

## ***Interactive comment on “Emissions of trace gases from Australian temperate forest fires: emission factors and dependence on modified combustion efficiency” by Elise-Andrée Guérette et al.***

**V. Selimovic (Referee)**

vanessa.selimovic@umconnect.umt.edu

Received and published: 14 November 2017

This reviewer would first like to thank the authors for submitting their article entitled “Emissions of trace gases from Australian temperate forest fires: emission factors and dependence on modified combustion efficiency” to Atmospheric Chemistry and Physics for potential publication in this journal, and finds the subject matter appropriate. In the article presented, the authors measure trace-gases and VOCs from nine prescribed fires, seven of which were in New South Wales and two in Victoria. Three different instruments were used in sampling, including an open-path FTIR, SIFT-MS, and White cell for grab sampling. While the results are relevant and attempt to close some gaps

C1

in ecosystem specific emission factors, the manner in which the data are presented and manipulated needs work. The manuscript presented lacks critical information as to how sampling was conducted and how components were measured by different instrumentation. Additionally, the manipulation and presentation of the data collected suffers from inconsistencies that reduce the significance of the overall message the authors are attempting to present. This manuscript would benefit significantly from clarification as well as further discussion into how the data was analyzed, including justification for the methods used. Therefore, it is the opinion of this reviewer that this manuscript not be accepted until these issues are addressed in detail.

Abstract: The fires studied are prescribed fires and may not represent wildfires. See: Liu et al., 2017: “Airborne measurements of western U.S wildfire emissions: Comparison with prescribed burning and air quality implications”

Introduction

P1, L21-22: The following sentence “The mix of VOCs emitted during biomass burning may be ecosystem specific, especially for VOCs that are associated with biogenic processes (as opposed to combustion processes) and that are distilled from vegetation in the early stages. . .” is somewhat unclear. Are you arguing that fuel type can impact emissions? If so, this is true, but raising biogenic emissions here is confusing and the message could be clarified or omitted. For example, some biogenic compounds like monoterpenes are stored in plant tissue and can be emitted due to heat from a fire, but others (like isoprene) are made and emitted immediately. Therefore, isoprene is emitted all the time, but made in fires not by heating stored isoprene but breaking down solid biomass. Also, the concept of ‘early stages’ has no meaning in a moving landscape fire.

P2, L1: The OVOC are not distilled but are pyrolysis products instead.

P3, L17: Maybe include “we compare our results with the emission factors listed in Akagi et al. . .for temperate forests and to emission factors measured for Australian

C2

savannah fires and find significant differences in both cases” in the abstract, with a quantitative comparison and list of differences for some compounds. You already sort of do it in the abstract, but elaborate a little more. I.E: “Some species agree within 20%, others differ by a factor of 2 or more.” Which ones?

#### Methods

Sect 2.2, P4, “Open-path FTIR system”: How do you measure pressure and temperature with the OP-FTIR? Looked to Paton-Walsh 2014 and didn’t find anything explicit on how that was done. You mention temperature and pressure for the white cell later on, so having it for the OP-FTIR should be just as important.

Sect 2.3, P5, “Grab sampling”: How were the glass grab samples filled? Was there a sample line? P6, L7: “As for the OP-FTIR spectra, mole fractions were retrieved using the Multiple Atmospheric Layer Transmission (MALT) model. . .” You already mention this in the OP-FTIR section. How were the spectra from the White cell analyzed? Were they also analyzed using MALT?

P6, L25: The authors mention mass to charge ratios and calibration factors used to quantify them in the supplemental. According to Table S2, H<sub>3</sub>O<sup>+</sup> is used as a reagent ion for HCN and formaldehyde which were both additionally assigned the same sensitivity. Did the authors compare HCN and formaldehyde values to any other instruments, for instance, results from OP-FTIR or grab samples? HCN and formaldehyde both have proton affinities that aren’t much higher than water, and sometimes this can be an issue, especially for instruments like a PTR-MS that use H<sub>3</sub>O<sup>+</sup> as its reagent ion. Does SIFT-MS have similar issues? If so, they should be addressed with instrument comparisons. A figure like Figure 3 would be nice for compounds like HCN or formaldehyde.

