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 open-path FTIR measurements and selective ion flow tube mass spectrometry (SIFT-MS) and White cell FTIR analysis 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 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. 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 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 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, with species such as monoterpenes being distilled from the vegetation as it is heated by the approaching fire (Ciccioli et al., 2014). 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; Malekenia 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; Siddaway and Petelina, 2011; de Laat et al., 2012) 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 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).

Volkova et al. (2014) reported emission factors for carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4) 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, 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 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.

5   In Victoria, 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

10   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)

15   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

20   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

25   was positioned along a 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 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).

30   The OP-FTIR spectra collected during the fires were subsequently analysed to derive mole fractions of carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), acetic acid (CH_3COOH), ammonia (NH_3), ethene (C_2H_4), formaldehyde (H_2CO), formic acid (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 ($\sim$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), carbon monoxide (CO), methane (CH_4), 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, 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 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. 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 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 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 (as in, for example, 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. 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:

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

5   where MM_X is the 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:

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

10   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
15 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):

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

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).

25   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. 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. 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 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.

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).

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).

5 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 Gulguer Plateau fire samples are excluded from the emission ratio for acetonitrile derived from combining data from all fires, since including 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.

10 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 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 ecosystem-average emission factors for all VOC species are listed in Table 5.

20 **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.

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, and the emission factors from Victoria agree within the uncertainties with those 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 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, 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.

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 plotted in Fig. 6. 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. 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 $\pm$ 13 to -96 $\pm$ 10), methanol (with slopes ranging from -21 $\pm$ 6 to -39 $\pm$ 2) and furan (-6 $\pm$ 3 to -8 $\pm$ 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 $\pm$ 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 $\pm$ 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 $\pm$ 5, R^2 = 0.98) but no relationship is found when all the fires are considered. For formic acid, both North American studies find

5   a relationship for conifer forest fires (with slopes of -1.8 $\pm$ 0.6 and -3.1 $\pm$ 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 $\pm$ 2 for formaldehyde and -11 $\pm$ 2 for ethene) and a weak or insignificant relationship to MCE for fires in chaparral. For fires in

10   Australian temperate forests, we observed similar slopes of -21 $\pm$ 10 for formaldehyde and -13 $\pm$ 4 for ethene.

Akagi et al. (2013) report a slope of -16 $\pm$ 4 for acetone, which is larger than the one observed for the sum of acetone and propanal in this study (-5 $\pm$ 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

15   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. This variability limits the usefulness of MCE as a means of extrapolating emission factors for these species. Nevertheless, the MCE measured

20   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

25   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. 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,

30   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 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 PM1 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 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 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). 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.

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.

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.

5   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

10   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

15   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.

20   *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

25   of vegetation at the fires in Victoria. All authors contributed to manuscript editing.

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References

Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, Atmospheric Chemistry and Physics, 11, 4039–4072, https://doi.org/10.5194/acp-11-4039-2011, 2011.

5 Akagi, S. K., Craven, J. S., Taylor, J. W., McMeeking, G. R., Yokelson, R. J., Burling, I. R., Urbanski, S. P., Wold, C. E., Seinfeld, J. H., Coe, H., Alvarado, M. J., and Weise, D. R.: Evolution of trace gases and particles emitted by a chaparral fire in California, Atmospheric Chemistry and Physics, 12, 1397–1421, https://doi.org/10.5194/acp-12-1397-2012, 2012.

Akagi, S. K., Yokelson, R. J., Burling, I. R., Meinardi, S., Simpson, I., Blake, D. R., McMeeking, G. R., Sullivan, A., Lee, T., Kreiden-weis, S., Urbanski, S., Reardon, J., Griffith, D. W. T., Johnson, T. J., and Weise, D. R.: Measurements of reactive trace gases and

10 variable O3 formation rates in some South Carolina biomass burning plumes, Atmospheric Chemistry and Physics, 13, 1141–1165, https://doi.org/10.5194/acp-13-1141-2013, 2013.

Akagi, S. K., Burling, I. R., Mendoza, A., Johnson, T. J., Cameron, M., Griffith, D. W. T., Paton-Walsh, C., Weise, D. R., Reardon, J., and Yokelson, R. J.: Field measurements of trace gases emitted by prescribed fires in southeastern US pine forests using an open-path FTIR system, Atmospheric Chemistry and Physics, 14, 199–215, https://doi.org/10.5194/acp-14-199-2014, 2014.

15 Alvarado, M. J., Lonsdale, C. R., Yokelson, R. J., Akagi, S. K., Coe, H., Craven, J. S., Fischer, E. V., McMeeking, G. R., Seinfeld, J. H., Soni, T., Taylor, J. W., Weise, D. R., and Wold, C. E.: Investigating the links between ozone and organic aerosol chemistry in a biomass burning plume from a prescribed fire in California chaparral, Atmos. Chem. Phys., 15, 6667–6688, https://doi.org/10.5194/acp-15-6667-2015, 2015.

Andreae, M. O. and Merlet, P.: Emission of trace gases and aerosols from biomass burning, Global Biogeochemical Cycles, 15, 955–966,

20 https://doi.org/10.1029/2000gb001382, 2001.

Bange, H. and Williams, J.: New Directions: Acetonitrile in atmospheric and biogeochemical cycles, Atmospheric Environment, 34, 4959–4960, https://doi.org/10.1016/S1352-2310(00)00364-2, 2000.

