Interactive comment on "Greenhouse gas emissions from laboratory-scale fires in wildland fuels depend on fire spread mode and phase of combustion" by N.C. Surawski et al.

N.C. Surawski et al.

Correspondence to: Nic Surawski (Nicholas.Surawski@csiro.au)

Our responses to the first reviewer's comments are detailed below.

Overall comment: The reviewer states that: "The sampling approach is not validated, the math is described in a misleading and inconsistent manner, and there is no practical application of the results even if the experiment had been done correctly."

Response: The revised version of the manuscript comprehensively addresses the three areas of the manuscript requiring improvement; namely, validating the sampling approach, discussing our emission factor calculations in a more transparent fashion and demonstrating practical application of our results.

Major comment 1 on measurement approach: There is an important place for lab measurements in fire research. For instance, smoke data can be obtained with instruments that might not be field worthy. However, when working close to a fire, elucidation of the impact of fire behavior on emissions is only valid if it can be shown that the sampling is representative of the overall lab fire emissions for all the behavior types considered. In other words, it needs to be shown that the smoke is well mixed so that data acquired at the sampling point do not reflect a fire-behavior impact on the height at which emissions from different processes are released. As an example, Christian et al., (2004) show that temperature and mixing ratios are constant across the stack at the level where sampling occurs for their lab fires. (Prior to that test, they published results based on an optical path that spanned the whole stack.) The good mixing Christian et al confirmed was due largely to a torus surrounding the base of the stack that promotes turbulent mixing. In contrast, wind tunnels are designed to eliminate turbulence, which discourages good mixing. In fact, Christian et al considered wind tunnel measurements, but found that wind tunnel fires produced a strong vertical temperature gradient with hot gases (flaming emissions) mostly at the top of the wind tunnel and cooler

1   gases (smoldering emissions) lower. Thus, the CO/CO_2 ratio depends strongly on the point-

2   sampling height selected. This separation of process-specific emissions likely varies strongly

3   by fire spread mode. In other words, the author's CO/CO_2 data could be reproducible, but not

4   be representative of fire behavior effects if the emissions are not well mixed and flaming

5   emissions have greater tendency to rise above their one fixed sampling point for some spread

6   modes. Without evidence that this artifact does not occur the data are not of value.

7   **Response:** The same comment was made by the second reviewer as well. We have added a

8   new section to the discussion section of this article called "Representativeness of combustion

9   wind tunnel emissions measurements" (section 4.1 in revised version of manuscript) and a

10   new Table of supporting data (Table 3 in revised manuscript) which together provide further

11   analysis supporting our measurement approach. In this new section, we calculate the reaction

12   Damköhler number (*Da*) which is the ratio of the flow time scale to the chemical reaction

13   time scale (Law, 2006). We calculate *Da* at two flame heights and axial positions within the

14   flow with *Da* exceeding 10^6 in all cases. Therefore, for the species we measure in this

15   experimental effort, the timescale required for chemical reaction is very short relative to the

16   flow timescale in our combustion wind tunnel. Therefore, the chemical reactions are at

17   equilibrium (or are "frozen") by the time our sampling manifold is reached and furthermore

18   do not depend on sampling height.

19

20   The new section in the discussion (section 4.1) reads: "Since emissions sampling was

21   conducted at a single fixed height above the wind tunnel floor (see section 2.1), further

22   analysis needs to be conducted to ensure the representativeness of measurements. If chemical

23   reactions were still occurring at the axial position of sampling, and if those reactions had a

24   dependence on sampling height, then the emissions measurements obtained would not be

25   representative of the entire plume. Here we calculate the reaction Damköhler number (*Da*)

26   (Law, 2006, p. 189) which characterises the ratio of the flow time scale (τ_F) to the chemical

27   reaction time scale (τ_C). The reaction Damköhler number is given by:

$$Da = \frac{\text{Characteristic flow time}}{\text{Characteristic reaction time}} \tag{11}$$

$$= \frac{\tau_F}{\tau_C}$$

$$= \frac{kL}{\bar{U}},$$

1   where τ_F is given by the characteristic length scale (L) divided by the characteristic velocity

2   ($\bar{U}$) (Law, 2006) and τ_C is the reciprocal of the reaction rate (k). We choose L as the axial

3   distance from the flame position to the sampling manifold (either 3.6 or 8.4 m), $\bar{U}$ as the

4   mean wind speed employed during testing (1.5 m s^{-1}) with k given by the lumped kinetic

5   scheme of Ranzi et al. (2008), which describes the production of CO_2, CH_4 and CO (plus

6   other carbon compounds) from biomass pyrolysis. We calculate k at two heights within the

7   flame, with maximum temperatures at the flame base being based on those recorded by

8   thermocouples on the CSIRO Pyrotron floor, whilst flame tip temperatures are based on

9   measurements made in eucalypt shrubs by Wotton et al. (2012). Calculation of the reaction

10   Damköhler number enables us to assess how close the relevant chemical reactions are to

11   equilibrium at two flame heights and axial positions within the flow, with the results of this

12   calculation being shown in Table 3.

13

14   We see that the reaction Damköhler number depends on vertical position within the

15   flame, with smaller Da being observed at the flame tip (i.e. 3.0 x 10^6) compared to the

16   flame base (1.8 x 10^8–2.9 x 10^8). There is also variation in the Da observed with different

17   fire spread modes which is due to differences in the maximum flame base temperature and

18   the influence it has on reaction kinetics. Whilst we see variation in Da with respect to fire

19   spread mode and vertical position within the flame, all of the Da exceed 10^6 (rounded to the

20   nearest order of magnitude) which does not change the conclusion that the reactions are

1 near equilibrium or "frozen" (Jenkins et al., 1993). Hence, we can conclude from this analysis

2 that our emissions sampling is representative of the entire plume since the timescale

3 required for the relevant chemical reactions to occur is very short relative to the flow

4 timescale.

5

6 Table 3 in the revised manuscript reads:

Table 3. Calculation of the reaction Damköhler number (Da) for several axial positions and flame heights within the flame.

Fire spread mode	$T_{\text{flame tip}}$ (K)	$T_{\text{flame base}}$ (K)	τ_F (s)	$\tau C_{\text{flame tip}}$	$\tau C_{\text{flame base}}$	$Da_{\text{flame tip}}$	$Da_{\text{flame base}}$
Heading	540	1170	5.6	8.0×10^{-7}	2.2×10^{-8}	7.0×10^{6}	2.6×10^{8}
Heading	540	1170	2.4	8.0×10^{-7}	2.2×10^{-8}	3.0×10^{6}	1.1×10^{8}
Flanking	540	1050	5.6	8.0×10^{-7}	3.1×10^{-8}	7.0×10^{6}	1.8×10^{8}
Flanking	540	1050	2.4	8.0×10^{-7}	3.1×10^{-8}	3.0×10^{6}	7.7×10^{7}
Backing	540	1220	5.6	8.0×10^{-7}	1.9×10^{-8}	7.0×10^{6}	2.9×10^{8}
Backing	540	1220	2.4	8.0×10^{-7}	1.9×10^{-8}	3.0×10^{6}	1.3×10^{8}

13 **Major comments 2a-d on EF's.**

14 **Comment 2a:** The reviewer states that: "Emission factors (EF) are meant to be used with fuel
15 consumption data and fuel consumption data explicitly doesn't count unburned carbon that
16 remains on the site".

17 **Response 2a:** One factor that the reviewer has neglected to consider in their comment is that
18 burnt fuel carbon does not necessarily have to be emitted to the atmosphere, even though most
19 of it is. As we detail in later in this set of responses (i.e. major comment 2), burnt carbon
20 could be present in the post-fire combustion residues as black carbon, ash or partially
21 charred/combusted fuel.

22

23 Based on our literature research we conducted, Andreae and Merlet (2001) suggest that best
24 practices in fire research **should** consider burnt carbon present in the post-fire residue. For
25 example, Andreae and Merlet suggest: "Calculation of this parameter (i.e. emissions factors)
26 requires knowledge of the carbon content of the biomass burned **and the carbon budget of**
27 **the fire**; both parameters are difficult to establish in the field as opposed to laboratory
28 experiments where they are readily determined."

It is generally common practice in atmospheric chemistry research to only consider carbon emitted to the atmosphere and to neglect carbon remaining in the post-fire combustion residue that has been burnt. Since this was a laboratory based study we considered the complete carbon budget of the fire, which as Andreae and Merlet suggest is simpler to do in a laboratory, rather than field, setting. Considering that we have taken this additional factor into account does not indicate that we have done anything it wrong, it merely suggests that we have considered **the complete carbon budget of the fire** as recommended by Andreae and Merlet.

Comment 2b: Following on from this point, the reviewer then suggests: "The authors are confused about this and make misleading statements about emission factors in other work. Further, they express EF both in the normal g/kg and as unspecified percentages." Related to this point, the reviewer then states: "Further, they express EF both in the normal g/kg and as unspecified percentages."

Response 2b: This comment was also made by the second reviewer (please see major comments 2a-b on EF's). In this article we have reported emissions factors two ways; namely: 1) as a percentage of the burnt carbon or nitrogen, or 2) on a per unit dry fuel consumed basis. We have modified the sentence on page 23133 (line 17) to make it clear that when we report emission factors as a percentage, it is a percentage of the total carbon or nitrogen burnt and not some "unspecified percentage" as claimed by both reviewers. Furthermore, we have furnished this revised sentence with several references to indicate that reporting emission factors this way has occurred widely in the emissions literature since the method was developed by Radke et al. in 1988. This revised sentence now reads: "A carbon mass balance approach developed by Radke et al. (1988), and applied (for example) by Lobert et al. (1990), Hurst et al. (1994a), Hurst et al. (1994b), and more recently by Meyer et al. (2012), was used to calculate emissions factors for different carbon- and nitrogen-based pollutants on a per unit element burnt basis."

Comment 2c: The reviewer then states: "The authors are correct that some burned C is converted to charcoal and this is a source of a small error in some standard carbon balance approaches. However charcoal yields are generally small and should not be confused with remnants of unburned carbon. For instance, Kuhlbusch et al. (1996) noted: "The ratio of black carbon produced to the carbon exposed to the fire in this field study (0.6–1.5%) was somewhat lower than in experimental fires under laboratory conditions (1.0–1.8%) which

may be due to less complete combustion." Some of their black carbon was in the emitted particles and some in the ash, with the ash portion representing the error in the carbon mass balance method due to C in the residue. When charcoal yields are high, as in the case of purposeful charcoal production, a method to adjust the CMB for this has already been published (Bertschi et al., 2003)."

Response 2c: Kuhlbusch report black carbon production percentages of 1.0-1.8% (relative to total carbon exposed) based on laboratory testing; however, based on preliminary ^{13}C NMR results conducted by the authors (which we reserve for presentation in a future publication) we think this percentage varies from 3% for heading fires to 7.5% for backing fires. This percentage is calculated by ascribing aryl structures from the NMR spectrum as being aromatic in nature and relatively resistant to degradation. Recent field work conducted by Volkova et al. (2014) on carbon emissions from prescribed burning and wildfire has noted increased charring of combustion residues from lower intensity fires (such as those conducted in this study) compared to wildfire. Thus, there is empirical evidence to support our results suggesting greater black carbon production relative to Kuhlbusch et al. More importantly though, Kuhlbusch et al. report on a number of carbon possibilities post-fire with black carbon representing only a portion of the carbon forms present. There will also be partially charred/combusted material, ash and also some unburnt (but nonetheless thermally exposed and altered) leaf, bark and twig remnants. Thus, the reviewer is incorrect in suggesting that post-fire carbon is composed merely of black carbon and an unburnt carbon pool.

Comment 2d: The reviewer also makes the suggestion that our combustion factors are small and that only non-carbon containing elements can be significant in the post-fire combustion residue.

Response 2d: Kuhlbusch et al. (1996) report backing fire carbon volatilisation percentages of 72% for the FP 4/2 fire and 78.2% for the FP 4/1 fire which is in excellent agreement with ours (74.8%). For heading fires Kuhlbusch et al. report carbon volatilisation percentages between 85.4% (KPE/1 fire) and 95.5% (KP3/3) which is, once again, very similar to ours (88.3%). Therefore, our carbon volatilisation percentages are in agreement with the Kuhlbusch et al study. It should also be noted that combustion factors near 100% could occur in extreme wildfire situations; however, in our experimental fires (please see Table 1) the Byram fireline intensity is more indicative of a prescribed fire situation. As a result, we would expect combustion factors less than 100% as indicated by our results. Furthermore,

1   our results and those of Kuhlbusch et al suggest that it is possible to get 30% of total fuel

2   carbon deposited in the post-fire combustion residue despite claims being made to the

3   contrary by the reviewer.

