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

We would like to thank both reviewers for their helpful review of our manuscript. In attempting to keep the methods section brief, we had omitted important information. We are grateful to the reviewers for pointing this out. In response to their comments, there were many additions to the text, which are shown as answers to specific comments below, and highlighted in the manuscript.

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.

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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.

As the ecosystem-specific emissions are only statistically significant for some of the gases, we feel that changing the title may be misleading and have decided to keep the original title.

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.

We modified the abstract to address your comments and those of the other reviewer:

… We then compare our average emission factors to those measured for temperate forest fires elsewhere (North America) and for fires in another dominant Australian ecosystem (savanna) and find significant differences in both cases. Indeed, we find that although the emission factors of some species agree within 20%, including those of hydrogen cyanide, ethene, methanol, formaldehyde and 1,3-butadiene; others, such as acetic acid, ethanol, monoterpenes, ammonia, acetonitrile and pyrrole, differ by a factor of two or more.

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

The correction was made.

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.

The other reviewer also had misgivings about this paragraph. We removed “rapid” and added a reference.

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

Thank you. We have added the suggested references.

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

We have added more detail in parentheses:
…under weather conditions (low wind speeds, stable atmosphere) that are conducive to pollution build up…

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

We only meant that the emission factors contained in this compilation are widely used (and do not include any results from Australian forest fires). The sentence was rephrased:

Currently, widely used compilations of emission factors …

Methods.
Line 30. Presumably bark litter was present too?

Yes, although it was not a dominant component of the ground litter. We added it to the list:

The ground cover was generally made up of native grasses and a litter of eucalypt leaves, bark and twigs, as well as fallen tree limbs of varying sizes.

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

The two sentences were merged to remove the word “canopy”:

In Victoria, dominant overstorey species were …

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

Both “forest road” and “forest track” have been replaced by “fire trail” in the text, which is the term used on the maps provided by fire personnel.

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

This sentence has been rewritten to clarify the meaning:

A spectrum consisting of 78 scans was acquired for each grab sample.

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

The dilution ratio was not measured, but is estimated from the temperature, pressure and flows of sample and carrier gases.

The flow tube dilution ratio under standard operating conditions is about 1:15.

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.

The vertical error bars are small, hence difficult to see. The revised version has a slightly larger figure, and was plotted without data symbols/dots, which makes the error bars more visible. The error bars on the y-axis are the standard deviation of the mean of the 8 measurements made by the SIFT-MS. On the x-axis, the error bars are the error on the fit reported by MALT. This information has been added to the text in the appropriate sections:

The uncertainty on individual grab sample measurements is the error on the retrieval reported by MALT. (Sect 2.3.1)

The standard deviation of the mean was taken as the uncertainty on the average mole fraction. (Sect. 2.3.2)

and to the caption:

Error bars for the SIFT-MS are the standard deviation of the measurement, for the White cell FTIR they are the error on the retrieval.

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.

Restricted major axis regression (RMA), major axis regression (MA) and orthogonal regression (also known as Deming regression) are all variants of "error-in-variable" regression models – they all minimize the deviations from the line of fit in both the x and y axes. They differ in the assumptions made about the error ratio λ – the ratio of the total error variances of X and Y. RMA assumes $\lambda = s_x/s_y$, MA assumes λ = 1 and orthogonal regression lets you specify the weights ω for each data point individually, with $\lambda = \omega_x/\omega_y$, where $\omega_{xi} = 1/\sigma_{xi}^2$.

In this study, we used orthogonal regression because it let us take into account the uncertainty of individual measurements. This means that the line of best fit has greater dependence on the more precise data points. This is also the type of regression that gave the best results in a recent comparison of several regression techniques for application in atmospheric science (Wu and Yu, 2017).

Wu and Yu (2017) also noted that the effect of which regression method is used on the resulting slope is minimized for data that are highly correlated.

The following has been added to the text:

The regression is also weighted by the uncertainties in both x and y, which, in this case, are the measurement uncertainties as described above, so that the line of best fit has greater dependence on the more precise data points. As noted in a recent evaluation of linear regression techniques (Wu and Yu 2017), the type of linear regression applied has little impact on the resulting slope as long as the correlation coefficient is high. For this reason, we chose pairs of species that were best correlated to derive emission ratios and do not report results when $R^2 < 0.5$, as this should yield the most robust results.

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?

We chose species that correlate well with each other as this should lead to more robust slope values (as explained above); however, strong correlation may also have a physical meaning, indicating that the species are co-emitted. This has been added to the text at the end of Sect 2.4:

Good correlation between VOC species may indicate co-emission.

Section 2.5 Page 8. Line 19. molar mass not molecular mass.

The correction was made.

Page 9. Line 18. "...uncertainties in quadrature". Are you able to shed more light on what this technique does?

This is a standard error propagation technique. Assuming that errors are not correlated, then they can be added in quadrature: $\sigma z^2 = z^2 *[(\sigma_x/x)^2 + \sigma_y/y)^2]$

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.

Both have already been defined in the introduction, in the order suggested by the reviewer. In this section, we are introducing the equations used in the analysis (MCE).

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.

Agreed. We have moved this to the methods:

The uncertainty on individual measurements is the error on the retrieval reported by MALT. For a complete uncertainty budget on the OP-FTIR smoke measurements in smoke, see Appendix B in Paton-Walsh et al. (2014).

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

The p-value is the probability that the slope is in fact zero (null hypothesis). This is one of the standard diagnostics of linear regression. We added the following to the text:

The strength of the relationship is judged from the coefficient of determination (R^2) and the p-value (the probability that there is no correlation between x and y).

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.

The caption now reads:

Summary of regression statistics for the emission factor dependence on modified combustion efficiency (MCE) of carbon-containing species measured by open-path FTIR in temperate forest fires in Australia

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

The sentence was removed from the text in response to comments from the other reviewer.

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.

No, we do not have a physical explanation. A similar MCE indicates that a similar mix of flaming and smouldering combustion was captured. This could be coincidental, or an artefact of the sampling approaches, or could mean that the fires sampled did burn at a similar MCE. There is not enough data to draw definite conclusions. Even if the fires did burn at a similar MCE, this does not guarantee that their emissions would be the same: as the other reviewer pointed out, Liu et al. (2017) saw higher PM emission from wildfires than for prescribed fires burning at the same MCE. The following was added to the MCE discussion in Section 4.2:

The good agreement for MCE between platforms and fire type could be coincidental, or an artefact of the sampling approaches, or may in fact indicate that the prescribed and wild fires sampled burnt at a similar MCE. Liu et al. (2017) report EF for PM that are a factor of two higher for wildfires than for prescribed fires burning at the same MCE but do not observe the same for trace gases such as CH_4.

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

The Akagi compilation only includes studies that sampled smoke that was less than 20 minutes old. However, we agree that this was not helpful, and have replaced this by “Prescribed & wild fires” since these are the types of fires sampled in the studies included in the compilation.

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

Yes, thank you. The correction has been made.

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.

Acetonitrile is somewhat long-lived in the atmosphere (months) and is considered a tracer for transported biomass plumes whereas more reactive nitrogen-containing species such as pyrrole may be tracers for fresher plumes. The observed variability in emission factors would be an important factor when interpreting plume age.

The difference with the North American fires may be due to differences in fuel nitrogen content. Most studies do not report fuel composition (this one included) so it is difficult to draw conclusions. Acacias are nitrogen-fixing and tend to have higher nitrogen content in their leaves than many other trees, which translates to higher N in the leaf litter as well (Snowdon et al., 2005). Acacias were present in the understorey of many of the fires sampled in this study, so this may be a contributing factor.
The following has been added to the discussion:

Nitrogen-containing VOCs make little contribution to the overall reactivity of a smoke plume (Gilman et al., 2015). Acetonitrile has an atmospheric lifetime on the order of months and is a tracer for long-range transport of biomass plumes (Bange and Williams, 2000) whereas more reactive nitrogen containing-species may be tracers for fresh plumes (Gilman et al., 2015, Coggon et al., 2016). Higher emissions may affect estimates of plume age based on these species.
The difference with the North American fires may be due to higher fuel nitrogen content. *Acacia* are nitrogen-fixing species that have high leaf N content (1.50-3.55%) which is partly conserved through leaf fall, leading to higher nitrogen in the leaf litter (Snowdon et al., 2005). Acacia are some of the dominant understorey species in the forests investigated in this study, and their presence may have contributed to the high emissions of nitrogen-containing species; however, without fuel composition measurements, it is impossible to draw definitive conclusions.

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.

We have replaced the abbreviations by the full names of the molecules (MACR = methacrolein, MCK = methyl vinyl ketone). The abbreviations were also added in the text. The question marks represented compounds that were detected but unidentified in the reference. The question marks were removed and the caption modified:

Unidentified species that are likely to contribute to the signal measured by SIFT-MS are listed by their molar mass in the last column.

Also, you have the use of MM (molecular mass) and MW (molecular weight) in the manuscript. Stick to one term.

We have replaced MW by MM in Table 5 so that it is used consistently throughout the manuscript.

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.

The sentence was modified to be more general (instead of focused on monoterpenes):

The initial mixture of trace gases emitted by a fire is one of the factors (along with meteorology and the presence of other sources) that influences plume aging (Akagi et al., 2012, Jaffe and Wigder, 2012) and therefore air quality outcomes downwind of the fires.

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

2017.

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.

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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”

Thank you. I have added this reference to the discussion of MCE measured from different platforms for prescribed and wild fires (Section 4.2).

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.

The sentence has been modified:
The mix of VOCs emitted during biomass burning may be ecosystem-specific, with species such as monoterpenes being distilled from the vegetation as it is heated by the approaching fire …

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

The mechanism of release is not always specified in the studies cited, so we use the general term ‘heated’.

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?

We did not add the reference to Akagi et al., (2011), as referencing is not recommended in the abstract, but we have modified the abstract as per your recommendations and those of the other reviewer:

We then compare our average emission factors to those measured for temperate forest fires elsewhere (North America) and for fires in another dominant Australian ecosystem (savanna) and find significant differences in both cases. Indeed, we find that although the emission factors of some species agree within 20%, including those of hydrogen cyanide, ethene, methanol, formaldehyde and 1,3-butadiene; others, such as acetic acid, ethanol, monoterpenes, ammonia, acetonitrile and pyrrole, differ by a factor of two or more.

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.

Thanks for pointing this out. The temperature and pressure are measured with sensors located near the spectrometer. The following has been added to the text:

Ambient pressure and temperature are monitored at one end of the path, through a barometer (Vaisala PTB110) and a resistance temperature detector (RTD PT100) connected to the computer controlling the spectrometer via an I/O box. The output is logged at the same time resolution as the spectral measurements.

Sect 2.3, P5, “Grab sampling”: How were the glass grab samples filled? Was there a sample line?

No. This has been clarified in the text:

Samples were collected in 600 ml glass flasks, except at the Gulguer Plateau fire, where samples were collected into 1 L Tedlar bags. The glass flasks were pre-evacuated using a turbo-molecular pump (Pfeiffer TCS 010) prior to deployment to the fires, and filled with smoke on site by opening them for a few seconds. **No sample line was affixed to the flasks for sampling; flasks were positioned in the smoke prior to opening them.** The bags were flushed with high purity nitrogen and brought to the Gulguer Plateau fire where they were filled with smoke using a differential pressure system or 'vacuum box' powered by a generator. **As the generator had to be placed away from the fire, a sample line (~5 meters) was attached to the vacuum box**. Filling the bags took a few minutes, and consequently, most samples were collected from large smouldering targets after the fire front had moved through the sampling area.

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?

Yes, they were analyzed using MALT. The sentence was unclear and has been modified:

Mole fractions were retrieved using the Multiple Atmospheric Layer Transmission (MALT) model …

P6, L25: The authors mention mass to charge ratios and calibration factors used to quantify them in the supplemental. According to Table S2, H_3O^+ 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_3O^+ 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.

The OP-FTIR system is fitted with a mercury cadmium telluride (MCT) detector, which does not allow us to measure HCN in the open-path. The OP-FTIR does measure formaldehyde however, and the results from the grab samples (SIFT-MS) are in good agreement (average of 2.3 vs 1.7 g/kg fuel) considering that the instruments sampled different fires.

It was not possible to determine formaldehyde by FTIR in the grab samples directly, since the in situ system is equipped with an indium antimony (InSb) detector which does not cover the appropriate spectral range. In fact, the only species that was measured by all three instruments was ethene.

It is true that both formaldehyde and HCN have proton affinities close to that of water and this can cause issues such as low sensitivity and dependence on water density in PTR measurements. However, these issues are much reduced in SIFT-MS measurements. Španěl et al. (1999) find that the [H3CO+]/[H3O+] ratio does not depend on [H2O]. Similarly, Španěl et al. (2004) find that:

“…the ratio of the count rate of H_2CN^+ to that of H_3O^+ does not change dramatically with the H_2O number density in the carrier gas, [H_2O]. Actually, the change is only 20% within the range of water concentration covered by these measurements (ranging from those typical of laboratory air and exhaled breath samples, i.e. relative humidity range 1–6%).”

Since HCN and formaldehyde have similar m/z (and are therefore likely to be transmitted in a similar way through the instrument), similar proton affinities, similar kinetics and little water dependence when measured by SIFT-MS, it seems reasonable to estimate the sensitivity of HCN from that of formaldehyde.

The following has been added to the supplementary ():

It should be noted that hydrogen cyanide was assigned the same calibration factor as formaldehyde. Both species have a similar m/z (and are therefore likely to be transmitted in a similar way through the instrument), similar proton affinities, similar kinetics and little water dependence when measured by SIFT-MS (Španěl et al., 1999, Španěl et al., 2004). Similarly, pyrrole was assigned the same calibration factor as isoprene.

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.

A single sample is meaningful only if background values are known, which is not the case in our study. Most of the background values were below the limit of detection of the SIFT-MS. Therefore we chose to derive ER using linear regression. This has been clarified in the text:

More generally, we chose to use linear regression to derive ER instead of calculating a value from each measurement (e.g. Burling et al., 2011) because the background mole fractions of many measured species were poorly defined, often being below the detection limit of the SIFT-MS. Deriving emission ratio through regression without first subtracting background values introduces very little error (< 0.1%, Wooster et al., 2011).

