**Atmospheric
Chemistry
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Discussions**

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.**

T. G. Karl et al.

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We are thankful for the thorough reviews provided by both reviewers, which have helped to improve the manuscript to a point where we think we have been able to address all issues pointed out during this reviewing process. Below is our specific response to individual comments.

Comments:

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

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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.

Response: The new version now explicitly lists calibration factors and/or rate constants used for the concentration calculation using PTRMS. The acetic acid calibration factor was obtained from a gravimetrically prepared liquid standard. We updated the methods section and now present a very detailed description of how individual compounds were derived. It is true that our primary means for deriving concentrations for formaldehyde during this study is based on the FTIR instrument. The main reason that we do not show much intercomparison in the field is that the FTIR instrument in the field was set up for grab sampling, while the PTRMS was monitoring continuously, as described in detail in section 3.2. In other words the FTIR cell was flushed for a variable amount of time during each plume penetration. A valving system was manually operated to shut off the airstream to the FTIR cell, e.g. after some lines on the FTIR spectrum showed a high enough signal. It is therefore not accurate to intercompare a line average concentration signal obtained by the FTIR with a continuous concentration time series obtained from the PTRMS in the field. During laboratory experiments both instruments were setup for real-time monitoring. Thus, we only intercompare VOC concentration data directly for the laboratory experiment. Instead we use VOC/methanol ratios to compare the instruments in the field. These ratios are consistent with laboratory measurements and are included in the compound discussion section of this paper where applicable. We also note that the overlap of VOCs measured in the field is somewhat limited due to the detection limit of the FTIR and the fact that most compounds that the FTIR can measure well in the field are either not measured by PTRMS (e.g. ethene, methane) or have been used to obtain a calibration for the PTRMS instrument (e.g.

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HCHO, HCN, formic acid).

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?

Response: NMHC measurements were based on FTIR measurements as stated in section 2.5 (e.g. ethylene), PTRMS as stated in section 3 (e.g. isoprene, aromatics) and stainless steel canisters (NMHC) as mentioned in the introduction. More detail on canister samples is presented elsewhere (Yokelson et al., 2007). We added more information on canister sampling in the methods section. The data needed to calculate the 4:1 ratio is listed in detail in Table 2 of the cited paper (Yokelson et al 2007).

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

Response: ok changed.

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

Response: Ok changed to: VOC concentration measurements in biomass burning plumes are also needed to assess our understanding of photochemical oxidation in smoke plumes.

p.8760 What types of fuel were burned?

Response: Added more information on fuels burned in the laboratory (section 2.1) and on fires in section 2.2.

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?

Response: We have added a more detailed description on measurement inlets for the FTIR and PTRMS instruments. Tests showed that the residence times in our inlet lines

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(on the order of 2-4 seconds) did not result in significant sampling losses. For example the rise time of VOCs in the plume shown in figure 7a is very similar for different VOCs (including acetic acid). The acetic acid concentration reached 10% of its peak value within ~7 seconds. A less-sticky compound like methanol showed slightly faster decline in this particular plume (e.g. it was at 10% of its peak value within 3-4 seconds). Overall this observation is confirmed by laboratory tests, showing that sampling losses in the PTR-MS inlet design are not major.

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 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).

Response: This is now explained in more detail in the methods section. We also extended Table 2, which now specifically indicates how each compound was calibrated and what rate constants were used. Overall calculated and measured calibration values were generally within the stated uncertainty of 30% for compounds that did not show significant fragmentation. The transmission generally becomes important for higher molecular weight compounds (e.g. >130 amu). We used a measured transmission curve for laboratory experiments to account for a declining transmission in the higher mass range.

p. 8762. Line 5. It wasn't clearly explained in the text the usefulness of the GCPTRMS 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?

Response: The usefulness of the GC-PTRMS coupling in the laboratory was to assess

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the specificity of the instrument as discussed in detail in section 3. The influence of fragmentation was not a primary concern for these measurements, since this is usually done by spiking the instrument with the pure vapor pressure of a particular VOC. Under the same operational conditions the fragmentation patterns in the instrument do not change and are therefore the same between laboratory and field measurements.