4   **Major comment 3 on application of results:** A serious problem is that real fires present a

5   mix of fire spread modes (as the authors themselves state) and in any case there is no way to

6   operationally monitor fire spread modes for all the fires of importance, especially since the

7   majority of global biomass burning goes undetected from space (Yokelson et al., 2011). Even

8   if single spread modes were applicable to real fires, and they could be routine measured,

9   many other factors effect emissions interactively such as fuel geometry, moisture, RH, etc.;

10   and wind effects on the ability of a fire to propagate are probably far more important than

11   subtle emissions differences. I.e. wind has other impacts such as aiding fire spread in

12   dispersed fuel, making fire control more difficult, and possibly enabling ignition of live fuels

13   that might not burn otherwise. Wind interacts with fire induced convection in complex ways.

14   None of variables can be operationally monitored in complex fire environment and realistic

15   replication of some complex fuel beds including live, moist, or large fuels etc. is probably not

16   feasible. If the numerous variables could be controlled one at time there are likely still non-

17   linear interactions between driving variables.

18   **Response:** We agree with the reviewer that most global fires cannot be managed; however, in

19   the section of the manuscript where we apply our results (section 4.5 of the revised

20   manuscript) we are considering prescribed fire where there is explicit choice (i.e. selected

21   before the burn) regarding the range of variables that the reviewer discusses in their comment;

22   such as: wind speed, fuel moisture as well as the ignition pattern. This is operationally

23   achieved by carefully selecting the ignition timing to correspond with fire weather conditions

24   that are appropriate for achieving the objectives of the burn. Furthermore, the ignition pattern

25   selected is based on a judicious choice regarding the moisture, load and contiguity of fuels,

26   the prevailing wind speed and direction as well as topography and the presence of firebreaks.

27   In our current article, we argue that mitigation of greenhouse gas emissions could become

28   part of the overall prescribed burn design; of which we assess the potential of by applying

29   single fire spread modes over a landscape. Whilst we agree that a single or universal fire

30   spread mode cannot be achieved in a prescribed fire situation; in practice, a variety of ignition

31   patterns are commonly employed in such operations that enable the fire spread modes we

32   considered (i.e. heading, flanking and backing) to predominate in different fuel, weather and

topographical conditions. We add a sentence to the 1st paragraph in section 4.5 (page 21of revised manuscript) stating that ignition patterns exist which enable a single fire spread mode to predominate. This new sentence reads: "Whilst it would not be possible to apply a single fire spread mode to a forested landscape in a prescribed fire situation, ignition patterns are practised in Victoria which enable a single fire spread mode to predominate (Tolhurst and Cheney, 1999), such as the three investigated in this study.

Other miscellaneous comments: Real fires burn with a mix of smoldering and flaming that is further not operationally available. Both main hypotheses are already in literature. Keene et al showed fire spread mode impacts MCE and countless papers have already shown that CH_4 correlates with MCE.

Response: The unique aspect of our study was outlined on page 23128 where we state "In this study, we re-examine the burning methodology of Keene et al. in a controlled laboratory study with an explicit experimental design combined with statistical testing of results. As such, examining the hypothesis that greenhouse gas emissions could depend on fire spread

mode is the major focus of this article." The only greenhouse gas species measured in the study of Keene et al. was CO_2 (which we stated on page 23128 line 14 of the original manuscript) which motivated us to revisit their burning methodology (i.e. heading, flanking and backing) to assess its impact on other greenhouse gas species. This is the basis of our original contribution in this article; not the other foci suggested by the reviewer.

Comments below were put in a Page, Line format by the reviewer.

Comment 1: 2, 4: diameter?

Response: Change made.

Comment 2: 2, 14: twice as much CO as what?

Response: We've added to some more detail to the end of this sentence to make it clear that heading fires produced twice as CO as flanking and backing fires.

Comment 3: 4, 1: Actually there are an infinite number of possible angles, they are normally mixed, plus any real fire has multiple wind directions.

Response: We emphasise that we are referring to the three "mutually independent" fire spread modes in this article, whereas the reviewer is referring to an infinity of directions

1   obtained by linear combinations of the fires spread modes we considered. To avoid confusion

2   though, we have changed the word "different" in this sentence to "main" to account for the

3   possibility of having many fire spread modes.

4   **Comment 4:** 4, 20-24: There is no way to operationally monitor fire spread modes and in fact

5   the majority of global fires go completely un-detected, plus no single fire spread mode applies

6   to a whole fire.

7   **Response:** For wildfire this may be true, but this is not the case for a prescribed fire where

8   monitoring the fire spread mode is an explicit consideration in the conduct of such a burn

9   (Tolhurst and Cheney, 1999). (please see our response to major comment 3 on

10   representativeness of experiments).

11   **Comment 5:** 6, 1: all gas sampling at one height – no evidence well mixed for all fire types

12   **Response:** We have added a new section to the manuscript (section 4.1 in the revised version

13   of the manuscript) which addresses this comment. Please see our response to reviewer 1's

14   major comment on our sampling design (major comment 1).

15   **Comment 6:** 7, 15: windspeed of 1.5 m/s or ~5 km/h kind of low

16   **Response:** This wind speed is one that is relevant for prescribed fire.

17   **Comment 7:** Pages 9-11: un-needed lengthy discussion of old math, plus a misprint in eqn 7

18   **Response:** These points were also raised by reviewer 2. Considering that both reviewers

19   questioned the reporting of emission factors on a per unit element burnt basis (as a

20   percentage), we thought it would be good practice to methodically work through our methods

21   of calculation including relevant references to make our calculations transparent to the readers

22   of this paper. The typographical error in equation (7) has been corrected.

23   **Comment 8:** 14, 21-24: "Fire spread mode had a statistically significant effect on CO_2

24   ($p<0.0001$), CO ($p<0.0001$) and carbon residue emissions ($p<0.0001$) but did not have a

25   statistically significant effect on CH_4 ($p = 0.269$) or N_2O emissions ($p = 0.261$)." Something

26   went wrong here because fire spread mode effects MCE and CH_4 is strongly correlated with

27   MCE and the authors claim N2O is strongly correlated with CH_4.

28   **Response:** The reviewer is incorrect in suggesting that something has "gone wrong" with our

29   MCE versus CH_4 results. Below we have included a plot of CH_4 emissions factors which

30   shows a statistically significant relationship with MCE ($p < 0.0001$, $R^2=0.68$). The source of

confusion for the reviewer is, perhaps, that we don't get a statistically significant relationship between CH_4 emission factors and fire spread mode due to the observed variability in our data set.

Also, the reviewer is mistaken in stating that we claimed a correlation between CH_4 and N_2O emissions. Whilst on page 23139 lines 3-18 we say (in a general way) that CH_4 and N_2O emissions are increased during smouldering combustion, but we do not claim that they are correlated.

Comment 9: 14, 23: "carbon residue emissions"?

Response: Changed to carbon residue production.

Comment 10: 15, 17-18: On the same page the authors first claim that CH_4 increases during smoldering and N_2O doesn't, then a few lines below they make opposite claim.

Response: The source of confusion for the reviewer here is that lines 3-18 (page 14) discuss the results numerically, whereas formal testing of results for statistical significance occurs on lines 19-27. What appears like a trend numerically may not pass the test as being statistically significant. To alleviate this confusion we have added two sentences on page 14.

We add the first sentence in line 8 stating: "In this paragraph we discuss the numerical trends found, whilst the next paragraph discusses testing of our results for statistical significance."

The second sentence is added in line 25 stating: "Whilst the non-significant result for CH_4 may appear to contradict the trends discussed in the previous paragraph, the CH_4 results are more variable which prevents a statistically significant result from being found."

Comment 11: Page 17:In general: The EF has to be multiplied by fuel consumption to get emissions!

Response: We are aware of that, but for equivalence of the two methods in reporting total emissions we need to multiply emissions estimates (obtained from an emissions factor

1   reported per unit dry fuel consumed) by $\sum C_{emit} / C_{fuel}$ at some point as we correctly

2   suggested on page 17.

3   **Comment 12:** 17, 11-12: Wrong, the widely used CMB approach assumes that burned fuel
4   carbon (except for charcoal) is emitted to the atmosphere

5   **Response:** We disagree with the reviewer. This is merely the assumption we want to relax by
6   considering the fraction of burnt carbon that is emitted to the atmosphere by explicitly

7   multiplying by $\sum C_{emit} / C_{fuel}$. For example, in one of the references provided by the reviewer

8   (Bertschi et al., 2003) they state in paragraph [21] (2nd sentence): **"we assume that all the**
9   burned carbon is volatilized ...". As discussed in our response to the major comment on EF's
10   by the 1st reviewer (please see major comments 2a-d) burnt carbon is not completely emitted

11   to the atmosphere. Once again, to be in a position to estimate $\sum C_{emit} / C_{fuel}$ one needs to

12   consider **the complete carbon budget of the fire** (i.e. emitted to the atmosphere and burnt
13   and remaining in the post-fire residue) as suggested by Andreae and Merlet (2001). In
14   addition, charcoal (although a small fraction of total fire exposed carbon but larger in our
15   results) is not the only carbon form present in the post-fire combustion residue **not** emitted to
16   the atmosphere. In our results, we show that a significant fraction (between 10-30%) of total
17   (fire exposed) carbon is left in the post-fire combustion residue in a variety of forms
18   including: black carbon, ash, partially charred/combusted material and some thermally
19   exposed/altered fuel.

20   **Comment 13:** 17, 17: If fuel carbon remains on site and is not counted as fuel consumption
21   then the authors approach will incorrectly estimate carbon emissions.
22   **Response:** We disagree with the reviewer. To be counted as fuel consumption the fuel has to
23   be burnt and emitted to the atmosphere. Burnt carbon remaining on site does not get counted
24   as consumed because it is not emitted to the atmosphere.

25

26   Furthermore, it is apparent to the authors of this paper (based on comments 12 and 13) that
27   there is some confusion regarding the difference between the terms burnt and consumed. We

have added two sentences in the first paragraph of section 4.2 (page 17 lines 20-24 in the revised manuscript) stating: "For our purposes, we define 'burnt' as fuel that has been thermally altered as a result of exposure to fire and either emitted to the atmosphere or left in the post-fire residue. We define 'consumed' as that component of the fuel that is emitted to the atmosphere as a result of exposure to fire.

Comment 14: 18, 6: How can EF be expressed as a percent?

Response: This comment was also made by the second reviewer. We described this in section 2.4.1 of the original manuscript (Calculation of emissions factors). As stated earlier under the major comment on EFs (please see major comments 2a-d) we added a sentence showing that reporting emission factors per unit of element burnt has been done widely since the 1980's in the atmospheric chemistry literature.

Comment 15: 18, 12-14: Here the authors explain perfectly why their work has no realistic application, real fires, they state, have mixed spread modes.

Response: We addressed this earlier under the major comment on Application of our results (please see major comment 3). In prescribed fire situations in Australia, the ignition location (and hence the fire spread mode) is a controllable parameter (Tolhurst and Cheney, 1999).

Comment 16: Table 1: Does not label the fire spread modes?

Response: We added fire spread mode and fuel moisture content as two extra columns to this table in the revised manuscript.

Comment 17: Table 2: The footnote discusses comparisons that are not in the table

Response: We have removed the footnote to Table 2 as its contents appear elsewhere in the manuscript.

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1 **Interactive comment on "Greenhouse gas emissions from**
2 **laboratory-scale fires in wildland fuels depend on fire**
3 **spread mode and phase of combustion" by N.C. Surawski**
4 **et al.**
5

6 **N.C. Surawski et al.**

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8

9 Our responses to the second reviewer's comments are detailed below.

10 **Major comment 1 on sampling methodology:** The reviewer states: "the experimental setup
11 of plume sampling (only at one point) is probably not representative of the average emission
12 composition as result of in-homogeneity of the plume in tunnel effluent as result low
13 turbulence and temperature gradient."

14 **Response:** We have added a new section to the discussion section of this article called
15 "Representativeness of combustion wind tunnel emissions measurements" (section 4.1 in
16 revised version of manuscript) and a new Table of supporting data (Table 3 in revised
17 manuscript) which together provide further analysis supporting our measurement approach.
18 In this new section, we calculate the reaction Damköhler number (Da) which is the ratio of
19 the flow time scale to the chemical reaction time scale (Law, 2006). We calculate Da at two
20 flame heights and axial positions within the flow with Da exceeding 10^6 in all cases.
21 Therefore, for the species we measure in this experimental effort, the timescale required for
22 chemical reaction is very short relative to the flow timescale in our combustion wind tunnel.
23 Therefore, the chemical reactions are at equilibrium (or are "frozen") by the time our
24 sampling manifold is reached and furthermore do not depend on sampling height.