Bertschi, I., Yokelson, R. J., Ward, D. E., Babbitt, R. E., Susott, R. A., Goode, J. G., and Hao, W. M.: Trace gas and particle emissions from fires in large diameter and belowground biomass fuels, Journal of Geophysical Research: Atmospheres, 108, 8472,

25 https://doi.org/10.1029/2002jd002100, 2003.

Blake, R. S., Monks, P. S., and Ellis, A. M.: Proton-Transfer Reaction Mass Spectrometry, Chemical Reviews, 109, 861–896, https://doi.org/10.1021/cr800364q, 2009.

Boer, M. M., Sadler, R. J., Wittkuhn, R. S., McCaw, L., and Grierson, P. F.: Long-term impacts of prescribed burning on regional extent and incidence of wildfires-Evidence from 50 years of active fire management in SW Australian forests, Forest Ecology and Management, 259,

30 132–142, https://doi.org/10.1016/j.foreco.2009.10.005, 2009.

Bradstock, R. A., Cohn, J. S., Gill, A. M., Bedward, M., and Lucas, C.: Prediction of the probability of large fires in the Sydney region of south-eastern Australia using fire weather, International Journal of Wildland Fire, 18, 932–943, https://doi.org/10.1071/WF08133, 2009.

Burling, I. R., Yokelson, R. J., Akagi, S. K., Urbanski, S. P., Wold, C. E., Griffith, D. W. T., Johnson, T. J., Reardon, J., and Weise, D. R.: Airborne and ground-based measurements of the trace gases and particles emitted by prescribed fires in the United States, Atmospheric

35 Chemistry and Physics, 11, 12 197–12 216, https://doi.org/10.5194/acp-11-12197-2011, 2011.

Cai, W., Cowan, T., and Raupach, M.: Positive Indian Ocean Dipole events precondition southeast Australia bushfires, Geophysical Research Letters, 36, L19 710, https://doi.org/10.1029/2009GL039902, 2009.

Ciccioli, P., Centritto, M., and Loreto, F.: Biogenic volatile organic compound emissions from vegetation fires, Plant, Cell & Environment, 37, 1810–1825, https://doi.org/10.1111/pce.12336, 2014.

Coggon, M. M., Veres, P. R., Yuan, B., Koss, A., Warneke, C., Gilman, J. B., Lerner, B. M., Peischl, J., Aikin, K. C., Stockwell, C. E., Hatch, L. E., Ryerson, T. B., Roberts, J. M., Yokelson, R. J., and de Gouw, J. A.: Emissions of nitrogen-containing organic compounds from the burning of herbaceous and arboraceous biomass: Fuel composition dependence and the variability of commonly used nitrile tracers, Geophysical Research Letters, 43, 9903–9912, https://doi.org/10.1002/2016GL070562, 2016.

de Laat, A. T. J., Stein Zweers, D. C., Boers, R., and Tuinder, O. N. E.: A solar escalator: Observational evidence of the self-lifting of smoke and aerosols by absorption of solar radiation in the February 2009 Australian Black Saturday plume, Journal of Geophysical Research: Atmospheres, 117, n/a–n/a, https://doi.org/10.1029/2011JD017016, 2012.

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

Dirksen, R. J., Folkert Boersma, K., de Laat, J., Stammes, P., van der Werf, G. R., Val Martin, M., and Kelder, H. M.: An aerosol boomerang: Rapid around-the-world transport of smoke from the December 2006 Australian forest fires observed from space, Journal of Geophysical Research: Atmospheres, 114, D21 201, https://doi.org/10.1029/2009JD012360, 2009.

Edwards, D. P., Emmons, L. K., Hauglustaine, D. A., Chu, D. A., Gille, J. C., Kaufman, Y. J., Pétron, G., Yurganov, L. N., Giglio, L., Deeter, M. N., Yudin, V., Ziskin, D. C., Warner, J., Lamarque, J. F., Francis, G. L., Ho, S. P., Mao, D., Chen, J., Grechko, E. I., and Drummond, J. R.: Observations of carbon monoxide and aerosols from the Terra satellite: Northern Hemisphere variability, Journal of Geophysical Research: Atmospheres, 109, D24 202, https://doi.org/10.1029/2004JD004727, 2004.

Edwards, D. P., Pétron, G., Novelli, P. C., Emmons, L. K., Gille, J. C., and Drummond, J. R.: Southern Hemisphere carbon monoxide interannual variability observed by Terra/Measurement of Pollution in the Troposphere (MOPITT), Journal of Geophysical Research: Atmospheres, 111, D16 303, https://doi.org/10.1029/2006JD007079, 2006.

Fromm, M., Tupper, A., Rosenfeld, D., Servranckx, R., and McRae, R.: Violent pyro-convective storm devastates Australia's capital and pollutes the stratosphere, Geophysical Research Letters, 33, L05 815, https://doi.org/10.1029/2005GL025161, 2006.

Gilman, J. B., Lerner, B. M., Kuster, W. C., Goldan, P. D., Warneke, C., Veres, P. R., Roberts, J. M., de Gouw, J. A., Burling, I. R., and Yokelson, R. J.: Biomass burning emissions and potential air quality impacts of volatile organic compounds and other trace gases from fuels common in the US, Atmospheric Chemistry and Physics, 15, 13 915–13 938, https://doi.org/10.5194/acp-15-13915-2015, 2015.

Glatthor, N., Höpfner, M., Semeniuk, K., Lupu, A., Palmer, P. I., McConnell, J. C., Kaminski, J. W., von Clarmann, T., Stiller, G. P., Funke, B., Kellmann, S., Linden, A., and Wiegele, A.: The Australian bushfires of February 2009: MIPAS observations and GEM-AQ model results, Atmospheric Chemistry and Physics, 13, 1637–1658, https://doi.org/10.5194/acp-13-1637-2013, 2013.