P7, L15: “Also, not every trace gas species was present at a detectable level in every sample. For some fires, this resulted in too few samples to allow an emission ratio to be meaningfully derived by regression for that species. For this reason, emission

C3

ratios for each species were also derived through combining samples from all fires.” Can you elaborate on this? The authors mention earlier in the paper that emissions vary based on fuel type, so how can you justify combining samples from all fires? The authors also mention further in the paper on P10 Line 17 that some species show important site-to-site variability. In the supplement it looks like fuel types from the fires were mostly dry sclerophyll, but the understory seemed to vary. Are you worried about understory components contributing differences in ER? Selimovic et al., 2017 (currently in ACP discussion) found that emissions vary based on fuel component, so this might be something to consider reworking using a different method. The one presented in Yokelson et al 2011, Figure 2 might be valid. Also, poor correlation or low sample number is no reason not to report data, even a single sample is meaningful and should be included.

P8, L1-4: This doesn’t make sense mathematically. If benzene is not highly correlated to CO or CO<sub>2</sub>, then that is real. If it has better correlation with ethene, it doesn’t matter. The uncertainty in benzene to ethene coupled with the uncertainty in ethene to CO or CO<sub>2</sub> should have the same overall uncertainty.

P9, L13: Using only three species in “CT” inflates the EF. It’s easy enough to include all C-containing gases and is also more accurate.

P10, L4: “These are indicative of the type of combustion (e.g flaming vs. smoldering) captured by the grab sampling, and are not necessarily representative of the whole fire. As an example, the average MCE of the grab samples collected at the Gulguer Plateau fires was 0.78 +/- 0.09 whereas a fire-integrated value of 0.90 was measured by OP-FTIR.” Which MCE did the authors use in the data analysis stage? It is not explicitly stated in the paper. For EF that were calculated using grab samples, was grab sample MCE used or fire-integrated? 0.78 indicates a fire that is more smoldering, but 0.90 indicates a fire that is more flaming. This could be problematic when trying to make the case for compounds emitted during the smoldering stage versus compounds emitted during the flaming stage, especially in relation to MCE. It would be helpful if the data

C4

analysis process was described in detail with all of the specifics. Results

P10, L17-32: I have issues with the authors choosing to exclude emissions of certain compounds from the Gulguer fire because it does not fit within the observed mean ratio without it, but then choosing to include emissions combined from all fires, despite site-to-site variability, which the Gulguer fire clearly shows. You should stick to one method or the other. Either include all of the samples regardless of how they affect the mean, or keep the ER fire-specific. Switching between the two reduces the significance of the message you're trying to get across. Additionally, fires are naturally variable and it's not representative to exclude data because of a low r-squared value. All samples without high instrumental error are valid and any number of samples from 1 to 'n' at some level of ecosystem specificity will give you your best results.

P11, Table1: Convert all of the ER to the same reference species for ease of use and eliminate the r-squared column, which isn't useful.

P13, L14: Within what % uncertainty? Be more quantitative.

P14, L5: What is meant by "fire-averaged?" Which fires?

P14, L8, Table 3: What p value? How was this calculated? Maybe include this in the table caption, or in detail in the paragraph.

P15, Fig 6. There is no inherent value in a high r-squared for EF vs. MCE. The r-squared is simply an indication of the dependence on flaming and smoldering and if other things like fuel chemistry or multiple formation mechanisms impact the EF vs. MCE then that is useful to see. The Lawson et al fire was in a heath land and seems less relevant than the Gulguer Plateau fire.

P16, L5: Why was methanol not included for the Gulguer Plateau fire? Nothing about this is mentioned earlier in the paper, and it's included as part of Table 2.

P16, L16-17: Burling et al. was spring fires and Akagi et al. sampled fires in the fall so a seasonal difference can contribute to the variability.

C5

## Discussion

P17, L8: Can you elaborate on why you think there is a relationship for the NSW but not when you include all fires? This seems to be further suggestion of site-to-site variability.

P17, L17: "that are biogenically produced by vegetation and are not only a product of combustion..." Please clarify. See comment 1 earlier, regarding a similar statement in the introduction.

P17, L28-29: "...relatively low average MCE of 0.91." Relatively low compared to what? Table 4 shows an even lower MCE of 0.89 for the same study.

P18, Table 4: Filling in the Akagi et al MCE based on the CO CO2 EF shown might make it easier to compare that aspect of studies quickly.

P19, L7: The results of the study should be included, even if the discussion isn't repeated. You should at least discuss how the comparison worked out.

P19, L10: The Lawson fire was not a temperate forest fire.

