Author Response

We thank the reviewer for the very helpful suggestions and additional references which in almost all cases have been incorporated into the manuscript

After encouragement from both reviewers we decided to calculate Emission Factors (EF) using the carbon mass balance and we have reported EF using this method in the manuscript. This method gives modified combustion efficiencies (MCEs) which are realistic for this type of fire (as pointed out by Reviewer 1) and gives EF that are approx 50% higher than those calculated using our original method, which as Reviewer 2 pointed out had uncertainty regarding the selected EF for CO. We have included the original EF in supplementary material so that the EF calculated using both methods can be compared if desired. A description and justification for use of the Carbon Mass Balance Method is given in Section 3.2.5.

Responses to specific reviewer comments are given below.

Anonymous Reviewer #1

The paper presents high-quality, opportunistic measurements of a heathland fire that impacted a measurement station at Cape Grim in the Australian State of Tasmania.While only one fire was sampled, it was sampled for almost 14 hours (split out over two occasions over several days) and also sampled when the smoke mixed with somewhat aged urban emissions for an additional period of hours. Thus, it provides an interesting case study of a rarely-sampled fire type and of urban/BB mixing. I recommend publication in ACP, but suggest a tighter focus on biomass burning and source mixing and that some of the data discussion (especially about particle growth during BB1-B) be moved to a planned companion paper where it might be treated more thoroughly. Unless some simple, brief text can be added to make the interpretation of BB1-B and some other periods completely obvious, it is better not to lengthen this paper inconclusively and instead discuss all the possibilities aided by a model in the companion paper

>as suggested we have removed discussion surrounding the drivers of particle growth during BB1-B. Section 3.1.3 (“Discussion – determination of drivers of O3 formation and particle growth in BB event 1’) has been removed from the manuscript. We have modified and clarified our description of BB1-B in section 3.1.1 to remove any speculative discussion. This tightens the focus of the paper significantly.

I also think that the authors could at least attempt calculating emission factors using the carbon mass balance method for comparison (at least in the supplement).

>As suggested by both reviewers we have calculated emission factors using the carbon mass balance method (section 3.2.5 and Table 3). After considering the reviewer’s comments we concluded that the EF calculated this way are likely to be more representative of the fire emissions than the original method we used, and so EF from the carbon mass balance method

are reported in the manuscript. For comparison we have included EF from the original ER to CO method in the supplementary section.

Title: is “41S” needed?

> removed

P17600, L9-14: This is about the BB1-B period that, as currently written, has a confusing interpretation because Cape Grim and Robbins Island don’t move so when, where, how did more dilution occur and get sampled? The particles that arrive at Cape Grim evidently change in size with time, but a packet of particles is not followed to see what happens to it. Unless the discussion of this period can be easily improved without lengthening the paper it should be left to the companion paper. If it is retained, the previous sentence describes nighttime observations and so some transition would be needed to discuss photochemistry.

>paragraph was originally written to suggest that Cape Grim was on the edge of the plume during this period, and hence the BB emissions were more diluted during this period. However, as discussed in more detail in responses to Reviewer 1 below, we cannot be completely sure that emissions from the fire were still present during the particle growth period due to an absence of CO enhancement. We have modified the paragraph as follows:

“During the first plume strike event (BB1), a four hour enhancement of CO (max ~2100 ppb), BC (~1400 ng m-3) and particles > 3 nm (~13,000 cm-3) with dominant particle mode of 120 nm were observed overnight. A wind direction change lead to a dramatic reduction in BB tracers and a drop in the dominant particle mode to 50 nm. The dominant mode increased in size to 80 nm over 5 hours in calm sunny conditions, accompanied by an increase in ozone. Due to an enhancement in BC but not CO during particle growth, the presence of BB emissions during this period could not be confirmed.”

L16-17: include uncertainties

>uncertainties included

L21: The paper puts too much emphasis on how high concentrations can be in fresh plumes, which is completely normal and ultimately not that important unless plumes are also widespread or extensive. I’d eliminate some of the plume/background ratios throughout the paper as these ratios are expected to be high and it detracts from the flow of the paper to rattle off a list.

>as suggested we have removed most of the plume/background ratios from the paper, in particular from Section 3.2. However we have retained the plume/background ratios for CCN in the abstract and in Section 3.1.2 because we think the absolute enhancement of CCN provides important context when considering the percentage of particles which are able to activate as CCN.

P17601, L5: “conditions” > “fires”

>replaced conditions with fires

L9: I would add “can” before “have” to avoid possibly implying these events are common which was not assessed

>have added ‘can’ before ‘have’

L11: The mixing with other sources is not clear here yet, because no other sources have been mentioned yet. Maybe add a few words?

> as suggested have added terrestrial, aged urban and marine emission sources to following sentence “….and the significant changes that can occur as the plume is diluted and interacts with terrestrial, aged urban and marine emission sources. “

P17603, L28: Probably the key precursor is NOx since BB plumes are NOx limited and mixing with urban NOx can promote O3 formation as in the case study of Akagi et al. (2013) and references there-in. With this NOx issue in mind, at the appropriate point, the age of the Melbourne emissions that mixed with the fire should be given.

Akagi, S. K., Yokelson, R. J., Burling, I. R., Meinardi, S., Simpson, I., Blake, D. R., McMeeking, G. R., Sullivan, A., Lee, T., Kreidenweis, S., Urbanski, S., Reardon, J., Griffith, D. W. T., Johnson, T. J., and Weise, D. R.: Measurements of reactive trace gases and variable O3 formation rates in some South Carolina biomass burning plumes, Atmos. Chem. Phys., 13, 1141-1165, doi:10.5194/acp-13-1141-2013, 2013.

> have incorporated Akagi et al 2013 reference in latter part of introduction when discussing mixing of urban and BB emissions

“….For example Jaffe and Wigder (2012), Wigder et al., (2013) and Akagi et al., (2013) show that O3 formation is enhanced when NOx-limited BB plumes mix with NOx- rich urban emissions.”

A detailed analysis of the impact of urban emissions on the ozone formation observed will be the focus of the follow up modelling paper (Lawson et al 2015 in prep). We think the follow up paper is therefore the most appropriate place to provide an estimate of the plume age from Melbourne.

P17604, L15: To be consistent, the EF in this work are for heathland, which is unforested so also unlikely to represent Australian forests. The significance of this work may be more as a rare (or unique?) set of EF for Australian heathlands than as a good model for Australian forests.

> This sentence is intended to give an example of why using EF specific to certain regions is important, rather than stating specifically what this study adds to the literature. We have added ‘for example’ to make this clear “….may not be representative of, for example, Australia’s temperate dry sclerophyll forests.” We agree that the significance of this work is to contribute a unique set of EF for Australian heathlands and have stated this in the abstract and summary.

Abstract:

“Emission factors (EF) were derived for a range of trace gases, some never before reported for Australian fires, (including hydrogen, phenol and toluene) using the carbon mass balance method. This provides a unique set of EF for Australian coastal heathland fires.”

Summary:

“These EF, which were calculated from nocturnal measurements of the BB plume, provide a unique set of emission estimates for a wide range of trace gases from burning of coastal heathland in temperate Australia.”

L29: Sentence seems better without “either”

>either removed

P17605, L4: A good reference for putting unknown compounds in models could be: Alvarado, M. J., Lonsdale, C. R., Yokelson, R. J., Akagi, S. K., Coe, H., Craven, J. S., Fischer, E. V., McMeeking, G. R., Seinfeld, J. H., Soni, T., Taylor, J. W., Weise, D. R., and Wold, C. E.: Investigating the links between ozone and organic aerosol chemistry in a biomass burning plume from a prescribed fire in California chaparral, Atmos. Chem. Phys., 15, 6667-6688, doi:10.5194/acp-15-6667-2015, 2015.

>Thank you for this reference which we have included.

“…Inclusion of unidentified semi volatile organics in a recent photochemical modelling study of young BB plumes allowed successful simulation of O3 and OA, if reasonable assumptions were made about the chemistry of the unidentified organics (Alvarado et al., 2015)”

L5-17: Akagi et al. (2013) note the increased likelihood of urban/BB mixing in the future. In that study and references there-in, the NOx from urban areas enhances formation of O3 so it is likely the BB plumes are NOx-limited. More NOx should lead to more nitrate formation as well so this may be one of the better understood aspects of plume chemistry. An interesting related factor may be higher NOx emissions from burning biomass impacted by deposition from an urban area (Yokelson et al 2007).

Yokelson, R.J., S.P. Urbanski, E.L. Atlas, D.W. Toohey, E.C. Alvarado, J.D. Crounse, P.O. Wennberg, M.E. Fisher, C.E. Wold, T.L. Campos, K. Adachi, P.R. Buseck, and W.M. Hao, Emissions from forest fires near Mexico City, Atmos. Chem. Phys., 7, 5569- 5584, 2007.

>we have incorporated the Akagi et al 2013 reference in this section as stated above. We have also incorporated the Yokelson et al 2007 reference:

“……Deposition of nitrogen-containing pollutants from major urban areas may also enhance emission of NOx and other nitrogen-containing trace gases in BB plumes (Yokelson et al., 2007).

P17606, L5: “on top of a cliff”

>added

L11: WS = windspeed? Also, I think it is more common to put the standard deviation before the units?

>have replaced WS with windspeed. Standard deviation is now before units.

L22: Coastal heath may not represent Australian temperate forests very well.

>we agree, and as discussed previously, due to the reviewers suggestion we have stated in the abstract and summary that the EF from this study are unique for Australian coastal heathland and do not claim that they are representative of Australian temperate forests.

L26: “occurred”

>corrected

P17607, L6: is “molar mixing ratios” the right term?

>Have replaced with volume mixing ratio

L13-149: A PTR-QMS that scanned sequentially thru 26 masses?

> original text retained “The PTR-MS ran in multiple ion detection (MID) mode in which 26 masses were selected.” Sequentially scanned may imply that 26 adjacent masses were measured which was not the case.

P17608, L1-2: From Stockwell et al. (2015) data for shrubland fires and references there-in, m/z 85 and 87 are likely furanone and butanedione, respectively. In any case, in what general way have the unknown masses been included?

