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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Comparison of the chemical evolution and characteristics of 495 biomass burning plumes intercepted by the NASA DC-8 aircraft during the ARCTAS/CARB-2008 field campaign” *by* A. Hecobian et al.

Anonymous Referee #2

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I did not get a chance to provide a quick review and so I am providing something similar to that now. I will make detailed comments later on a revised paper if one is provided using improved analysis.

Flying a world-class instrument package in complex smoke plumes will usually yield interesting results, but perhaps not in the way originally envisioned. Thus I will point out both concerns with the current analysis and a simple alternate analysis that could be quite productive.

Because of high variability in the source emissions versus time within single fires and high variability from fire to fire and high age uncertainty for most of the plumes in this study, the initial attempt to investigate photochemistry in aging plumes as shown in Figure 3 is not convincing or useful.

To support the high age uncertainty, the climatological cloud cover for July in western Canada is about 50% meaning many fires would go undetected by active fire detection and sources would be mislocated when relying on hotspots. See: Stubenrauch, C.J., Cros, S., Guignard, A., & Lamquin, N. (2010). A 6-year global cloud climatology from the Atmospheric InfraRed Sounder AIRS and a statistical analysis in synergy with CALIPSO and CloudSat. Atmospheric Chemistry Physics, 10, 7197-7214

In general, in science, one can test if a diagnostic approach is working by seeing if it gets the right answer for a question where the right answer is well-known. In Figure 3, the authors plot normalized excess mixing ratios (NEMR) as a function of estimated plume age in an attempt to probe the photochemical changes in smoke. Thus, one suitable test of the approach is as follows: Since there is no photochemical source of HCN or CH3CN in biomass burning plumes, the NEMRs for CH3CN or HCN to CO should not vary over the timescales shown unless the NEMR at the source was varying. In fact, in the data shown, the HCN and CH3CN NEMRs vary a lot with age, especially for the 29 June plume. Thus in these plumes the data is a history of the source variability rather than a measurement of photochemical evolution of the plume. Alternatively if one looks at the bulk properties of the plots one sees an apparent increase in the NEMR for toluene to CO when in fact, at the cited/measured OH of 2-3 times ten to the sixth molecules/cc, the toluene lifetime is known to be about 1 day. The apparent toluene increase in the bulk data set is likely caused by much higher initial NEMR for toluene at the source of the plumes that randomly happened to be intercepted only at longer ages. Thus, since the bulk reductionist approach is failing to yield the correct conclusion about species with known photochemistry (or known lack of photochemistry), we see that we cannot have confidence in the conclusions for the other species where the evolution is still an open question: when based either on the bulk data or individual plumes.

Thus, all the trend analysis as shown is only telling us about variability and not photochemical evolution; except for O3 where the initial ER is always zero (Akagi et al 2011a, b). Happily, the O3 data shows fascinating potential for an alternate diagnostic approach for the data expanded upon below. Plume aging section in: Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, Atmos. Chem. Phys., 11, 4039-4072, doi:10.5194/acp-11-4039-2011, 2011a. Akagi, S. K., Craven, J. S., Taylor, J. W., McMeeking, G. R., Yokelson, R. J., Burling, I. R., Urbanski, S. P., Wold, C. E., Seinfeld, J. H., Coe, H., Alvarado, M. J., and Weise, D. R.: Evolution of trace gases and particles emitted by a chaparral fire in California, submitted June 6 to Atmos. Chem. Phys. Discuss., acp-2011-438, 2011b.

Before getting to that alternate approach its worth one more point on the existing approach. It's possible that the approach used in Fig 3 might work for a subset of the data shown. E.G. if a subset of the data currently in Fig 3 can be shown to be pseudo-Lagrangian as in Yokelson et al., (2009) then the comparison of those samples is likely useful. For instance, in this study, if the dCO/dCO2 ratio (or, alternatively dBC/dCO) is the same for two different aged samples from the same plume then they likely were emitted with the same flaming/smoldering ratio and subsequent differences are more likely due largely to post emission photochemical processing than changes in NEMR at the source (barring large changes in the fuel burned). Even better, one could calculate the emission time for two different downwind samples from the same plume and if they are close subsequent differences are likely due largely to post emission processing (Akagi et al., 2011b). My guess is that unfortunately not a lot of sample pairs in this work will meet either of these criteria. In any case the authors need to check the y-axis label on Figure 3c. The points appear to be reasonable values for CO/CO2 not CO2/CO. Also please check units on 3i (ppt or ppb for PAN?) and define "organics" in

3m.

