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Atmospheric Chemistry and Physics 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.

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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 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. Results are presented for some tropical fuels and there are some very useful

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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. 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, 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.

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. 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. 2. For masses like 61 and 75 that have multiple compounds both of which fragment how is accounted for in the quantification? 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-PTR-MS? 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? 5. m/z 75 - In the discussion only acetol is discussed, but in Table 2 two compounds are identified methyl formate and hyrdoxyacetone. The naming of acetol/hydroxyacetone

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should be consistent. Again both of these compounds fragment. 6. m/z 83 - Hexanal is listed here - It is important to indicate that hexanal fragments to this mass. 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 2e-9 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 2.5e-9 ml/s. If a rate constant of 2.5e-9 were used then the ratio would be 0.8 and one might conclude that vinyl furan is more important than is being reported. 8. All of the aromatics - it appears that canister samples were collected during the field 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. 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.

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