

Interactive comment on “The Tropical Forest and fire emissions experiment: overview and airborne fire emission factor measurements” by R. J. Yokelson et al.

R. J. Yokelson et al.

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Response to Anonymous Referee #2

R2.1. The manuscript by Yokelson et al., presents an overview of the measurements conducted within the TROFFEE field experiment in Brazil 2004. This paper presents the motivation for this airborne and ground-based field effort and presents background information on fire activity in Brazil. The main results obtained in this field experiment, i.e., emission factors for numerous, mainly organic, compounds from deforestation fires mainly obtained within individual smoke plumes, are presented. On one flight a highly polluted air mass was chemically characterized and the location of the responsible fires

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was determined. The manuscript is in general well written and contains a good description of the motivation, the experimental concept and observational strategy, and the main results. Some parts, however, should be more focused and maybe restructured as suggested in the specific comments below. The data analysis and interpretation of the results is sound and clear. The currently available data for emission factors from deforestation fires is very limited (especially for the oxygenated VOC presented in this study), thus the present work presents a significant contribution to our knowledge of tropical fires and will help to establish a better representation of these types of fires in larger-scale models. Hence, the manuscript is well suited for publication in ACP.

Enclosed are my specific comments that should be considered before publication of the manuscript in ACP.

Specific Comments:

R2.2. Introduction: Presently the introduction is written rather unconventional in the sense, that first (after only one paragraph of general introduction) details of the field experiment are presented (page 6905 to 6908) before some more motivation for the field experiment is given (page 6908/6909). I suggest to reorganize the introduction in the more conventional way, starting with the more general motivation and then presenting the details of the field experiments.

Au2.2. We are attempting to accomplish two things with this paper: (1) a brief overview of the whole field campaign, and (2) details the airborne fire results. Because of paper length we gave only one paragraph of background on the general atmospheric significance of tropical forests. Then we described the full scope of the campaign, which covered both vegetative and fire emissions. Then we narrow the focus to the fire emissions and the final bit of material that seems introductory in nature is actually the detailed justification for the approach and study design used. We have tried to make this clear with minor revisions. If we move the introductory material about fires before the description of the whole campaign, the subject of vegetative emissions seems out

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of place

R2.3. In addition, more general information that is included in the later sections of the manuscript should be moved into the introduction. Section 3.3, for example, contains interesting information about Brazilian deforestation fires that should be included in the introduction. Section 3.4 deals with the description of the fires sampled within TROFFEE and should be included into the 'Experimental Details' section.

Au2.3. Reviewer 2 suggests moving the material from section 3.3 into the introduction and the material from section 3.4 into section 2 (Experimental details). These comments are reasonable, but we also note that reviewer 3 says the introduction is already "too long." We have compromised by shortening both original sections 3.3 and 3.4 and moving the remaining text as follows:

- (1) The first paragraph in the original section 3.3 on the global significance of deforestation fires was moved to the first paragraph of the introduction.
- (2) We moved the material on comparison of annual amounts of burning from the original section 3.4 to the beginning of the new section 3.3 on emission factors where it addresses representativeness.
- (3) The remaining material was moved to a new section 2.3 that summarizes Brazilian biomass burning and compares it to the fires we actually sampled.

In the process, we also shortened the overall length of our working copy of the paper from 53 to 50 pages.

R2.4. Page 6911, Section 2.1.2: This section contains the description of the IR spectral analysis for the different compounds accessible with FTIR. While for some compounds, mixing ratios can be determined, for most of the compounds excess mixing ratios are determined by the spectral subtraction routine. I suggest to make this point more clearer, e.g., by dividing the first paragraph on page 6911 into two, the second paragraph possible starting on line 11 ('Excess mixing ratios of NO...').

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- Page 6911, line 11: Please expand a little bit on the determination of the NO and NO₂ excess mixing ratios. Are those determined ‘directly from the smoke-plume absorbance spectra’? If so, why is this excess mixing ratio (as opposed to mixing ratio)? Or do you subtract background air mixing ratios to derive excess mixing ratios?

Au2.4. Reviewer 3 had a closely related comment, which we insert out of order next and then reply to both comments.

R3.4. Page 6911, lines 20-22: I may be missing something here, but, if the detection limits for the AFTIR were 15-20 ppbv for NO_x, O₃, and a few other compounds, how is it possible to estimate the enhancements of these compounds from these measurements? Aren't the background concentrations of these compounds lower than the detection limits?

