We thank Referee #1 for their comments and suggestions: all of which were helpful in improving the manuscript. We detail our response to each item below.

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.

This is an important point that we were greatly concerned with in a companion paper, but did not address clearly enough in this paper. We now address this in three additional ways.

(1) We mention early on in the introduction that the representativeness of the FLAME-4 fire emissions was explored in great detail by examining agreement with field measurements in an already published companion paper (Stockwell et al. 2014). In that paper we show that much of the FLAME-4 data is representative as is and - for fuel types warranted - we suggest simple, specific adjustment procedures to make the laboratory data more representative of field data.

Changes in the text are as follows:

P22167, L15-20: Old text: “In this work, we perform, to our knowledge, the first application of PTR-TOF-MS technology to laboratory biomass burning smoke to characterize emissions from a variety of authentic globally significant fuels. We report on several new or rarely measured gases and present a large set of useful emission ratios (ERs) and emission factors (EFs) for major fuel types that can inform/update current atmospheric models.”

New text: “In a companion paper the FLAME-4 emissions were compared extensively to field measurements of fire emissions and they were shown to be representative of “real-world” biomass burning either as is or after straightforward adjustment procedures detailed therein (Stockwell et al., 2014). In this work, we describe, to our knowledge, the first application of PTR-TOF-MS technology to laboratory biomass burning smoke to characterize emissions from a variety of authentic globally significant fuels. We report on several new or rarely measured gases and present a large set of useful emission ratios (ERs) and emission factors (EFs) that can represent major fuel types and inform/update current atmospheric models.”

(2) We now better clarify that the main compilation of new recommended EF is in Table S3. This important table appears in the supplement simply because of its large size. We also better clarify that any adjustment procedures required based on the comparisons in the companion paper have been applied to the data in Table S3. One exception is for cooking fires. We did not have enough TOF data from analyzing just three fires to get a useful EF vs MCE relationship so we instead computed adjusted EF for any NMOC “X” as the average X/CH4 ratio from FLAME-4 times the literature average EF(CH4) for cooking fires from Akagi et al., (2011).

Changes in text are as follows:

P22173 L5-7, Old text: "Finally, the EFs reported in Supplement Table S3 were adjusted according to procedures established in Stockwell et al. (2014) to improve laboratory representation of real-world biomass burning emissions."

New text: "Finally, the EFs reported in Supplement Table S3 were adjusted (when needed) according to procedures established in Stockwell et al. (2014) to improve laboratory representation of real-world biomass burning emissions. This table contains the EF we recommend other workers use and it appears in the Supplement only because of its large size."

P22173, L17: changed "S1 and S2" to "S1-S3"

To further clarify the relative importance of Tables S3 and Table 2 we made the following change:

P22176, L14-20: Existing text: "To facilitate discussion we grouped many of the assigned (or tentatively assigned) mass peak features into categories including: aromatic hydrocarbons; phenolic compounds; furan and its derivatives; nitrogen-containing compounds; sulfur-containing compounds; and miscellaneous compounds at increasing m/z."

New text: "To facilitate discussion we grouped many of the assigned (or tentatively assigned) mass peak features into categories including: aromatic hydrocarbons; phenolic compounds; furans; nitrogen-containing compounds; and sulfur-containing compounds. These categories do not account for the majority of the emitted NMOC mass, but account for most of the rarely-measured species reported in this work. We then also discuss miscellaneous compounds at increasing *m/z*."

P22190, L1, changed "and should aid" to "and (especially the recommended values in Table S3) should aid"

(3) We found two recent additional field studies of biomass burning to compare to (Geron and Hays, 2013; Kudo et al., 2014). They both support the "realism" of our FLAME-4 EF in Table S3.

Changes in text are as follows:

We include the following sentence in the text immediately following the above mentioned sentence at P22173 L7: "In addition to the comparisons considered in Stockwell et al. (2014), we find that our EFs in Table S3 are consistent (for the limited number of overlap species) with additional, recent field studies including Kudo et al. (2014) for Chinese crop residue fires and Geron and Hays (2013) for NC peat fires."

These additional references were added to the paper:

"Kudo, S., Tanimoto, H., Inomata, S., Saito, S., Pan, X., Kanaya, Y., Taketani, F., Wang, Z., Chen, H., Dong, H., Zhang, M., and Yamaji, K.: Emissions of nonmethane volatile organic compounds from open crop residue burning in the Yangtze River Delta region, China, J. Geophys. Res. Atmos., 119, 7684-7698, doi: 10.1002/2013JD021044, 2014."

