**Atmospheric
Chemistry
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Discussions

Interactive comment on "Trace gas emissions from combustion of peat, crop residue, biofuels, grasses, and other fuels: configuration and FTIR component of the fourth Fire Lab at Missoula Experiment (FLAME-4)" *by* C. E. Stockwell et al.

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Response to Referee #2

We thank the Referee #2 for their comments and suggestions, many of which have been taken into account and were helpful in improving the manuscript. We address their specific comments below

R2 main comments:

R2: It's no doubt that OP-FTIR is a good instrument to provide an opportunity to measure a large number of gases in a high time resolution. Since optical measurements are usually associated with relatively high variations and uncertainties compared to the methods like traditional chemical analysis and GC separation with ECD, FID or MS detectors, is there any previous calibration work in the data obtained from OP-FTIR?

To our knowledge there is no inherent accuracy advantage of any general approach. But this comment is helpful and we've added additional references showing good agreement between our OP-FTIR and GC-FID and PTR-MS for the species stable enough to be measured by extractive approaches (Goode et al., 1999; Christian et al., 2004). We've also clarified the relevance of the Akagi et al. (2013) reference in this respect:

On P10077, L2-5: we change: "The uncertainties in the individual mixing ratios vary by spectrum and molecule and are dominated by uncertainty in the reference spectra (1–5 %) or the detection limit (0.5–15 ppb), whichever is larger as described elsewhere (Akagi et al., 2013)."

To: "The uncertainties in the individual mixing ratios vary by spectrum and molecule and are dominated by uncertainty in the reference spectra (1–5 %) or the detection limit (0.5–15 ppb), whichever is larger. Comparisons with other techniques and calibration standards are described elsewhere (Goode et al., 1999; Christian et al., 2004; Akagi et al., 2013)."

R2: The carbon mass balance method is used to calculate EFs. The method has been widely used in emission measurements by using CO2 as a reference species, although CO is also sometimes used as a refer compound. In the cited reference, Burling et al., used CO2 as the refer target to calculate pollutant EFs. Therefore, it may be interesting to compare some representative results calcu-

lated from CMB using CO and CO2 as refer compounds, respectively. In addition, is it possible to calculate the total mass of pollutants with the data of chamber volume and compare the results from the CMB method? The difference may be expected. This may be one important reason for the difference between the present study and those in the literatures.

Regardless of the reference species, all CMB EF calculations are based on estimates of total carbon as opposed to any single species. To clarify this we've added "The denominator of the third term in Eq. (1) estimates total carbon and" to the beginning of the sentence on P10079, L9. The chamber volume method suggested is interesting and might work for the room burns, but not for the stack burns, which were the majority of the fires.

R2: It would be interesting to look into the relationship between fuel element content and pollutant emission factors, and the relationship among measured 20 gases using statistical analysis, for example using CO as the main incomplete pollutant to investigate its correlation with other air pollutants.

We have discussed how N and Cl content impact emissions. All the emission ratios to CO are in the supplement and some are in the main tables, but we suspect that adding more analysis of this type, while interesting, would make the paper too long.

R2: In data comparison part, different chemical analytical methods and EF calculation methods between the present study and others should be taken into account, and these factors can hardly be reflected by the parameter, MCE, which is mainly related to the different fuel properties and burning performance.

We compare to data collected by other FTIR systems and analyzed by the same EF calculation method (CMB). In any case, we can only assume other studies are accurate and that any differences are real.

R2 technical comments:

R2: Title: crop residue and grasses are typical types of "Biofuels". Please consider to revise the word here.

Following most other workers, we use "biomass" as a generic term for "biomass" and "biofuel" to refer specifically to biomass used as a domestic fuel. However, we acknowledge that some workers use "biofuel" to refer to all biomass. We have added "domestic" before "biofuel" in the title to help clarify.

R2: Abstract line 16-17, "cooking fires" are not fuel types. In this study, indoor cookstove burning using different wood fuels were done. It may be "different fuel burning activities", instead of "fuel types", in my opinion.

We changed "fuel types" to "fire types" to be brief but more general.

R2: Abstract line 22, and throughout the text, does "crop residue fires" mean "simulated open crop straw burning"? Please clarify.

Yes. We think the Referee#2 is referring to line 23 and we think we clarified this on line 25, but we also changed "crops" on line 25 to "crop residues."

R2: Abstract line 29, what are "other reactive oxygenate organics" emitted from the burning of sugar cane?

We think the Referee#2 is referring to line 28 and have added "such as HCHO, HCOOH, and CH_3COOH." following "reactive oxygenate organics"

R2: Method, for each fuel type, the burning duration in stack and room burnings should be added, maybe into the table 1.

We don't know length of fire for room burns because the fire was ignited and then we left the room, but we added the duration of each stack burn in (hr:min:s) to row 6 of the new Supplementary Table S5 which provides ER to CO.