>Section 2.2.1 and Table 3 have been updated to include 2-furanone and 2,3-butanedione. Concentration data has been reported for the unidentified masses. The following sentence has been modified to clarify this:

“…..Protonated masses m/z 46, m/z 101, m/z 113 and m/z 153 were measured but not identified, but their concentrations have been reported in this work with the aim of quantifying as much emitted volatile carbon as possible.”

L4: “campaign”

>corrected

L16: m/z 137 likely has contributions from many isobaric species, some with different fragmentation, and many not even monoterpenes (see Fig 8 in Stockwell et al., 2015).

>thank you for this useful information. We have added “+ unknowns” after monoterpenes in the text and in Table 3

P17609, L24-26: This is the problematic period BB1-B that I mention above. Why is period B cleaner than A when the back trajectories shown for both seem to go right over Robbins Island? (By the way, the fire (and Melbourne) should be indicated in the supplemental figures.)

>the fire and Melbourne have been indicated on supplementary figures as requested

>We agree that the back trajectories during periods A and B are very similar, however the wind direction measured at Cape Grim becomes slightly more southerly at the end of Period A and start of Period B, indicating that the plume is likely just missing Cape Grim (or Cape Grim is on the edge of the plume – see responses further below) during Period B.

P17610, L1-14: The discussion of period B is confusing and unless it can be simply all cleared up, just leave it for a thorough, model-assisted examination of all the possibilities in the companion paper, while only stating that a possible particle–growth event was observed at this time that will be discussed elsewhere. Problems include: 1) It's stated earlier that the BB plume stopped impacting the site, but then said in various places that the plume was diluted 1-14% and that the CO may have missed the plume that was actually there, 2) It's not clear that particle growth is the only explanation for a gradual increase in particle size since no air masses were followed in Lagrangian fashion and a later increase in particle size is dismissed as an "influx of larger particles," 3) It's not clear what we learn about particle growth from this data. It seems better not to discuss this section in any detail, which will create a more focused paper. I also recommend against lengthening this paper by dragging the reader through a series of complex scenarios, when a more powerful model-assisted discussion will be possible elsewhere. The scope of this paper is big enough if you discuss BB1A and BB2A to learn about pure BB smoke, backgrounds (terrestrial (e.g. BB1-C) and marine (e.g. BB1-E)), aged urban (e.g. BB1-D), and then discuss BB2-B to learn about BB/urban mixing.

> General comment: We apologise for the confusion. This is a complex period in the time series and is challenging to interpret. We have tried to clarify several points below and in the manuscript which makes the interpretation of this period clearer and simpler. We agree that there are many unknowns surrounding this event so we have refrained from speculating as to the drivers or discussed this event at length in this manuscript.

Response to specific points 1, 2 and 3 raised:

1) It's stated earlier that the BB plume stopped impacting the site, but then said in various places that the plume was diluted 1-14% and that the CO may have missed the plume that was actually there,

>we stated that the plume stopped *directly* impacting the site due to sudden reduction in BB tracers. However as stated, the BC is elevated above typically background levels by 12-194 nm m3 during this period, and the back trajectory (supp figure 1B) and HFC 134s (urban tracer) do not indicate urban sources of BC are likely. As the back trajectories and wind direction during period A and B are very similar, we had concluded that the source of the

elevated BC is the Robbins Island fire, and that Cape Grim is on the edge of the plume during Period B. However we concede that the lack of CO elevation during period B means that we cannot be certain about the influence of fire emissions during this time. CO measurements are discrete (every 40 minutes) and may miss enhancements in a highly variably environment – nevertheless without enhancement of CO we agree fire emissions cannot be confirmed.

>This section now reads:

"Period B. Just after 06:00 (Fig. 3.), a slight wind direction change results in dramatically reduced particle concentration, CO and BC. The dominant mode of the particles drops from about 120 nm to 50 nm, but the distribution remains broad and uni-modal (Fig. 4a). From 7:00 – 12:00 there is a gradual increase in the dominant mode of particles from 50 nm to 80 nm, suggesting a particle growth event, which is accompanied by an increase in ozone from 12 to 20 ppb. The winds were light (1 m s-1) and variable, the temperature mild (19ºC) and skies clear during this period. There is an enhancement of BC above background concentrations (12 - 194 ng m-3) while the particle size is increasing, suggesting that the station may be on the edge of the BB plume during this period, however no CO enhancement is observed and so influence of BB emissions cannot be confirmed. The HYSPLIT trajectory (Supp Fig. 1b) shows that air arriving at the station is almost entirely of marine origin but had some contact with the vegetated and sparsely populated North West coast of Tasmania and appears to pass over Robbins Island before arriving at Cape Grim."

2) It's not clear that particle growth is the only explanation for a gradual increase in particle size since no air masses were followed in Lagrangian fashion and a later increase in particle size is dismissed as an "influx of larger particles,"

> During period BB1-B there was a single dominant mode of particles which gradually increased in size over several hours. This increase in the size occurred during warm sunny conditions and light (1 m s-1) and variable winds which would provide suitable conditions for the oxidation of gas phase precursors and condensation of low volatility products within the air parcel. Details of the meteorological conditions have been now added to the manuscript as we think this information further supports likelihood of particle growth. We acknowledge that being a single ground based observation site we were not able to follow air masses in a Lagrangian fashion – however given the information available, we think it is reasonable to conclude that the particles were growing in size during this period. The alternative is that the light and variable winds were bringing increasingly larger particles to the station over several hours which we think is less likely.

The particle growth period (BB1-B) is in contrast to the later increase in particle size (BB1-F), where some increase in particle size in the 40-60 nm range (which is less defined than during BB1-B) is accompanied by an increase in particle number for all sizes up to 200nm which is suggestive of an air parcel impacting the station (in this case terrestrial air) which has a different particle size and number profile to the previous air parcel (marine air). For this reason we have not classified Period F as a particle growth event. On the basis of the reasons above we have removed reference to a possible particle growth event in Period F. This section now reads

"At midnight on the 18th February, (Fig. 3.) terrestrial influence from mainland Australia is visible (Supp Fig. 1f), with an increase in O_3, HFC-134a and an increase in particle number in the 60 – 200nm size range,"

3) It's not clear what we learn about particle growth from this data.

> We observe a gradual increase in particle size alongside a modest increase in ozone, in marine air in calm sunny conditions, which has been recently influenced by a biomass burning plume and may still have some biomass burning emissions present. We think that this is an interesting event worth reporting. However we agree it is difficult to make definitive conclusions about the drivers of this event and we have removed speculation about the drivers of the event or composition of aerosol from the manuscript.

L9-11: Peak BC during period A is about ten times the BC during period B according to the text: the BC trace in the figures doesn't seem elevated in the figures. The BC in period A can only come from the fire according to the single back trajectory shown. The lower BC in period B seems like it could result from Cape Grim being on the edge of the fire plume or from transported urban BC according to the back trajectories? Is being on the edge of the plume what the authors mean by dilution? Clarify on line 18 if this period can be rationalized?

>yes, peak BC during Period A (1381 ng m3) is 7 times higher than the peak BC in Period B (193 ng m3). The elevation is visible as a 'hump' in Fig 3 but may not be obvious to the reviewer due to the large range on the y axis. As stated above, the lower BC during period B is unlikely to be from urban sources as shown by low levels of urban tracer HFC134a and marine back trajectories indicated by Supp figure 1b. Yes, we think that Cape Grim was likely on the edge of the plume during this period, and so the fire emissions were mixed with background air, hence the reference to dilution. However as stated above, the absence of an elevation in CO does not conclusively support the presence of fire emissions.

P17612. L3-4: Is learning about chemical composition from physical measurements really the main focus of this section? Also, re rest of section, I think there are lots of measurements of the % of BB particles that activate as CCN going back to the 1980's and if I recall some of those percentages are much higher than seen here. It would be helpful to compare to some of the other work for context.

> this section has been renamed "Ability of particles in BB event 1 (BB1) to act as CCN" We have compared the % activation with the comprehensive laboratory measurements of different fuel burning reported by Petters et al 2009

"Petters et al., (2009) show that in laboratory BB measurements the CCN activation of 80 nm particles ranges from a few % for low or weakly hygroscopic fuels to up to 60% for more hygroscopic fuels such as chamise, suggesting that the particles produced from coastal heath burned here may be more hygroscopic than those from other fuel types."

L11: “Petters”

>corrected

L18-19: I’m not sure what CCN/CN adds unless it would help to compare to other work?

>have removed CCN/CN ratio

P17613, L12-20: Why do the volatility/hygroscopicity measurements suggest an outer later at 60 nm when the period A particles are 120 nm? Briefly, what technique was used for these measurements? How would a hydrophobic outer layer form?

> Technique used was VH-TDMA (volatility and hygroscopic tandem differential mobility analyser) which has been defined in the manuscript. Particles of 60 nm were selected for characterisation with this instrument – this has been clarified as below.

“Volatility and hygroscopicity measurements of particles are available from Period A using a volatility and hygroscopic tandem differential mobility analysis (VH-TDMA) system (Fletcher et al., 2007). These measurements focused on the composition of 60nm particles, and suggested they consisted of a non-hygroscopic 23-nm core, a hygroscopic layer to 50 nm and a hydrophobic outer layer to 60 nm (possible homogeneously mixed).”

The following paragraph has been added to discuss how a hydrophobic outer layer could form.

“While the composition of the fresh BB particles may only be inferred from these measurements, the non-hygroscopic core may be black carbon or primary organic aerosol, the hygroscopic component an inorganic material such as sea salt or ammonium nitrate or sulphate or a hydroscopic organic such as MSA which is abundant in the marine boundary layer at Cape Grim in summer. The hydrophobic outer layer may be a hydrocarbon-type organic, with a low O:C ratio, which was co-emitted in the fire and condensed on to the particle as the plume cooled and was transported to Cape Grim (Fletcher et al., 2007).”

P17614, L11-14: Going from period A to period B, the factor of three drop in CCN is much smaller than the much larger drop in BC and both are explained as dilution of smoke (or being on plume edge?). The BC/CCN ratio can change during a fire though and if the CCN change is computed for excess CCN above the 320 background, then the drop is a factor 4.5.

