

Our responses and changes to the manuscript are detailed below. Referee comments are highlighted in bold text, with additions to the manuscript noted in plain text. In the revised manuscript, changes are also highlighted in red.

We note the jointly prepared comment by Clare Paton-Walsh and Bob Yokelson, which is an interesting and very useful addition. Given the conclusion of the comment is that no changes are required to the manuscript, a response is not necessary.

We have corrected some typographical errors in the manuscript as follows:

P5, L28: missing 'a' in 'interpreted as relative'.

P5, L28: 'degress' should be 'degrees'.

P12, L3. 'balanaced' should be 'balanced'.

P24, F1: 'Plume interception' in caption has an errant '1' on the end.

We have also added two additional studies to the comparisons and tables:

Stockwell, C. E., Jayarathne, T., Cochrane, M. A., Ryan, K. C., Putra, E. I., Saharjo, B. H., Nurhayati, A. D., Albar, I. Blake, D. R., Simpson, I. J., Stone, E. A., and Yokelson, R. J. (2016). Field measurements of trace gases and aerosols emitted by peat fires in Central Kalimantan, Indonesia, during the 2015 El Niño. *Atmospheric Chemistry and Physics*, 16(18), 11711–11732. <http://doi.org/10.5194/acp-16-11711-2016>

Desservettaz, M., Paton-Walsh, C., Griffith, David W. T., Kettlewell, G., Keywood, M. D., Vanderschoot, M. V., Ward, J., Mallet, M. D., Milic, A., Miljevic, B., Ristovski, Z. D., Howard, D., Edwards, G. C., and Atkinson, B. (2017). Emission factors of trace gases and particles from tropical savanna fires in Australia. *Journal of Geophysical Research: Atmospheres*, 122(11), 6059–6074. <http://doi.org/10.1002/2016JD025925>

Co-Editor: M. O. Andreae comment

I'd like to request a minor addition: I found the discussion in the additional comment by Yokelson and Paton-Walsh very useful and relevant, in particular as it supports the authors' approach of background subtraction and forcing through zero. Please add one or two sentences to your manuscript that reflect this discussion and cite the discussion with its DOI in your references, so that it will be noted by readers who otherwise would not access the interactive discussion.

We thank the co-editor for their suggestion. We have added the following text to section 2.2.3:

'This method utilises a simple linear regression that only minimises the sum of the square of the deviations in the y-axis. An alternative method is a more complex regression that minimises the sum of the square of the deviations in both the x and y-axis weighted by the uncertainty in each individual data point; Paton-Walsh and Yokelson (2017) conclude that the uncertainty associated with the simpler method is insignificant compared to the real overall uncertainty in fire emission ratios. Therefore we use the simpler method in this study, where the excess concentrations of species x and the reference species concentration are integrated over the plume intercept, with the regression slope of these species giving ER_x .'

Referee #1: R. J. Yokelson comments

We very much thank the reviewer for his detailed comments, which have significantly improved the manuscript.

Several savanna fires and one forest fire were sampled in the near-field with a heavily instrumented aircraft in Brazil to measure emission factors (EF). These are the first EF measurements in Brazil since 2004 and 1996. The earlier studies sampled more fires, but there is way too little sampling of these extremely important, but variable sources. Further, this study used some instruments not previously deployed on fires in Brazil. The data should be published without a doubt. Since fires are variable, any EFs measured will fall on a Bell curve. Thus, the expectation is not that this data must agree with previous averages, but that it can be combined with previous data to nudge an evolving global average. At the same time, the authors find no evidence that erroneously low EF in previous work caused the ubiquitous low a-priori emissions in regional to global models.

We thank the reviewer for his positive comments.

There is one serious oversight that needs to be fixed. Ferek et al., (1998) reported EF as gC/KgC not g of species /Kg fuel. Assuming the fuel is about 50% C, their EF for BC need to be divided by two to compare to the work here. The EF for CO₂ should be divided by two and then multiplied by (44/12) to convert to g CO₂/ kg fuel, etc. The authors should recalculate all the Ferek et al numbers correctly and then update their comparisons, which come much closer in many cases if this step is taken.

We thank the reviewer for highlighting this mistake in the manuscript. We note that Akagi et al. (2011) reported updated emission factors in their supplementary material for Ferek et al. (1998) based on correspondence with the authors and reanalysis of their published fire types. Given the revisions presented in Akagi et al. (2011), we have updated our figures for Ferek et al. (1998) to match.

Upon updating the values from Ferek et al. (1998), the major difference in our comparisons is for OC, which is now much closer to the Rondonia fire. This has been noted in the revised manuscript.

Minor terminology point: “rainforest” is kind of colloquial. I suggest evergreen tropical forest throughout as distinct from seasonally dry tropical forest or just tropical forest if they are not sure which type. It is important to distinguish between understory and deforestation fires, which they do.

We have replaced ‘rainforest’ with ‘tropical forest’ throughout the manuscript. This change includes the title of the manuscript, which is now ‘Near-field emission profiling of Tropical Forest and Cerrado fires in Brazil during SAMBBA 2012’.

One topic not mentioned that might make a good addition to the paper if possible. Were any aerosol optical properties measured? If so, did they scale with EC/OC or MCE as in Pokhrel et al., (2016)?

Aerosol scattering and absorption were measured by a nephelometer and PSAP respectively. However the performance and time-resolution of the PSAP was not sufficient to calculate the single scattering albedo. We do not report scattering-related measurements as we prefer to focus on the chemical properties of the aerosol. Furthermore, measurements of aerosol optical properties will be a focus of a forthcoming manuscript detailing regional pollution during SAMBBA.

P1, L12: I suggest defining organic aerosol as “(OA)”. OA is the primary measurement, but OC is reported by dividing OA by 1.6. Reporting OC facilitates comparison with more historical data, but it might be worth reporting OA too?

We have added the emission factor values for organic matter (OM) to the abstract so that the nomenclature is consistent with the rest of the manuscript.

P1, L15: “fuel content” to “fuel mixture” maybe?

Replaced.

P1, L17: Perhaps change “scaling” to “scaling up” to set the context for why the possibility of low EF was interesting.

Amended.

P1, L18: Maybe simplify the end of this sentence as e.g. “. . . one potential cause of low a-priori emissions in modeling studies.

Left as is.

P2, L12: delete “to”

Deleted.

P2, L15: There is a far more complex mix of burning in Brazil than just two fire types as discussed at length elsewhere (section 2.3, Yokelson et al., 2007). Referees complained about the length of that section, but maybe a broader summary is in order here. Something like ~”a range of climate and fire types occurs in Brazil and fire-impacted ecosystems include pure grassland, a gradient of wooded savannah into dry (seasonal) tropical forest (aka Cerrado), and evergreen tropical forest (Ward et al., 1992). In forested areas understory fires can occur, but deforestation fires to establish pastures or croplands, along with pasture maintenance and agricultural residue fires are the most common types of burning on an evolving heterogeneous landscape.” You could cite our 2007 paper or any of the excellent papers cited there-in. Then mention (move here) the later statements (already with citations) about burning shifting from forests to savannas.

We have added the following to the manuscript:

‘A range of climate and fire types occurs in Brazil, with fire-impacted ecosystems including pure grassland, a gradient of wooded savannah into dry (seasonal) tropical forest and evergreen tropical forest (Ward et al., 1992, Yamasoe et al., 2000). Deforestation and Cerrado (savannah-like) fires are commonly used for land clearing and pasture maintenance (Martin et al., 2010),

which leads to high levels of black carbon, organic matter and gas phase species in the atmosphere.'

P2, L23: Actual landscape fires can rarely be characterized by a single stage, but instead there is a dynamic, variable mix of flaming and smoldering processes.

We have added that fires are made up of 'a dynamic, variable mix of combustion phases'.

P2, L29-30: By sampling more we get a better idea of the mean and range. We can also learn about the factors driving the variability, which I think this study may do thru its analysis.

Noted.

P3, L1: Insert "and other" before "regions" as the mix of AMS and SP2 been used in the US on chaparral fires (Akagi et al., 2012), prescribed forest fires (May et al., 2014), agricultural fires (Liu et al 2016), etc.

We have added the additional references to the manuscript.

P3, L1-4: The historical context and the contrast with the current effort is a bit oversimplified. Previous work was not necessarily less sensitive or unable to probe individual plumes. Yokelson et al., (2007) flew Artaxo's calibrated nephelometer to get real-time PM10 in numerous single plumes and computed PM10 EFs for Brazilian fires. Light scattering measurements are pretty sensitive. It could be that PM based on light scattering is not as accurate as an AMS, but evidently a nephelometer was used to scale the AMS data in this work. In SCAR-B in Brazil and SAFARI 2000 in Africa, a very large bag sampler was used and instantaneously filled in numerous individual plumes at multiple ages per plume. This allowed sensitive filter sampling, though filter artifacts can occur (e.g. Ferek et al., 1998; Sinha et al., 2003). Also, real-time data was acquired with a suite of PM instruments in individual plumes in the Mexican tropics in Yokelson et al., (2007, 2009, 2011). I think Capes et al., (2008) deployed an AMS on North African fires. To my knowledge this was the first study to use both AMS and SP2 in individual smoke plumes in the tropics. However, the sentence implying this is particularly true for airborne work should be deleted unless the authors can cite a ground-based study of individual tropical BB plumes that used both SP2 and AMS. Finally, depending on performance, different approaches have a different set of strengths and weaknesses.

We appreciate the reviewer's comments on this section and have re-written the text to focus more on the ability to measure aerosol chemical composition, which we feel is the major instrumental advance presented in our manuscript given the known biases for filter-based sampling. We have also omitted the text in relation to low time resolution given the reviewer's note that a large bag sampler was used in previous measurements. We have also deleted the sentence regarding airborne and ground-based sampling.

The new discussion is as follows:

'Previous measurements of the chemical composition of particulate emissions from South American tropical biomass burning were conducted over a decade ago using filter-based

sampling, which have known biases (e.g. Bond and Bergstrom, 2006; Chow et al., 2007; Lack et al., 2008; Petzold et al., 2013; Bond et al., 2013).’

P4, L1-5: The authors estimated the mass of PM from scattering data to scale the AMS mass. They should report what mass scattering efficiency they used and an error estimate. Then a scaling factor of 2.69 +/- ? Further, if the SMPS could be used to measure the AMS collection efficiency, it seems like it could also be used for an independent estimate of the AMS scaling factor. On L5 add “forest fire” before “data”.

We calculated a mass scattering efficiency of $5.98 \text{ m}^2/\text{g}$ based on four biomass burning flights unaffected by the pinhole blockage. We will report this and the uncertainty in the scaling factor (2.69 ± 0.3) in the updated manuscript.

We have updated the sentence in the manuscript, which now reads as:

‘The applied scaling factor was 2.69 ± 0.3 based on measured mass scattering efficiencies of $16.1 \pm 0.3 \text{ m}^2/\text{g}$ and $5.98 \pm 0.3 \text{ m}^2/\text{g}$ for the partially blocked and unblocked flights respectively and is applied to the data for B737 in this study’.

We used the nephelometer rather than the SMPS or GRIMM data due to better instrument coverage during the campaign and to eliminate changes in the size distribution of the aerosol as a conflating factor in the comparison.

For the sake of comparison, we calculated a scaling factor of 3.02 using the GRIMM data.

P4, L15: It’s not super clear how coincidence was solved. Evidently they did not account for small rBC particles below the SP2 size cutoff as is sometimes done, but the figures seem to indicate this correction is not needed in this case.

See response to referee #2 regarding the SP2 operation.

P5, L15-20: Perhaps report both OA and OC and use OA along with the other species to estimate and compare fine PM?

We have reported both organic matter (the AMS native measurement) and organic carbon.

P5, L23: Technically “hydrocarbons” should be non-methane organic gases (NMOGs) since O-containing VOC dominate. Likewise on P6, L17

Amended.

P6, L2-3 don’t need, smoke dilution rates slow down exponentially with time and can be even faster on ground-based measurements closer to the source.

We have deleted ‘The absolute concentration of trace gases and particulates in fire plumes cannot directly be used to interpret emissions due to the dilution of the species with the ambient background air. This is particularly important when sampling smoke from aircraft platforms.’

P6, L22: A “few” percent is probably more accurate than 1-2% if particulate carbon, which was measured is not included in total C.

Amended.

P6, L26 “molecular” should be “atomic in the case of carbon (an error I have made many times).

Amended.

P7, L15: This is a nice description of the fire. Hotspots are shown in the figure on the day of sampling. It is stated there were no hotspots the previous day and the fire may have started the same day it was sampled. The fire seems a bit large to emerge in one morning and the authors could check a few of the previous days for hotspots since, due to cloud cover or orbital gaps any particular day may have no hotspot data. Brazilian fires can be anthropogenic and off-road due to the presence of indigenous peoples. We likely sampled some of these in an indigenous preserve along the Xingu River.