P19, L22-23: Do you think Nitrogen emissions higher due to seasonal high fuel N?

P23, L1: Can you elaborate on how they would impact plume chemistry and influence air quality outcomes downwind of the fires? Some discussion would be helpful.

## Technical Corrections:

P1, L17: Change "At a national level, average gross annual emissions of total carbon from fires.." to "..annual emissions of total carbon from some fires.." since not all vegetation grows back fast.

P3, L3: You already mention Hurst et al. 1996 in page 2, line 31. You should remove the sentence from the third page and add it to the second, or vice versa. Either way I think consolidating the statements would be helpful, since having it in two locations essentially saying the same thing seems redundant.

C6

P3, L6: Abbreviate New South Wales National Parks as NSW. You mention it in Page 3, Line 11, but don't abbreviate it before then.

P5, L5: "CO<sub>2</sub>, CO, CH<sub>4</sub>, acetic acid, ammonia, ethene,..." and "CO<sub>2</sub>, CO, CH<sub>4</sub>, ethane and ethene..." This could be considered "picky" but I think it would be useful to include the chemical formulas and names of all the compounds to maintain consistency (I.E: Carbon Dioxide (CO<sub>2</sub>), Carbon monoxide (CO), Methane (CH<sub>4</sub>), acetic Acid (CH<sub>3</sub>COOH), ammonia (NH<sub>3</sub>), etc).

P19, L17: "...emission factors listed in 5.." Do you mean Table 5?

Supplemental: No issues on the supplemental

References: Brilli, F., Gioli, B., Ciccioli, P., Zona, D., Loreto, F., Janssens, I. A., and Ceulemans, R.: Proton Transfer Reaction Time-of-Flight Mass Spectrometric (PTR-TOF-MS) determination of volatile organic compounds (VOCs) emitted from a biomass fire developed under stable nocturnal conditions, *Atmospheric Environment*, 97, 54-67, <https://doi.org/10.1016/j.atmosenv.2014.08.007>, 2014.

Liu, X., Huey, G. L., Yokelson, R. J., Selimovic, V., Simpson, I. J., Müller, M., Jimenez, J. L., Campuzano-Jost, P., Beyersdorf, A. J., Blake, D. R., Butterfield, Z., Choi, Y., Crouse, J. D., Day, D. A., Diskin, G. S., Dubey, M. K., Fortner, E., Hanisco, T. F., Hu, W., King, L. E., Kleinman, L., Meinardi, S., Mikoviny, T., Onasch, T. B., Palm, B. B., Peischl, J., Pollack, I. B., Ryerson, T. B., Sachse, G. W., Sedlacek, A. J., Shilling, J. E., Springston, S., St. Clair, J. M., Tanner, D. J., Peng, A. P., Wennberg, P. O., Wisthaler, A., and Wolfe, G. M.: Airborne measurements of western U.S wildfire emissions: Comparison with prescribed burning and air quality implications, *J. Geophys. Res. Atmos.*, 122, 6108-6129, doi:10.1002/2016JD026315, 2017.

Koss, A. R., Sekimoto, K., Gilman, J. B., Selimovic, V., Coggon, M. M., Zarzana, K. J., Yuan, B., Lerner, B. M., Brown, S. S., Jimenez, J. L., Krechmer, J., Roberts, J. M., Warneke, C., Yokelson, R. J., and de Gouw, J.: Non-methane organic gas emissions

C7

from biomass burning: identification, quantification, and emission factors from PTR-ToF during the FIREX 2016 laboratory experiment, *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2017-924>, in review, 2017.

Knighton, W. B., Fortner, E. C., Midey, A. J., Viggiano, A. A., Herndon, S. C., Wood, E. C., and Kolb, C. E.: HCN detection with a proton transfer mass reaction spectrometer, *International Journal of Mass Spectrometry*, 283, 112-121, <https://doi.org/10.1016/j.ijms.2009.02.013>, 2009. Selimovic, V., Yokelson, R. J., Warneke, C., Roberts, J. M., de Gouw, J., Reardon, J., and Griffith, D. W. T.: Aerosol optical properties and trace gas emissions by PAX and OP-FTIR for laboratory-simulated western US wildfires during FIREX, *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2017-859>, in review, 2017.

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, <https://doi.org/10.5194/acp-11-6787-2011>, 2011.

---

Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2017-883>, 2017.

C8