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 (see main text).

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 mentioned 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 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)

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

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	0.0104 ± 0.0004	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	0.010 (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 (0.001)
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	0.010 ± 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			0.0017 ± 0.0002	0.85	0.0020 (0.0003)
Methanol	CO	0.023 ± 0.007	0.88	0.028 ± 0.003	0.95	0.023 ± 0.006	0.30	0.016 ± 0.004	0.52	0.027 ± 0.009	0.66	0.023 (0.005)
Toluene	CO	0.0004 ± 0.0002	0.81	0.00086 ± 0.00003	0.98			0.00045 ± 0.00009	0.63	0.0007 ± 0.0004	0.89	0.0006 (0.0002)
mean MCE of samples		0.88 ± 0.07		0.93 ± 0.02		0.77 ± 0.09		0.92 ± 0.03		0.88 ± 0.06		0.88 (0.07)

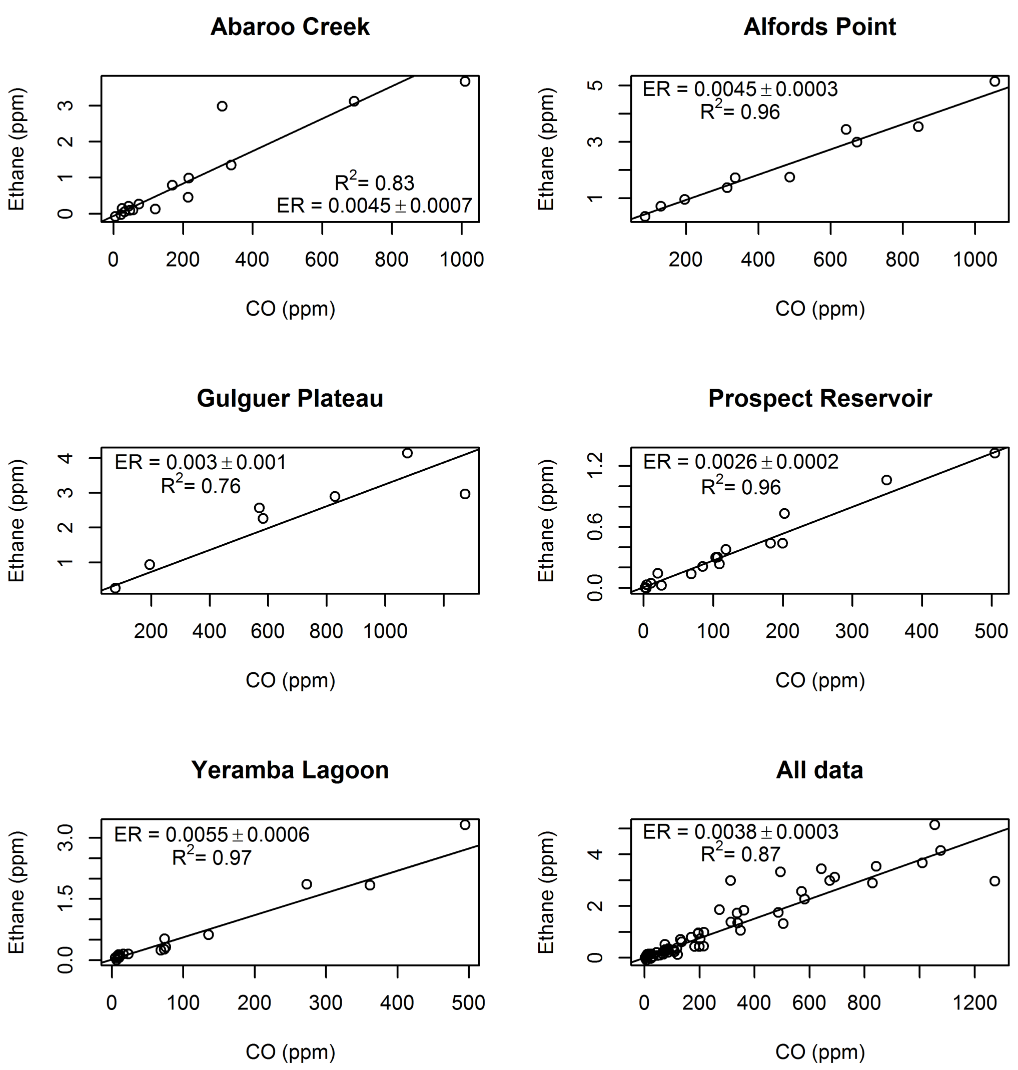

Figure S1. Emission ratios of ethane to CO for each individual fire sampled by grab sampling and for all the fires combined.

