Dear Delphine: Thank you for your hard work. Our posted responses to all comments are followed by the complete manuscript with all revisions shown in track changes. Thanks again! Bob

Response to Referee #1

5 We thank the Referee for their encouraging assessment and constructive suggestions, which will improve the paper. The Referee comments are reproduced below followed by our detailed response.

Anonymous Referee #1

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The manuscript "Field measurements of trace gases and aerosols emitted by peat fires in Central Kalimantan, Indonesia during the 2015 El Niño" presents the first field emission measurements of comprehensive atmospheric

- 10 compositions from peat fires burning in Southeast Asia. This kind of field measurements is extremely rare and thus very valuable to the scientific community of Atmospheric Chemistry and Physics. The measurement methods used in the study are well established and the field experiment design is reasonable and justified. I expected this manuscript would only reported emissions from a rarely studied environment (which itself would add values to literature), but the discussion on the representativeness of the field measurements, comparison to previously
- 15 available emission factors for the same type of emissions is very useful too. The authors also compare the field measured emission factors to those obtained from lab experiments, and discuss the value and importance of lab data. Peat fire burning in Southeast Asia is such an interesting and important topic from atmospheric chemistry and climate perspectives but many questions still remain as first order research problems due to the limited field data. I believe the manuscript could be much improved in terms of how to scale the field data to a large spatial area in this
- 20 region, but I understand that the study is also limited by prior data and resource that could be deployed. The manuscript is well written in general, while the readability could be improved by properly introducing acronyms. In summary, I think this manuscript could be published and I list a few minor suggestions as below:

R1.1: The manuscript points the importance and uniqueness of 2015 El Niño event. The authors need to comment on how this field measurements during a El Niño event apply to other 'normal' years, or do the authors suggest that these field measured emission factors can only apply to El Niño events? Can the difference between lab and field comparison be partly explained by the special El Niño event?

Authors: This is an excellent question. The emissions are "possibly" of greatest interest during El Niño years when the "acute" impacts are greatest. For now we can only assume that the emission factors for burning peat (g/kg peat burned) are probably similar in all years, but the total emissions (Tg/yr) are smaller in non-El Niño years when the fire season is not as severe and the amount of peat burned is reduced. However, the summed emissions from several

- non-El Niño years will surely rival the emissions from an El Niño year. We don't know enough about what drives the variability in peat-fire emission factors at this point to speculate whether El Niño will drive interannual variability in peat-fire emission factors or lab/field differences, but we do plan future measurements designed in part to probe geographic and inter-annual differences. We're not sure if we should address these questions in this paper,
- 35 but we now clarify that despite the recent increase in non-El-Niño year emissions, the El Niño year emissions are still anomalously large at P3, L19:

Old text: "With accelerated deforestation and building of drainage canals (e.g. 4000 km of canals as part of the Ex Mega Rice Project (EMRP) started in 1996 (Putra et al., 2008; Hamada et al., 2013)), peat fires and their impacts are now extensive on an annual basis (van der Werf et al., 2010; Wiedinmyer et al., 2011; Gaveau et al., 2014)."

40 New text: "With accelerated deforestation and building of drainage canals (e.g. 4000 km of canals as part of the Ex Mega Rice Project (EMRP) started in 1996 (Putra et al., 2008; Hamada et al., 2013)), peat fires and their impacts are now extensive on an annual basis (van der Werf et al., 2010; Wiedinmyer et al., 2011; Gaveau et al., 2014) and even more pronounced in El Niño years (Huijnen et al., 2016)."

Regarding the difference between lab and field results, while the 2015 El Niño explains larger overall emissions, the lab/field comparison is based on emission factors (g/kg) relative to units of peat burned, and as a result we believe the comparison should be useful.

R1.2: Related to point 1: This manuscript finds that many significant revisions of emission factors compared previously widely used EFs, mostly reductions (CO2, CH4, NH3). But as the authors point in the introduction, previous studies suggest "in Southeast Asia, in the 1980s-1990s, peatland fires were a major source of carbon to the atmosphere mainly during El Niño induced droughts : : .: " How can the authors reconcile this? The manuscript uses

10 "the 2015 El Niño" in the title, and the authors would be expected to comment more on this event. However, such comments are very rare in this version of the manuscript.

Authors: We think the Referee is wondering if we mentioned El Niño in the title because we think El-Niño changes the chemical nature of emissions. Our inclusion of El Nino in the title was just to point out the data was collected in a year responsible for a large fraction of the total emissions from the region on a multi-year time-scale. I.e. we went

in a year when the conditions were associated with more emissions than most other years. This doesn't prove the data is more relevant, but it is a good choice in case the peat-fire emission factors do change inter-annually. Hopefully this is clear now that we clarify (as described above) that the largest "acute" impacts occur in El Niño years.

R1.3: P5 L14: the definition of fuel moisture is not clear. What is 'wet', what is 'dry'? Here and many places in the
manuscript, the authors assume all readers know most of acronyms related to fire studies. Properly introducing them
could help the manuscript reach a broad audience of atmospheric scientists.

Authors: Thank you for this comment. We have changed text to read: "Peat deposits can burn at > 100% fuel moisture (defined as $100 \times (wet-dry)/dry$)), where "wet" refers to the weight of a fresh fuel sample and "dry" refers to the fuel weight after oven drying until mass loss ceases. This is because the glowing front pre-dries the fuel as it advances."

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R1.4: P7 L29: 'cyclones' should be 'cyclone samplers'? The authors need to avoid using 'field language' as much as possible and try to use its formal name.

Authors: Changed (P7, L31 in the revised text).

R1.5: P8 L15: poorly written.

30 **Authors:** We made this more definitive by changing to: "Styrene is known to decay in canisters and the styrene data should be taken as lower limits."

R1.6: P8 L21-22: here and other places, the instrument modes and manufactures should be listed as full names with company names and locations.

Authors: We added this information here and in many other places. In just a few cases we skipped to avoid overly long sentences since the supplied info is enough to locate further info on the web.

R1.7: P 9, session 2.2.5: it is unclear if any control (or blank) samples were deployed for these offline measurements? For example, pre-cleaned filters shipped with other filters but without any sampling.

Authors: We did collect field blanks, but since we elected to subtract background filters from source sample filters the field blank correction cancels mathematically. I.e. S-B = (S-c) - (B-c) = S-c-B+c. At P10, L10 we added:

"While field blanks were collected, subtracting the background from smoke samples made the field blank correction unnecessary."

R1.8: P13 L13-15: it would be very valuable if those peat characteristics were mapped and it could help to scale these point measurements to large areas and perhaps devise a parameterization to study other peat fire emission. It is very unfortunate that this study did not attempt such an analysis. What would be the authors' recommendations to future field studies? It would be useful for other researchers who are interested in this area.

Authors: We agree this is a logical, important thing to wonder about and that is why we mentioned it. However, we are not sure if there are peat characteristics that correlate with emission differences. We also don't know how well characteristics such as peat type, moisture, etc could be mapped in 3-D along with burn depth. If these connections

10 exist and could be mapped/scaled it would require a substantial additional study. Another Referee questioned the relevance of this inconclusive text so we ultimately deleted it.

R1.9: P15 L 36: what is 'rapid green-up'. Again, the manuscript could be improved and reach a broader audience if these words were properly defined.

Authors: "Green-up" is a forestry term to describe the emergence of fresh new vegetative growth, which is "green"
rather than the "black" as might be expected for a burn scar, or "brown" due to a drought, etc. We changed "rapid green-up," to "rapid growth of new vegetation,"

Response to Referee #2

We thank the Referee for their encouraging assessment and constructive suggestions, which will improve the paper. The Referee comments are reproduced below followed by our detailed response.

20 Anonymous Referee #2

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Review of "Field measurements of trace gases and aerosols emitted by peat fires in Central Kalimantan, Indonesia during the 2015 El Niño", by C. E. Stockwell et al., 2016. The manuscript by Stockwell et al. presents measurements from 2015 peatland fires in the Indonesian province Kalimantan. The findings presented in this manuscript both add to and modify previous lab-based measurements of peat combustion, amending a handful of

25 key EFs that were previously only available from laboratory studies, while confirming the validity of laboratory studies for estimating EFs for species that are not easily measured in the field. The paper is well-written, cohesive and thorough, and my assessment is that it merits publication in ACP after the following issues are addressed.

Specific Comments

R2.1: Page 2, line 19 – "(2012)" - is that a reference? It should be included properly here.

30 **Authors:** We found "(2012)" on P2, L8. The year of the recent measurements was included because our field data did not agree well with the lab measurements made in 2001 that IPCC uses, but did agree well with lab measurements made in 2012. It's probably safe to delete the year and we have done so.

R2.2: Page 4, line 32 and Page 19, line 10 – I don't think it's necessary to put "in preparation" here – it is included
in the reference itself. However, please include a full reference for this work if possible, including a full author list and title.

Authors: We removed "in preparation" throughout and updated the reference as suggested.

R2.3: Page 5, lines 11-12 – please explain what n=1 is in reference to, or simply state, if this is the case, that there was only a single sample of each type analyzed in the lab study.

Authors: Within both parentheses we changed "n=1" to "one sample"

R2.4: Page 5, line 33 – it would be helpful to the reader to direct them to Table S1 at this point, rather than making them wait to find out about the table until the next page. **Authors:** Good suggestion and we now call out Table S1 earlier on P5, L27.

5 **R2.5:** Page 6, lines 4-25 – a map/diagram of the sites would help put this entire sampling description into context. **Authors:** A site map has now been provided as Supplementary Figure 2 (now referenced on P6 L4).

R2.6: Page 12, lines 20-25 – where are the ERs if I want to look at them? A lot of this discussion is very qualitative and vague (i.e. "seven of these nine cases agree: ::" – what about the other two? And what were they? It would

- 10 seem reasonable to spell that out or offer something specific about the differences between the FTIR and the WAS sample that would alleviate the reader's concern that there is something we should know about the alleged differences. I understand that the analysis were not set up to evaluate differences, and yet to just allude to it but not give us anything further is more suspicious.
- Authors: This is an excellent comment and we considered adding this comparison to the supplement in response.
 For background, we had two WAS cans that the field notes indicated were filled from the FTIR cell. While changes could theoretically occur to some species during storage in the FTIR cell, this seemed like a valid opportunity to compare the data for the overlap species fairly directly. Unfortunately, in attempting to further clarify this comparison, we have now realized that the FTIR cell was actually re-filled after the FTIR measurements and before
- the cans were filled. Thus, the comparison included an unknown contribution from natural plume variability and was not semi-rigorous after all so we have deleted this text. Ideally we would be able to compare overlapping techniques at least semi-rigorously and often we have in previous studies. For instance, most recently in Hatch et al. (2016), the WAS vs FTIR slope for overlap species that were nearly the same as in this study was 1.01 ± 0.001 , $r^2 = 1.0$. Unfortunately, the resources we could import to the field were limited and we did not perform conclusive tests. We have made the following changes to the text.
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Old text: "There were nine instances when the same gas was measured by both WAS and FTIR in nearly the same place and seven of these nine cases agree within the combined uncertainty. The other two cases are less close, but this experiment was not well-designed for comparison. We have noted excellent WAS/FTIR agreement previously under more rigorous, but drier conditions (Christian et al., 2003) and we found that these 2015 field WAS results compared well with on line measurements during FLAME 4 neat fire sampling for many major species as discussed

30 compared well with on-line measurements during FLAME-4 peat fire sampling for many major species as discussed later in the paper."

New text: "This experiment was not well-designed for comparison, but we have noted excellent WAS/FTIR agreement previously under more rigorous, but drier conditions (e.g. Christian et al., 2003; Hatch et al., 2016) and we found that these 2015 field WAS results compared well with on-line measurements during FLAME-4 peat fire sampling for many major species as discussed later in the paper."

Hatch, L. E., Yokelson, R. J., Stockwell, C. E., Veres, P. R., Simpson, I. J., Blake, D. R., Orlando, J. J., and Barsanti, K. C.: Multi-instrument comparison and compilation of non-methane organic gas emissions from biomass burning and implications for smoke-derived secondary organic aerosol precursors, Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-598, in review, 2016.

R2.7a: Page 12, lines 33-35 - many of the uncertainties are unreasonably precise -i.e., 0.867 ± 0.479 and 0.860 ± 0.433 . Please round these to make them more reasonable for reporting.

- 45 Authors: We have rounded uncertainties in cases where the level of significance did not match (e.g. propylene 1.07 \pm 0.531 now changed to 1.07 \pm 0.53). However we like to report our results with any potentially useful amount of digits for several reasons that include minimizing round-off error if the number is used by others. The variability should be propagated for all terms used in any calculations done with these numbers and reported along with the result to avoid misleading uncertainties.
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R2.7b: Page 13, lines 2-3 the "overlap" isn't very surprising, considering that the range in your work is from 0.3 to 1.44. Overlap isn't hard, and likely shouldn't be emphasized like this. "Are consistent", perhaps. **Authors:** We did not mean to imply overlap between a variable data set and a single point is difficult, but it is a typical reality check in comparing sets of data. A lack of overlap would imply serious questions about the relevance.

55 We changed: "which overlaps with" to "roughly consistent with" – hopefully the point that significant emissions of large alkanes likely occur from real peat fires is made.

R2.8: Page 13, lines 10-15 – I'm not fond of the idea of alluding to something that should be done, and then just saying "we haven't attempted this yet." Why bring it up? Or why not attempt to include the analysis here? **Authors:** Referee #1 also commented on this. Our thought in including this was that the reader would wonder if

- 5 peat characteristics correlated with emissions and that therefore mapping peat characteristics would improve estimates. We wanted to point out that we don't see a way forward. However, as the Referee points out we can just delete it this text, which is what we have done.
- R2.9: Page 14, lines 5-16 I have issues with this plot, and with the implication that the overlap in time is so
 fortuitously going to take something with 7 points, eliminate 3, and leave you with a four point plot that has an r² of 0.674, and that you're going to give it any actual credence. I don't think you "confirmed" the MAC near 0.1 at all. You just eliminated points until the remainder of your points came slightly close to giving you a line. This either needs far more justification, or it shouldn't be included.
- Authors: Figure 3 shows that the emissions may change with time so looking at the ratio of absorption to mass from data collected at the exact same time is important to consider and gives the value from the plot of 0.071 ± 0.03 . If we relax our time-overlap restriction to tap into more data and compare all data as a straight average (a plot would have low r²) we get nearly the same number 0.09 ± 0.08 . These values overlap within uncertainty and because the mass measurement has a larger size cut-off, both approaches imply a MAC value "near 0.1" – note that in this case we restrict ourselves to one significant figure as we are not quoting a measured uncertainty. As with the MSE estimate,
- 20 we get similar values using just the perfectly overlapped data as we do with using all the data. To remind the reader why we considered temporal overlap in a dynamic environment we made the following change: Old text: "If instead we plot EF $B_{abs-405}$ versus EF OC just for the four plumes sampled over the exact same time period (but different size cutoffs; blue points in Fig. 6) we get a slope of $0.071 \pm 0.03 \text{ m}^2/\text{g}$." New text: "Keeping the dynamic nature of the emissions chemistry shown in Fig. 3 in mind, if we restrict our
- 25 analysis to the same four plumes where sample timing was identical (but different size cutoffs; blue points in Fig. 6) and plot EF $B_{abs-405}$ versus EF OC we get a slope of $0.071 \pm 0.03 \text{ m}^2/\text{g.}$ "

R2.10: Page 14, line 36 – please comment on the differences between the Liu et al. paper using SSA 781 and you using SSA 870 nm, and what kind of linearity you expect for the two different locations, and how that affects your

30 comparison. Also, this comparison of the observed aerosol parameters with literature values would benefit from having a table like S3 included.
Authors: At both 781 and 870, the absorption by BrC should be very small so the high SSA is consistent with minimal BC emissions. The amount of data available to compare here is limited and so we have elected to present this in the text rather than adding a very small table in the supplement. We did reformat the text to make it easier to

35 read.