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

Response: As mentioned in the manuscript (p8764, line9) we used an orthogonal regression.

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.

Response: see our comments above on calibration procedures. Phenol: We stated the general uncertainty of our measurements based on rate constants in the experimental section. We show an intercomparison between two independent techniques, which gives us confidence that we can measure phenol within the stated uncertainty. We believe that this is a first step towards a better understanding of phenol emissions from fires. We have not in particular evaluated sampling losses of phenols occurring in cans etc, but,we do believe that the large difference for phenol could indicate analytical challenges for conventional GC-analysis, similar to what we observed during the present study by coupling a GC setup to the PTRMS.

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,

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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 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.

Response: We decided to omit this figure in the revised version. The main reason for the large scatter of data points is due to uncertainties of lining up FTIR and PTRMS field data directly due to different sampling strategies. This results in a higher variability which is not accurately captured by the instrumental uncertainty alone. Instead we show a similar figure, but now plotting the HCHO/MeOH (PTRMS) to MeOH/HCHO(Ftir) ratios versus ambient humidity. It shows that the standard deviation of this calibration curve (slope) is reasonable considering extremely variable concentration measurements in smoke plumes. Due to variability, always associated with measurements in the real atmosphere, the variation of a single data point should not be used to assess the goodness of a fit (as the reviewer seems to imply); the overall standard deviation of the fit shown is 25% with an R-square of 0.73. Since we base the field PTRMS HCHO calibration on the FTIR, we do not elaborate on the theoretical calculation in great detail (for the more interested reader we refer to Hansel et al.), but added more information in the revised manuscript to a point that might be useful to the reader. We demonstrate that humidity effects are linear within the range encountered

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for ambient air measurements and can be used to correct HCHO measurements obtained by PTRMS. Ligand switching is not important under typical PTRMS conditions; the revised manuscript also lists the backward reaction rate constant (obtained from a non-linear least squares fit).

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.

Response: Well mixed along the flight path. The reason for this is because the FTIR takes grab samples and the PTR-MS measures continuously.

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?

Response: Figure 7a shows that the rise time for all VOCs is of similar order, suggesting that sampling losses in our inlet system are not significant. We also note that mixing ratios in figure 7a are shown on a logarithmic scale. The mixing ratios of acetone and methanol declined to their 10% value within 2-4 seconds. Acetic acid mixing ratios declined to within 10% of the peak mixing ratio within ˜7seconds. The somewhat longer time constant for acetic could indicate some small memory effects in the sampling line. Since we compare integrated emission ratios along the flight path, uncertainties due to memory effects in this particular case would be on the order of 10%. We performed periodic background measurements using a catalytic converter and spiked VOCs in our inlets (not during flight operations though). These measurements are consistent with figure 7a, showing that organic acids have a longer time constant (e.g. 5-7 seconds). The excess mixing ratio was calculated from the background subtracted signal before and after each plume penetration. This procedure therefore eliminated any effect due

to changing instrumental background.

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?

Response: The background values are simply the average value before and after the plume penetrations, which accounts for the vast majority of the flight time. The small pre-post average background values were simply subtracted from the very high values in the plume resulting in excess values with very small potential error due to potential errors in the background value.

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

Response: As noted above, we intercompare FTIR and PTRMS datasets in the laboratory, where both instruments were measuring in real-time and measured a number of species simultaneously. In the field however the FTIR was grab sampling and the PTR was still measuring continuously, so no absolute concentration comparison can be done. We also note that the overlap of VOCs measured in the field is somewhat limited due to the detection limit of the FTIR and the fact that most compounds that the FTIR can measure well in the field are either not measured by PTRMS (e.g. ethene, methane) or have been used to obtain a calibration for the PTRMS instrument (e.g. HCHO, HCN, formic acid). We added VOC/MEOH ratios for field data where applicable.

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

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