25

26 The new section in the discussion (section 4.1) reads: "Since emissions sampling was
27 conducted at a single fixed height above the wind tunnel floor (see section 2.1), further
28 analysis needs to be conducted to ensure the representativeness of measurements. If chemical
29 reactions were still occurring at the axial position of sampling, and if those reactions had a
30 dependence on sampling height, then the emissions measurements obtained would not be
31 representative of the entire plume. Here we calculate the reaction Damköhler number (Da)

1   (Law, 2006, p. 189) which characterises the ratio of the flow time scale (τ_F) to the chemical

2   reaction time scale (τ_C). The reaction Damköhler number is given by:

$$Da = \frac{\text{Characteristic flow time}}{\text{Characteristic reaction time}}$$

$$= \frac{\tau_F}{\tau_C}$$

$$= \frac{kL}{\bar{U}},$$

(11)

3   where τ_F is given by the characteristic length scale (L) divided by the characteristic velocity

4   ($\bar{U}$) (Law, 2006) and τ_C is the reciprocal of the reaction rate (k). We choose L as the axial

5   distance from the flame position to the sampling manifold (either 3.6 or 8.4 m), $\bar{U}$ as the

6   mean wind speed employed during testing (1.5 m s^{-1}) with k given by the lumped kinetic

7   scheme of Ranzi et al. (2008), which describes the production of CO_2, CH_4 and CO (plus

8   other carbon compounds) from biomass pyrolysis. We calculate k at two heights within the

9   flame, with maximum temperatures at the flame base being based on those recorded by

10   thermocouples on the CSIRO Pyrotron floor, whilst flame tip temperatures are based on

11   measurements made in eucalypt shrubs by Wotton et al. (2012). Calculation of the reaction

12   Damköhler number enables us to assess how close the relevant chemical reactions are to

13   equilibrium at two flame heights and axial positions within the flow, with the results of this

14   calculation being shown in Table 3.

15

16   We see that the reaction Damköhler number depends on vertical position within the

17   flame, with smaller Da being observed at the flame tip (i.e. 3.0 x 10^6) compared to the

18   flame base (1.8 x 10^8–2.9 x 10^8). There is also variation in the Da observed with different

1 fire spread modes which is due to differences in the maximum flame base temperature and

2 the influence it has on reaction kinetics. Whilst we see variation in *Da* with respect to fire

3 spread mode and vertical position within the flame, all of the *Da* exceed 10^6 (rounded to the

4 nearest order of magnitude) which does not change the conclusion that the reactions are

5 near equilibrium or "frozen" (Jenkins et al., 1993). Hence, we can conclude from this analysis

6 that our emissions sampling is representative of the entire plume since the timescale

7 required for the relevant chemical reactions to occur is very short relative to the flow

8 timescale.

9 Table 3 in the revised manuscript reads:

10

Table 3. Calculation of the reaction Damköhler number (Da) for several axial positions and flame
11 heights within the flame.

12
Fire spread mode	$T_{\text{flame tip}}$ (K)	$T_{\text{flame base}}$ (K)	τ_F (s)	$\tau_{C\text{flame tip}}$	$\tau_{C\text{flame base}}$	$Da_{\text{flame tip}}$	$Da_{\text{flame base}}$
Heading	540	1170	5.6	8.0×10^{-7}	2.2×10^{-8}	7.0×10^6	2.6×10^8
Heading	540	1170	2.4	8.0×10^{-7}	2.2×10^{-8}	3.0×10^6	1.1×10^8
Flanking	540	1050	5.6	8.0×10^{-7}	3.1×10^{-8}	7.0×10^6	1.8×10^8
Flanking	540	1050	2.4	8.0×10^{-7}	3.1×10^{-8}	3.0×10^6	7.7×10^7
Backing	540	1220	5.6	8.0×10^{-7}	1.9×10^{-8}	7.0×10^6	2.9×10^8
Backing	540	1220	2.4	8.0×10^{-7}	1.9×10^{-8}	3.0×10^6	1.3×10^8

15

16 **Major comments 2a-b on EF's.**

17 **Comment 2a:** The reviewer states that "the data treatment and presented formulation is given

18 in a very confusing way with a unnecessary long discussion of equations for Emission Ratios

19 and Emission Factors that in several cases are inaccurate, using unclear symbology."

20 **Response 2a:** As discussed in detail in the next paragraph, given that we report emission

21 factors in two equally valid ways (either as a percentage of the burnt carbon or nitrogen and

22 on a mass per unit of dry fuel consumed basis) we thought it would be good scientific practice

23 to clearly describe and cite the calculation methods used. We thought this would add

24 transparency to our analysis, but regrettably, the reviewers have correctly identified one

25 typographical error in both equations (3) and (7) which we have now corrected. With these

26 two errors rectified we believe that sufficient detail (and no more) has been provided for

27 readers to understand our methods.   As for unclear symbology, we have used the

28 nomenclature present in the papers we have cited which involve terms commonly used in

1   wildfire emissions science. As such equations (2-4) are based on Hurst et al. (1994b), (5-6)

2   on Yokelson et al. (1999), whilst (7) is based on Andreae and Merlet (2001).

3   **Comment 2b:** The reviewer then states: "Emission Factors are given as a fraction of

4   burned/fired carbon, as a fraction (g/Kg) of burned biomass and in Section 4.2 as an un-

5   specified percentage of something."

6   **Response 2b:** In this article we have reported emissions factors two ways; namely: 1) as a

7   percentage of the burnt carbon or nitrogen, or 2) on a per unit dry fuel consumed basis. We

8   have modified the sentence on page 23133 (line 17) to make it clear that when we report

9   emission factors as a percentage, it is a percentage of the total carbon or nitrogen burnt and

10   not some "unspecified percentage" as claimed by both reviewers (please see also major

11   comments 2a-d by reviewer 1). Furthermore, we have furnished this revised sentence with

12   several references to indicate that reporting emission factors this way has occurred widely in

13   the emissions literature since the method was developed by Radke et al. in 1988.

14

15   This revised sentence now reads: "A carbon mass balance approach developed by Radke et al.

16   (1988), and applied (for example) by Lobert et al. (1990), Hurst et al. (1994a), Hurst et al.

17   (1994b), and more recently by Meyer et al. (2012), was used to calculate emissions factors for

18   different carbon- and nitrogen-based pollutants on a per unit element burnt basis."

19   **Major comment 3 on representativeness of experiments:** My doubts are that these

20   laboratory experiments with quite uniform and low litter sizes and humidity conditions, can

21   be representative of prescribed fires that are done in less extreme dried conditions with winds

22   that produce a mixture of processes (heading/flank/back).

23   **Response:** We selected the fuel load, fuel moisture content and wind speed to obtain Byram

24   fireline intensities which are representative of that which occurs during many prescribed

25   burning operations. We have now added a sentence at the end of section 2.2 (last sentence)

26   explaining why these various parameters were chosen. This new sentence reads: "Altogether,

27   the selection of fuel loads, fuel moisture content and wind speed were selected to achieve

28   Byram fireline intensities (Byram, 1959) (which is the product of the lower heating value of

29   the fuel, fuel consumed and the forward rate of spread) indicative of those during prescribed

30   burning conditions in temperate eucalypt forest in Australia (i.e. approximately < 500 kW m^{-1}

31   (Cheney, 1981) or approximately < 345 kW m^{-1} (McArthur, 1962))"

The comment the reviewer makes about having a mix of fire spread modes was also raised by the first reviewer (please see major comment 3 by reviewer 1 on application of results). Whilst we agree that a single or universal fire spread mode cannot be achieved in a prescribed fire situation; in practice, a variety of ignition patterns are commonly employed in such operations that enable the fire spread modes we considered (i.e. heading, flanking and backing) to predominate in different fuel, weather and topographical conditions. We add a sentence to the 1st paragraph in section 4.5 (page 21of revised manuscript) stating that ignition patterns exist which enable a single fire spread mode to predominate. This new sentence reads: "Whilst it would not be possible to apply a single fire spread mode to a forested landscape in a prescribed fire situation, ignition patterns are practised in Victoria which enable a single fire spread mode to predominate (Tolhurst and Cheney, 1999), such as the three investigated in this study.

Comment 1: Line 25, page 23129- develop experiments positioning the tube at different heights above the floor of combustion to access the homogeneity of the plume.

Response: The new section we added to the revised manuscript (section 4.1: Representativeness of combustion wind tunnel emissions measurements) has addressed this comment.

Comment 2: Line 13, page 23130- removal of fragmented material will not produce a combustible less representative of natural conditions?

Response: The comment made by the reviewer is correct but adding a duff layer to the fuel bed would have added an extra level of complexity that we did not want in our first set of emissions experiments. It was beyond the scope of the current set of experiments to include another fuel stratum in our experiments.

Comment 3: Line 1-2, page 23131- To dry the combustible to this low humidity is representative of conditions of burning in prescribed fires? Usually prescribed fires are taken during periods of lower fire hazard, therefore more humid.

Response: Prescribed burns in Victoria are usually conducted between 9-16% (Tolhurst and Cheney, 1999) but in the current work we dried the fuel to give Byram fireline intensities indicative of those at the higher-end of prescribed fire. We have added a sentence at the end of section 2.2 to explain why the fuel moisture was dried to such a low level (please see major comment 3 by reviewer 2 on the representativeness of results).

Comment 4: What means dilution with zero air? Is it normal external air, with usual CO_2 content, or air without CO_2? Clarify. If it is air with normal ambient CO_2 (and CH_4, etc) which is the imprecision resulting from the subtraction for conditions when burning is producing less emissions (in the end of experiments)?

Response: We have used air consisting of 20.5% O_2 in N_2. Hence there are no additional sources of carbon that need to be accounted for when correcting for the dilution ratio. We have modified line 7 on page 23132 to add this compositional information on what we mean by zero air.

Comment 5: Lines 13-15, page 23132- Unclear

Response: All we are saying is that the initial dilution ratio applied was increased during the heading fire experiments, but this did not happen for backing and flanking fires. We thought it was written clearly so have not modified this sentence.

Comment 6: Pages 23132-23133- I think that this discussion about ER is probably not necessary. It is only a methodology to calculate emission factors from concentration measurements. The associated figure 4 is also not very enlightening. Is it for heading, flanking or backfires?

Response: We have decided to keep the discussion on emission ratios as a choice needs to be made about which reference gas to use for calculating emission factors. The associated figure (i.e. Figure 4) is enlightening as it indicates that CO_2, CO and CH_4 would all be good choices as a reference gas for calculating emissions factors based on the quality of the linear fits. The caption for Figure 4 has been modified to make it clearer that the results from all 18 experimental fires appear in each panel.

The new caption for Figure 4 reads (with a modified first sentence in the caption): "Linear fits of excess mixing ratios for all 18 experimental fires (not corrected for the overall dilution ratio) using either CO_2, CO or CH_4 as a reference gas.

Comment 7: Equation 2- This equation is not exact. With basis in in concentration molar ratios (ppm) the values for NMHC should take into account that all hydrocarbons have more than a C atom. Also molar ratio for PC is not well defined.

1 **Response:** The fact that non-methane hydrocarbons have more than one carbon atom is
2 addressed explicitly by the parameter n in the next equation (i.e. equation 3). Whilst the
3 emissions factor for particulate carbon is not well defined it nonetheless contributes to the
4 carbon being emitted to the atmosphere and hence should be in the equation.

5 **Comment 8:** Equation 3- lacks a delta before CO_2

6 **Response:** Change made and thanks for spotting this typographical error.

7 **Comment 9:** Lines 16-18, page 23134. To adapt equation 3 to N_2O it needs also to substitute
8 in for the ratio between N_2O and CO_2 number of atoms in the molecule (that is- 2). The

9 consequent emission factor is in fraction of N emission per N present in the combustible

10 burned? Clarify.

11 **Response:** There is no need to do this (as described in Hurst et al. (1994b) and Meyer et al.
12 (2012)) as the molar nitrogen-to-carbon ratio (which we divide equation 3 by) takes into
13 account the fact that N_2O has two nitrogen atoms.
14
15 To alleviate this potential confusion the sentence on page 10 of the revised manuscript (lines
16 15-17) has been modified to read: "To estimate emissions factors for N_2O, the excess mixing
17 ratio for N_2O is substituted into the numerator of equation (3) and is then divided by the molar
18 nitrogen-to-carbon ratio of the fuel to account for the fact that every mole of N_2O has two
19 moles of N.