Old text: "Turning to optical properties, Liu et al. (2014) reported some SSA values and the AAE for smoldering Kalimantan peat (Fire 114) from FLAME-4: MCE (0.74), SSA 405 (0.94), SSA 781 (1.00), and AAE (6.06). These are very consistent with our data (Table 2) and especially with our lowest MCE field sample: MCE (0.726), SSA 405 (0.941), SSA 870 (0.997), and AAE (6.23)."

New text: "Turning to optical properties, Liu et al. (2014) reported some SSA values and the AAE for smoldering Kalimantan peat (Fire 114) from FLAME-4: MCE (0.74), AAE (6.06), SSA-405 (0.94), and SSA-781 (1.00). These are very consistent with our data (Table 2) and especially with our lowest MCE field sample: MCE (0.726), AAE (6.23), SSA-405 (0.941), and SSA-870 (0.997)."

The requested comment on the comparison was added a few lines further down: "BrC absorption is very small at both 781 and 870 nm so the high SSA at the long wavelengths in both studies and similar AAEs are consistent with minimal BC absorption and dominant absorption by BrC."

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R2.11: Page 15, line 36 – "and other factors" is very vague. Please expound. Authors: Quantifying the amount of fire emissions is extremely challenging, especially for peat fires and in SE Asia, as discussed at length in the cited reference by Reid et al. In bottom-up approaches, fires and burned area are missed due to cloud cover, which approaches 90% on average in SE Asia and also due to an aggressive "cloud mask" that

rejects smoky pixels. MODIS only scans areas near the equator 2 out of every 3 days and at the edges of the scans the resolution is degraded to about 6 km, which misses numerous small, smoldering peat fires even if clouds (and

canopy) don't interfere. In top-down (inverse modeling) approaches, fires and burned area can be underestimated due to the same factors above and general uncertainty is added due to problems such as uncertainty in air mass factors, emission factors, smoke injection altitude, meteorology, and the evolution of species used as constraints. Thus, most often the initial amount of fire emissions in inventories needs to be increased in models by factors of

- 5 ~1.5-10 to match observations. Some of many examples of this adjustment procedure include Lu and Sokolik (2013), Reddington et al. (2016), and extensive references cited within these papers. Rather than a long digression in the paper, we have edited this sentence and added more references showing that a-priori fire emissions are usually too low.
- 10 Old text: On the other hand, burned area is likely underestimated in inventories since they rely on remote sensing data that misses hotspots, burned area, and the fire products used in top-down approaches. This is due to high regional cloud cover; orbital gaps; rapid green-up, which is strongly associated with shallow burn depth (Cypert, 1961; Kotze, 2013); and other factors (Reid et al., 2013). Thus, overestimating burn depth and underestimating burned area tend to cancel.

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New text: On the other hand, burned area is likely underestimated in inventories since they rely on remote sensing data that misses some of the hotspots and burned area used in bottom-up estimates, as well as some of the fire products (e.g. CO, aerosol) used in top-down approaches. The information gap is caused by high regional cloud cover; orbital gaps; rapid growth of new vegetation, which is strongly associated with shallow burn depth (Cypert,

20 1961; Kotze, 2013); and other factors (Lu and Sokolik, 2013; Reddington et al., 2016; Reid et al., 2013). Thus, overestimating burn depth and underestimating burned area tend to cancel when coupling these terms to estimate fuel consumption.

Lu, Z., and Sokolik, I. N.: The effect of smoke emission amount on changes in cloud properties and precipitation: A
 case study of Canadian boreal wildfires of 2007, J. Geophys. Res., 118, 11777–11793, doi:10.1002/2013JD019860, 2013.

Reddington, C. L., Spracklen, D. V., Artaxo, P., Ridley, D., Rizzo, L. V., and Arana, A.: Analysis of particulate emissions from tropical biomass burning using a global aerosol model and long-term surface observations, Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-967, in review, 2016.

R2.12: Page 16, line 13 – you "interpolated" between two points to find something. How did you do this? Was it linear? Why? How do you know?

Authors: We don't have any data or theory to support anything other than a simple linear interpolation and we now specify that this was what we did.

Old text: This is close to our 530 nm value if we interpolate between 870 and 405 nm (0.981).

New text: We can estimate an SSA at 530 nm by linear interpolation between 870 and 405 nm and obtain a similar value (0.981).

R2.13: Page 15-16, Section 3.3. This section feels very hand-wavy. I would like to see a more quantitative and stepwise analysis presented for the comparisons mentioned to previous studies and other kinds of peat BB observations in this paragraph. Some of the comparisons mentioned are presented with little defense as to their relevance and/or the validity of the comparison (i.e., the interpolation mentioned above.)

- 45 the validity of the comparison (i.e., the interpolation mentioned above.) Authors: There are very little data to compare to so we compared to everything with any relevance. In addition, we have now added comparisons to two more papers that came to our attention after we submitted our paper (and we updated the text and Table S3 to reflect this). Hopefully by addressing the specific comments and adding these new comparisons this section will be more useful. Even if we cannot address the comparisons in this section as
- 50 conclusively as might be liked, representativeness is an important issue and we have attempted to raise and discuss it to the extent possible.

P16, L30 (end of section 3.3) added text: "Two very recent studies probed peat fire emissions during the 2015 El-Niño. Huijnen et al. (2016) measured three EFs for peat fires also near Palangkaraya. Their "peat-only" EFs are 255 \pm 39, 1594 \pm 61, and 7.4 \pm 2.3 g/kg for CO, CO₂ and CH₄, respectively. Their means are all within one standard deviation of our means and their EFs are within +1.9, -13, and -22% percent of ours, respectively. Not many details of the measurements are given, but the agreement is good. Parker et al. (2016) report three space-based measurements of the ER for Kalimantan fires in Sept-Oct 2015 for CH_4/CO_2 ranging from 0.0062 to 0.0136. This is lower on average than the CH_4/CO_2 ERs reported for peat combustion in the in-situ studies cited above (range ~0.011 – 0.035). The difference is consistent with our expectation noted above that some flaming-dominated

- 5 consumption of surface fuels likely contributed to regional emissions in 2015. However, a glance at Figure 6 in Parker et al. (2016) shows that some of highest retrieved levels of these gases, which they attribute to fires, are far off-shore and/or upwind of the fires. Thus, more evaluation is clearly needed to determine if space-based approaches can accurately measure CH_4/CO_2 ERs (e.g. Agustí-Panareda et al., 2016)."
- 10 Agustí-Panareda, A., Massart, S., Chevallier, F., Balsamo, G., Boussetta, S., Dutra, E., and Beljaars, A.: A biogenic CO₂ flux adjustment scheme for the mitigation of large-scale biases in global atmospheric CO₂ analyses and forecasts, Atmos. Chem. Phys., 16, 10399-10418, doi:10.5194/acp-16-10399-2016, 2016.

Huijnen, V., Wooster, M. J., Kaiser, J. W., Gaveau, D. L. A., Flemming, J., Parrington, M., Inness, A., Murdiyarso,
D., Main, B., and van Weele, M.: Fire carbon emissions over maritime southeast Asia in 2015 largest since 1997,
Scientific Reports, 6, 26886, doi:10.1038/srep26886, 2016.

Parker, R. J., Boesch, H., Wooster, M. J., Moore, D. P., Webb, A. J., Gaveau, D., and Murdiyarso, D.: Atmospheric CH_4 and CO_2 enhancements and biomass burning emission ratios derived from satellite observations of the 2015 Indonesian fire plumes, Atmos. Chem. Phys., 16, 10111-10131, doi:10.5194/acp-16-10111-2016, 2016.

R2.14: Page 17, line 33 - "the lab value is actually the sum of isomers compared to a single isomer from the GC analysis: : :" please explain this more, including references to the table, in which I see no evidence of a difference between a sum of isomers and a single isomer. Is this for a particular compound or set of compounds? Be specific.

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Authors: This is a very helpful and important comment. One thing that was clear in the FLAME-4 papers, but we failed to specify in this paper was that the mass spec assignments in the lab study were "nominal" in some cases: or in other words a best guess at the most abundant species when many isomers could contribute. For example, mass 137.132 in the lab studies was calibrated with alpha-pinene and shown as that compound in Table S3, but there are

30 numerous isomers that have the same exact mass (Hatch et al., 2015; 2016). In addition, fragments of higher masses can contribute to the mass spec signals. Thus it is not surprising that the lab MS value for all of mass 137.132 is much larger than the field WAS value more specific to alpha-pinene. In addition, one of the FLAME-4 PTR-TOF-MS calibrations was just revised based on the work described in Hatch et al., (2016). Thus, we have revisited this in detail. We have revised the text and the species impacted by isomers are now clearly flagged in Table S3.

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P17, L30: Old text: "Table S3 compares all 31 gases measured for Kalimantan samples in both the lab (FLAME-4) and the field. The average of the two lab EFs is within a factor of two of the field mean for 20 of 31 species, which is adequate given that a factor of two is essentially also the field coefficient of variation (n = 35). In 7 of the 11 cases with more than a factor of two difference, the lab value is actually the sum of isomers compared to a single isomer

- 40 from the GC analysis of the field WAS samples. For the remaining 4 species the lab values tend to be higher for unclear reasons. For instance formic acid is higher in the lab where an open-path system was used instead of the closed cell system in the field, which could be subject to sample losses. However, HCl and NH₃ are likely more prone to adsorption than formic acid (Yokelson et al., 2003) and they were higher as measured with the field system suggesting the Teflon sample line and coating on the closed cell were effective in limiting line losses. The lab
- 45 average for NO is higher, but NO was below detection in one lab fire and high in the other where flaming briefly occurred. The one field fire where flaming was briefly observed (Plume C, Table S2) had a higher EF for NO than the lab fire where it was detected. Thus, further comparisons with more lab fires will clearly be useful, but it appears the trace gas EFs from the lab are reasonable proxies for the EFs for species that have not been measured in the field"

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New text: "Table S3 compares all 31 gases nominally measured for Kalimantan samples in both the lab (FLAME-4) and the field. (We clarify the need for the term "nominal" below.) Due to the natural high variability in the field data, the low number of lab measurements (two), the use of different peat samples, etc., we start by proposing that the lab measurements provide useful EFs for species not measured in the field if the average of the two lab EFs is

⁵⁵ within a factor of two of the field mean for species measured in both locations. Next, we find in the right-hand column of Table S3 that 15 of 31 species fail this initial factor-of-two test (ratios shown in red). However, this result

is somewhat misleading since the lab data for 8 of these species (shown in blue) is actually comparing a best guess at the identity of the most abundant isomer for an exact mass measured in the lab to a WAS-based analysis for a specific isomer. Thus, these ratios could be larger than two because of contributions from other isomers (or fragments) to the mass spectrometer signal, higher than normal sensitivity in the mass spectrometer, WAS error, or

- 5 unusually high variability for some species; with no way of knowing the individual contribution of these factors. We do note that a generally good comparison of the WAS and mass spectrometer was obtained when they were compared more directly in peat smoke in the lab (Hatch et al., 2016). Thus, only 7 out of 23 compounds fail the factor-of-two test, if we eliminate species that are ambiguous due to isomers. Of these 7 species, three are very close to the factor-of-two cutoff and are of less concern (ammonia, acetaldehyde, and hydroxyacetone). For the remaining
- 4 species (formic acid, NO, 1,3-butadiyne, styrene) the lab values tend to be higher for unclear reasons. For instance 10 formic acid was higher in the lab where an open-path FTIR system was used instead of the closed cell FTIR system in the field, which could be subject to sample losses. However, HCl (below detection in lab) and NH₃ are likely more prone to adsorption than formic acid (Yokelson et al., 2003) and they were higher as measured with the field system suggesting the Teflon sample line and coating on the closed cell were effective in minimizing losses and
- sampling losses were not the source of the discrepancy. The lab "average" for NO was more than four times higher 15 than the field value implicating high variability. NO was below detection in one lab fire and "high" in the other lab fire where flaming briefly occurred. The one field fire where flaming was briefly observed (Plume C, Table S2) had an even higher EF for NO than in the lab fire where it was detected. The other two species of concern are styrene and 1,3-butadiyne. These two ratios could be high due to decay in the canisters, fragments in the mass spectrometer,
- 20 or perhaps other less likely reasons. In summary, more lab/field comparisons should be carried out, but our rough analysis suggests that trace gas EFs measured in the lab are useful estimates (i.e. within a factor of two) for the emissions of most gases not yet measured in the field."

R2.15: Page 18, line 14 – you should reassure the reader that the 37% of unidentified or tentatively assigned mass 25 peaks of the NMOG mass is not going to negatively affect your assumption that you are measuring all the carbon to be factored into your EF calculations. I'm sure it's not significant, considering the major non-NMOG carbon species, but this should be recognized.

Authors: P19 L 33-35 we added: "The missing NMOG mass in the field measurements is not large enough to cause significant error in our field carbon mass balance, but would impact estimates of secondary formation of aerosol and O₃ (Yokelson et al., 2013; Hatch et al., 2015)."

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R2.16: In Table 1, Table 2, Figure 1, etc., there are numbers that are both too precise considering the standard deviations reported, and I dislike the excel-style presentation of numbers with exponents written as (e.g.) 1.67E-3. Authors: We have changed the tables so they are no longer in the excel-type format. . The number of figures in the

35 table values is to avoid round-off error, though we have changed values where the significant figures did not match: e.g. CH3I, 0.0125(0.00448) corrected to 0.0125(0.0045).

R2.17: Re: Table S1 – there are a handful of things that would make this table easier to digest, without having to search out other information.

Authors: We have italicized the Referees suggestions in the rest of this comment and reply point by point in un-40 italicized text.

Instead of "Y/N type" or "Y/N what" as a header, eliminate Y/N and just include the type/what or put "none" or "unknown" where applicable.

45 Au: Done.

50

Also, please spell out here what the peat fuel types are, so that I don't have to go back and find that in the paper (in *the footnote would be fine.*)

Au: They are now spelled out in each cell.

"day-mon" should be "DD-Mon". Au: Done.

Why are there some plumes included that aren't lettered? These don't seem to add anything to the paper.

55 Au: The unlettered plumes represent occasions when it was possible to quickly collect a WAS canister, but not deploy all the instruments. These samples add important emissions information.

"seec" is not a word or a shortform (as a direction). Au: *"seec" was changed to "sec"*

5 *For Depth of Burn, " site avg" is redundant. "site avg" is fine.* Au: We changed to "approx. site avg" and deleted the "~" where they appeared before entries.

Why is so little known about site 6?

Au: The team member collecting site data was unable to participate on the last day of the field campaign. The emissions team was able to collect some data.

Re: Winds – "av, max, dir" implies you'll have numeric values below. Maybe leave the "av, max, dir" part out, and just consider it a verbal description of the winds. Au: Done.

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Be consistent with spacing and vertical cell centering. Au: This was checked.

Also, for all three supporting information tables (S1-S3), please be consistent about font size and styles and remove bold settings.

Au: The journal has requested that we use 9 pt Times New Roman with bold headings for our print tables and we assumed they want that for the supplement as well. However, Table S1 was clearly outside the normal journal format so we changed the font and font size to optimize readability.

25 *Table titles should all be uniformly sized.* Au: Please see above.

For all supplement tables, if these are being submitted as they are now in an excel file, a san serif font is likely best for readability. If you're preparing a printed document, a simple serif font is also acceptable (i.e., Times New Roman.)

Au: We have been asked to use Times New Roman 9 pt for tables by the journal so we did that. On Table S1 we used a more readable font since it is clearly a non-standard table.

Referee #2 (Continued) Technical Comments

R2.18: Page 5, lines 4-5 – don't us semicolons in place of commas.
 Authors: We separated the items in the list with semi colons because one item has multiple terms separated by commas: "...; charred logs, char, and ash from previous burns;"

R2.19: Page 5, line 26 – remove the hyphen from "at six-different peatland: : :" **Authors:** removed

R2.20: Page 6, line 10 – no need for "(#2)" after "This site: : :" **Authors:** deleted

45 **R2:21:** Page 11, line 12 – there is a missing or extra parenthesis here. **Authors:** The first "(" was deleted and now reads " $1/(1+\Delta CO/\Delta CO_2)$ "

R2.22: Page 18, line $28 - 0.35 \pm 1 \times 10$: 0.10 ± 0.10 . Authors: fixed

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40

R2.23: Page 19, line 1 – "Six of the nine: : :" **Authors:** changed to "six of the eleven"

R2.24: Page 19, line 11 – the Putra et al. paper in preparation needs to be included in the reference list.
 Authors: added

R2.25: Tables 1, S2 and S3: "ethyne", "ethene", "propene" (and in the text and Figure 1, where applicable). **Authors:** We think the common name for these species and many others (e.g. formaldehyde, formic acid, methanol and many more) is more or reasonably common, but added the requested formal names in the parentheses with the formula at the first appearance of these species in the text (P7).