We have clarified the following sentence ‘MODIS hotspot data from the TERRA overpass at 14:26 UTC on 19 September 2012 indicated that this fire was likely started that day’ in the manuscript as we realise that it was unclear that we were stating that the fire likely started on the day prior to our flight (20 September 2012).

The revised sentence now reads as:

‘MODIS hotspot data from the TERRA overpass at 14:26 UTC on 19 September 2012 indicated that this fire likely started on the day before our flight.’

We have added the following sentence to acknowledge that the fire may have been started by indigenous people:

‘However, we cannot rule out that the fire may have been started by the presence of indigenous people, which would mean the fire was anthropogenic in origin.’

P7, L26: 30 ppm is really fresh! That’s a good sign that the EF are not distorted by mixing.

Noted. No amendment made.

P8, L24: The high r-squared likely indicates that the plume was well-mixed and the fire burned a homogeneous fuel bed as opposed to a “common source.” (relevant also to P10, L8)

Amended. Revised sentence:

‘The trace gas species measured on the aircraft are very strongly correlated, with r-squared values between 0.92 and 0.99 illustrating that the plumes are well-mixed and that these active fires likely burned a homogeneous fuel bed.’

P8, L25-26: Perhaps the authors are trying to say that there is more variability when sampling a group of fires than a single fire, but the group of fires has a fairly high r-squared nonetheless.

This is correct. No amendment required.

P9, L4-5: Also a general comment. The data for the Rondonia fire is in good agreement for PM and CH₄ with the data for tropical dry forest fires in Mexico (Table 3 in Yokelson et al., (2011)). Yokelson, R. J., Burling, I. R., Urbanski, S. P., Atlas, E. L., Adachi, K., Buseck, P. R., Wiedinmyer, C., Akagi, S. K., Toohey, D. W., and Wold, C. E.: Trace gas and particle emissions from open biomass burning in Mexico, *Atmos. Chem. Phys.*, **11, 6787-6808, doi:10.5194/acp-11-6787-2011, 2011.**

We thank the reviewer for highlighting this and note that the study is included in our comparison tables. Rather than comparing to every study detailed in our tables, we limited the comparisons to mainly studies in Brazil to improve the readability of the manuscript. No amendment required.

P10, L2: It's worth clarifying if they are showing the size of the BC core or the core plus coating, and also confirming that coated BC particles were included in the computation of BC mass.

We have noted that the size distributions refer to the BC core size. The instrumentation section states that the 'total mass of particles containing refractory black carbon' is determined i.e. all particles (both coated and uncoated) that contain BC are measured.

P10, L15: I would delete "more than" and possibly add "approximately" in light of the uncertainties.

Amended.

P10, L25 – P11, L6: Several things can be quickly fixed in here and throughout. The Ferek et al values that are compared to need to be converted to g species per kg of fuel. After doing that, the Akagi et al review paper lists these values for Ferek et al as examples: Savanna (OC 2.94, BC 0.35 (note good agreement with Sinha et al., (2003) for African savannas)) and Tropical Forest (OC 4.34, BC 0.46). So for instance, on P11, L3, the Ferek et al value is 0.35 and not 0.7 for EFBC. The authors should go thru all the text, tables, and also figures if applicable, and update the values quoted for Ferek et al and the comparisons as well. Further, most of the "BC" measurements they compare to are actually "EC" measurements that can be impacted by charring of OC. (The PAX measurement in Stockwell et al are an exception.) This should probably be mentioned here (along with later mention) and might inform the comparison.

See response to prior comment on this mistake.

P11, L2: The Stockwell measurements were by in-situ photoacoustic spectroscopy. This may be a good place to mention EC artifacts and the possibility of lower EFBC because of an unusually smoldering fire. Nonetheless, the data can be factored into the global average nudging it down.

We have added a reference to the Stockwell et al. (2016) results for black carbon and elemental carbon to the discussion:

'Stockwell et al. (2016) reported emission factors for black carbon and elemental carbon of 0.0055 ± 0.0016 g kg⁻¹ and 0.24 ± 0.10 g kg⁻¹ respectively, illustrating the significant

differences in what is usually assumed to represent EFBC when using different measurement techniques.'

P12, L22: change "to" to "as"

Amended.

P13, L9: change "is" to "was"

Amended.

P13, L26: Re "the instrument" – was the SAMBBA SP2 or the May et al SP2 or both SP2's calibrated with urban-BC relevant material? Suggest clarifying by changing to "our instrument" "both instruments", etc as appropriate.

Amended. Both the May et al. and our SP2 were calibrated using urban-BC relevant material.

P13, L27-28: Informational only, we have just completed such a comparison in FIREX

Noted.

P14, L19: If there is no clearing then a fire is not a deforestation fire, but understory fires can be indigenous/anthropogenic to promote favored tree species, for hunting, or to improve access.

We have noted the following in the conclusion, which is supported earlier in our discussion of the fire in the results (section 3.1.1):

'We believe that the Rondonia fire was most likely a wildfire.'

P14, L20: "numerous" may be a bit overstated for what looks like about ten hotspots in 3 groups. Maybe "several" or "a group of" is better.

Amended.

P14, L24: "illustrate" to "confirm" since the differences in initial emissions is a fairly well-known topic.

Amended.

Fig. 1. Nice fire pics, perhaps a larger version in supplement would be worthwhile?

We will add the pictures as a supplement to the paper.

Fig. 4. It seems odd that the values are larger for the Tocantins fires given the lower emissions??

We're unsure what the referee is referring to here. The rBC number and mass values are indeed larger for the Tocantins fires given the rBC emissions were much greater than the Rondonia fire. Perhaps the referee has not seen the difference in the scales? With that in mind, we did note in the figure caption that the scales differ.

Table 1: header, reference 9 is Akagi et al., (2012). “laboratory” entry could be “lab/field” since the cottonwood log was in lab, but the Zambian log was in the field.

Amended.

Table 2: There should not be any missing (“-”) values since all three gases were measured in all cited studies. For the Brazil smoldering logs (ref 2) the value for CH₄/CO (X1000) is 143 not 14.3. This value for ref 7 may also be a factor of ten low?

We have added the missing values and corrected the typographical error for ref. 2.

Table 3: Third and thirteenth entries down for EFCO₂ (ref 3) looks suspicious.

We have updated these values (for Ferek et al. (1998)) following the previous comments.

Referee #2: G. R. McMeeking comments

We thank the reviewer for their comments.

The manuscript presents biomass burning emission measurements during a series of research flights over several fires in Brazil. This is a region of global significance in terms of both total particulate matter as well as black carbon emissions. While there have been several previous campaigns focused on characterizing emissions in this region, none have used more modern instruments, and the relative scarcity of data from this area coupled with its importance certainly merits publication in my opinion.

I have little to add beyond Dr. Yokelson’s thorough comments, but do recommend addressing a couple of smaller issues/areas in more detail in the manuscript in a revised version:

It would be helpful to others in the SP2 community to know a bit more about how the instrument was operated in these more challenging conditions. Some small details regarding the sample flow rate and dilution (if any) could be provided. In addition, an estimate of the concentration limit where true particle coincidence (multiple BC present in the laser beam at the same time) would be helpful, and a verification that the field data remained below this value.

We have noted the SP2 sampling conditions in the revised text as follows:

‘The SP2 sample flowrate was approximately 120 vccm and operated without sample dilution.’

We have also added more details regarding the particle coincidence citing a subsequent analysis for very high direct diesel emissions using the Manchester aerosol chamber as described in Liu et al. (2017):

‘An offline comparison of the SP2 with a Sunset OC/EC measurement at very high BC mass loadings was performed by measuring the direct diesel emissions using the Manchester aerosol chamber (Liu et al., 2017), which suggested a high correlation between both measurements under high BC mass loading (up to approximately 15 µgsm⁻³). Above this limit, the SP2

measurement was biased low. However, the BC masses in this study were well below this threshold, thus would not be affected by the coincidence issue.'

Liu, D., Whitehead, J., Alfarra, M. R., Reyes-Villegas, E., Spracklen, D. V., Reddington, C. L., ... Allan, J. D. (2017). Black-carbon absorption enhancement in the atmosphere determined by particle mixing state. *Nature Geoscience*, 10(3). <http://doi.org/10.1038/ngeo2901>

The manuscript mentions the use of dryers on the AMS and SP2 inlet line, but does not discuss losses. Deriving correction factors for losses in nafion dryers can be difficult, but some short discussion of potential impacts on measurement uncertainties would be useful. On a related point, I assume the nephelometer inlet line RH was at times quite different from the AMS/SP2 line, else the nephelometer could be used to apply corrections for the pin-hole issue earlier in the study at all times. I am curious if the pinhole blockage effects may have varied with sample line RH. Any systematic relationships between emission ratios to CO and RH might hint at this.

We have added that nafion driers are subject to particle losses and that they represent an additional uncertainty, which we have not considered in our analysis as we assume these to be small compared to the instrument and variation in the ambient sampling.

We discovered an error in the text, which mistakenly stated that the pin-hole correction was applied to data where the sample line humidity was below 40%. We actually used all of the data during low-altitude segments as we did not observe a dependence on relative humidity. This has been corrected in the revised manuscript. We have also added that only slow-mode data from the AMS was used given the difficulty in matching 1Hz data from the AMS, SP2 and nephelometer data together.

Suggest referring to BC "core" diameters rather than BC diameter to avoid potential confusion with the mixed particle size.

Amended throughout.

I recommend reporting an average OA mass concentration in Table 6. This can be useful for any future comparisons with EF measured at different concentrations and can help untangle potential impacts of semi-volatile partitioning.

We note the comment but we have reported the range in OA mass concentration in Figure 2 and sections 3.1.1 and 3.1.2. We feel this is the most transparent method for describing the experimental conditions given the range in concentrations spanning two orders of magnitude, whereas a simple average would be misleading given this range.

No changes made to manuscript.

Referee #3: C. Paton-Walsh comments

We thank the reviewer for their comments.

This is an excellent paper presenting some very valuable measurements of emissions from fires in Brazil, a poorly sampled region of the globe. The paper is definitely suitable for

publication in ACP, and has been expertly reviewed already by Bob Yokelson and Gavin McMeeking. I have a few minor additional comments below:

1. It has become traditional (following Yokelson et al., [1999]), when calculating emission ratios via the best straight-line fit to a plot of one species against the reference species, to first subtract the background amounts and then force the regression to go through zero. However, subtracting background amounts is not required, because this has no mathematical impact on the gradient of the best line fit. Forcing the line through zero may change the gradient, but it puts unnecessary weight to the background concentrations measured/assumed. If these are very close to the real (and unchanging) background amounts, then the change to the gradient that occurs when you force the line through zero will be small. If the background assumed is incorrect, or is changing, the effect can be quite significant, as pointed out in a later paper by Yokelson et al., [2013]. A generalised least squares regression (that takes into consideration the uncertainties in both x and y) is a mathematically simpler and more accurate way to determine the emission ratio. I recommend this way to calculate emission ratios. It will not avoid all of the issues pointed out in Yokelson et al., [2013] if the background amounts are hugely variable, but it will minimize them compared to the calculation the authors have used in this study. Having said that, the high r-squared values lend confidence to the results in this study. If the authors are confident that they haven't biased their results significantly and do not wish to go back and recalculate the emission ratios, then I recommend that a sentence is added on this matter. The sentence should point out that forcing the regression through zero can bias the emission ratio if the background amounts assumed are wrong or change, but in this case they are confident they are not subject to the pitfalls described in Yokelson et al., [2013].

We thank the reviewer for their comment and their previously referred to joint-comment with referee #1 on this issue, the conclusion of which is that no changes to the manuscript are necessary.

No changes made to manuscript.

2. The use of the 1 sigma uncertainty of the best line fit as the total uncertainty in the emission ratio is not valid when the uncertainties in the individual points are correlated with one another (which they are in this case). Ideally you should undertake a proper uncertainty analysis of your measurements. As a minimum you should acknowledge that the uncertainties in each point are correlated and so your value of the uncertainties will be an underestimate (since it will include the random errors only).

We have added the following to section 2.2.2:

'Uncertainties in the ERs are derived as the one standard deviation error in the slope of the line of best fit following e.g. Akagi et al. (2012). Such uncertainties will represent an underestimate as they only include random errors given that the uncertainties in each point are correlated.'

3. Finally, I assume that the correction to the AMS data that was required as a result of the partial blockage of the inlet would have added to the measurement uncertainties? Again, if it

is not feasible to undertake a proper uncertainty analysis, you should at least acknowledge this has not been done and mention the additional uncertainty in the text.

This has been partially covered in the response to referee #1. We have added that this represents an additional uncertainty to our calculations.