"Geron, C., and Hays, M.: Air emissions from organic soil burning on the coastal plain of North Carolina, Atmos. Environ., 64, 192-199, doi: 10.1016/j.atmosenv.2012.09.065, 2013."

The authors report a conservative bound of +/- 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 contains 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.

We agree that additional calibration gases would be useful. This would be especially true for stand-alone use of the PTR-TOF-MS and we do note that we used the OP-FTIR furan data in this work. In our case, the instrument was rented for only three months and calibration gases were ordered ahead of time to meet the needs of several different experiments. We chose a variety of gases that were already known to be emitted by fires (including hydrocarbons and C-H-O heteroatoms), but operationally could not add calibration gases during the experiment. It is no longer possible to run more calibration gases, but for any group that owns or rents a TOF for smoke characterization in the future we recommend including more calibration species and measuring more fragmentation patterns. We now mention these issues in the conclusions where we summarized the lessons learned from our first attempt.

P22189 L2 before sentence beginning with: "Despite these practical…" add: "We were limited to our pre-chosen calibration mixture based primarily on gases previously observed in smoke. For future experiments we suggest adding more standards to generate more accurate calibration factors, specifically including major species such as furan and phenol and more compounds with S and N heteroatoms. In addition, measuring the fragmentation, if any, of more of the species identified in this work would be of great value."

On the subject of our treatment of heteroatoms, such as in the case of DMS and Acetonitrile, we agree with the reviewers that perhaps this is not the best treatment of these species. One would expect that approximation of sensitivities would most accurately be calculated *via* grouping families of compounds (e.g. alcohols, carbonyls, alkenes) rather than general subgroups of oxygenates and hydrocarbons. Unfortunately due to the limitations in this study and the lack of additional calibration standards as mentioned above we are forced to make some assumptions as in the case of compounds containing heteroatoms. Here we only have two calibrated examples both of which show a wide range in sensitivities. While sulfur and nitrogen containing compounds should be treated separately in a more complete analysis, we have chosen to consider these species collectively in order to increase sample size. When considered as a group these compounds more closely follow the trend for the oxygenated family. This does result in an increased error on the calculated calibration factors which has been approximated using the scatter on the fits derived from the oxygenated + heteroatom relationship. Unfortunately without any additional information we cannot more accurately approximate the error though we do admit the cited error is likely a lower limit on the actual errors associated with this method of determination. This is a valid criticism of this work and the approximation of calibrations factors is a problem that is and will continue to be an issue with the analysis of TOF data moving forward, however, a detailed treatment is beyond the scope of this paper.

P22170, L16: Existing text: “In cases where a compound contains a non-oxygen heteroatom (such as methanethiol), the mass dependent calibration factor was determined using the relationship established using the oxygenated species.”

New text: “Sulfur and nitrogen-containing compounds were considered collectively and together they more closely followed the trend of the oxygenated species. Thus, in cases where a compound contains a non-oxygen heteroatom (such as methanethiol), the mass dependent calibration factor was determined using the relationship established using the oxygenated species.”

Then in addition to recognize the higher uncertainty for these species we added this change:

P22171, L6: We append after “prescribed” “, but with larger errors possible for compounds with N and S heteroatoms.”

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.

Thank you for bringing this to our attention. Table 2 should include the following footnote “Note: "nm" indicates not measured; blank indicates species remained below the detection limits; values in parenthesis indicate one standard deviation”

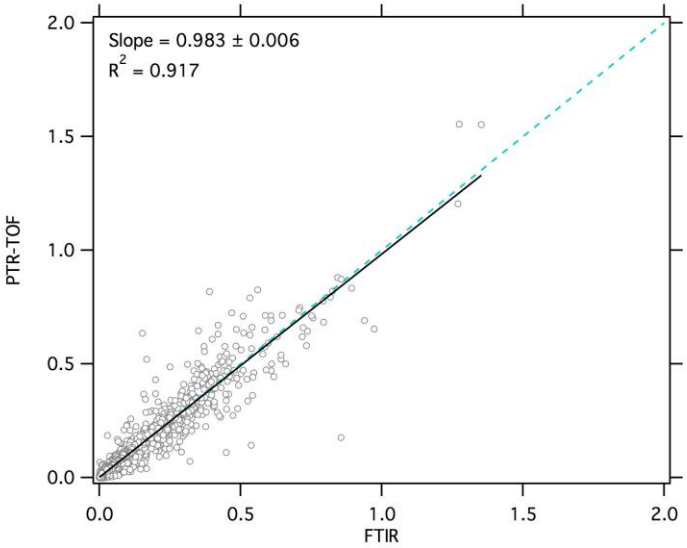
The authors use methanol concentrations, as measured by OP FTIR, as an internal standard to account for variations associated with PTR-MS instrument. This is an innovative approach and one that will likely reduce measurement variability. Inclusion of more intercomparison data between the PTR and FTIR 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.

