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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. Continued from Part 1

R13. 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.

A13. To keep the paper to a reasonable length, we limited the discussion of BB OM emissions to emissions from tropical forest fires and crop residue fires, which is what we sampled. There are a large number of savanna fire measurements that could be

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discussed, but it would greatly lengthen the paper.

R14. P794, L25: which of the points are cloud impacted?

A14. The cloud-processed points are given as 1.27-1.47 h on line 6 of page 781. We should point out that we do not have good information on the extent of cloud-processing because the location and size of clouds is dynamic. We do know that the RH exceeded 100% as the aircraft sampled these points suggesting that cloud-processing could have been occurring at the time of sampling. We also see a response in the HCHO/CO ratio similar to that in cloud-processed smoke sampled in Africa by Yokelson et al. (2003).

R15. P794-5: 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.

A15. We have added error bars to the source and downwind points in the revised figures.

R16. 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?

A16. We will clarify that the large variability in PAN/CO demonstrates possible variability in either the initial emissions or the processing or both.

Original text:

ACPD

9, S2638–S2647, 2009

"This demonstrates the large variability in both initial emissions and photochemical rates that are associated with BB plumes."

New text:

"This demonstrates that large variability in initial emissions and/or photochemical processing can be associated with BB plumes."

R17. 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.

A17. Addressed above and in our earlier response.

R18. 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.

A18. 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

ACPD

9, S2638–S2647, 2009

agreeing with the Referee's earlier statement that this is a subject worthy of future research.

R19. P800, final paragraph: This discussion also appears to support a rather rapid initial processing of the plume.

A19. 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.

R20. 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.

A20. 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. . . .

R21. 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.

A21. 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.

ACPD

9, S2638–S2647, 2009

R22. 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.

A22. As indicated above we prefer to confine the discussion to tropical forest fires because a discussion of savanna fires would significantly increase the paper length.

R23. P809: Capes et al does not appear in the reference list.

A23. First author error! Thanks! Fixed.

Other minor voluntary changes (VC#):

VC1.

Page 770, Line 13 and Page 786 Line 18:

The data in the private communication attributed to J. Crounse is now in a paper. Thus, we have changed to a citation to Crounse et al., 2009 and added the reference.

Crounse, J. D., DeCarlo, P. F., Blake, D. R., Emmons, L. K., Campos, T. L., Apel, E. C., Clarke, A. D., Weinheimer, A. J., McCabe, D. C., Yokelson, R. J., Jimenez, J. L., and Wennberg, P. O.: Biomass burning and urban air pollution over the Central Mexican Plateau, Atmos. Chem. Phys. Discuss., 9, 2699-2734, 2009.

VC2.

Tables 3 and 4 had incorrect entries for NO_2 for fire #1 on March 23. Those values were corrected, which also affected the NO_x and NO_x/NO_y entries for that fire. This then increased the average NO_2, NO_x, and NO_x/NO_y values for the complete set of C-130 fires upwards by about 5% of the previous value. In turn, on line 23 of page 799, the estimated average fraction of NO_x converted to nitrate was decreased from 0.26 to 0.25.

VC3.

Due to a misunderstanding by the first author, the wrong data was entered in Table 3

ACPD

9, S2638–S2647, 2009

Interactive Comment

for the values of the HCN/CO ratios as determined by the proxy method. The existing values were 0.0196, 0.0047, and 0.0081. The correct values are 0.0148, 0.0063, and 0.0088, which actually agree better on average with the slope-based determination of the ER. The new ratios for "slope/proxy" in Table 3 are 1.03, 1.17, and 0.92 with an average of 1.04 $\pm$ 0.13. This then led to a minor revision of the text discussion of the agreement between the two methods on page 777 lines 12-20. (Note, we calculated HONO by both methods, but because of its short lifetime we did not include it in the comparison of the slope and proxy methods.)

Original text:

"For two species measured discretely by the Caltech CIMS (SO_2 and HCN) it was possible to compare the "integral-based" ER to CO to the "plot-based" ER to CO. Compared to the integral-based ER, the plot-based approach returned individual fire ER that were identical when a few minutes were spent in plume and up to 57% different for brief sample periods with an average difference of $\pm$ 21%. It is important to note, however, that the ER obtained from the plot-based method did not show significant bias when averaged over several fires. Specifically, the plot-based ER was within 7% of the integral based ER averaged over 2 fires for SO_2, and within 5 % averaged over three fires for HCN."

New text:

"For two species measured discretely by the Caltech CIMS (SO_2 and HCN) it was meaningful to compare the "integral-based" ER to CO to the "plot-based" ER to CO. In comparison to the integral-based ER, the plot-based approach returned individual fire ER that were less than 10% different when 2-3 minutes were spent in plume and up to 19% different for brief sample periods. The ER obtained from the plot-based method did not show significant bias when averaged over all five comparable samples (the plot-based ER was 0.998 $\pm$ 0.14 of the integral based ER)."

VC4.

ACPD

9, S2638–S2647, 2009

Because the HCN values changed in Table 3 slightly, we also had to make slight changes in the values for HCN in Table 4.