Response to Referee #3

We thank the Referee for their encouraging assessment and constructive suggestions, which will improve the paper. The Referee comments are reproduced below followed by our detailed response.

10 Anonymous Referee #3

5

This paper presents results of a field campaign measuring emissions from burning Indonesian peat in-situ, during the intense burning during the intense 2015 El Nino event. These very challenging measurements were collected with mobile sampling set up incorporating FTIR to measure a range of gas phase species, several photoacoustic extinctiometers to measure aerosol light absorption and scattering at two wavelengths and filter and canister

15 samplers to collected integrated samples of condensed- and gas-phase species, respectively. 35 separate plumes were measured with different combinations of instruments, resulting in measurements constraining both the central tendency and the (relatively large) variability in emission factors resulting from combustion of this fuel.

As evidenced by the startlingly high PM concentrations (>3000 ug/m3) observed in nearby cities, peat combustion can and does make an enormous contribution to loadings of atmospheric aerosols and a wide range of gas-phases

- 20 species. Considering that the only extant emission factors come from a handful of laboratory burns, which a) do not capture the potential variability in emissions and, ,b) may not recreate combustion conditions observed when the fuel is in place, there is great value in the results of this study. The measurements of gas and aerosol species and aerosol optical properties appear to be carefully conducted and are well documented in this manuscript, and I particularly applaud attention to uncertainty in measurements and the resulting propagated uncertainty in EFs
- 25 (though echo the other referees' comments concerning their presentation in tables). A rather extensive effort is made to compare the results with those measured in earlier lab measurements, showing general consistency but some very significant differences. The resulting emission factors will be of great use for emission inventory development and chemical transport modeling to understand the impacts of the dramatic land use transformation taking place in this region. Therefore, the manuscript is certainly suitable for publication in ACP. Below I list several points of
- 30 clarification that would enhance the readability and utility of the manuscript.

R3.1: One general comment is that there is a relatively large number of portions of the text that seem overly detailed and make the paper harder to read than it might otherwise be. Ideally, these could be moved to an online supplemental section. While I understand the use of a spreadsheet for the supplement in this case, perhaps a second file could be used or some of these details moved to aid readers. Examples include: P. 6, L1-25 (description of

35 sampling sites), P. 8, L22-28 (description of PAX operating principle), P. 10, L20-28 (description of alternate data reduction approaches).

40

Authors: There are two schools of thought on whether to include details in the main paper, which lengthens it, or in a supplement where they may be ignored. The Referees have done an excellent job of reading the entire paper in detail, and while we agree with the Referee, the suggested supplement content would be a bit fragmented and have the unwieldy task of containing both text and spreadsheets. Thus, we prefer to skip this suggestion.

Minor Points:

R3.2: P9, L23-24 – This description is not clear and imprecise; for example, what is the standard deviation of smoke PM? I think I understand this to be the standard deviation of PM mass concentration, but since this is from a single filter, how is a standard deviation determined? And why is 10% of PM concentration used?

Authors: The standard deviation corresponds to the standard deviation of three replicate measurements of filter preand post-weights. The inclusion of 10% of the PM mass is a conservative estimate of the analytical uncertainty in this measurement. The reasoning is, the standard deviations of the filter weights and background PM are very small (ug). For filters with high mass loadings, the absolute error estimated on standard deviations alone would be very small (<0.1%), so we add in this relative error.

To clarify, we changed this text to read: "Uncertainty in the excess mass in the smoke plumes was propagated using the standard deviation of triplicate measurements of pre- and post-sampling filter weights, the standard deviation of background PM masses, and 10 % of the PM mass concentration, which is a conservative estimate of the analytical error associated with this measurement."

R3.3: P12, L3-4 – this is imprecise, BC does not absorb light 'proportional to frequency'.

Authors: To a first approximation sp2 hybridized carbon (including BC) absorbs light proportional to frequency
 (e.g. <u>https://en.wikipedia.org/wiki/Aethalometer</u>), which is mathematically equivalent to the more common statement that BC has an AAE of one (Bond and Bergstrom, 2006).

R3.4: P12, L25 – Unclear. What is meant by 'less close', and what do you mean 'not well-designed for comparison'?

Authors: This text has been deleted as explained in the response to Referee #2.

20 **R3.5:** P13, L11-12- While I get what you're saying, this is also imprecise. It doesn't necessarily follow that fires with both smoldering and flaming will have a linkage between MCE and EFs. I think what you mean is that in cases where you have a wider range of MCEs you tend to see a (anti) correlation between MCE and EFs, but the small range of low MCEs observed here means you don't see such a trend.

Authors: Good point. The MCE range is small, but more importantly, it is shifted below the range where it would
 help indicate the mix of flaming and smoldering, which have different products. We have changed the text as follows.

Old text: "For most biomass fires there is both flaming and smoldering and so EFs correlate with MCE, but these fires burned by smoldering only with no high MCE values (e.g. >0.9) and little or no correlation of EFs with MCE."

New text: "For most biomass fires there is both flaming and smoldering combustion and EFs for flaming compounds
 are observed to correlate with MCE while EFs for smoldering compounds (most NMOGs) tend to be anti-correlated with MCE (Burling et al., 2011). However, these fires burned by smoldering only with no high MCE values (e.g. >0.9) and little or no dependence of EFs on MCE was observed."

R3.6: P13, L13-14 – Awkward sentence, what would such characteristics be?

Authors: As noted in our response to the other Referees, we did not note a clear dependence of EFs on any peat
 characteristic. We also did not have very good capabilities to characterize the peat or map the peat types, so rather
 than discuss this in detail we have just deleted the text.

R3.7: P13, L18-19 – This evolution in the absorption in this plume seems to be also linked with CO emissions, with Bap(405nm) and CO very tightly correlated in the early stage of the burn, and much less so later on. Were stages of combustion typically seen? Is there any somewhat consistent trajectory in emissions during a burn? I assume that

because you measured a relatively large number of plumes that you captured emissions from a range of stages, but it would be interesting to learn of any consistency to give some insights into how laboratory tests can be more representative of combustion observed in large fuel beds in-situ.

Authors: Good point. Babs-405 and CO are actually tightly correlated throughout the sampling, but the ratio of 5 Babs-405 to CO decreases towards the end, which is consistent with an increase in the glowing to pyrolysis ratio. We're not sure what the most representative mix of these processes is, but hope we captured it with our sample size. To acknowledge this signature of the types of smoldering we added text at P13, L21: "Babs at 405 and CO remain correlated, but the ratio of Babs at 405 to CO decreases towards the end of the 5 Nov data, which is consistent with an increase in the glowing/pyrolysis ratio (Yokelson et al., 1997). Variation in the mix of these smoldering processes

10 likely causes some of the variation in EFs."

30

R3.8: P14, L3-4 – 'obtained closer to 500 nm' is unclear, presumably this refers to illumination wavelength? Would be best to make these MSE values more directly comparable if at all possible.

Authors: We changed "Either value of the MSE is close to MSEs obtained closer to 500 nm" to "Either value of the MSE is close to MSEs obtained at illumination wavelengths in the range 532 - 550 nm."

- 15 On the comparison: We have data at 405 and 870 nm and most of the literature MSE values are at wavelengths such as 532 or 550 nm, which is much closer to 405 nm than 870 nm. We have seen (and discuss) SSA measurements for peat aerosol at 781 nm, which is close to 870 nm and, having some idea that it was reasonable, we estimated an SSA at wavelengths between our data. We have not seen MSE measurements for peat aerosol at 405, 781 or 870 nm and are not confident about how to interpolate or otherwise estimate a value closer to 540 ± 10 nm based on our data.
- 20 R3.9: P15, L16-18 – This sentence is very hard to read/understand. Overestimated by what, relative to what?

Authors: There is a tendency to time field campaigns to capture peak behavior, which makes sense, but that is not the only valid time to sample. We changed: "should not be overestimated" to "is difficult to estimate"

R3.10: P15, L33 – Not sure what is meant by 'significant areas' or 'deep burn depth'. Please clarify.

Authors: Upon reflection, this sentence just repeated the point of the previous sentence, which was that our measured burn depths are too high for some burned areas. We've deleted the sentence. 25

R3.11: P15, L35 – What is distinctly wrong about 'fire products used in top-down approaches'? This sentence is unclear.

Authors: We explained and modified the text as described in response to Referee #2. Briefly, in top-down (inverse modeling) approaches, fires and burned area can be uncertain due to factors such as uncertainty in air mass factors, emission factors, smoke injection altitude, meteorology, and the evolution of species used as constraints.

The new text on P16 L10-17 now reads: "On the other hand, burned area is likely underestimated in inventories since they rely on remote sensing data that misses some of the hotspots and burned area used in bottom-up estimates, as well as some of the fire products (e.g. CO, aerosol) used in top-down approaches. The information gap is caused by high regional cloud cover; orbital gaps; rapid growth of new vegetation, which is strongly associated

35 with shallow burn depth (Cypert, 1961; Kotze, 2013); and other factors (Lu and Sokolik, 2013; Reddington et al., 2016; Reid et al., 2013). Thus, overestimating burn depth and underestimating burned area tend to cancel when coupling these terms to estimate fuel consumption."

R3.12: P16, L1 – Following from previous confusing sentences, not sure what is meant by 'tend to cancel'.

Authors: In addition to the above new text, please see the detailed response to Referee #2.

R3.13: P19, L4-7 – This is a bit of a non-sequitur as you are talking about exposure and health impacts, and then shift to an EF comparison concerning lab/field measurements which doesn't really so much apply to these very 'high level' estimates. If anything a consistency in air toxic/PM ratio could be highlighted, as this is what you're using to estimate air toxic exposure concentrations.

5 **Authors:** Six of the air toxics were only measured in the lab study so we needed to show the relevance of the lab data if we intended to use it, especially for the two more potent pollutants measured in both settings. The Referee points out correctly that some sort of transition was needed and we have added this at P19, L4: "Two of these key species were measured in both the field and the lab and we compare the results."

The companion paper on PM will be based on a much larger, and thus more representative, set of filter data and provide a better comparison to CO and other air toxics.

Field measurements of trace gases and aerosols emitted by peat fires in Central Kalimantan, Indonesia during the 2015 El Niño

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Abstract

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Peat fires in Southeast Asia have become a major annual source of trace gases and particles to the regional-global atmosphere. The assessment of their influence on atmospheric chemistry, climate, air quality, and health has been uncertain partly due to a lack of field measurements of the smoke characteristics. During the strong 2015 El Niño event we deployed a mobile smoke sampling team in the Indonesian province of Central Kalimantan on the island of Borneo and made the first, or rare, field measurements of trace gases, aerosol optical properties, and aerosol mass

- emissions for authentic peat fires burning at various depths in different peat types. This paper reports the trace gas and aerosol measurements obtained by Fourier transform infrared spectroscopy, whole air sampling, photoacoustic extinctiometers (405 and 870 nm), and a small subset of the data from analyses of particulate filters. The trace gas
- 25 measurements provide emission factors (EFs, g compound per kg biomass burned) for CO₂, CO, CH₄, non-methane hydrocarbons up to C₁₀, 15 oxygenated organic compounds, NH₃, HCN, NO_x, OCS, HCl, etc.; up to ~90 gases in all. The modified combustion efficiency (MCE) of the smoke sources ranged from 0.693 to 0.835 with an average of 0.772 ± 0.053 (*n*=35) indicating essentially pure smoldering combustion and the emissions were not initially strongly lofted. The major trace gas emissions by mass (EF as g/kg) were: carbon dioxide (1564 ± 77), carbon monoxide (291 ± 49), methane (9.51 ± 4.74), hydrogen cyanide (5.75 ± 1.60), acetic acid (3.89 ± 1.65), ammonia
- (2.86 ± 1.00) , methanol (2.14 ± 1.22) , ethane (1.52 ± 0.66) , dihydrogen (1.22 ± 1.01) , propylene (1.07 ± 0.53) ,

propane (0.989 \pm 0.644), ethylene (0.961 \pm 0.528), benzene (0.954 \pm 0.394), formaldehyde (0.867 \pm 0.479), hydroxyacetone (0.860 \pm 0.433), furan (0.772 \pm 0.035), acetaldehyde (0.697 \pm 0.460), and acetone (0.691 \pm 0.356). These field data support significant revision of the EFs for CO₂ (-8%), CH₄ (-55%), NH₃ (-86%), CO (+39%) and other gases compared with widely-used recommendations for tropical peat fires based on a lab study of a single

- 5 sample published in 2003. BTEX compounds (benzene, toluene, ethylbenzene, xylenes) are important air toxics and aerosol precursors and were emitted in total at 1.5 ± 0.6 g/kg. Formaldehyde is probably the air toxic gas most likely to cause local exposures that exceed recommended levels. The field results from Kalimantan were in reasonable agreement with recent (2012)-lab measurements of smoldering Kalimantan peat for "overlap species," lending importance to the lab finding that burning peat produces large emissions of acetamide, acrolein, methylglyoxal, etc.,
- 10 which were not measureable in the field with the deployed equipment and implying value in continued similar efforts.

The aerosol optical data measured include EFs for the scattering and absorption coefficients (EF B_{scat} and EF B_{abs} , m^2/kg fuel burned) and the single scattering albedo (SSA) at 870 and 405 nm, as well as the absorption Ångström exponents (AAE). By coupling the absorption and co-located trace gas and filter data we estimated black carbon

- (BC) EFs (g/kg) and the mass absorption coefficient (MAC, m²/g) for the bulk organic carbon (OC) due to brown carbon (BrC). Consistent with the minimal flaming, the emissions of BC were negligible (0.0055 ± 0.0016 g/kg). Aerosol absorption at 405 nm was ~52 times larger than at 870 nm and BrC contributed ~96% of the absorption at 405 nm. Average AAE was 4.97 ± 0.65 (range, 4.29-6.23). The average SSA at 405 nm (0.974 ± 0.016) was marginally lower than the average SSA at 870 nm (0.998 ± 0.001). These data facilitate modeling climate-relevant aerosol optical properties across much of the UV/visible spectrum and the high AAE and lower SSA at 405 nm to the simultaneously measured OC mass on filters suggests a low MAC (~0.1) for the bulk OC, as expected for the low
 - BC/OC ratio in the aerosol. The importance of pyrolysis (at lower MCE), as opposed to glowing (at higher MCE), in producing BrC is seen in the increase of AAE with lower MCE ($r^2 = 0.65$).