Greenberg, J. P., Friedli, H., Guenther, A. B., Hanson, D., Harley, P., and Karl, T.: Volatile organic emissions from the distillation and pyrolysis of vegetation, Atmospheric Chemistry and Physics, pp. 81–91, https://doi.org/10.5194/acp-6-81-2006, 2006.

Griffith, D. W. T.: Synthetic Calibration and Quantitative Analysis of Gas-Phase FT-IR Spectra, Applied Spectroscopy, 50, 59–70, 1996.

Griffith, D. W. T., Deutscher, N. M., Caldow, C., Kettlewell, G., Riggenbach, M., and Hammer, S.: A Fourier transform infrared trace gas and isotope analyser for atmospheric applications, Atmospheric Measurement Techniques, 5, 2481–2498, https://doi.org/10.5194/amt-5-2481-2012, 2012.

Guan, H., Esswein, R., Lopez, J., Bergstrom, R., Warnock, A., Follette-Cook, M., Fromm, M., and Iraci, L. T.: A multi-decadal history of biomass burning plume heights identified using aerosol index measurements, Atmos. Chem. Phys., 10, 6461–6469, https://doi.org/10.5194/acp-10-6461-2010, 2010.

Haikerwal, A., Reisen, F., Sim, M. R., Abramson, M. J., Meyer, C. P., Johnston, F. H., and Dennekamp, M.: Impact of smoke from prescribed burning: Is it a public health concern?, Journal of the Air & Waste Management Association, 65, 592–598, https://doi.org/10.1080/10962247.2015.1032445, 2015.

Hao, W. M. and Ward, D. E.: Methane production from global biomass burning, Journal of Geophysical Research: Atmospheres, 98, 20 657–20 661, https://doi.org/10.1029/93jd01908, 1993.

Haverd, V., Raupach, M. R., Briggs, P. R., Canadell, J. G., Davis, S. J., Law, R. M., Meyer, C. P., Peters, G. P., Pickett-Heaps, C., and Sherman, B.: The Australian terrestrial carbon budget, Biogeosciences, 10, 851–869, https://doi.org/10.5194/bg-10-851-2013, 2013.

Hurst, D., Griffith, D. T., Carras, J., Williams, D., and Fraser, P.: Measurements of trace gases emitted by Australian savanna fires during the 1990 dry season, Journal of Atmospheric Chemistry, 18, 33–56, https://doi.org/10.1007/bf00694373, 1994a.

Hurst, D. F., Griffith, D. W. T., and Cook, G. D.: Trace gas emissions from biomass burning in tropical Australian savannas, Journal of Geophysical Research: Atmospheres, 99, 16 441–16 456, https://doi.org/10.1029/94jd00670, 1994b.

Hurst, D. F., Griffith, D. W. T., and Cook, G. D.: Trace-Gas Emissions from Biomass Burning in Australia, in: Biomass Burning and Global Change, edited by Levine, J. S., The MIT Press, London, England, 1996.

Ito, A. and Penner, J. E.: Global estimates of biomass burning emissions based on satellite imagery for the year 2000, Journal of Geophysical Research: Atmospheres, 109, D14S05, https://doi.org/10.1029/2003jd004423, 2004.

Jaffe, D. A. and Wigder, N. L.: Ozone production from wildfires: A critical review, Atmospheric Environment, 51, 1–10, https://doi.org/http://dx.doi.org/10.1016/j.atmosenv.2011.11.063, 2012.

Johnston, F. H., Henderson, S. B., Chen, Y., Randerson, J. T., Marlier, M., DeFries, R. S., Kinney, P., Bowman, D. M., and Brauer, M.: Estimated Global Mortality Attributable to Smoke from Landscape Fires, Environmental Health Perspectives, 120, 695–701, https://doi.org/DOI:10.1289/ehp.1104422, 2012.

Johnston, F. H., Purdie, S., Jalaludin, B., Martin, K. L., Henderson, S. B., and Morgan, G. G.: Air pollution events from forest fires and emergency department attendances in Sydney, Australia 1996-2007: a case-crossover analysis, Environmental Health, 13, 105, https://doi.org/10.1186/1476-069x-13-105, 2014.

Keywood, M., Kanakidou, M., Stohl, A., Dentener, F., Grassi, G., Meyer, C. P., Torseth, K., Edwards, D., Thompson, A. M., Lohmann, U., and Burrows, J.: Fire in the Air-Biomass burning impacts in a changing climate, Critical Reviews in Environmental Science and Technology, 43, 40–83, https://doi.org/10.1080/10643389.2011.604248, 2013.

Keywood, M., Cope, M., Meyer, C. P. M., Iinuma, Y., and Emmerson, K.: When smoke comes to town: The impact of biomass burning smoke on air quality, Atmospheric Environment, 121, 13–21, https://doi.org/http://dx.doi.org/10.1016/j.atmosenv.2015.03.050, 2015.

King, K. J., Cary, G. J., Bradstock, R. A., and Marsden-Smedley, J. B.: Contrasting fire responses to climate and management: insights from two Australian ecosystems, Global Change Biology, 19, 1223–1235, https://doi.org/10.1111/gcb.12115, 2013.

Landry, J.-S. and Matthews, H. D.: Non-deforestation fire vs. fossil fuel combustion: the source of CO2 emissions affects the global carbon cycle and climate responses, Biogeosciences, 13, 2137–2149, https://doi.org/10.5194/bg-13-2137-2016, 2016.