In light of the above, the diagnostic approach with more general potential is described next. I develop this approach with a series of observations.

In contrast to the author's bulk discussion and model output, their data shows some amazingly fast O3 production in several of the samples in Fig 3h. As background information, Andreae et al. (1994) reported NEMR for dO3/dCO for numerous tropical biomass burning plumes and they observed important enhancements from 11 to 89% after 7 to 10 days of aging.

Andreae, M. O., Anderson, B. E., Blake, D. R., Bradshaw, J. D., Collins, J. E., Gergory, G. L., Sachse, G. W., and Shipham, M. C.: Influence of plumes from biomass burning on atmospheric chemistry over the equatorial and tropical South Atlantic during CITE 3, J. Geophys Res., 99, 12793–12808, doi:10.1029/94JD00263, 1994.

In comparison to the above paper, the author's report of 60% dO3/dCO after one hour and almost 120% in 6 h in the July 8 plume is perhaps the fastest photochemistry ever reported in the literature on BB plumes (or maybe all plumes) just from my memory. Andreae et al were able to show that dO3/dCO correlated positively with dNOy/dCO and further they noted that the lower average dO3/dCO seen in the tundra fire plumes that were measured during the earlier ABLE campaign could be rationalized by lower average dNOy/dCO in the ABLE plumes.

The authors Fig 3h shows 4 samples with extreme photochemical processing, ~3 fast, and ~11 minimal. Step 1 would be; does the NOy based analysis explain the different O3 outcomes or can other driving factors (NOy/VOC, transport altitude, vertical position within the plume (i.e. top or bottom), time of transport (i.e. mid-day vs nighttime), OH, degree of high cloud cover, be identified? The authors include one sentence that the "These infrequent high ozone episodes were not associated with clear enhancements of other species, either gaseous or aerosol phase." That seems unlikely. If all the instrumentation on the aircraft truly yields no insight into the reasons for the huge differences in O3 production, then only a short paper presenting the average PILS dWSOC/dCO for all quality samples is needed as the average values for the other species have already been published by Singh, Simpson, Hornbrook, Cubison, etc?

In the short paper there would be no need for statements about “nothing happening overall.” Table 3 can be eliminated in any case as it is not clear what it means if anything. The model does not seem relevant if it concluded that O3 production was minimal in the July 1 plume. Looking at Figure 3h one sees a dO3/dCO point of almost 50% in less than one hour in the July 1 plume!

Then, since this is ostensibly a PILS theme paper, regardless of the explanation (or lack there-of) for the different “degree of processing” outcomes, the major theme of paper might be: (1) In the limit where photochemistry has no discernable effect on the PILS samples, just the average dWSOC/dCO for the campaign and how that compared to the dWSOC/dCO in other campaigns. (2) If possible, a paper elucidating the variable processing outcomes that probes questions such as: a) How did the different amounts of processing impact the WSOC observations? E.G. is dWSOC/dOC or (species of WSOC)/(sum WSOC) related to photochemical activity? These ratios within the bulk PM will probably normalize to some extent for the variability in overall PM. (b) Why do some plumes have fast photochemistry and other do not? (c) Does increased photochemical processing (as evidenced by high dO3/dCO) infer more oxidized aerosol and/or a greater portion of WSOC/OC or OA/OC? (d) Or are WSOC trends with "degree of processing" more related to RH, NOx, etc… (e) How does processing, when observed, affect the optical properties, etc… Are the particles in the samples with high O3 more likely to be coated or have brown carbon, which has many interesting applications?

Also note: If the plot is retained for some reason I recommend changing the NOx units to ppb/ppm in Figure 3.

I agree with Referee #1 that the modeling portion could be dropped or developed in

more detail in a separate paper.

The title is a bit misleading since it’s really 495 samples, but the chemical evolution is only compared using about 20 samples? Further, among the ~20 samples shown there are many incomplete samples where the data is not displayed for all the variables.

Page 18605, Lines 6-7: A reanalysis of the data in Hobbs et al. (2003) concluded that there was significant SOA in the Timbavati plume. See: Alvarado, M. J. and Prinn, R. G.: Formation of ozone and growth of aerosols in young smoke plumes from biomass burning: 1. Lagrangian parcel studies, J. Geophys. Res., 114, D09306, doi:10.1029/2008JD011144, 2009.

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