25 1 Introduction

Many major atmospheric sources have been studied extensively with a wide range of instrumentation. This includes, for example, temperate forest biogenic emissions (e.g. Ortega et al., 2014) and developed-world fossil-fuel based emissions (e.g. Ryerson et al., 2013). Biomass burning (BB) is the second largest global emitter of CO₂, total greenhouse gases, and non-methane organic gases (NMOGs), with the latter being precursors for ozone (O₃) and

- 30 secondary organic aerosol (OA). BB is the largest global source of fine primary OA, black carbon (BC) and brown carbon (BrC) (Akagi et al., 2011; Bond et al., 2004, 2013). However, many important, complex, BB emission sources have been rarely, if ever, characterized by comprehensive field measurements (Akagi et al., 2011). The largest of these undersampled BB sources is peatland fires, which occur primarily in boreal forests and in the tropics, especially the Indonesian provinces of Sumatra, Kalimantan, and Papua as well as Malaysian Borneo.
- 35 Peatland fires in the tropics usually start in surface fuels with surface fuel consumption commonly ranging from ~1-20 MgC/ha as a result of land-clearing and agricultural activities common throughout the tropics (Page et al., 2009;

Akagi et al., 2011). As the surface fuels are consumed, the much larger store of belowground biomass (mostly peat) at loadings of ~500-600 MgC/ha per meter depth, and up to 20 m deep, can become ignited and propagate as a glowing front that dries and pyrolyzes the fuel ahead of it (Yokelson et al., 1997; Page et al., 2002; Usup et al., 2004; Huang et al., 2016). Once the glowing fronts are burning under a layer of ash or have undercut the peat, the

- 5 fire is virtually impossible to extinguish by commonly available means and it can burn slowly, both horizontally and downward to the water table for months. Peat fires can also re-emerge and ignite surface fuels, but the smoldering consumption of large quantities of belowground fuel, which produces smoke that is initially weakly-lofted, is a key ecological and atmospheric characteristic of peatland fires (Tosca et al., 2011).
- The local air quality impacts of peat fires can be dramatic. As an example PM_{10} levels in Palangkaraya, Indonesia reached 3741 ug/m³ on 20 October, 2015 (BMKG, 2015) during a months-long pollution crisis that had simultaneous counterparts in Sumatra and Papua. With unfavorable transport, locally-generated smoke may be dispersed to numerous major population centers regionally where much reduced but more widespread exposure and health effects are a potential concern (e.g. Aouizerats et al., 2015).
- Since peat is a semi-fossilized fuel (accumulation rates are a few mm per year; Wieder et al., 1994; Page et al., 15 1999), the impacts on the carbon cycle are larger for the same amount of biomass burned than for most other BB types, and the carbon emissions may be significant in comparison to total fossil fuel carbon emissions in some years (e.g. 13-40% in 1997, Page et al., 2002). In Southeast Asia, in the 1980s and 1990s, peatland fires were a major source of <u>carbon emissions</u> to the atmosphere mainly during El-Niño-induced droughts when fire danger was higher, the fire season was longer, and water tables were lower. With accelerated deforestation and building of drainage
- 20 canals (e.g. 4000 km of canals as part of the Ex Mega Rice Project (EMRP) started in 1996 (Putra et al., 2008; Hamada et al., 2013)), peat fires and their impacts are now extensive on an annual basis (van der Werf et al., 2010; Wiedinmyer et al., 2011; Gaveau et al., 2014) and even more pronounced in El Niño years (Huijnen et al., 2016). In many disturbed areas the absence of the original peat swamp forest's moist under-canopy microclimate that acted to deter ignition or slow fire spread results in increased fire activity (Cochrane et al., 1999). In these areas ferns,
- 25 plantations, or patches of secondary forest overlie peat that has often already been impacted by previous fires and/or by roads and canals that also increase access and fire activity. The disturbed-area surface fuels are usually a minor component of the total available fuel, but are present in sufficient amounts to be an ignition source for the peat. Previously, tropical peat fire emissions had only been measured in detail in a few laboratory experiments (e.g. Christian et al., 2003) and most recently during the fourth Fire Lab at Missoula Experiment (FLAME-4, Hatch et al.,
- 30 2015; Jayarathne et al., 2014; Stockwell et al., 2014, 2015). The lab emissions measurements featured an extensive suite of instruments, many of which would be difficult to deploy in remote field conditions, but the realism of the lab burning conditions was hard to judge except qualitatively/visually. Further, the emissions from burning one peat sample from Sumatra (Christian et al., 2003) were quite different from the average emissions generated by burning three samples of Kalimantan peat during FLAME-4. For example, the "Sumatra/Kalimantan" emission ratio was ~2
- for CH_4 and ~11 for NH_3 (Stockwell et al., 2014). This variability makes it unclear how to optimize regional emissions inventories and the mean and variability in lab studies could also potentially reflect artifacts arising from sample collection, storage, or handling procedures. As a result, field measurements were a critical priority.

Beginning in 2013, an international team involving South Dakota State University, Bogor Agricultural University (IPB), the University of Montana, University of Iowa, University of California at Irvine, the United States Forest Service, and the Borneo Orangutan Survival Foundation (a Kalimantan NGO) initiated a multi-faceted study of peat fires in the Central Kalimantan province of Indonesia. The activities built on earlier work by the Kalimantan Forest

- 5 and Climate Partnership (KFCP, Applegate et al., 2012; Ichsan et al., 2013, Graham et al., 2014a, b; Hooijer et al., 2014) established in 2009 and included fire-scene investigations; fire history documentation; vegetation and fuels mapping; hydraulic conductivity, water table, and subsidence monitoring with an extensive series of 515 wells and 81 subsidence poles along 70 km of transects; collecting peat samples for the FLAME-4 laboratory emissions measurements; burned area mapping; and Lidar transects to quantify depth of burn (Ballhorn et al., 2009). In this
- 10 paper we present our October-November, 2015 ground-based field measurements of trace gases and aerosols directly in 35 different peat fire plumes in the vicinity of Palangkaraya, Central Kalimantan, in the mostly-disturbed western part of the EMRP (Page et al., 2002, 2009; Usup et al., 2004). We describe the sampling sites, peat characteristics, and our instrument selection, which aimed to optimize the trade-offs between the required mobility and the need for detailed measurements to understand atmospheric impacts and compare with a suite of "overlap
- 15 species" also measured in the FLAME-4 lab studies. We present and discuss our trace gas emission factors (EFs, g compound produced per kg peat burned) measured by a cart-based, mobile Fourier transform infrared spectrometer (FTIR) and by filling whole air sampling (WAS) canisters for subsequent lab analyses. The EFs provided include: CO₂, CO, NH₃, NO_x, CH₄, and numerous non-methane organic gases (NMOG) up to C₁₀, as many as ~90 gases in all. We present and discuss our measurements of aerosol optical properties and mass measured by photoacoustic
- 20 extinctiometers (PAX) and gravimetric filter sampling. The aerosol data include: EFs for scattering and absorption coefficients (EF B_{scat}, EF B_{abs}, m²/kg peat burned) at 870 and 405 nm, the single scattering albedo (SSA) at 870 and 405 nm, and the absorption Ångström exponents (AAE). These data facilitate modeling of aerosol optical properties across much of the UV-visible spectrum. We also present and discuss BC emission factors (g/kg fuel burned) and the mass absorption coefficient (MAC, m²/g) for the bulk organic carbon (OC) due to BrC emissions that are based
- 25 on combining the PAX absorption data with co-located trace gas and filter measurements. Our field measurements enable us to assess emissions of the main greenhouse gases emitted by fires, many ozone and organic aerosol precursors, several air toxics, and the absorbing BrC that dominates the direct radiative forcing of peat fire smoke. Finally, we compare our field data to lab results published in 2003, IPCC guidelines, and the recent FLAME-4 lab measurements of burning Indonesian peat to gain additional insight into the emissions of air toxics and precursors
- 30

not measured in the field and assess the overall value of lab studies of burning peat. Additional aerosol results based on our filter sampling in the field coupled with a large suite of subsequent analyses will be reported in a companion paper (Jayarathne et al., 2016, in preparation).

2 Experimental details

2.1 Site descriptions

Peat is an accumulation of partially decayed vegetation or organic matter that can be further classified as fibric, hemic, or sapric (by increasing degree of decomposition and density (Wüst et al., 2003)). Different amounts of roots;

- 5 sound or rotten logs; charred logs, char, and ash from previous burns; and mineral soil are frequently mixed in with the peat along with varying amounts of water. On undisturbed sites deeper peat is normally more decomposed and denser, but on disturbed sites the upper layer is sometimes already removed by previous fires, while dredging for canals can place "older peat" on top of younger peat, and road-building can compact the peat. Traditional peat classification schemes can be less straightforward for disturbed areas. For instance, ferns and grasses can contribute
- 10 fibrous roots to a layer of older, even sapric, material. We note that the Kalimantan peat burned in the FLAME-4 lab study that we will compare to was sampled in both undisturbed forest (n=1<u>one sample</u>) and previously logged/burned forest (n=1<u>one sample</u>), whereas the peat fires sampled in this field work were all on moderately to heavily disturbed sites, which is generally where fire activity is the highest.

Peat <u>deposits</u> can burn at <u>above > 100%</u> fuel moisture (defined as $100 \times (wet-dry)/dry$)), where "wet" refers to the

- 15 weight of a fresh fuel sample and "dry" refers to the fuel weight after oven drying until mass loss ceases. This is because the glowing front pre-dries the fuel as it advances. Peat combustion can occur as a glowing front in an expanding pit or undercut, but with direct access to surface air (Huang et al., 2016), which we term "lateral spreading." The glowing front can be covered by ash or initially propagate downward on inclusions or in cracks in initially, mostly-unburned peat, which we refer to as "downward" spreading, but this is much less common. Figure
- 20 S1 shows photographs of these spread modes. The glowing front is the site of gasification reactions (O₂-oxidation of char) that produce mostly CO₂, CO, CH₄, NH₃, and little visible aerosol. The heat from glowing combustion pyrolyzes the adjacent peat, producing relatively more organic gases and copious amounts of white smoke (with high OA content) (e.g. Fig. 3 in Yokelson et al., 1997). Wind increases the glowing front temperature. Oxygen availability is likely higher for lateral spreading than downward spreading fire and the overburden in downward
- spreading fires may scavenge some emissions. Occasionally peat can support brief, small flames if the surface peat is not too dense, or has high flammable inclusion content, or at high wind speeds (Yokelson et al., 1996; 1997).
 During eight days from 31 October through 7 November, we sampled 35 separate plumes at six differentsix different peatland areas with two areas being revisited (Table S1). All smoke sampling was conducted directly in the visible plumes (Fig. S1) and all background sampling was conducted just outside (usually upwind) of the plumes in paired
- 30 fashion. The surface fuels at all sites were non-existent or limited to ferns, charred logs, or patchy second growth forest, but they were neither present in heavy loading nor burning in most cases. This facilitated sampling "pure emissions" from the smoldering peat. On each day from 1-7 November, about four plumes originating from various peat types or depths were grab sampled about ten times each by FTIR, at least once by WAS, and usually by filters. This provided data for 27 plumes each assigned a letter identifier in our tables from A-Z-AA. Eight additional
- 35 plumes were quickly, opportunistically, sampled by just WAS, which was the fastest sampling method to complete. On 5 and 6 November, seven of the plumes with letter identifiers were also sampled continuously between 10-30 minutes apiece with both PAXs (coincident with FTIR, WAS, and filter sampling). Twenty-two filter samples were

collected from 19 different "lettered" plumes from 1-7 November. The full set of filter based analyses will be reported separately (Jayarathne et al., 2016). The sites and fires sampled included a variety of peat types, disturbance levels, spread modes, burn depths, etc. A brief chronological narrative of the sampling follows and most of the site characteristics that we were able to document are shown in Table S1. <u>A site map is given in Figure S2.</u>

5 *31 October (Site 1).* Two WAS samples were collected while scouting this site known locally as "South Bridge West" late in the afternoon. The site (Site #1 in Tab. S1) had hemic and fibric peat burning at 30-60 cm depth and was the most disturbed of all the sites sampled.

1 November (Site 1), plumes A-D. The "South Bridge West" site #1 was revisited and sampled by WAS, FTIR, and filters, which began the series of intensively sampled plumes designated by letters. Plume C included emissions from surface peat that were partially impacted by flames during wind gusts.

- 2 *November (Site 2), plumes E-H.* This site (#2)-was the least disturbed of the sites we sampled, but had been logged and was known to have burned once before the fire we sampled. In addition, site #2 was close enough to a canal that its hydrology would have been impacted. The site is known locally as "South Bridge East." The peat was hemic and fibric and burn depth ranged from 18-28 cm.
- 15 *3 November (Site 3), plumes I-L.* The "White Shark (Hiu Putih)" site comprised hemic and fibric peat burning at depths of 33-52 cm.

4 November: (Site 4) plumes M-N; (Site 5) Plume P. Site 4 was known locally as the "Mahir Mahar" site and plume M provided our best measurements of the emissions from burning sapric peat. The other plumes sampled were burning in hemic and fibric peat types. The burn depths sampled on this day varied over a narrow range near 21-22

20 cm.

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5 November (Site 1), plumes Q-T. The South Bridge West site was revisited. Burn depths were 25-50 cm and the peat was hemic and fibric.

6 November (Site 2), plumes U-W. The South Bridge East site was revisited. The peat was hemic and fibric and burn depths were 20-30 cm.

25 *7 November (Site 6), plumes X-Z-AA.* Some shallow peat combustion was sampled at this site, known locally as Tangkiling Road.

2.2 Instrument descriptions and calculations

2.2.1 Land-based Fourier transform infrared (LA-FTIR) spectrometer

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A rugged, cart-based, mobile FTIR (Midac, Corp., Westfield, MA) designed to access remote sampling locations was used for trace gas measurements (Christian et al., 2007). We note for other researchers that the soft peat surface was not easily traversed with the rolling cart, which usually had to be carried. In addition, all equipment was protected from underlying ash and dust with a tarp. The vibration-isolated optical bench consists of a Midac spectrometer with a Stirling cycle cooled mercury-cadmium-telluride (MCT) detector (Ricor <u>USA</u>, Inc., <u>Salem</u>, NH) interfaced with a closed multipass White cell (Infrared Analysis, Inc., <u>Anaheim</u>, <u>CA</u>) that is coated with a halocarbon wax (1500 Grade, Halocarbon Products Corp., <u>Norcross</u>, <u>GA</u>) to minimize surface losses (Yokelson et al., 2003). In the grab sampling mode air samples are drawn into the cell by a downstream pump through several

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meters of 0.635 cm o.d. corrugated Teflon tubing. The air samples are then trapped in the closed cell by Teflon valves and held for several minutes for signal averaging to increase sensitivity. Once the IR spectra of a grab sample are logged with cell temperature and pressure (Minco TT176 RTD, MKS Baratron 722A) on the system computer, a new grab sample can be obtained resulting in many grab samples for each peat fire smoke plume and "paired"

- backgrounds. Spectra were collected at a resolution of 0.50 cm⁻¹ covering a frequency range of 600-4200 cm⁻¹. Since some other recent reports of the use of this system (Akagi et al., 2013), several upgrades/changes have been made:
 (1) addition of a retroreflector to the White cell mirrors increased the optical pathlength from 11 m to 17.2 m, lowering previous instrument detection limits, (2) replaced in the Teflon cell coating with halocarbon wax to enable-maintain good measurements of ammonia (NH₃), hydrogen chloride (HCl), and other species prone to
- 10 adsorption on surfaces, (3) mounting the mirrors to a stable carriage rather than the previous method of gluing them to the cell walls, (4) the above mentioned Stirling cycle detector, which gave the same performance as a liquidnitrogen-cooled detector without the need for cryogens, (5) the addition of two logged flow meters (APEX, Inc.) and filter holders to enable the system to collect particulate matter on Teflon and quartz filters for subsequent laboratory analyses. The new lower detection limits vary by gas from less than 1 ppb to ~100 ppb, but are more than sufficient
- for near-source ground-based sampling since concentrations are much higher (e.g. ppm range) than in lofted smoke (Burling et al., 2011). Gas-phase species including carbon dioxide (CO₂), carbon monoxide (CO), methane (CH₄), acetylene (ethyne, C₂H₂), ethylene (ethene, C₂H₄), propylene (propene, C₃H₆), formaldehyde (HCHO), formic acid (HCOOH), methanol (CH₃OH), acetic acid (CH₃COOH), furan (C₄H₄O), hydroxyacetone (C₃H₆O₂), phenol (C₆H₅OH), 1,3-butadiene (C₄H₆), nitric oxide (NO), nitrogen dioxide (NO₂), nitrous acid (HONO), NH₃, hydrogen
- 20 cyanide (HCN), hydrogen chloride (HCl), sulfur dioxide (SO₂) were quantified by fitting selected regions of the mid-IR transmission spectra with a synthetic calibration non-linear least-squares method (Griffith, 1996; Yokelson et al., 2007). A few species were sometimes not above the detection limit in background air, but are retrieved from absorption spectra made from smoke/background so the excess amounts are inherently returned. SO₂ and NO₂ were not observed above the detection limit in the background or the most concentrated smoke and are not discussed
- further. An upper limit 1 σ uncertainty for most mixing ratios is ±10%. Pre-mission calibrations with NIST-traceable standards indicated that CO, CO₂, and CH₄ had an uncertainty between 1-2%, suggesting an upper limit on the field measurement uncertainties for CO, CO₂, and CH₄ of 3-5%. The NO_x species have the highest interference from water lines under the humid conditions in Borneo and the uncertainty for NO is ~25%.
- In addition to the primary grab sample mode, the FTIR system was also used in a real-time mode to support the 30 PAX (vide infra) and filter sampling when grab samples were not being obtained. Side by side Teflon and quartz 51 filter holders preceded by cyclone <u>samplers</u> to reject particles with an aerodynamic diameter > 2.5 microns were 52 followed by logged flow meters. The flow exiting the meters was then combined and directed to the multipass cell 53 where IR spectra were recorded at ~1.1 second time resolution. The PAX sample line was co-located with the filter 54 inlet and sampled in parallel from the same location. In real-time filter/PAX mode we did not employ signal
- 35 averaging of multiple FTIR scans and the signal to noise is lower at high time resolution. In addition, there could be sampling losses of sticky species such as NH_3 on the filters so we did not analyze the real-time data for these species. However, the data quality was still excellent for CO_2 , CO, and CH_4 . This allowed the time-integrated

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particle mass and PAX signals to be compared to the simultaneously measured time-integrated mass of the three gases most needed for EF calculations (Sect 2.3) and provided additional measurements of the emissions for these three gases as described in detail in the filter sampling companion paper (Jayarathne et al., 2016).