Near-field emission profiling of Tropical Forest and Cerrado fires in Brazil during SAMBBA 2012

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Abstract. We profile trace gas and particulate emissions from near-field airborne measurements of discrete smoke plumes in Brazil during the 2012 biomass burning season. The South American Biomass Burning Analysis (SAMBBA) Project conducted during September and October 2012 sampled across two distinct fire regimes prevalent in the Amazon Basin. Combined measurements from a Compact Time Of Flight Aerosol Mass Spectrometer (C-ToF-AMS) and a Single Particle Soot Photometer (SP2) are reported for the first time in a tropical biomass burning environment. Emissions from a mostly-smouldering tropical forest wildfire in Rondônia state and numerous smaller flaming Cerrado fires in Tocantins state are presented. While the Cerrado fires appear to be representative of typical fire conditions in the existing literature, the tropical forest wildfire likely represents a more extreme example of biomass burning with a bias towards mostly-smouldering emissions. We determined fire integrated modified combustion efficiencies, emission ratios and emission factors for trace gas and particulate components for these two fire types, alongside aerosol microphysical properties. Seven times more black carbon was emitted from the Cerrado fires per unit of fuel combustion (EF_{BC} of $0.13 \pm 0.04 \text{ g kg}^{-1}$) compared to the tropical forest fire (EF_{BC} of $0.019 \pm 0.006 \text{ g kg}^{-1}$) and more than six times the amount of organic aerosol was emitted from the tropical forest fire per unit of fuel combustion (EF_{OM} of $8.00 \pm 2.53 \text{ g kg}^{-1}$, EF_{OC} of $5.00 \pm 1.58 \text{ g kg}^{-1}$) compared to the Cerrado fires (EF_{OM} of $1.31 \pm 0.42 \text{ g kg}^{-1}$, EF_{OC} of $0.82 \pm 0.26 \text{ g kg}^{-1}$).

Particulate phase species emitted from the fires sampled are generally lower than those reported in previous studies and in emission inventories, which is likely a combination of differences in fire combustion efficiency and fuel mixture, along with different measurement techniques. Previous modelling studies focussed on the biomass burning season in tropical South America have required significant scaling up of emissions to reproduce in-situ and satellite aerosol concentrations over the region. Our results do not indicate that emission factors used in inventories are biased low, which could be one potential cause of the reported underestimates in modelling studies. This study supplements and updates trace gas and particulate emission factors for fire type specific biomass burning in Brazil for use in weather and climate models. The study illustrates that initial fire conditions can result in substantial differences in terms of their emitted chemical components, which can potentially perturb the Earth system.

1 Introduction

Atmospheric aerosols represent the largest uncertainty in current understanding of radiative forcing of climate (Boucher et al., 2013), with biomass burning aerosol (BBA) aerosol-radiation interactions estimated to have a radiative forcing of 0.0 Wm^{-2} but with a very large uncertainty of $\pm 0.2 \text{ Wm}^{-2}$ and significant perturbations on the regional scale (Boucher et al., 2013). BBA have both a global and regional effect on weather and climate via perturbation of the atmospheric radiation balance and cloud microphysical properties (Ramanathan et al., 2001; Andreae et al., 2004) and visibility (Andreae et al., 1988) but can also affect human health (Cançado et al., 2006; Arbex et al., 2007; Carmo et al., 2013). Biomass burning in the tropics contributes more than 80% of all the emissions produced from total biomass burning globally (Ward et al., 1992). The Amazon Basin in Brazil contains approximately $4 \times 10^6 \text{ km}^2$ of evergreen tropical forest (Christian et al., 2007) and during the dry season (August–October) intense widespread burning occurs leading to high levels of atmospheric particulate matter (Chand et al., 2006). A range of climate and fire types occurs in Brazil, with fire-impacted ecosystems including pure grassland, a gradient of wooded savannah into dry (seasonal) tropical forest and evergreen tropical forest (Ward et al., 1992; Yamasoe et al., 2000). Deforestation and Cerrado (savannah-like) fires are commonly used for land clearing and pasture maintenance (Martin et al., 2010), which leads to high levels of black carbon, organic matter and gas phase species in the atmosphere. Detailed representation of the emissions and properties of gas and particulate phase species from BB in Brazil are therefore required in global climate models for their outputs to be accurate and reliable (Bowman et al., 2009).

Emissions from BB are quantified either by emission ratios (ERs or $\text{ER}_{x/y}$, the relative excess amounts of two smoke species, x and y) or emission factors (EFs, grams of species released per kg of dry fuel burnt) and these are used in order to compute trace gas and particulates released from biomass burning fires. Numerous scientific studies have taken place to study smoke from biomass burning both in the field (e.g. Reid and Hobbs, 1998) and in the laboratory (e.g. McMeeking et al., 2009). Every fire is unique, differing in vegetation type and a dynamic, variable mix of combustion phases e.g. flaming or smouldering, while other factors such as moisture content of the fuel, the environmental conditions and whether the vegetation is dead or alive can alter the emissions of certain BB species (e.g. Ward et al., 1996; Yokelson et al., 1996). However, while there is significant inter-fire variability, fires over a particular region often exist within broader distinct regimes depending on the dominant fuel type and combustion properties. Recent studies by McMeeking et al. (2009) and Akagi et al. (2011) have compiled emissions from different vegetation types and showed large variations in the composition of the emitted species and their overall abundance. All of these previous studies provide data for emission inventories, which can then be directly used in atmospheric models. However, due to the large uncertainties and factors influencing BB emissions, further understanding of these emission variations are needed.

Recent instrument developments including the Time of Flight Aerosol Mass Spectrometer (ToF-AMS, Aerodyne Research, Inc., Billerica, MA, USA, Canagaratna et al., 2007) and a Single Particle Soot Photometer (SP2, Droplet Measurement Technologies, Boulder, CO, USA, Stephens et al., 2003) have been used recently to study biomass burning emissions in North America (e.g. Kondo et al., 2011; Akagi et al., 2012; May et al., 2014; Jolleys et al., 2015; Liu et al., 2016). Previous measurements of the chemical composition of particulate emissions from South American tropical biomass burning were conducted over a decade ago using filter-based sampling, which have known biases (e.g. Bond and Bergstrom, 2006; Chow et al., 2007; Lack et al., 2008; Petzold et al., 2013; Bond et al., 2013). The South American Biomass Burning Analysis Project (SAMBBA) is the first experiment to utilise both of these instruments in a tropical environment for studies of biomass burning. These fire type specific measurements are important as recent biomass burning studies in Brazil have found a shift from forest to savannah burning, which will impact trace gas and particulate emissions in the region (Ten Hoeve et al., 2012; Chen et al., 2013).

The airborne campaign of SAMBBA conducted twenty flights from 13 September to 4 October 2012. Two of the flights focused on near-source biomass burning emissions, sampling across contrasting environments in terms of vegetation and fire regime. We present emission ratios and emission factors for a range of gas and particle phase species, alongside measurements of the physical and chemical properties of the plumes sampled by the aircraft.

2 Experimental Details & Methodology

2.1 Instrumentation

In-situ measurements presented here took place on the UK Facility for Airborne Atmospheric Measurement (FAAM) Airborne Research Aircraft, BAe-146. The BAe 146 aircraft has a wide range of instruments on board, but only those relevant to the analysis are discussed below. Mass concentrations of particulate species are reported at standard temperature and pressure in μgsm^{-3} (where sm^{-3} refers to standard cubic metre at 273.15 K and 1013.25 hPa).

A compact variant of the ToF-AMS provided real time size-resolved mass measurements of non-refractory (NR) organic aerosol (OA) and inorganic component mass: sulphate, nitrate, chloride and ammonium (Drewnick et al., 2005; Canagaratna

et al., 2007). This instrument provides quantitative high time resolution data with high precision and accuracy making it ideal for use on aircraft campaigns. Measured mass concentrations for the C-ToF-AMS have an uncertainty of approximately 30% (Bahreini et al., 2009). Previous studies by Crosier et al. (2007), Morgan et al. (2009) and Morgan et al. (2010) have detailed the sampling strategy and calibration protocols for the AMS on the BAe 146. Plume interceptions utilised the ‘fast mass spectrum’ mode of the AMS (Kimmel et al., 2011), which provided data at 1 second time resolution. The instrument was calibrated using monodisperse ammonium nitrate and ammonium sulphate to provide the ionisation efficiency of nitrate, along with relative ionisation efficiencies for sulphate and ammonium. A collection efficiency of 1.0 was applied to the data based on comparisons with a Scanning Mobility Particle Sizer (SMPS) using data from the entire campaign (further details available in Allan et al., 2014). This is supported by the independent measurements of Brito et al. (2014) who also reported a collection efficiency of 1.0 for their Aerosol Chemical Speciation Monitor (ACSM) measurements conducted at a ground-site in Porto Velho during the SAMBBA experiment.

The early flights of the campaign (up to and including B737 on 20 September 2012) suffered from a partial blockage of the AMS pinhole (part of the inlet system where particles enter the instrument aerodynamic lens), which reduced the reported mass concentrations. When comparing the AMS concentrations with optical particle counter and total scattering measurements, a clear and consistent discrepancy was evident pre- and post-blockage. In order to correct for this, a scaling factor was applied to recover the mass concentrations by comparing the mass concentrations to total scattering coefficients measured by a TSI nephelometer during low-altitude sampling while the AMS was operating in slow-mode. The applied scaling factor was 2.69 ± 0.3 based on measured mass scattering efficiencies of $16.1 \pm 0.3 \text{ m}^2 \text{ g}^{-1}$ and $5.98 \pm 0.3 \text{ m}^2 \text{ g}^{-1}$ for the partially blocked and unblocked flights respectively and is applied to the data for B737 in this study. The scaling factor represents an additional uncertainty in the AMS mass concentrations for this flight.

The SP2 provides a determination of the single particle BC mass, the number of particles containing BC and the total mass of particles containing refractory black carbon (rBC) species (Baumgardner et al., 2004; Schwarz et al., 2006). The term rBC is defined as the incandescent material measured by the SP2, following the definition of Petzold et al. (2013). The SP2 instrument operation and subsequent data interpretation have been described elsewhere (Liu et al., 2010; McMeeking et al., 2010). Calibration of the SP2 incandescence signal in order to calculate single particle rBC mass was accomplished using monodisperse Aquadag BC particle standards (Aqueous Deflocculated Acheson Graphite, manufactured by Acheson Inc., USA) using a scaling factor of 0.75 (Baumgardner et al., 2012). A 30% uncertainty in the SP2 black carbon mass is used as in previous studies (e.g. McMeeking et al., 2010, 2012). The SP2 sample flowrate was approximately 120 vccm and operated without sample dilution. During near-source plume sampling, multiple coincident particles may be sampled at the same time by the instrument and such peaks in each single particle event are identified by the data analysis software, with the mass loading being the summation of the single particle masses from the identified peak signals. An offline comparison of the SP2 with a Sunset OC/EC measurement at very high BC mass loadings was performed by measuring the direct diesel emissions using the Manchester aerosol chamber (Liu et al., 2017), which suggested a high correlation between both measurements under high BC mass loading (up to approximately $15 \mu\text{gsm}^{-3}$). Above this limit, the SP2 measurement was biased low. However, the BC masses in this study were well below this threshold, thus would not be affected by the coincidence issue.

The C-ToF-AMS and SP2 both sampled via Rosemount inlets (Foltescu et al., 1995). These have been shown to enhance aerosol concentrations dependent on the mean bulk density of the aerosol sample (Trembath et al., 2012), with the enhancement being largest for the super-micron size range (e.g. up to a factor of 10 for Saharan dust). For European pollution aerosol, which has a comparable density to BBA, the enhancement is negligible for particles below an optical diameter of $0.6 \mu\text{m}$. Given the size ranges of the C-ToF-AMS and SP2 and the general dominance of sub-micron aerosol in this environment based on size distribution measurements, limited enhancement is expected for the measurements presented here.

The C-ToF-AMS and SP2 measured downstream of nafion driers to prevent condensation of water in the inlet lines, which combined with the cabin temperature exceeding the ambient temperature, resulted in the sample being dried to a significant extent. Nafion driers are subject to losses, which will add additional uncertainties to the measured concentrations that have been ignored in our subsequent uncertainty calculations. Sample line relative humidity measurements were typically between 20–60% during flights in Rondônia and from 20–30% in Tocantins at the flight altitudes of interest here.

The Fast Greenhouse Gas Analyzer (FGGA, Model RMT-200, Los Gatos Research Ltd., USA) utilises a cavity-enhanced absorption spectrometer to provide high accuracy, 1 Hz measurements of carbon dioxide and methane mixing ratios with a 0.1% uncertainty (O’Shea et al., 2013) and the VUV Fast Fluorescence CO Analyser measures carbon monoxide mixing ratios with a 2% uncertainty (Hopkins et al., 2006; O’Shea et al., 2013).