Author reply to both comments. All molecules absorb IR radiation, but sometimes the measured reduction in IR energy transmitted through a sample, at a particular frequency, is smaller than the peak to peak noise in the spectrum baseline. When this is the case, the molecule is below the detection limit. Or, alternatively, the potential error in the measurement due to system noise is the stated detection limit. For CO₂, CO, H₂O, and CH₄, there is always enough in the troposphere so that they are above the detection limit. We analyze the background and smoke spectra separately to obtain mixing ratios in this case and we calculate the excess mixing ratios from the difference. The other molecules reported are well above the detection limit in fresh smoke plumes, but normally below the detection limit in background air. Because of the usual huge enhancements in the plumes, the error associated with uncertainty in the background is usually negligible and the most important error term is the accuracy of the measure of the absorbing strength of the molecule (its “cross-section”). The error in the cross-section is typically 5% and this is why our errors are reported for these molecules as “5% or the detection limit, whichever is larger.” We obtain excess mixing ratios for these molecules directly from absorbance spectra. An absorbance spectrum is simply $\log(\text{smoke spectrum}/\text{background spectrum})$. The resulting spectrum has reduced

noise and absorbance peaks that are (linearly) related to the difference in concentration between the two samples. We ensure that the background and sample spectra are at the same pressure so that the difference in mixing ratios follows directly from the difference in concentration, although differences in pressure can be corrected for in the case when the spectra are obtained at different altitudes. Since the paper is long and this response will be published we do not reproduce this whole explanation in the paper. We added a reference about basic IR spectroscopy and we slightly reorganized the text as follows:

Original: “We used the same background-sample spectra pairs to generate absorbance spectra of the smoke plume samples. Excess mixing ratios for NO and NO₂ in smoke plumes were obtained directly from the smoke plume absorbance spectra using peak integration and a multipoint calibration.”

Revised: (including a new paragraph started) “We used the same background-sample spectra pairs to generate absorbance spectra of the smoke plume samples. Excess mixing ratios are retrieved directly from the absorbance spectra (Hanst and Hanst, 1994). Excess mixing ratios for NO and NO₂ in smoke plumes were obtained from the absorbance spectra using peak integration and a multipoint calibration.”

Hanst, P. L., and Hanst, S. T.: Gas measurement in the fundamental infrared region, in *Air Monitoring by Spectroscopic Techniques*, edited by M.W. Sigrist, pp. 335 - 470, John Wiley, New York, 1994.

R2.5. Page 6912, line 21: Please give some more detail (e.g., a reference) on the mass-calibrated nephelometer. In particular I am wondering how the aerosol mass is determined based on measurements of the aerosol scattering (I assume that aerosol scattering is the quantity that is measured by the nephelometer). Do you make an assumption about the aerosol mass scattering efficiency to convert aerosol scattering into aerosol mass? If so, please motivate the choice of the value you are using.

Au2.5. According to the detailed explanation in the instrument manual, the particle

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mass is determined from the intensity of scattering at two wavelengths and the ratio of the scattering intensity at these two wavelengths. Further relative humidity is measured and an RH correction is built in. Artaxo's group has run this instrument along side a TEOM under very smoky conditions in the Amazon and obtained good agreement. We realized that we also needed to define PM10 and provide the manufacturer of the nephelometer so we rewrote this section as follows:

“A list of the instruments deployed by the University of São Paulo and their measurement frequency follows. (1) DataRAM4 (Thermolectron Corp), which measures the mass of particles with an aerodynamic diameter <10 microns (PM10) and mean particle diameter (microns) at 0.5 Hz.. (2) 3-channel nephelometer (RBG) at 0.2857 Hz.. (3) 7-channel aethalometer (Magee Scientific) measuring particle absorbance from 950-450 nm every 2 minutes.. (4) Ozone by UV absorbance (1 min time resolution). (5) GPS (Garmin) measuring UTC time, latitude, longitude, and altitude at 1 Hz. Instruments 1-4 had specialized inlets located on the front belly of the aircraft adjacent to the PTR-MS inlet. The PM10 measurements reported here were measured by the DataRAM4, which is a two-wavelength nephelometer with a built in humidity correction. The instrument has been run side by side with a TEOM (Tapered Element Oscillating Microbalance) under smoky conditions in the Amazon and good agreement was observed.”