> because we cannot definitively state that the BC observed during Period B was from the fire, we have removed the statement “the decrease driven by dilution of the fresh smoke plume”. Hence the comparison between the drop in CCN and BC due to dilution of the smoke is not discussed.

17614, L25-26: The introduction was focused almost completely on biomass burning. At the outset, this section appears like it will continue the trend of trying to do too much with too little evidence in a growing series of speculative diversions that can detract from the main message.

>this section (3.1.3) has been removed from the manuscript. The paragraph about determining the production of ozone from biomass burning has been moved to Section 3.1.1. Removal of this section removes speculative discussion about aerosol composition and particle growth from the manuscript.

P17615, L8: “Several” should probably be “Many”

>this section has been removed (see above)

L9-10: Coagulation could be contributing to particle growth.

>this section has been removed (see above)

L15: What is meant by “size distributions for individual particle growth events in BB plumes”? How is it different from any generic measurement of particle size changes?

>this section has been removed (see above)

L23-29: It seems unlikely that coating of fresh BB particles (that had average diameter of 120 nm) explains particle growth in period B when the particles were only half as large unless the fire started putting much smaller fresh particles.

>this section has been removed (see above)

P17617, L4: “others” > “other”

>this section has been removed (see above)

General, less ratios needed as the point made on lines 15-17 is obvious from a glance at the figure.

>as suggested, most of the ratios have been removed from this section

L23: “that very light patchy” (delete “at”)

> ‘at’ deleted

L29: change “dynamics” to “processes” or “chemistry”

>changed to processes

P17618, L10 what is meant by “(minutely)” here and earlier?

> minute data rather than hourly averaged data. Changed to ‘minute data’ in manuscript to clarify

L17: “is impacting”

>added ‘is’

L18: “into”

>changed to‘into’

L26: total emissions or emission ratios?

>changed to emission ratios

L27: Plumes influencing background seems wrong since plumes should contrast with background not influence it. The background is defined as something unaffected by plumes.

>replaced with “This work also highlights the large influence that BB plumes can have on the composition of air in the marine boundary layer”

P17619, L1-7: Comparisons of CN numbers at different distances from fire sources are not that useful since thy change with dilution and other processes. See figures 6 and 17 in Hobbs et al. (2003).

Hobbs, P.V., P. Sinha, R.J. Yokelson, T.J. Christian, D.R. Blake, S. Gao, T.W. Kirchstetter, T. Novakov, and P. Pilewskie, Evolution of gases and particles from a savanna fire in South Africa, J. Geophys. Res., 108, 8485, doi:10.1029/2002JD002352, 2003.

P17621, L11: “Emission ratios (ER)”

>the paragraph comparing CN numbers with different studies has been removed

L17: “particle number to CO”

>added

P17621, L23 – P17622, L2: Fires are variable and you don’t necessarily need a high rˆ2 to have representative data. This is especially true for two species mostly from different combustion processes (e.g. CO2 from flaming and CO from smoldering). While variability in background CO2 likely does introduce some uncertainty to the dCO/dCO2 ratio, actually the ratio of dCO/dCO2 implied from the fit or simple subtraction of aver-ages is 0.16 or 0.12 (from Table 3), which are both perfectly normal for a smoldering fire filling the nocturnal boundary layer. The implied MCE is then 0.86 or 0.89, which is in good agreement with the BC/CO ratio the authors report on P17621, L21 according to Fig. 2 in May et al., (2015). So realistic EF and perhaps better EF could be calculated using the carbon mass balance method (Yokelson et al., 1999) and they are worth reporting.

May, A., McMeeking, G., Lee, T., Taylor, J., Craven, J., Burling, I., Sullivan, A., Akagi, S., Collett, Jr., J., Flynn, M., Coe, H., Urbanski, S., Seinfeld, J., Yokelson, R. J., and Kreidenweis, S.: Aerosol emissions from prescribed fires in the United States: A synthesis of laboratory and aircraft measurements, J. Geophys. Res., 119, 11826–11849, doi:10.1002/2014JD021848, 2014.

> as discussed previously, after considering comments of both reviewers we have calculated EF using the carbon mass balance approach as suggested (Table 3, Section 3.2.5) and agree that these are likely more realistic EF than the previous approach. We have incorporated the BC/CO ratio and the May et al reference suggested into the text (3.2.5).

"The ER of BC to CO reported here is in good agreement with BC to CO ERs in smouldering fires (MCE <0.9) reported by Kondo et al (2011)and May et al (2014) which suggests that the excess CO2, and MCE has been determined reliably."

>We have also noted in the text that the low r^2 for CO and CO2 is likely because these two species are from different combustion processes, as the reviewer points out (Section 3.2.4).

"There is a low correlation between mixing ratios of CO and CO2 (ER to CO R2 = 0.15, see Table 3). This is in part because CO and CO2 are emitted in different ratios from different combustion processes (smouldering and flaming respectively) and may also be influence by variability in background levels of CO2 (Andreae et al., 2012)."

P17622, L8: I would delete "as observed by Christian et al. (2004)" since that paper compared PTR-MS to an FTIR that used old values for the HCOOH IR cross-section that are now known to be in error by about a factor two (see, http://www.atmos-chemphys-discuss.net/12/C11864/2013/acpd-12-C11864-2013.pdf)

>deleted and replaced with Stockwell et al., 2014

L21-22: Here species are given with capital "X" and with lower case "x" earlier.

>x is now used consistently instead

P17623, L2: I would include these gases with low rˆ2 for reasons given above. For these gases and any others (see line 4), the uncertainty could be estimated from the uncertainty in the slope.

>EF have now been reported for all gases including those with low r^2 using the carbon mass balance method as suggested. Uncertainty in the slope was not estimated because the ER method was not used to calculate the EF reported in the manuscript.

L14: "though it lacks" – in general this section gives a better description of the veg than earlier.

>this section has been moved to Methods section 2.1 to strengthen the description of vegetation given there

L27: In Yokelson et al. (2013) the EFCO is 73.8 g/kg.

> text has been removed as this section has been simplified in response to Reviewer comment below (P17624-5, General)

P17624, L23: Reference without year.

> text has been removed as this section has been simplified in response to Reviewer comment below (P17624-5, General)

P17624-5, General: It’s my opinion that extensive species by species text-based comparisons for large data sets are tedious and obscure the real message. I think it is better to summarize the overall level agreement with statements such as _ “50% of species agree within 20%” - or something like that. Minor point, the EF in Akagi et al 2011 were updated in May 2014 by including the Yokelson et al. (2013) values into an evolving average and are available at the website indicated. However, this update did not have a large effect on the EFCO for chaparral or temperate forest. In this long comparison section, the only thing that really stands out is the low acetic acid EF? Could this be shortened? Post emission production of acetic acid in BB plumes has been noted many times making this an interesting issue (Akagi et al., 2012). The low EFCH3COOH in this work could be due to sample line losses, but also maybe there are loss processes at night such as sticking to wet aerosols that have not been measured in the field before since other studies were done during the day (see Fig. 3 Stockwell et al 2014).

>we agree. This section has been shortened considerably, and now includes only one paragraph which makes broad statements about the level of agreement between studies.

“EF from this study reported in Table 4 are within 50% of the EFs from the other South Eastern Australian studies except for acetic acid, which is 5 times lower than the EF reported by Paton-Walsh et al., (2014). EF from this study are also within 50% of temperate NH EF (temperate forests and chaparral) except for hydrogen, acetic acid and the methyl halides and within 80% of the average tropical savannah EF, with the exception of acetic acid and the methyl halides.”

The possible reasons for the discrepancy in EF for acetic acid (below) and methyl halides (next response) is discussed.

“The acetic acid EF from this study is significantly lower than reported from Australian and NH temperate studies, though the variability reported elsewhere is large. Acetic acid may form rapidly in BB plumes (Akagi et al., 2012), which adds uncertainty to the EF in plumes which are sampled some distance downwind of emission. The lower EF reported in this work may be due to inlet losses, or another loss process such as nocturnal uptake of acetic acid on to wet aerosols (Stockwell et al., 2014).”

Updated temperate EF values from Akagi et al 2011 have been incorporated into Table 4 from the website indicated by the reviewer.

P17625, L6-20: High halogen content in the fuel seems likely as Stockwell et al., 2014 observed high HCl emissions from burning coastal grasses. Note also McKenzie reference there-in.

Stockwell, C. E., Yokelson, R. J., Kreidenweis, S. M., Robinson, A. L., DeMott, P. J., Sullivan, R. C., Reardon, J., Ryan, K. C., Griffith, D. W. T., and Stevens, L.: Trace gas emissions from combustion of peat, crop residue, domestic biofuels, grasses, and other fuels: configuration and Fourier transform infrared (FTIR) component of the fourth Fire Lab at Missoula Experiment (FLAME-4), Atmos. Chem. Phys., 14, 9727-9754, doi:10.5194/acp-14-9727-2014, 2014.

>thank you for these helpful additional references (Stockwell, McKenzie and references therein) which we have incorporated into this section. After reading these references we agree that high halogen content in fuels is the most likely cause and have stated this in the manuscript. We have removed the less likely alternative explanation of coastal methyl halide emissions. This section now reads:

"It is likely that the high methyl halide EFs reported here are due to high halogen content of soil and vegetation on the island, due to very close proximity to the ocean, and transfer of halogens to the soil via sea spray (McKenzie et al., 1996). Chlorine and bromine content in vegetation has been shown to increase with proximity to the coast (McKenzie et al., 1996;Stockwell et al., 2014) and methyl chloride and hydrochloric acid EF are impacted by the chlorine content of vegetation (Reinhardt and Ward, 1995, Stockwell et al 2014) ."

P17627, L6: "the observations" since observations that are possible with current technology could help.

>This paragraph has been removed in order to reduce speculative discussion of particle growth event

L18: It's only one fire, but it was sampled for many hours, which is really nice and is also possibly unique from heath land and rare night-time smoke composition data.

>Thanks. We have changed this sentence to

…"These EF, which were calculated from nocturnal measurements of the BB plume, provide a unique set of emission estimates for a wide range of trace gases from burning of coastal heathland in temperate Australia."

P17628, General: Of course, changing model input will change model output, but the problem is there is no easy way to accurately predict deviations from the average operationally.