Lawson, S. J., Keywood, M. D., Galbally, I. E., Gras, J. L., Cainey, J. M., Cope, M. E., Krummel, P. B., Fraser, P. J., Steele, L. P., Bentley, S. T., Meyer, C. P., Ristovski, Z., and Goldstein, A. H.: Biomass burning emissions of trace gases and particles in marine air at Cape Grim, Tasmania, Atmospheric Chemistry and Physics, 15, 13 393–13 411, https://doi.org/10.5194/acp-15-13393-2015, 2015.

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

Maleknia, S. D., Bell, T. L., and Adams, M. A.: PTR-MS analysis of reference and plant-emitted volatile organic compounds, International Journal of Mass Spectrometry, 262, 203–210, https://doi.org/10.1016/j.ijms.2006.11.010, 2007.

Maleknia, S. D., Bell, T. L., and Adams, M. A.: Eucalypt smoke and wildfires: Temperature dependent emissions of biogenic volatile organic compounds, International Journal of Mass Spectrometry, 279, 126–133, https://doi.org/10.1016/j.ijms.2008.10.027, 2009.

Meyer, C. P., Cook, G. D., Reisen, F., Smith, T. E. L., Tattaris, M., Russell-Smith, J., Maier, S. W., Yates, C. P., and Wooster, M. J.: Direct measurements of the seasonality of emission factors from savanna fires in northern Australia, Journal of Geophysical Research: Atmospheres, 117, D20 305, https://doi.org/10.1029/2012jd017671, 2012.

Milligan, D. B., Francis, G. J., Prince, B. J., and McEwan, M. J.: Demonstration of Selected Ion Flow Tube MS Detection in the Parts per Trillion Range, Analytical Chemistry, 79, 2537–2540, https://doi.org/10.1021/ac0622678, 2007.

Paton-Walsh, C., Jones, N. B., Wilson, S. R., Haverd, V., Meier, A., Griffith, D. W. T., and Rinsland, C. P.: Measurements of trace gas emissions from Australian forest fires and correlations with coincident measurements of aerosol optical depth, Journal of Geophysical Research, 110, D24 305, https://doi.org/10.1029/2005jd006202, 2005.

Paton-Walsh, C., Wilson, S. R., Jones, N. B., and Griffith, D. W. T.: Measurement of methanol emissions from Australian wildfires by ground-based solar Fourier transform spectroscopy, Geophysical Research Letters, 35, L08 810, https://doi.org/10.1029/2007gl032951, 2008.

Paton-Walsh, C., Deutscher, N. M., Griffith, D. W. T., Forgan, B. W., Wilson, S. R., Jones, N. B., and Edwards, D. P.: Trace gas emissions from savanna fires in northern Australia, Journal of Geophysical Research: Atmospheres, 115, D16 314, https://doi.org/10.1029/2009JD013309, 2010.

Paton-Walsh, C., Smith, T. E. L., Young, E. L., Griffith, D. W. T., and Guérette, A.: New emission factors for Australian vegetation fires measured using open-path Fourier transform infrared spectroscopy - Part 1: Methods and Australian temperate forest fires, Atmospheric Chemistry and Physics, 14, 11 313–11 333, https://doi.org/10.5194/acp-14-11313-2014, 2014.

Pfister, G. G., Wiedinmyer, C., and Emmons, L. K.: Impacts of the fall 2007 California wildfires on surface ozone: Integrating local observations with global model simulations, Geophysical Research Letters, 35, L19 814, https://doi.org/10.1029/2008gl034747, 2008.

Possell, M. and Bell, T. L.: The influence of fuel moisture content on the combustion of Eucalyptus foliage, International Journal of Wildland Fire, 22, 343–352, https://doi.org/10.1071/WF12077, 2013.

Possell, M., Jenkins, M., Bell, T. L., and Adams, M. A.: Emissions from prescribed fires in temperate forest in south-east Australia: implications for carbon accounting, Biogeosciences, 12, 257–268, https://doi.org/10.5194/bg-12-257-2015, 2015.

Price, O. F., Williamson, G. J., Henderson, S. B., Johnston, F., and Bowman, D. M. J. S.: The Relationship between Particulate Pollution Levels in Australian Cities, Meteorology, and Landscape Fire Activity Detected from MODIS Hotspots, PLOS ONE, 7, e47 327, https://doi.org/10.1371/journal.pone.0047327, 2012.

Rea, G., Paton-Walsh, C., Turquety, S., Cope, M., and Griffith, D.: Impact of the New South Wales fires during October 2013 on regional air quality in eastern Australia, Atmospheric Environment, 131, 150–163, https://doi.org/10.1016/j.atmosenv.2016.01.034, 2016.

Reid, C. E., Brauer, M., Johnston, F. H., Jerrett, M., Balmes, J. R., and Elliott, C.: Critical review of health impacts of wildfire smoke exposure, Environmental Health Perspectives, 124, 1334–1343, https://doi.org/10.1289/ehp.1409277, 2016.

Reisen, F. and Brown, S. K.: Implications for Community Health from Exposure to Bushfire Air Toxics, Environmental Chemistry, 3, 235–243, https://doi.org/10.1071/EN06008, 2006.

5 Reisen, F., Meyer, C. P., McCaw, L., Powell, J. C., Tolhurst, K., Keywood, M. D., and Gras, J. L.: Impact of smoke from biomass burning on air quality in rural communities in southern Australia, Atmospheric Environment, 45, 3944–3953, https://doi.org/10.1016/j.atmosenv.2011.04.060, 2011.