2.2 Biomass burning emission calculations

2.2.1 Background ambient and in-plume measurements

Excess mixing ratios of species x (Δx) are needed in order to calculate the ER and EF of a species. In order to calculate Δx , the ambient background mixing ratios of species x must be subtracted from the values measured in the smoke plume. The ambient background mixing ratio was defined as the fifth percentile for each species while outside the plume during constant-altitude runs in the boundary layer for each flight respectively. Plume identification was performed manually based on the time series of CO, OA and rBC. We note the discussion by Yokelson et al. (2013) that examines the limitations of the excess mixing ratios approach due to changes in background air composition through tropospheric mixing; as our measurements were made close to initial source through numerous plume intercepts on both flights and background concentrations were constant throughout, we do not consider this mixing of background air into the plume to be a significant effect in this study.

The numerous instruments on-board the BAe-146 each had different response times and inlet lag times leading to difficulties when comparing data from different instruments. Therefore, an integral based approach was used which helps to compensate for these different response times (Yokelson et al., 1996; Karl et al., 2007; Yokelson et al., 2009, 2011). Integrated methods have been found to be more robust and decrease uncertainty compared to the direct point by point method (Karl et al., 2007).

Given the AMS measures Organic Matter (OM), rather than Organic Carbon (OC), which is the most typical reported value for OA in the literature and emission inventories, OM/OC is converted using a value of 1.6 following the work of Yokelson et al. (2009) and Akagi et al. (2012) for fresh biomass burning. The OM/OC ratio value is composition, source and age dependent, with values ranging from 1.4 for fresh urban aerosol to 2.2 for aged non-urban aerosol (Turpin and Lim, 2001), therefore this adds another source of uncertainty to the calculated OC emissions.

2.2.2 Modified combustion efficiency

The combustion efficiency (CE) and modified combustion efficiency (MCE) can be used to define the relative amount of flaming or smouldering combustion taking place. The CE is defined as the ratio of carbon emitted as CO₂ to the total carbon emitted. Total carbon emitted includes CO₂, CO, CH₄, non-methane organic gases and carbon containing particulates (Ward and Radke, 1993). Measuring all of these emitted carbon species can be difficult in field campaigns, therefore we use the MCE which is defined below following Ward and Radke (1993):

$$MCE = \frac{\Delta CO_2}{\Delta CO_2 + \Delta CO} \quad (1)$$

CE and MCE are closely related with a difference of only a few percent, as CO and CO₂ represent the majority of the carbon species emitted (Ward and Radke, 1993; Ferek et al., 1998). MCE can be interpreted as a relative scale of varying degrees of smouldering and flaming combustion; values greater than 90% are typically biased towards a fire in the flaming stage, whereas a MCE less than 90% is defined as being biased towards the smouldering phase (Ward and Radke, 1993). The excess concentrations of CO and CO₂ were integrated over the plume interception time to give integrated excess values. These values for each plume interception were then plotted with the intercept forced to zero to give the fire average MCE.

2.2.3 Emission ratio

ERs are calculated to give the relative emission of species x to a simultaneously measured reference gas, usually CO or CO₂ as these gases are non-reactive and conserved (Andreae and Merlet, 2001; Sinha et al., 2003). The ER of species x using CO as the reference gas is defined below:

$$ER_x = \frac{\Delta x}{\Delta CO} \quad (2)$$

For gas phase species, ER_x is usually given as the molar ratio and for aerosol species ER is stated as the mass ratio at 273.15 K and 1013.25 hPa. When only one pass is made through a BB plume the calculation of ER_x is trivial using the equation above. The ER_x can also be derived when multiple passes are made through the BB plume by using the regression slope of the excess species concentration of x versus the reference species with the line forced through zero (Yokelson et al., 1999). This method utilises a simple linear regression that only minimises the sum of the square of the deviations in the y-axis. An alternative method is a more complex regression that minimises the sum of the square of the deviations in both the x and y-axis weighted by the uncertainty in each individual data point; Paton-Walsh and Yokelson (2017) conclude that the uncertainty associated with the simpler method is insignificant compared to the real overall uncertainty in fire emission ratios. Therefore

we use the simpler method in this study, where the excess concentrations of species x and the reference species concentration are integrated over the plume intercept, with the regression slope of these species giving ER_x .

Uncertainties in the ERs are derived as the one standard deviation error in the slope of the line of best fit following e.g. Akagi et al. (2012). Such uncertainties will represent an underestimate as they only include random errors given that the uncertainties in each point are correlated.

2.2.4 Emission factor

Another parameter used to define the emission of a particulate species from fires is the EF. EF is reported as the mass of species x emitted per kg of dry fuel burnt. The dry fuel burnt is approximated by the total mass of carbon species released in the form of CO_2 , CO , CH_4 , **non-methane organic gases**, particulate carbon etc (Yokelson et al., 2013; Stockwell et al., 2015). EFs were calculated using the carbon mass balance method (Ward and Radke, 1993; Yokelson et al., 1996). The mass fraction of carbon in the fuel is needed for EF calculation and as this quantity was not measured during the campaign we used a value of 0.5 ± 0.05 , which is typical in the literature (e.g. Wooster et al., 2011). Susott et al. (1996) presented data that shows the carbon content of Brazilian vegetation ranges from 45–55%. As we only used CO_2 , CO , CH_4 as the carbon containing species in the EF calculations, our EFs are likely to be overestimated by **a few percent** (Susott et al., 1996; Andreae and Merlet, 2001), although the particulate phase carbon is usually only a small fraction of the carbon emitted (Lipsky and Robinson, 2006; McMeeking et al., 2009). The EF for species x ($g\ kg^{-1}$) is defined below following Yokelson et al. (1999) and Wooster et al. (2011):

$$EF_x = F_c 1000 \frac{MM_x}{MM_{carbon}} \frac{C_x}{C_T} \quad (3)$$

Where $1000\ g\ kg^{-1}$ is a unit conversion factor, MM_x is the molecular mass of species $x(g)$, MM_{carbon} is the **atomic** mass of carbon (12) and C_x/C_T is the ratio of the number of moles of species x in the plume interception to the total number of moles of carbon, which is calculated following Yokelson et al. (2009) and Wooster et al. (2011):

$$\frac{C_x}{C_T} = \frac{ER_{x/CO_2}}{\sum_{j=1}^n (NC_j ER_{j/CO_2})} \quad (4)$$

Where ER_{x/CO_2} is the ER of species x to CO_2 , NC_j is the number of carbon atoms in compound j , and the sum is over all carbon species including CO_2 (e.g. Wooster et al., 2011).

Uncertainties in the EFs are derived in quadrature from the uncertainty in the carbon content of the fuel (0.05) and the uncertainty in the associated ER values.

3 Results

3.1 Flight Overview

Two of the flights during SAMBBA focussed on near-field in-situ measurements of active fires. The fires were sampled within the boundary layer, with out-of-plume aerosol samples dominated by biomass burning haze. The general features of the fires are summarised below.

3.1.1 Rondônia flight

Flight B737 took place in Rondônia State in the West of Brazil on 20 September 2012, with take-off at 14:45 UTC (10:45 local time) and a duration of 3 hours 45 minutes. The natural vegetation in Rondônia is characterised by dense Amazonian **tropical forest**, but the region has become one of the most deforested areas of the Amazon. Fig. 1a shows a large smouldering **tropical forest** fire, which was suspected to be a natural wildfire, likely initiated by lightning. The fire was located in a National Park many kilometres from the nearest road, in a region well away from any deforestation. **However, we cannot rule out that the fire may have been started by the presence of indigenous people, which would mean the fire was anthropogenic in origin.** It is unlikely the fire was a deforestation fire, which is the dominant form of fire in the region and the typical focus of previous campaigns. MODIS hotspot data from the TERRA overpass at 14:26 UTC on 19 September 2012 indicated that this fire **likely started on the day before our flight**. The near field plume interceptions shown on the flight track for B737 on Fig. 1b took place at an altitude of 1800m (above sea-level) with far field interceptions at an altitude of 2500m (above sea-level). The fire was located on a 900m high plateau, therefore the plume was intercepted at 900m above the fire, with smoke estimated to be approximately 6 minutes old (based on vertical wind velocity measurements). This paper only focuses on the near-field

measurements to understand initial emissions, while a future publication (Morgan et al., in prep) will characterise the ageing and transformation of the plume downwind.

Some mid-level cloud was present in central Rondônia and a large pyro-cumulus cloud was observed over the BB plume above the boundary layer. Winds were from the North-North-West and relative humidity outside of plume interceptions was high with values of around 70% at 900m. During this flight, 9 separate plume interceptions took place, each lasting approximately 15 seconds, shown in Fig. 1c with large increases in CO, rBC and OA clearly visible. Plume interceptions were made prior to the pyrocumulus cloud. Background concentrations of CO, OA and rBC were 213 ppbv, 9.81 μgsm^{-3} and 0.31 μgsm^{-3} respectively. Plume maxima ranged between 1261-29554 ppbv for CO, 134-3661 μgsm^{-3} for OA and 1-9 μgsm^{-3} for rBC.

The Rondônia fire MCE of 0.79 ± 0.02 is effectively identical to the MCE of 0.788 for residual smouldering combustion of logs in Brazil from a ground-based experiment (Christian et al., 2007), although compared to other **tropical forest**-like fires reported in the literature that are summarised in Table 1, the MCE for Rondônia fire is much lower e.g. Ferek et al. (1998) reported a value of 0.87 for **tropical deforestation** fires in Brazil measured on an aircraft.

3.1.2 Tocantins flight

Flight B742 took place in the Tocantins State of Brazil on 27 September 2012, with take-off at 13:00 UTC (10:00 local) and a flight duration of 3 hours 15 minutes. Tocantins State is characterized by Cerrado vegetation, in particular grasslands (campo limpo/campo sujo) and open woodland (Cerrado sensu) forms (Mistry, 1998). Fig. 1a shows an example of some of the fires sampled during the Tocantins flight with flames visible in the closest fire. The vegetation consists mainly of grassland with some trees. During the flight, numerous new fires were starting, which are likely a consequence of man-made agricultural burning based on existing knowledge of fire in the region (e.g. Longo et al., 2013). The BB smoke plumes were sampled at an altitude of 600m above the fires, with smoke sampled being approximately 4 minutes old, which we define as initial smoke. The flight track is shown in 1b, with the MODIS hotspot data from NASA's Terra satellite (Kaufman et al., 1998, 2003; Giglio et al., 2006), shown by the red markers to indicate the fire locations and the plume interceptions shown by the blue markers.

There was little cloud cover in the area, with low relative humidity values of around 30% at an altitude of 600m outside of plume interceptions and winds were light coming from the South East at 950 hPa. During this flight, 23 plume interceptions took place each lasting between 5 to 10 seconds. The plume interceptions can clearly be seen in the time series of CO, rBC and OA shown in Fig. 1c. Background concentrations at 600m altitude were 228 ppbv for CO, 0.77 μgsm^{-3} for rBC and 9.31 μgsm^{-3} for OA. Maximum concentrations in the plume interceptions ranged between 750-17732 ppbv for CO, 10-110 μgsm^{-3} for rBC and 65-1636 μgsm^{-3} for OA.

The MCE of the Tocantins fires was 0.94 ± 0.02 , identical to similar aircraft measurements of Cerrado fire emissions reported by Ferek et al. (1998). Compared with the existing literature on savannah/Cerrado fires (see Table 1), the Tocantins MCE is very similar e.g. African savannah fires (Yokelson et al., 2003), California chaparral fires (Akagi et al., 2012) and **Australian savannah fires** (Desservettaz et al., 2017) have similar MCE values of 0.94, 0.93 and 0.86-0.99 respectively.

3.2 Trace gas emissions

Fig. 2 shows the scatter plots used for derivation of the trace gas ERs, with the derived values shown in Table 2, with an uncertainty of one standard deviation in the line of best fit. The trace gas species measured on the aircraft are very strongly correlated, with r-squared values between 0.92 and 0.99 illustrating **that the plumes are well-mixed and that these active fires likely burned a homogeneous fuel bed**. The different points in the Tocantins figures are derived from data from multiple fires and the lack of variability indicates similarity between the fires, although the level of emission does vary significantly. Table 3 shows the calculated EF values for CO₂, CO and CH₄. Also presented are reported values from other studies from the literature.