We combined data from all fires to get an "ecosystem" ER, that hopefully captures variability due to different fuel types. These "ecosystem" ER agree well with the average ER calculated from the individual fires. We have added this clarification in the text:

Emission ratios were derived from the open-path measurements for each fire separately. The mean ER from all the fires sampled is then our best estimate for the ecosystem.
For the grab samples, emission ratios were derived for individual fires when possible; however, the VOC results from the targeted grab sampling were more highly variable than the open-path measurements in the well-mixed smoke, as is common for this type of sampling (Yokelson et al., 2008, 2013; Burling et al., 2011; Akagi et al., 2013). This resulted in poor correlations ($R^2 < 0.5$) for some species for certain fires. 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. As ER were not successfully derived for each fire for some species, a mean ER was not necessarily the best estimate for the ecosystem. To derive a best estimate for the ecosystem, all valid samples were combined irrespective of which fire they were collected at and a single ER derived through orthogonal regression.

P8, L1-4: This doesn't make sense mathematically. If benzene is not highly correlated to CO or CO_2, 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_2 should have the same overall uncertainty.

This method was not chosen to reduce uncertainties as such. We chose to only use pairs of well correlated trace gases as this reduces the impact of which regression method is used. There are several ways to handle data that has error in both the y and x axes, and although we chose a regression method that gives reliable results, it is noted that more robust slopes are obtained at higher correlation coefficients, i.e. the same slope is obtained whatever the regression method used at very high R^2 values, but differences between methods become more apparent as R^2 decreases (Wu and Yu, 2017).

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.

Although many carbon-containing gases were measured in the grab samples, only CO_2, CO and CH_4 were measured successfully in all samples. So that we can be consistent in the way we calculate EF from the grab samples, we therefore only use these three species in our calculations. It is true that this inflates the EF slightly (a few percent). We have added the following to the text:

For this analysis, emission factors for CO_2, CO and CH_4 were calculated for each individual grab sample using Eq. 4, with C_T calculated as the sum of CO_2, CO and CH_4 only. Although many more carbon-containing species were measured in the grab samples, only CO_2, CO and CH_4 were successfully quantified in every single grab sample. For consistency, they were therefore the only species included in the calculation. Doing so inflates the emission factors by up to a few percent (< 5 %).

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.

We have clarified what analysis was done for each type of measurements in the methods. To derive EF from the grab samples, we used the OP-FTIR CO and CO2 EF from the NSW fires, as mentioned in Sect 2.5:

Similarly, the MCE of a fire sampled by OP-FTIR was determined from the total excess amounts of CO_2 and CO detected by the open-path system (i.e. by summing the excess amounts from each measurement recorded). These MCE values are used to determine whether the emission factors of the species measured by OP-FTIR have a dependence on MCE.

For grab samples, two variants of the analysis were completed. The first one was used to derive emission factors and MCE values to evaluate whether the emission factors of the species measured only in the grab samples have a dependence on MCE.

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.

Agreed. The mean emission ratio in Table 1 includes the Gulguer Plateau fire. This mean value is not significantly different from the ER derived by combining the data from the four other fires.

Similarly, the emission ratio of acetonitrile to CO is markedly lower at Gulguer Plateau than at the other fires. This could be due to the lower nitrogen content of logs compared to foliage and twigs (Susott et al., 1996, Snowdon et al., 2005), resulting in lower emissions of nitrogen-containing species (Coggon et al., 2016). ~~The emission ratio measured for acetonitrile at Gulguer Plateau is excluded from the mean emission ratio listed in Table \ref{table:grab}. Including this emission ratio reduces the mean ER from 0.05 ± 0.01 to 0.04 ± 0.02.~~
The Gulguer Plateau fire is excluded from the emission ratio for acetonitrile derived from combining data from all fires, since including it results in $R^2 < 0.5$. Figure 5 shows the correlations of acetonitrile with CO; the Gulguer Plateau fire is shown in red, the other four fires are shown in black. The emission ratio derived from the black line is not significantly different from the mean ER that includes the Gulguer Plateau data (see Table 1).

As for results with low R^2, see our comments above concerning the robustness of slopes derived from poorly correlated pairs of species.

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.

ER to CO (or CO_2) for all species are listed in Table 5. Table 1 is meant to be a transparent summary of how the grab sample data was processed, and as such we would like to keep Table 1 as it is now. And for reasons stated above, we believe that R^2 is a useful metric, indicating how robust the ER are likely to be.

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

The uncertainties are listed in Table 2. We have clarified the text:

The differences are slight however, and the emission factors from Victoria agree within the uncertainties with those from NSW.

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

The fires measured by OP-FTIR. We have removed "fire-averaged" from the sentence.

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

The p-value is the probability that there is in fact zero no correlation between x and y (null hypothesis). This is one of the standard diagnostics of linear regression. We added the following to the text:

The strength of the relationship is judged from the coefficient of determination (R^2) and the p-value (the probability that there is no correlation between x and y).

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.

We report R^2 exactly for the reasons mentioned by the reviewer – as a means a judging to what extent MCE explains the variability observed in the EF. We have added this to the text:

A poor R^2 indicates that MCE alone cannot explain the variability in EF.

The OP-FTIR results from the Gulguer Plateau fire are included in Figure 6, only the grab sample results from this fire are not shown. For methanol, this is because no value is available (Table 1 shows the average of the 4 other fires, I have added a note to the table). For methane, there is a value, but the average MCE is 0.78 and falls outside the range measured by OP-FTIR. We have clarified the text:

Figure 6 also shows the average results derived for CH_4 and methanol from the grab samples. The grab sampling results from the Gulguer Plateau fire are either not available (methanol) or fall outside the range measured by OP-FTIR (methane) and therefore do not appear in Fig. 6.

and the caption for Figure 6:

The black circles represent average results from grab samples at four fires (The grab sampling results from the Gulguer Plateau fire are either not available (methanol) or fall outside the range measured by OP-FTIR (methane) and therefore do not appear).

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.

No ER could be determined for methanol for the Gulguer fire in the grab samples. This is now indicated by a note in Table 1. The OP-FTIR data from that fire is included in Figure 6 (and the MCE analysis).

Discussion
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.
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.

It does suggest site-to-site variability. This was touched on earlier, in Sect. 3.2: "This indicates a difference in emissions from the different regions sampled that is not explained by the difference in modified combustion efficiency". We have added the following to the discussion:

Considering the variability of relationships to MCE observed even for similar ecosystems, it seems likely that other factors are influencing emissions. Burling et al. (2011) sampled spring fires whereas Akagi et al. (2013) sampled autumn fires so it is possible that some of the variability is due to seasonal differences. In this study, fires were sampled over several years, both in spring (August-

September) and in autumn (April-May). There is no obvious seasonal effect in the data, however there seems to be regional effects, especially for formic acid and acetic acid, and these may be due to differences in vegetation.

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.

The sentence was removed.

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.

Low for a very large wildfire. The sentence was removed.

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.

A value of ~0.92 was estimated and added to Table 4.

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.

The following sentence has been added:

They found good agreement for methanol and formaldehyde, and evidence for depletion of ammonia and ethene and formation of formic acid in aged smoke.

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

True. However, the vegetation that burned on Robbins Island was similar in structure to the understorey that burnt in the prescribed fires we sampled. It is also the only other study in Australia to have calculated emission factors for a large number of species, so the comparison is still useful. This has been clarified in the text:

The plume was advected to the Station from a fire in coastal heath on a nearby island, mostly at night (from 23:00 AEST until 09:00 AEST). The vegetation burnt in the Robbins Island fire is similar to what typically burns in a prescribed fire, so their emission ratios and emission factors for VOCs are listed alongside ours in Table 5.

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

We sampled fires both in spring (Aug-Sep) and autumn (Apr-May), and see no obvious differences in emissions between the seasons. We do not have fuel composition data so it is difficult to draw conclusions. One potential factor is the presence of Acacia species in the understorey, which are nitrogen-fixing:

The difference with the North American fires may be due to higher fuel nitrogen content. *Acacia* are nitrogen-fixing species that have high leaf N content (1.50-3.55%) which is partly conserved through leaf fall, leading to higher nitrogen in the leaf litter (Snowdon et al., 2005). Acacia are some of the dominant understorey species in the forests investigated in this study, and their presence may have contributed to the high emissions of nitrogen-containing species; however, without fuel composition measurements, it is impossible to draw definitive conclusions.

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.

The sentence was modified to be more general (instead of focused on monoterpenes):

The initial mixture of trace gases emitted by a fire is one of the factors (along with meteorology and the presence of other sources) that influences plume aging (Akagi et al., 2012, Jaffe and Wigder, 2012) and therefore air quality outcomes downwind of the fires.

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.

The other reviewer also had misgivings about this paragraph. We removed “rapid” and added a reference.

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.

We removed the sentence from P2.

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.

The abbreviation was added:

New South Wales (NSW) National Parks and Wildlife Service

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).

Done.

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

Yes, thank you. The correction has been made.

Supplemental: No issues on the supplemental

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Emissions of trace gases from Australian temperate forest fires: emission factors and dependence on modified combustion efficiency

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Abstract. We characterised trace gas emissions from Australian temperate forest fires through a mixture of in situ open-path FTIR measurements spectroscopy and selective ion flow tube mass spectrometry (SIFT-MS) and White cell FTIR spectroscopy of grab samples. We report emission factors for a total of 25 trace gas species measured in smoke from nine prescribed fires. We find significant dependence on modified combustion efficiency (MCE) for some species, although regional differences indicate that the use of MCE as a proxy may be limited. We also find that the fire-integrated MCE values derived from our in situ on-the-ground open-path measurements are not significantly different from those reported for airborne measurements of smoke from fires in the same ecosystem. We then compare our average emission factors to those measured for ~~fires in North American temperate ecosystems~~ temperate forest fires elsewhere (North America) and for fires in ~~Australian savanna and find that, although~~ another dominant Australian ecosystem (savanna) and find significant differences in both cases. Indeed, we find that although the emission factors of some species agree within 20%, ~~others~~ including those of hydrogen cyanide, ethene, methanol, formaldehyde and 1,3-butadiene; others, such as acetic acid, ethanol, monoterpenes, ammonia, acetonitrile and pyrrole, differ by a factor of ~~2~~ two or more. This indicates that the use of ecosystem-specific emission factors is warranted for applications involving emissions from Australian forest fires.

1 Introduction

Biomass burning emits a wide range of trace species, including greenhouse gases, particulate matter and volatile organic compounds (VOCs). Globally, fires are the second largest source of VOCs, with emissions estimated at 400 Tg yr^{-1} on average (Yokelson et al., 2008; Akagi et al., 2011). Fires are also the main driver of inter-annual variability for species such as carbon monoxide and ~~aerosol~~ particulate matter (Edwards et al., 2004, 2006; Voulgarakis et al., 2015).

Australia emits 7-8 % of global annual biomass burning carbon emissions (Ito and Penner, 2004; van der Werf et al., 2010). At a national level, average gross annual emissions of total carbon from fires (127 Tg C yr^{-1}) actually exceed those from burning fossil fuels (95 Tg C yr^{-1}) (Haverd et al., 2013). While net emissions of carbon from fires are lower due to ~~rapid~~

~~regrowth~~ regrowth (Haverd et al., 2013; Landry and Matthews, 2016), volatile organic species emitted by those fires are not subject to uptake by the regenerating vegetation and can therefore be considered net emissions.

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~~ with species such as monoterpenes being distilled from the vegetation ~~in the early stages of the~~ as it is heated by the approaching fire (Ciccioli et al., 2014). ~~Species such as methanol~~Methanol, acetic acid, acetaldehyde, acetone and monoterpenes have all been detected from heated *Eucalyptus* leaves in laboratory experiments, with differences observed between fresh leaves and senescent leaves (Greenberg et al., 2006; Maleknia et al., 2007, 2009; Possell and Bell, 2013). Other factors that impact smoke composition include fuel composition (e.g. nitrogen content, Coggon et al., 2016) and fire behaviour (e.g. Wooster et al., 2011). Changes in fire behaviour can be reflected in the combustion efficiency of the fire, i.e. in the proportion of total carbon that is emitted as CO_2. A useful proxy for combustion efficiency is modified combustion efficiency (MCE), which is defined as the ratio of CO_2 released to the sum of CO and CO_2 (Hao and Ward, 1993; Yokelson et al., 1996). Emission factors of several trace gases have been found to correlate to MCE in a number of ecosystems (e.g. Akagi et al., 2013; Burling et al., 2011; Meyer et al., 2012).

The composition of fresh smoke matters as it affects plume chemistry as the smoke ages, contributing to varying rates of ozone and aerosol formation (Yokelson et al., 2009; Akagi et al., 2012; Alvarado et al., 2015) and elevated ozone and particulates downwind of the fires (Pfister et al., 2008; Yan et al., 2008).

Most of the area burnt in Australia annually is in the semi-arid and tropical savannas in the north of the country (Russell-Smith et al., 2007), but large bushfires also occur regularly in the temperate forests that cover extensive areas of the south-east of Australia (Cai et al., 2009). These fires can be intense enough to create pyro-convective lofting and inject smoke at high altitudes ~~(Fromm et al., 2006; Dirksen et al., 2009; Guan et al., 2010)~~ (Fromm et al., 2006; Dirksen et al., 2009; Guan et al., 2010; Siddaway and P
and are expected to become more frequent under a changing climate (Bradstock et al., 2009; Cai et al., 2009; Keywood et al., 2013; King et al., 2013). There has been growing interest in characterising the composition of smoke from Australian temperate forest fires in recent years, mostly arising from increased awareness of the significant impacts of bushfire smoke on regional air quality (Reisen et al., 2011, 2013; Price et al., 2012; Keywood et al., 2015; Rea et al., 2016) and its associated repercussions on human health (Reisen and Brown, 2006; Johnston et al., 2012, 2014; Reisen et al., 2015; Reid et al., 2016), coincident with a mandate for state agencies to increase prescribed burning in the wake of the catastrophic 2009 forest fires in Victoria (Teague et al., 2010). Prescribed burning is widely used in Australia as a means of reducing bushfire risk (Boer et al., 2009); however, these low to moderate intensity fires often take place close to population centres, under weather conditions (low wind speeds, stable atmosphere) that are conducive to pollution build up, sometimes on a regional scale (e.g., Williamson et al., 2016, Fig. 2), with potential health impacts on nearby population (Haikerwal et al., 2015).