Reisen, F., Meyer, C. P., and Keywood, M. D.: Impact of biomass burning sources on seasonal aerosol air quality, Atmospheric Environment, 67, 437–447, https://doi.org/10.1016/j.atmosenv.2012.11.004, 2013.

10 Reisen, F., Duran, S. M., Flannigan, M., Elliott, C., and Rideout, K.: Wildfire smoke and public health risk, International Journal of Wildland Fire, 24, 1029–1044, https://doi.org/10.1071/WF15034, 2015.

Russell-Smith, J., Yates, C. P., Whitehead, P. J., Smith, R., Craig, R., Allan, G. E., Thackway, R., Frakes, I., Cridland, S., Meyer, M. C. P., and Gill, A. M.: Bushfires 'down under': patterns and implications of contemporary Australian landscape burning, International Journal of Wildland Fire, 16, 361–377, https://doi.org/10.1071/WF07018, 2007.

15 Shirai, T., Blake, D. R., Meinardi, S., Rowland, F. S., Russell-Smith, J., Edwards, A., Kondo, Y., Koike, M., Kita, K., Machida, T., Takegawa, N., Nishi, N., Kawakami, S., and Ogawa, T.: Emission estimates of selected volatile organic compounds from tropical savanna burning in northern Australia, Journal of Geophysical Research: Atmospheres, 108, 8406, https://doi.org/10.1029/2001JD000841, 2003.

Siddaway, J. M. and Petelina, S. V.: Transport and evolution of the 2009 Australian Black Saturday bushfire smoke in the lower stratosphere observed by OSIRIS on Odin, Journal of Geophysical Research, 116, D06 203, https://doi.org/10.1029/2010JD015162, 2011.

20 Smith, T. E. L., Paton-Walsh, C., Meyer, C. P., Cook, G. D., Maier, S. W., Russell-Smith, J., Wooster, M. J., and Yates, C. P.: New emission factors for Australian vegetation fires measured using open-path Fourier transform infrared spectroscopy - Part 2: Australian tropical savanna fires, Atmospheric Chemistry and Physics, 14, 11 335–11 352, https://doi.org/10.5194/acp-14-11335-2014, 2014.

Snowdon, P., Ryan, P., and Raison, J.: Review of the C:N Ratios in Vegetation, Litter and Soil Under Australian Native Forests and Plantations, Tech. Rep. National Carbon Accounting System Technical Report No. 45, Department of the Environment and Heritage,
25 http://www.greenhouse.gov.au/ncas/, 2005.

Surawski, N. C., Sullivan, A. L., Meyer, C. P., Roxburgh, S. H., and Polglase, P. J.: Greenhouse gas emissions from laboratory-scale fires in wildland fuels depend on fire spread mode and phase of combustion, Atmospheric Chemistry and Physics, 15, 5259–5273, https://doi.org/10.5194/acp-15-5259-2015, 2015.

Susott, R. A., Olbu, G. J., Baker, S. P., Ward, D. E., Kauffman, J. B., and Shea, R. W.: Carbon, hydrogen, nitrogen, and thermogravimetric
30 analysis of tropical ecosystem biomass, in: Biomass Burning and Global Change, edited by Levine, J. S., vol. 1, chap. 24, pp. 249–259, The MIT Press, Cambridge, Mass., 1996.

Teague, B., McLeod, R., Pascoe, S., and of Victoria, P.: Final Report, http://royalcommission.vic.gov.au/Commission-Reports/Final-Report.html, 2010.

van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S., Morton, D. C., DeFries, R. S., Jin, Y., and van
35 Leeuwen, T. T.: Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997-2009), Atmospheric Chemistry and Physics, 10, 11 707–11 735, https://doi.org/10.5194/acp-10-11707-2010, 2010.

Volkova, L., Meyer, C. P., Murphy, S., Fairman, T., Reisen, F., and Weston, C.: Fuel reduction burning mitigates wildfire effects on forest carbon and greenhouse gas emission, International Journal of Wildland Fire, 23, 771–780, https://doi.org/10.1071/WF14009, 2014.

Voulgarakis, A., Marlier, M. E., Faluvegi, G., Shindell, D. T., Tsigaridis, K., and Mangeon, S.: Interannual variability of tropospheric trace gases and aerosols: The role of biomass burning emissions, Journal of Geophysical Research: Atmospheres, 120, 7157–7173, https://doi.org/10.1002/2014JD022926, 2015.

Wang, X., Meyer, C. P., Reisen, F., Keywood, M., Thai, P. K., Hawker, D. W., Powell, J., and Mueller, J. F.: Emission Factors for Selected Semivolatile Organic Chemicals from Burning of Tropical Biomass Fuels and Estimation of Annual Australian Emissions, Environmental Science & Technology, 51, 9644–9652, https://doi.org/10.1021/acs.est.7b01392, 2017a.

Wang, X., Thai, P. K., Mallet, M., Desservettaz, M., Hawker, D. W., Keywood, M., Miljevic, B., Paton-Walsh, C., Gallen, M., and Mueller, J. F.: Emissions of Selected Semivolatile Organic Chemicals from Forest and Savannah Fires, Environmental Science & Technology, 51, 1293–1302, https://doi.org/10.1021/acs.est.6b03503, 2017b.