20 **Comment 10:** Equation 5- to use the same symbol EF for this and equation 3 is confusing. Fc
21 needs to be in fraction in the equation and not in % as it is suggested. In the equation there

22 is confusion between molecules and atoms of carbon.

23 **Response:** We've made many changes to the manuscript (please see major comment 2 by
24 both reviewers and comments 16 and 17 by reviewer 2) articulating how we've used two
25 methods of reporting emissions factors in this paper. The context of which of the two
26 approaches and where it's used is now clear in the revised manuscript.

27 We've changed the part of line 4 page 23135 which refers to F_C to read "F_C is the fractional
28 fuel carbon content (measured before burning: 0.516)." Given our nomenclature follows that
29 of Yokelson et al. (1999) we don't see any confusion between molecules and atoms of carbon
30 in equation (5) as suggested by the reviewer.

1   **Comment 11:** Equation 6- The symbol NCj is used to specify the same than the symbol n in

2   equation 3. Equation 6 is unnecessary to explain the evaluation methodology.

3   **Response:** We believe that equation (6) is necessary to explain how the calculations are

4   performed as it shows, explicitly, that CO_2 is selected as the reference gas for calculations;

5   which is not the only choice. For example, Figure 4 in our manuscript shows that CO or CH_4

6   would have been acceptable choices for the reference gas as well. Besides, as stated in the

7   previous response, our nomenclature follows that of Yokelson et al. (1999) who reported this

8   equation in their paper and we think it is necessary for transparently communicating the

9   methods we chose.

10   **Comment 12:** Equation 7- What is the meaning of EFN_2O/CO_2?

11   **Response:** This should read $ER_{N2O}/_{CO2}$. This typographical error has been corrected.

12   **Comment 13:** Table1- No specification about which data corresponds to which fire process

13   (heading/flanking/back). Define Byram fire line intensity.

14   **Response:** We added fire spread mode and fuel moisture content as two extra columns to this

15   table. We have also defined Byram fireline intensity in the caption to Table 1.

16   **Comment 14:** Figure 5- The colors for lines representing flanking and backfires are difficult

17   to discriminate.

18   **Response:** We have halved the font size of each experimental fire to make it more readable.

19   **Comment 15:** Lines 19-25, page 23138- I did not understand this discussion. As far as I

20   understood from the experimental part, the humidity of the combustible was always the same.

21   So no influence of humidity variability on emissions could be detected because there was no

22   humidity variability.

23   **Response:** It is the moisture content of the fuel and not the atmospheric humidity which we

24   were trying to control. If we had significant variation in the fuel moisture content this would

25   have added extra (unwanted) variability to our data. As stated on lines 1-2 page 23131 (and

26   from column two in the revised version of Table 1) we achieved fuel moisture contents

27   between 4.6-6.8% after oven drying. As a result, there was still some variability in fuel

28   moisture for different experimental fires. Therefore, fuel moisture was not a "fixed" quantity

29   as suggested by the reviewer. The fact that there was still some residual variation in fuel

30   moisture content motivated us to statistically test for whether this subtle variation in fuel

moisture content influenced emissions factors. On lines 19-25 page 23138 we merely state that the covariate (i.e. fuel moisture content) did not affect emission factors with a p value of 0.60 (a highly non-significant result). In summary, we thought it would be better scientific practice to measure fuel moisture content for every burn and to statistically test for its impact on emissions factors, rather than to assume it was not a source of variation.

Comment 16: Section 4.1 is confusing because it is not clear which definition of EF is being discussed at each moment.

Response: We have added three extra sentences to the start of section 4.2 (in the revised manuscript) to remedy any potential confusion as to which emissions factor reporting method we are referring to. These three new sentences read: "In this section, we discuss a comparison between the two methods for reporting emission factors which are both based on a carbon mass balance approach (see section 2.4.1). As such, we switch interchangeably between reporting on a per unit element burnt basis (i.e. either carbon or nitrogen) or a per unit dry fuel consumed basis. The relevant equation number or associated units are provided to make it clear which emissions factor reporting method we are using."

As stated in the last of these three sentences we provide equation numbers or units to make it clear which method of reporting emission factors we are using.

Comment 17: Section 4.2- I could not understand and follow most of this discussion that now uses Emission Factors in percentages, mixed with the previous definitions of EFs.

Response: Several changes to this section have been made to make it clearer which emissions factor reporting method we are using. In all four paragraphs of section 4.3 (in revised version of the manuscript), when the term "emissions factors" appears we have added extra detail in parentheses following this term to indicate which emissions factor reporting method we are using. In addition, on line 1 page 23143 the emissions factors (per unit element burnt) have been changed from ratios to percentages to provide a consistent method of reporting them throughout the manuscript.

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Greenhouse gas emissions from laboratory-scale fires in wildland fuels depend on fire spread mode and phase of combustion

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Abstract

~~Experimental~~ Free-burning experimental fires were conducted in a ~~combustion wind tunnel facility~~ wind tunnel to explore the role of ignition type and thus fire spread mode on the resulting emissions profile from combustion of fine ($\sim$< 6 mm in diameter) Eucalyptus litter fu-
els. Fires were burnt spreading with the wind (heading fire), perpendicular to the wind (flanking fire) and against the wind (backing fire). Greenhouse gas compounds (i.e. CO_2, CH_4 and N_2O) and CO were quantified using off-axis integrated-cavity-output spectroscopy ~~(off-axis ICOS). A dilution system was employed with the off-axis ICOS technique to prevent spectral broadening of the CO emissions peak and to enable simultaneous quantification of N_2O~~
~~and CO. The forward rate of spread was 20 times faster and the Byram fireline intensity~~
~~was 20 times higher for heading fires compared to flanking and backing fires.~~. Emissions factors calculated using a carbon mass balance technique (along with statistical testing) showed that most of the carbon was emitted as CO_2, with heading fires emitting 17% more CO_2 than flanking and 9.5% more CO_2 than backing fires, and about twice as much CO
as flanking and backing fires. Heading fires had less than half as much carbon remaining in combustion residues. Statistically significant differences in CH_4 and N_2O emissions factors were not found with respect to fire spread mode. Emissions factors calculated per unit of dry fuel consumed showed that combustion phase (i.e. flaming or smouldering) had a statistically significant impact, with CO and N_2O emissions increasing during smouldering
combustion and CO_2 emissions factors decreasing. Findings on the equivalence of different emissions factor reporting methods are discussed along with the impact of our results for emissions accounting. The primary implication of this study is that prescribed fire practices ~~might~~ could be modified to mitigate greenhouse gas emissions from ~~forested landscapes by the preferential application of~~ forests by judicial use of ignition methods to induce flanking
and backing fires over heading fires. ~~Future research could involve wind tunnel testing with more realistic fuel architectures and could also quantify particulate emissions with different fire spread modes.~~

2

1 Introduction

Wildfires emit a variety of pollutants to the atmosphere which have impacts on global warming, biogeochemical cycles, ambient air quality and human health (Mack et al., 2011; Monks et al., 2009; Weinhold, 2011). Globally, wildfires contribute approximately 23% of
5 total anthropogenic greenhouse gas equivalent emissions (Houghton et al., 2009; van der Werf et al., 2010) although there can be significant year-to-year variability. Furthermore, increases in wildfire occurrence have been observed in many parts of the world during the last decade, including the Western United States (Running, 2006), the Mediterranean region (Portugal, Spain and Greece) (Vicente et al., 2011) and Australia (Cai et al., 2009).
10 The main greenhouse gas species of interest emitted by wildfire include CO_2, CH_4 and N_2O. Wildfires also emit particulate matter (PM) to the atmosphere that has an impact on climate due to its ability to absorb and scatter light (Reid et al., 2005). In addition, the effect of wildfire PM on the aerosol indirect effect (i.e. cloud formation) remains poorly quantified at present (Bowman et al., 2009).
15 Despite considerable progress since the pioneering works on ~~biomass burning emissions~~ emissions from biomass burning by Crutzen et al. (1979), and Seiler and Crutzen (1980), only recently has the chemical composition of biomass burning smoke been quantified in ~~significant~~ detail. Yokelson et al. (2013) deployed a Fourier Transform Infra-Red Spectrometer (FTIR) and a range of different mass spectrometry systems to quantify 204 trace gas
20 species, with a further 153 species being quantified but not able to be identified from the resulting mass spectra. Most of these compounds were non-methane hydrocarbons which play a role in ozone and secondary organic aerosol formation (Akagi et al., 2011). Based on this work there now appears to be ~~state-of-the-art~~ detailed knowledge on the chemical composition of ~~biomass burning smoke~~ smoke from biomass burning from fuels located in
25 the south-east and south-west of the United States~~; however~~. Despite this new knowledge, measurements of N_2O emissions from biomass burning ~~(such as those made in the current study)~~ are not commonly reported (Meyer and Cook, 2015, In press).

3

~~It is known that sections of wildfire~~ The various sections of free-burning wildland fire perimeters propagate with three ~~different orientations with respect~~ distinct orientations in response to the prevailing wind direction. Fire perimeters can propagate with the wind (i.e. a heading fire) against the wind (i.e. a backing fire) and ~~they can also spread~~ perpendicular to the wind (i.e. a flanking fire) (Sullivan et al., 2012). The ~~key observation is that the~~

5   individual fire spread modes (i.e. heading, flanking and backing) within a larger overall fire exhibit different fire ~~behaviour~~ behavior (such as different rates of spread, flame heights, combustion factors and fireline intensities) which could lead to differences in emissions with respect to fire spread mode ~~.~~ (Sullivan and Ball, 2012) .

Laboratory experiments testing the role of fire spread mode on fire ~~behaviour~~ behavior

10 and emissions have been conducted ~~once before~~ previously with Keene et al. (2006) referring to flanking fires as mixed combustion fires. Keene et al. reported differences in modified combustion efficiency (MCE) with different fire spread modes and report higher emissions factors for acetic acid (CH_3COOH) for heading and flanking fires compared to backing fires.

~~The~~ However, the only greenhouse gas compound measured in the study of Keene et al.

15 was CO_2~~; however,~~, although, detailed particulate emissions measurements were made.

In this study, we ~~revisit~~ re-examine the burning methodology of Keene et al. in a controlled laboratory study ~~with~~ involving a free-moving fire. We developed an explicit experimental design combined with statistical testing of results ~~for significance. As such, examining~~ to examine the hypothesis that greenhouse gas emissions could depend on fire spread

20 mode~~is the major focus of this article. Testing this~~ . The validity of this hypothesis has the implication that if emissions were dependent on fire spread mode, opportunities could open up to dramatically improve the precision with which greenhouse gas estimates of wildfire events are made and, perhaps more importantly, to strategically manage prescribed burning operations in forested landscapes to minimise greenhouse gas emissions by changing

25 the applied fire spread mode of such fires.

In this study, the impact of fire spread mode on greenhouse gas (CO_2, CH_4, N_2O) emissions (plus CO) profiles from the combustion of dry eucalypt forest litter was tested in a combustion wind tunnel facility. Dry eucalypt forest fuel was selected for this study as it is

4

the dominant flora of south-eastern Australia with this region being representative of fire activity in Australian temperate forests. Emissions estimates derived from this study build upon previous research efforts undertaken globally in temperate forest, where it is noted that emissions estimates from this ecological biome are rare in Australia (van Leeuwen and van der Werf, 2011).

5   In addition to testing the role of fire spread mode (i.e. heading, flanking and backing) on greenhouse gas emissions, the role of combustion phase (i.e. flaming or smouldering) and the temporal progression of emissions factors during a complete fire are explicitly tested ~~in the experimental design~~ with appropriate statistical methods. We also report findings on different methods for reporting emission factors and demonstrate the impact of our results

10   with reference to greenhouse gas emissions accounting from prescribed burning in Australia. Overall, the results from this study provide a new body of information on biomass burning emission estimates from a region that has been poorly characterised in the past.