Most of what is known about the VOC emissions from Australian temperate ~~forest~~ fires to date comes from opportunistic measurements of bushfire plumes impacting measurement sites such as the University of Wollongong (Paton-Walsh et al., 2005, 2008; Rea et al., 2016) or the Cape Grim Baseline Air Pollution Station (Lawson et al., 2015) or captured from space using satellite sensors (Young and Paton-Walsh, 2011; Glatthor et al., 2013). Dedicated field and laboratory measurement campaigns have mostly focused on greenhouse gases (Hurst et al., 1996; Volkova et al., 2014; Possell et al., 2015; Surawski et al., 2015)~~and only one study reports emission factors that can be deemed representative of whole fires (Hurst et al., 1996)~~.

Volkova et al. (2014) reported emission factors for carbon dioxide (CO_2~~, CO,~~), carbon monoxide (CO), methane (CH_4~~and~~) and nitrous oxide (N_2O) separately for burning fine fuels and logs from measurements made on the ground at prescribed fires in the State of Victoria. Surawski et al. (2015) measured emissions of CO_2, CO, CH_4 and N_2O from fine *Eucalyptus* litter fuels in a combustion wind tunnel and found that emissions from these fuels vary depending on the mode of fire spread and on the phase of combustion. Possell et al. (2015) reported emission factors for CO_2 and CO for several fuel classes combusted in a mass-loss calorimeter and estimated the total fraction of fuel carbon that would be emitted as CH_4, particulates and non-methane hydrocarbons using a carbon mass balance approach. The only whole fire emission factors available are those from Hurst et al. (1996), who sampled smoke plumes from fires in the greater Sydney region from an aircraft and reported emission factors for CO_2, CO and CH_4.

This paper presents results from a dedicated ground measurement program that sampled smoke at several prescribed fires organised by the New South Wales (NSW) National Parks and Wildlife Service in the greater Sydney area and by the Department of Environment, Land, Water and Planning in the State of Victoria. Measurements made at a subset of these fires were presented in Paton-Walsh et al. (2014) along with a detailed description of the open-path Fourier Transform Infrared system (OP-FTIR) and a discussion of the uncertainties associated with deriving emission factors using this technique. Here, we present emission factors for 15 additional VOC species, measured by selected ion flow tube mass spectrometry (SIFT-MS) from grab samples collected at prescribed fires in NSW, as well as additional OP-FTIR results from fires in the State of Victoria. We then investigate the dependence of the measured emission factors on MCE, using all the data collected to date. We also compare the average MCE values observed in our ground measurements to MCE values reported for measurements from other platforms, including airborne measurements. Finally, we compare our average emission factors to values reported in the literature for other ecosystems. Currently, ~~highly cited~~ widely used compilations of emission factors (e.g., Akagi et al., 2011) do not include any results from Australian forests fires. In fact, the emission factors listed for temperate forests in Akagi et al. (2011) are sourced exclusively from measurements made at North American fires. We compare our results with the emission factors listed in Akagi et al. (2011, Table S4, February 2015 update) for temperate forests and to emission factors measured for Australian savanna fires (Smith et al., 2014) and find significant differences in both cases.

2 Methods

2.1 Prescribed fires

Between 2010 and 2015, we sampled a total of nine prescribed fires in Australian temperate forests. Seven of those fires took place in New South Wales (NSW) in 2010-2013, the other two fires were sampled in the State of Victoria in April 2015. The locations of the fires sampled are indicated on the maps shown in Fig. 1. All fires took place in variants of dry sclerophyll forests, dominated by eucalypt species. Table S1 lists the fires, their location, the dates on which they were sampled, the main

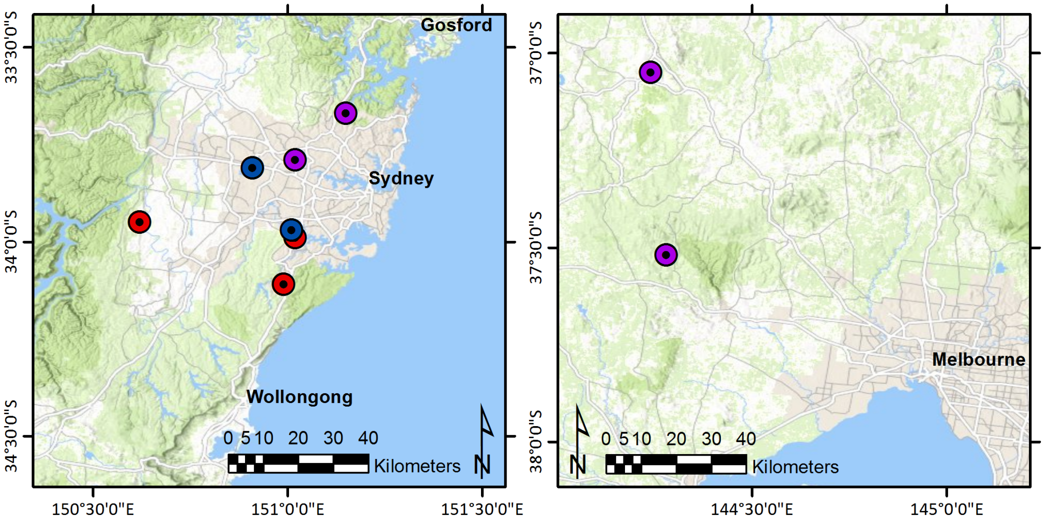

Figure 1. Locations of the nine prescribed fires in Australian temperate forests sampled between 2010 and 2015. The NSW fires are on the left, and the fires in Victoria on the right. The red dots represent fires where both open-path FTIR (OP-FTIR) and grab sampling took place, the blue dots indicate fires where only grab sampling took place, and the purple dots indicate fires where only OP-FTIR sampling took place.

vegetation type, the area burnt, the fuel loading, the time elapsed since the previous fire, the coordinates of the sampling sites and the method(s) of sampling deployed (these methods correspond to the colour coding on the maps in Fig. 1).

In NSW, all fires took place in the Greater Sydney area, as seen in Fig. 1. Dominant overstorey species included eucalypts (including *Eucalyptus*, *Corymbia* and *Angophora* species), with *Melaleuca*, *Acacia* and *Banksia* species in the sub-canopy and the shrubby understorey. The ground cover was generally made up of native grasses and a litter of eucalypt leaves, bark and twigs, as well as fallen tree limbs of varying sizes.

In Victoria, dominant ~~canopy species were mostly eucalypts. Dominant~~ overstorey species were *E. radiata* (Sieb. ex. DC.), *E. obliqua* (L'Hérit.), *E. dives* (Schau.), *E. leucoxylon* (F. Muell.) and *E. macrorhyncha* (F. Muell.). *Acacia* and *Banksia* species dominated the understorey. Ground cover was dominated by tree litter, with gorse (*Ulex europaeus*) and blackberry (*Rubus fruticosus*) recorded in some areas.

2.2 Open-path FTIR system (OP-FTIR)

An open-path FTIR system was deployed at five prescribed fires in NSW and at the two prescribed fires in Victoria, as indicated in the last column of Table S1. The system used in this project is described in detail in Paton-Walsh et al. (2014). Briefly, the spectrometer (Bomem MB-100 Series, 1 cm^{-1} resolution) has a built-in infrared source and is placed 20-50 meters away from a set of retro-reflectors positioned so that smoke from the fire crosses the path in between. The system can run autonomously and records a spectrum consisting of three scans, approximately every twenty seconds. Ambient pressure and temperature are monitored at one end of the path, through a barometer (Vaisala PTB110) and a resistance temperature detector (RTD PT100)

Figure 2. The instrumental set-up for the open-path FTIR measurements of smoke at Greendale on April 13th, 2015 (left) and Castlemaine on April 23rd, 2015 (right).

connected to the computer controlling the spectrometer via an I/O box. The output is logged at the same time resolution as the spectral measurements.

Typically, the system is set up and starts recording before the fire is ignited, and is left to run until mole fractions return to ambient values. As the measurement is integrated over a path of several meters and is continuous over the duration of the fire, the emissions measured using this technique are likely to capture smoke from all stages of the fire, and therefore to be representative of the whole fire. One of the great advantages of OP-FTIR is that there is no sample capture, avoiding losses due to walls or sample lines.

In April 2015, the OP-FTIR was deployed at two prescribed burns in temperate forests in Victoria, several hundred kilometres away from the fires sampled in 2010-2013. The first fire, on April 13th, was near Greendale, Victoria, and the second, on April 23rd, was in Kalimna Park, Castlemaine, Victoria (see Fig. 1 for a map of the locations). At the Greendale fire, the spectrometer was positioned along a ~~forest road~~ fire trail and the retro-reflectors were installed 45 m away within the woodland area to be burned, so that both smoke and flames passed through the line of sight of the instrument. At the Castlemaine fire, both the spectrometer and the retro-reflectors were positioned along a ~~forest track~~ fire trail downwind of the fire, so that smoke would blow through the 50 m measurement path. The instrument set-up at both fires is shown in Fig. 2. The details of the NSW deployments are in Paton-Walsh et al. (2014).

The OP-FTIR spectra collected during the fires were subsequently analysed to derive mole fractions of carbon dioxide (CO_2~~, CO,~~), carbon monoxide (CO), methane (CH_4), acetic acid (CH_3COOH), ammonia (NH_3), ethene (C_2H_4), formaldehyde (H_2CO), ~~ammonia, ethene, formaldehyde,~~ formic acid ~~and methanol~~ (HCOOH) and methanol (CH_3OH) using the Multiple Atmospheric Layer Transmission (MALT) model (Griffith, 1996; Griffith et al., 2012) and the spectral windows described in Paton-Walsh et al. (2014). The uncertainty on individual measurements is the error on the retrieval reported by MALT. For a complete uncertainty budget for the OP-FTIR measurements in smoke, see Appendix B of Paton-Walsh et al. (2014).

2.3 Grab sampling

A total of 67 smoke samples were collected over seven days of sampling at five prescribed fires in NSW. Of those samples, over half were of well mixed, rising smoke. The others were from various targets, including smouldering litter and logs and burning grass and shrubs. The number of samples collected at each fire is indicated in brackets in the last column of Table S1. Samples were collected in 600 ml glass flasks, except at the Gulguer Plateau fire, where samples were collected into 1 L Tedlar bags. The glass flasks were pre-evacuated using a turbo-molecular pump (Pfeiffer TCS 010) prior to deployment to the fires, and filled with smoke on site by opening them for a few seconds. No sample line was affixed to the flasks for sampling; flasks were positioned in the smoke prior to opening them. The bags were flushed with high purity nitrogen and brought to the Gulguer Plateau fire where they were filled with smoke using a differential pressure system or 'vacuum box' powered by a generator. As the generator had to be placed away from the fire, a sample line (∼5 meters) was attached to the vacuum box. Filling the bags took a few minutes, and consequently, most samples were collected from large smouldering targets after the fire front had moved through the sampling area.

All grab samples were brought back to the lab and analysed within 24 hours of collection. A Fourier Transform Infrared (FTIR) spectrometer coupled to a White cell was used to measure carbon dioxide (CO_2~~, CO, ~~), carbon monoxide (CO), methane (CH_4~~, ethane and ethene~~), ethane (C_2H_6) and ethene (C_2H_4). VOC mole fractions were measured using selective ion flow tube mass spectrometry (SIFT-MS).

2.3.1 Fourier Transform Infrared (FTIR) spectrometer coupled to a White cell (White cell FTIR)

Mole fractions of CO_2, CO, CH_4, ~~ethane and ethene~~ C_2H_6 and C_2H_4 in the grab samples of smoke collected at the fires were measured using a Bomem MB-100 Series FTIR spectrometer (1 cm^{-1} resolution). This spectrometer is coupled to a multi-pass optical (White) cell with a path of 22.2 m and is fitted with ~~a InSb~~an indium antimony (InSb) detector cooled with liquid nitrogen.

Part of the sample was transferred to the evacuated White cell and the temperature and pressure inside the cell were logged. Typical temperatures and pressures inside the White cell were 22°C and 220 hPa, respectively. A spectrum consisting of 78 scans was acquired for each grab sample~~by co-adding 78 scans. As for the OP-FTIR spectra, mole~~. Mole fractions were retrieved using the Multiple Atmospheric Layer Transmission (MALT) model (Griffith, 1996; Griffith et al., 2012). The uncertainty on individual grab sample measurements is taken as the error reported by MALT for the retrieval.

2.3.2 Selective Ion Flow Tube Mass Spectrometry (SIFT-MS)

SIFT-MS is a technique for the on-line analysis of gas samples that is akin to the better-known Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) (Blake et al., 2009). Both instruments use chemical ionization to ionize the VOCs present in air and both are equipped with quadrupole mass filters. The main advantage of SIFT-MS is its capability to switch between three reagent ions (H_3O^+, NO^+ and O_2^+) within a single measurement cycle, allowing the detection of species such as acetylene and ethene in addition to the species commonly detected using PTR-MS within the same analysis. It does this by producing all three reagent ions simultaneously in a microwave discharge and then selecting one or the other (switching) using a quadrupole mass filter (the instrument therefore has two quadrupole mass filters). By contrast, PTR-MS is typically equipped with a hollow-cathode discharge that produces a pure stream of a single reagent ion (most commonly H_3O^+) and therefore requires a single quadrupole. Another difference is that PTR-MS uses a drift tube as its reaction chamber (in which ions are carried by an electric field), whereas SIFT-MS is equipped with a flow tube. The specific instrument used in this study (Syft Voice 100) uses a stream of helium and argon to thermalize and carry the ions (Milligan et al., 2007). This means that the instrument dilutes the sample by a factor that is a function of the pressure and temperature inside the flow tube, and of the flows of sample and carrier gases. This makes the instrument less sensitive than PTR-MS (Blake et al., 2009) but ideally suited for the analysis of highly polluted air, such as smoke samples. The flow tube dilution ratio ~~in this study was~~ under standard operating conditions is about 1:15.