Developing detailed inter-comparisons for more species for numerous fires is a large body of work that is the focus of an in-progress companion paper describing both contributions and inter-comparisons for the PTR-TOF-MS, OP-

FTIR, WAS, and 2D-GC data from FLAME-4. The in-progress study comparing and identifying the strengths of four techniques promises to be more valuable than comparing two techniques. Thus, we prefer not to lengthen the current already-long paper, which is focused on expanding the amount of data concerning NMOCs emitted by BB.

The point of using methanol as the internal standard for calculating fire-integrated ERs is that it actually cancels errors even if the PTR-MS and OP-FTIR disagree on occasion for methanol due to reagent ion depletion, timing, etc. We have already included the slope and R^2 value for this comparison in the manuscript. The lack of overall bias between the two instruments for methanol that we observed is nice, but already a departure from the main point. As noted above, adding more comparisons or the 1:1 methanol comparison plot would lengthen the manuscript and shift focus when a separate, comprehensive paper detailing measurement issues is already in progress. Thus, while the Referees concerns are warranted we address them elsewhere and did not add figures or comparisons at this time.

It is also important to note that depending on how we define the intercomparison (e.g. fire-integrated or real-time, etc.) the results vary a bit - and this takes time/space to describe, thus further supporting our decision to devote a separate paper to the topic of the intercomparison. As an example we show (in this response only) an FTIR/PTR methanol comparison with a slightly different filter applied than in the example quoted in the text. The slope and R^2 are then different, but still good. We trust the forthcoming companion paper comparing four techniques will provide the best way to gain insights into the bulk of the FLAME-4 NMOC fuel-specific emission factor results.



The good agreement for several species measured by both proton-transfer-reaction mass spectrometry and OP-FTIR spectroscopy has been demonstrated in numerous past manuscripts focused on laboratory biomass burning emissions (Christian et al., 2004; Karl et al., 2007; Veres et al. 2010; Warneke et al., 2011). To reflect this discussion in the paper we modified the sentence on P22172, L1-2 as follows:

Old sentence: “The agreement between these two measurements is within the uncertainties of both instruments.”

New sentence: "This result is consistent with the good agreement for several species measured by both PTR-MS and OP-FTIR observed in numerous past studies of laboratory biomass burning emissions (Christian et al., 2004; Karl et al., 2007; Veres et al. 2010; Warneke et al., 2011)."

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?

We simply chose to mass-produce the data with enough places after the decimal point to account for the large range in EF/ER. The co-tabulated standard deviations should make the actual number of significant figures clear. The important table (S3) uses 3 significant figures and researchers can use less if they prefer. It seems unnecessary to go through such large tables and manually edit them because there is so much variation on how many 0s are in front of the numbers. In addition, the rounding off the CO_2 emission factors to less than four digits could be warranted, but is never done in the literature. Reporting significant figures only introduces "round-off error" into any subsequent calculations with the 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.

Thank you for pointing out that this figure needs a more detailed explanation. The data in these figures are based on the synthesis of the FTIR and PTR measurements and do not compare the two. Instead we lumped the emissions into the following categories: non-methane hydrocarbons, oxygenates containing only 1 oxygen, oxygenates containing 2 oxygen atoms, and oxygenates containing 3 oxygen atoms. To give an even greater level of detail we then indicated within each category what emissions were directly from phenolic compounds or furan and substituted furans.

To clarify these changes in the text are as follows:

Added sentence before "As shown in Fig. 3…" P 22176 L8: "Figure 3 includes both FTIR and PTR emissions grouped into the following categories: non-methane hydrocarbons, oxygenates containing only one oxygen, oxygenates containing two oxygen atoms, and oxygenates containing three oxygen atoms. Within these categories, the contribution from aromatics, phenolic compounds, and furans are further indicated."

Also change the figure description to add further clarity, P22210:

"Figure 3. The emission factors (g kg^{-1}) of total observed hydrocarbons and total observed species oxygenated to different degrees averaged for each fire type based on a synthesis of PTR-TOF-MS and OP-FTIR data. The patterned sections indicate the contribution to each of the above categories by selected functionalities discussed in the text (aromatic hydrocarbons, phenolics, furans). The parenthetical expressions indicate how many oxygen atoms are present."