2.2.2 Whole air sampling (WAS) in canisters

- 5 Whole air samples were collected in evacuated 2 L stainless steel canisters equipped with a bellows valve that were pre-conditioned by pump-and-flush procedures (Simpson et al., 2006). The canisters were filled to ambient pressure directly in plumes or adjacent background air to enable subsequent measurement and analysis of a large number of gases at the University of California, Irvine. Species quantified included CO₂, CO, CH₄ and up to 100 non-methane organic gases by gas chromatography (GC) coupled with flame ionization detection, electron capture detection, and
- 10 quadrupole mass spectrometer detection as discussed in greater detail by Simpson et al. (2011). Typically ~70 of the NMOGs were enhanced in the source plumes and we do not report the results for most multiply-halogenated species, which are generally not emitted by combustion (Simpson et al., 2011). We also do not report the higherchain alkyl nitrates, which are often secondary photochemical products and were not enhanced in these fresh peat fire plumes. Peaks of interest in the chromatograms were individually inspected and manually integrated. The limit
- 15

of detection for most NMOGs was less than 20 pptv, well below the concentrations that were sampled. Styrene is known to decay in canisters and the styrene data <u>may should be taken as lower limits</u>.

2.2.3 Photoacoustic extinctiometers (PAX) at 405 nm and 870 nm

Particle absorption and scattering coefficients (B_{abs}, B_{scat}), single scattering albedo (SSA), and absorption Ångström exponent (AAE) at 405 nm and 870 nm were measured directly at 1 s time resolution using two photoacoustic
extinctiometers (PAX, Droplet Measurement Technologies, Inc., CO). This monitored the real-time absorption and scattering resulting from BC and (indirectly) BrC. The two units were mounted with a common inlet, desiccator (Silica Gel, 4-10 mesh, Fisher Scientific), and gas scrubber (Purafil SP blend media, Purafil, Inc., Doraville, GA) in rugged, shock-mounted, Pelican military-style hard cases. Air samples were drawn in through conductive tubing to 1.0 μm size-cutoff cyclones (URG Corp., Chapel Hill, NC) at 1 L/min. The continuously sampled air was split
between a nephelometer and photoacoustic resonator enabling simultaneous measurements of scattering and absorption at high time resolution. Once drawn into the acoustic section, modulated laser radiation was transferred to the surrounding air as heat and the resulting pressure changes were detected by a sensitive microphone. Scattering coefficients at each wavelength were measured by a wide-angle integrating reciprocal

30 nephelometer, using photodiodes to detect the scattering of the laser light. The estimated uncertainty in PAX absorption and scattering measurements has been estimated as ~4-11% (Nakayama et al., 2015). Additional details on the PAX instrument can be found elsewhere (Arnott et al., 2006; Nakayama et al., 2015). For logistics reasons it was only practical to sample fresh peat fire plumes with the PAXs on two days.

Calibrations of the two PAXs were performed during the deployment using the manufacturer recommended 35 absorption and scattering calibration procedures utilizing ammonium sulfate particles and a kerosene lamp to generate pure scattering and strongly absorbing aerosols, respectively. The calibrations of scattering and absorption of light were directly compared to measured extinction by applying the Beer-Lambert Law to laser intensity attenuation in the optical cavity (Arnott et al., 2000). As a quality control measure, we frequently compared the measured total light extinction ($B_{abs} + B_{scat}$) to the independently measured laser attenuation. For nearly all the 1 s

5 data checked, the agreement was within 10% with no statistically significant bias, consistent with (though not proof of) the error estimates in Nakayama et al. (2015). Finally, after the mission a factory measurement of the 405 nm absorption in the PAX was performed with NO₂ gas that was within 1% of the expected result (Nakayama et al., 2015). As part of this factory calibration, to account for the NO₂ quantum yield, the laser wavelength was precisely measured as 401 nm. This difference from the nominal 405 nm wavelength is common and we continue to refer to the wavelength as 405 nm since this is a standard nominal wavelength for aerosol optical measurements. This

impacts the calculated values for AAE by only 0.3 % and the absorption attribution by 1.0 % (Sect. 2.3).

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2.2.4 Other measurements

Peat samples were collected just ahead of the burning front for fuel moisture measurements. A brief description of the filter collection process is given here and the details of the post-mission analyses will be described elsewhere (Jayarathne et al., 2016).

2.2.5 PM_{2.5} filter collection for offline analysis

 $PM_{2.5}$ was collected through 0.635 cm o.d. Cu tubing and $PM_{2.5}$ cyclones onto pre-weighed 47 mm Teflon filters and pre-cleaned 47 mm quartz fiber filters (QFF) (PALL, Life Sciences, Port Washington, NY) in both smoke plumes and directly-upwind background air. QFF were pre-baked at 550°C for 18 hours before sampling to remove contaminants and stored in cleaned, aluminum foil-lined petri dishes sealed with Teflon tape.

- 20 PM2.5 mass measurements. Before and after sample collection Teflon filters were conditioned for 48 hours in a desiccator and weighed using an analytical microbalance (Mettler Toledo XP26) in a temperature and humidity controlled room. Particulate mass (PM) was calculated from the difference between pre-and post-sampling filter weights, which were determined in triplicate. PM per filter was converted to mass concentration using the sampled
- 25 air volume. Uncertainty in the excess mass in the smoke plumes was propagated using the standard deviation of triplicate measurements of pre- and post-sampling filter weights the smoke PM, the standard deviation of the background PM masses, and 10 % of the PM mass concentration, which is a conservative estimate of the analytical error associated with this measurement.

EC OC analysis. EC and OC were measured by thermal optical analysis (Sunset Laboratory, Forest Grove, OR)

- following the NIOSH 5040 method (NIOSH, 1999) using 1.00 cm² sub-samples of the quartz fiber filters. The 30 EC/OC split was determined by thermal optical transmittance (TOT). The OC and EC concentrations ($\mu g m^3$) were calculated using the total filter area and the sampled air volume. The OC uncertainty was propagated using the standard deviation of the field blanks, the standard deviation of background filters, and 10 % of the OC concentration. Instrumental uncertainty (0.05 µg cm⁻²), 5 % of the EC concentration, and 5 % of the measured
- pyrolyzed carbon concentration were used to propagate EC uncertainty. 35

Back-up filter collection. In order to assess the positive sampling artifacts from carbonaceous gas adsorption, a second QFF (back-up) filter was placed following the first QFF (front) filter. These QFF filters were analyzed for EC and OC as described previously. EC was not detected on any of the back-up filters. On average, the OC concentration on backup filters was 4.8 % of OC on front filters. At the high concentrations sampled both QFF

- 5 would saturate with respect to gas adsorption indicating that ~5 % of the front filter OC was due to positive sampling artifacts (Kirchstetter et al., 2001). *Background filter collection.* In order to correct for ambient background PM_{2.5}, background filter samples were collected in background air outside, but adjacent to the smoke plumes for 20 minutes (similar to the smoke sampling times). These filters were also analyzed for PM_{2.5} mass, EC and OC as described above. EC was not detected on any
- 10 of the background filters, while OC levels were consistent with gas adsorption described previously. The backgrounds were very similar and on average, the background contributed 0.60 % of PM_{2.5} mass, indicating that background contributions to PM mass were very minor in relation to the peat burning smoke. Nonetheless, the average background value was subtracted from the smoke samples during data workup to calculate the contributions from the smoke plumes. While field blanks were collected, subtracting the background from smoke samples made
- 15 the field blank correction unnecessary.

2.3 Emission ratio and emission factor determination

The excess mixing ratios above the background level (denoted ΔX for each gas-phase species "X") were calculated for all the gas-phase species in the grab samples and CO₂, CO, and CH₄ in the real-time data. The grab samples were collected in a way that avoided possible artifacts for some gases due to adsorption on filters or in flow meters and they were used to produce a self-consistent complete set of data on trace gas emissions as described next. The molar emission ratio (ER, e.g. ΔX/ΔCO) for each gaseous species X relative to CO or CO₂ was calculated for all the FTIR and WAS species. The plume-average ER for each FTIR or WAS species measured in multiple grab samples was estimated from the slope of the linear least-squares line (with the intercept forced to zero) when plotting ΔX versus ΔCO (or ΔCO₂) for all samples of the source (Yokelson et al., 2009; Christian et al., 2010; Simpson et al., 2011).

- Forcing the intercept decreases the weight of the lower points relative to those obtained at higher concentrations that reflect more emissions and have greater signal to noise. Alternate data reduction methods usually have little effect on the results as discussed elsewhere (Yokelson et al., 1999). For a handful of species measured by both FTIR and WAS it is possible to average the ERs from each instrument for a source together as in Yokelson et al. (2009). However, in this study, we either worked up the independently sampled WAS data as a separate set of ER or used
- 30 the more extensive FTIR ERs when there were a few "overlap species" (primarily CH₃OH, C₂H₄, C₂H₂, and CH₄). From the ERs, emission factors (EFs) were derived in units of grams of species X emitted per kilogram of dry biomass burned by the carbon mass balance method, which assumes all of major carbon-containing emissions have been measured (Ward and Radke, 1993; Yokelson et al., 1996, 1999):

$$EF(X)(gkg^{-1}) = F_{C} \times 1000 \times \frac{MM_{x}}{AM_{C}} \times \frac{\frac{\Delta X}{\Delta CO}}{\sum_{j=1}^{n} \left(NC_{j} \times \frac{\Delta C_{j}}{\Delta CO}\right)}$$
(1)

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where F_C is the measured carbon mass fraction of the fuel; MM_x is the molar mass of species X; AM_C is the atomic mass of carbon (12 g mol⁻¹); NC_i is the number of carbon atoms in species j; ΔC_i or ΔX referenced to ΔCO are the fire-average molar emission ratios for the respective species. The carbon fraction was measured (ALS Analytics, Tucson) for seven samples of Kalimantan peat from sites ranging from heavy to no disturbance and averaged 0.5793

- \pm 0.025² (Stockwell et al., 2014). EFs are proportional to assumed carbon content, making future adjustments to evolving literature-average EFs trivial if warranted based on additional carbon content measurements. The denominator of the last term in Eqn. (1) estimates total carbon. For nearly all the plumes, the mass ratio of EC and OC to the simultaneous co-located CO, measured by the FTIR (see below), was added to the estimate of total carbon. Thus, our total carbon estimate for the grab samples includes all the gases measured by the FTIR or WAS in 10 grab samples of a source and the carbon in the aerosol measured on the filters. Ignoring the carbon emissions not included or not measureable by our suite of instrumentation (typically higher molecular weight oxygenated organic gases) likely inflates the EF estimates by less than ~1-2 % (Yokelson et al., 2013; Stockwell et al., 2015), which is
- Biomass fire emissions vary naturally as the mix of combustion processes varies. The relative amount of smoldering 15 and flaming combustion during a fire can be roughly estimated from the modified combustion efficiency (MCE). MCE is defined as the ratio $\Delta CO_2/(\Delta CO_2 + \Delta CO)$ and is mathematically equivalent to $(1/(1 + \Delta CO/\Delta CO_2))$ (Yokelson et al., 1996). Flaming and smoldering combustion often occur simultaneously during biomass fires, but a very high MCE (~0.99) designates nearly pure flaming (more complete oxidation) while a lower MCE (~0.75-0.84 for biomass fuels) designates pure smoldering. Plume-average MCE was computed for all plumes using the plume

small compared to the 4% uncertainty due to natural variability in peat carbon content.

20 average $\Delta CO/\Delta CO_2$ ratio as above. In the context of biomass or other solid fuels, smoldering refers to a mix of solid-fuel pyrolysis (producing NMOG and OA) and gasification (producing mainly NH₃, CH₄, and inorganic gases with little visible aerosol) (Yokelson et al., 1997).

The time-integrated excess B_{abs} and B_{scat} from the PAXs were used to directly calculate the plume average single scattering albedo (SSA, defined as B_{scat} /(B_{scat} + B_{abs})) at both 870 and 405 nm for each source. The PAX time-25 integrated excess Babs at 870 and 405 was used directly to calculate each plume-average absorption Ångström exponent (AAE, Eqn. 2).

$$AAE = -\frac{\log\left(\frac{B_{abs,1}}{B_{abs,2}}\right)}{\log\left(\frac{\lambda_1}{\lambda_2}\right)}$$
(2)

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Aerosol absorption is a key parameter in climate models, however, inferring absorption from total attenuation of light by particles trapped on a filter, or from the assumed optical properties of a mass measured by thermal/optical processing, incandescence, etc. can sometimes suffer from artifacts (Andreae and Gelencsér, 2006; Subramanian et al., 2007). In the PAX, the 870 nm laser is absorbed in-situ by black carbon containing particles only, without filter or filter-loading effects that can be difficult to correct. We directly measured aerosol absorption (B_{abs}, Mm⁻¹) and used the literature-recommended mass absorption coefficient (MAC) (4.74 m²/g at 870 nm) to estimate the BC concentration (µg/m³) (Bond and Bergstrom, 2006). The PAXs (and filters) were co-sampled with the FTIR measuring CO_2 , CO, and CH_4 in real-time. The mass ratio of the integrated excess BC in the plume measured on the PAX to the integrated excess CO measured by the FTIR was multiplied by the EF CO based on the real-time FTIR data to determine EFs for BC (g/kg). Note the total C for the carbon mass balance for the EFs calculated for real-time data is based on the integrated excess amounts of just the three main gases and aerosol carbon, which will

5 inflate the EFs by a small amount (typically 1-3 %) compared to the larger suite of gases used for the grab sample calculations.

To a good approximation, sp^2 -hybridized carbon (i.e. BC) has an AAE of 1.0 ± 0.2 and absorbs light proportional to frequency. Thus, B_{abs} due only to BC at 405 nm would be expected to equal $2.148 \times B_{abs}$ at 870 nm and we assumed that excess absorption at 405 nm, above the projected amount, is associated with BrC absorption. This method of

- 10 attributing BrC absorption is based on several assumptions discussed in detail elsewhere that are likely most valid in cases where the BrC absorption is dominant such as in these peat fire smoke plumes (Lack and Langridge 2013). In theory, a BrC concentration (μ g/m³) could be calculated using a literature-recommended BrC MAC of 0.98 m²/g at 404 nm (Lack and Langridge, 2013). The BrC mass calculated this way would be intended to be roughly equivalent to the total OA mass, which as a whole weakly absorbs UV light, and not the mass of the actual chromophores.
- However, the MAC of Lack and Langridge (2013) is appropriate for more typical biomass burning with a mix of flaming and smoldering, whereas the peat aerosol is overwhelmingly organic and at low BC/OA ratios the MAC is much smaller (Saleh et al., 2014; Olson et al., 2015). Thus, instead we divided the B_{abs} at 405 nm assigned to BrC by the co-measured OC mass to estimate the peat smoke MAC referenced to bulk OC. The EFs for scattering and absorption at 870 and 405 nm (EF B_{abs}, EF B_{scat}) are reported directly in units of m² per kg of dry fuel burned by multiplying the ratios of B_{abs} and B_{scat} to co-measured real-time CO by the real-time EF CO. We note that most of the related measurements of elemental and organic carbon on the filters will be discussed separately by Jayarathne et

al. (2016).