The Rondônia fire EF_{CO₂} of $1447 \pm 145 \text{ g kg}^{-1}$ and EF_{CO} of $237 \pm 24 \text{ g kg}^{-1}$ are very similar to those reported by Christian et al. (2007) for smouldering logs in Brazil, which were 1346 g kg^{-1} and 229 g kg^{-1} respectively. **Similarly, measurements of tropical peat fires in Indonesia by Stockwell et al. (2016) are within experimental uncertainties for EF_{CO₂} and EF_{CO} compared to our measurements.** Our EF_{CO₂} is similar to previous studies reporting emission factors for deforestation fires in Brazil e.g. Ward et al. (1992), Kaufman et al. (1992), Ferek et al. (1998) and Yokelson et al. (2007). However, our EF_{CO} is typically 2-3 times larger than other previous studies in Brazil, other than the Christian et al. (2007) study. Global average values reported in the literature are typically slightly larger in the case of EF_{CO₂} and significantly lower in the case of EF_{CO}. Andreae and Merlet (2001) and Akagi et al. (2011) determined tropical forest global averages that were 11% and 14% larger than our reported EF_{CO₂}, while the GFEDv3/4 and GFASv1.0 emission inventories (van der Werf et al., 2010; Kaiser et al., 2012) report a value that is 12-14% greater; EF_{CO} values are 56%, 61% and 57-61% lower.

Our value of $5.17 \pm 0.53 \text{ g kg}^{-1}$ for EF_{CH_4} is around 3 times lower than was reported by Christian et al. (2007), while being similar to those reported by Ferek et al. (1998), Kaufman et al. (1992) and Yokelson et al. (2007). The global averages for tropical forest also agree well ($5.07 \pm 1.98 \text{ g kg}^{-1}$ (Akagi et al., 2011) and $6.8 \pm 2.0 \text{ g kg}^{-1}$ (Andreae and Merlet, 2001)). The value of 6.6 g kg^{-1} used in the GFEDv3 and GFASv1.0 emission inventories for deforestation fires is 28% higher than our reported value for the Rondônia tropical forest fire, although the latest GFEDv4 release reports a value of 5.07 g kg^{-1} , which is very similar to ours.

Emission factors for CO_2 and CO for the Tocantins were $1711 \pm 175 \text{ g kg}^{-1}$ and $74 \pm 8 \text{ g kg}^{-1}$, which are similar to existing values reported in the literature for Cerrado fires in Brazil. Similarly, our observed EF_{CO_2} is comparable to global average savannah and grassland values from Andreae and Merlet (2001) and Akagi et al. (2011), which are 6% and 1% lower respectively, while being 4% higher than the value of 1646 g kg^{-1} used in the GFEDv3 and GFASv1.0 emission inventories for savannah fires. For EF_{CO} , our value is 14%, 17%, 21% and 17% larger than those reported by Andreae and Merlet (2001), Akagi et al. (2011), GFEDv3/GFASv1.0 and GFEDv4 emission inventories respectively. The Tocantins fires EF_{CH_4} value of $2.23 \pm 0.23 \text{ g kg}^{-1}$ is similar to previous measurements of Cerrado fires in Brazil and global average savannah fires.

3.3 Particulate emissions

The total excess mass of aerosol species integrated over the plume interceptions as a percentage of the total mass of aerosols measured (BC, OA, chloride, ammonium, sulphate and nitrate) are presented in Fig. 3 and Table 4.

The aerosol emitted by the Rondônia fire was composed of over 97% organic mass, greater than the value of 91.3% reported by Ferek et al. (1998) for a smouldering Brazilian tropical forest fire. The Ferek et al. (1998) value of 6.04% for BC mass is over an order of magnitude greater than our value for smouldering tropical forest BC mass of 0.3%.

The value of 88.4% for OM for Cerrado fires in Brazil reported by Ferek et al. (1998) is similar to our value of 84.4% for the Tocantins Cerrado fires. Ferek et al. (1998) values for BC (6.58%), chloride (4.32%) and nitrate (0.301%) for Cerrado fires are also all comparable to our measurements for Brazilian Cerrado of 7.99%, 5.08% and 1.29% respectively.

The Rondônia fire emitted 12.7% more OA than the Tocantins fire in terms of their average mass fraction. The flaming Cerrado fires emitted over twenty five times more BC by mass to the total particulate mass than the smouldering tropical forest fire. Yamasoe et al. (2000) found the difference was only three times as much when comparing tropical deforestation and cerrado fires in Brazil. The Tocantins fires emitted almost ten times more Cl⁻ by mass of total particulates than the Rondônia fire, which is similar to Yamasoe et al. (2000) who found the difference was approximately eleven times more for the flaming Cerrado fires compared to the smouldering tropical forest fire. Grass is known to be high in chlorine (Lobert et al., 1999), which would explain the relative abundance of chloride sampled from the Tocantins fires.

Fig. 4 shows the black carbon mass and number core size distributions for the Rondônia and Tocantins fires which gives an indication of the size of particles at source. The grey shading shows the minimum and maximum size distributions from the plume intercepts on each flight to show the plume to plume variations, with the solid black line indicating the average mean. There is little difference in the BC size distributions of the two fires despite the large difference in fuel and burning characteristics. Average mass median core diameters are 0.19 μm and 0.20 μm for B737 and B742 respectively, while average number median core diameters are 0.10 μm for both fires, calculated from the log-normal fits based on the distributions shown in Fig. 4.

Fig. 2 includes the scatter plots used to derive the particulate species ERs, while their derived values are listed in Table 5. Particulate phase species and trace gas emissions are strongly correlated, with r-squared values of between 0.72 and 0.98. Table 6 shows the calculated EF values for particulate species with their associated uncertainties, alongside reported values from the literature for comparison. Given that directly comparable measurements from fires in Brazil are more scarce for particulate emissions than trace gases and the substantial range from region-to-region reported in the literature (e.g. Jolleys et al., 2012), in the following text we focus on comparing with global average values and those used in emission inventories in the absence of Brazil-specific emission factors.

3.3.1 Organic aerosol

The Rondônia and Tocantins fire EF_{OC} values were $5.00 \pm 1.58 \text{ g kg}^{-1}$ and $0.82 \pm 0.26 \text{ g kg}^{-1}$ respectively, representing approximately a six-fold increase in OC per kg fuel burnt when comparing the two fires.

The Rondônia fire EF_{OC} is similar to the deforestation value of 4.34 reported by Ferek et al. (1998). From a global perspective, our value is very similar to those reported by Akagi et al. (2011) and Andreae and Merlet (2001) for average global tropical forests, which were $4.71 \pm 2.73 \text{ g kg}^{-1}$ and $5.2 \pm 1.5 \text{ g kg}^{-1}$ respectively. Our value is 16% higher than the EF_{OC} value of 4.3 g kg^{-1} used for deforestation fires in the GFEDv3 and GFASv1.0 emission inventories.

Ferek et al. (1998) reported a EF_{OC} of 2.94 g kg^{-1} for Cerrado burning, which is 3.5 times greater than our EF_{OC} for the Tocantins fire. Global averaged savannah values for EF_{OC} reported by Akagi et al. (2011) and Andreae and Merlet (2001), which were $2.62 \pm 1.24 \text{ g kg}^{-1}$ and $3.4 \pm 1.4 \text{ g kg}^{-1}$ respectively, are 3-4 times greater than our value. Similarly, the GFEDv3 and GFASv1.0 emission inventories value of 3.2 g kg^{-1} for savannah fires is almost four times higher than the value we calculated for the Tocantins fire.

3.3.2 Black carbon

Our EF_{BC} values were $0.019 \pm 0.006 \text{ g kg}^{-1}$ and $0.13 \pm 0.04 \text{ g kg}^{-1}$ for the Rondônia and Tocantins fires respectively, approximately one order of magnitude apart.

Our EF_{BC} value for the Rondônia fire is an order of magnitude smaller than the value of 0.46 g kg^{-1} reported by Ferek et al. (1998) for deforestation fires in Brazil. This divergence between our EF_{BC} value and those in the literature is similar when comparing with global averages; values of $0.52 \pm 0.28 \text{ g kg}^{-1}$ (Akagi et al., 2011) and $0.66 \pm 0.31 \text{ g kg}^{-1}$ (Andreae and Merlet, 2001) for global average tropical forest fires are more than an order of magnitude greater than our reported value. The GFEDv3 and GFASv1.0 emission inventories use a value of 0.57 g kg^{-1} for deforestation fires, which is again over an order of magnitude greater than our value for the Rondônia fire. Our value is most similar to those measured for smouldering Indonesian peat by Stockwell et al. (2016) using in-situ photoacoustic spectroscopy, with a value that is approximately 3 times lower than our measurement.

Compared with Ferek et al. (1998), our EF_{BC} is more than a factor of 2.5 smaller than their value of 0.35 g kg^{-1} for Cerrado fires in Brazil. EF_{BC} values for African savannah fires and global average savannah fires are also larger than our value, $0.39 \pm 0.19 \text{ g kg}^{-1}$ (Sinha et al., 2003) and $0.37 \pm 0.20 \text{ g kg}^{-1}$ (Akagi et al., 2011) respectively. The GFEDv3 and GFASv1.0 emission inventories use a value 0.46 g kg^{-1} , which is 3.5 times greater than the value we calculated for the Tocantins fires.

3.3.3 Inorganic aerosol

Values for EF_{Cl} of $0.04 \pm 0.01 \text{ g kg}^{-1}$ and $0.09 \pm 0.03 \text{ g kg}^{-1}$ for the Rondônia and Tocantins fires respectively and are 2-4 times smaller than global averages reported by Akagi et al. (2011) for tropical forest and savannah fires. For the Rondônia and Tocantins fires, values for EF_{NO_3} were $0.078 \pm 0.025 \text{ g kg}^{-1}$ and $0.013 \pm 0.004 \text{ g kg}^{-1}$; global average tropical forest and savannah fires reported in Akagi et al. (2011) are 41% and 23% greater than our reported values respectively. The Rondônia fire EF_{SO_4} value of $0.034 \pm 0.011 \text{ g kg}^{-1}$ is close to a factor of four smaller than the value of 0.133 g kg^{-1} for the global tropical forest average reported in Akagi et al. (2011). The Tocantins fire EF_{SO_4} value of $0.0006 \pm 0.0002 \text{ g kg}^{-1}$ is thirty times smaller than the value of 0.018 g kg^{-1} for the global average of savannah fires in Akagi et al. (2011). Values for EF_{NH_4} were $0.033 \pm 0.011 \text{ g kg}^{-1}$ and $0.015 \pm 0.005 \text{ g kg}^{-1}$ for the Rondônia and Tocantins fires respectively, which are approximately six and four times greater than the global averaged tropical forest and savannah fires reported by Akagi et al. (2011).

4 Discussion

4.1 How representative are the Rondônia and Tocantins fires?

Section 3.2 reports comparisons between our gas phase emission factors and those in the existing literature and emission inventories, which can serve as a basis for judging the representativeness of our particle phase measurements. Gas phase emission factors are more numerous, up-to-date and robust than their particle phase counterparts, so we focus on those to place our measurements in the context of the existing literature.

For the major trace gas emissions reported here, the Tocantins fire emission factors are very similar to previous measurements in the Brazilian Cerrado as well as global average savannah and grassland fires; this suggests from a gas-phase perspective, the Tocantins fires are consistent with previous measurements and likely representative of typical flaming Cerrado fires. Flaming combustion is predominant in Cerrado fires due to the dry fine fuel, which burns quickly with high combustion efficiency (generally of 0.93 or greater e.g. Ward et al. (1992); Ferek et al. (1998)), which is consistent with our observations of the Tocantins fires.

For the Rondônia wildfire, our EF_{CO_2} value is similar to previous emission factors reported for deforestation fires in Brazil, as well as global average values and those used in emission inventories. However, our value for EF_{CO} is 2-3 times greater than those reported in previous studies aside from measurements by Christian et al. (2007) focussing on smouldering logs in Brazil and Stockwell et al. (2016) investigating Indonesian peat fires. For EF_{CH_4} , there is no clear discrepancy between our value and those reported across the literature, although the range of values is large for deforestation and tropical fires. This suggests that the Rondônia fire represents a mostly-smouldering example of biomass burning in Brazil; deforestation fires in Brazil have

been shown to have a more **balanced** mix of flaming and smouldering combustion e.g. Ward et al. (1992) observed combustion efficiencies ranging from 0.88 to less than 0.80. A further factor that will lower the combustion efficiency is the water content of the fuel, which was likely much greater for the Rondônia fire as a growing forest, whereas typical deforestation fires may have seen the fuel dried for a season before burning. A key outstanding question is how different stages of combustion evolve for these types of fires, with our Rondônia example likely representing one extreme of this evolution as a mature wildfire.

4.2 Particulate emissions compared to existing literature

For the Rondônia fire, organic aerosol made up 97% of the emitted particulate mass on average, which is very similar to global average values for tropical forests and those used for deforestation fires in emission inventories. Values of EF_{OC} are scarce in the literature for Brazilian biomass burning fires, with the only other comparable value from Ferek et al. (1998) being **similar** to our value. Major differences are found between our emission factors for the other particulate species measured by our study when compared with existing literature, particularly in the case of rBC, which was more than an order of magnitude smaller. These differences are likely due to the mostly smouldering nature of the fire, with EF_{BC} being strongly coupled to combustion efficiency and the fuel type of the vegetation. rBC made up just 0.3% of the emitted mass of particulate species, which is much less than that observed at the regional scale during SAMBBA (5.5–6.1%) as reported by Darbyshire et al. (in prep.). In order for conditions during the Rondônia fire to be typical of biomass burning emissions during the study, substantial evaporation or loss of non-rBC aerosol species would be required, which is not observed when assessing transformations at the plume or regional scale (Morgan et al., in prep.). Therefore we conclude that the conditions prevalent during the Rondônia fire are unlikely to represent the dominant mode of biomass burning emissions during the wider study.