The SIFT-MS was operated in multiple ion mode, targeting eighteen VOC species. Table S2 lists the species targeted, the reagent ion used, the mass-to-charge ratios measured and the calibration factors used to quantify them. The list includes aromatic species, nitrogen-containing species, some oxygenated species, some small hydrocarbons and some biogenic species, targeting a breadth of chemical classes. The species targeted were for the most part the most abundant reported at their nominal molecular mass by Yokelson et al. (2013), who deployed extensive instrumentation in a laboratory setting and calculated emission factors for 357 species. A notable exception is the signal at NO^+ 68, which is calibrated using isoprene, but is expected to be dominated by furan in smoke samples. Also, the signal at H_3O^+ 71 is expected to include 2-butenal as well as methacrolein (MACR) and methyl vinyl ketone (MVK). The measurement cycle took approximately 7 seconds to complete and was repeated 8 times on each smoke sample. Mole fractions of VOCs were computed from raw SIFT-MS spectra using the calibration factors listed in Table S2. For each sample, an average mole fraction was calculated for each species by taking the mean over all repeats. The standard deviation of the mean was taken as the uncertainty on the average mole fraction. An average mole fraction was reported for a given species only if its signal-to-noise ratio was greater than three, i.e. if the average signal was at least three times greater than the standard deviation of its mean.

The linearity of the SIFT-MS response was checked by plotting the mole fractions measured for ethene against those measured by White cell FTIR in the same grab samples. Figure 3 shows the good agreement for ethene between the two methods. The plot demonstrates that there was no loss of linearity in the SIFT-MS response even at high mole fractions, which is a result of the sample dilution that occurs within the flow tube of the instrument.

2.4 Determination of emission ratios (ER)

Emission ratios (ER) were derived by plotting VOC mole fractions against those of CO or CO_2 (or another reference VOC species in some cases, see below) and applying an orthogonal regression. Orthogonal regression finds the best line of fit by minimising squared distances between (x, y) points and their projection on the line of best fit. The regression is also weighted by the uncertainties in both x and y, which, in this case, are the measurement uncertainties ~~.~~ described above, so that the line of best fit has greater dependence on the more precise data points. The slope of the line of best fit is the emission ratio. As noted in a recent evaluation of linear regression techniques (Wu and Yu, 2017), the type of linear regression applied has little impact on the resulting slope as long as the correlation coefficient is high. For this reason, we chose pairs of species that

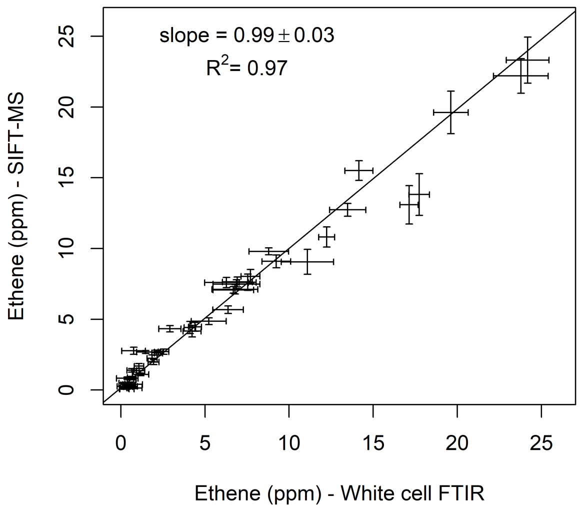

Figure 3. Comparison of ethene mole fractions measured by SIFT-MS with those measured by White cell FTIR in grab samples of smoke collected at Australian temperate forest fires. Error bars for the SIFT-MS are the standard deviation of the measurement, for the White cell FTIR they are the error on the retrieval. The line of best fit was determined using orthogonal regression.

were well correlated to derive emission ratios and do not report results when $R^2 < 0.5$, as this should yield the most robust results. More generally, we chose to use linear regression to derive ER instead of calculating a value from each measurement (e.g. Burling et al., 2011) because the background mole fractions of many measured species were poorly defined, often being below the detection limit of the SIFT-MS. Deriving emission ratio through regression without first subtracting background values introduces very little error (< 0.1%, Wooster et al., 2011).

Emission ratios were derived from the open-path measurements for each fire separately. The mean ER from all the fires sampled is then our best estimate for the ecosystem. For the grab samples, emission ratios were derived for individual fires when possible; however, the VOC results from the targeted grab sampling were more highly variable than the open-path measurements in the well-mixed smoke, as is common for this type of sampling (Yokelson et al., 2008, 2013; Burling et al., 2011; Akagi et al., 2013). This resulted in poor correlations ($R^2 < 0.5$) for some species for certain fires. 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~~As ER were not successfully derived for each fire for some species, a mean ER was not necessarily the best estimate for the ecosystem. To derive a best estimate for the ecosystem, all valid samples were combined irrespective of which fire they were collected at and a single ER derived through orthogonal regression. Certain VOC species measured in the grab samples did not correlate strongly with either CO or CO_2. In those cases, emission ratios were derived using another reference species, e.g. an emission ratio to acetonitrile was derived for pyrrole, and ethene was used as a reference species to derive an emission ratio for benzene, 1,3-butadiene and acetylene. Good correlation between VOC species may indicate co-emission.

2.5 Determination of emission factors (EF) and modified combustion efficiency (MCE)

An emission factor (EF) is defined as the mass of trace gas of interest (X) released per amount of dry biomass burnt and is typically expressed in units of g kg^{-1}:

$$EF_X = 1000 \times \frac{mass_X}{mass_{dryfuelburnt}} \tag{1}$$

This is a very direct method of estimating emissions, but can only be used if all the emissions are captured (so that the total mass of gas X can be measured) and if the mass of biomass burnt in the fire is known (Andreae and Merlet, 2001), which is rarely the case except in laboratory experiments. In the absence of such knowledge, the total mass of biomass burnt can be derived from the total mass of carbon emitted and the fractional carbon content of the biomass burnt (F$_{carbon}$), which is sometimes measured but often estimated:

$$EF_X = F_{carbon} \times 1000 \times \frac{mass_X}{mass_{dryfuelburnt}} \tag{2}$$

In this study, F$_{carbon}$ was assigned a value of 0.5, as in Akagi et al. (2011),Yokelson et al. (2011) and Paton-Walsh et al. (2014). Similarly, the total mass of carbon emitted by a fire is usually not known, and is estimated by measuring the most abundant carbon-containing species emitted by the fire. The emission factor for species X is then:

$$EF_X = F_{carbon} \times 1000 \times \frac{MM_X}{12} \times \frac{C_X}{C_T} \tag{3}$$

where MM$_X$ is the ~~molecular~~ molar mass of the species of interest, 12 is the atomic mass of carbon and $\frac{C_X}{C_T}$ is the number of moles of species X emitted divided by the total number of moles of carbon emitted. In general, only a subset of the smoke from a fire is sampled. If that sample is representative of the whole fire, then the observed ratio of a species to the sum of all other species $\frac{C_X}{C_T}$ should be representative of the entire fire. $\frac{C_X}{C_T}$ can be calculated directly from the excess amounts measured:

$$EF_X = F_{carbon} \times 1000 \times \frac{MM_X}{12} \times \frac{\Delta[X]}{\sum_{y=1}^{n} NC_y \times \Delta[Y]} \tag{4}$$

where $\Delta[X]$ and $\Delta[Y]$ are the total excess mole fraction of the species of interest and of another carbon-containing species, respectively, NC$_y$ is the number of carbon atoms in species Y and the sum is over all carbon-containing species measured in the smoke. Equation 4 can also be written as:

$$EF_X = F_{carbon} \times 1000 \times \frac{MM_X}{12} \times \frac{ER_{X/ref}}{\sum_{y=1}^{n} NC_y \times ER_{Y/ref}} \tag{5}$$

and it follows that the emission factor for a given species of interest can be calculated from the emission ratio of that species to the reference species, and the emission factor of the reference species:

$$EF_X = ER_{X/ref} \times \frac{MM_X}{MM_{ref}} \times EF_{ref} \tag{6}$$

MCE is a proxy for combustion efficiency, which is defined as the proportion of total carbon emitted by a fire released as CO_2. MCE is defined as the excess mole fraction of CO_2 divided by the sum of the excess mole fractions of CO_2 and CO (Hao and Ward, 1993; Yokelson et al., 1996):

$$MCE = \frac{\Delta CO_2}{\Delta CO_2 + \Delta CO} \tag{7}$$

When the fire is dominated by flaming combustion, the modified combustion efficiency is high, meaning that the emissions are dominated by CO_2. The combustion efficiency decreases as smouldering combustion and emissions of CO become more dominant. Flaming combustion is generally associated with MCE values greater than 0.9 and smouldering combustion with values below 0.9 (Yokelson et al., 1996; Bertschi et al., 2003).

There are variants on how to apply the equations above, see Paton-Walsh et al. (2014) for a discussion. In this project, we chose the same approach as in Paton-Walsh et al. (2014) to process the open-path FTIR data and calculated emission factors for CO and CO_2 using Eq. 4 with $\frac{C_X}{C_T}$ calculated using the total excess amounts of each gas detected by summing over the excess amounts from each measurement. The emission factors of other species were calculated using Eq. 6.

~~Emission factors for CO, CO~~Similarly, the MCE of a fire sampled by OP-FTIR was determined from the total excess amounts of CO_2 and CO detected by the open-path system (i.e. by summing the excess amounts from each measurement recorded). These MCE values are used to determine whether the emission factors of the species measured by OP-FTIR have a dependence on MCE.

For grab samples, two variants of the analysis were completed. The first one was used to derive emission factors and MCE values to evaluate whether the emission factors of the species measured only in the grab samples have a dependence on MCE. For this analysis, emission factors for CO_2, CO and CH_4 were calculated for each individual grab sample using Eq. 4, with C_T calculated as the sum of CO_2, CO and CH_4 only. ~~These were~~ Although many more carbon-containing species were measured in the grab samples, only CO_2, CO and CH_4 were successfully quantified in every single grab sample. For consistency, they were therefore the only species included in the calculation. Doing so inflates the emission factors by up to a few percent ($<$ 5%) (Gilman et al., 2015; Yokelson et al., 2013). The emission factors for CO and CO_2 were then used with Eq. 6 and the emission ratios determined for individual fires, to derive emission factors for ~~individual fires. To determine study-average emission factors from the grab sample data~~each fire. MCE was calculated for each sample using Eq. 7 and an average value determined for each fire. These MCE values are indicative of the type of combustion (e.g. flaming vs. smouldering) 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 fire - where grab samples were mostly collected from smouldering logs - was 0.78 ± 0.09, whereas a fire-integrated value of 0.90 was measured by OP-FTIR (Paton-Walsh et al., 2014).

The second variant was used to determine ecosystem-average emission factors for the species measured only in the grab samples. In this case, we used Eq. 6 with the emission ratios derived from combining all data together, and the emission factors for CO and CO_2 derived from the in situ OP-FTIR measurements at the NSW fires. If the emission ratio for a given VOC was derived using another VOC (instead of CO or CO_2), their emission ratio was first converted to an emission ratio to CO or CO_2 using the emission ratio of their reference VOC to CO or CO_2. The uncertainty on the resulting emission ratio to CO (or CO_2) was calculated by adding the uncertainties in quadrature.

2.6 ~~Calculation of modified combustion efficiency (MCE)~~

~~MCE is a proxy for combustion efficiency, which is defined as the proportion of total carbon emitted by a fire released as CO_2. MCE is defined as the excess mole fraction of CO_2 divided by the sum of the excess mole fractions of CO_2 and CO (Hao and Ward, 1993; Yokelson et al., 1996):~~

$$\cancel{MCE = \frac{\Delta CO_2}{\Delta CO_2 + \Delta CO}}$$

~~When the fire is dominated by flaming combustion, the modified combustion efficiency is high, meaning that the emissions are dominated by CO_2. The combustion efficiency decreases as smouldering combustion and emissions of CO become more dominant. Flaming combustion is generally associated with MCE values greater than 0.9 and smouldering combustion with values below 0.9 (Yokelson et al., 1996; Bertschi et al., 2003).~~

~~In this project, the MCE of a fire sampled by OP-FTIR was determined from the total excess amounts of CO_2 and CO detected by the open-path system (i.e. by summing the excess amounts from each measurement recorded). For grab samples, MCE was calculated for each individual sample using Eq. 7. These are indicative of the type of combustion (e.g. flaming vs. smouldering) 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 (Paton-Walsh et al., 2014).~~

3 Results

3.1 Emission ratios and emission factors determined from grab samples collected at prescribed fires in NSW and analysed using SIFT-MS and White-cell FTIR

Emission ratios (ER) were derived for all species measured in the grab samples by White cell FTIR and SIFT-MS as per Sect. 2.4. Emission ratios for individual fires, when available, are listed in Table S3. Table 1 lists the emission ratios derived from combining data from all fires ('all data combined'). When emission ratios for individual fires are available (see Table S3), the mean emission ratio is also included in Table 1. Figure S1 shows the correlation of ethane with CO for each of the five individual fires, and for all fires combined, as an example. Figure 4 shows the "all data combined" correlations for six species (hydrogen cyanide, formaldehyde, acetylene, pyrrole, monoterpenes, and the sum of C_8H_{10} species)~~for which only an 'all data combined' emission ratio could be derived~~.

The emission ratios of some species show important site-to-site variability (see Table S3). For example, the emission ratio of CH_4 to CO measured at Prospect Reservoir is lower than the average (0.06 (0.01), see Table S3). The site at Prospect Reservoir was mostly grassy, and the emission ratio measured there (0.037 ± 0.004) is close to the one measured in tussock- and hummock-grass savanna open woodland fires in northern Australia (0.040 ± 0.007) by Smith et al. (2014).

