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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.***

**T. G. Karl et al.**

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We are thankful for the thorough reviews provided by both reviewers, which has 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.

Response to Reviewer #1:

I feel that this manuscript is not presently suitable for publication for a variety of reasons. The authors present results from a biomass burning study in which a PTR-MS and a

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FTIR were used to quantify the volatile organic compounds being emitted. This work essentially repeats an earlier study previously published by a subset of the present authors (Christian et al. 2004) using a different PTR-MS instrument. There is some new information presented which could be very valuable to the biomass emissions community.

Response: We do not believe that this is a simple repetition of earlier experiments for 2 reasons: 1) Christian et al. 2004 focused on a different fuel type (African savanna grass) and 2) for the first time to our knowledge we combined GC and PTR-MS for biomass burning experiments to identify the selectivity of PTR-MS.

Results are presented for some tropical fuels and there are some very useful and informative results reported from a GC-PTR-MS experiment. My biggest complaint with the present manuscript is that while it indicates it is a method evaluation paper, it lacks sufficient experimental detail for any informed reader to judge the validity of the PTR-MS data that is reported. Without any description of how the different PTR species were quantified, such as calibration factors, reaction rate constants, branching fractions for each species, interested practitioners like myself gain no useable information on how to use our own PTR-MS instruments for quantifying VOCs arising from biomass burning.

Response: We added a new column in Table 2 indicating calibration factors obtained during this study. We also clarify for which VOCs standard calibrations were used and when the concentration was based on reaction rate constants and fragmentation patterns. However, we do not want to encourage people to just use calibration factors from this study and apply these to their own measurement for a lack of VOC standards. The goal of this paper is to provide a critical assessment of the specificity of PTRMS for measuring VOCs from biomass burning.

Another point where the manuscript could have a substantial impact, but falls short, is that while PTR-MS data is reported from both laboratory and field measurements,

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the intercomparison discussion is restricted to only the laboratory data. Why isn't there any comparison of the field data? The manuscript indicated that both the PTR-MS and the FTIR instruments were deployed on the same platform in the field study.

Response: The main reason for this 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 for the laboratory experiment. The new manuscript lists a field intercomparison of Acetic Acid/methanol ratios between both FTIR and PTRMS. We 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).

Specific comments: 1. Specific details describing how each mass was quantified should be included such as calibration factors and/or reaction rate constants and branching fractions.

Response: We included 2 new columns in Table 2 listing calibration factors and compounds used for calibration for each ptrms mass channel.

In particular greater details are needed for HCN and formaldehyde that are reported in Table 2 as being calibrated using the FTIR results. Presently there is no discussion of how this was done in the experimental or results section.

Response: Figure 4 shows an intercomparison for HCN between PTRMS and FTIR

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in the laboratory. The signal to noise ratio for HCN in the field with the FTIR was insufficient for similarly accurate comparison, so we assume that the lab relationship would be true for field data. For formaldehyde we do have data obtained from the FTIR in the field and a comparison is shown in figure 5. The reviewer states that there is no discussion, yet we describe both compounds with two figures and a detailed discussion for HCHO starting from page 8766 line 25 on. We added calibration factors used in Table 2.

2. For masses like 61 and 75 that have multiple compounds both of which fragment how is accounted for in the quantification?

Response: We assume that the reviewer refers to the fragmentation pattern of these compounds. We have calibrated acetic acid which takes care of the fragmentation (it is typically 25%(m/z 43) and 75% (m/z 61). For m/z 75 see our response below.

3. For isoprene and furan - Your calibration standard contains isoprene so was this calibration factor applied to both isoprene and furan? Also how did the distribution of isoprene and furan measured by the FTIR compare with that determined by the GC/MS?

Response: Yes we used the same calibration for isoprene and furan. Zhang et al. (2004) for example reported reaction rates for both compounds which are within 9%. Within the experimental uncertainty (30%) the study average FTIR and PTRMS isoprene/furan ratio agreed.

4. m/z 71 contains a number of compounds. It appears that this measured distribution is assumed to be constant over all conditions - ie flaming vs smoldering. How valid is this assumption for different fire conditions. What about different fuels?

Response: In general fires always consist of flaming and smoldering parts. It is impossible to separate these phases out independently as suggested by the reviewer. Results shown here represent tropical fuels. M/z 71 consists mostly of three structural

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isomers all of which are probably emitted mostly by smoldering combustion. Therefore, the distribution was probably stable over the course of the fires.

5.  $m/z$  75 - In the discussion only acetol is discussed, but in Table 2 two compounds are identified methyl formate and hydroxyacetone. The naming of acetol/hydroxyacetone should be consistent. Again both of these compounds fragment.

Response: Ok we changed the naming to be consistent throughout the text (now hydroxyacetone). The previous version of the manuscript already noted that the fragmentation of hydroxyacetone is about 20%. We did not identify methyl formate on  $m/z$  75? Methyl formate would have a parent ion of  $m/z$  61+. FTIR measurements in the laboratory suggest that mostly hydroxyacetone contributes to this PTR-MS mass channel. A contribution of methyl acetate is possible, however small (<3% assuming no fragmentation and a reaction rate constant of  $2.8 \times 10^{-9} \text{ cm}^3/\text{s}$ ), which is now explicitly stated. Due to a lack of a calibration standard we rely on results obtained from the FTIR.

6.  $m/z$  83 - Hexanal is listed here - It is important to indicate that hexanal fragments to this mass.

Response: Ok we added a comment that hexanal fragments to  $m/z$  83.

7. Phenol - The discussion on this compound demonstrates the need for new information about how the PTR signals were quantified. If a rate constant of  $2\text{e-}9 \text{ ml/s}$  was used for this calculation then reported ratio of 1.02 while appearing to be good is actually quite wrong since the calculated rate constant for phenol is  $2.5\text{e-}9 \text{ ml/s}$ . If a rate constant of  $2.5\text{e-}9$  were used then the ratio would be 0.8 and one might conclude that vinyl furan is more important than is being reported.

Response: We use  $2.5 \times 10^{-9} \text{ cm}^3/\text{s}$  as a reaction rate constant and applied this for phenol, the concentration should lie within our stated uncertainty of  $\pm 30\%$  when using calibration factors scaled to reaction rate constants. We clarified this in the new version.

8. All of the aromatics - it appears that canister samples were collected during the field

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campaign, it would be logical to show the comparison between this data and that of the PTR-MS. This would strengthen the assertion that these compounds can be accurately analyzed by the PTR-MS.

Response: Unfortunately we do not have aromatic concentration data from these cans. Previous intercomparisons (as listed in the reference sections) and our GC-PTRMS measurements however show that the PTRMS is able to measure these compounds within the stated uncertainty.

9. Comparison of lab vs field data - This section should contain a comparison of the PTR vs FTIR data. At the very least do the FTIR measurements support the conclusions derived in Table 2? At the end of this section it is shown that acetonitrile/CO ratios are almost a factor of two different between the laboratory and field measurements. On this basis I do not understand why the results in Table 2 should average to 1.

Response: 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 PTRMS was still measuring continuously; this means that no absolute concentration comparison can be done. However we added VOC/MeOH comparisons for field data where applicable. While the VOC/acetonitrile ratio between field and laboratory are similar, it does not necessarily imply that acetonitrile/CO ratios have to be similar too. Indeed, CO emissions in the field were smaller compared to VOC/acetonitrile emissions. The VOC/Acetonitrile ratios demonstrate that the PTRMS dataset between field and lab are consistent.

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

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