While particulate emission factors for the Tocantins fire were generally of the same order of magnitude as values for average global savannah and grassland emissions, they were lower by factors of 2–4. Emission factors for inorganic particulate species from these environments are severely lacking, so drawing specific conclusions would be unwise. For OC and BC, more emission factors are available in the literature, so consideration of these differences is more warranted. Given that the combustion efficiency of the fires were very similar to those previously reported in the literature, the most likely candidates for the differences are the fuel type and sampling methods.

Assessing the role of fuel type is not possible within this study but we can discuss potential biases due to sampling methods. Previous measurements have relied on a variety of methods involving prior collection on a filter followed by thermal, optical or combined thermal-optical techniques, which are then either analysed off-line or in real time. Thermal-based approaches are prone to biases due to pyrolysis or charring of carbonaceous material during the analytical protocol, which can make separation of the OC and BC components challenging and uncertain (e.g. Chow et al., 2007; Petzold et al., 2013). Optical measurements can overestimate BC due the presence of other absorbers such as OA as well as optical interactions between particles and the filter matrix (Bond and Bergstrom, 2006; Lack et al., 2008; Bond et al., 2013). Furthermore, such measurements rely on converting absorption to BC mass, which can vary significantly and is a major strand of current research into BC (e.g. Bond et al., 2013).

Determination of ER_{OC} and EF_{OC} using the cTOF-AMS relies on converting OM to OC using an uncertain ratio, which typically ranges from 1.4 for fresh urban aerosol to 2.2 for aged non-urban aerosol (Turpin and Lim, 2001). We used a value of 1.6 in this study, which is considered typical for fresh biomass burning (Yokelson et al., 2009; Akagi et al., 2012). Given the differences between our reported EF_{OC} and those in the literature are much larger than the range in OM/OC previously observed, this is unlikely to be a major driver of the differences reported here. Due to the significant concentrations of OA relative to inorganic species in this environment, the default fragmentation table (Allan et al., 2004) used to apportion measured signals in the cToF-AMS to gas and particle phase chemical components **was** modified based on calibrating the response of the instrument to sulphate. This methods follows established protocols for biomass burning (Ortega et al., 2013), yielding a change in OA of only a few percent and can therefore be discounted as a potential major source of bias and uncertainty in our reported ER_{OC} and EF_{OC} .

The SP2 measures BC mass directly without relying on converting from absorption, so is likely better suited to sampling in this environment. The SP2 however will not detect BC containing particles with a **core** diameter less than 60nm, which would bias the reported BC mass concentrations lower. The closed BC-mass size distributions in Fig. 4 though render this unlikely without a very large amount of BC-containing particles below the SP2 size cut-off, which would be required to substantially increase the BC mass concentration. Furthermore, while we do not have SMPS size distributions in the plumes, in the near-field at the regional scale we do not observe a highly enhanced ultrafine mode which would be expected if there was a large BC contribution at these sizes. Kondo et al. (2011) studied BC emissions from biomass burning in North America and Asia using the SP2 instrument. While the study is not directly comparable to ours due to the emissions being a few hours old rather than a few minutes old and from a different environment, they found BC emission ratios were similarly lower (factor of 2–5) than other literature values. This would support a potential reason for the differences between our reported BC emissions being at

least in part due to differences in the measurement techniques. However, May et al. (2014) when studying prescribed fires in the United States found that laboratory and airborne derived EFs using a SP2 were generally higher than values previously reported in the literature. Uncertainties relating to the SP2 instrument response to different types of BC is a potential source of bias given that **both instruments were calibrated using a reference standard for urban anthropogenic BC rather than one specific to biomass burning.** Stockwell et al. (2016) reported emission factors for black carbon and elemental carbon of $0.0055 \pm 0.0016 \text{ g kg}^{-1}$ and $0.24 \pm 0.10 \text{ g kg}^{-1}$ respectively, illustrating the significant differences in what is usually assumed to represent EF_{BC} when using different measurement techniques. Future studies in both the laboratory and field environments utilising a range of measurement techniques would be highly beneficial in terms of examining potential biases in different methods.

4.3 Implications

Global and regional numerical models are typically unable to reproduce aerosol optical depth (AOD) using standard configurations for emission inventories without scaling emissions by factors that vary both model-to-model and region-by-region (Kaiser et al., 2012; Tosca et al., 2013). Scaling factors can range from 1.5–5, representing a significant under-prediction of aerosol abundance in the atmospheric column. The EF values presented here are generally either similar to or lower than previous values reported for this biomass burning environment, suggesting that the EFs used in models are not responsible for the underestimate of AOD over tropical South America; several modelling studies have been undertaken during SAMBBA (Archer-Nicholls et al., 2015; Reddington et al., 2016; Pereira et al., 2016; Johnson et al., 2016) and have required scaling of their emissions to match in-situ and satellite measurements. Consequently, scaling emission factors to match observations implies that the discrepancy lies elsewhere if it does relate to emissions (e.g. fire detections being biased low, uncertainties in the evolution of fires), or other aspects of models such as their processes and assumptions.

We observe significant contrasts between the chemical components emitted by the Rondônia and Tocantins fires that are consistent with the differences in fuel and combustion efficiency of the fires. The Tocantins fire emitted 18% more CO_2 than the Rondônia fire, while for the particulate phase species, 97% of the total mass for the Rondônia **tropical forest** fire was composed of organic aerosol compared to 84% for the Tocantins Cerrado fires. These results illustrate how the combustion efficiency and fuel content of a fire can strongly influence the composition of the emissions, particularly in the case of the relative contribution of BC. Such contrasts will strongly control the single scattering albedo of the emitted smoke (e.g. Pokhrel et al., 2016) and perturb atmospheric heating rates and radiative forcing. Greater relative emissions of OA can significantly affect cloud droplet formation given that 45–75% of biomass burning OA has been shown to be water soluble (Reid et al., 2005; Asa-Awuku et al., 2008), which can again perturb the radiative balance of the atmosphere. Consequently, the initial conditions at source can potentially play a large role in determining the weather, climate and air quality implications of the significant atmospheric burden of biomass burning across the region.

5 Conclusions

In-situ observations of near-field biomass burning emissions from two distinct fire types in Brazil are presented and evaluated. We presented fire integrated emission ratios and emission factors from a large smouldering **tropical forest** fire in Rondônia state and **several** smaller man-made flaming Cerrado fires in Tocantins state. **We believe that the Rondônia fire was most likely a wildfire.** The two fires differed substantially in emissions of CO and CO_2 , resulting in MCEs of 0.79 and 0.94 for the Rondônia and Tocantins fires respectively. OA emissions also varied with the Rondônia smouldering **tropical forest** fire having a higher emission factor for OA than the Tocantins flaming Cerrado fires, with OA comprising 97% of the emitted sub-micron mass in the former and 84% in the latter. The BC emission per kg fuel burnt was an order of magnitude higher for the Tocantins fires than the Rondônia fire. These results **confirm** that the initial fire conditions can play a significant role in determining the impacts on the Earth system by biomass burning emissions. In particular, the relative contribution of BC can vary significantly, which will represent a major control on the single scattering albedo of the aerosol burden over a given region and fire regime.

Compared with previous deforestation fire EFs in the literature and in emission inventories, the Rondônia particulate emissions differ substantially, with the only exception being the EF value for OA. This was likely due to the bias towards smouldering emissions of the wildfire, which represents the lower extreme in terms of combustion efficiency compared to previous deforestation fire measurements. Gas phase EFs for the Cerrado environment suggest that the fires are representative of previous measurements in the literature. However, particulate emission factors for the Tocantins fire were 2–4 times lower for BC and OA than those reported in the literature for Cerrado or savannah type fires. One potential reason for this discrepancy is the different measurement techniques used in this study, which measure OA and BC more directly than the filter-based measurements typically used in past studies. We recommend that comparisons of techniques are made in the future to assess the size of any such potential biases. Our calculated EFs do not indicate that the scaling of emissions that is required within

global and regional numerical models to reproduce in-situ and satellite aerosol concentrations over Brazil (Kaiser et al., 2012; Tosca et al., 2013; Archer-Nicholls et al., 2015; Reddington et al., 2016; Pereira et al., 2016; Johnson et al., 2016) is related to underestimates in EFs used in emission inventories.

Data availability

All raw time series data used to derive the emission ratios and factors from the FAAM research aircraft are publically available from the Centre for Environmental Data Analysis website (<http://www.ceda.ac.uk/>). SP2 size distribution data is available on request due to the size of the data files. Data masks for categorising flight patterns into plume-sampling and other sampling types (vertical profiles and SLRs) are currently available on request. Active fire data used in the manuscript is available publically from NASA (see acknowledgements for further details).

Author contributions. A. K. Hodgson and W. T. Morgan analysed the data and wrote the manuscript. S. O'Shea, J. D. Allan, E. Darbyshire, D. Liu and J. Lee provided additional data analysis support, including data processing and quality assurance. S. Bauguitte and M. J. Flynn operated the gas-phase and aerosol instruments respectively during the field campaign. B. Johnson, J. Haywood, K. M. Longo, P. E. Artaxo and H. Coe led the planning of the field campaign and were co-principal investigators on the SAMBBA project.

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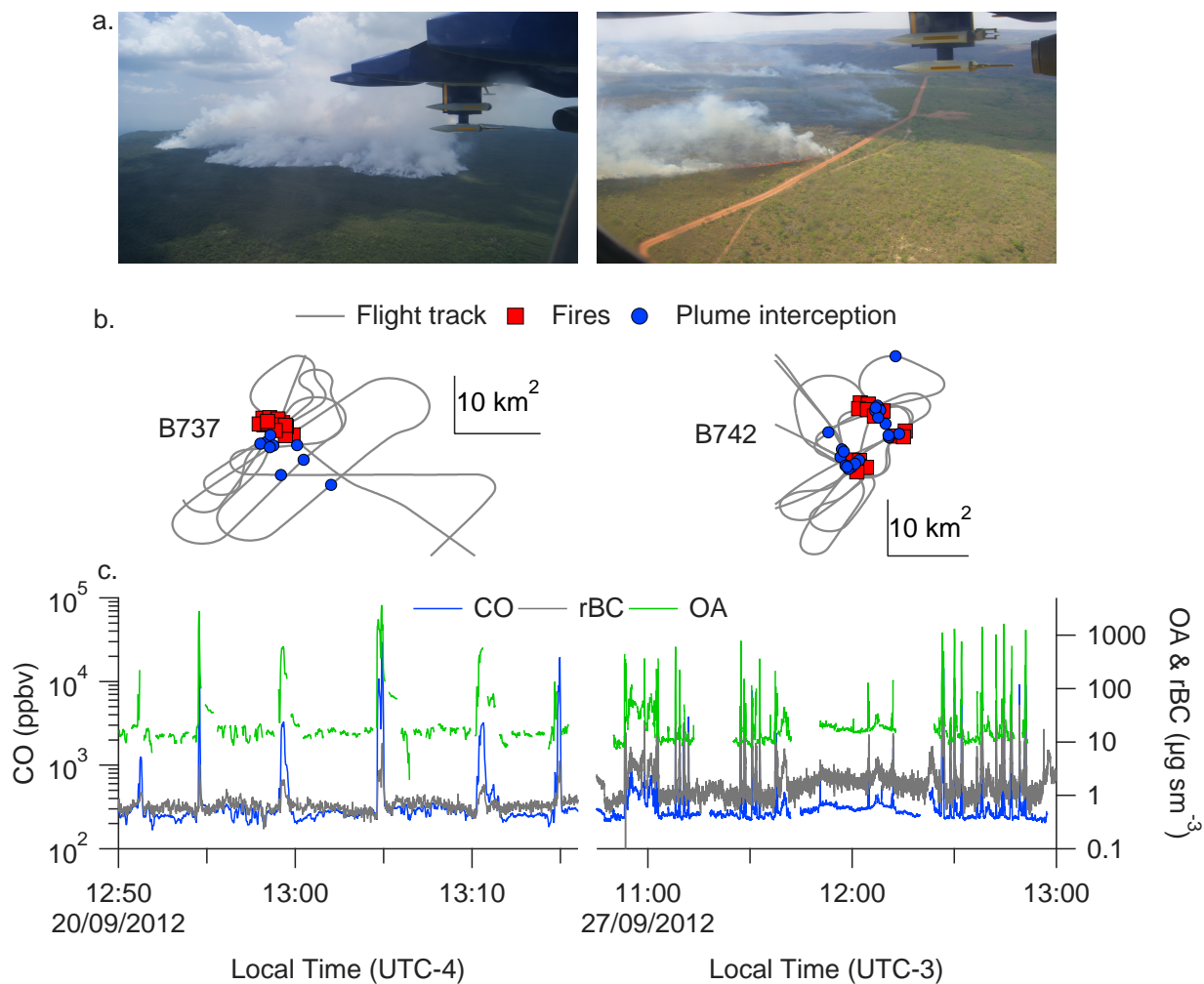


Figure 1. Overview of case studies used in the analysis with the Rondônia flight (B737) shown on the left and the Tocantins flight (B742) shown on the right. Panel a. Photographs taken from the aircraft of the Rondônia and Tocantins fires courtesy of William T. Morgan and Axel Wellpott respectively. **Full-size photographs are included in the supplementary material.** Panel b. Low-level flight tracks including MODIS hotspot data from TERRA and AQUA overpasses for the dates of interest. Plume interceptions are also marked. 10 km² box represents scale for flight-track. Panel c. Time series of CO, rBC and OA during the near-field fire sampling periods of the flight.