Similarly, the emission ratio of acetonitrile to CO is markedly lower at Gulguer Plateau than at the other fires. This could be due to the lower nitrogen content of logs compared to foliage and twigs (Susott et al., 1996; Snowdon et al., 2005), resulting in lower emissions of nitrogen-containing species (Coggon et al., 2016). ~~The emission ratio measured for acetonitrile at Gulguer Plateau is excluded from the mean emission ratio listed in Table 1. Including this emission ratio reduces the mean ER from 0.05 ± 0.01 to 0.04 ± 0.02. The Gulguer fire is also~~ The Gulguer Plateau fire samples are excluded from the emission ratio for acetonitrile derived from combining data from all fires, since including ~~it~~ them results in $R^2 < 0.5$. Figure 5 shows the correlations of acetonitrile with CO; the Gulguer Plateau fire is shown in red, the other four fires are shown in black. The emission ratio derived from the black line is not significantly different from the mean ER that includes the Gulguer Plateau data (see Table 1). Pyrrole showed the same behaviour against CO as acetonitrile. Its emission ratio was therefore derived to acetonitrile instead of CO.

Despite this site-to-site variability in the emission ratio of certain species, the mean emission ratio is usually the same, within the uncertainties, as the value derived from combining samples from all fires. This indicates that the 'all data combined' emission ratios listed in Table~~1 should be similarly~~ 1 are representative of the ecosystem sampled - a useful result since this is the only ER available for some species. Whole-fire emission factors were then calculated using the 'all data combined' emission ratios listed in Table 1 and the average fire-integrated emission factors for CO and CO_2 measured by OP-FTIR at the NSW fires by Paton-Walsh et al. (2014) and reproduced in the last column of Table 2. The resulting ~~whole-fire~~ ecosystem-average emission factors for all VOC species are listed in Table 5.

3.2 Open-path FTIR results from prescribed fires in temperate forests in Victoria

All trace gases measured by OP-FTIR at the prescribed fires in Victoria exhibited strong correlations with either CO or CO_2. Correlations between the measured species at the Castlemaine fire are shown in Figure S2 as an example. The calculated emission ratios and emission factors are listed in Table 2. ~~Uncertainties were calculated as per Appendix B of Paton-Walsh et al. (2014)~~ ~~.~~

There is little variability seen between the two fires sampled in Victoria. The emission ratios measured at the two fires are comparable, and the emission factors agree within their uncertainties. The emission ratios measured in Victoria are within the range of values measured at the NSW fires for all species except formic acid and acetic acid (Table 2). The average observed MCE of 0.92 at the Victorian fires is higher than that reported by Paton-Walsh et al. (2014) for the NSW fires (average 0.90, range: 0.88-0.91). The emission factors listed in Table 2 generally reflect this difference, with species typically associated with smouldering combustion having slightly lower emission factors at the Victorian fires. The differences are slight however,

Table 1. Summary of emission ratios (ER) determined for species measured by SIFT-MS and White cell FTIR in grab samples collected at the NSW fires. Mean ER is the average ER measured at individual fires. The "all data combined" ER was derived ~~using a linear~~ through orthogonal regression on all available samples irrespective of which fire they were collected at.

Species	Reference species	Mean ER (std. dev.)	ER (all data combined)	# of samples	R^2
White cell FTIR					
CO	CO_2	0.19 (0.15)	0.17 ± 0.06	67	0.47
CH_4	CO	0.06 (0.01)	0.059 ± 0.003	67	0.89
Ethane	CO	0.004 (0.001)	0.0038 ± 0.0003	67	0.87
Ethene	CO_2		0.0017 ± 0.0002	58	0.71
SIFT-MS					
Ethene	CO_2		0.0018 ± 0.0002	54	0.77
Acetaldehyde	CO	0.009 (0.002)	0.007 ± 0.001	50	0.75
Acetone	CO	0.005 (0.002)	0.0034 ± 0.0005	47	0.74
Acetonitrile ~~[a]~~	CO	~~0.0039 (0.0008~~0.004 (0.001)	0.0038 ± 0.0005[a]	42	0.91
Acetylene	Ethene		0.21 ± 0.04	29	0.59
Benzene	Ethene	0.08 (0.01)	0.078 ± 0.006	43	0.84
Butadiene	Ethene	0.042 (0.006)	0.042 ± 0.002	38	0.95
Butanone	CO		0.00082 ± 0.00007	45	0.69
Ethanol[b]	CO		0.00021 ± 0.00005	7	0.97
Formaldehyde	Hydrogen cyanide		2.9 ± 0.3	50	0.65
Furan + isoprene	CO	0.0018 (0.0006)	0.0019 ± 0.0003	37	0.87
Hydrogen cyanide	CO		0.0063 ± 0.0007	50	0.46
sum of MACR, MVK and 2-butenal	CO		0.0035 ± 0.0009	44	0.73
Methanol	CO	0.025 (0.006)[c]	0.022 ± 0.002	54	0.72
Monoterpenes	Methanol		0.042 ± 0.006	33	0.86
Pyrrole	Acetonitrile		0.15 ± 0.07	25	0.78
Toluene	CO	0.0006 (0.0002)	0.0006 ± 0.0001	40	0.75
sum of C_8H_{10} species	Toluene		0.42 ± 0.04	36	0.75

[a] this ER excludes samples from the Gulguer Plateau fire - see text and Figure 5 for detail

[b] value reported is for the Alfords Point fire

[c] this mean value was derived from four fires only as no ER could be determined for methanol for the Gulguer Plateau fire

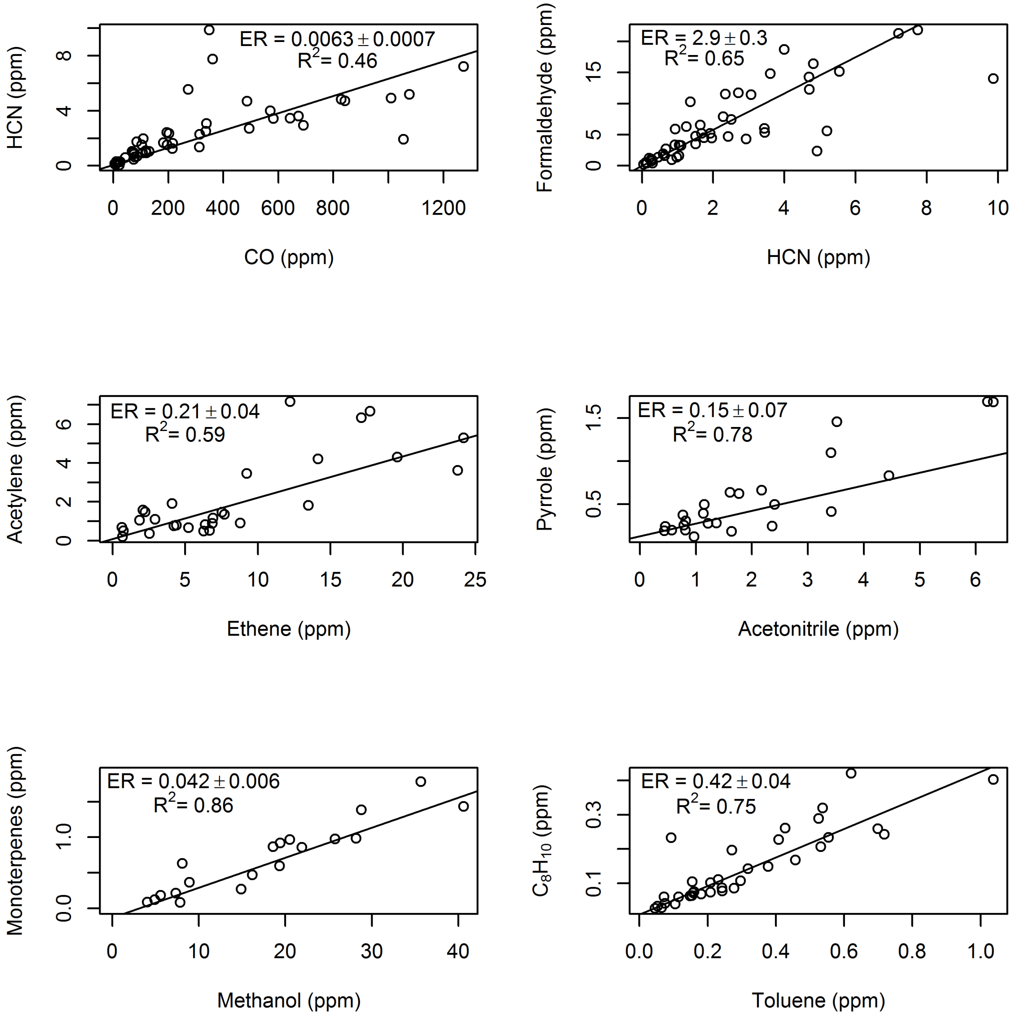

Figure 4. Examples of ~~correlations for species for which only a single~~ ’all data combined’ ~~emission ratio (ER) could be derived~~ correlations from the grab sample measurements. Top left is hydrogen cyanide (HCN) to CO, top right is formaldehyde to HCN, middle left is acetylene to ethene, middle right is pyrrole to acetonitrile, bottom left is monoterpenes to methanol and bottom right is the sum of C_8H_{10} species to toluene.

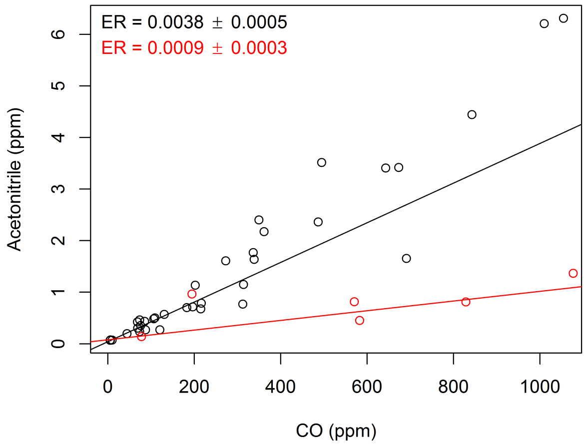

Figure 5. Emission ratio (ER) for acetonitrile to CO for the Gulguer Plateau fire grab samples (in red) and for the other four fires (in black).

and the emission factors ~~measured at the fires in Victoria generally~~ from Victoria agree within the ~~stated~~ uncertainties with those ~~reported for the NSWfires~~from NSW. One major exception is acetic acid. Its emission ratio at the fires in Victoria was double that seen at the NSW fires, and this is reflected in the emission factors. This indicates a difference in emissions from the different regions sampled that is not explained by the difference in modified combustion efficiency. The dependence of emission factors derived from the OP-FTIR measurements on MCE is explored more fully in the next section.

3.3 Dependence of emission factors of trace gases from Australian temperate forest fires on modified combustion efficiency (MCE)

The MCE dependence of the emissions of carbon-containing species from all fires sampled using OP-FTIR as part of this ground-based study is explored in this section. The emission factors calculated for each fire sampled by OP-FTIR are plotted as a function of ~~fire-averaged~~ MCE in Fig. 6. The regression statistics are listed in Table 3. As the range of observed MCE is relatively narrow, the relationship is well represented using a linear regression. For larger MCE ranges, an exponential fit may be more appropriate (e.g. Meyer et al. (2012) suggest an exponential fit for CH_4).

The magnitude of the slope and the intercept listed in Table 3 reflects the magnitude of the emission factor for that species. The strength of the relationship is judged from the coefficient of determination (R^2) and the p-value ~~.~~ (the probability that there is no correlation between x and y). A poor R^2 indicates that MCE alone cannot explain the variability in EF.

For some species, there is no significant relationship with MCE when including data from all seven fires. This is the case for formic acid and acetic acid, for which significantly different emission ratios were measured at the fires in Victoria. Similarly,

Table 2. Summary of open-path FTIR measurements at prescribed fires in temperate forest in the State of Victoria and comparison with similar results obtained at prescribed fires in New South Wales. Values in parentheses are standard deviations of the mean.

		Castlemaine			Greendale			NSW fires[a]	
Species	Reference species	ER	R^2	EF	ER	R^2	EF	ER	EF
CO_2				1650 ± 170			1670 ± 170		1620 (160)
CO				101 ± 16			84 ± 13		118 (19)
CH_4	CO	0.0571 ± 0.0006	0.97	3.3 ± 0.2	0.0633 ± 0.0005	0.99	3.1 ± 0.2	0.05 (0.01)	3.6 (1.1)
Ammonia	CO	0.0276 ± 0.0003	0.98	1.7 ± 0.2	0.0291 ± 0.0004	0.95	1.5 ± 0.2	0.021 (0.008)	1.6 (0.6)
Ethene	CO_2	0.00118 ± 0.00001	0.97	1.2 ± 0.3	0.00105 ± 0.00002	0.91	1.1 ± 0.2	0 .0012 (0.0003)	1.3 (0.3)
Formaldehyde	CO_2	0.00133 ± 0.00002	0.94	1.5 ± 0.3	0.00113 ± 0.00003	0.82	1.3 ± 0.2	0.0016 (0.0004)	1.7 (0.4)
Methanol	CO	0.0144 ± 0.0002	0.96	1.7 ±0.3	0.0154 ± 0.0006	0.95	1.5 ±0.4	0.017 (0.006)	2.4 (1.2)
Formic acid	CO	0.00321 ± 0.00005	0.94	0.5 ± 0.2	0.00414 ± 0.00007	0.93	0.6 ± 0.1	0.0021 (0.0007)	0.4 (0.2)
Acetic acid	CO	0.0303 ± 0.0003	0.98	6.5 ± 1.2	0.0331 ± 0.0005	0.95	6.0 ± 0.9	0.015 (0.003)	3.8 (1.3)

[a] Paton-Walsh et al. (2014)

Table 3. Summary of regression statistics for the emission factor dependence on modified combustion efficiency (MCE) of carbon-containing species measured by open-path FTIR in temperate forest fires in Australia