R2: Page 8 line 23, "the entire space" here means the sealed combustion chamber or the adjacent room with analytical instruments? Also, in the room burning,

where are the emissions "stored", sealed chamber or adjacent room? Line 30, where is "greater detailed elsewhere"? A reference should be added, and it is may be necessary to describe a little more why the room burning is needed here to allow the analysis of optical and ice-nucleating properties of smoke, more samples required or simulated short aging process?

The smoke was stored in the combustion room only and not to investigate aging but to allow for 1-2 hour scans by the ice nuclei instrument and other equipment. To clarify we made these changes:

L23: changed "entire space" to "entire combustion room"

L28: changed "extensive analysis" to "time-consuming analyses"

L29: added reference to paper recently submitted to AS&T "(Levin et al., 2014)"

And added the following reference:

Levin, E. J. T., McMeeking, G. R., DeMott, P. J., McCluskey, C. S., Stockwell, C. E., Yokelson, R. J., and Kreidenweis, S. M.: A new method to determine the number concentrations of refractory black carbon ice nucleating particles, Aerosol Sci. Technol., submitted, 2014.

R2: Page 11, 2.2.3. Was the Water Boiling Test (WBT) used in the simulated burning in cooking stoves? If so, or not, please describe more about the burning procedure, as this may be also one important reason behind the differences in EFs among different studies.

We did continue our cooking fire simulations until the water boiled, but not according to an exact international protocol. Rather our collaborator endeavored to faithfully simulate cooking procedures he had actually observed in extensive field studies. Despite this attempt, not surprisingly and for a variety of reasons, the lab fires burned differently for some cooking fire types. We note that lab-field differences are "normal" and discussed at length in Yokelson et al., (2013) and elsewhere. To clarify that our goal

was realistic simulations of field use as opposed to following a strict test procedure we made the following change:

P10071, L25: We changed "In this study, we investigated trace gas emissions from four cookstove types . . . " to "In this study, an experienced field researcher (L'Orange et al., 2012a, 2012b) simulated "field" cooking with four cookstove types . . . "

Add following references:

L'Orange, C., Volckens, J., and DeFoort, M.: Influences of stove type and cooking pot temperature on particulate matter emissions from biomass cook stoves, Energy Sustainable Dev., 16, 448-455, doi: 10.1016/j.esd.2012.08.008, 2012a.

L'Orange, C., DeFoort, M., and Willson, B.: Influence of testing parameters on biomass stove performance and development of an improved testing protocol, Energy Sustainable Dev., 16, 3-12, doi:10.1016/j.esd.2011.10.008, 2012b.

R2: Page 19, line 13-15, it is very good to see the re-calculation of EFs in the case of higher missing carbon. It is strongly recommended to analyze all data available in the experiment and confirm the amount of missing carbon. This is also a way of evaluation of EF calculation method.

A great benefit of the FLAME-4 experiment was the involvement of many instruments. But this means the results have to be divided among several papers. The changes due to missing C are smaller than we anticipated and so we have noted that slightly different EF appear for these species in other papers because of small changes in the total carbon. Using only the FTIR data in this paper also provides the most direct comparison to the field work. Once all the papers are finished we may explore the idea of recommending final best values, but some EF may eventually get superseded by planned field work anyway so our goal is to make useful data available now.

Specifically we changed "In the case of peat fires, the overestimate of these EF by the CMB because of "missing carbon" is ∼5% and those EF will be recalculated with

higher accuracy after analyzing full mass scans by the PTR-TOF-MS." To "Because of EF dependence on assumed total carbon, slightly different EF will appear in papers (Stockwell et al., 2014; Hatch et al., 2014) describing other instruments. However these differences are only a few percent (except for peat fires where they are ~5%) and insignificant compared to other uncertainties in global BB."

Add following references:

Hatch, L. E., Luo, W., Pankow, J. F., Yokelson, R. J., Stockwell, C. E., and Barsanti, K. C.: Identification and quantification of gaseous organic compounds emitted from biomass burning using two-dimensional gas chromatography/time-of-flight mass spectrometry, in prep., 2014.

Stockwell, C. E., Veres, P. R., Williams, J., and Yokelson, R. J.: 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, Atmos. Chem. Phys., in preparation, 2014.

R2: Page 21, results and discussion, did the fuel moisture measured in the experiment? And is there any relationship found between fuel moisture and MCE, for different fuel types or all 157 burning experiments?

There is some uncertainty in measuring fuel moisture for complex fuel beds where the degree of consumption of different fuel elements is not always trivially measured. We measured fuel moisture for about one-half the burns and only observed weak trends with MCE. We note that McMeeking et al. (2009) also observed a weak relationship between estimated fuel moisture and MCE which didn't offer very useful constraints.