2   Methodology

2.1   Combustion wind tunnel details

15 Experiments were conducted in the CSIRO Pyrotron (see Fig. 1) which is a 25.6 ~~m~~ m long combustion wind tunnel facility designed to investigate the behaviour and emissions of laboratory-scale fires ~~(?)~~ (Sullivan et al., 2013) . Wind for experiments is generated upstream from the working section by a 1.372 ~~m~~ m diameter centrifugal fan (model 54LSW) from Fans and Blowers Australia Pty Ltd. Positioned downstream of the fan in the settling

20 section are four perforated screens and a flow straightener for removing as much turbulence from the air stream as possible (turbulence intensity < 0.6%) ~~(?)~~ (Sullivan et al., 2013) . The working section, where fuel is placed for experimental burns and where combustion takes place, is 1.5 ~~m^{-1}~~ m wide and 4.8 m long. Gas phase emissions samples were obtained from the exit section of the wind tunnel, downstream of the working section. Two 12.7 ~~mm~~ mm di-

25 ameter stainless steel tubes positioned at a height of 840 mm above the floor of the combus-

tion wind tunnel were used to sample gas and particle phase samples separately. An array of K type thermocouples are positioned on the floor of the CSIRO Pyrotron with a spacing of 500 mm in the direction of wind flow with a least 11 thermocouples spanning the width of the working section to record temperatures at the flame base (Sullivan et al., 2013). The design of the CSIRO Pyrotron enables sampling from the plume of a low intensity
5 free-moving fire, driven by the wind, which may be contrasted with the approaches used by, for example, Lobert et al. (1990), McMeeking et al. (2009) and Jenkins et al. (1993) which all involve stack sampling without capturing either the free-moving or wind-driven characteristics of wildland fires.

2.2 Fuel collection and preparation

10 Forest litter fuel was collected from Kowen Forest in the north-east of the Australian Capital Territory (ACT), Australia during late summer (see Fig. 2), in a stand dominated by *Eucalyptus macrorhyncha* (F. Muell.) and *E. rossii* (R.T. Bak. & H.G. Sm.). The fine fuel (< 6 mm diameter) litter layer was collected because it is the primary fuel layer combusted during forest fires in south-eastern Australia (Sullivan et al., 2012) and was comprised of leaf,
15 bark and twig components. An attempt was made during the fuel collection not to include coarse fuel elements (such as large pieces of bark, twigs, logs and branches) greater than 6 mm in diameter. ~~After fuel collection, it was sieved~~ Fuel was sieved after collection to remove coarse fuel fractions that were not removed in the field. Fuel sieving also removed fragmented material from the soil fermentation layer which can affect the ability of a fire to
20 propagate and its combustion phase.

A dry fine fuel load of 1.1 $kg\,m^{-2}$ (or 11 $t\,ha^{-1}$) was used which is typical of dry sclerophyll forest and is equivalent to that experienced during a major Australian wildfire (the 2009 Kilmore East fire) in dry sclerophyll forest (with a low understorey) in Victoria (Cruz et al., 2012)). The moisture content of the fuel was measured prior to weighing to ensure that the
25 correct dry fuel weight was achieved. Fuel moisture measurements before fuel drying were performed with a Wiltronics fine fuel moisture meter (Chatto and Tolhurst, 1997) which uses the electrical resistance of a plant sample to measure its water content.

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After weighing out the fuel with ambient moisture content it was dried in an oven at 50°C for 24 hours to reduce the fuel moisture content to a level typical of that for fine fuels during major Australian wildfires (< 5% oven-dry weight) (Cruz et al., 2012; McArthur, 1967; Sullivan and Matthews, 2013). Prior to each experimental burn, three to five ~~samples~~ sub-samples were collected in tins from the fuel bed to measure the fuel moisture con-
5 tent. The tins were oven-dried at 105°C for 24 hours (Matthews, 2010) with fuel moisture contents between 4.6–6.8% being achieved (see Table 1).

Fuel was spread in the working section of the wind tunnel to make the fuel bed as homogeneous as possible in terms of depth and the structural arrangement of leaf, bark and twig components. Mean fuel depths were between 24.2 and 33.6 mm for the experimental
10 fires. Three unburnt fuel samples were sorted and weighed throughout the course of the experiment to establish the relative proportions of leaf ~~, bark and twig components. Based on this sampling, the mean fuel composition was~~ (23.2% ~~leaf material,~~), bark (28.6% ~~bark material and~~) and twig (48.2% ~~twig material~~) components. The size of the fuel bed was 6 m^2 (4 m × 1.5 m) for heading fires and 2.25 m^2 (1.5 m × 1.5 m) for flanking and backing
15 fires.

Fires were ignited using a 1.5 m channel filled with ethanol (60 ml volume), which was placed in a different position (relative to the air flow) for each fire spread mode and lit with a gas lighter. Each fire spread mode was replicated six times (with the level of replication being based on Mulvaney (2012) ~~and ?)~~ to enable the experimental uncertainty to be re-
20 duced to a satisfactory level. This level of replication resulted in a total of 18 fires. A wind speed of 1.5 m s^{-1} was used in all fire experiments. Altogether, the selection of fuel loads, fuel moisture content and wind speed were selected to achieve Byram fireline intensities (Byram, 1959) (which is the product of the lower heating value of the fuel, fuel consumed and the forward rate of spread) indicative of those during prescribed burning conditions in
25 temperate eucalypt forest in Australia (i.e. approximately < 500 kW m^{-1} (Cheney, 1981) or approximately < 345 kW m^{-1} (McArthur, 1962)).

2.3 Emissions measurements

Gas phase measurements were performed using off-axis ~~ICOS~~integrated-cavity-output spectroscopy (off-axis ICOS), a laser-based absorption technique used in commercially available instruments from Los Gatos Research (http: //www.lgrinc.com/). One instrument measured CO_2/CH_4 (Greenhouse Gas Analyser GGA-24r-EP) and the other measured N_2O/CO (N_2O/CO Analyser 907-0015) with both instruments operating in slow flow mode. The method works

[5] by directing a laser beam into an optical cavity equipped with high reflectivity dielectric coated mirrors (with mirror losses around 100 ppm capable of being achieved) (Baer et al., 2002). The absorption signal is determined by the temporal decay (or 'ringdown') of the light transmitted through the cavity due to absorption (based on the Beer-Lambert law) which is modelled as an exponential decay process (O'Keefe and Deacon, 1988).

[10] Due to the highly reflective nature of the mirrors, optical path lengths of several kilometres can be achieved, making the technique highly suited for the detection of trace gas species (Baer et al., 2002). Off-axis ICOS is a relatively new method in cavity ring down spectroscopy that is simpler to operate as the optical alignment of the laser beam with respect to the optical cavity does not need to be mode-matched (Baer et al., 2002). Both

[15] instruments collected data with a 1 Hz sampling frequency. Particle phase emissions measurements were also made during experiments, but we reserve the presentation of those results for a future publication.

For gas ~~phase~~ measurements, the sample flow was diluted with zero air (i.e. 20.5% O_2 in N_2) to enable simultaneous quantification of N_2O and CO. During calibrations (Fig. 3)

[20] there was spectral broadening of the CO absorbance peak with smouldering combustion (CO concentrations in excess of 10 ppm) which prevented the N_2O absorbance peak from being quantified accurately. To keep the CO concentration below 10 ppm and prevent the spectral broadening, a dilution ratio between 5.7 and 6.0 for flanking and backing fires and between 5.9 and 10.7 for heading fires were used. Heading fires required the initial dilution ratio to be increased during the experiment which is why these dilution ratios are greater than those for flanking and backing fires.

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Calibration of the N_2O/CO instrument (before and after experiments) against bottled CO gas gave coefficients of determination of 0.9993 and 0.9996 based on a linear fit between the measured CO concentration and the concentration provided by the calibration system, with slopes of these linear fits being 0.94 and 1.07. Overall, the calibrations performed before and after experiments confirmed the linear response and accuracy of the off-axis ICOS technique.

2.4 Data analysis

2.4.1 Calculation of emissions factors

Emissions ratios are widely used in biomass burning ~~science~~ research to rectify the problems associated with plume sampling in environments subject to variable levels of dilution (Le Canut et al., 1996) and as such are used as an input to enable the calculation of emission factors. An emissions ratio (ER) is calculated via the following equation (Levine and Cofer III, 2000):

$$ER = \frac{\Delta X}{\Delta \text{Reference Gas}}, \tag{1}$$

where X is the gas of interest, the reference gas is usually either CO or CO_2 (although CH_4 is sometimes used), and Δ is the excess mixing ratio which denotes that the smoke-free ambient concentration is subtracted from the plume concentration (i.e. $\Delta X = X_{plume} - X_{ambient}$).

The selection of the reference gas is based on the quality of a linear fit between excess mixing ratios of the gas of interest (Y axis) and the reference gas (X axis). The slope of the resulting linear fit therefore provides another method for quantifying an emissions ratio. Figure 4 shows correlation plots for incomplete combustion products using either CO_2, CO, or CH_4 as a reference gas. The best linear fit was obtained for CH_4 using CO as a reference gas (R^2=0.942) and by using CH_4 as a reference gas for N_2O emissions (R^2=0.822). Overall, the degree of fit with all three reference gases was similar, so CO_2 was used as a

reference gas since it is the dominant carbon-containing compound in the plume and it is also a relatively simple gas to measure (Levine and Cofer III, 2000).

A carbon mass balance approach developed by Radke et al. (1988), and applied (for example) by Lobert et al. (1990), Hurst et al. (1994a), Hurst et al. (1994b) and more recently by Meyer et al. (2012), was used to calculate emissions factors for different carbon- and nitrogen-based pollutants on a per unit element burnt basis. Calculating emissions factors this way enables the fraction of carbon (or nitrogen) emitted from different chemical compounds containing that element to be quantified. Using CO_2 as a reference gas for all carbon containing species, the emissions factor for carbon dioxide (EF_{CO_2}) is given by:

$$EF_{CO_2} = \frac{\frac{\sum C_{emit}}{C_{fuel}}}{1 + \frac{\Delta CO}{\Delta CO_2} + \frac{\Delta CH_4}{\Delta CO_2} + \frac{\Delta \sum NMHC}{\Delta CO_2} + \frac{\Delta PC}{\Delta CO_2}}, \tag{2}$$

where C_{emit} is the mass of carbon emitted to the atmosphere, C_{fuel} is the mass of ~~carbon exposed to fire~~fuel carbon burnt, NMHC represents the sum of all non-methane hydrocarbons, and PC represents particulate carbon. NMHC have not been quantified in the current study; however, to complete the calculation of emissions factors in the above equation, an NMHC emissions factor of 0.0091 has been used based on the fire emissions work of Hurst et al. (1994a) in Australian savanna's. Note that there are no published estimates of PC emissions factors in Australian temperate forest so this term has been removed from the calculation of emissions factors. Removing PC emissions factors from the calculation of emission factors would have a very marginal impact on the final results with an upwards bias of < 1–2% being likely (Yokelson et al., 1999).

To calculate carbon-based emission factors for compounds other than CO_2 the following equation was used:

$$EF_X = \frac{\Delta X}{CO_2} \frac{\Delta X}{\Delta CO_2} n EF_{CO_2}, \tag{3}$$

where n is the number of carbon atoms in the compound of interest.

10

By definition, the sum of all carbon-based emission factors equals the fraction of fuel carbon that is emitted to the atmosphere. This expression is given by:

$$\sum_X EF_X = \frac{\sum C_{emit}}{C_{fuel}}. \tag{4}$$

To estimate emissions factors for N_2O, the excess mixing ratio for N_2O is substituted into the numerator of equation (3) and is then divided by the molar nitrogen-to-carbon ratio of the fuel to account for the fact that every mole of N_2O has two moles of N. Performing this calculation makes nitrogen-based emission factors independent of the nitrogen content of the fuel (Hurst et al., 1994b). Nitrogen-to-carbon ratios (0.73%) were measured from unburnt fuel samples, consisting of leaf, bark and twig components, using Isotope Ratio Mass Spectrometry.

Whilst reporting emissions factors on a per unit element basis is common in inventory reporting, in atmospheric chemistry it is common to report emissions factors per unit of dry fuel consumed. The carbon mass balance method used to present emissions factors this way is discussed by Yokelson et al. (1999) and Paton-Walsh et al. (2014) and for carbon containing species is given by the following equation:

$$EF_i = F_c \times 1000 \times \frac{MM_i}{12} \times \frac{C_i}{C_T}, \tag{5}$$

where EF_i is the mass of compound i emitted per kg of dry fuel consumed, F_C is the fractional fuel carbon content (measured before burning: 51.6%0.516), 1000 is a units conversion factor (1000 g kg^{-1}), MM_i is the molecular mass of species i, 12 is the atomic mass of carbon, C_i/C_T is the number of moles of species i emitted divided by the total number of moles of carbon emitted.