Species	Data used in regression calculation	Slope	Intercept	R^2	p value
CH_4	NSW and VIC fires	-65 ± 20	62 ± 17	0.61	0.02
Ethene	NSW and VIC fires	-13 ± 4	13 ± 3	0.75	0.007
Formadehyde	NSW and VIC fires	-21 ± 10	21 ± 9	0.79	0.005
Methanol	NSW and VIC fires	-64 ± 16	60 ± 14	0.79	0.005
Formic acid	NSW fires only	-12 ± 6	11 ± 5	0.74	0.04
Acetic acid	NSW fires only	-86 ± 5	81 ± 4	0.98	0.004
sum of furan and isoprene	Grab samples	-9 ± 5	9 ± 4	0.95	0.005
sum of acetone and propanal	Grab samples	-5 ± 2	6 ± 1	0.94	0.009

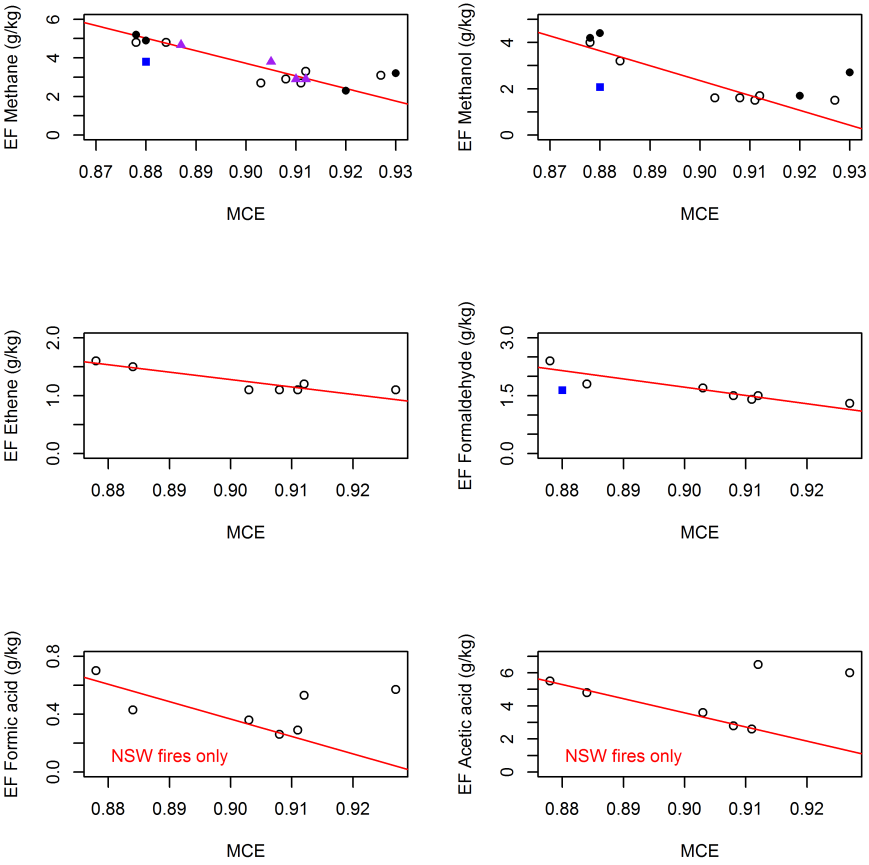

Figure 6. Dependence of emission factors on MCE. Open circles represent the seven fires sampled using OP-FTIR with the line of best fit shown in red. For formic acid and acetic acid, this regression line was derived using the measurements from the NSW fires only. The black circles represent average results from grab samples at four fires (The grab sampling results from the Gulguer Plateau fire ~~falls~~ are either not available (methanol) or fall outside the range ~~of MCE values~~ measured by OP-FTIR (methane) and ~~is~~ therefore do not ~~shown~~appear). ~~Purple~~ The purple triangles represent the methane results from the airborne measurements of Hurst et al. (1996) and the blue squares represent the emission factors measured for methane, methanol, and formaldehyde by Lawson et al. (2015) in a transported plume impacting the Cape Grim Baseline Air Pollution Station in Tasmania.

the emission factor for CH_4 has a stronger relationship with MCE when considering only the NSW fires. This indicates that combustion efficiency is not the only factor that controls differences in emissions for these species.

~~The~~ For comparison purposes, the emission factors measured by Hurst et al. (1996) for CH_4 and Lawson et al. (2015) for CH_4, methanol and formaldehyde are also ~~included~~ plotted in Fig. 6~~for comparison~~. Figure 6 also ~~includes~~ shows the average results derived ~~from the grab samples for both~~ for CH_4 and methanol ~~for each fire except the~~ from the grab samples. The grab sampling results from the Gulguer Plateau fire ~~. The reasonable agreement with the~~ are either not available (methanol) or fall outside the range measured by OP-FTIR ~~measurements seen~~ (methane) and therefore do not appear in Fig. 6~~means that it may be possible to estimate the~~ . The MCE-dependence of the species that were only measured in the grab samples (by SIFT-MS or White-cell FTIR) was also tested. For this analysis, average values from the five fires were used, spanning a range of average MCE of 0.78 to 0.93. No statistically significant trend was found for acetaldehyde, acetonitrile, benzene, butadiene, ethane and toluene, but there were significant trends for the sum of furan and isoprene and for the sum of acetone and propanal. The statistics for these trends are listed in Table 3. The MCE dependence of the other measured species could not be determined because fire-specific emission ratios were not available.

4 Discussion

4.1 Comparison with MCE-dependent emission factors from North American temperate forests

The MCE dependence of emission factors listed in Table 3 were compared to those reported by Akagi et al. (2013) for fires in conifer forests in South Carolina, and by Burling et al. (2011) for fires in conifer forests in North Carolina and for chaparral fires in California. There is considerable variability between the two North American studies, even for the similar conifer ecosystems sampled. Both studies found negative relationships to MCE for CH_4 (with slopes ranging from -65 ± 13 to -96 ± 10), methanol (with slopes ranging from -21 ± 6 to -39 ± 2) and furan (-6 ± 3 to -8 ± 1). These results are consistent with the ones listed in Table 3 for these species, although the slope measured in Australian temperate forests for methanol is larger (-64 ± 16).

For other species, the results are mixed, with Akagi et al. (2013) finding no relationship to MCE for acetic acid but Burling et al. (2011) finding a strong one (with a slope of -45 ± 3 and $R^2 = 0.98$) in a similar conifer ecosystem. This is analogous to the results presented here, where a strong relationship to MCE is found for a subset of the data (NSW fires only, slope = -86 ± 5, $R^2 = 0.98$) but no relationship is found when all the fires are considered. For formic acid, both North American studies find a relationship for conifer forest fires (with slopes of -1.8 ± 0.6 and -3.1 ± 0.2), but Burling et al. (2011) found no relationship for chaparral fires. In this study, we find a relationship for the NSW fires, but no relationship when including all fires.

For formaldehyde and ethene, Akagi et al. (2013) reports a weak or insignificant relationship to MCE whereas Burling et al. (2011) reports strong relationships to MCE for both species for fires in a similar conifer ecosystem (with slopes of -21 ± 2 for formaldehyde and -11 ± 2 for ethene) and a weak or insignificant relationship to MCE for fires in chaparral. For fires in Australian temperate forests, we observed similar slopes of -21 ± 10 for formaldehyde and -13 ± 4 for ethene.

Akagi et al. (2013) report a slope of -16 ± 4 for acetone, which is larger than the one observed for the sum of acetone and propanal in this study (-5 ± 2). Akagi et al. (2013) also report significant relationships to MCE for ethane, benzene, toluene, xylenes, acetonitrile and acetaldehyde whereas no relationship was observed for these species in our study.

Considering the variability of relationships to MCE observed even for similar ecosystems, it seems likely that other factors are influencing emissions~~, especially of those species that are biogenically produced by vegetation and are not only a product of combustion. This~~. Burling et al. (2011) sampled spring fires whereas Akagi et al. (2013) sampled autumn fires so it is possible that some of the variability is due to seasonal differences. In this study, fires were sampled over several years, both in spring (August-September) and in autumn (April-May). There is no obvious seasonal effect in the data, however there seems to be regional effects, especially for formic acid and acetic acid, and these may be due to differences in vegetation. This variability limits the usefulness of MCE as a means of extrapolating emission factors for these species. Nevertheless, the MCE measured at a fire can be a good indication of whether a representative sample has been captured. This is explored in the next section by comparing MCE values observed from different measurement platforms for Australian temperate forest fires.

4.2 Comparison of MCE, CO_2, CO and CH_4 emission factors measured for Australian temperate ecosystems from various platforms

MCE and emission factors for CO_2, CO and CH_4 for Australian temperate ecosystems have been measured from a variety of platforms, including airborne measurements (Hurst et al., 1996) and measurements of plumes transported short distances to fixed monitoring stations (Lawson et al., 2015; Rea et al., 2016). Comparing these results to our ground-based measurements (see Table 4) reveals that there is a relatively small spread of MCE values measured for fires in Australian temperate ecosystems. ~~Even airborne measurements over the very large Sydney wildfires of January 1994 have a relatively low average MCE of 0.91 (Hurst et al., 1996). Furthermore, there~~ There is no significant difference in the MCE observed for wild or prescribed fires, or between measurement platforms (Kruskal-Wallis rank sum test, $p > 0.7$). This is in contrast with measurements conducted at prescribed fires in North America, where higher average MCE values were observed for airborne measurements than for open-path measurements on the ground (0.93 vs. 0.91 on average for the same fires in Akagi et al. (2014), for example). MCE values of 0.93 or greater for airborne measurements have also been reported by other US studies (Burling et al., 2011; Akagi et al., 2013). The top left panel of Fig. 6 shows the CH_4 emission factors reported by Hurst et al. (1996) plotted alongside the OP-FTIR measurements conducted as part of this study and as part of Paton-Walsh et al. (2014). The agreement between the two platforms is excellent.

~~The~~ The good agreement for MCE between platforms and fire type could be coincidental, or an artefact of the sampling approaches, or may in fact indicate that the prescribed and wild fires sampled burnt at a similar MCE. Liu et al. (2017), studying wildfires in the western US, report EF for PM that are a factor of two higher for wildfires than for prescribed fires burning at the same MCE, but do not observe the same for trace gases such as CH_4. No PM data are available from the studies listed in Table 4, but CH_4 data are. The average emission factor measured for CH_4 in Australian temperate forests is 3.5 (0.8) g kg^{-1} dry fuel burnt (this value excludes the emission factor reported by Rea et al. (2016) as it may have been influenced by other sources). The average for the ground-based OP-FTIR measurements is 3.5 (0.9) g kg^{-1} dry fuel burnt. These are in excellent

Table 4. Comparison of whole-fire modified combustion efficiency (MCE) and whole-fire emission factors for CO_2, CO and CH_4 reported in the literature for fires in Australian temperate forests and temperate forests in North America.

Study	Location	MCE	EF CO_2	EF CO	EF CH_4	Platform	Type of fire
Hurst et al. (1996)[a]	Helensburgh, NSW, Australia	0.91	1577	99	2.9	Airborne	Wildfire
	Worragee, NSW, Australia	0.89	1540	125	4.7	Airborne	Wildfire
	Sydney, NSW, Australia	0.91	1558	104	3.8	Airborne	Wildfire
	Bateman's Bay, NSW, Australia	0.91	1577	97	2.9	Airborne	Prescribed fire
Lawson et al. (2015)	Robbin Island, TAS, Australia	0.88	1621	127	3.8	Transported plume	Wildfire
Paton-Walsh et al. (2014)	Greater Sydney Area, NSW, Australia	0.90 (0.2)	1620 (160)	118 (19)	36 (1.1)	Ground-based OP-FTIR	Prescribed fires
Rea et al. (2016)	Greater Sydney Area, NSW, Australia	0.91	1640	107	7.8[b]	Transported plume	Wildfires
This study	Central Highlands, VIC, Australia	0.92 (0.01)	1660 (170)	93 (15)	3.2 (0.2)	Ground-based OP-FTIR	Prescribed fires
Akagi et al. (2011)[c]	North America	~~–~~ ∼0.92	1647 (37)	88 (19)	3.4 (0.9)	Mixed	~~Smoke~~ Prescribed ~~<20 min~~ & wild fires

[a] Hurst et al. (1996) assume 6 % of carbon is emitted as ash, which explains the lower emission factors reported for CO_2

[b] this value may be influenced by other sources - see Rea et al. (2016)

[c] Table S4, February 2015 update. MCE estimated from reported emission factors for CO_2 and CO.

agreement with the emission factor for CH_4 of 3.4 (0.9) g kg^{-1} dry fuel burnt listed for temperate forests in Akagi et al. (2011, Table S4, February 2015 update).

4.3 Comparison of VOC emission ratios and emission factors measured for temperate ecosystems

Measurements of VOC emission factors have been more limited for Australian temperate forests. Enhancement ratios to CO for methanol, ammonia, formic acid, formaldehyde, acetylene, ethene and ethane were measured in lofted plumes from wildfires by ground-based solar remote sensing Fourier transform spectrometry (Paton-Walsh et al., 2005, 2008) and satellite-based spectroscopic measurements (Young and Paton-Walsh, 2011; Glatthor et al., 2013). These were compared to the emission ratios measured in fresh smoke by OP-FTIR in NSW ~~in Paton-Walsh et al. (2014)and this discussion is not repeated here~~by Paton-Walsh et al. (2014). They found good agreement for methanol and formaldehyde, and evidence for depletion of ammonia and ethene and formation of formic acid in aged smoke.

The only other study to have reported emission factors for a significant number of trace gas species is that of Lawson et al. (2015). They report emission ratios and emission factors for trace gases and aerosol from opportunistic measurement of a biomass burning plume impacting Cape Grim Baseline Air Pollution Station in Tasmania in February 2006. The plume was advected to the Station from a fire in coastal heath on a nearby island, mostly at night (from 23:00 AEST until 09:00 AEST). ~~Their~~ The vegetation burnt in the Robbins Island fire is similar to what typically burns in a prescribed fire, so their emission ratios and emission factors for VOCs are listed alongside ours in Table 5. Emission factors from Akagi et al. (2011, Table S4, February 2015 update) are also included for comparison. For some of the species measured by SIFT-MS in this study and by PTR-MS in Lawson et al. (2015), the reported emission factors are sum measurements of several species, including potential contributions from unidentified compounds. In these cases, the emission factors of all species that could contribute were sourced from Akagi et al. (2011, Table S4, February 2015 update) and listed in the last column of Table 5.