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3 Results and Discussion

3.1 Trace gas emission factors

- In general, we found very high correlation in the ER plots indicating the plumes were well-mixed and implying low uncertainty in the individual plume EFs. Figure 1 shows a selection of such plots for plume N and it is also seen that the smoke mixing ratios were far above background. There were nine instances when the same gas was measured by both WAS and FTIR in nearly the same place and seven of these nine cases agree within the combined uncertainty. The other two cases are less close, but this experiment was not well-designed for comparison, but w. We have noted excellent WAS/FTIR agreement previously under more rigorous, but drier conditions (e.g. Christian et al., 2003;
- Hatch et al., 2016) and we found that these 2015 field WAS results compared well with on-line measurements during FLAME-4 peat fire sampling for many major species as discussed later in the paper.

Table S2 presents all the trace gas EFs for all 35 plumes sampled while Table 1 shows all our study-average EFs and one standard deviation of the means for all the gases that were significantly elevated in the smoke plumes. In the pure peat combustion that we were able to sample, the major trace gas emissions by mass (EF > \sim 0.5 g/kg) were:

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carbon dioxide (1564 \pm 77), carbon monoxide (291 \pm 49), methane (9.51 \pm 4.74), hydrogen cyanide (5.75 \pm 1.60), acetic acid (3.89 \pm 1.65), ammonia (2.86 \pm 1.00), methanol (2.14 \pm 1.22), ethane (1.52 \pm 0.66), dihydrogen (1.22 \pm 1.01), propylene (1.07 \pm 0.534), propane (0.989 \pm 0.644), ethylene (0.961 \pm 0.528), benzene (0.954 \pm 0.394), formaldehyde (0.867 \pm 0.479), hydroxyacetone (0.860 \pm 0.433), furan (0.772 \pm 0.035), acetaldehyde (0.697 \pm

5 0.460), and acetone (0.691 \pm 0.356). These results are shown in a bar chart in Fig. 2. C₆-C₁₀ alkanes summed to 0.87 \pm 0.57 g/kg, which overlapsroughly consistent with the 0.59 g/kg of C₆-C₁₀ alkanes emitted by a peat fire sampled by two-dimensional gas chromatography in the FLAME-4 lab study (Hatch et al., 2015). Hatch et al. (2015) also measured 0.43 g/kg of C₁₁-C₁₅ alkanes, which is probably a reasonable estimate for our field fires. The larger alkanes (> C₁₀) are efficient OA precursors (Presto et al., 2010). BTEX (benzene, toluene, ethylbenzene, xylenes)

- 10 compounds are also high-yield OA precursors (Wang et al., 2014) and important air toxics; they were emitted in total at 1.49 ± 0.64 g/kg. Air toxics are discussed further in Sect 3.5.2 with the FLAME-4 lab data included. Additional discussion of NMOG emissions and detailed comparison with previous (e.g. FLAME-4) trace gas measurements on lab peat fires is presented in Section 3.5.1.
- The modified combustion efficiency (MCE) of the smoke sources ranged from 0.693 to 0.835 with an average of
 0.772 ± 0.035 (n = 35) indicating essentially pure smoldering combustion. For most biomass fires there is both
 flaming and smoldering combustion and so EFs for flaming compounds are observed to correlate with MCE while
 EFs for smoldering compounds (most NMOGs) tend to be anti-correlated with MCE (Burling et al., 2011). butHowever, these fires burned by smoldering only with no high MCE values (e.g. >0.9) and little or no correlation
 dependence of EFs withon MCE was observed. It is important to consider if EFs are related to peat characteristics,
 especially peat characteristics that could be mapped. However, given our sample size and some mixing of peat types
 by the disturbance regimes, we have not attempted such an analysis yet.

3.2 Aerosol optical properties and emission factors

Figure 3 shows an example of the PAX real-time B_{abs} at 870 and 405 nm collected on 5 Nov along with the colocated CO data. Note the scaling of the axes and the dominance of B_{abs} at 405 nm, though the ratio of 870/405 is seen to increase towards the end of the sampling period (the traces are slightly offset so that the background trace is visible.) The excess values above background that were used to calculate all the quantities described above had similar excellent signal to noise in all cases. <u>B_{abs} at 405 and CO remain correlated</u>, but the ratio of B_{abs} at 405 to CO decreases towards the end of the 5 Nov data, which is consistent with an increase in the glowing/pyrolysis ratio (Yokelson et al., 1997). Variation in the mix of these smoldering processes likely causes some of the variation in

30 <u>EFs.</u>

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Table 2 shows all PAX-measured quantities, the MCE from the co-sampled real-time FTIR data, and the small subset of filter EC, OC, and PM_{2.5} data that were co-sampled with the PAXs for all 7 plumes along with the study averages and standard deviations. Consistent with the lack of flaming, the emissions of BC were negligible (0.0055 \pm 0.0016 g/kg) (Christian et al., 2003; Liu et al., 2014). Aerosol absorption at 405 nm was 52 times larger than at 870 nm and BrC contributed an estimated 96% of the absorption at 405 nm. Average AAE was 4.97 \pm 0.65 (range

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 $(0.998 \pm 0.001$, range 0.997-0.999). Clearly, estimating aerosol absorption from BC measurements alone would be inadequate for this source.

Pure pyrolysis has lower MCE than glowing and thus, pyrolysis is implicated as the source of BrC via the correlation of AAE with lower MCE ($r^2 = 0.65$) (Fig. 4a). We note the data cover a small MCE range and thus the relationship shown is not well constrained for extrapolation much beyond the range shown. We also find that AAE correlates strongly with SSA at 405 nm (Fig. 4b). In this case, the trend line shown is likely illustrative of peat fire

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aerosol, but again, not suitable for extrapolation to other fuels or beyond the range shown. By plotting EF B_{scat} versus EF $PM_{2.5}$ for all seven plumes sampled by PAX and filters (Fig. 5) we get a rough estimate of the mass-scattering efficiency (MSE) of the peat fire aerosol at 405 nm based on the slope of 2.96 ± 0.67

- 10 m^2/g ($r^2 = 0.80$). The plot compared EFs measured in the same plumes, but in some cases at slightly different times due to a PAX auto-zero or a filter clogging. If we restrict the plot to the four plumes where the timing of the sampling was identical, the slope is $3.05 m^2/g$ ($r^2 = 0.81$). Either value of the MSE is close to MSEs obtained <u>at</u> <u>illumination wavelengths closer toin the range</u> 532 - 5500 nm ($3 - 5 m^2/g$) in other studies of biomass burning aerosol with lower values characteristic of fresher smoke (Tangren, 1982; Patterson and McMahon, 1984; Nance et
- 15 al., 1993; Burling et al., 2011). However, based on average BB aerosol size distributions (Reid et al., 2005), our MSE may be underestimated on the order of 5-10% due to the difference in sampling cut-offs (2.5 microns for filters and 1.0 microns for PAX). By comparing the EF B_{abs} at 405 nm assigned to BrC with EF OC from the filters on the same plumes (Fig. 6) we can estimate the mass absorption coefficient (MAC) of the bulk OC. As above, two MAC estimates are possible. Using the mean value for all 7 plumes we get $0.09 \pm 0.08 \text{ m}^2/\text{g}$ where the large coefficient of
- 20 variation is due to one larger MAC value near 0.27 m²/g. Keeping the dynamic nature of the emissions chemistry shown in Fig. 3 in mind, Hif we restrict our analysis to the same four plumes where sample timing was identical (but different size cutoffs; blue points in Fig. 6) instead weand plot EF B_{abs-405} versus EF OC just for the four plumes sampled over the exact same time period (but different size cutoffs; blue points in Fig. 6) we get a slope of 0.071 ± 0.03 m²/g. The MACs obtained either way are similar, but again underestimated by a few percent due to cutoff
- 25 differences and much smaller than MACs for average biomass burning OA (0.98; Lack and Langridge, 2013). However, we confirm the expected MAC near 0.1 m²/g for the extremely low BC (or EC) to OA ratio in the aerosol (Saleh et al., 2014; Olson et al., 2015).

While EC and BC are considered approximately equivalent for some combustion sources (e.g. diesel fuel combustion), our EF EC for peat fires is noticeably larger than the EF BC although both EC and BC values are very

- 30 small (Table 2) compared to typical values for combustion aerosol. This is the expected result in this case for several reasons. The peat smoke plumes sampled outdoors likely contain very small amounts of soot from rare instances of flaming and also a small amount of entrained small char particles produced by pyrolysis of the peat on site by the glowing combustion front (Santín et al., 2016). Both soot and char are detected to some extent as EC (Andreae and Gelencsér, 2006; Han et al., 2007; 2010; 2016) and our EC sub-fractions evolving at lower temperatures confirm
- 35 some char was present (NIOSH, 1999). The char particles tend to be larger (1-100 microns, Han et al., 2010) and would be more efficiently sampled by the filters, which had a 2.5 micron cut-off as opposed to the PAX with a 1.0 micron cut-off. Char tends to absorb long wavelengths less efficiently than soot (Han et al., 2010) and the PAX

would therefore be relatively insensitive to any sampled char for this reason also. The accuracy of both the PAX and the thermal optical EC detection is challenged by the low EC or BC to OC ratio (Andreae and Gelencsér, 2006). Yet, both measurements are useful and point to the same key results: that the aerosol is overwhelmingly organic and the organic fraction contributes most of the light absorption.

5 In a previous study of aerosol emissions from burning Sumatran peat in a lab setting, Christian et al. (2003) measured an EF for OC + EC by the thermal optical technique of $\sim 6 \text{ g/kg}$ that had OC/EC of 151. More extensive comparison of our field PM2.5, EC, and OC data with lab measurements, including the FLAME-4 EC/OC data will be presented in Jayarathne et al. (2016).

Turning to optical properties, Liu et al. (2014) reported some SSA values and the AAE for smoldering Kalimantan

- peat (Fire 114) from FLAME-4: MCE (0.74), AAE (6.06), SSA--405 (0.94), and SSA--781 (1.00), and AAE (6.06). 10 These are very consistent with our data (Table 2) and especially with our lowest MCE field sample: MCE (0.726), AAE (6.23), SSA--405 (0.941), and SSA--870 (0.997), and AAE (6.23). They also report data for a FLAME-4 peat fire with some brief flaming (Fire 154) and obtain for example an AAE of 3.02, which is below our lowest AAE of 4.28. Their average AAE 4.45 \pm 2.19 for Indonesian peat is not significantly smaller than ours (4.97 \pm 0.65) and it
- 15 should be kept in mind that the determination and comparisons of AAE can be affected by the use of different wavelength pairs (Lewis et al., 2008; Chakbarty et al., 2016). BrC absorption is very small at both 781 and 870 nm so the high SSA at the long wavelengths in both studies and similar AAEs are consistent with minimal BC absorption and dominant absorption by BrC. In summary, when comparing to published laboratory studies of tropical peat burning, especially for smoldering combustion in the lab, we get good agreement in the sense of extremely low EC or BC to OC ratios and for the aerosol optical properties.

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3.3 Representativeness and comparison to other field studies

The biomass of the surface layer in logged/disturbed peatlands is small compared to the peat, and even the biomass of intact peat-swamp forest is small compared to peat loading as noted by Page et al. (2002). However, peat is only one component of the total peatland fuel and potentially a diminishing component as exploitation and repeated fires 25 are continued over many years (Konecny et al., 2016). As the peat fuels are consumed on a site, the loading of surface fuels likely also decreases. We did not see much evidence of active surface fuel combustion, but our sampling was just after the peak regional PM_{10} levels, which may have had a larger contribution from surface fuels. Numerous "hotspots" were detected in the region and both flaming and smoldering were evident in the news media coverage (https://worldview.earthdata.nasa.gov/). The fraction of total, annual regional emissions due to emissions

- generated during the peak regional impacts should not be overis difficult to estimated since a long period of 30 moderately elevated emissions could produce as much or more emissions as a shorter, higher level of emissions. The overall mix of fuels burning in the region during the peak regional pollution would have been hard to assess in any case since visibility dropped to ~10 m making driving dangerous and even a regional fire survey with an aircraft problematic. Further, surface fuel emissions would likely be associated with some amount of flaming combustion
- 35 that would be hard to sample properly with most ground-based instruments. Finally, under extremely polluted conditions it is hard to acquire background samples or isolate and measure individual fuel contributions/EFs so that

the variable relative contributions of peat and surface fuels (primary and secondary forest, cropland, grassland, etc.) can be explicitly modeled on a regional scale. Our sampling, somewhat fortuitously, unambiguously probed the emissions from the major fuel component, peat, of special concern in Southeast Asia.

- Our sampling was also near the end of the fire season when the relative amount of total annual deep burning versus total annual surface burning could potentially be measured (an earlier assessment would underestimate the deep peat burning). We sampled and observed areas with peat burning at depths from 18 to 60 cm. However, we also accessed our sites at times across areas that had recently burned with consumption of some surface fuels, but with only shallow consumption of the organic soil layer. Thus, applying an average peat burn depth for all burned area from our sampled burn depths would be biased high and a better estimate of the average burn depth will likely result from
- 10 the Lidar data collected. There were significant areas where a deep burn depth is clearly not accurate. On the other hand, burned area is likely underestimated in inventories since they rely on remote sensing data that misses <u>some of</u> the hotspots <u>and</u>, burned area <u>used in bottom-up estimates</u>, <u>and as well as some of</u> the fire products (e.g. CO, <u>aerosol)</u> used in top-down approaches. This The information is due togap is caused by high regional cloud cover; orbital gaps; rapid green upgrowth of new vegetation, which is strongly associated with shallow burn depth (Cypert,
- 15 1961; Kotze, 2013); and other factors (Lu and Sokolik, 2013; Reddington et al., 2016; Reid et al., 2013). Thus, overestimating burn depth and underestimating burned area tend to cancel when coupling these terms to estimate fuel consumption. A 2015 airborne campaign surveying regional smoke could have theoretically assessed the overall regional smoke characteristics, but did not occur. With the caveat that fire use has evolved in Kalimantan over the years, we can compare to airborne atmospheric chemistry measurements conducted during the 1997 El Niño haze
- 20 event as detailed next.

We now compare our ground-based measurements of "pure" peat smoke to the only available airborne regional smoke measurements, which were part of the Pacific Atmospheric Chemistry Experiment 5 (PACE-5) campaign in Kalimantan during the peak of another El Niño event (Sawa et al., 1999). During late October 1997, airborne sampling was conducted west of Banjarmasin along a flight leg several hundred km long at four flight levels

- between 1.3 and 4.4 km altitude. The flight was ~100 km south of Palangkaraya and encountered 3-9 ppm of CO and ~500 m visibility at lower altitudes (Sawa et al., 1999). Gras et al. (1999) noted that no visible flame fronts were observed from the aircraft and estimated one SSA for a Kalimantan smoke plume as 0.98. This is close to our<u>We can estimate an SSA at 530 nm value if weby linear interpolatione between 870 and 405 nm and obtain a similar value (0.981). They measured large hygroscopic growth factors of 1.65 which agreed well with tests of peat
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- 30 combustion they cite by Golitsyn et al. (1988). From the same flight Sawa et al. (1999) reported NO_x/CO ERs of 0.00019 to 0.00045, which they attributed to a lack of flaming combustion, but also possibly faster losses of NO_x than CO. We observed several individual values in their range (our minimum was 0.00028), but our average NO_x/CO ER is higher (0.0012 \pm 0.0007). The comparison is good in that the ranges overlap and are consistent with smoldering combustion, but some fast NO_x losses probably also impacted the airborne ERs. The PACE-5 team
- 35 speculated that high SO_2 emissions could contribute to the hygroscopicity and cited unpublished lab tests that confirmed high SO_2 from burning peat. We did not see evidence of elevated SO_2 , but our measurements were conducted further inland, possibly away from Holocene coastal sulfidic sediments invoked by Gras et al. (1999) as a

possible source of SO₂. During FLAME-4, no SO₂ was detected from burning peat in the lab except for the one sample of coastal peat which was collected in North Carolina (Table S2 in Stockwell et al., 2015). This suggests that the emissions from burning coastal peat deposits are impacted by their known chemical differences (Cohen and Stack, 1996).