When using CO_2 as a reference gas, C_i/C_T is given by:

$$\frac{C_i}{C_T} = \frac{\frac{\Delta C_i}{\Delta CO_2}}{\sum_j NC_j \frac{\Delta C_j}{\Delta CO_2}}, \tag{6}$$

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5 where ΔC_i and ΔC_j are the excess mixing ratios for species i and j and NC_j is the number of carbon atoms in species j.

To calculate N_2O emissions factors per unit of dry fuel consumed, the following equation (based on Andreae and Merlet (2001)) was used:

$$EF_{N_2O} = \underline{EF}\underline{ER}_{N_2O/CO_2} \times \frac{MM_{N_2O}}{MM_{CO_2}} \times EF_{CO_2}. \qquad (7)$$

10 This equation uses a molar emissions ratio for N_2O/CO_2, the CO_2 emissions factor and the respective molecular masses to calculate an emissions factor.

2.4.2 Other calculations

Time series data of excess mixing ratios was calculated by subtracting the diluted ambient readings for emissions before the test from the plume diluted concentrations, as the emis-
15 sions from the fire only (and not ambient air) were of interest. Concentrations were then multiplied by the dilution ratio to enable undiluted plume concentrations to be calculated.

Emissions factors reported on a per unit dry fuel consumed basis were estimated (using equation (5) for carbon containing species and equation (7) for N_2O) separately for the flaming and smouldering combustion phases of each fire. Furthermore, plotting the results
20 of equations (5) and (7) versus time enabled time series of emissions factors (g kg^{-1}) to be calculated.

2.4.3 Statistical analysis of data

Multivariate Analysis of Covariance (MANCOVA) was performed to test for the statistical significance of fire spread mode (a categorical factor) and fine fuel moisture content (a numerical covariate) on the emissions factors measured. The one-way MANCOVA analysis involved testing hypotheses related to a single categorical variable and a single numerical

covariate. The statistical models fitted to the data were of the following form:

$$Y_{ijk} = \underbrace{\mu}_{\substack{\text{Grand} \\ \text{mean}}} + \underbrace{\alpha_{ij}}_{\substack{\text{Treatment} \\ \text{effect}}} + \underbrace{\beta_{ij}}_{\substack{\text{Covariate} \\ \text{effect}}} + \underbrace{\epsilon_{ijk}}_{\text{Residual}}, \tag{8}$$

where Y_{ijk} is the response (i.e. the emissions factor) for the ith emissions species for the jth fire spread mode and for the kth replicate.

The null hypothesis (H_0) being tested for the categorical variable (fire spread mode) was:

$$H_0 : \mu_{iH} = \mu_{iF} = \mu_{iB} \text{ for } \forall \, i, \tag{9}$$

where H, F and B denote the levels of the fire spread mode factor (i.e. heading, flanking and backing fires).

This hypothesis states that different fire spread modes (i.e. heading, backing and flanking) do not lead to significant differences in emissions for all species investigated (i.e. CO_2, CO, CH_4, N_2O and residue carbon).

The alternative hypothesis (H_1) being tested was that at least one of the μ_{ij} comparisons in equation (9) were concluded to differ.

The null hypothesis being tested for the covariate (fine fuel moisture content) was:

$$H_0 : \beta_{iH} = \beta_{iF} = \beta_{iB} \text{ for } \forall \, i, \tag{10}$$

while the alternative hypothesis tested that at least one of the β_{ij} slope comparisons in equation (10) were concluded to differ.

In addition, Multivariate Analysis of Variance (MANOVA) was performed to test whether fire spread mode and combustion phase (i.e. flaming or smouldering combustion) had a statistically significant impact on emissions factors reported on a per unit dry fuel consumed basis. The statistical models fitted and hypotheses tested had the same structure as equation (8), except instead of having a single factor and a covariate, two categorical factors (i.e.

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fire spread mode and combustion phase) were fitted in this two-way MANOVA. All statistical tests were conducted using R v 3.03 and a significance level of 5% was used to determine statistical significance.

3 Results

Table 1 reports summary statistics from the fire experiments which shows that flanking and backing fires are quite similar in terms of their Byram fireline intensity (Byram, 1959), rate of spread and duration of smouldering combustion. Heading fires burnt about 20 times faster (~~in terms of~~ for rate of forward spread) and with approximately 20 times higher fireline intensity than flanking or backing fires. Furthermore, the duration of flaming combustion was about 75% less with heading fires and smouldering combustion was more than twice as long. Table 2 reports emissions factors for all four emissions species per unit dry fuel consumed.

Time series data for the excess mixing ratios of CO_2, CO, CH_4, and N_2O are shown in Fig. 5. The two most striking aspects are the relative magnitudes of the emissions peaks, and also differences in the combustion duration for different fire spread modes. Heading fires produced very pronounced peaks during flaming combustion for all emissions species considered, whereas flanking and backing fires exhibit less temporal variability in their emissions with less pronounced peaks. The temporal variability in emissions is very similar for flanking and backing fires.

Emissions factors for carbon- and nitrogen-based species using the carbon mass balance approach show that between 63–74% of fuel carbon is emitted to the atmosphere as CO_2, and about 5.7–13% is emitted as CO (Fig. 6), 0.36–0.53% as CH_4 and 0.35–0.57% of fuel nitrogen as N_2O (Fig. 6). For heading fires, the CO_2 emissions factor was about 17% greater than flanking fires and 9.5% higher than backing fires and CO emission factors were about twice as high for heading fires than for the other two fire spread modes. The fraction of unburnt and partially burnt fuel (residue) ranges from 12% of fuel carbon for heading fires up to 30% of fuel carbon for flanking fires. During some experiments, it was difficult to get

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flanking fires to propagate with a continuous flame front which offers an explanation for the greater production of combustion residue (due to patchiness) during these fires.

Statistical testing of the results with MANCOVA indicated that fine fuel moisture content (i.e. the covariate) did not have an impact on emissions factors ($p = 0.60$); however, fire spread mode was a statistically significant factor ($p < 0.0001$). Fire spread mode had a

5   statistically significant effect on CO_2 ($p < 0.0001$), CO ($p < 0.0001$) and carbon residue ~~emissions~~ production ($p < 0.0001$) but did not have a statistically significant effect on CH_4 ($p = 0.269$) or N_2O emissions ($p = 0.261$). Testing with pairwise comparisons showed that CO_2 emissions factors for all paired combinations of fire spread mode (i.e. heading versus backing, heading versus flanking and flanking versus backing) were statistically different (p

10   < 0.0001 for all comparisons). For CO emissions, heading versus backing and heading versus flanking emissions factors were statistically different ($p < 0.0001$ for all comparisons); however, flanking emissions factors were not statistically different to backing emissions factors ($p = 0.962$).

As shown previously (see Fig. 6), emissions factors for different chemical species varied

15   significantly with respect to fire spread mode. In addition, the different phases of combustion (e.g. flaming, smouldering, and glowing) during a fire have different fire behaviour and, therefore, potentially different emissions profiles (Lee et al., 2010). To test this hypothesis, emissions factors (per unit of dry fuel consumed) were calculated separately for flaming and smouldering phases for the 18 experimental fires (see Fig. 7). ~~The results~~ In this paragraph

20   we discuss the numerical trends found, whilst the next paragraph discusses testing of our results for statistical significance. Numerically, the results confirm that both CO and CH_4 emissions ~~ratios~~ factors were substantially increased during smouldering combustion. CO emissions factors ranged from 72–102 g kg^{-1} during flaming combustion and ranged from 189–221 g kg^{-1} during smouldering combustion. CH_4 emissions factors ranged from 2.4–

25   3.8 g kg^{-1} during flaming combustion and 5.0–10.5 g kg^{-1} during smouldering combustion. With more carbon being emitted as either CO or CH_4 during smouldering combustion, this led to decreases in the CO_2 emissions factor, with CO_2 emissions factors ranging from 1705–1750 g kg^{-1} during flaming combustion and from 1515–1550 g kg^{-1} during smoul-

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dering combustion. ~~Alternatively~~Numerically, N_2O emissions factors did not increase during smouldering combustion for heading fires but did increase for both backing and flanking fires.

The MANOVA analysis confirms that combustion phase ($p < 0.0001$) had a statistically significant impact on emissions factors (reported per unit of dry fuel consumed) and so did fire spread mode, but only for the heading fire versus flanking fire comparison ($p = 0.04$). CO_2 emissions factors were lower during smouldering combustion ($p < 0.0001$) whilst CO emissions factors were increased ($p < 0.0001$). CH_4 emissions factors did not exhibit statistically significant differences with respect to combustion phase ($p = 0.12$) but N_2O emissions factors did ($p = 0.04$). Whilst the non-significant result for CH_4 may appear to contradict the trends discussed in the previous paragraph, the CH_4 results are more variable which prevents a statistically significant result from being found. Furthermore, N_2O emissions factors exhibited a relationship with fire spread mode ($p = 6.5 \times 10^{-3}$) with heading fires producing less N_2O than flanking or backing fires.

Time resolved emissions factors (on a per dry fuel consumed basis) were calculated and are shown in Fig. 8. This graph shows that the CO_2 emissions factor peaks early in the burn during flaming combustion with a pronounced decrease (with an increase in CO) after the passage of the flame front through the fuel bed. CH_4 and CO emissions factors are quite low during flaming combustion, but increase significantly once smouldering combustion starts to dominate. N_2O emissions show a significant contribution from both flaming and smouldering combustion.

4 Discussion

4.1 Representativeness of combustion wind tunnel emissions measurements

Since emissions sampling was conducted at a single fixed height above the wind tunnel floor (see section 2.1), further analysis needs to be conducted to ensure the representativeness of measurements. If chemical reactions were still occurring at the axial position of sampling,

and if those reactions had a dependence on sampling height, then the emissions measurements obtained would not be representative of the entire plume. Here we calculate the reaction Damköhler number (Da) (Law, 2006, p. 189) which characterises the ratio of the flow time scale (τ_F) to the chemical reaction time scale (τ_C). The reaction Damköhler number is given by:

$$
\begin{aligned}
Da &\equiv \frac{\text{Characteristic flow time}}{\text{Characteristic reaction time}} \\
&\equiv \frac{\tau_F}{\tau_C} \\
&\equiv \frac{kL}{\overline{U}}
\end{aligned}
\tag{11}
$$

where τ_F is given by the characteristic length scale (L) divided by the characteristic velocity ($\overline{U}$) (Law, 2006) and τ_C is the reciprocal of the reaction rate (k). We choose L as the axial distance from the flame position to the sampling manifold (either 3.6 or 8.4 m), $\overline{U}$ as the mean wind speed employed during testing (1.5 m s^{-1}) with k given by the lumped kinetic scheme of Ranzi et al. (2008) , which describes the production of CO_2, CH_4 and CO (plus other carbon compounds) from biomass pyrolysis. We calculate k at two heights within the flame, with maximum temperatures at the flame base being based on those recorded by thermocouples on the CSIRO Pyrotron floor, whilst flame tip temperatures are based on measurements made in eucalypt shrubs by Wotton et al. (2012) . Calculation of the reaction Damköhler number enables us to assess how close the relevant chemical reactions are to equilibrium at two flame heights and axial positions within the flow, with the results of this calculation being shown in Table 3.

We see that the reaction Damköhler number depends on vertical position within the flame, with smaller Da being observed at the flame tip (i.e. 3.0×10^6) compared to the flame base (1.8×10^8–2.9×10^8). There is also variation in the Da observed with different fire spread modes which is due to differences in the maximum flame base temperature and the

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influence it has on reaction kinetics. Whilst we see variation in Da with respect to fire spread mode and vertical position within the flame, all of the Da exceed 10^6 (rounded to the nearest order of magnitude) which does not change the conclusion that the reactions are near equilibrium or "frozen" (Jenkins et al., 1993) . Hence, we can conclude from this analysis that our emissions sampling is representative of the entire plume since the timescale required for the relevant chemical reactions to occur is very short relative to the flow timescale.

4.2 Equivalence of emissions factor reporting

In this section, we discuss a comparison between the two methods for reporting emission factors which are both based on a carbon mass balance approach (see section 2.4.1). As such, we switch interchangeably between reporting on a per unit element burnt basis (i.e. either fuel carbon or nitrogen) or a per unit dry fuel consumed basis. For our purposes, we define 'burnt' as fuel that has been thermally altered as a result of exposure to fire and either emitted to the atmosphere or left in the post-fire residue. We define 'consumed' as that component of the fuel that is emitted to the atmosphere as a result of exposure to fire. The relevant equation number or associated units are provided to make it clear which emissions factor reporting method we are using.