> this sentence has been removed

References: order Pratt, Prinn, Pratt, Prinn

>these references appear to be in order and we are unsure what is referred to here.

Figure 1. Show fire location here and in supplement!

>Figures have been modified to include fire (area burned) and Melbourne

Figs 2, 3, and 6: y-axis labels not very high quality.

>figures have been reformatted so y axis is clearer

Also would be helpful to indicate the times selected for the back trajectories shown in supplement. I’m also curious if more than one back trajectory was run for each period and if so, how reproducible they are

> individual back trajectories were run which finished at different times within each period of interest, to show how the back trajectories changed over time. Times selected for the back trajectories have been included under each figure in the supplementary material.

Fig 6: what is “N3” in legend in top panel?

>this was an error and has been removed

Anonymous Reviewer #2

We thank the reviewer for the very helpful suggestions and additional references which in almost all cases have been incorporated into the manuscript

Responses to specific reviewer comments are given below (responses denoted by > before text)

This paper presents an extensive set of opportunistic measurements of bushfire emissions made when a bushfire impacted the Cape Grim station during a campaign aimed at studying particle formation in the clean marine environment. The paper is well written and contains significant new information on the emissions from fires in a poorly sampled region of the world. Thus I recommend publication after a number of minor issues are addressed.

Page 17605 line 18: “fresh and diluted BB plumes” - rephrase please- (the degree of dilution may vary but both are diluted by ambient air).

> in response to comments made by reviewer 1 we are no longer referring to Period B as a diluted plume (due to a lack of CO enhancement observed). We have therefore changed the sentence to remove reference to dilution:

“In this study we have investigated the chemical composition of fresh BB plumes in marine air at the Cape Grim Baseline Air Pollution Station”

2. Page 17606 line 10, please define whether the _ symbol refers to standard deviation? - if so at what confidence interval?

> has been defined as ±1 std dev.

3. Page 17611 line 12, do you really need to use the acronym “nss”? You probably do not use it enough for it to be necessary.

>Have removed acronym

4. Page 17613, end of line 3 “particle” should be “particles”?

>yes, corrected

5. Page 17615, line 1 “produce” should be “produces”?

>this text has been removed in response to comments from reviewer 1

6. Page 17617-17618 and page 17627 line 25: you imply that there is a change in the absolute magnitude of the emissions from the fire (as well as the emission ratios) as a result of rain/changing combustion efficiency but I am not convinced that you present sufficient evidence for this. The concentrations increase dramatically at the measurement site but the amounts reaching the site depend both on the emissions and on the degree of mixing. A change in meteorological conditions (accompanying the rainfall) could significantly alter the degree of (e,g. vertical) mixing and produce greater concentrations at the measurement site. A change in the emissions from fully oxidised products (like CO2) to partially oxidised products (like CO), would be fully expected with a reduction in combustion efficiency due to rain, nevertheless the changes in the ratios of acetonitrile and black carbon to CO are very interesting.

>we agree and we have modified the text in this section, as well as in the conclusion and abstract, to state that we see a change in emission ratios due to rainfall and decreased combustion efficiency. We have removed any reference to absolute emissions magnitude of emissions changing as a result of the rainfall/decreased combustion efficiency.

7. Page 17619, the comparison of number concentrations from different sites should also point out that the degree of mixing will be a major factor in the concentrations measured.

> comparison of particle number concentrations with other studies has been removed, due to similar comments raised by reviewer 1

8. Page 17620: (or somewhere else!) Somewhere you should add a sentence saying that it is assumed that the enhancement ratios measured are unaltered from the original emission ratios because of the short transport time to the measurement site.

> the following additional sentence has been added after the following paragraph:

Existing text:

“During the selected time period, wind speeds of 16 m s-1 meant that the plume travelled the 20 km to Cape Grim over a period of about 20 minutes, which allows the plume to cool to ambient temperatures but ensures minimum photochemical processing of the plume (Akagi et al., 2011). Advection of the plume to the site occurred primarily at night so minimal impact of photochemical reactions on the plume composition is expected (Vakkari et al., 2014).

Additional sentence: “It is therefore assumed that the enhancement ratios measured at Cape Grim are unaltered from the original emission ratios.”

9. Page 17621: why do you remove background amounts and then force the straight line fit through the origin? The slope of the regression should be the same regardless of what the background values are. This probably doesn’t make a great deal of difference but you are likely adding unnecessary uncertainty to the results.

> as stated in Yokelson et al 1999 (page 30,117), and in agreement with the statement of Reviewer 2 above, there are several different methods of calculating ER to CO, which produce essentially the same result. The method used here was used successfully by Yokelson et al 1999 and found to agree closely with alternative methods.

10. Page 17621 last paragraph: CO and CO2 are often poorly correlated when sampling a fire plume if the combustion efficiency of the fire varies during the measurement period. Thus poor correlation in itself should not be a problem, if you can determine the actual enhancement in CO2 and CO as you can simply sum the total enhancements of each throughout the fire. The single grab sample measurement for CO2 every 40 minutes may be more problematic when attempting to do this, so I don’t have an issue with the use of a literature value for the emission factor of CO if you are really not confident that you can obtain a trustworthy one from your own data. However you do not explain the choice of the EF from Akagi et al. This seems like an odd choice to me when you point out on page 17604 “EFs from NH coniferous forests are unlikely to be representative of Australia’s temperate dry sclerophyll forests”. Why not use the EF from Volkova et al?? If you don’t want to recalculate - just explain the choice and/or maybe comment on how much (or little) difference a different choice of EF for CO would make to your results.

>thank you for this advice. As mentioned in general response and specific response to reviewer 1, we have calculated the EF based on the carbon mass balance method as suggested by both reviewers. Due to the realistic MCE obtained, and agreement between ER and MCE, we believe we have reliably measured the excess CO and CO2 during the fire.

The EF calculated using the CO EF from Akagi et al are now reported for comparison in supplementary material and are not the focus of the paper. However, to respond to the comment above, we selected the Akagi et al CO EF because this was an average temperate forest EF, calculated from several independent studies, and we believe be a robust average value. We could have used an Australian EF from a single study as suggested but were unsure about the representativeness of this value.

11. Page 17624 line 11: delete “a factor of” before “almost a factor of”

>This detailed comparison of EF with other studies has been removed from manuscript in response to comments from Reviewer 1

12. Page 17626: insert “for” before “NH temperate forests”

>This detailed comparison of EF with other studies has been removed from manuscript in response to comments from Reviewer 1

13. Page 17626: consider changing section title to “summary and future work” ???

>changed to ‘Summary and future work’ as suggested

Biomass burning emissions of trace gases and particles in marine air at Cape Grim, Tasmania~~, 41ºS~~.

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Abstract

Biomass burning (BB) plumes were measured at the Cape Grim Baseline Air Pollution Station during the 2006 Precursors to Particles campaign, when emissions from a fire on nearby Robbins Island impacted the station. Measurements made included non methane organic compounds (NMOCs) (PTR-MS), particle number size distribution, condensation nuclei (CN) > 3 nm, black carbon (BC) concentration, cloud condensation nuclei (CCN) number, ozone (O_3), methane (CH_4), carbon ~~monixide~~ monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), nitrous oxide (N_2O), halocarbons and meteorology.

During the first plume strike event (BB1), a four hour enhancement of CO (max ~2100 ppb), BC (~1400 ng m^{-3}) and particles > 3 nm (~13,000 cm^{-3}) with dominant particle mode of 120 nm were observed overnight. A wind direction change lead to a dramatic reduction in BB tracers and ~~Dilution of the plume resulted in~~ a drop in the dominant particle mode to 50 nm.~~ ,~~ The dominant mode increased in size to 80 nm over 5 hours in calm sunny conditions, accompanied by an increase in ozone.~~and then growth to 80 nm over 5 hours~~ Due to an enhancement in BC but not CO during particle growth, the presence of BB emissions during this period could not be confirmed. ~~. This was accompanied by an increase in O_3, suggesting that photochemical processing of air and condensation of low volatility oxidation products may be driving particle growth.~~

The ability of particles > 80 nm (CN80) to act as CCN at 0.5% supersaturation was investigated. The ΔCCN/ΔCN80 ratio was lowest during the fresh BB plume (56±8%), higher during the particle growth ~~event ~~period (77±4%) and higher still (104±3%) in background marine air. Particle size distributions indicate that changes to particle chemical composition, rather than particle size, are driving these changes. Hourly average CCN during both BB events were between 2000-5000 CCN cm^{-3}, which were enhanced above typical background levels by a factor of 6-34, highlighting the dramatic impact BB plumes can have on CCN number in clean marine regions.

During the 29 hours of the second plume strike event (BB2) CO, BC and a range of NMOCs including acetonitrile and hydrogen cyanide (HCN) were clearly enhanced and some enhancements in O_3 were observed ($\Delta O_3/\Delta CO$ 0.001-0.074). A shortlived increase in NMOCs by a factor of 10 corresponded with a large CO enhancement, an increase of the NMOC/CO emission ratio (ER) by a factor of 2 – 4 and a halving of the BC/CO ratio. Rainfall on Robbins Island was observed by radar during this period which likely resulted in a lower fire combustion efficiency, and higher emission of compounds associated with smouldering. This highlights the importance of relatively minor meterological events on BB emission ratios~~s~~.