- 5 Hamada et al. (2013) measured CO₂, CO, and CH₄ emissions from a peat fire near Palangkaraya during the 2009 El Niño. Based on 23 samples, they report CO/CO₂ and CH₄/CO₂ ERs of 0.382 and 0.0261; 31 and 56% higher than our study averages, respectively, but within our range for individual plume averages. Their data are consistent with a smoldering-dominated burn and an MCE of 0.724, which is within our range for individual fires (one of ours was lower (0.693), though our study average was higher (0.772 \pm 0.035).
- 10 Two very recent studies probed peat fire emissions during the 2015 El-Niño. Huijnen et al. (2016) measured three EFs for peat fires also near Palangkaraya. Their "peat-only" EFs are 255 ± 39 , 1594 ± 61 , and 7.4 ± 2.3 g/kg for CO, CO₂ and CH₄, respectively. Their means are all within one standard deviation of our means and their EFs are within ± 1.9 , ± 1.3 , and $\pm 22\%$ percent of ours, respectively. Not many details of the measurements are given, but the agreement is good. Parker et al. (2016) report three space-based measurements of the ER for Kalimantan fires in
- 15 Sept-Oct 2015 for CH_4/CO_2 ranging from 0.0062 to 0.0136. This is lower on average than the CH_4/CO_2 ERs reported for peat combustion in the in-situ studies cited above (range ~0.011 – 0.035). The difference is consistent with our expectation noted above that some flaming-dominated consumption of surface fuels likely contributed to regional emissions in 2015. However, a glance at Figure 6 in Parker et al. (2016) shows that some of highest retrieved levels of these gases, which they attribute to fires, are far off-shore and/or upwind of the fires. Thus, more
- 20 <u>evaluation is clearly needed to determine if space-based approaches can accurately measure CH_4/CO_2 ERs (e.g. Agustí-Panareda et al., 2016).</u>

3.4 Application of emission factors

The basic application of emission factors is to multiply them by a total fuel consumption to generate total emissions for a desired region (Seiler and Crutzen, 1980). Our EFs in this work are intended for use with peat consumption 25 estimates to calculate total emissions from the peat component. Major uncertainties would include natural variation of the EFs (e.g. the standard deviations of the EFs given in Table 2) and variation in %C, density, and burn depth of the peat. Konecny et al. (2016) list some other %C and burn depth measurements, which are generally close to our values. We plan to present further data on these issues in a separate paper. We note that in a previous review of BB EFs Akagi et al. (2011) estimated literature average values for EFs for pure peat. Following Page et al. (2002) they 30 also computed "peatland" EFs by combining the peat EFs and fuel consumption with EFs and fuel consumption for tropical peat swamp forest, which was considered as the only surface fuel type. This was potentially appropriate for 1997. However, given on-going land-use trajectories, it is now clear that many different types of surface fuels and a variety of fuel combinations are important (Miettinen et al., 2016). The work here presents EFs specific for the major peat component that can be coupled with peat fuel consumption estimates and that ideally contribute to 35 emissions estimates after combining with fuel consumption estimates and EFs for the relevant surface fuel types.

- Many of the EFs and fuel consumption values for other surface fuel types are tabulated in Akagi et al., (2011).
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Another earlier set of trace gas EF previously available for tropical peat burning was from a laboratory study (Christian et al., 2003) and was also adopted in IPCC guidelines (Table 2.7 in IPCC, 2014). We suggest our new and more extensive field-measured values are more appropriate and that this involves significant adjustments for the EFs for most gases compared to the 2003 study notably: CO_2 (-8%), CH_4 (-55%), NH_3 (-86%) and CO (+39%).

5 Improved EFs, at least for Kalimantan, for numerous other gases are found in Table 2. Finally, this work also provides previously unavailable field measurements of aerosol optical properties. Both the aerosol and trace gas data in this study should be used with the understanding that many quantities will be affected by smoke evolution (e.g. Hobbs et al., 2003; Abel et al., 2003; Yokelson et al., 2009; Akagi et al., 2012; Alvarado et al., 2015).

3.5 Comparison to, assessment of, and synthesis with FLAME-4 lab data for peat fires

10 In this section we explore combining our new field data with the FLAME-4 lab data to develop an even more comprehensive set of EFs for the peat component of peatland fires.

3.5.1. Lab/Field Comparison

Reasonable agreement for FLAME-4 lab measurements with our field measurements of aerosol properties was already demonstrated above. The comparison for the larger body of trace gas data is detailed next. For gases measured in FLAME-4 and the field for Kalimantan peat, and by Christian et al. (2003) in the lab for Sumatran peat,

- 15 measured in FLAME-4 and the field for Kalimantan peat, and by Christian et al. (2003) in the lab for Sumatran peat, we present the comparison graphically in Figure 7. Despite the high inherent variability, the Kalimantan field data overlap well with the Kalimantan samples burned in FLAME-4 (Stockwell et al., 2015). However, the one Sumatran peat sample is noticeably different. For the 21 compounds shown, 16 out of 21 field average EFs fall closer to Kalimantan lab mean EFs than the Sumatran lab EFs. However, based on one Sumatran sample alone we cannot yet say if the lab work is capable of resolving regional differences that may occur in peat fire emissions.
- Table S3 compares all 31 gases nominally measured for Kalimantan samples in both the lab (FLAME-4) and the field. (We clarify the need for the term "nominal" below.) Due to the natural high variability in the field data, the low number of lab measurements (two), the use of different peat samples, etc.;, we start by proposing that the lab measurements provide useful EFs for species not measured in the field if the average of the two lab EFs is within a
- 25 factor of two of the field mean for species measured in both locations. Next, we find in the right-hand column of Table S3 that 15 of 31 species fail this initial factor-of-two test (ratios shown in red). However, this result is somewhat misleading since the lab data for 8 of these species (shown in blue) is actually comparing a best guess at the identity of the most abundant isomer for an exact mass measured in the lab to a WAS-based analysis for a specific isomer. Thus, these ratios could be larger than two because of contributions from other isomers (or
- 30 fragments) to the mass spectrometer signal, higher than normal sensitivity in the mass spectrometer, WAS error, or unusually high variability for some species; with no way of knowing the individual contribution of these factors. We do note that a generally good comparison of the WAS and mass spectrometer was obtained when they were compared more directly in peat smoke in the lab (Hatch et al., 2016). Thus, only 7 out of 23 compounds fail the factor-of-two test, if we eliminate species that are ambiguous due to isomers. Of these 7 species, three are very close
- 35 to the factor-of-two cutoff and notare of less concern (ammonia, acetaldehyde, and hydroxyacetone). For the

remaining 4 species (formic acid, NO, 1,3-butadiyne, styrene) the lab values tend to be higher for unclear reasons. For instance formic acid iswas higher in the lab where an open-path FTIR system was used instead of the closed cell FTIR system in the field, which could be subject to sample losses. However, HCl (below detection in lab) and NH₃ are likely more prone to adsorption than formic acid (Yokelson et al., 2003) and they were higher as measured with

- 5 the field system suggesting the Teflon sample line and coating on the closed cell were effective in minimizing losses and sampling losses were not the source of the discrepancy. The lab "average" for NO was more than four times higher than the field value implicating high variability. NO was below detection in one lab fire and "high" in the other lab fire where flaming briefly occurred. The one field fire where flaming was briefly observed (Plume C, Table S2) had an even higher EF for NO than in the lab fire where it was detected. The other two species of concern
- 10 are styrene and 1,3-butadiyne. These two ratios could be high due to decay in the canisters, fragments in the mass spectrometer, or perhaps other less likely reasons. In summary, more lab/field comparisons should be carried out, but our rough analysis suggests that trace gas EFs measured in the lab are useful estimates (i.e. within a factor of two) for the emissions of most gases not yet measured in the field."Table S3 compares all 31 gases measured for Kalimantan samples in both the lab (FLAME 4) and the field. The average of the two lab EFs is within a factor of
- 15 two of the field mean for 20 of 31 species, which is adequate given that a factor of two is essentially also the field coefficient of variation (n = 35). In 7 of the 11 cases with more than a factor of two difference, the lab value is actually the sum of isomers compared to a single isomer from the GC analysis of the field WAS samples. For the remaining 4 species the lab values tend to be higher for unclear reasons. For instance formic acid is higher in the lab where an open-path system was used instead of the closed cell system in the field, which could be subject to sample
- losses. However, HCl and NH₃ are likely more prone to adsorption than formic acid (Yokelson et al., 2003) and they were higher as measured with the field system suggesting the Teflon sample line and coating on the closed cell were effective in limiting line losses. The lab average for NO is higher, but NO was below detection in one lab fire and high in the other where flaming briefly occurred. The one field fire where flaming was briefly observed (Plume C, Table S2) had a higher EF for NO than the lab fire where it was detected. Thus, further comparisons with more lab fires will clearly be useful, but it appears the trace gas EFs from the lab are reasonable proxies for the EFs for

3.5.2 Value of lab data

species that have not been measured in the field.

The value of lab NMOG EFs for peat burning is evident in at least two ways. First, with more powerful-broadlysensitive instruments in the FLAME-4 study a significantly larger amount of NMOG mass was measureable. For the

- 30 two FLAME-4 "stack" burns of Kalimantan peat (fires 114 and 125) where losses on the laboratory walls cannot occur during storage as with "room" burns (Stockwell et al. 2014), the high-resolution mass spectrometer and FTIR combined to measure 52.7 ± 5.0 g/kg total NMOG on average (Stockwell et al., 2015). This includes unidentified or tentatively assigned mass peaks that accounted for ~37% of detected NMOG mass. Our field equipment (with higher mobility requirements) measured 22.5 ± 6.7 (max 30.3) g/kg of total NMOG emissions on average. An alternate
- 35 metric is to note that the species measured in both the field and lab accounted for 52-68% of the total NMOG measured in the lab. The missing NMOG mass in the field measurements is not large enough to cause significant
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error in our field carbon mass balance, but would impact estimates of secondary formation of aerosol and O_3 (Yokelson et al., 2013; Hatch et al., 2015). In addition, a much larger number of species (>400) including extensive speciation of isomers by 2D-GC was reported in FLAME-4 although most of them were not emitted in large amounts (Hatch et al., 2015). Perhaps most importantly, the FLAME-4 lab experiment provides EFs for some key

- 5 individual species not measured in the field including: acrolein (an important air toxic, EF 0.19 ± 0.03 g/kg); methylgyloxal (important in the formation of both aqueous SOA and BrC (Lin et al., 2015), EF 0.19 ± 0.04 g/kg); and acetamide and other air toxics, which we discuss in more detail next. The pure smoldering Kalimantan peat in FLAME-4 (fire 114) emitted acetamide (4.21 g/kg) at twice the mass of
- NH₃ (2.02 g/kg) (Stockwell et al., 2015). Acetamide can have numerous serious health effects (Ge et al., 2011) and is considered a carcinogen by the International Agency for Research on Cancer (www.iarc.fr). Barnes et al. (2010) report that isocyanic acid (HNCO) and CO are the major oxidation products of acetamide, and small amounts of CH₃OH and HCOOH formation are also seen. The acetamide lifetime would be ~3.3 days based on the measured
 OH rate constant (0.35 ± 0.1 × 10¹¹ cm³ molecule⁻¹ s⁻¹) (Barnes et al., 2010). Acetamide also reacts quickly with Cl atoms, which could be important given Indonesia's common description as the "Maritime Continent." The main
- 15 oxidation product HNCO has a longer lifetime and is also of major concern for health effects as discussed by Roberts et al. (2011).

Akagi et al. (2014) discussed air toxic gases measured in biomass burning smoke in general terms and George et al. (2016) discussed hazardous air pollutants observed in lab measurements of burning coastal North Carolina peat. In Table 4 of Akagi et al. (2014), 26 air toxic gases in addition to CO that have been measured in smoke on a

- reasonably frequent basis are shown along with recommended exposure limits. We measured 15 of these gases in the field (namely acetaldehyde, acetone, ammonia, benzene, 1,3-butadiene, ethylene, formaldehyde, HCl, *n*-hexane, hydrogen cyanide (also a biomass burning tracer), methanol, phenol, styrene, toluene, and xylene). Six of the 9 eleven others were measured for lab peat fires in FLAME-4 (acetonitrile [also a biomass burning tracer], acrolein, acrylonitrile, crotonaldehyde, methylethylketone, and naphthalene). Three of the 26 air toxics have markedly lower
- 25 exposure limits than the others: formaldehyde, acrolein, and benzene. <u>Two of these key species were measured in</u> <u>both the field and the lab and we compare the results.</u> Our field-WAS EF benzene and lab measurement by on-line mass spectrometry of EF benzene for smoldering Kalimantan peat burning agreed within 5 %. Our lab FTIR average EF HCHO is 77 % higher than our field FTIR average EF HCHO though 6 of the field fires had EF HCHO that were similar to or higher than the lab average (*n*=2).
- Akagi et al. (2014) outline a method to estimate exposures using emission ratios that we can adapt here as a simple screening procedure for local exposure to air toxics in Kalimantan. We plan more detailed assessment of health effects using the filter data (Jayarathne et al., in preparation, 2016) and regional PM₁₀ and visibility monitoring (Putra et al., in preparation, 2016). As mentioned earlier, regional PM₁₀ hit a maximum reported hourly reading of 3741 µg/m³ in Palangkaraya, which, based on preliminary CO/PM ratios derived from Tables 1 and 2, would
- 35 suggest a maximum hourly average of about 40 ppm CO (note, we did not monitor CO in Palangkaraya). This is similar to the recommended 8-hr limits (25-50 ppm) and well below the peak exposure limit of 200 ppm (Table 3, Akagi et al., 2014). Using our HCHO/CO ratio from Table 1, the peak HCHO (ignoring chemical evolution) would
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be about 0.1 ppm. This is near the low end of various recommended peak exposure limits for HCHO indicating that HCHO exposure could be a concern for local residents. In addition, the synergistic health effects of multiple pollutants need more attention (Akagi et al., 2014).

4 Conclusions

- 5 During the strong 2015 El Niño event we deployed a mobile suite of ground-based trace gas and aerosol instruments in Central Kalimantan on the island of Borneo to make rare or unique field measurements of the fresh smoke emissions from fires burning peat of various types and at a range of depths. We report emission factors (EFs, g/kg) for the major greenhouse gases and about 90 gases in all obtained by Fourier transform infrared spectroscopy and whole air sampling. The EFs can be used with estimates of peat fuel consumption to improve regional emissions inventories and assessments of the climate and health impacts of peatland fires. Our field data provide regionally-appropriate EFs for most of the measured gases that should be preferable to previously recommended EFs that were based on lab measurements of a single sample of smoldering Sumatran peat. Many of our new EF differ considerably from the previous recommendations; for example; CO₂ (-8%), CH₄ (-55%), NH₃ (-86%), CO (+39%), etc. The modified combustion efficiency of the peat fire smoke ranged from 0.693 to 0.835 with an average of 0.772
- ± 0.035 (n=35) indicating essentially pure smoldering combustion and no significant lofting of the initial emissions was observed. EFs (g/kg) for major gas-phase tracers, air toxics, or carcinogens measured include: HCN (5.8 ± 1.6), formaldehyde (0.87 ± 0.48), BTEX (benzene, toluene, ethylbenzene, xylenes, 1.5 ± 0.6), and 1,3-butadiene (0.19 ± 0.16). The field results from Kalimantan were in reasonable agreement with recent (FLAME-4) lab measurements of the trace gases and aerosol from smoldering Kalimantan peat for species measured in both studies. This suggests lab
- 20 measurements can provide useful EFs for species not yet measured in the field such as the air toxics acrolein $(0.19 \pm 0.03 \text{ g/kg})$, and acetamide $(2.54 \pm 2.36 \text{ g/kg})$. Except for HCN (lifetime in months) and benzene (lifetime in days), these air toxics observed in the field and FLAME-4 are all reactive and, therefore, of most concern for local exposure. A simple screening procedure suggests that formaldehyde and the synergistic effects of multiple pollutants are most likely to challenge recommended exposure limits locally. HNCO as a longer-lived photochemical product
- 25 of acetamide could be a health concern regionally. In addition, we measured in-situ aerosol optical properties at 405 and 870 nm with two photoacoustic extinctiometers and analyzed particulate collected on filters. The aerosol optical data measured include EFs for the scattering and absorption coefficients (EF B_{scat} and EF B_{abs} , m²/kg fuel burned) and SSA at both wavelengths. Consistent with the minimal flaming combustion, the emissions of BC were negligible (0.0055 ± 0.0016 g/kg) and
- aerosol absorption was overwhelmingly due to the organic component. For example, brown carbon contributed ~96% of aerosol absorption at 405 nm and absorption at 405 nm was ~52 times larger than at 870 nm. The importance of the organic absorption was also seen in the high average AAE (4.97 ± 0.65, range 4.29-6.23) and the average SSA at 405 nm (0.974 ± 0.016) being lower than the average SSA at 870 nm (0.998 ± 0.001). However, comparing the B_{abs} at 405 nm to the simultaneously measured organic carbon mass on filters suggests a low MAC (~0.1 m²/g) for the bulk OC, as expected for the low BC/OC ratio in the aerosol.