Williamson, G. J., Bowman, D. M. J. S., Price, O. F., Henderson, S. B., and Johnston, F. H.: A transdisciplinary approach to understanding the health effects of wildfire and prescribed fire smoke regimes, Environmental Research Letters, 11, 125 009, http://stacks.iop.org/1748-9326/11/i=12/a=125009, 2016.

Wooster, M. J., Freeborn, P. H., Archibald, S., Oppenheimer, C., Roberts, G. J., Smith, T. E. L., Govender, N., Burton, M., and Palumbo, I.: Field determination of biomass burning emission ratios and factors via open-path FTIR spectroscopy and fire radiative power assessment: headfire, backfire and residual smouldering combustion in African savannahs, Atmospheric Chemistry and Physics, 11, 11 591–11 615, https://doi.org/10.5194/acp-11-11591-2011, 2011.

Wu, C. and Yu, J. Z.: Evaluation of linear regression techniques for atmospheric applications : The importance of appropriate weighting, Atmospheric Measurement Techniques Discussions, pp. 1–31, https://doi.org/10.5194/amt-2017-300, 2017.

Yan, B., Zheng, M., Hu, Y. T., Lee, S., Kim, H. K., and Russell, A. G.: Organic composition of carbonaceous aerosols in an aged prescribed fire plume, Atmospheric Chemistry and Physics, 8, 6381–6394, https://doi.org/10.5194/acp-8-6381-2008, 2008.

Yokelson, R. J., Griffith, D. W. T., and Ward, D. E.: Open-path Fourier transform infrared studies of large-scale laboratory biomass fires, Journal of Geophysical Research, 101, 21 067–21 080, https://doi.org/10.1029/96jd01800, 1996.

Yokelson, R. J., Christian, T. J., Karl, T. G., and Guenther, A.: The tropical forest and fire emissions experiment: laboratory fire measurements and synthesis of campaign data, Atmospheric Chemistry and Physics, 8, 3509–3527, https://doi.org/10.5194/acp-8-3509-2008, 2008.

Yokelson, R. J., Crounse, J. D., DeCarlo, P. F., Karl, T., Urbanski, S., Atlas, E., Campos, T., Shinozuka, Y., Kapustin, V., Clarke, A. D., Weinheimer, A., Knapp, D. J., Montzka, D. D., Holloway, J., Weibring, P., Flocke, F., Zheng, W., Toohey, D., Wennberg, P. O., Wiedinmyer, C., Mauldin, L., Fried, A., Richter, D., Walega, J., Jimenez, J. L., Adachi, K., Buseck, P. R., Hall, S. R., and Shetter, R.: Emissions from biomass burning in the Yucatan, Atmospheric Chemistry and Physics, 9, 5785–5812, https://doi.org/10.5194/acp-9-5785-2009, 2009.

Yokelson, R. J., Burling, I. R., Urbanski, S. P., Atlas, E. L., Adachi, K., Buseck, P. R., Wiedinmyer, C., Akagi, S. K., Toohey, D. W., and Wold, C. E.: Trace gas and particle emissions from open biomass burning in Mexico, Atmospheric Chemistry and Physics, 11, 6787–6808, https://doi.org/10.5194/acp-11-6787-2011, 2011.

Yokelson, R. J., Burling, I. R., Gilman, J. B., Warneke, C., Stockwell, C. E., de Gouw, J., Akagi, S. K., Urbanski, S. P., Veres, P., Roberts, J. M., Kuster, W. C., Reardon, J., Griffith, D. W. T., Johnson, T. J., Hosseini, S., Miller, J. W., Cocker Iii, D. R., Jung, H., and Weise, D. R.: Coupling field and laboratory measurements to estimate the emission factors of identified and unidentified trace gases for prescribed fires, Atmospheric Chemistry and Physics, 13, 89–116, https://doi.org/10.5194/acp-13-89-2013, 2013.

Young, E. and Paton-Walsh, C.: Emission Ratios of the Tropospheric Ozone Precursors Nitrogen Dioxide and Formaldehyde from Australia's Black Saturday Fires, Atmosphere, 2, 617–632, http://www.mdpi.com/2073-4433/2/4/617/, 2011.

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 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	CO	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

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.

Species	Reference species	Castlemaine ER	R^2	EF	Greendale ER	R^2	EF	NSW fires[a] 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

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	Prescribed & 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.

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)

