**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.**

**N. Surawski (Referee)**

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The reviewer thanks 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. In this article, the authors undertake trace gas measurements from nine prescribed fires in South-Eastern Australia (seven in NSW and two in Victoria). In this study, the main focus is on VOC measurements as well as trace gas emissions such as CO2, CO and CH4 that support analysis behind the measurements (i.e. they enable MCE to be calculated, for example). The authors use a combination of open-path FTIR, SIFT-MS and White Cell spectroscopy as tools to quantify trace gas species. Within this field, state-of-the-art (at least from a North American perspective) has been advanced by authors such as R. J. Yokelson et al. and S. K. Akagi et al. which the authors of the current manuscript have cited. The opinion of the reviewer is that the current study presented by the authors is a timely addition to the literature. The authors demonstrate that ecosystem specific EFs should be used for VOC emissions accounting in Australia and also demonstrate that some VOC species differ significantly from those measured in North America. On these grounds I find the current contribution useful, and furthermore recommend publication after minor revisions and attending to some technical issues.

Whilst the reviewer is not an expert in VOC measurement and chemistry, Figure 3 demonstrates some nice results showing excellent agreement between ethene mixing ratios quantified with SIFT-MS and White cell FTIR spectroscopy. This gives the reviewer some confidence that the instrumentation used in this study is quantitatively reliable.

The manuscript is currently in fairly good shape; however, an accepted manuscript would have to attend to a few matters.

Title:

The reviewer has a preference for titles that indicate the outcome. This would

help to promote the findings of this paper and get more people to read it. Something in

the title that indicates the recommendation of ecosystem-specific VOC emissions may

help.

Abstract:

Line 8. "... compare with Australian savanna". This is presumably due to

a paucity of data in Australia. May help to indicate why comparison was done with a

different biome.

Line 9. "... disagree by a factor of two or more". May help to indicate which VOCs differ

by that amount.

Introduction:

Line 15. "... carbon monoxide and aerosol". Probably reads better as ... particulate matter.

Line 19. May help to be careful regarding the comment "... lower due to rapid regrowth". If there was a change in fire regime e.g. fire frequency then the rapid regrowth would not occur. Net C emissions would increase.

Line 15. "... pyro-convective lofting". I believe the authors have missed two papers here. Please consult:

de Laat, A. T. J., D. C. S. Zweers, R. Boers, and O. N. E. Tuinder (2012), A solar escalator: Observational evidence of the self-lifting of smokeand aerosols by absorption of solar radiation in the February 2009 Australian Black Saturday plume, J. Geophys. Res., 117, D04204,doi:10.1029/2011JD017016.

Siddaway, J. M., and S. V. Petelina (2011), Transport and evolution of the 2009 Australian Black Saturday bushïnˇA˛re smoke in the lower stratosphere observed by OSIRIS on Odin, J. Geophys. Res., 116, D06203, doi:10.1029/2010JD015162

Line 23. "... weather conditions that are conducive to pollution build up". What conditions are these - a stable atmosphere? More detail required.

Line 15. Page 3. "... highly cited compilations". This phrase should not appear in a scientific article. It appears a bit like a sales job.

Methods.

Line 30. Presumably bark litter was present too?

Line 32. "... canopy species" then "... overstorey species". Choose one term and stick with it.

Section 2.2. Line 16. "... forest road ": looks like a firebreak to me.

Section 2.3.1. I’m not sure what the phrase "co-adding scans" means?

Section 2.3.2 Line 23. Is the dilution ratio measured or assumed? If measured, how was this done?

Figure 3. Can’t see the vertical errors bars < 10 ppm. Have they been calculated?

Also, how were these uncertainties calculated? This information should go into the Figure caption.

Section 2.4. Line 8. Orthogonal regression. Please check this terminology. Greg Ayers refers to this as restricted major axis regression. It may help to cite this paper too - it’s in Atmospheric Environment from memory.

Page 8. Lines 3-4. RE selection of reference species. Not really sure what the chemical reasoning is for these selections? Is this just a matter of choosing a reference species that correlates with your results, or is there some more fundamental reasoning sitting behind this?

Section 2.5 Page 8. Line 19. molar mass not molecular mass. Page 9. Line 18. "...

uncertainties in quadrature". Are you able to shed more light on what this technique does?

Section 2.6. Line 20. The first part of this sentence mentions MCE then it moves to combustion efficiency. I think it should be the other way round? Define combustion efficiency and then define MCE as an approximation.

Section 3.2. Page 13. Line 6-7. RE uncertainties. It may help to bring this information forward i.e. uncertainties calculated according to Paton-Walsh. The first mention of uncertainties in the methods may be a good locus for this information.

Section 3.3. Line 9. The p-value. Not sure what test was done to obtain this p-value?

Table 3. The table caption is not self-contained for the reader. How are the +/- values calculated? What test was done for the p-values? Putting some of this detail in the Table caption may help.

Section 4.1. Page 17. Lines 17-18. "... not only a product of combustion". Are there any quantitative insights regarding non-combustion emissions?

Section 4.2. Lines 29-30. "... wild or prescribed fires, or between measurement platforms".

Just wondering whether you have a physical explanation for why wild versus prescribed MCEs are similar.

Table 4. Last row. Smoke < 20 min. Not sure what this fire type relates too? Further details may help.

Section 4.3. Line 17. I think you mean Table 5?

Line 23. "... two to ten times more acetonitrile and pyrrole". Just a two-fold suggestion here. What is the role of these compounds in atmospheric chemistry and why, perhaps, you got the differences you did compared to Northern American fires.

Table 5. The last column needs to be tidied up a bit. There are question marks and undefined acronyms. Not sure what MACR and MVK relate to for example. Also, you have the use of MM (molecular mass) and MW (molecular weight) in the manuscript. Stick to one term.

Section 5. Page 23. Line 2. "... impacts plume chemistry". In what ways? Some discussion of these impacts in the discussion may round it out a bit more - at least in terms of impact.

Supplementary Information Supporting Data. These aspects of the submission look satisfactory.

Thanks again to the authors for a timely submission regarding VOC emissions from temperate forest fires. The reviewer wishes the authors good luck with the resubmission of this paper to ACP.

Reviewed by: N. Surawski, Sydney, Australia.

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**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)**

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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 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 temperature forests and to emission factors measured for Australian 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, H3O+ 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 H3O+ 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 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 CO2, 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 CO2 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 OPFTIR.” 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 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 that 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.

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.

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: “CO2, CO, CH4, acetic acid, ammonia, ethene … and “CO2, CO, CH4, 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 (CO2), Carbon monoxide (CO), Methane (CH4), acetic Acid (CH3COOH), ammonia (NH3), etc).

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

Supplemental: No issues on the supplemental

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