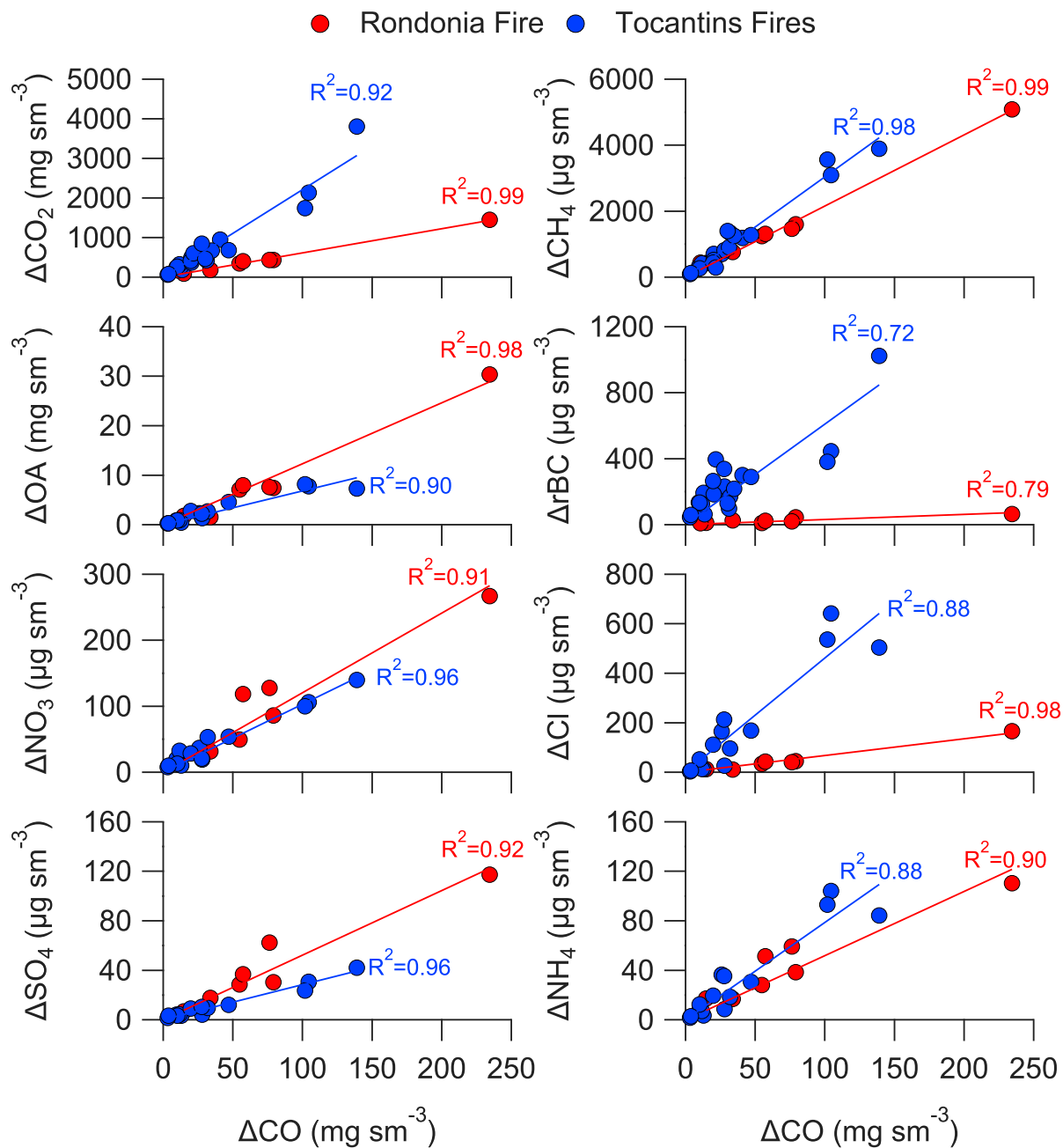


Figure 2. Relationship between excess concentrations of trace gas and particulate phase species relative to excess carbon monoxide for the Rondonia and Tocantins fires. Solid lines show line of best fit from linear regressions forced through zero.

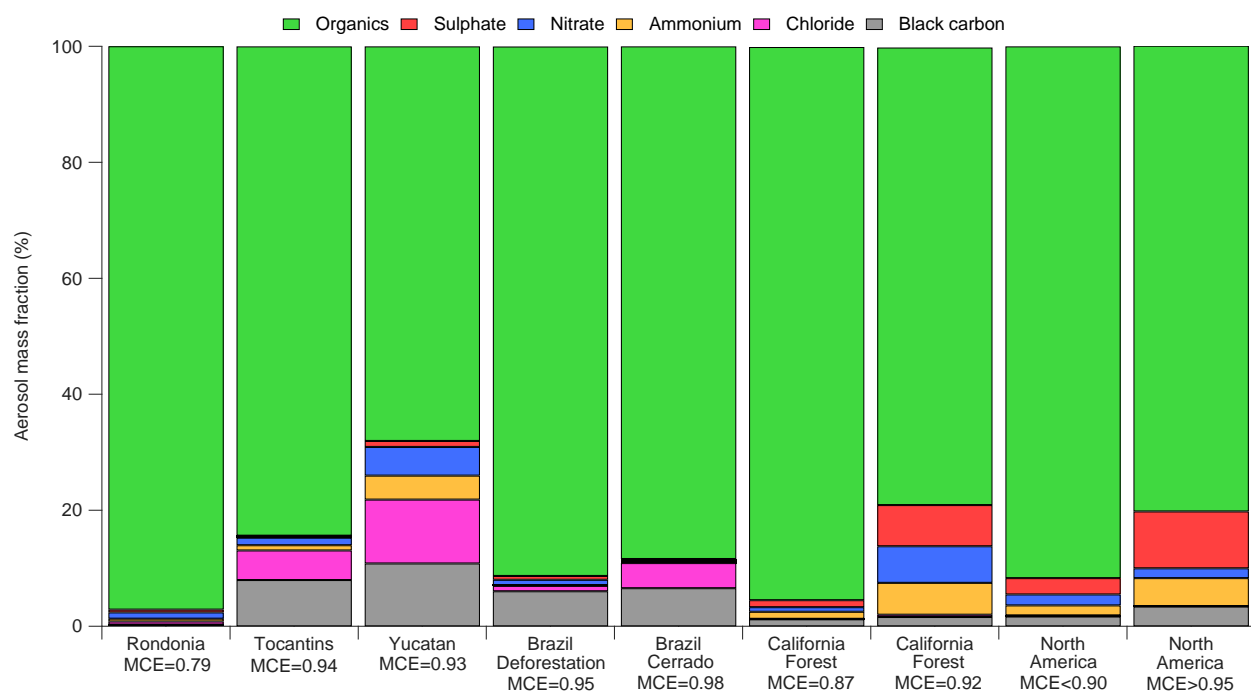


Figure 3. Mass fraction of aerosol components as a percentage of total aerosol mass, including black carbon, organic aerosol, chloride, ammonium, sulphate and nitrate for the Rondônia fire, Tocantins fires and values for previous studies from the Yucatan (Yokelson et al., 2003), Brazil (Ferek et al., 1998), California (Sahu et al., 2012) and North America (Kondo et al., 2011).

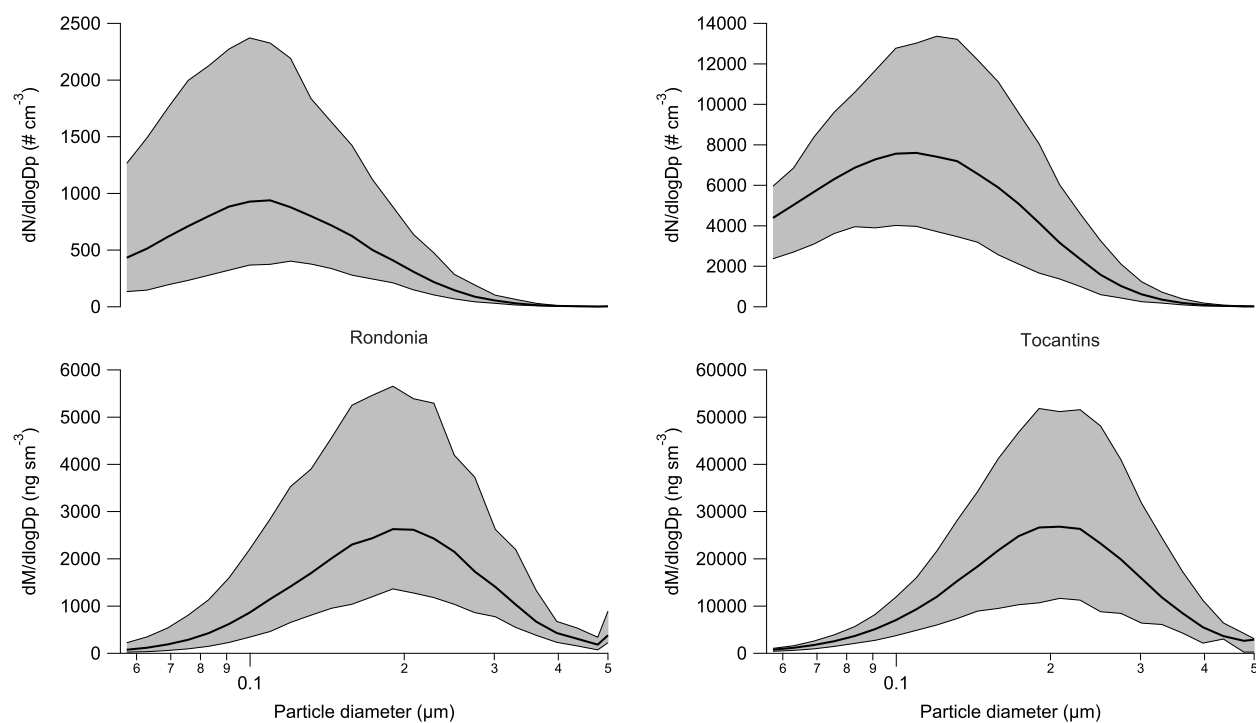


Figure 4. Black carbon number and mass-size distributions for in plume measurements of the Rondônia and Tocantins fires. The grey bound shading indicates the minimum and maximum size distributions from the plume intercepts on each flight and the solid black line gives the average over all plume interceptions. Note the difference in scales between Rondônia and Tocantins size distributions.

Table 1. Modified Combustion Efficiency (MCE) for the Rondônia fire and the Tocantins fires. Calculation methods as described in section 2.2.2. Also included are other studies MCE's from Brazil and from other locations with the specific fuel type quoted. ¹This study, ²Yokelson et al. (2007), ³Christian et al. (2007), ⁴Stockwell et al. (2016), ⁸Bertschi et al. (2003), ⁶Ferek et al. (1998) following Akagi et al. (2011), ⁷Kaufman et al. (1992), ⁸Yokelson et al. (2009), ⁹Yokelson et al. (2003), ¹⁰Akagi et al. (2011), ¹¹Desservettaz et al. (2017), ¹²McMeeking et al. (2009).