R2.6. Page 6913, line 3: ‘Septemember’ should read ‘September’

Au2.6. Done

R2.7. Page 6913, line 9: Maybe add another sentence to give some more details about the ZF-14 Tower (who is running this tower, what kind of instrumentation: aerosol vs gas phase). This information could instead be included in the introduction, page 6907, line 21 (in fact, it might be better placed in the introduction).

Au2.7. To avoid excess length we just added the reference to the paper that describes the tower in more detail.

R2.8. Page 6913, line 14: It is not clear if in total 21 canisters were sampled, or if this number relates to the canisters sampled in Manaus. Please specify.

Au2.8. There were 22 background can samples and one smoke can sample over campaign as a whole. The new text in context is:

“When sampling background air in either region, the PTR-MS continuously cycled through a suite of mass channels with a resulting measurement frequency for individual species ranging from 10-20 s. Overall, twenty-one canisters were used to “grab” background samples at key locations. The airborne FTIR (AFTIR) was operated either continuously (time resolution of 0.83 to 18 s) or to acquire 133 grab samples of background air.

To measure the initial emissions from fires in both regions, . . .”

R2.9. Page 6913, line 15: I suggest to start a new paragraph before ‘To measure....’ to increase readability.

Au2.9. Done as seen above.

R2.10. Page 6913, line 25: What is meant by ‘..profiles on an emission source...’? Please specify.

Au2.10. The phrase was changed to: “measured their species continuously.”

R2.11. Figure 2: The axis labels should read ΔCO and ΔCO_2 (for 2a, and accordingly for 2b, 2c, and 2d). I suggest to include error bars on the measurements. Figure 2: There seems to be a misprint in Figure 2c, since CH_3CO is a radical, which almost certainly has not been measured with the employed instrumentation.

Au2.11. Thanks for pointing out all 3 mistakes, which have all been fixed. CH_3CO was changed to CH_3CHO (the structural formula for acetaldehyde).

R2.12. Page 6915, line 4: Please motivate the use of the integrated excess mixing ratio to determine the ER from PTR-MS measurements. From my perspective it seems that

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using the continuous plume measurements from the PTR-MS would be the natural way to determine ER. Please specify, how the integrated excess mixing ratios are calculated from PTR-MS measurements (e.g., how do you define the plume, how do you derive the unit of ppbv s?)

Au2.12. Basically the PTRMS species are measured sequentially while passing rapidly through a plume. Also the time response varies a bit for some molecules. The comparison of integrals compensates for both of these shortcomings. The units ppbv s are simply the units of the integral. The enhancements in the plume are enormous making the plume locations obvious. The backgrounds are the average of a section of data just outside the plume. This is discussed at great length in the companion paper reference now provided. We added the sentence, “Comparison of integrals provides more accurate ER (Karl et al., 2007a).”

R2.13. Page 6916, line 7: I suggest to refer to Table 2 only in the ‘Results and Discussion’ Section, and not already in the Section on ‘Experimental Details’.

Au2.13. Done. We moved the two references to Table 2 that were here to the beginning of what is now section 3.3.1.

R2.14. Page 6916, line 11: How is the emission factor for ‘NO_x as NO’ calculated?

Au2.14. We added the sentence: “We computed this EF from the NO_x/CO₂ molar ER obtained as described in section 2.2.1, but it can also be estimated from Table 2 data using: $EF_{NO} + (30/46) \times EF_{NO_2}$.”

R2.15. Figures 3 and 4: The use of ‘percent’ as the unit for water vapor is rather uncommon, maybe this value can be converted to more common ways to report atmospheric humidity, like dew point, specific or relative humidity. At least it should be stated somewhere, how this unit can be transferred to more common units.

Au2.15. In principle, vertical profiles of RH could be obtained from the DataRAM4, but the intent of these figures is to compare CO mixing ratios directly to H₂O mixing ratios.

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We changed the words “water vertical profile” to “water mixing ratios” in the text to clarify this. Mixing ratios are also the preferred unit of the modelers that use our data. The percent water data shown from the AFTIR (measured in same cell as CO shown) could be converted to partial pressures of water using the temperature and pressure in the IR cell. But then the comparison would not be direct and the conversion is not simplistic or based on data already in the paper.

We added a sentence to the Figure 4 caption which reads: “(The water vertical profiles can be obtained in other units from the authors.)”

R2.16. Page 6919, line 15: ‘Christian07b’ should read ‘Christian et al., 2007b’ (I guess).

Au2.16. Fixed.