There is considerable variability in the emission factors listed in Table 5, and most species agree within their stated uncertainties. Nevertheless, comparing average values highlights potential differences between emissions from Australian temperate forests and emissions from North American temperate forests. Emission factors for both hydrogen cyanide and ethene are in excellent agreement, and emission factors for methanol, formaldehyde and 1,3-butadiene are within 20% of each other. Emission factors for ethane, acetylene and toluene also agree quite well, being within about 30% of each other. However, Australian forest fires potentially emit 50% more formic acid, twice as much acetic acid and ammonia, less than half as much ethanol and monoterpenes, and two to ten times more acetonitrile and pyrrole than North American fires. ~~Lower emissions of compounds such as monoterpenes would impact downwind plume chemistry as the smoke is photochemically processed (Akagi et al. 2013)~~

Nitrogen-containing VOCs make little contribution to the overall reactivity of a smoke plume (Gilman et al., 2015). Acetonitrile has an atmospheric lifetime on the order of months and is a tracer for long-range transport of biomass plumes (Bange and Williams, 2000), whereas more reactive nitrogen-containing species may be tracers for fresh plumes (Gilman et al., 2015; Coggon et al., 2016). Higher emissions may affect estimates of plume age based on these species. The difference with the North American fires may be due to higher fuel nitrogen content. Acacia are nitrogen-fixing species that have high leaf N content (1.50-3.55%) which is partly conserved through leaf fall, leading to higher nitrogen in the leaf litter (Snowdon et al., 2005). Acacia are some of the dominant understorey species in the forests investigated in this study, and their presence may have contributed to the high emissions of nitrogen-containing species; however, without fuel composition measurements, it is impossible to draw definitive conclusions.

The initial mixture of trace gases emitted by a fire is one of the factors (along with meteorology and the presence of other sources) that influences plume aging (Akagi et al., 2012; Jaffe and Wigder, 2012) and air quality outcomes downwind of the fires. The use of Australian-specific emission factors is therefore recommended in studies looking at the regional impact of fires in Australian temperate forests.

Table 5. Comparison of VOC emission ratios and emission factors reported in the literature for fires in temperate forests in Australia and in North America. Emission ratios (ER) are in mol mol^{-1} and emission factors (EF) are in g kg^{-1} dry fuel burnt. Unidentified species that are likely to contribute to the signal measured by SIFT-MS are listed by their molar mass in the last column.

			This study				References		
			White cell FTIR and SIFT-MS analysis of grab samples - prescribed fires in NSW		Open-path FTIR - average values		Lawson et al. 2015		Akagi et al. 2011
Species	MM	ref.	ER	EF	ER	EF	ER	EF	EF
Ammonia	17	CO			0.023 (0.007)	1.6 (0.6)			0.8 (0.4)
Acetylene	26	CO_2	0.00037 ± 0.00008	0.35 ± 0.09					0.26 (0.04)
Hydrogen cyanide	27	CO	0.0063 ± 0.0007	0.7 ± 0.2			0.0057	0.7	0.7 (0.2)
Ethene	28	CO	0.009 ± 0.001	1.1 ± 0.2	0.011 (0.003)	1.2 (0.2)			1.2 (0.2)
Ethane	30	CO	0.0038 ± 0.0003	0.48 ± 0.09	0.004 (0.001)	0.5 (0.2)	0.0032	0.41	0.6 (0.2)
Formaldehyde	30	CO	0.018 ± 0.003	2.3 ± 0.5		1.7 (0.4)	0.011	1.6	2.1 (0.4)
Methanol	32	CO	0.022 ± 0.002	3.0 ± 0.5	0.016 (0.005)	2 (1)	0.014	2.1	1.7 (0.5)
Acetonitrile	41	CO	0.0038 ± 0.0005	0.7 ± 0.1			0.0013	0.25	0.12 (0.05)
Acetaldehyde	44	CO	0.007 ± 0.001	1.3 ± 0.3			0.0044	0.92	0.8 (0.2)
Ethanol	46	CO	0.00021	0.04 ± 0.01					0.10 (0.05)
Formic acid	46	CO			0.003 (0.001)	0.45 (0.16)			0.29 (0.09)
Butadiene	54	CO_2	0.000074 ± 0.000009	0.23 ± 0.04					0.19 (0.05)
sum of acetone and propanal	58	CO	0.0034 ± 0.0005	0.8 ± 0.2			0.002	0.54	0.54 (0.15) (acetone) 0.11 (0.05) (propanal)
[20mm] Acetic acid	60	CO			0.020 (0.009)	4.5 (1.6)			2.1 (0.7)
~~14mm~~Pyrrole	67	CO	0.0006 ± 0.0003	0.16 ± 0.08					0.012 (0.009) (pyrrole)

			This study				References		
			White cell FTIR and SIFT-MS analysis of grab samples - prescribed fires in NSW		Open-path FTIR - average values		Lawson et al. 2015		Akagi et al. 2011
Species	MM	ref.	ER	EF	ER	EF	ER	EF	EF
sum of furan and isoprene	68	CO	0.0019 ± 0.0003	0.5 ± 0.1			0.0053	1.7	0.047 (0.026) ~~(? MW67~~(MM67) 0.3 (0.1) (furan) 0.10(0.004) (isoprene)
sum of MACR, MVK and 2-butenal	70	CO	0.0035 ± 0.0009	1.0 ± 0.3			0.0012	0.38	0.18 (0.08) ~~(? MW68~~(MM68) 0.05 (0.02) (~~MACR)~~methacrolein)) 0.16 (0.04) (~~MVK~~methyl vinyl ketone) 0.2 (0.1) (2-butenal)
Butanone	72	CO	0.00082 ± 0.00007	0.25 ± 0.05			0.001	0.35	0.3 (0.2) ~~(? MW70~~(MM70) 0.13 (0.04) (butanone)
Benzene	78	CO_2	0.00014 ± 0.00002	0.39 ± 0.07				0.69	0.09 (0.04) ~~(? MW72~~(MM72) 0.3 (0.1)
Toluene	92	CO	0.0006 ± 0.0001	0.23 ± 0.05			0.00069	0.30	0.19 (0.05)
sum of C_8H_{10} species	106	CO	0.00025 ± 0.00005	0.11 ± 0.03			0.00053	0.26	0.17 (0.14) (C_8 aromatics) 0.2 (0.1) (benzaldehyde)
Monoterpenes	136	CO	0.0009 ± 0.0002	0.5 ± 0.1			0.00018	0.11	0.9 (0.3)

4.4 Comparison with emission factors reported for Australian savanna

As mentioned earlier, most of the area burnt in Australia annually is in the semi-arid and tropical savannas in the north of the country. A number of studies have characterised smoke from these fires (Hurst et al., 1994a, b, 1996; Shirai et al., 2003; Paton-Walsh et al., 2010; Meyer et al., 2012; Smith et al., 2014; Desservettaz et al., 2017; Wang et al., 2017a, b). Smith et al. (2014) used an OP-FTIR system to derive emission factors for CO_2, CO, CH_4, ethane, ethene, acetylene, formaldehyde, methanol, formic acid, acetic acid, ammonia and hydrogen cyanide. Comparing our OP-FTIR emission factors for temperate forests listed in Table 5 to those reported in Table 5 of Smith et al. (2014) indicates that both ecosystems have similar emission factors for formaldehyde and hydrogen cyanide (1.7 (0.4) vs. 1.6 (0.4) and 0.7 (0.2) vs 0.5 (0.3) g kg^{-1} dry fuel burnt). Methane, methanol and ammonia show high variability in both ecosystems, and although the emission factors measured for temperate forests fires are higher, the emission factors agree within the uncertainties quoted (3.5 (0.9) vs. 2.2 (1.2), 2 (1) vs. 1.1 (0.8) and 1.6 (0.6) vs. 0.7 (0.4) g kg^{-1} dry fuel burnt for methane, methanol and ammonia, respectively). The comparison also reveals that fires in Australian temperate forests emit up to five times more ethane, three times more acetic acid, formic acid and acetylene, and twice as much ethene than Australian savanna fires on a kg of dry fuel basis. This highlights the need for ecosystem-specific emission factors for Australia, especially when looking at regional impacts of biomass burning events.

5 Summary and Conclusions

In this study, emission factors were derived for a total of 25 trace gas species using a mixture of in situ open-path FTIR and grab sampling at nine prescribed fires in Australian temperate forests. MCE values measured during these ground-based measurements were not significantly different from those reported in the literature from airborne measurements, which contrasts with what has been observed in temperate ecosystems in North America. The emission factors for CH_4, ethene, formaldehyde, methanol, formic acid, acetic acid, the sum of furan and isoprene and the sum of acetone and propanal exhibited significant MCE dependence, although there were regional differences for formic acid, acetic acid and CH_4 that indicate that the use of MCE may be of limited use to extrapolate emission factors. There were also differences between the MCE dependences observed in this study compared to those observed for fires in North American temperate ecosystems.

The average emission factors measured for Australian temperate forest fires were compared to those measured for fires in North American temperate ecosystems. The average emission factors for hydrogen cyanide and ethene were in excellent agreement, and those of methanol, formaldehyde, ethane, toluene and 1,3-butadiene were in good agreement (within 30%). The emission factors measured in this study for other species however, indicate that Australian temperate forests may emit 50% more formic acid, twice as much acetic acid and ammonia, half as much ethanol and monoterpenes, and two to ten times more acetonitrile and pyrrole than North American fires on a per kg of dry fuel burnt basis.

We also find that the emission factors for hydrogen cyanide and formaldehyde for Australian temperate forest fires are in excellent agreement with those measured for Australian savanna fires, but that the forest fires have emission factors that are up to five times higher for ethane, three times higher for acetic acid, formic acid and acetylene, and twice higher for ethene.

These differences would impact plume chemistry and influence air quality outcomes downwind of the fires. We therefore recommend that the emission factors presented here and in other studies such as those of Lawson et al. (2015) and Paton-Walsh et al. (2014) be used in studies of biomass burning that require ecosystem-specific emission factors to represent emissions from Australian forest fires.

Data availability. All the emission ratios and the emission factors measured as part of this study are summarized in .csv files provided as a supplement to the main text.

Author contributions. EAG contributed to field work in NSW, oversaw collection, instrumental analysis and data analysis for the grab samples, contributed to QA/QC of all data and wrote the manuscript. CPW conceived of the project, contributed to field work, oversaw measurements, spectral analysis, data analysis and QA/QC for all open-path FTIR measurements. MJD deployed the open-path system at fires in Victoria and contributed to data analysis. TELS contributed to FTIR spectral analysis and MCE analysis. LV, CJW and CPM coordinated with the Department of Environment, Land, Water and Planning to make attendence at the fires in Victoria possible and contributed details of vegetation at the fires in Victoria. All authors contributed to manuscript editing.

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Emissions of trace gases from Australian temperate forest fires: emission factors and dependence on modified combustion efficiency

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S1 Additional information on prescribed fires

As mentioned in the main text, we attended nine prescribed fires between 2010 and 2015. Seven of these fires were in the greater Sydney area in NSW, and two were in the State of Victoria. Table S1 lists the fires, their location, the dates on which they were sampled, the main vegetation type, the area burnt, the fuel loading, the time elapsed since the previous fire, the coordinates of the sampling sites and the method(s) of sampling deployed. The number of grab samples collected at each fire is indicated in brackets in the last column of Table S1. For the NSW fires, the vegetation type, the area burnt, the fuel load and the time since last fire were sourced from the burn plans provided by the New South Wales National Parks and Wildlife Service. For the fires in Victoria, this information was gathered by the research team.

The emission factors from the open-path FTIR measurements at the Lane Cove, Turramurra, Abaroo Creek, Gulguer Plateau and Alfords Point fires were reported in Paton-Walsh et al. (2014) but are reanalysed here to evaluate their dependence on modified combustion efficiency (MCE).

S2 Details of the SIFT-MS analysis

As described in the main text, the SIFT-MS was operated in multiple ion mode, targeting eighteen VOC species. The list includes aromatic species, nitrogen-containing species, some oxygenated species, some small hydrocarbons and some biogenic species, targeting a breadth of chemical classes. Table S2 lists the species targeted, the reagent ion used, the mass-to-charge ratios measured and the calibration factors used to quantify them. It should be noted that hydrogen cyanide was assigned the same calibration factor as formaldehyde~~and~~. Both species have a similar m/z (and are therefore likely to be transmitted in a similar way through the instrument), similar proton affinities, similar kinetics and little water dependence when measured by SIFT-MS (Španěl et al., 1999, 2004). Similarly, pyrrole was assigned the same calibration factor as isoprene. The instrument response to monoterpenes was determined using α-pinene and eucalyptol (1,8-cineole).

Table S1. Summary of prescribed fires in Australian temperate forest sampled in 2010-2013 and April 2015, including location, date, vegetation type, area burnt, pre-fire fuel loading, time elapsed since the area was last exposed to fire and sampling method(s) deployed. The number of grab samples collected at each fire is indicated in parentheses.