			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
Acetic acid	60	CO			0.020 (0.009)	4.5 (1.6)			2.1 (0.7)
Pyrrole	67	CO	0.0006 ± 0.0003	0.16 ± 0.08					0.012 (0.009) (pyrrole) 0.047 (0.026) (MM67)
sum of furan and isoprene	68	CO	0.0019 ± 0.0003	0.5 ± 0.1			0.0053	1.7	0.3 (0.1) (furan) 0.10(0.004) (isoprene) 0.18 (0.08) (MM68)
sum of MACR, MVK and 2-butenal	70	CO	0.0035 ± 0.0009	1.0 ± 0.3			0.0012	0.38	0.05 (0.02) (methacrolein)) 0.16 (0.04) (methyl vinyl ketone) 0.2 (0.1) (2-butenal) 0.3 (0.2) (MM70)
Butanone	72	CO	0.00082 ± 0.00007	0.25 ± 0.05			0.001	0.35	0.13 (0.04) (butanone) 0.09 (0.04) (MM72)
Benzene	78	CO_2	0.00014 ± 0.00002	0.39 ± 0.07				0.69	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)
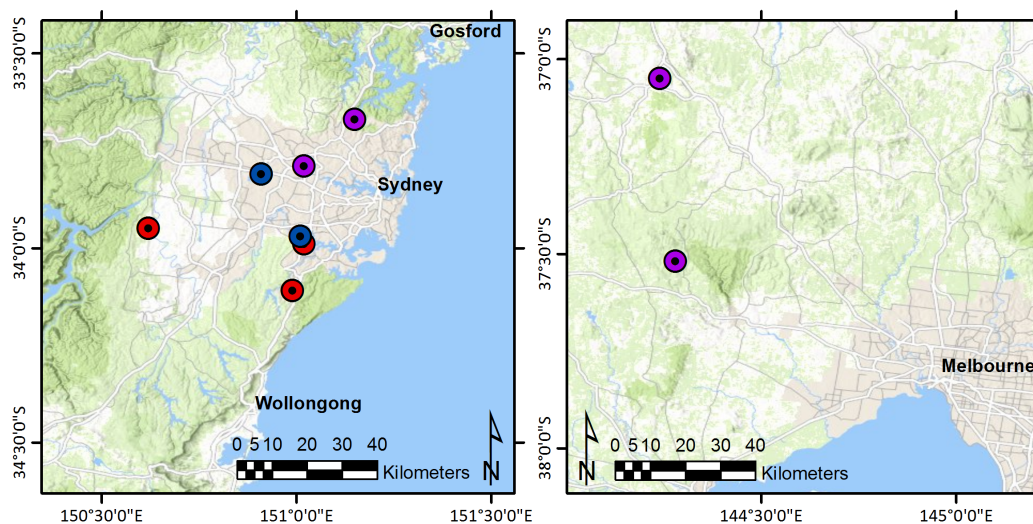
Figure 1. Locations of the nine prescribed fires in Australian temperate forests sampled between 2010 and 2015. The NSW fires are on the left, and the fires in Victoria on the right. The red dots represent fires where both open-path FTIR (OP-FTIR) and grab sampling took place, the blue dots indicate fires where only grab sampling took place, and the purple dots indicate fires where only OP-FTIR sampling took place.