Emission factors (EF) were derived for a range of trace gases, some never before reported for Australian ~~conditions~~fires, (including hydrogen, phenol and toluene) using ~~a calculated ER to CO and a published CO Ef~~the carbon mass balance method. This provides a unique set of EF for Australian coastal heathland fires. Methyl halide EFs were higher than EF reported from other studies in Australia and the Northern Hemisphere which is likely due to high halogen content in vegetation on Robbins Island due to close proximity to ocean. ~~The EF derived for most species are comparable to other temperate Australian studies but lower than Northern Hemisphere temperate studies.~~

This work demonstrates the substantial impact that BB plumes can have on the composition of marine air, and the significant changes that can occur as the plume ~~is diluted and ~~interacts with ~~other ~~terrestrial, aged urban and marine emission sources. ~~We also provide new trace gas and particle EF for temperate southern Australia.~~

1 Introduction

Biomass burning (BB) is the largest global source of primary carbonaceous fine aerosols and the second largest source of trace gases (Akagi et al., 2011). Species directly emitted from fires include carbon dioxide (CO_2), methane (CH_4), carbon monoxide (CO), nitrogen oxides (NO_x), ammonia (NH_3), non methane organic compounds (NMOCs), carbonyl sulfide (COS), sulfur dioxide (SO_2) and elemental and organic carbonaceous and sulphate-containing particles (Keywood et al., 2011). Secondary species that are formed from BB precursors include ozone (O_3), oxygenated NMOCs and inorganic and organic aerosol (OA). The complex mixture of reactive gases and aerosol that make up BB plumes can act as short lived climate forcers (Keywood et al., 2011). While BB plumes often have the greatest impact on the atmopshere close to the source of the fire, once injected into the free troposphere ~~(FT)~~ plumes may travel long distances, so that climate and air quality affects may be regional or even global. A recent modelling study by Lewis et al., (2013) for example highlighted the large contribution that BB emissions make to the burden of several NMOC in the background atmosphere, particularly in the Southern Hemisphere.

With some studies predicting that future changes to the climate will result in increasing fire frequency (Keywood et al., 2011), it is essential to understand the composition of fresh plumes, how they vary temporally and spatially, and the way in which the chemical composition is transformed with aging. This will provide the process understanding to allow models to more accurately predict regional air quality impacts and long term climate affects of BB.

Characterising BB plumes is challenging for several reasons, and significant knowledge gaps still exist. BB plumes contain extremely complex mixtures of trace gases and aerosols, which vary substantially both spatially and temporally. The initial composition of BB plumes is dependent on the combustion process and efficiency of combustion, which has a complex relationship with environmental variables. Combustion efficiency (CE) is a measure of the fraction of fuel carbon completely oxidised to CO_2. However it is difficult to measure all the carbon species required to calculate CE, and so modified combustion efficiency (MCE), which closely approximates the CE, is often used instead, where MCE = $\Delta CO_2/(\Delta CO+\Delta CO_2)$ (Ferek et al., 1998) where Δ refers to excess or above-background quantities. The efficiency of fire combustion depends on fuel size, density and spacing, fuel moisture content, local meteorology (including temperature, windspeed and precipitation), and terrain (van Leeuwen and van der Werf, 2011), and MCE can vary substantially spatially and temporally within one fire. The EF of trace gas and aerosol species are in many cases strongly tied to the efficiency of combustion. Species such as CO, organic carbon, and NMOCs tend to be emitted at higher rates in smouldering fires which burn with low MCE (i.e. have a negative relationship with MCE), while other species such as CO_2 and black carbon (BC) are emitted at higher rates in flaming fires with higher MCE (e.g. have a positive relationship with MCE) (Andreae and Merlet, 2001).

Once emitted, the composition of BB plumes can change very rapidly, with destruction of highly reactive species, coagulation of particles, and formation of secondary species such as O_3, oxygenated NMOCs and secondary organic and inorganic aerosol occuring on a timescale of minutes to hours (Akagi et al., 2012; Vakkari et al., 2014). Particles typically become more oxygenated, and particle size often increases as primary particles are coated either with low-volatility oxidation products of co-emited organic and inorganic gases, or with co-emited semi volatile primary organics (Sahu et al., 2012; Akagi et al., 2012; Vakkari et al., 2014). Changes that occur in the composition of the plume can be highly variable and drivers of variability are difficult to quantify. One example is the large variability in the net OA enhancement in aged BB plumes, with studies reporting both enhancements and decreases in the OA/CO ratio with plume aging (Yokelson et al., 2009; Hennigan et al., 2011; Cubison et al., 2011; Akagi et al., 2012; Hecobian et al., 2012).

While BB is recognised as a major source of CCN (Andreae et al., 2002), the hygroscopicity of fresh BB particles varies enormously from weakly to highly hygroscopic and fuel type appears to be a major driver of the variability (Pratt et al., 2011; Engelhart et al., 2012; Petters et al., 2009) along with particle morphology (Martin et al., 2013). As particles age, in addition to becoming larger, they also generally become more hygroscopic and more easily activated to CCN. However, this is dependent on the initial composition and hygroscopicity of the particle, as well as the hygroscopicity of the coating material (Martin et al., 2013; Engelhart et al., 2012). Most studies of CCN in BB plumes to date have been chamber studies, and there are few ambient studies which have examined the ability of BB particles to act as CCN in fresh and aged plumes.

Ozone is typically destroyed by reaction with nitric oxide (NO) in close proximity to the fire, however once the plume is diluted, O_3 enhancement is often observed (typically normalised to CO). In a recent summary of a number of studies, the enhancement of O_3 to CO typically increases with the age of the plume (Jaffe and Wigder, 2012). However there is significant variation in O_3 enhancements observed between studies which is thought to be dependent on several factors such as precursor emissions (resulting from fuel and combustion efficiency), meteorology, the aerosol affect on plume chemistry and radiation, and photochemical reactions. Many challenges remain in modelling the transformation processes that occur in BB plumes, such as O_3 formation and changes to particle properties, in part due to a lack of high-quality real-time observations (Jaffe and Wigder, 2012; Akagi et al., 2012).

In recent years there have been a number of intensive field and laboratory studies which have characterised both fresh emissions and aged BB emissions. However there are several regions of the globe where BB emissions, including emission factors (EF), have been sparsely characterised. For example, EF data has been published for only a few trace gases in the temperate forests of Southern Australian (Volkova et al., 2014; Paton-Walsh et al., 2012; Paton-Walsh et al., 2005; Paton-Walsh et al., 2014; Paton-Walsh et al., 2008). The lack of Australian temperate EF was evident in a recent compilation of EF by Akagi et al (2011), in which all temperate EF reported were from the Northern Hemisphere (NH) from mostly coniferous forests. Species emitted during combustion can be strongly dependent on vegetation type (e.g. Simpson et al 2011), and EFs from NH coniferous forests are unlikely to be representative of for example Australia's temperate dry sclerophyll forests. Using EF from boreal and tropical forest fires to model BB plumes in temperate regions adds uncertainty to the model outcomes (Akagi et al., 2011), and more detailed chemical measurements of BB plumes in the Southern Hemisphere temperate regions are needed.

An increasingly wide range of sophisticated instruments are being used to measure the trace gas and aerosol composition and microphysical properties in BB plumes. This has lead to a higher proportion of NMOC being quantified than ever. Despite this, there is significant evidence that a large proportion of NMOCs in BB plumes are still not being identified. A compilation of NMOC measurements from 71 laboratory fires using a range of techniques, found that the mass of unidentified NMOC was significant (up to 50%) (Yokelson et al., 2013), though recent work using high-resolution proton transfer reaction – time of flight – mass spectrometry (PTR-TOF-MS) has allowed at least tentative identification of up to 93% of NMOC (Stockwell et al., 2015). Flow reactor experiments have indicated the mass of OA formed in aged BB plumes exceeds the mass of known NMOC precursors, suggesting ~~either~~ unknown NMOC precursors, and/or highlighting the important contribution of semi and intermediate volatile species to the increase in OA observed (Ortega et al., 2013). ~~These studies highlight t~~ Inclusion of unidentified semi volatile organics in a recent photochemical modelling study of young BB plumes allowed successful simulation of O_3 and OA, if

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reasonable assumptions were made about the chemistry of the unidentified organics (Alvarado et al., 2015). ~~he need to include these unidentified and tentatively identified gas phase organics in models to capture the additional reactivity and contribution to OA they provide.~~

Finally, with increasing global population and urbanisation, it is likely that BB events will increasingly impact human settlements, either through close proximity of fires or transport of plumes to urban areas. Consequently a greater understanding is needed of the interactions between BB and urban emissions. These interactions are complex and have not been significantly studied to date, although there is evidence that interactions between these two sources may significantly change the resulting processes and products in plume aging. For example Jaffe and Wigder (2012) Wigder et al., (2013) and Akagi et al., (2013) show ~~summarise several studies which show~~ that O_3 formation is enhanced when NO_x-limited BB plumes mix with NO_x- rich urban emissions. Deposition of nitrogen-containing pollutants from major urban areas may also enhance emission of NO_x and other nitrogen containing trace gases in BB plumes (Yokelson et al., 2007). ~~O_3 enhancement in aged BB plumes is greater when the plumes mix with urban emissions, however the mechanisms for this enhancement remain unclear.~~ Hecobian et al (2012) found higher concentrations of inorganic aerosol components in aged BB plumes that had mixed with urban emissions compared to BB plumes, which were attributed to higher degree of oxidative processing in the mixed plumes.

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In this study we have investigated the chemical composition of ~~both~~ fresh ~~and diluted~~ BB plumes in marine air at the Cape Grim Baseline Air Pollution Station. The BB event occurred unexpectedly during the Precursors to Particles campaign (Cainey et al., 2007), which aimed to investigate new particle formation in clean marine air. Despite the opportunistic nature of this work and lack of targeted BB measurements, a wide variety of trace gas and aerosol species were quantified which provide valuable information on the composition of BB plumes in this sparsely studied region of the world.

2 Methods

2.1 Cape Grim station location and location of fire

The Cape Grim Baseline Air Pollution Station is located near the north-west tip of the island state of Tasmania, Australia, 40.7° S latitude and 144.7° E longitude (see Fig 1). The station is situated on top of a cliff 94 m above mean sea level. When the wind blows from the south west sector (the Roaring Forties) the air that impacts the station is defined as Baseline and typically has back trajectories over the Southern Ocean of several days. In northerly wind directions, urban air from the city of Melbourne some 300 km away is transported across the ocean (Bass Strait) to the station. North west Tasmania has a mild temperate climate, with average February temperatues of 15~~-~~±2° C ~~± 2~~, RH 75±12%~~ ± 12~~, ~~WS~~ windspeed of 9±4 m s^{-1} ~~± 4~~ (where ±~~-~~is 1 std dev) and 25 mm precipitation.