Future lab measurements of burning peat should be useful to screen for regional differences in emissions based on geographic origin, distance from the coast, etc., and to extend the measurement capability to new gases (e.g. highly oxygenated NMOG) and aerosol properties (e.g. size distribution, cloud condensation nuclei activity, OA volatility, etc.). Ground-based measurements of peat fire emissions in other regions of Southeast Asia are needed. In addition,

5 an extensive regional airborne campaign is critically needed for characterization of the mix of fire types that currently dominate the overall region and to measure the detailed evolution of the peatland fire smoke plumes and the coalesced regional haze.

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15 References

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Table 1. Study-average emission factors (g/kg) and one standard deviation (stdev) for trace gases significantly elevated above background in Kalimantan peat fire plumes.

Compound (formula)	Study avg (stdev) 35 plumes
MCE	0.772(0.035)
Carbon Dioxide (CO ₂)	1564(77)
Carbon Monoxide (CO)	291(49)
Methane (CH ₄)	9.51(4.74)
Dihydrogen (H_2)	1.22(1.01)
Acetylene (C_2H_2)	0.121(0.066)
Ethylene (C_2H_4)	0.961(0.528)
Propylene (C_3H_6)	1.07(0.53)
Formaldehyde (HCHO)	0.867(0.479)
Methanol (CH ₃ OH)	2.14(1.22)
Formic Acid (HCOOH)	0.180(0.085)
Acetic Acid (CH ₃ COOH)	3.89(1.65)
Glycolaldehyde ($C_2H_4O_2$)	0.108(0.089)
Furan (C_4H_4O)	0.736(0.392)
Hydroxyacetone ($C_2H_2O_2$)	0.860(0.433)
Phenol ($C_{\epsilon}H_{\epsilon}OH$)	0 419(0 226)
1 3-Butadiene (C_4H_2)	0.189(0.157)
Isoprene $(C_{+}H_{0})$	0.0528(0.0433)5.28E.2(4.33E.2)
Ammonia (NH ₂)	2 86(1 00)
Hydrogen Cyanide (HCN)	5 75(1.60)
Nitrous Acid (HONO)	0.208(0.059)
Hydrogen chloride (HCl)	0.208(0.039)
Nitric Oxide (NO)	$\frac{0.0340(0.0203)}{0.0340(0.0203)} = \frac{0.0340(0.0203)}{0.0307(0.360)}$
Carbonyl sulfide (OCS)	0.507(0.500)
$DMS(C \parallel S)$	0.00282(0.00224)2.82E.2(2.24E.2)
Chloromethane (CH-Cl)	$\frac{0.00282(0.00234)}{2.82E^{-3}(2.34E^{-3})}$
Promomethane (CH Pr)	0.147(0.057)
Mother indida (CILI)	$\frac{0.0101(0.0035)}{1.012}$
Dibromomothana (CH \mathbf{Pr})	$\frac{0.0125(0.0045)}{1.25E} \frac{1.25E}{2(4.48E-5)}$
Ethena (C, H)	$\frac{0.000104(0.000077)}{1.04E} + \frac{4(7.70E}{5})}{1.52}$
Dropana (C, H)	1.52(0.00)
i Putana (C H)	0.989(0.044)
<i>i</i> -Butane ($C_4 \Pi_{10}$)	$\frac{0.091(0.102)}{0.221(0.225)}$
1 Dutane (C II)	0.321(0.225)
i Butana (C II)	0.182(0.085)
<i>t</i> -Butelle ($C_4 \Pi_8$)	0.311(0.160)
trans-2-Butene (C ₄ H ₈)	$\frac{0.0775(0.0380)}{7.75E} \frac{2(3.80E-2)}{2(3.80E-2)}$
$CIS-2$ -Butelle (C ₄ Π_8)	<u>0.0615(0.0334)</u> 0.13E 2(3.34E 2)
<i>i</i> -Pentane (C_5H_{12})	0.123(0.135)
<i>n</i> -Pentane (C_5H_{12})	0.243(0.131)
$1,2$ -Propadiene (C_3H_4)	$\frac{0.00184(0.00227)}{1.84\pm 3(2.27\pm 3)}$
Propyne (C_3H_4)	<u>0.00565(0.00857)</u> 5.65E 3(8.57E 3)
1-Butyne (C_4H_6)	<u>0.00198(0.00137)</u> 1.98E 3(1.37E 3)
2-Butyne (C_4H_6)	<u>0.00115(0.00151)</u> 1.15E 3(1.51E 3)
1,3-Butadyne (C_4H_2)	<u>0.000299(0.000242)</u> 2.99E 4(2.42E 4)
1,2-Butadiene (C_4H_6)	<u>0.000615(0.000639)</u> 6.15E-4(6.39E-4)
1-Pentene (C_5H_{10})	0.110(0.066)
<i>trans</i> -2-Pentene (C_5H_{10})	<u>0.0397(0.0276)</u> 3.97E 2(2.76E 2)
cis-2-Pentene (C ₅ H ₁₀)	<u>0.0224(0.0152)</u> 2.24E 2(1.52E 2)
3-Methyl-1-butene (C_5H_{10})	<u>0.0303(0.0198)</u> 3.03E 2(1.98E 2)
2-Methyl-1-butene (C_5H_{10})	<u>0.0299(0.0161)</u> 2.99E 2(1.61E 2)
2-Methyl-2-butene (C_5H_{10})	<u>0.0647(0.0372)</u> 6.47E 2(3.72E 2)
2-Methyl-1-Pentene (C_6H_{12})	0.109(0.076)
1,3-Pentadiene (C_5H_8)	<u>0.0198(0.0104)</u> 1.98E 2(1.04E 2)
1,3-Cyclopentadiene (C_5H_6)	0.00998(0.00585)9.98E 3(5.85E 3)
Cyclopentene (C_5H_8)	<u>0.0246(0.0157)</u> 2.46E 2(1.57E 2)
1-Heptene (C_7H_{14})	<u>0.0790(0.0540)</u> 7.90E 2(5.40E 2)

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0.0652(0.0424)6.52E-2(4.24E-2) 1-Octene (C₈H₁₆) 1-Decene (C₁₀H₂₀) *n*-Hexane (C_6H_{14}) *n*-Heptane (C_7H_{16}) *n*-Octane (C_8H_{18}) *n*-Nonane (C_9H_{20}) *n*-Decane ($C_{10}H_{22}$) 2,3-Dimethylbutane (C_6H_{14}) 2-Methylpentane (C_6H_{14}) 3-Methylpentane (C_6H_{14}) Benzene (C_6H_6) Toluene (C₇H₈) Ethylbenzene (C₈H₁₀) m/p-Xylene (C₈H₁₀) o-Xylene (C₈H₁₀) Styrene (C_8H_8) *i*-Propylbenzene (C_9H_{12}) *n*-Propylbenzene (C₉H₁₂) 3-Ethyltoluene (C_9H_{12}) 4-Ethyltoluene (C₉H₁₂) 2-Ethyltoluene (C₉H₁₂) 1,3,5-Trimethylbenzene (C₉H₁₂) 1,2,4-Trimethylbenzene (C₉H₁₂) 1,2,3-Trimethylbenzene (C₉H₁₂) alpha-Pinene (C₁₀H₁₆) *beta*-Pinene ($C_{10}H_{16}$) 2-Methylfuran (C5H6O) Nitromethane (CH₃NO₂) Acetaldehyde (C₂H₄O) Butanal (C_4H_8O) Furfural $(C_5H_4O_2)$ Acetone (C_3H_6O) Butanone (C_4H_8O) Methyl vinyl ketone (C_4H_6O)

0.0498(0.0388)4.98E 2(3.88E 2) 0.143(0.087) 0.112(0.074) 0.0980(0.0690)9.80E 2(6.90E 2) 0.0895(0.0633)8.95E-2(6.33E-2) 0.0744(0.0509)7.44E 2(5.09E 2) 0.00531(0.00415)5.31E 3(4.15E 3) 0.0397(0.0358)3.97E 2(3.58E 2) 0.00931(0.00800)9.31E 3(8.00E 3) 0.954(0.394) 0.370(0.306) 0.0417(0.0202)4.17E 2(2.02E 2) 0.122(0.055) 0.103(0.059) 0.0271(0.0131)2.71E 2(1.31E 2) 0.00534(0.00374)5.34E 3(3.74E 3) 0.0118(0.0082)1.18E 2(8.20E 3) 0.0270(0.0228)2.70E 2(2.28E 2) 0.0235(0.0213)2.35E 2(2.13E 2) <u>0.0416(0.0335)</u>4.16E-2(3.35E-2) <u>0.0108(0.0085)</u>1.08E 2(8.55E 3) <u>0.0696(0.0552)</u>6.96E 2(5.52E 2) 0.0639(0.0457)6.39E 2(4.57E 2) 0.00299(0.00288)2.99E 3(2.88E 3) 0.00167(0.00176)1.67E 3(1.76E 3) 0.121(0.123) 0.0601(0.0310)6.01E 2(3.10E 2) 0.697(0.460) 0.0238(0.0191)2.38E 2(1.91E 2) 0.124(0.116) 0.691(0.356) 0.136(0.068) 0.0569(0.0427)5.69E 2(4.27E 2)

Plume ID>	Q	R ^a	S	T ^a	V	$\mathbf{W}^{\mathbf{a}}$	$\mathbf{W}^{\mathbf{a}}$	
Date>	5-Nov	5-Nov	5-Nov	5-Nov	6-Nov	6-Nov	6-Nov	PAX (7) avg (stdev)
Filter #	21	22	23	24	25	27	28	
EF BC (g/kg)	5.23E <u>30.00523</u> 2.48E	5.49E <u>30.00549</u> 2.60E	5.27E <u>30.00527</u> 2.50E	6.62E <u>30.00662</u> 3.14E	8.32E 30.00832 3.95E	4 .45E <u>30.00445</u> 2.11E	3.22E <u>30.00322</u> 1.53E	5.52E 3(1.62E 3)0.00552(0.00162) 2.61E 2(7.66E
EF B _{abs} 870 (m ² /kg)	$\frac{2.461}{20.0248}$	2.001 2 <u>0.0260</u>	$\frac{2.501}{20.0250}$	$\frac{3.141}{20.0314}$	$\frac{3.9512}{20.0395}$	$\frac{2.112}{20.0211}$	$\frac{1.05E}{20.0153}$	3) 0.0261(0.0077)
$EF B_{scat} 870 (m^2/kg)$	7.84	26.9	19.3	21.2	21.4	17.9	13.5	18.3(6.1)
EF B _{abs} 405 (m ² /kg)	2.91	1.33	0.787	1.61	1.78	0.651	0.405	1.35(0.85)
$EF B_{scat} 405 (m^2/kg)$	46.2	60.9	37.3	78.6	52.7	43.6	34.9	50.6(15.2)
EF B_{abs} 405 just BrC (m ² /kg)	2.85	1.29 4.22E	0.733 5.36E	1.54 6.74E	1.69 <u>8.48E</u>	0.606 4-54E	0.374 3.13E	1.30(0.85)
EF B _{abs} 405 just BC (m ² /kg)	$\frac{20.0532}{2}$	2 0.0422	$\frac{20.0536}{2}$	$\frac{20.0674}{2}$	$\frac{20.0848}{2}$	2 0.0454	$\frac{20.0313}{2}$	2) <u>0.0540(0.0176)</u>
SSA 870 nm	0.997	0.999	0.999	0.999	0.998	0.999	0.999	0.998(0.001)
SSA 405 nm	0.941	0.979	0.979	0.980	0.967	0.985	0.989	0.974(0.016)
AAE	6.23	5.14	4.51	5.15	4.98	4.49	4.29	4.97(0.65)
MCE real-time	0.726	0.763	0.773	0.778	0.824	0.833	0.831	0.790(0.041)
MCE grab sample	0.693	0.761	0.779	0.795	0.824	0.835	0.835	0.789(0.051)
$\mathrm{EF}\mathrm{PM}_{2.5}\left(\mathrm{g/kg}\right)^\mathrm{b}$	19.3	21.5	17.9	29.6	24.3	22.5	15.7	21.5(4.6) ^{<u>b</u>}
EF OC (g/kg) ^b	10.5	16.7	13.6	26.9	14.9	17.6	11.6 8 985	16.0(5.5) ^{<u>b</u>}
EF EC (g/kg) ^b	0.386	0.175	0.196	0.258	0.354	0.237	<u>020.0898</u>	0.242(0.103) ^b
MAC est. (405) (m ² /g)	0.271	7.69⊑ <u>20.0769</u>	3.40⊭ <u>20.0540</u>	3./1⊭ <u>20.0571</u>	1.14E <u>40.114</u>	3.45E <u>20.0345</u>	3.22E <u>20.0322</u>	9.13E 2(8.38E <u>2)</u> 0.0913(0.0838)

Table 2. Aerosol emission factors and optical properties measured by the PAX and filter sampling.

a-For these plumes, PAX and filter collection times are completely in sync.

b-For these quantities an preferred average based on all the filter samples will be reported by Jayarathne et al., (2016 in prep).



Figure 1. ER plots from plume N for (a) carbon monoxide, (b) methane, (c) acetylene, (d) ammonia, (e) HCN, (f) methanol, (g) furan, (h) formaldehyde, and (i) acetic acid measured by FTIR.



Figure 2. The emission factors (g/kg) and \pm one standard deviation for the 20 most abundant trace gases (excluding CO₂, CO, CH₄) in this dataset.



Figure 3. PAX real-time B_{abs} at 870 (black) and 405 (red) nm collected on 5 November showing the dominance of absorbing aerosol at 405 nm. The co-located CO mixing ratio measurement from the real-time FTIR data is shown in blue. CO background was obtained from grab samples for increased accuracy. A transition to more glowing dominated combustion with a lower aerosol to CO ratio (and lower AAE and higher MCE, not shown) is observed at



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about 2:37 pm.



Figure 4. Correlations of (a) AAE versus MCE and (b) AAE vs SSA (405 nm).



Figure 5. The emission factor of B_{scat} at 405 nm versus $PM_{2.5}$ EF. The slope is an estimate of the mass scattering efficiency.



Figure 6. The estimated mass absorption coefficient of the bulk OC from the B_{abs} assigned to BrC versus simultaneously measured OC mass on filters. Only 4 plumes were sampled by both techniques over the exact same time period (blue symbols) and they were used in fit shown to estimate the MAC.



Figure 7. Study overlap (minimum, maximum, and average) including field Kalimantan samples from this study (green), Kalimantan laboratory stack burns (blue; Stockwell et al., 2014; 2015) and a single laboratory burn of Sumatran peat (red; Christian et al., 2003).