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).
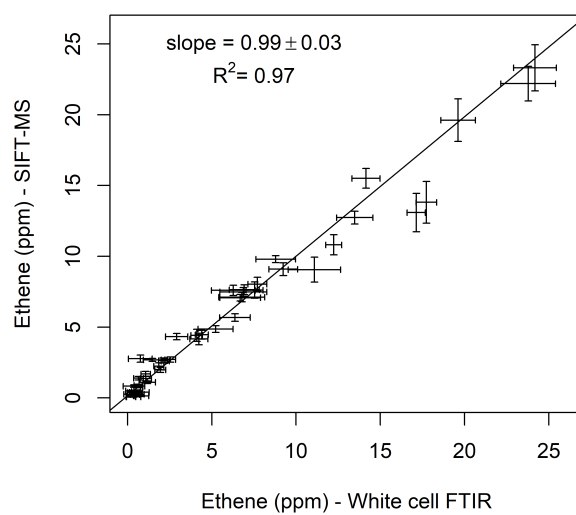
Figure 3. Comparison of ethene mole fractions measured by SIFT-MS with those measured by White cell FTIR in grab samples of smoke collected at Australian temperate forest fires. Error bars for the SIFT-MS are the standard deviation of the measurement, for the White cell FTIR they are the error on the retrieval. The line of best fit was determined using orthogonal regression.
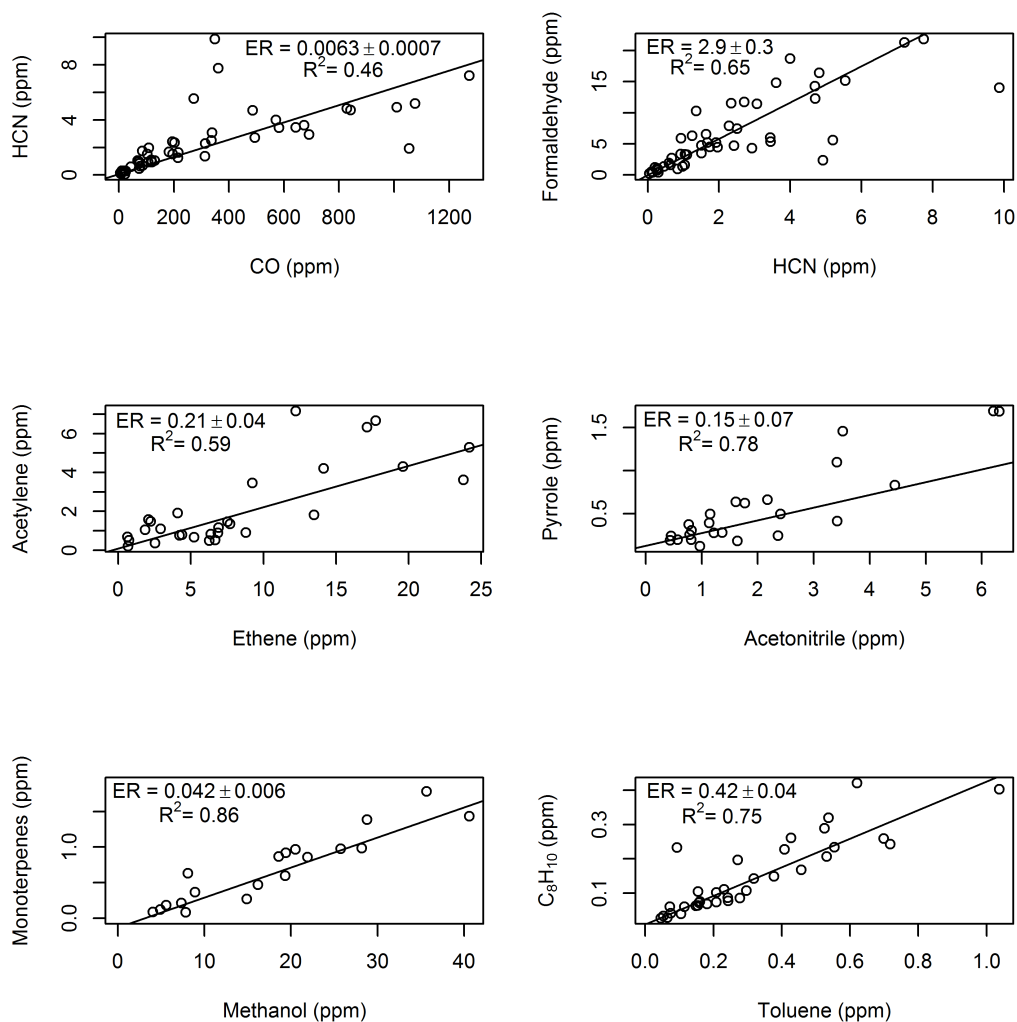
Figure 4. Examples of 'all data combined' correlations from the grab sample measurements. Top left is hydrogen cyanide (HCN) to CO, top right is formaldehyde to HCN, middle left is acetylene to ethene, middle right is pyrrole to acetonitrile, bottom left is monoterpenes to methanol and bottom right is the sum of C_8H_{10} species to toluene.
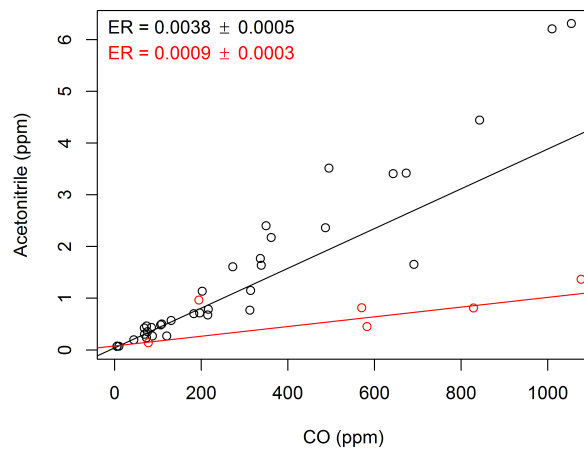
Figure 5. Emission ratio (ER) for acetonitrile to CO for the Gulguer Plateau fire grab samples (in red) and for the other four fires (in black).
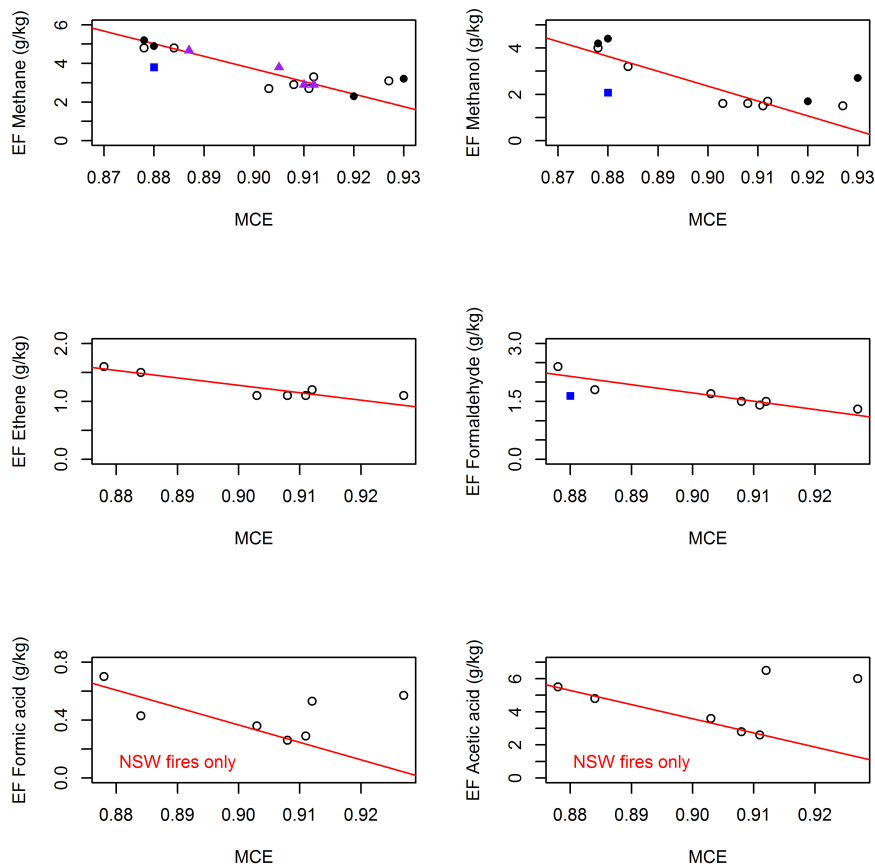
Figure 6. Dependence of emission factors on MCE. Open circles represent the seven fires sampled using OP-FTIR with the line of best fit shown in red. For formic acid and acetic acid, this regression line was derived using the measurements from the NSW fires only. The black circles represent average results from grab samples at four fires (The grab sampling results from the Gulguer Plateau fire are either not available (methanol) or fall outside the range measured by OP-FTIR (methane) and therefore do not appear). 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.