Fire Name	Location	Date(s)	Vegetation	Area (ha)	Fuel load ($t\ ha^{-1}$)	Time since last fire	Lat, Lon of sampling site	Method(s) (# of samples)
Lane Cove	Lane Cove National Park, NSW	31 Aug 2010	Dry sclerophyll open woodland	4.8	18-26	unknown	-33.79, 151.15	OP-FTIR^a
Turramurra	Ku-Ring-Gai Chase National Park, NSW	28 Sep 2010	Dry sclerophyll shrubby forest/heath	148.5	20-25	unknown	-33.67, 151.15	OP-FTIR^a
Abaroo Creek	Heathcote National Park, NSW	11&12 May 2012	Dry sclerophyll shrubby forest/heath	115	12.5	10 years	-34.10, 150.99 -34.13, 150.99	Grab sampling (17) and OP-FTIR^a
Gulguer Plateau	Gulguer Nature Reserve,NSW	16 May 2012	Dry scleropyll forest, grassy understorey	32	8-10	30 years	-33.95, 150.62	Grab sampling (9) and OP-FTIR^a
Alfords Point	Georges River National Park, NSW	23 May 2012	Dry sclerophyll shrubby forest	18	14-18	9 years	-33.99, 151.02	Grab sampling (11) and OP-FTIR^a
Prospect Reservoir	Prospect Nature Reserve, NSW	27 Apr 2013	Open woodland, grassy/shrubby understorey	12.5	10-12	>30 years	-33.81, 150.91	Grab sampling (17)
Yeramba Lagoon	Georges River National Park, NSW	26&27 Aug 2013	Dry sclerophyll shrubby forest	14	18	unknown	-33.97,151.01	Grab sampling (18)
Greendale	King Track, Greendale, VIC	13 Apr 2015	Heathy dry sclerophyll forest	254	17 ± 2	32 years	-37.52,144.28	OP-FTIR
Castlemaine	Kalimna Park, Castlemaine, VIC	23 Apr 2015	Heathy dry sclerophyll forest	22	16 ± 2	>30 years	-37.05, 144.24	OP-FTIR

[a] the emission factors from these OP-FTIR measurements were published in Paton-Walsh et al. (2014). The data are re-analysed to look at the dependence of emission factors on modified combustion efficiency (MCE) (see main text)

Table S2. Summary of SIFT-MS analysis of smoke samples: targeted species, selected masses, dwell time and sensitivity.

Species Targeted	Reagent ion	m/z	Dwell time (ms)	Sensitivity (ncps ppb^{-1})
H_3O^+ and clusters	H_3O^+	19, 37, 55	50	–
NO^+ and clusters	NO^+	30, 48	50	–
O_2^+	O_2^+	32	50	–
Acetaldehyde	H_3O^+	45	100	11.3
Acetone	H_3O^+	59	100	14.1
Acetonitrile	H_3O^+	42, 60	100	18.3
Acetylene	O_2^+	26	100	4.4
Benzene	NO^+	78	100	5.2
1,3-butadiene	NO^+	54	100	7.9
Butanone	NO^+	102	100	11.4
Ethanol	NO^+	45, 63	100	4.8
Ethene	O_2^+	28	100	4.5
Eucalyptol	NO^+	154	100	12
Formaldehyde	H_3O^+	31	100	7.3
Hydrogen cyanide	H_3O^+	28	100	7.3[a]
Isoprene (and furan)	NO^+	68	100	7.9
Methacrolein (and methyl vinyl ketone)	H_3O^+	71	100	11.8
Methanol	H_3O^+	33, 5	100	6.5
Monoterpenes[b]	H_3O^+	81, 137	100	10.4
Pyrrole	H_3O^+	68	100	7.9[c]
Toluene	NO^+	92	100	10.7
Xylenes	NO^+	106	100	12

[a] assigned the same sensitivity as formaldehyde

[b] determined using α-pinene and eucalyptol (1,8-cineole)

[c] assigned the same sensitivity as isoprene

S3 Additional grab sampling results

Emission ratios (ER) were derived for individual fires for all species measured by White cell FTIR and SIFT-MS in the grab samples. For some species at some fires, the correlations were poor ($R^2 < 0.5$) and these were excluded. 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 a specific fire. Emission ratios for individual fires are listed in Table S3.

Figure S1 shows the correlation of ethane with CO for each of the five individual fires, and for all fires combined, as an example.

S4 Additional open-path FTIR results

All trace gases measured by open-path FTIR at the prescribed fires in Victoria exhibited strong correlations with either CO or CO_2. Correlations between the measured species at the Castlemaine fire are shown in Figure S2 as an example.

Table S3. Emission ratios determined at individual fires for species measured by SIFT-MS and White cell FTIR in grab samples of smoke

Species	Ref. species	Abaroo Creek	R^2	Alfords Point	R^2	Gulguer Plateau	R^2	Prospect Reservoir	R^2	Yeramba Lagoon	R^2	Mean (std. dev.)
White cell FTIR												
CO	CO_2	0.15 ± 0.03	0.57	0.08 ± 0.02	0.62	0.44 ± 0.08	0.83	0.08 ± 0.02	0.89	0.18 ± 0.03	0.92	0.19 (0.15)
CH_4	CO	0.067 ± 0.009	0.86	0.065 ± 0.004	0.98	0.060 ± 0.009	0.79	0.037 ± 0.004	0.92	0.07 ± 0.01	0.89	0.06 (0.01)
Ethane	CO	0.0045 ± 0.0007	0.83	0.0045 ± 0.0003	0.96	0.003 ± 0.001	0.76	0.0026 ± 0.0002	0.96	0.0055 ± 0.0006	0.97	0.004 (0.001)
SIFT-MS												
Acetaldehyde	CO	0.006 ± 0.004	0.99	0.0101 ± 0.0007	0.99	0.006 ± 0.002	0.63	0.010 ± 0.002	0.90	0.011 ± 0.005	0.96	0.009 (0.002)
Acetone	CO	0.0034 ± 0.0009	0.85	0.0052 ± 0.0006	0.98	0.003 ± 0.001	0.80	0.0040 ± 0.0009	0.90	0.004 0.003	0.90	0.0039 (0.0008)
Acetonitrile	CO	0.0031 ± 0.0009	0.82	0.0050 ± 0.0005	0.98	0.0009 ± 0.0003	0.83	0.006 ± 0.002	0.94	0.005 ± 0.001	0.98	0.005 (0.001)
Benzene	Ethene	0.09 ± 0.02	0.64	0.068 ± 0.004	0.98	0.10 ± 0.02	0.58	0.088 ± 0.002	0.99	0.07 ± 0.01	0.99	0.08 (0.01)
Butadiene	Ethene	0.048 ± 0.003	0.93	0.047 ± 0.003	0.97	0.037 ± 0.005	0.82	0.04 ± 0.01	0.95	0.045 ± 0.005	0.96	0.042 (0.006)
Ethanol[b]	CO			0.00021 ± 0.00005	0.97							
Furan + isoprene	CO	0.0022 ± 0.0003	0.83	0.0018 ± 0.0002	0.96	0.0023 ± 0.0009	0.75	0.0009 0.0005	0.65	0.0017 ± 0.0002	0.85	0.0018 (0.0006)
Methanol	CO	0.029 ± 0.004	0.88	0.028 ± 0.003	0.95			0.016 ± 0.004	0.52	0.027 ± 0.009	0.66	0.025 (0.006)
Toluene	CO	0.0004 ± 0.0002	0.81	0.00086 ± 0.00003	0.98	0.0004 0.0003	0.63	0.00045 ± 0.00009	0.63	0.0007 ± 0.0004	0.89	0.0006 (0.0002)
mean MCE of samples		0.89 ± 0.05		0.93 ± 0.02		0.78 ± 0.09		0.92 ± 0.03		0.89 ± 0.06		0.88 (0.07)

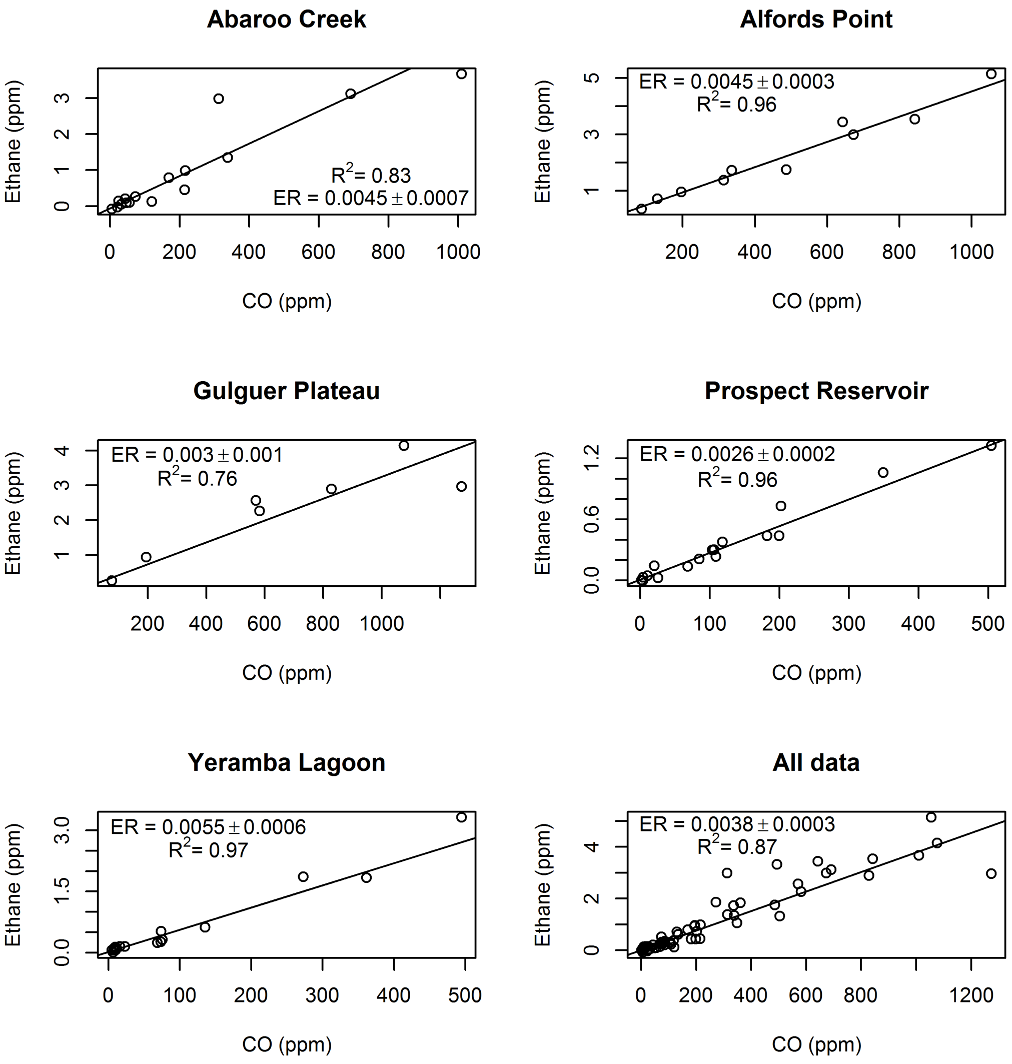

Figure S1. Emission ratio of ethane to CO for each individual fire sampled by grab sampling and for all the fires combined.

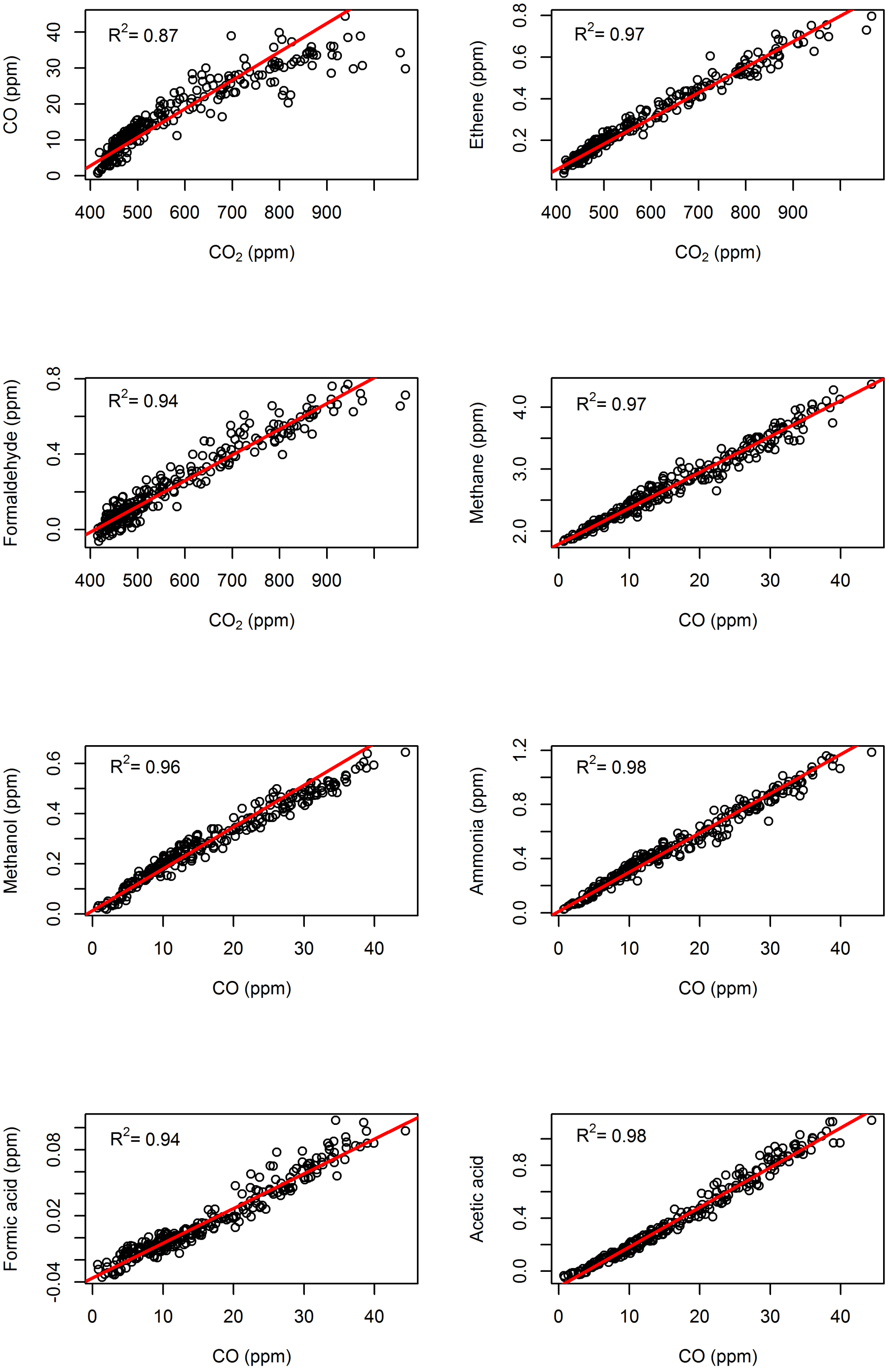

Figure S2. Correlation plots for open-path FTIR measurements at the Castlemaine, VIC fire.

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