Comparison of the emissions factors reported per unit element burnt (Fig. 6) with those reported per unit of dry fuel consumed (Table 2) led to the apparently anomalous conclusion that CO_2 emission factors are greater for flanking and backing fires; a result which directly contradicts those reported in Fig. 6. To properly resolve this apparent inconsistency, it is important to realise that emissions factors calculated using either equation (2) or (5) are only estimates and there are several sources of error. A source of error common to both equations (2) or (5) is the fact that arises because it is not possible to measure all the carbon compounds present in the smoke plume.

If carbon-based emissions factors were to be calculated using only CO_2, CO and CH_4 (which is a common approach), the total amount of carbon emitted would be underestimated by 1–2% due to omitting NMHC and by a further 1–2% for neglecting PC (Yokelson et al., 1999). The implication of not measuring all carbon emitted in the plume is that the

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emissions factor would be over-estimated. Further sources of error include estimating the carbon fraction deposited in ash ~~in~~ (equation (2)) and estimating the fuel carbon content before burning takes place ~~in~~ (equation (5)). In atmospheric chemistry studies it is common to assume a fuel carbon content of 50% (Paton-Walsh et al., 2014; Yokelson et al., 1999) whilst Hurst et al. (1996) assumed that 6% of fuel carbon was deposited in ash. In this study, both the fuel carbon fraction before burning and the fraction of carbon deposited in ash were measured, meaning that these sources of error have been eliminated from the analysis.

A further source of error which has received limited discussion in the literature relates to the equivalence of the methods described in equations (2) or (5). In particular, the calculation of total emissions from a fire should not depend on which metric is used to calculate emissions factors. The method described in equation (2) is commonly used in inventory reporting and is a ~~sound and~~ well-established methodology. In contrast, applying equation (5) to estimate total emissions would involve multiplying the area burnt, fuel load, combustion factor and emissions factor and would not report the same result as equation (2). The reason for this discrepancy is that the method described in equation (5) does not explicitly consider the fraction of total fuel carbon emitted to the atmosphere. Instead, this method implicitly assumes that all fuel carbon is emitted to the atmosphere.

Making the assumption that all fuel carbon is emitted to the atmosphere might be acceptable in the headfire of a high intensity wildfire; however, in the current work a significant fraction of fuel carbon (12–30%) is contained in the post-fire residue and furthermore displays a trend with respect to fire spread mode. As a result, in burning conditions representative of prescribed burning it is not acceptable to assume that all fuel carbon is emitted to the atmosphere and instead this fraction should be estimated, as recommended by Andreae and Merlet (2001) and as done in the current work. Multiplication of equation (5) by $\sum C_{emit}/C_{fuel}$ would enable the per unit dry fuel consumed method of reporting emissions factors to report the same total emissions as the per unit element burnt method. Performing this correction leads to the correct trend in CO_2 emission factors with respect to fire spread

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mode, with heading fires (1407 g kg^{-1}) emitting more CO_2 than flanking (1200 g kg^{-1}) or backing fires (1284 g kg^{-1}).

4.3 Comparison with field derived measurements

This emissions study was performed in a combustion wind tunnel facility with the relationship of the results obtained with those acquired in the field constituting a very important validation exercise. Recently Volkova et al. (2014) explored the relationship of fuel reduction burning on the carbon and greenhouse gas emissions from subsequent wildfire in temperate forest in Victoria, Australia. Measurements of CH_4 and N_2O emission factors over a very wide MCE range (0.7-1) were made during fuel reduction burning. ~~Our~~ The laboratory-derived CH_4 and N_2O emissions factors are in very good agreement with those measured by Volkova et al. who measured CH_4 emission factors (reported per unit element burnt) between 0.5-1.5% and N_2O emission factors between 0.4-1% over the MCE range relevant to the laboratory measurements (0.82-0.93).

Another valuable source of data for comparison is the dataset of Paton-Walsh et al. (2014) who recently measured trace gas emissions factors with an FTIR system during prescribed fires in temperate forests in New South Wales, Australia. Our CO_2 emissions factors (reported per unit of dry fuel consumed) are slightly smaller for heading fires ($\sim$1.5%) and are larger for flanking ($\sim$5%) and backing fires ($\sim$6%) compared to Paton-Walsh et al. Keeping in mind that emissions sampling from an active fire front will involve contributions from different fire spread modes (especially heading and flanking) makes the overall CO_2 emissions profile from our measurements consistent with those reported by Paton-Walsh et al.

Our CO emissions ~~measurements~~ factors (reported per unit of dry fuel consumed) are significantly higher for heading fires ($\sim$45%) due to significant smouldering after the progression of the flame front (see Fig. 8), but are lower for flanking ($\sim$17%) and backing fires ($\sim$19%). Our CH_4 emission factors (reported per unit of dry fuel consumed) are higher for heading (20%) and flanking ($\sim$23%) fires but are slightly lower for backing ($\sim$6%) fires. Increases in ~~the~~ our CH_4 and CO emissions factors are consistent with sampling at a lower

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MCE in the combustion wind tunnel compared to the results of Paton-Walsh et al. Our MCE range was 0.82–0.93, whereas the recommended emissions factors reported by Paton-Walsh et al. are based on an MCE average of 0.90. In contrast ~~the~~ our N_2O emissions factors (reported per unit of dry fuel consumed) are lower for heading (~41%), flanking
5 (22%) and backing (~57%) compared to Paton-Walsh et al.

The only other published estimates of greenhouse gas emissions from temperate forest fires in Australia are those of Hurst et al. (1996) who measured CO_2, CO and CH_4 emission factors for two wildfires in the Sydney region in February 1991, another wildfire in January 1994 and also a prescribed fire in March 1994. Averaged over four fires, they measured
10 emission factors ~~of 0.85~~ (reported per unit element burnt) of 85% for CO_2, ~~0.091~~ 9.1% for CO and ~~0.0054~~ 0.54% for CH_4. They did not measure fuel consumption; however, the production of ash was assumed to be 6% of total fuel carbon. As seen from Fig. 6, the post-burn residue fraction in our study was much larger than that reported by Hurst et al. (1996), which places an upper limit on how much fuel carbon can be released as CO_2. As a
15 result, CO_2 emissions factors measured by Hurst et al. are substantially higher than those we measured; however our range of CO emissions factors was similar to those reported by Hurst et al. CH_4 emission factors for heading fires were very similar in magnitude to those reported by Hurst et al. with CH_4 emissions factors from flanking and backing fires being slightly less than those from heading fires. ~~Despite some differences,~~ Therefore, based on
20 comparison of our results with three field sampling studies suggests that the design of the CSIRO Pyrotron has successfully captured the combustion and emissions dynamics that typically occur under prescribed burning conditions.

4.4 A comment on N_2O emissions production

As highlighted by van Leeuwen et al. (2013), exploring the temporal variability of emissions
25 factors from biomass burning is an important consideration but is rarely undertaken. Despite reports in the literature of N_2O emissions factors being dominant in flaming combustion (Lobert et al., 1990; Urbanski, 2013), there is strong evidence from Fig. 8 of contributions to N_2O emissions from both flaming and smouldering combustion. This fact is evident from Fig.

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8B̶ b̲ by looking at the limited temporal variability in the N_2O emissions factor (with respect to time) compared to other emissions species. Clearly further measurements and modelling
5 work is required to develop a mechanistic understanding of N_2O emissions production from fire.

4.5 Implications for carbon accounting and sequestration

The results from this study have implications for both the mitigation of greenhouse gas emissions from fire and also carbon accounting methods which we discuss with reference
10 to prescribed burning in Victoria. The Royal Commission into the 2009 bushfires in Victoria recommended that 5% of Victoria's public land (approximately 390 000 hectares) should be burnt by prescribed fires each year to reduce the risk of bushfires (Teague et al., 2010). Using state-based and country specific data from Australia's National Inventory System (Commonwealth of Australia, 2014) it is estimated that 5630 Gigagrams (Gg) of CO_2 equiv-
15 alent (CO_2-e) emissions would be emitted from the burning of 390 000 hectares. Using the emission and combustion factors derived from our experimental study (as an estimate of prescribed burning emission and combustion factors) and keeping all other inputs fixed yields estimates of: 5640 Gg of CO_2-e emissions if all the area is burnt by heading fire, 4200 Gg CO_2-e if burnt by flanking fire and 4990 Gg CO_2-e if burnt as a backing fire. Whilst
20 it would not be possible to apply a single fire spread mode to a forested landscape in a prescribed fire situation, ignition patterns are practised in Victoria which enable a single fire spread mode to predominate (Tolhurst and Cheney, 1999) , such as the three investigated in this study.

This calculation suggests that the preferential application of flanking fires over heading
25 fires during prescribed burning operations would save approximately 1280 Gg of CO_2 emissions with 420 Gg being saved with backing fires. In addition, the application of flanking fires would leave an extra 265 Gg of carbon as a post-fire combustion residue (compared to heading fires) and backing fires would leave an extra 250 Gg; preventing further carbon emissions to the atmosphere. A further benefit to the application of non-heading fires during prescribed burning would be a reduction in CO emissions, which are implicated in respira-

tory health effects, with flanking fires emitting 330 Gg less CO (compared to heading fires)
and backing fires emitting 290 Gg less.

In addition, the results have implications for carbon accounting methods considering that
the Australia's National Inventory System does not currently discriminate between types of
fire other than whether they are prescribed or wildfires. Given that, compared with heading
fires, CO_2-e emissions are about 26% lower for flanking fires and 11% lower for backing
fires, there is potentially scope for more accurate greenhouse inventory reporting by taking
into account the mode of fire spread.

5 Conclusions

This study has explored the hypothesis (which was formulated and tested statistically) that
fire spread mode and phase of combustion could lead to differences in emission factors of
greenhouse gases from laboratory-scale fires conducted in a wind tunnel facility. We found
that both fire spread mode and combustion phase had statistically significant impacts on
emissions of greenhouse gases. Furthermore, the temporal progression of emission factors
were markedly different for the three different fire spread modes.

In particular, we found that flanking and backing fires emitted less CO_2 and CO than
heading fires and had more carbon remaining in combustion residues on a per unit car-
bon basis. These results have direct relevance to the management of forested landscapes
that are affected by fire. Given the lower magnitude of greenhouse emissions species from
flanking and backing fires this (potentially) opens up an opportunity to reduce carbon emis-
sions from fire by the strategic use of these fire spread modes over heading fires. Future
research activities could involve investigating greenhouse gas emissions for different fire
spread modes but with more strata in the fuel bed which would better represent the way in
which forest fuels burn in the field. In addition, the measurement of particulate emissions
factors continues to be a significant avenue for future research.

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Author contributions

All authors were involved in the experimental design. NCS, ALS and SHR performed the experiments with guidance from PJP. NCS performed the data analysis with input from ALS
10 and CPM. NCS prepared the manuscript with contributions from all co-authors.