R2: Page 22-23, did you measure CH3Cl in addition to HCl? And in the cited reference, did inorganic HCl measured together with CH3Cl? If not, the comparison between HCl/CO in the present study and CH3Cl/CO in other studies may be difficult to address the question that organic or inorganic Cl is the major form in

biomass burning exhaust.

The cited reference did not measure HCl and the CH3Cl measurements in FLAME-4 have been delayed indefinitely. Therefore we specify that this is an indirect, but still compelling, comparison because of the very large difference.

P23, L4: change "Thus," to "This indirect comparison suggests that"

R2: Page 23 line 24, Is there any relationship found between Cl content and Cl EF.

As discussed, the emission factor of HCl depends on both Cl content and MCE. There may be other relationships, but, if so, we could not clarify them conclusively enough to expand beyond the existing discussion.

R2: Page 28, line 5-10, it is suggested to check and confirm the data from ToFMS, and revise the EFs here, instead of in a later publication, if you had already found 28% of carbon in NMOC.

We now have near-final PTR-TOF-MS data and found that the change to the EF reported here is not that significant so we have deleted this entire paragraph.

R2: Page 31, did the EF of NH3 statistically correlate with N contents of crop residues? what is in HCl EF-Cl content?

The main N emissions are NH3 from smoldering and NOx and HONO from flaming. The distribution of these emissions is complex because it depends on fuel N and MCE as discussed in detail elsewhere (Burling et al., 2011, McMeeking et al., 2009, Fig. 10). We observe higher EFNH3 across a range of MCE in Fig. 11 for the "feed" fuels. We added "at all MCE" after the word "crops" on line 10 to illustrate the general consistency with high fuel N.

Apologies, we don't understand the second comment.

R2: Table 2-3, what is the data shown in parentheses?

In the title of Tables 2, 3, and 5 we added a sentence: "Values in parentheses are one standard deviation."

R2: Fig.1, how did the MCE, or CO/CO2 ratio change over time?

We can't add a third axis to the CO and CO2 plot and having 8 plots seems excessive. Therefore we added "or as a time series" before the Yokelson et al. (1996) reference on P10080, L5 since examples of MCE vs time are shown for several lab fires in that paper.

R2: Fig.3, does "the maximum value" here mean the maximum concentration of each species?

In order to clarify we inserted "by their maximum mixing ratio (shown in legend)" after "normalized"

R2: Fig.8. There is a very large difference found in CO EF from the burning in Philips HD4012. Is there any explanation?

It could be that the other test focused on following manufacturer instructions while we focused on simulating normal use in developing countries. This is just a possibility, but our less efficient combustion may be more understandable and relevant now that we have clarified our approach earlier.

R2: Fig.9, how did the CO/CO2 ratio change over time, and what is the difference in the temporal change of the ratio between the 3-stone and rocket stove?

We have added a short plot of MCE vs time for each of the two cooking stoves in Fig. 9 to further illustrate the dynamic mix of combustion processes.

Also added to text of Fig. 9: "The profiles of MCE versus time are included for both stove types."

Author updates:

We were able to obtain additional subsamples of the Indonesian peat we burned and had additional elemental analysis performed. This slightly changed the elemental data in Table 1 including the average %C for each sample and the range of %C. As a result we revised the EF (Supplement tables and Table 3) and figures (Fig. 6, 7) showing EF, but all the changes were minor.

We've added a legend for CO and CO2 in Fig. 9

We've changed the color of the misc. fuels in Fig. 12 to help the reader distinguish between categories.

In Supplemental tables, we've added captions for each tab. Also reorganized with the addition of OP-FTIR spectral regions as Table S2.

In Table S3, updated the U-Miami contribution to "WAS, cartridges"

L22, P10072 Changed "The emissions from these fires have a large atmospheric influence, but are not yet well characterized (Streets et al., 2003; Yevich and Logan, 2003; Chang and Song, 2010; Lin et al., 2010; Yokelson et al., 2011; Sinha et al., 2013)." To "The fires enable faster crop rotation with less risk of topsoil loss; reduce weeds, disease, and pests, and return some nutrients to the soil, but they are not yet well characterized and have a large atmospheric influence (Streets et al., 2003; Yevich and Logan, 2003; Chang and Song, 2010; Lin et al., 2010; Oanh et al., 2010; Yokelson et al., 2011; Sinha et al., 2014)."

Added reference Oanh et al., 2010 and updated Sinha et al as follows:

Oanh, N. T. K., Bich, T. L., Tipayarom, D., Manadhar, B. R., Prapat, P., Simpson, C. D., and Liu, L.-J. S.: Characterization of particulate matter emission from open burning of rice straw, Atmos. Environ., 45, 493–502, 2011.

Sinha, V., Kumar, V., and Sarkar, C.: Chemical composition of pre-monsoon air in the Indo-Gangetic Plain measured using a new air quality facility and PTR-MS: high surface ozone and strong influence of biomass burning, Atmos. Chem. Phys., 14,

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