From 30 January to 24 February 2006 (the Austral late summer), the Precursors to Particles (P2P) campaign was undertaken (Cainey et al., 2007). On the 15th of February 2006, in the middle of P2P, a fire was ignited on nearby Robbins Island, which lies across farmland 20km east of Cape Grim. Robbins Island (9748 ha) is separated from the Tasmanian mainland by a tidal passage 2km across, and has been a freehold property used for the grazing of sheep and cattle since the 1830s (Buckby, 1988). The vegetation consists of grazed pastures and native vegetation, mostly disturbed coastal heathland (largely endemic *Epacridaceae*, *Leptospermum*) and woodland (*Leptospermum*, *Melaleuca* and *Eucalyptus nitida)* with shrubs interspersed by tussock grasses (Poa spp) and sedges (Kitchener and Harris, 2013). The fire burned 2000 ha, mostly coastal heath, over a period of 2 weeks. The vegetation burned is comparable in structure to the mid and lower story vegetation in Australian temperate forest and savannah woodland, though lacks the coarse woody debris and the dominant upper story of trees found particularly in temperate Australian forests.~~The fire burned 2000 ha, mostly coastal heath, over a period of 2 weeks~~. On two occasions an easterly wind advected the BB plume directly to the Cape Grim Station. The first plume strike (BB1) occured from 02:00 – 06:00 (Australian Eastern Standard Time - AEST) on the 16th February, with light easterly winds of 3 m s^{-1} and temperature of 13 ºC and RH of 96 %. The second, more prolonged plume strike (BB2) occurred from 23:00 on 23rd February to 05:00 on the 25th February, with strong easterly winds ranging from 10-16 m s^{-1}, temperatures of 16-22 ºC and RH from 75-95 %.

2.2 Measurements

During P2P, a number of additional instruments were deployed to run alongside the routine measurements. All the measurements made during BB1 and BB2 (routine and P2P measurements) are listed in Table 1, with references supplied for further information. Some additional information is provided here. All levels of trace gases are expressed as ~~molar~~ volume mixing ratios. As the focus of P2P was clean marine air, PM2.5 and PM10 filter samples were not collected during the BB events.

2.2.1 NMOCs (PTR-MS)

Details on PTR-MS measurements are given in Galbally et al (2007) and some additional information is provided here.

The PTR-MS ran with inlet and drift tube temperature of 75°C, 600V drift tube, 2.2 mbar drift tube pressure, which equates to an energy field of 140 Td. The O_2^+ signal was ~2% of the primary ion H_3O^+ signal. The PTR-MS ran in multiple ion detection (MID) mode in which 26 masses were selected. Masses included in this work were identified by reviewing instrument intercomparison studies of BB plumes (Christian et al., 2004; Karl et al., 2007b; de Gouw and Warneke, 2007; Stockwell et al., 2015). Protonated masses were identified as m/z 28 hydrogen cyanide (HCN), m/z 31 formaldehyde (HCHO), m/z 33 methanol (CH_3OH), m/z 42 acetonitrile (C_2H_3CN), m/z 45 acetadehyde (C_2H_4O), m/z 47 formic acid (HCOOH), m/z 59 acetone and propanal (C_3H_6O), m/z 61 acetic acid (CH_3COOH), m/z 63 dimethyl sulphide - DMS (C_2H_6S), m/z 69 furan/isoprene (C_4H_4O/C_5H_8), m/z 71 methacrolein/methyl vinyl ketone - MVK (C_4H_6O), m/z 73 methylglyoxal ($C_3H_4O_2$)/methyl ethyl ketone - MEK (C_4H_8O), m/z 79 benzene (C_6H_6), m/z 85 2-furanone ($C_4H_4O_2$), m/z 87 2,3-butanedione ($C_4H_6O_2$) m/z 93 toluene (C_7H_8), m/z 95 phenol (C_6H_6O), m/z 107 ethylbenzene + xylenes (C_8H_{10}), m/z 121 C_3 benzenes (C_9H_{12}), m/z 137 monoterpenes ($C_{10}H_{16}$) + unknowns ($C_8H_8O_2$). These are expected to be the dominant compounds contributing to these masses. However, due to the inability of the PTR-MS to differentiate between species with the same molecular mass, a contribution from other compounds not listed here cannot be ruled out. Protonated masses m/z 46, ~~m/z 85, m/z 87,~~ m/z 101, m/z 113 and m/z 153 were measured but not identified, but their concentrations have been ~~included~~ reported in this work ~~here~~ with the aim of quantifying as much emitted volatile carbon as possible.

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During the campaign the PTR-MS was calibrated for the following compounds using certified gas standards from Scott Specialty Gases, USA and National Physical Laboratory, UK: methanol, acetaldehyde, acetone, isoprene, MVK and methacrolein, MEK, benzene, toluene, ethylbenzene, 1,2,4 trimethylbenzene and formaldehyde. Calibration data were used to construct sensitivity plots which were used to calculate approximate response factors for other masses not specifically calibrated. Due to having proton affinities similar to water, formaldehyde and HCN responses are highly dependent on humidity of the sample air. The changing response of the PTR-MS for these compounds was calculated every 10 minutes by taking the response of the dry formaldehyde calibration gas, then adjusting this based on the measured water content of the sample air and relationship between response and humidity as reported in Inomata et al (2008). Corrections were made to the response of m/z 61 and m/z 137 for known losses due to fragmentation of acetic acid and monoterpenes at those masses. Dunne et al (2012) reported a significant interference to the acetonitrile signal at m/z 42 from the ^{13}C isotopologues of $C_3H_5^+$ and the product ion $C_3H_6^+$ from reactions involving O_2^+ and alkanes/alkenes. A detailed correction for this interference was not possible here, due to an absence of m/z 41, and alkane and alkene measurements. However, during a BB event, Dunne et al., (2012) calculated a 20% contribution to m/z 42 from non-acetonitrile ions: to reflect this interference the m/z 42 signal during the BB events has been reduced by 20%. Minimum detectable limits (MDLs) were calculated according to the principles of ISO 6869 (ISO, 1995) and ranged from 2 – 563 ppt for a one hour measurement. Where measured levels were below the MDL, a half MDL value was substituted.

3 Results and discussion

A time series of CO, BC and particle number > 3nm clearly shows the two events (BB1 and BB2) where plumes from the Robbins Island fire impacted the Cape Grim Station (Fig. 2). A detailed times series of these two events are presented here, with discussion of the influence of photochemistry, meteorology and air mass back trajectory on changing composition of trace gases and aerosol.

3.1 Biomass burning event 1 (BB1) February 16th 2006

3.1.1 Brief plume strike, particle growth and ozone enhancement

Fig. 3. shows a time series plot from BB1, including both the fresh plume and the changing composition with changing wind direction. A particle size and number contour plot, wind direction, O_3, CO, BC and urban tracer HFC-134a are shown. Periods of interest are labelled asd Periods A-F (Fig 3.) which are discussed below and summarised in Table 2. Average particle size distributions for periods corresponding to Periods A-F are presented in Fig. 4. NMOC data is not available from BB1. The matching air mass back trajectories for periods corresponding to Periods A-F are shown in Supp Fig. 1a-f.

Period A. The fresh BB plume is visible from ~02:00-06:00 (Fig. 3.) through high particle number concentrations corresponding with elevated CO and BC. The BB particles have a single, broad size distribution with a dominant mode of 120 nm (Fig. 4a), indicating fresh BB aerosol (Janhäll et al., 2010). The O_3 mixing ratio during this period is 10 ppb which is lower than background concentration of about ~15 ppb, likely due to titration by NO emitted from the fire. The HYSPLIT back trajectory (Supp Fig. 1a) indicates that air which brought the plume to Cape Grim had previously passed over the north west corner of Tasmania and the Southern Ocean.

Period B. Just after 06:00 (Fig. 3.), a slight wind direction change results in dramatically reduced particle concentration, CO and BC.~~, indicating the BB plume is no longer directly impacting the station~~. ~~With the sudden reduction in BB tracers,~~ T~~t~~he dominant mode of the particles drops from about 120 nm to 50 nm, but the distribution remains broad and uni-modal (Fig. 4a). From 7:00 – 12:00 there is ~~At around 07:00, O_3 increases, accompanied by~~ a gradual increase in the dominant mode of particles from 50 nm to 80 nm~~, indicating~~ suggesting a particle growth event, which is accompanied by an increase in ozone from 12 to 20 ppb~~.~~ The winds were light (1 m s^{-1}) and variable, the temperature mild (19ºC) and skies clear during this period ~~. The mean diameter of the particles increases from 50nm to 80nm over a period of 5 hours (corresponding to a growth rate of ~6 nm hr^{-1}), with an O_3 increase from 12 to 20 ppb. This daytime increase in O_3 alongside particle growth is suggestive of photochemical processing of the air, and an increase in particle size due to condensation of low volatility oxidation products. The emission source/s driving this particle growth event are not clear.~~ There is a small enhancement of BC above ~~The BC is elevated above~~ background concentrations ~~between~~ (12 - 194 ng m^{-3}~~,~~) while the particle size is increasing, suggesting that the station may be on the edge of the plume during this period, however CO is not enhanced alongside BC and so influence of BB emissions cannot be confirmed. ~~versus 2 ng m^{-3} in background air, suggesting the BB plume is diluted to between 1 – 14 % during particle growth. CO is elevated only 10 ppb above background during this period. However, unlike the integrated BC measurements, CO is an instanteous measurement every 40 minutes (Table 1) and it is likely these CO observations have not captured the BB plume influence during this period of high variability (e.g. during mixing of air masses).~~ The HYSPLIT trajectory (Supp Fig. 1b) shows that air arriving at the station ~~during the particle growth event~~ is almost entirely of marine origin but had some contact with the vegetated and sparsely populated North West coast of Tasmania and appears to pass over ~~passes close to the~~ Robbins Island ~~fire~~ before arriving at Cape Grim.

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Period C. At midday, the dominant particle mode stops increasing and is stable, and BC drops to background levels.~~, indicating that fire emissions are no longer impacting the station~~. An easterly wind overnight brings air from the sparsely populated and forrested coast of south eastern Australia (Supp Fig. 1 c) which leads to a further decrease in particle number, but a continued increase in O_3. The meteorology and nightime increase in O_3 is suggestive of a transported continental aged air mass arriving at Cape Grim, rather than local production. The average particle size distribution over this period (Fig. 4b) is a single broad distribution with a dominant mode of around 60nm, and is similar in shape to the distribution during the particle growth event.