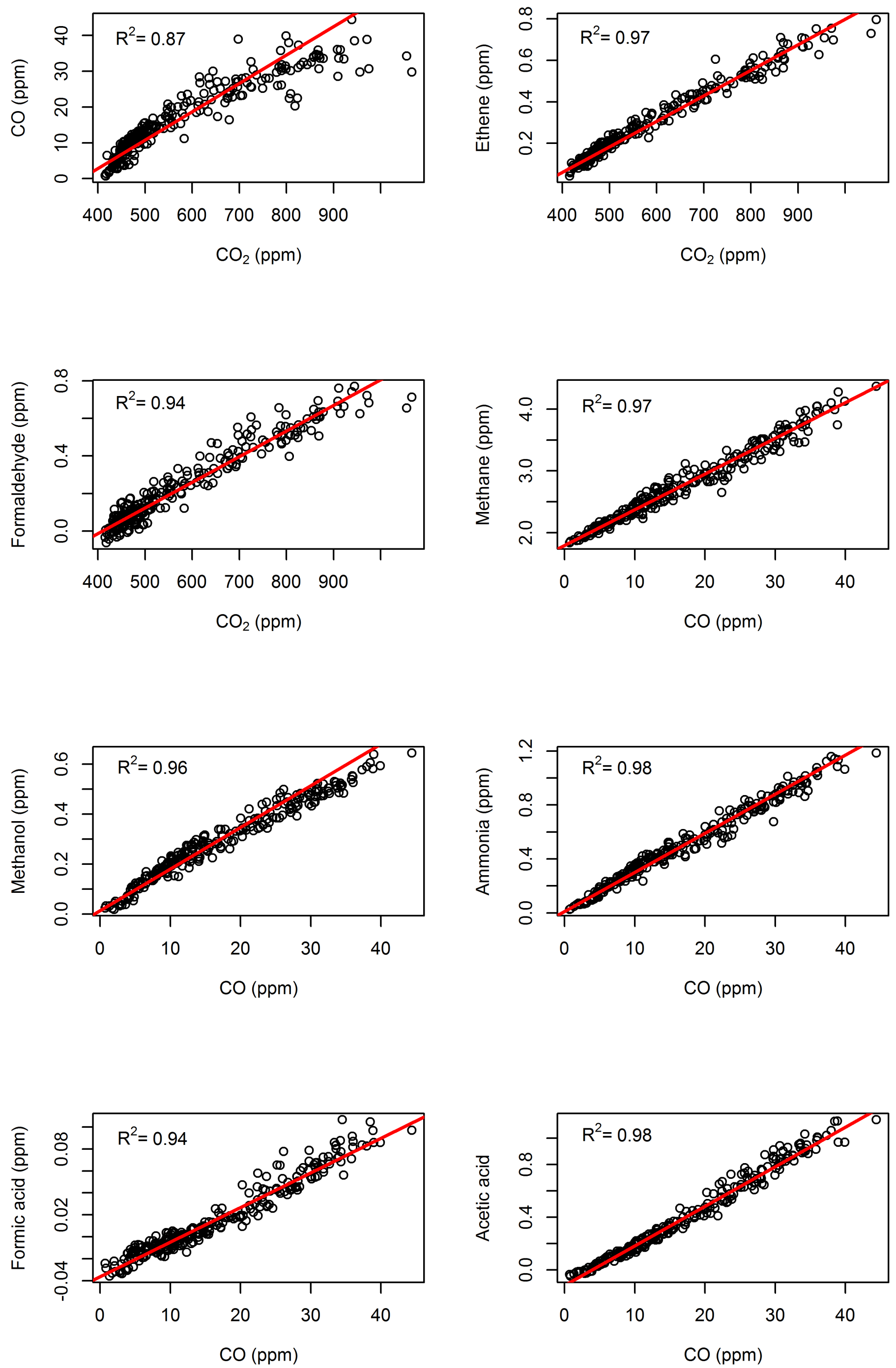

Figure S2. Correlation plots for open-path FTIR measurements at the Castlemaine fire.

References

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.