For the emissions factors tables, can the authors indicate which tests were true replicates? 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).

If by true replicates the author means burning "the exact same fire again and seeing how the emissions changed" then we have no true replicates. This is partly because on the scale of the fires we burned (several cubic meters of fuel) no exact duplicates could be constructed, but also because we instead aimed to vary the fires (moisture, geometry, etc.) in hope of capturing the natural EF dependence on MCE. We did perform replications of the smog chamber perturbations that will be described elsewhere.

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.

We thank the reviewer for bringing this to our attention and we have scaled Figures 4a, 5a, and 6a accordingly.

Voluntary changes:

P22190, L11: "was" changed to "were" – L12: changed "regions biofuel" to "regions where biofuel" - L18: changed "chlorine organic gases were not readily detectable" to "chlorine containing organic gases were not readily observed"

We changed "Ringed Aromatics" to "Aromatics" on the y axis label of Figure 4.

We eliminated m/z 81 from the Supplementary Tables because it is a fragment considered in the calculation of total carbon, but not a primary emission.

We added the EFs for the tire fire to the supplementary tables based on using HCOOH as an internal standard

We've also added several rows of additional species to Table S3. We have also extended the column averages in the supplemental tables for fuel types to include extended species even if there was no standard deviation.

We added an extra row for MCE in Tables 2a and 2b.

At the end of the acknowledgements we added: "We thank C. Geron for providing a sample of NC peat."

In the reference section the following reference we should eliminate misplaced "5" : "Müller, M., Mikoviny, T., Jud, W., D'Anna, B., and Wisthaler, A.: A new software tool for the 5analysis of high resolution PTR-TOF mass spectra, Chemometr. Intell. Lab., 127, 158–165, doi:10.1016/j.chemolab.2013.06.011, 2013."

It was changed to: “Müller, M., Mikoviny, T., Jud, W., D’Anna, B., and Wisthaler, A.: A new software tool for the analysis of high resolution PTR-TOF mass spectra, Chemometr. Intell. Lab., 127, 158–165, doi:10.1016/j.chemolab.2013.06.011, 2013.”

In Figure 6’s caption we’ve changed “furan derivatives” to “substituted furans”. We’ve also clarified which compounds are not averaged: The caption now reads “Figure 6. (a) The distribution in average fuel EF for furan and substituted furans, where individual contributions are indicated by color. The EFs for substituted furans additionally analyzed a single time are not true averages. (b) The linear correlation of furan with select substituted furans for an African grass fire (Fire 49).”

In Figure 4’s caption we’ve changed “The EF for p-Cymene is only calculated for select burns and should not be considered an average for each particular fuel type.” To: “The EFs for p-Cymene are only calculated for select fires and should not be considered a true average.”

Please update the following reference: “Yu, F. and Luo, G.: Modelling of gaseous dimethylamine in the global atmosphere: impacts of oxidation and aerosol uptake, Atmos. Chem. Phys. Discuss., 14, 17727–17748, doi:10.5194/acpd-14-17727-2014, 2014.” To “Yu, F. and Luo, G.: Modeling of gaseous methylamines in the global atmosphere: impacts of oxidation and aerosol uptake, Atmos. Chem. Phys., 14, 12455–12464, doi:10.5194/acp-14-12455-2014, 2014.”

Please update the following reference: “Stockwell, C. E., Yokelson, R. J., Kreidenweis, S. M., Robinson, A. L., DeMott, P. J., Sullivan, R. C., Reardon, J., Ryan, K. C., Griffith, D. W. T., and Stevens, L.: Trace gas emissions from combustion of peat, crop residue, biofuels, grasses, and other fuels: configuration ad FTIR component of the fourth Fire Lab at Missoula Experiment (FLAME-4), Atmos. Chem. Phys. Discuss., 14, 10061-10134, doi:10.5194/acpd-14-10061-2014, 2014. “ To: “Stockwell, C. E., Yokelson, R. J., Kreidenweis, S. M., Robinson, A. L., DeMott, P. J., Sullivan, R. C., Reardon, J., Ryan, K. C., Griffith, D. W. T., and Stevens, L.: Trace gas emissions from combustion of peat, crop residue, biofuels, grasses, and other fuels: configuration and Fourier transform infrared (FTIR) component of the fourth Fire Lab at Missoula Experiment (FLAME-4), Atmos. Chem. Phys., 14, 9727-9754, doi:10.5194/acp-14-9727-2014, 2014.”