Period D. A strong urban influence is visible in the early morning on the 17th February (Fig. 3.), when air is transported directly from metropolitan region of Melbourne ~300 km directly to the north (Supp Fig. 1d). O_3 peaks at ~30 ppb, accompanied by particle number concentrations of similar magnitude to the direct BB plume the previous day, but without the elevated CO or BC. The significant urban influence is confirmed by a peak in HFC-134a, an urban tracer which is widely used in motor vehicle air conditioning and domestic refrigeration (McCulloch et al., 2003). The average particle size distribution (Fig. 4b) shows a single broad distribution with a dominant mode of 90 nm.

Period E. In mid afternoon on the 17th February a westerly wind from the ocean sector leads to a sudden drop in HFC-134a, O_3 and particle number. HYSPLIT trajectories suggest the air mass passed over the ocean for at least 60 hours prior to arriving at Cape Grim (Supp Fig. 1 E). The particle size distribution changes from uni-modal to bi-modal, with dominant modes at around 50nm and 160 nm (Fig. 4c). This bi-modal distribution is typical of clean marine air and aerosols are likely dominated by non sea salt ~~(nss)~~ sulphate and sea salt particles, which in the larger mode have been cloud processed (Lawler et al., 2014; Cravigan et al., 2015).

Period F. At midnight on the 18th February, (Fig. 3.) terrestrial influence from mainland Australia is visible (Supp Fig. 1f), with an increase in O_3, HFC-134a and an increase in particle number in the 60 – 200nm size range. ~~, and possible a particle growth event between 0:00-03:00, though the increase in particle diameter is more likely due to an influx of larger particles.~~ Over the next 24 hours, decreasing O_3 and particle number suggests the air is becoming increasingly free of terrestrial influence. However the HYSPLIT trajectory (Supp 1F) shows that some terrestrial influence from mainland Australia remains for the next 24 hours. This is also shown by HFC-134a values which are slightly higher than during clean marine period (Event E), and a uni-model average particle size distribution (Fig. 4c), which resembles the terrestrially-influenced distributions corresponding to Periods B, C, D and F.

It is interesting to note that while size distributions have been described as uni-modal for Periods B, C, D and F, Fig. 4 a-c shows evidence of a second minor mode at around 160-170 nm in each of these terrestrially-influenced periods. Due to the strong marine influence of the air arriving at Cape Grim, the 160-170 nm mode in these periods can likely be attributed to cloud processed ~~nss-~~non sea salt sulphate and sea salt aerosol, and corresponds to the second larger mode (160 nm) in the clean marine period of Fig. 3 Period E.

Of interest is the contribution that the BB emissions from the Robbins Island fire had on the O_3 enhancement (Fig. 3). Determining the contribution is challenging given the variety of emission sources impacting Cape Grim (BB, terrestrial, marine, urban), and understanding the transport and mixing of these emissions. During BB1 The HFC-134a indicates an increasing influence from urban air from mainland Australia (indicating a likely source of O_3 or O_3 precursors), and indeed the O_3 and HFC-134a concentrations do increase in parallel (Fig. 3). However, some of the increases in O_3 occured when there was minimal urban influence, for example during the particle growth event (Fig. 3 Period B), and may have been driven by emissions from the local fire. Use of a chemical transport model to determine influence of fire emissions on O_3 formation will be reported in a follow up paper by Lawson et al (2015).

3.1.2 ~~Inferring chemical composition in~~Ability of particles in BB event 1 (BB1) ~~from CCN measurements~~to act as CCN

The ability of particles to act as CCN at 0.5% supersaturation was investigated during the fresh BB plume (Fig. 3 Period A) and the particle growth period (Period B). The CCN activity of particles was also calculated during the 24 hours of Period F, chosen due to the absence of BB tracers during this period, and predominance of marine air with some minor terrestrial influence. The average hourly ratio of CCN number to condensation nuclei (CN) number > 80 nm (CN80, measured using the SMPS) was calculated. CN80 was chosen based on a study by Petters et al., (2009) which suggested even weakly hygroscopic BB aerosols began to activate to CCN at a diameter of approximately 80 nm and larger. Given this, any observed difference in the CCN/CN80 ratio may then be due to either different chemical composition between the particles, and/or differences in particles size distributions, as larger particles are more easily activated to CCN. The CCN/CN80 ratio has only been calculated for BB1 because there are no aerosol size distribution measurements (and hence no CN80 measurements) for BB2. ~~The CCN/CN ratio for total CN measured with SMPS (CN> 14 nm) was also calculated.~~

Fig. 5a shows the CCN/CN80 expressed as a percentage for the fresh plume (Period A), particle growth event (Period B), and background marine/terrestrial (Period F). Error bars are ±1 standard error of the mean. Fig. 5b shows the absolute number concentration of CCN during these periods.

The CCN/CN80 ratio ~~is lowest~~ during the fresh BB plume strike (Period A) is ~~(~~56±8%. ~~), and is substantially higher during the particle growth event (Period B) (77±4%). For comparison, the CCN/ total CN ratio for the fresh BB plume strike is 37% (not shown).~~ Petters et al., (2009) show that in laboratory BB measurements the CCN activation of 80 nm particles ranges from a few % for low or weakly hygroscopic fuels to up to 60% for more hygroscopic fuels such as chamise, suggesting that the particles produced from coastal heath burned here may be more hygroscopic than those from other fuel types.

The CCN/CN80 ratio is substantially higher during the particle growth event (Period B) (77±4%). Fig. 4a shows that the average dominant diameter of particles shifts from around 120 nm during Period A to around 60nm during the period B. The smaller diameter during Period B suggests that particle size is not the reason for the increased CCN/CN80 ratio during the particle growth period, but is likely due to a changing chemical composition of particles between the two periods, with more hygroscopic particles measured during the particle growth period compared to the fresh BB particles. ~~As discussed above, an elevation of BC above typical background levels suggests dilute BB emissions are still present during this period. The changing chemical composition then is likely due to both a change in the source of particles (with a diminished BB influence and implied stronger marine inflence during Period B) but also possibly the change in properties of the diluted BB particles. The increase in CCN/CN80 ratio during period B and implied increased hygroscopicity, alongside the particle growth event suggests a coating of particles with a material more hygroscopic than the primary particle.~~

Volatility and hygroscopicity measurements of particles are available from Period A using a volatility and hygroscopic tandem differential mobility analysis (VH-TDMA) system(Fletcher et al., 2007). These measurements focused on the composition of 60 nm particles, and suggested ~~that 60 nm particles~~they consisted of a non-hygroscopic 23-nm core, a hygroscopic layer to 50 nm and a hydrophobic outer layer to 60 nm (possible

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Formatted: Font: (Default) Times New Roman, 12 pt, Font color: Black, German (Germany) homogeneously mixed). There was some evidence that the particle core contained two different types of particle, possibly due to merging of marine and BB particles. The suggested mix of hygroscopic and non-hygroscopic materials in fresh BB particles is in agreement with the fact that only 56% of these particles were hygroscopic enough to act as CCN. While the composition of the fresh BB particles may only be inferred from these measurements, the non-hygroscopic core may be black carbon or primary organic aerosol, the hygroscopic component an inorganic material such as sea salt or ammonium nitrate or sulphate or a hydroscopic organic such as MSA which is abundant in the marine boundary layer at Cape Grim in summer. The hydrophobic outer layer may be a hydrocarbon-type organic, with a low O:C ratio, which was co-emitted in the fire and condensed on to the particle as the plume cooled and was transported to Cape Grim (Fletcher et al., 2007). Unfortunately no hygroscopicity or volatility measurements are available from Period B (particle growth).

During background marine Period F, all (104 ± 3%) of the particles >80 nm could act as CCN (Fig. 5a). A value of more than 100% is not physically possible but is due to uncertainty associated with the different techniques (SMPS and CCN) and measurement synchronisation. This result is in agreement with the work of Fletcher et al (2007) who reported that the fresh BB particles from BB1-A had a lower hygroscopic growth factor than marine particles. Fig. 4 a and 4 c shows the average size distribution of particles during Period F (background marine/terrestrial) is very similar to period B (particle growth), despite the air masses coming from different directions (westerly and easterly respectively). As discussed previously, both these periods have a predominant marine back trajectory and some terrestrial influence. It is therefore likely that the main difference between the particle composition between these two periods, and the reason for the lower CCN/CN ratio during Period B is the presence of non or weakly-hygroscopic >80 nm particles, such as the BC which elevated above background levels during Period B.~~ from the recent BB emissions.~~

Sea salt and non sea salt~~nss~~ sulphate aerosol are important sources of CCN in the marine boundary layer (Korhonen et al., 2008; Quinn and Bates, 2011) and are likely the main source of CCN in Period F (and ~~possibly~~ probably Period B). The fact that all particles >80nm could act as CCN in Period F suggests that any non-hygroscopic terrestrial particles which reached Cape Grim during this time were likely to have been aged and oxidised during the several hundred kms during transport from the mainland.

Finally, the absolute number concentration ~~hourly average~~ of CCN ~~number~~ in the fresh plume (A) (hourly average) was ~2000 cm^{-3} (Fig. 5b), with minute average concentrations up to

~5500 CCN cm^{-3}~~-~~. In contrast, the average number of CCN during particle growth (Period B) was a factor of 3 lower at ~700 CCN cm^{-3}.~~, the decrease driven by dilution of the fresh smoke plume.~~ During the background marine/terrestrial Period (F) in BB1, the CCN is 320 CCN cm^{-3}, with low variability, a value which is within the range of typical pristine marine values (Gras, 2007). Overall, CCN were enhanced by a factor ~6 and a factor of ~30 above background levels in BB1 and BB2 respectively (see Sect. 3.2 and Table 3). Despite the modest ability of fresh BB particles to form CCN (CCN/CN80 ratio of 56%), the very high numbers of particles ejected into the marine boundary layer during the fire highlights the dramatic impact BB plumes can have on the CCN population, particularly in clean marine regions.

