highlight any altitude dependence, which could indicate fast initial chemistry, we computed the initial ratios of H_2SO_4 or MSA to SO_2. No trend was observed with altitude in these ratios, but due to the high variability and uncertain formation process we do not report initial emissions for these species in the Tables."

R4. I see little evidence for the validity of trend lines and regressions for many of the changes in concentration ratios shown.

A4.

This was discussed in detail in AC S1892. In response to this comment we have modified the text on page 793 lines 9-17 to clarify.

Old text:

"A rigorous error estimate is not possible for each of the above terms or the assumption of a similar windspeed before our sampling. Thus we point out obvious trends in the data and, in some cases, we fit a line to the data and compare the slope to the standard error in the slope to determine if there is a statistically significant trend. The fractional uncertainty in the rate of any process discussed is larger than the standard error divided by the slope due to the additional uncertainty in the sample ages. Probably all the samples have experienced more aging, or all the samples have experienced less aging, than estimated. The real uncertainty in the rate is probably about a factor of two."

The modified paragraph with the new text in context:

"A rigorous error estimate is not possible for each of the above terms or the assumption of a similar windspeed before our sampling. Thus we point out obvious trends in the data and, in some cases, we fit a line to the data and compare the slope to the standard error in the slope to determine if there is a statistically significant trend. The plume chemistry is not expected to be linear: the linear fit is employed as a simple test of

whether the values at the beginning and end of the aging sequence are significantly different from each other. Below, we show that the initial emissions were likely very similar for the samples probed at the beginning and the end of the sequence and so significant differences between these points are then evidence for a net change due mostly to photochemistry. The fractional uncertainty in the effective "rate" of any process that might be derived from the fit would be larger than the standard error divided by the slope due to the additional uncertainty in the sample ages. Probably all the samples have experienced more aging, or all the samples have experienced less aging, than estimated. The real uncertainty in the rate is probably about a factor of two."

In addition, error bars were added to the intercepts and representative points on the plots.

Further comment:

The trends shown with the linear fits are basically valid within the already shown 95% confidence interval as long as the following is true:

1. Instrument drift is negligible or any bias is relatively constant over the 2-3 minute sampling interval and errors are random.

2. If forcing the intercept to the measured initial value is valid, or if not, if the trend is evidenced without forcing the intercept.

It seems a safe assumption that condition 1 is met. To investigate condition 2 we can (a) compare the uncertainty in the initial vales to the uncertainty in the single downwind points and also (b) investigate if trends occur without forcing the intercept.

a) To compare the uncertainty in the initial values to the uncertainty in the single downwind points we proceed as follows. We use a generic error of 5% for the real time instruments (including CO) and take the error in the ratio of two real time integrals as SQRT($5^2 + 5^2$) or 7%. The average additional error due to using a multipoint slope

determination from the discrete instruments was 10.6% as shown in Table 3. So we compute an error in the intercept for slope based values from discrete measurements and CO of SQRT(7^2 + 10.6^2) or 13%. This is taken as the error in the intercept for Figures 5, 7a, and 7b. For Figure 9a (PM$_{2.5}$) we just take the error in the intercept as 25% assuming it is dominated by natural variation in the mass scattering efficiency. For Figure 10a-d we adopt the generic AMS calibration uncertainty of approximately 20% for the intercepts.

Next we probe the additional uncertainty due to acquiring single samples at points in the downwind plume. To do this we computed the difference between the ratio obtained from a multipoint slope determination and the ratio determined from a single point in the fresh plumes. The differences ranged from 1 to 597 percent, but averaged abut 36%. Taking 36% as the average additional uncertainty due to sampling only once, we use the same "sum of squares" formula used above to estimate total uncertainties for the single downwind points. In this way we obtain 38% uncertainty for single points in Figures 5, 7a, and 7b; 44% for single points in Figure 9a; and 41% for Figures 10a-d. Thus, the intercept values have 2-3 times less uncertainty than the single downwind points. This alone in our mind justifies forcing the intercept.