Original and new values are:

C-130 avg C-130 stdev ER/CO Avg EF Avg EF stdev

Original 0.0108 0.0078 0.0070 0.543 0.457

New 0.0100 0.0044 0.0066 0.512 0.316

And in the text page 786, lines 13-17 we corrected the CH_3CN/HCN molar ratio and modified the text on HCN/CO ratios slightly to read:

Original text:

"The ΔHCN/ΔCO ER measured on the C-130 was 0.0108 $\pm$ 0.008 (n=3) and the Twin Otter ΔHCN/ΔCO ER for all fires was 0.0032 $\pm$ 0.0016 (n=17). The combined average for both aircraft is about 0.007 $\pm$ 0.006, which is not significantly higher than the ΔHCN/ΔCO ER obtained for Brazilian DF (0.0063 $\pm$ 0.0054). The $\Delta CH_3CN/\Delta$HCN molar ER is fairly consistent for several recent field studies: 0.39 MC-area (Crounse et al., 2009), 0.41 Brazil DF (Yokelson et al., 2008) and $\sim$0.26 in the Yucatan if we only consider the fires where both species were measured."

Final text to reflect corrected values and the referee comment number 10:

The ΔHCN/ΔCO ER measured on the C-130 was 0.0100 $\pm$ 0.0044 (n=3) and the Twin Otter ΔHCN/ΔCO ER for all fires was 0.0032 $\pm$ 0.0014 (n=7). The combined average for both aircraft is about 0.0066 $\pm$ 0.0041, which is not significantly higher than the ΔHCN/ΔCO ER obtained for Brazilian DF (0.0063 $\pm$ 0.0054). The $\Delta CH_3CN/\Delta$HCN molar ER is fairly consistent for several recent field studies: 0.39 MC-area (Crounse et al., 2009), 0.41 Brazil DF (Yokelson et al., 2008) and $\sim$0.43 in the Yucatan if we only consider the fires where both species were measured.

VC5.

ACPD

9, S2638–S2647, 2009

The Caltech team realized they had HONO data for the three fires sampled in the Yucatan. Because of the importance of this species the following additions were made.

On page 774, line 25:

Nitrous acid (HONO) was added to Caltech CIMs species list

The following brief paragraph discussing this data was inserted on page 787, line 2 after the discussion of NO_x emissions and before the discussion of SO_2 emissions:

"Nitrous acid (HONO) is known to be a direct initial emission from fossil fuel combustion (Finlayson-Pitts and Pitts, 2000, pp 274) and Keene et al. (2006) and Yokelson et al. (2007b) observed direct emission of HONO from biomass burning in the lab and field, respectively. Photolysis with unit quantum yield to OH and NO is the only important daytime loss for HONO and occurs within 10-20 minutes (Finlayson-Pitts and Pitts, 2000). Thus we expect the lower altitude samples of the Yucatan BB plumes to have higher ΔHONO/ΔNO_y values (where this ratio should normalize for fuel N differences to some extent). This trend is evidenced in our samples since ΔHONO/ΔNO_y was the highest for Fire # 2 ($\sim$0.11, sampled at 390 m) and decreased for Fires 1 ($\sim$0.05, 1110 m) and 3 ($\sim$0.044, 1730 m). Since NO_y is about 75% NO_x (Table 3), a comparable value for ΔHONO/ΔNO_x of 0.14 was measured at lower altitudes (predominantly $\sim$580 m) in Brazil by Yokelson et al. (2007b). The lab BB study of Keene et al. (2006) reported a ΔHONO/ΔNO_x molar ratio of 0.13 $\pm$ 0.097. In the aging Fire #3 plume (Sect. 3.4) the ΔHONO/ΔCO dropped to about one-tenth of the initially observed value within $\sim$20 minutes and ΔHONO/ΔCO was even lower in the aged haze layers (Table 3, Sect. 3.5). Thus, we conclude that HONO accounts for about 10% of initial BB NO_y and that it makes a major contribution to both OH and NO in fresh BB plumes."

In the tables:

Additional values for Table 3, were added as shown below. In Table 4, we estimate the true initial EFHONO for the Yucatan based on assumption that initial HONO is $\sim$10%

ACPD

9, S2638–S2647, 2009

of NOy. This is indicated with a footnote.

	HONO/CO slope	HONO/CO proxy
Haze highest	.00033	nm
Haze lowest	8.2e-5	nm
Fire 1	.0022	.0023
Fire 2	.0075	.0031
Fire 3	.0028	.0029

Finally, we deemed the HONO results important enough to add to the abstract and conclusions as follows:

In abstract:

Original sentence:

The OH measurements revealed high initial OH levels $> 1 \times 10^7$ molecules/cm^3.

New sentence:

The OH measurements revealed high initial levels ($> 1 \times 10^7$ molecules/cm^3) that were likely caused in part by high initial HONO ($\sim$10% of NO$_y$).

In conclusions:

Original sentence:

The OH measurement in an aging BB plume confirmed the possibility of very high early OH (1.14×10^7 molecules/cm^3).

New sentence:

The OH measurement in an aging BB plume confirmed the possibility of very high early OH (1.14×10^7 molecules/cm^3) likely caused in part by high initial HONO ($\sim$10% of NO$_y$).

ACPD
9, S2638–S2647, 2009

VC6.

page 804, Lines 16-18.

Clarified and slightly corrected the text as follows:

Original text:

“The timing of the MODIS overpasses, closely spaced (∼90 minutes) midday and night-time pairs, leads to omission errors for short-lived fires or fire activity initiated following the last daytime pass.”

New text:

“The timing of the Terra and Aqua MODIS overpasses (at 20° N) results in close spacing (∼100 minutes) of the midday observations and leads to omission errors for short-lived fires or fire activity initiated following the last daytime pass.”

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9, S2638–S2647, 2009