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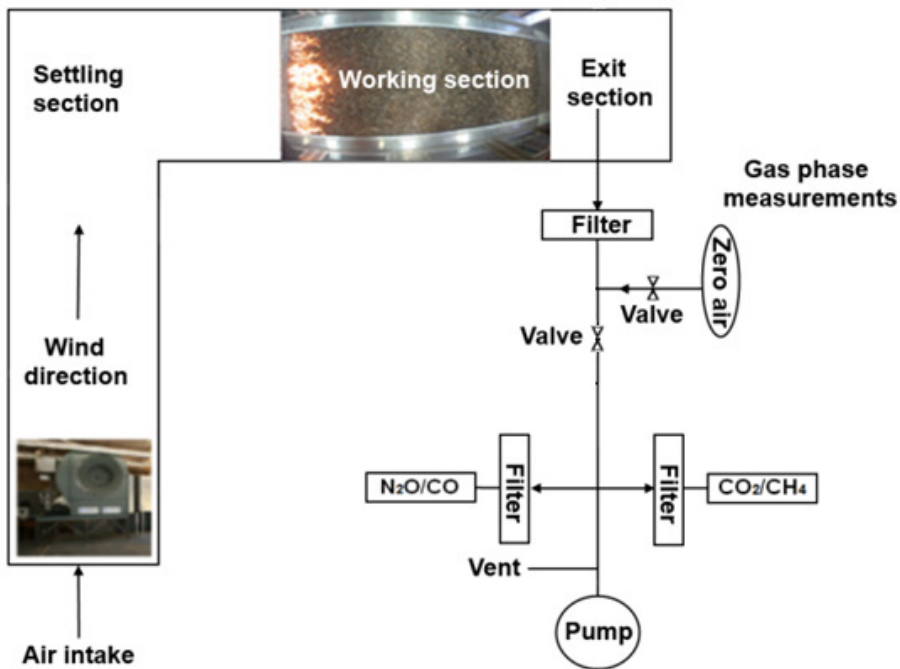
29

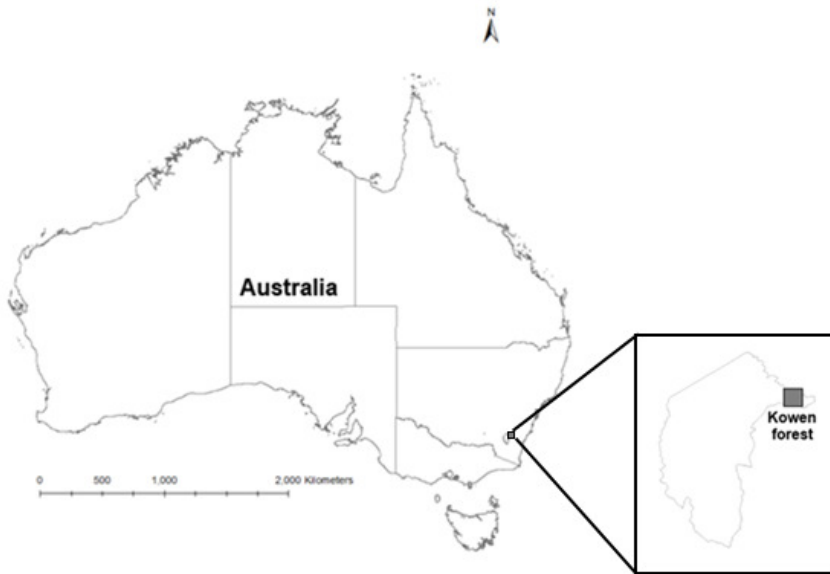**Figure 1.** A schematic (not to scale) of the experimental configuration used in the CSIRO Pyrotron for experimental fires.

Figure 2. Location of the dry sclerophyll eucalypt forest for collection of litter (35° 19' 30.07" S, 149° 15' 25.64" E). Shapefile of Australia sourced from Department of Agriculture (2014).
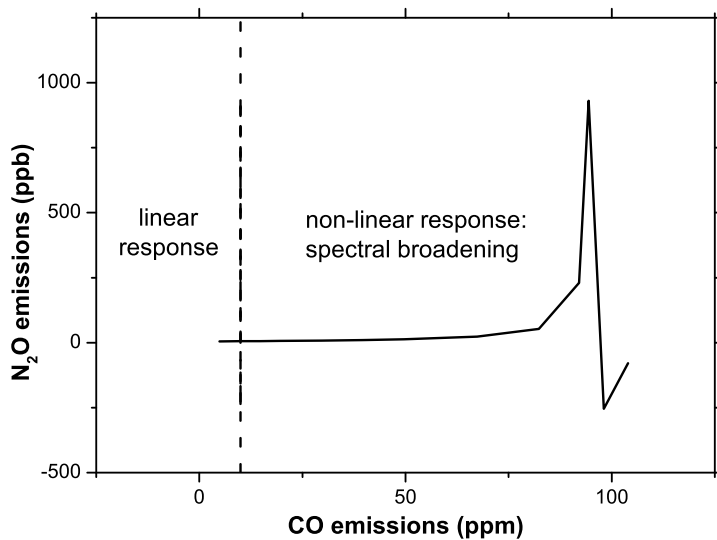
Figure 3. A graph of the interaction between N_2O and CO emissions measurements during routine calibrations which necessitated the use of a dilution system.
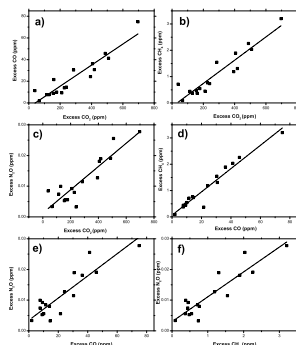
Figure 4. Linear fits of excess mixing ratios <u>for all 18 experimental fires</u> (not corrected for the overall dilution ratio) using either CO_2, CO or CH_4 as a reference gas. ~~A~~a): CO plotted against CO_2 (R^2=0.872, CO=-3.99+0.097CO_2). ~~B~~b): CH_4 plotted against CO_2 (R^2=0.871, CH_4=-0.14+0.0044CO_2). ~~C~~c): N_2O plotted against CO_2 (R^2=0.811, N_2O=0.0012+3.79$\times10^{-5}CO_2$). ~~D~~d): CH_4 plotted against CO (R^2=0.942, CH_4=-0.066+0.044CO). ~~E~~e): N_2O plotted against CO (R^2=0.788, N_2O=0.0035+3.61$\times10^{-4}$CO). ~~F~~f): N_2O plotted against CH_4 (R^2=0.822, N_2O=0.0030+0.0081CH_4).

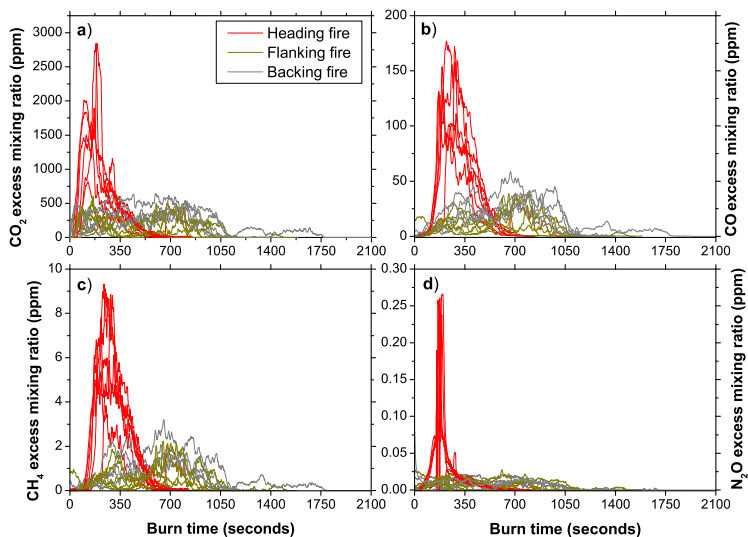**Figure 5.** Time series of excess mixing ratios for different emissions species and three different fire spread modes Aa): CO_2. Bb): CO. Cc): CH_4. Dd): N_2O. Note that each line of a particular colour represents one experimental replicate.
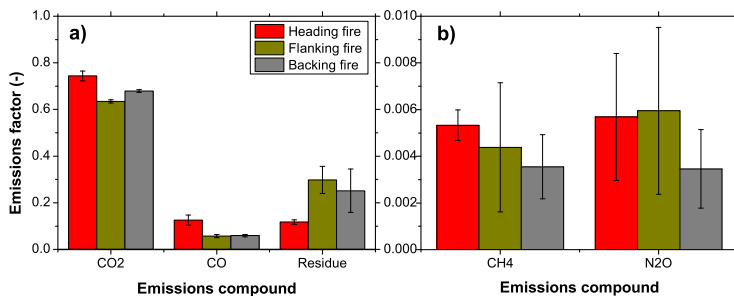
Figure 6. Carbon and nitrogen based emissions factors (per unit of carbon or nitrogen burnt) from the experimental burns. Aa): CO_2, CO and residue carbon emission factors. Bb): CH_4 and N_2O emission factors.
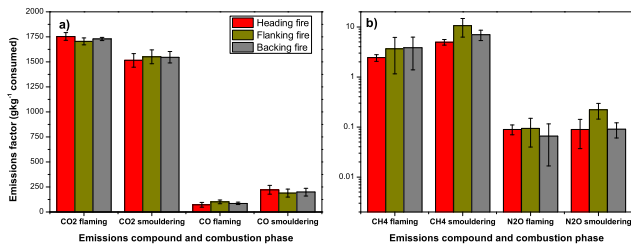
Figure 7. Carbon and nitrogen based emissions factors (per unit of dry matter burnt) for different combustion phases within the experimental burns. Aa): CO_2 and CO emission factors for flaming and smouldering combustion. Bb): CH_4 and N_2O emission factors for flaming and smouldering combustion.
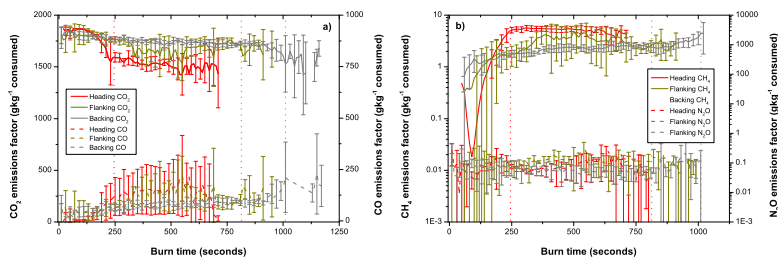
Figure 8. Time resolved emissions factors for the trace gas emissions species measured during the experimental burns. Aa): time resolved CO_2 and CO emissions factors. Bb): time resolved CH_4 and N_2O emissions factors. Coloured vertical and dotted bars represent the median end time for predominantly flaming combustion for each fire spread mode.

Table 1. Summary data from the fire experiments. Values are reported as the mean with the range reported as: (minimum value–maximum value). Byram fireline intensity is the product of the lower heating value of the fuel (kJ kg^{-1}), fuel consumed (kg m^{-2}) and the forward rate of spread (m s^{-1}) Byram (1959).

Fire spread mode	Fuel moisture content (%)	Fire duration (s)	Flaming combustion duration (s)	Smouldering combustion duration (s)	Rate of spread (m h^{-1})	Combustion factor (-)	Residue carbon content (%)	Byram fireline intensity (kW m^{-1})
Heading	5.6 (5.0–6.8)	715 (580–840)	256 (224–290)	459 (356–582)	123 (103–150)	81.8 (77.7–84.4)	33.3 (29.4–66.2)	553 (462–693)
Flanking	5.6 (5.1–6.2)	1085 (900–1530)	907 (763–1099)	178 (93–431)	6.6 (4.9–8.2)	71.6 (61.3–81.7)	54.0 (39.2–67.7)	26 (17–32)
Backing	5.4 (4.6–6.5)	1413 (1160–2230)	1196 (867–1988)	218 (72–533)	6.1 (4.2–7.5)	82.2 (77.3–86.4)	72.8 (34.8–78.9)	27 (20–32)

Table 2. Emissions factors ($\pm$ one standard deviation) for emissions species reported on a per unit of dry fuel burnt basis.

Data source	CO_2 (g kg^{-1})	CO (g kg^{-1})	CH_4 (g kg^{-1})	N_2O (g kg^{-1})
Heading fires (this study)	1594 ± 46	172 ± 30	4.2 ± 0.5	0.089 ± 0.043
Flanking fires (this study)	1709 ± 18	98 ± 11	4.3 ± 2.7	0.117 ± 0.071
Backing fires (this study)	1716 ± 14	95 ± 9	3.3 ± 1.3	0.064 ± 0.031
Andreae and Merlet (2001)	1569 ± 131	107 ± 37	4.7 ± 1.9	0.26 ± 0.07
Akagi et al. (2011)	1637 ± 71	89 ± 32	3.9 ± 2.4	0.16 ± 0.21
Paton-Walsh et al. (2014)	1620 ± 30	118 ± 16	3.5 ± 1.1	0.15 ± 0.09

Table 3. Calculation of the reaction Damköhler number (Da) for several axial positions and flame heights within the flame.

Fire spread mode	$T_{\text{flame tip}}$ (K)	$T_{\text{flame base}}$ (K)	τ_F (s)	$\tau_{C_{\text{flame-tip}}}$	$\tau_{C_{\text{flame-base}}}$	$Da_{\text{flame-tip}}$	$Da_{\text{flame-base}}$
Heading	540	1170	5.6	8.0×10^{-7}	2.2×10^{-8}	7.0×10^{6}	2.6×10^{8}
Heading	540	1170	2.4	8.0×10^{-7}	2.2×10^{-8}	3.0×10^{6}	1.1×10^{8}
Flanking	540	1050	5.6	8.0×10^{-7}	3.1×10^{-8}	7.0×10^{6}	1.8×10^{8}
Flanking	540	1050	2.4	8.0×10^{-7}	3.1×10^{-8}	3.0×10^{6}	7.7×10^{7}
Backing	540	1220	5.6	8.0×10^{-7}	1.9×10^{-8}	7.0×10^{6}	2.9×10^{8}
Backing	540	1220	2.4	8.0×10^{-7}	1.9×10^{-8}	3.0×10^{6}	1.3×10^{8}