R2.17. Section 3.2: The comparison of the measured pollutant concentrations with previous work is very valuable. Maybe there is some additional information available from the SMOCC experiment in 2002, e.g., Guyon et al. in the ACP Special issue.

Au2.17. The paper by Guyon et al is good, but they had a different study objective and design and did not present data directly comparable to the data we discuss in this section.

R2.18. Section 3.3: As mentioned previously I suggest moving this section on the Deforestation fires forward in the introduction section. In addition, it should be shortened, streamlined, and more focused on the information relevant for the present work. Page 6921/6922: The summary of fire types in Brazil (savanna, pasture and deforestation, if I understand correctly) is very interesting and helpful to evaluate the relevance of the obtained measurements. However, it is rather hard to read and therefore should be streamlined and the most relevant points (e.g., what is the contribution of the

different fire types to the Brazil biomass burning emissions?) should be highlighted more clearly. Page 6921, line 18ff: The presentation of the results from different studies

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on the biomass loading of deforestation fires should be shortened, maybe give a range of burned fuel derived in these studies that can be compared to the value of 5 - 10 t/ha from savanna fires. Section 3.4: This section describes fires sampled within TROFFEE and their relevance. I suggest to move this section into Section 2 'Experimental Details', potentially as Section 2.3, and present only results in Section 3.

Au2.18. These issues were addressed as described above.

R2.19. Page 6925, line 2: To motivate the statement of 'well above-average years' please include the average annual area of deforestation fires?

Au2.19. The new text reads: "The INPE deforestation data, however, shows 2004 (27429 km²) as the second highest year after 1995 (29059 km²) - the year of the SCAR-B campaign. Thus, both TROFFEE and SCAR-B were conducted in years when the deforested area was well above the long-term average of ~20000 km²."

R2.20. Section 3.5: Here, a reference to Table 2 should be included.

Au2.20. The sentences stating that the ER and EF appear in Table 2 was moved from section 2 to the end of the introductory paragraph to this section, which is now section 3.3.

R2.21. Table 2: Please specify what is meant by 'nm'.

Au2.21. "not measured." Footnote added to table.

R2.22. Table 2: I suggest presenting the data from the Mega-Plume in a separate table. Only the AFTIR conducted measurements listed in Table 2 for the Mega-Plume so the additional table should be much shorter than Table 2. This would make Table 2 more readable and would give more attention to the very nice results obtained from the Mega-Plume measurements. Especially the comparison of the effective emission factors from the Mega-Plume measurements with the emission factors determined from the plume measurements, and the calculation of the difference between the megaplume emission factor and the emission factors expressed using number of

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standard deviations in the study-average emission factor is very innovative and useful.

Au2.22. This suggestion definitely has some strong points and so we tried this. The current Table 2 includes the mega-plume data and fits on a landscape page. If we remove the mega-plume data, Table 2 would still require a landscape page, but also have wasted white space. A new Table 3 would then lengthen the paper and also require the reader to flip back and forth between tables to compare values. Therefore, we have left the tables as they were.

R2.23. Section 3.5.1/Figure 5: For selected compounds their emission factors as function of MCE are determined. What is the selection criterium for the selected six compounds?

Au2.23. NO_x as NO is the major flaming emission after CO₂ and so it exhibits a positive correlation with MCE (noted in new section 3.3.1 text). CH₄ and C₂H₄ are the most abundant hydrocarbon emissions. CH₃OH is the second most abundant organic compound in troposphere and also used as an internal standard in this work to couple the PTRMS and AFTIR data (noted earlier in text). PM₁₀ is the only particle species we measured and the fact that its MCE-dependence is similar to that of smoldering compounds is noted in the text in new section 3.3.1. CH₃CN is important as a biomass burning tracer and the fact that its emissions do not depend strongly on MCE makes it more attractive as a tracer since one average value can be roughly assumed for all deforestation fires regardless of seasonal or spatial variation in MCE. The latter point is made later in the text in new section 3.3.1. to clarify all these points, we replaced the last sentence in the Figure 5 caption, which simply stated that variation occurs as follows:

Original: “A range of EF can occur and the sign of the trend of EF vs MCE can vary (section 3.5.1).”

Revised “(See discussion in section 3.3.1.)”

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R2.24. For the use in models and for the broader understanding of fire emissions it could be valuable to determine the dependence of the emission ratios from the MCE for all measured compounds. If the authors find this relevant, maybe a Table that includes the parameters of the linear correlation between the MCE and the emission factor for each compound can be included.