We also investigated whether trends are still seen if the intercept is not forced. In all cases a trend was still observed and the changes were normally small and/or well within our stated uncertainty and do not effect the scientific conclusions. Specifi-cally, by species the slopes are shown in parentheses first for the forced and then the "free" intercept: Ammonium (0.00402, 0.00337); Nitrate (0.0107, 0.00902); OA (0.0348, 0.031); Sulfate (0.0052, 0.0037); PM2.5 (0.0737, 0.0523); Hydrogen Perox-ide (0.0031, 0.0033); Peroxyacetic Acid (0.000468, 0.000546); Formic Acid (0.0033, 0.0019). All the changes are within our stated factor of two uncertainty in effective rates and furthermore, letting the intercept float gave initial values outside the range dictated by our measurement plus or minus the stated uncertainty for the intercept in several cases. Thus, we opt to retain the slopes based on forcing the intercept.

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R5. 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.

A5. We meant in this sentence that there are only a few studies of the evolution of *individual isolated* BB plumes and cited the most detailed paper, which cites the other papers. For the sake of completeness we have now added the citations to Abel et al who also measured the evolution of a single isolated plume and all the other such measurements we know of. In addition we now reference all the modeling attempts to replicate measured changes we know of.

Original sentence:

"Only a few observations of the chemical evolution of BB smoke have been made (Hobbs et al., 2003) and they are only partially reproduced by models (Trentmann et al., 2005)."

New sentence Page 771, Line 19:

"Only a few observations of the chemical evolution of individual BB plumes have been made (Goode et al., 2000; Yokelson et al., 2003; Jost et al., 2003; Hobbs et al., 2003; Abel et al., 2003) and the observed evolution is only partially reproduced by models (Tabazadeh et al., 2004; Trentmann et al., 2005; Mason et al., 2006; Alvarado and Prinn, 2009)."

We added Jost et al and Abel et al to the references.

In addition the Abel et al. (2003) study measured an increase in the single scattering albedo from 0.84 to 0.885 over a 2.4 hour aging period within a single aging plume that they attributed to secondary aerosol formation. Further, the regional smoke haze had an even higher SSA ($\sim$0.9), which they estimated would be attained by the smoke

they sampled after 5 hours of total aging. Their measured changes are relevant to our findings and are now mentioned in our section 3.4 as shown next:

Page 797, Lines 27-28

Original text:

"Also shown in Figure 9b is the increase in SSA as the mass fraction of BC decreases in the $PM_{2.5}$. Secondary formation of the individual non-absorbing constituents was quantified by the AMS as described next."

New text:

"Also shown in Figure 9b is the increase in SSA from ∼0.75 to ∼0.93 as the mass fraction of BC decreases in the $PM_{2.5}$. This is analogous to the increase in SSA from 0.84 to 0.885 measured by Abel et al. (2003) over ∼2.4 hours of aging in an African BB plume. In this work, we also quantified the secondary formation of the individual non-absorbing constituents using the AMS as described next."

Further relevant discussion. In southern Africa at the time of Abel et al.'s measurements, the regional background was mostly aged BB smoke. The meteorology of southern Africa is dominated by recirculation as opposed to fast ventilation. Thus, they were justified in extrapolating the SSA evolution rate they observed over 2.4 h to estimate the total aging time (∼5 hours) needed to achieve the regional aged smoke average. In our case, the SSA at ∼1.5-2 h in the Fire #3 plume (∼0.93) was analogously lower than the regional background value of ∼0.95-0.96. This is consistent with our claim that the smoke evolution is not likely to be all finished in the "near field." However, we are less confident that the Yucatan background values are influenced only by aged BB smoke as it entails a significantly smaller land mass affected by fires than southern Africa and the transport of BB smoke away from the area seems quite efficient (see our Fig. 12). Thus, we don't add a similar extrapolation to our paper, but we note the issue here.

R6. 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.

A6. 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.

R7. Page (P), 776, Line (L) 9: reflect the degree - should be reflects

A7. Changed, thanks.

R8. P783, L9: Andrea should be Andreae

A8. fixed! Thanks.

R9. 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.

A9. 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.

R10. 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 deforesta-

tion 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)?

A10. The Twin Otter and C-130 HCN/CO ratios were averaged together simply because that was the simplest way to include all valid data, from what were essentially two independent measurements. 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. Finally small corrections were made to the HCN values as described at the end of this document where the final revised text is presented.

R11. 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?

A11. 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.

R12. 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?

A12. We are discussing the initial emissions at this point and they were not cloud-processed. We report sulfuric acid ER, but not EF.