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Interactive comment on “The tropical forest and fire emissions experiment: method evaluation of volatile organic compound emissions measured by PTR-MS, FTIR, and GC from tropical biomass burning” by T. G. Karl et al.

Anonymous Referee #2

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General Comments: The paper presents results on volatile organic compounds emitted from biomass burning measured during an 11 day aircraft based field experiment in Brazil in 2004 and from laboratory fires of tropical fuels performed at the United States Forest Service Fire Sciences lab. The principal focus of the paper is a comparison of the 2 analytical methods used for measuring VOCs in the field and laboratory experiments: an FTIR spectrometer and a proton transfer reaction mass spectrometer. This paper also reports average VOC emissions as molar ratios to acetonitrile for both the field experiments and lab experiments and compares these measured emission

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ratios to those reported in a recent review (Andrea et al., 2001). Companion papers noted by the author and also submitted to ACPD are presumably describing the field experiments and emissions factors in more detail.

The paper presents useful results although it can be faulted on the lack of specifics and experimental detail. The authors report mixing ratios for many oxygenated species such as acids and formaldehyde and rely upon calculated instrument sensitivity factors to determine ambient mixing ratios. No details are given on the rate constants used or whether ion transmission efficiencies were accounted for. I think this is a severe omission. This is principally an instrument intercomparison paper and as such it is a requirement that the reader understand how these instruments were calibrated in order to evaluate the results. Another omission is that there is no discussion of how the FTIR and PTRMS measurements compared in the field. Some discussion is warranted.

Specific Comments: In the abstract you state that OVOC/ NMHC ratio in fires is 4:1. Nowhere in the paper do you state what NMHC were measured or how. Are the NMHC those species measured by PTR-MS?

p. 8756 first use of acronym USFS - should spell out what it means.

p. 8758 line 10. Awkward sentence “.. how aging effects VOC, and other, concentrations in plumes ..”

p.8760 What types of fuel were burned?

p. 8760. How was air sampled into the aircraft and then measured by the PTR-MS and FTIR instruments? Could you comment on the potential for compounds to be lost to sampling lines in the aircraft?

p. 8762. It is not clear how the different species were quantified by PTR-MS. Was a transmission curve determined in the field in order to determine a theoretical sensitivity for compounds not in the multi-component mixture? How well did mixing ratios determined theoretically compare to those determined from using the multi-component

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calibration mixture? You should at least provide a table of the rate constants you used to calculate mixing ratios and identify their source (measured or calculated).

p. 8762. Line 5. It wasn't clearly explained in the text the usefulness of the GC-PTRMS coupling. As far as I could glean the usefulness arises in understanding the potential impact of fragmentation in quantifying particular species in the field (positive and negative artifacts). Is this correct? How were these effects accounted for in the field data?

p. 8764 Line 9. How was the regression weighted?

p. 8766. and elsewhere. To reiterate you need to describe in much more detail how you calculated the mixing ratios of species not included in your calibration tank - what rate constants were used, did you correct for transmission efficiency? You make the point that emissions of the oxygenated species such as phenol are important and underestimated in VOC emission budgets perhaps a result of poor techniques. That statement behooves you to prove to others you know how to calibrate the PTR-MS for phenol and that you know what the uncertainties of your measurement are.

p. 8767. The data in Figure 5 do not inspire much confidence in a simple humidity dependent correction factor - there is a lot of scatter in the relationship. For example there is more than a factor of 3 variation at low water content. Despite this scatter, without the low water content data points it would be hard to discern a positive correlation with water content implied by the reaction kinetics trend. However this is an interesting plot and provides valuable information on the quality of HCHO measurements from the PTR-MS instrument. The problem with this section is the lack of useful detail. For example you need to elaborate on how your theoretical line was calculated. The figure caption implies the Hansel et al. reference provides a water concentration dependent correction factor for the formaldehyde sensitivity which is mis-leading. The Hansel reference provides kinetic data from a SIFDT experiment using very different conditions than your drift experiment (He buffer, lower E/N). What kinetic data did you

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use? It is not obvious from your treatment if you accounted for ligand switching reactions. Perhaps this was not an important source of HCHO+ given your water cluster concentrations. In any event much more detail should be provided here to support the inclusion of Figure 5 and any contention that PTR-MS HCHO data can be reasonably corrected to account for water vapor effects.

p. 8772. Could explain what you mean by well mixed plume? Well mixed in the vertical? It isn't clear why you need to invoke "well mixed plume" to compare FTIR and PTR-MS measurements.

p. 8772. I would have expected that the acids would have had an appreciable memory effect from adsorption to sample lines and that the elevated mixing ratios encountered in plumes cause the instrument background to increase. Is this the reason for the tailing data in Figure 7a? Were backgrounds performed in flight to determine instrument backgrounds, response times, and memory effects?

p. 8772 How were "excess" mixing ratios determined? Did you have an independent tracer of smoke (particle concentration for example) to determine when you were in and out of the plume and thereby identify "regional background" periods for the PTR-MS?

p. 8772 How did the FTIR and PTRMS compare in the field?

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 8755, 2007.

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