

***Interactive comment on “Characterization of biomass burning smoke from cooking fires, peat, crop residue and other fuels with high resolution proton-transfer-reaction time-of-flight mass spectrometry” by C. E. Stockwell et al.***

**Anonymous Referee #1**

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Biomass combustion emissions represent a significant load of carbonaceous species to the atmosphere; such species are known to affect air quality, health, and atmospheric processes on local, regional, and global scales. The work by Stockwell et al. will make a nice contribution to the body of literature on biomass combustion, as the data presented here extend our understanding of species-specific emissions factors for a number of biomass fuels.

This work is a good candidate for publication in ACP and will certainly be of interest

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to many readers. Overall, the experimental approach appears carefully designed and well documented. The manuscript is well written and clearly laid out. Some ambiguity exists with Tables and Figures but these are minor issues that are easily resolved. A couple weaknesses do exist with the experimental approach, but these weaknesses should not preclude publication – such weaknesses can likely be addressed in future work as the results presented here represent a strong step towards achieving mass balance around species-specific emissions for biomass fuels.

Specific Comments:

As with all emissions inventory work, the key questions to pose are (1) How representative are these data (of actual emissions)? (2) how accurate (and uncertain) are these estimates?

The fuels themselves appear very representative; whether the emissions from the FLAME burns are representative of real-world emissions is a difficult question to answer and probably beyond the scope of this work. However, since the authors are experts in this area of research – some discussion on the validity of lab-to-field representativeness is warranted for the emissions factors reported here.

The authors report a conservative bound of  $\pm 50\%$  measurement uncertainty about emissions by compound. This uncertainty is not surprising given the inherent limitations of PTR-MS and the fact that their calibration standards were mostly hydrocarbon based (with only a few heteroatom molecules beyond C-H-O). Perhaps the biggest weakness of this work is the choice of calibration gasses. The authors report emissions factors for many previously unstudied compounds (especially oxygenates and a few S- and N- containing compounds), yet, they did not generate calibration curves for these compounds. Standards for S- and N- compounds are likely difficult to obtain (especially those that are semi-volatile), however, the development of a phenol- and furan-containing calibration mixture would have strengthened this work considerably.

P22170 lines 16-19. This sentence is awkward. “In cases where a compound con-

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tains a non-oxygen heteroatom (such as methanethiol), the mass dependent calibration factor was determined using the relationship established using the oxygenated species.” More importantly, it is unclear whether this approach is valid. What is the uncertainty associated with assuming that such heteroatomic compounds will follow the oxygenated calibration curve? The deviation of dimethylsulphide from the ‘oxygenates’ calibration line (Figure 3) indicates that this assumption may not be valid.

Table 2 (body text). Are the numbers in parentheses standard deviations or some other measure of variability? This comment applies to nearly every Table in the manuscript; footnotes should be added to each table to explain accordingly.

The authors use methanol concentrations, as measured by OP FTIR, as an internal standard to account for variations associated with PTR-MS instrument. This is an innovative approach and one that will likely reduce measurement variability. Inclusion of more intercomparison data between the PTR and FTIR instruments for other shared compounds (perhaps as supplementary material) would strengthen this manuscript as these data would shed light on PTR measurement reliability. Showing the methanol comparison plot (1:1) would be helpful, too.

The compound-specific emissions factors that are included as supplemental tables is a great contribution of this work; these data will likely be used by many researchers. Is the use of 3+ significant figures justified, given the uncertainty in these EF data?

Figure 3 is difficult to comprehend based on the information presented in the title and legend. Only a single reference to this figure appears in the text body, but that reference is not explanatory. Many questions follow. There are three categories for ‘oxygenates’, ‘phenolics’, and ‘furans’ for each fuel type. Why? What do the parentheses mean, number of independent tests? I ‘think’ this plot is meant to compare FTIR to PTR measurements, but if so, I don’t know which instrument is which since there are four bars per fuel.

For the emissions factors tables, can the authors indicate which tests were true repli-

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cates? I suspect such information exists elsewhere but it would be very helpful to know how repeatable the measurements were for repeat tests (i.e., EF’s determined from the same set of experimental conditions).

The authors might try breaking Figure 4a and 5a into two panels each. One panel would contain EF’s for those fuels whose sum exceeds > 1 g/kg and one for those fuels whose sum is less than 1 g/kg (the latter scaled appropriately). The bars for fuels with low EF’s (i.e., less than 1 g/kg) are practically unreadable in these figures.

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 22163, 2014.

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