Au2.24. This is an excellent suggestion. Since this paper is long already we plan to use it in a nearly-complete companion paper that will present the laboratory EF measurements and synthesize them with the ground-based and airborne field-measured EF.

R2.25. Page 6929, second paragraph: Is the difference in acetonitrile emission factor for the different fuel types consistent with the different N-content of the fuel, e.g., high emission factors for fuel with high N-content.

Au2.25. We don't have fuel nitrogen data for the individual fires in this study. Comparing the main fire types based on available, "typical" fuel N data in the literature, there is evidence that fuel N content is a factor, but maybe not the only factor. I.E. the acetonitrile emissions and fuel N content for peat are both very large. However, the forest fuels emitted more acetonitrile than the savanna fires even though the literature indication is that the grasses might have higher N content. That latter statement has a caveat in that fuel N varies seasonally and so we may not have sampled emissions from forest and savanna fuels with N content proportional to the literature average.

R2.26. Page 6929, Line 18: Please mention the particle emission factor measured during TROFFEE here.

Au2.26. Added in parentheses to revised paper.

R2.27. Page 6930, line 18: Can you speculate, why aerosol mass emission is related to fire size / intensity (and not MCE)?

Au2.27. Clearly the aerosol mass emission is related to MCE as shown in Figure 5. It

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may also be related to fire size and intensity and, in fact, the latter may correlate with MCE to some extent. Aerosol mass emission the lab can be enhanced by adding fresh green vegetation as fuel. Perhaps larger more intense fires have more capability to consume any live fuels in the area. But, without some careful experimental work in this area we prefer not to lengthen the paper by discussing this.

R2.28. Page 6930, line 20: maybe mention the three main types of burning you are referring to in this paragraph already in the beginning.

Au2.28. Added in parentheses in revised paper.

R2.29. Page 6930, line 29ff: Are the higher emission factors for deforestation fires compared to savanna fires related to the difference in MCE between these two fire types. Or is the statement valid even when you include the MCE dependency of the emissions?

Au2.29. Good question - there is no simple answer. When we compare savanna fires to deforestation fires at an MCE of 0.91 we find higher savanna fire emissions for C_2H_4 and HCOOH, lower for CH_4 and CH_3OH , and about the same for CH_3COOH , HCHO, and C_2H_2 .

R2.30. Page 6933, line 6ff: You mention that ‘only the AFTIR and the GPS acquired data on this flight’, but present PM10 mass mixing ratio. It seems that also the nephelometer was measuring during this flight.

Au2.30. We have clarified that high PM10 is “inferred” based on the typical $\Delta PM10/\Delta CO$ ratios observed in fresh plumes ($\sim 200 \mu g/m^3$ of PM10 per ppm CO).

R2.31. Page 6933, main paragraph: How do you determine the effective emission ratios? How do you determine the background mixing ratios to calculate the excess mixing ratio in the situation of the mega-plume?

Au2.31. As we approached the mega-plume from the north in clean air we saw a looming “wall of smoke” on the horizon, which turned out to be the edge of the mega-

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plume. In figure 7a one can see the last sample of clean background air obtained at 8°S. This was used as the background for the subsequent samples. This is analogous to the procedure for the smaller plumes, but on a larger spatial scale. New text reads:

“The last sample of clean air (at ~8oS, Fig. 7a) was used as the background for the mega-plume samples. The EEF were computed in the same way as EF (Sect. 2.2.2).”

Additional changes:

1) We originally included a short paragraph about phenol that mentioned possible sampling losses for the PTR-MS and we flagged the Table 2 values as lower limits. Subsequent work showed good agreement for phenol between open-path FTIR and PTR-MS. Thus we eliminated the flag (footnote) from Table 2 and also the short paragraph in the comparison to other work.

2) As described above, a footnote was added to Table 2 to define “nm” as “not measured.” (In most cases this was because a measurement was not attempted.) We also replaced the formulas for acetonitrile and acetaldehyde with their names as was already the case for the other PTR-MS compounds. Finally, the table entry “C6 hydrocarbons” was corrected to “C6 carbonyls.”

3) Slightly revised section 3.3.2 and conclusions to reflect the value of acetonitrile for source apportionment.

E.G. New: Still, these results suggest that (with proper attention to the type of fire), PTR-MS acetonitrile measurements could contribute to source apportionment or, with inverse modeling, estimates of the amount of biomass burned.

4) Updated references

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