Study	Modified Combustion Efficiency		
	Tropical Forest-like	Cerrado-like	Mixed
Rondônia: Tropical Forest¹	0.79 ± 0.02		
Tocantins: Cerrado¹		0.94 ± 0.02	
Brazil: forest, pasture, grass average ²			0.91 ± 0.02
Brazil: Residual smouldering combustion of logs ³	0.788 ± 0.059		
Central Kalimantan, Indonesia: tropical peat fires⁴	0.772 ± 0.053		
Laboratory/field study: smouldering cotton wood and Zambian logs ⁵	0.855		
Brazil: Deforestation and Cerrado ⁶	0.87	0.94	
Brazil: Deforestation and Cerrado ⁷	0.91	0.97	
Yucatan: Deforestation and Crop residue ⁸	0.927 ± 0.013	0.934 ± 0.023	
Africa: Savannah ⁹		0.938 ± 0.019	
California: Chaparral ¹⁰		0.933	
Australia: Savannah¹¹		0.86-0.99	
Laboratory study: range of fuel types ¹²			0.857-0.977

Table 2. Emission ratios (ppmv/ppmv) and uncertainties for CO and CH₄ with respect to CO (ER_{x/CO}) and CO₂ (ER_{x/CO₂}) for the Rondônia fire and the Tocantins fires. Uncertainties for the two fires shown are one standard deviation in the line of best fit. Calculation methods are described in section 2.2.3. Also included are other ERs from other studies conducted in Brazil and other locations with the specific fuel type quoted. ¹This study, ²Christian et al. (2007), ³Yokelson et al. (2009), ⁴Yokelson et al. (2003), ⁵Akagi et al. (2012), ⁶Wooster et al. (2011), ⁷Crutzen et al. (1985).

Study	ER _{CO/CO₂} (x100)	ER _{CH₄/CO₂} (x1000)	ER _{CH₄/CO} (x1000)
<i>Tropical Forest-like</i>			
Rondônia: Tropical Forest¹	25.8 ± 0.70	9.8 ± 0.20	38.0 ± 0.80
Brazil: Residual smouldering combustion of logs ²	27.5 ± 9.3	39.3	143 ± 86
Yucatan: Deforestation and Crop residue ³	7.68	8.48	110.4
<i>Cerrado-like</i>			
Tocantins: Cerrado¹	6.8 ± 0.30	3.6 ± 0.03	53.1 ± 1.60
Africa: Savannah ⁴	6.64 ± 2.14	3.53	53.1 ± 11.8
California: Chaparral ⁵	7.13 ± 0.55	6.22	87.2 ± 2.4
Africa: Savannah ⁶	9.60 ± 3.10	4.30 ± 1.70	46.0 ± 7.0
<i>Mixed</i>			
Brazil: Mix of fire types ⁷	15.4	1.2	7.79

Table 3. Trace gas emission factors (g kg^{-1} of dry fuel burned) for Rondônia and Tocantins fires determined using the calculations as shown in section 2.2.4. EF values from previous studies in Brazil are included for comparison with the specific fuel type stated. Also included are EFs from different geographical locations around the world and values used in GFEDv3/GFASv1.0 and GFEDv4 emission inventories (van der Werf et al., 2010; Kaiser et al., 2012). ¹This study, ²Christian et al. (2007), ³Ferek et al. (1998) following Akagi et al. (2011), ⁴Ward et al. (1992), ⁵Kaufman et al. (1992), ⁶Yokelson et al. (2009), ⁷Akagi et al. (2011), ⁸Andreae and Merlet (2001), ⁹Bertschi et al. (2003), ¹⁰Stockwell et al. (2016), ¹¹GFEDv3, ¹²GFEDv4, ¹³Sinha et al. (2003), ¹⁴Yokelson et al. (2003), ¹⁴Wooster et al. (2011), ¹⁵Desservettaz et al. (2017), ¹⁶McMeeking et al. (2009).

Study	CO ₂	CO	CH ₄
<i>Tropical Forest-like</i>			
Rondônia: Tropical Forest¹	1447 ± 148	237 ± 24	5.17 ± 0.53
Brazil: Residual smouldering combustion of logs ²	1346 ± 123	229 ± 64.6	17.1 ± 10.0
Brazil: Deforestation ³	1652 ± 30	91 ± 24	5.41 ± 1.75
Brazil: Deforestation ⁴	1614	110	6.6
Brazil: Deforestation ⁵	1664	89	5.0
Yucatan: Deforestation and Crop residue ⁶	1641 ± 40	80.18 ± 19.4	5.059 ± 2.369
Global: Tropical forest ⁷	1643 ± 58	93 ± 27	5.07 ± 1.98
Global: Tropical Forest ⁸	1580 ± 90	104 ± 20	6.8 ± 2.0
Laboratory study: smouldering cotton wood and Zambian logs ⁹	1461.5	156.5	19.7
Central Kalimantan, Indonesia: tropical peat fires¹⁰	1564 ± 77	291 ± 49	9.51 ± 4.74
GFEDv3/GFASv1.0: Deforestation ¹¹	1626	101	6.6
GFEDv4: Deforestation ¹²	1643	93	5.07
<i>Cerrado-like</i>			
Tocantins: Cerrado¹	1711 ± 175	74 ± 8	2.23 ± 0.23
Brazil: Cerrado ³	1737 ± 10	43.9 ± 1.2	1.19 ± 0.2
Brazil: Cerrado ⁴	1722	58	1.3
Brazil: Cerrado ⁵	1783	24	0.6
Global: Savannah ⁷	1686 ± 38	63 ± 17	1.94 ± 0.85
Global: Savannah and Grassland ⁸	1613 ± 95	65 ± 20	2.3 ± 0.9
Africa: Savannah ¹²	1700 ± 60	68 ± 30	1.7 ± 0.98
Africa: Savannah ¹³	1703 ± 39	71.5 ± 21.7	2.19 ± 1.0
African: Savannah ¹⁴	1665 ± 54	101 ± 30	2.5 ± 0.9
Australia: Savannah¹⁵	1536 ± 154	110 ± 13	5.65 ± 0.7
GFEDv3/GFASv1.0: Savannah ¹¹	1646	61	2.2
GFEDv4: Savannah ¹²	1686	63	1.94
<i>Mixed</i>			
Laboratory study: range of fuel types ¹⁶	1034 ± 175 to 1868 ± 5	43.0 ± 1.4 to 129.5 ± 4.9	0.2 to 5.9 ± 1.2

Table 4. Mass fraction of aerosol components as a percentage of total aerosol mass, including black carbon, organic aerosol, chloride, ammonium, sulphate and nitrate for the Rondônia fire, Tocantins fires and values from previous studies. Ferek et al. (1998) and Yokelson et al. (2009) reported a percentage total including other particulate matter that we did not measure in our study, therefore we recalculated the values presented just including BC, organics and inorganics in order to compare values. *OA for the two Brazilian values estimated assuming OM/OC is 1.6 in fresh smoke (Yokelson et al., 2009; Akagi et al., 2012). ¹This study, ²Ferek et al. (1998), ³Sahu et al. (2012), ⁴Kondo et al. (2011), ⁵Yokelson et al. (2009).

Study	OM	BC	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	Cl ⁻
<i>Smouldering fires</i>						
Rondônia¹	97.1	0.30	0.49	1.08	0.49	0.53
Brazil: Deforestation ²	91.3	6.04	0.66	1.05	0.013	0.92
California: Forest ³	95.4	1.2	1.2	0.8	1.2	0.10
North America: Boreal forest ⁴	91.7	1.7	2.8	1.9	1.7	0.2
<i>Flaming fires</i>						
Tocantins¹	84.4	7.99	0.34	1.29	0.92	5.08
Brazil: Cerrado ²	88.4	6.58	0.34	0.301	0.066	4.32
California: Forest ³	78.9	1.6	7.1	6.3	5.5	0.4
North America: Boreal forest ⁴	80.3	3.4	9.8	1.7	4.8	0.1
Yucatan: Deforestation & Crop residue ⁵	68.0	10.8	1.02	4.95	4.14	11.01

Table 5. Emission ratios and uncertainties for particulate species with respect to CO ($ER_{x/CO}$) and CO₂ (ER_{x/CO_2}) for the Rondônia fire and the Tocantins fires. The ERs are presented as molar ratios and are multiplied by 1000. Calculation methods are described in section 2.2.3. Also included are other ERs from other studies conducted in Brazil and other locations with the specific fuel type quoted. ¹This study, ²Akagi et al. (2012): California Chapparral, ³Yokelson et al. (2009): Mix of crop residue and deforestation, ⁴Jolleys et al. (2012), ⁵Capes et al. (2008) using OM/OC ratio of 1.4.

Study	ER	OM	OC	BC	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁻
Rondônia¹	x/CO_2	20.3	12.7	0.05	0.10	0.20	0.09	0.08
		±6.1	±3.8	±0.02	±0.03	±0.06	±0.03	±0.02
Tocantins¹		2.8	1.7	0.28	0.19	0.04	0.01	0.03
		±0.8	±0.5	±0.08	±0.06	±0.001	±0.003	±0.009
California ²		3.55	2.22	0.783Z	0.0497Z	0.0961	0.00358	0.06
		±0.857	±0.536	±0.536	±0.536	±0.536	±0.00328	±0.0395
Rondônia¹	x/CO	123.4	77.0	0.30	0.67	1.21	0.52	0.5
		±37.1	±37.1	±0.09	±0.2	±0.36	±0.16	±0.2
Tocantins¹		68.2	42.6	6.1	4.62	1.03	0.28	0.79
		±20.5	±12.8	±1.8	±1.39	±0.31	±0.08	±0.24
Yucatan ²		-	26.4	6.3	6.3	2.9	0.6	2.4
Northern Australia ⁴		329±23.0	-	-	-	-	-	-
SE Mexico City ⁴		51.0±1.0						
West Africa ⁵		65.0±2.0	41.0±2.0	7.2±0.9	-	-	-	-

Table 6. Particulate species emission factors (g kg^{-1} of dry fuel burned) for Rondônia and Tocantins fires determined using the calculations as shown in section 2.2.4. EF values from previous studies in Brazil are included for comparison with the specific fuel type stated. Also included are EF's from different geographical locations around the world and values used in GFEDv3/GFASv1.0 and GFEDv4 emission inventories (van der Werf et al., 2010; Kaiser et al., 2012). ¹This study, ²Ferek et al. (1998) following Akagi et al. (2011), ³Yokelson et al. (2009), ⁴Stockwell et al. (2016), ⁵Akagi et al. (2011), ⁶Andreae and Merlet (2001), ⁷van der Werf et al. (2010); Kaiser et al. (2012), ⁸Sinha et al. (2003), ⁹Desservettaz et al. (2017), ¹⁰McMeeking et al. (2009).

Study	OM	OC	BC	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁻
<i>Tropical Forest-like</i>							
Rondônia¹	8.00	5.00	0.019	0.04	0.078	0.034	0.033
	±2.53	±1.58	±0.006	±0.01	±0.025	±0.011	±0.011
Brazil: Deforestation ²	-	4.34	0.46	0.07	0.08	0.05	0.001
		-	-	±0.07	±0.02	±0.03	±0.002
Yucatan: Deforestation & Crop residue ³	3.254	2.117	0.541	0.509	0.233	0.047	0.192
	±0.690	±0.569	±0.569	±0.377	±0.056	±0.024	±0.136
Central Kalimantan, Indonesia: tropical peat fires ⁴	-	16.0	0.00552	-	-	-	-
		± 5.5	± 0.00162				
Global: Tropical forest ⁵	-	4.71	0.52	0.15	0.11	0.13	0.00564
		±2.73	±0.28	±0.16	±0.05	±0.088	±0.0172
Global: Tropical Forest ⁶	-	5.2	0.66	-	-	-	-
		±1.5	±0.31				
GFEDv3/GFASv1.0: Deforestation ⁷	-	4.3	0.57	-	-	-	-
GFEDv4: Deforestation ⁷	-	4.71	0.52	-	-	-	-
<i>Cerrado-like</i>							
Tocantins¹	1.31	0.82	0.13	0.09	0.013	0.0006	0.015
	±0.42	±0.26	±0.04	±0.03	±0.004	±0.0002	±0.005
Brazil: Cerrado ²	-	2.94	0.35	0.23	0.016	0.018	0.0035
		±1.23	±0.2	0.055	0.013	0.009	0.0035
Africa: Savannah ⁸	-	2.3	0.39	0.97	0.16	0.17	-
		±1.2	±0.19	±1.4	±0.11	±0.18	
Australia: Savannah ⁹	5.7	3.56	-	0.60	0.030	0.0024	0.20
	±1.4	±0.88	-	±0.1	±0.008	±0.006	±0.005
Global: Savannah ⁵	-	2.62	0.37	0.23	0.016	0.018	0.0035
		±1.24	±0.20	±0.055	±0.013	±0.009	±0.0035
Global: Savannah & Grassland ⁶	-	3.4	0.48	-	-	-	-
		±1.4	±0.18				
GFEDv3/GFASv1.0: Savannah ⁷	-	3.2	0.46	-	-	-	-
GFEDv4: Savannah ⁷	-	2.62	0.37	-	-	-	-
<i>Mixed</i>							
Laboratory study: range of fuel types ¹⁰		0.5 to 44.2	-	0.03±0.02 to 5.39	0.0±0.0 to 0.84±1.17	0.01 to 0.73±0.34	0.0±0.01 to 0.51