~~3.1.3 Discussion – determining drivers of ozone, particle growth and change in CCN/CN ratio in BB event 1 (BB1)~~

~~Of interest is the contribution that the BB emissions from the Robbins Island fire had on the particle growth event, and O_3 enhancement (Fig. 3). Determining the contribution from just one source is challenging given a) the variety of emission sources impacting Cape Grim during during BB1 (BB, terrestrial, marine, urban), and understanding the transport and mixing of these emissions b) the complexity of chemistry involved in particle growth processes including gas to aersosol phase transfer, and of O_3 production and c) the lack of specific BB tracers, such as levoglucosan and acetonitrile during this event (BC is a BB tracer but may also come from other combustion processes eg fossil fuel combustion). Similarly, without aerosol composition measurements, the changing composition of the particles during growth, and therefore the species responsible, cannot be determined.~~

~~Several studies have reported a larger diameter of particles in aged, diluted BB plumes compared to fresh BB plumes, due to coating of primary BB particles with low volatility organic and inorganic compounds (Janhäll et al., 2010; Kondo et al., 2011; Sahu et al., 2012; Akagi et al., 2012). The importance of photochemical reactions in driving the oxidation and condensation processes were higlighted recently by Vakkari et al (2014) who found that the degree of oxidation and diameter was enhanced when the plume was transported in daylight hours compared to nightime. Rather fewer studies have reported size distributions for individual particle growth events in BB plumes as reported here. Particle nucleation and subsequent growth in fresh BB plumes occured in chamber studies with rapid growth rates of~~

~~12 nm hour^{-1} (Hennigan et al., 2012), which is approximately twice the growth rate observed in this study. In summary, there is evidence elswhere that particle diameter increases with BB plume dilution and aging, particularly during daylight hours.~~

~~Similarly the sources and chemical drivers of the change in CCN/CN80 ratio during the fresh plume and particle growth period are difficult to determine from observations alone. As discussed above the dominant mode diameter of particles during the particle growth event was smaller than during the fresh plume and so a change in particle composition leading to enhanced hygroscopicity is the likely driver of the enhanced ratio during particle growth. Chamber studies have shown that primary BB particles become more hygroscopic when coated with inorganics and oxygenated secondary organics (Martin et al., 2013; Petters et al., 2009; Engelhart et al., 2012). The increase in O_3 alongside the particle growth event indicates photochemical processing of the diluted plume, which produce lower volatility organics and inorganics. However it is difficult to elucidate the mechanisms contributing to an increase in hygroscopicity when particles from the BB plume are externally mixed with particles and trace gases from a range of others sources.~~

~~Ozone production has been frequently reported in air impacted by BB, and there is some evidence of larger enhancements in air impacted by both BB and urban emissions (Jaffe and Wigder, 2012; Wigder et al., 2013). In BB1, the HFC-134a indicates an increasing influence from urban air from mainland Australia (indicating a likely source of O_3 or O_3 precursors), and indeed the O_3 and HFC-134a concentrations do increase in parallel (Fig. 3). However, some of the increases in O_3 occured when there was minimal urban influence, for example during the particle growth event (Fig. 3 Period B), and may have been driven by emissions from the local fire.~~

~~Use of a chemical transport model to determine the sources driving the particle growth, change in CCN/CN ratio and O_3 formation will be reported in a follow up paper by Lawson et al (2015).~~

3.2 BB event 2 (BB2) February 23rd 2006

3.2.1 Interplay between emissions, meteorology and sources

BB2 was of much longer duration than BB1, and lasted about 29 hours. Fig. 6 shows a time series including wind direction and rainfall, O_3, CO, BC, BB tracer acetonitrile, acetonitrile/CO ratio (where CO > 400 ppb) and urban tracer HFC-134a. Periods of interest are highlighted as A-D (Fig 6.), summarised in Table 2 and discussed below. Particle size distribution data is not available for BB2. The matching air mass back trajectories for the events highlighted in Fig. 6. are shown in Supplementary Fig. 2. a-d.

Period A. For the first 24 hours of BB2, there is clear elevation in CO, BC and acetonitrile, due to the easterly wind advecting the plume directly to Cape Grim. The acetonitrile mixing ratio is ~ 1 ppb and is enhanced by a factor of 30 above typical background levels at Cape Grim of ~35 ppt (Table 3). The acetonitrile ratio to CO is also relatively constant during this time (1-2 ppt/ppb). An ozone peak of 27 ppb (~~minutely~~minute data) occurs in mid afternoon on 24 February, corresponding to an hourly Normalised Excess Mixing Ratio (NEMR) $\Delta O_3/\Delta CO$ of 0.05 (where NEMR is an excess mixing ratio normalised to a non-reactive co-emitted tracer, in this case CO, see Akagi et al., 2011).

Period B. At 04:00 on 25th February acetonitrile peaks by a factor of 17 over 2 hours (Fig. 6 Period B) with a smaller peak at 23:00 on the 24th February~~ (factor of 5 increase)~~. Almost all masses on the PTR-MS increased at the same time as acetonitrile, including masses corresponding to HCN, methanol, acetaldehyde, acetone, furan/isoprene and benzene~~ which increased by a factor of 3-5 during the first peak at 23:00 and a factor of 6-16 during the second peak at 4:00 (hourly average values~~.). The corresponding CO peak at 04:00 (~1500 ppb) increased by a factor of 21 ~~over 2 hours ~~and is the largest peak from BB2. The corresponding ~~While~~ BC ~~has a corresponding ~~peak at 04:00 ~~(factor of 5 increase) this BC peak ~~is much smaller than peaks which occured earlier in BB2~~. CN number showed an increase in concentration by a factor of 4 during peak 1 and factor of 7 during peak 2. ~~This large enhancement in CO and NMOCs but modest enhancement in BC suggests a decrease in the combustion efficiency during this time. This is further supported by increases in the ratio of acetonitrile to CO (where CO > 400 ppb) by a factor of ~3 during the peak periods (Fig. 6), and a decrease in the ratios of BC to CO during peak periods (average 0.9± 0.3 ng m^{-3}ppb^{-1}) compared to non-peak periods (2.2± 0.1 ng m^{-3}ppb^{-1}).

A small amount of rainfall recorded at Cape Grim (1.4 mm) corresponds with the second peak (Fig. 6). Archived radar images from the Bureau of Meteorology (West Takone 128 km, 10 min resolution) confirm that ~~at ~~very light patchy rain showers occured on Robbins Island at 23:10 followed by intermittent rain showers of light to moderate intensity from 12:40 until 05:40, on the 25th February (S. Baly, pers com). The total rainfal amount that fell on Robbins Island was between 1-5 mm (www.bom.gov.au). Evidence of rainfall coinciding with an enhancement in NMOC ER to CO, and a decrease in BC ER to CO suggests that the rainfall changed the combustion ~~dynamics~~ processes of the fire. The enhanced ~~mixing ratios~~ERs of NMOCs ~~and~~ to CO which are associated with low-efficiency, smouldering combustion, can therefore attributed to a short term decrease in combustion efficiency, ~~enhancement in emissions~~, driven by rainfall. Due to the small number of data points (2) it is not possible to calculate reliable ER to CO during this shortlived event. But this time series highlights the importance of relatively minor meterological events on BB emission ratios~~s~~.

While the elevated concentrations of BB tracers CO, BC and acetonitrile during this period are attributed to emissions from the local fire, back trajectories (Supp Fig. 3B) show that ~~during this period~~ air arriving at Cape Grim had previously passed over the Australian mainland. The increasing anthropogenic influence is also supported by increasing levels of HFC-134a and a corresponding increase in O_3 which peaks at 34 ppb (minute~~l~~ data~~y~~) at 1:00-2:00, with an hourly NEMR for $\Delta O_3/\Delta CO$ of 0.07 (the highest observed).

Period C. With a change in wind direction further to the north from 5:00 onwards (Fig. 6), BB tracers BC, CO and acetonitrile all decrease to background levels, ~~suggesting~~ indicating fire emissions are no longer impacting the station. Ozone begins to increase at 8:00 and reaches ~40 ppb 3 hours later, corresponding with a maximum HFC-134a mixing ratio of ~ 35 ppt. The air mass back trajectory (Supp Fig. 2 C) confirms that air from Melbourne is impacting the station during this period

Period D. As wind moves further into the west in to the clean marine sector (Supp Fig. 2D), O_3 and HFC-134a decrease to background levels.

This time series highlights possible interplay of sources and meteorology on the observed trace gases and particles. The very large increase of NMOCs and CO observed during the rainfall period shows the potentially large affect of quite minor meteorological events on BB emission ratios~~s~~. While other studies have found a link between fuel moisture, MCE and emissions of PM2.5, (eg Watson et al., ~~(~~2011~~)~~ ; Hosseini et al., ~~(~~2013~~)~~) this is the first study to our knowledge which has linked rainfall with a large increase in trace gas emission ratios~~s~~ from BB.

This work also highlights the large influence that BB plumes can have on the composition of air in the marine boundary layer.~~the background atmosphere~~. During the direct plume strikes, absolute numbers of particles > 3nm increased from 600 to 25,000 particles cm^{-3} (hourly average). ~~These particle number concentrations are in good agreement with ground based measurements at background sites in the Amazon (20,000 particles cm~~$^{-3}$~~) (Artaxo et al., 2013)~~

~~and at a forested site in Finland (30,000 particles cm^{-3}) (Virkkula et al., 2014). The absolute number of CCN increased from 160 particles cm^{-3} in background air up to 5500 particles cm^{-3} in BB2, a factor of 34 increase, in agreement with a study who showed a dry season increase in CCN of a factor 10-20 in the Amazon, attributed to BB aerosols (Andreae et al., 2002).~~ In BB2, as was the case in BB1, the O_3 concentrations closely correspond with the HFC134a concentrations. This suggests that transport of photochemically processed air from urban areas to Cape Grim is the main driver of the O_3 observed but does not rule out possible local O_3 formation from BB emissions. NEMRs of $\Delta O_3/\Delta CO$ ranged from 0.001-0.074 during BB2 which are comparable to NEMRs observed elsewhere in BB plumes <1 hr old (Yokelson et al., 2003;Yokelson et al., 2009).

3.2.2 Chemical composition of BB2 and selection of in-plume and background periods

The composition of the fresh plume during BB2 was explored by determining for which trace gas and aerosol species the enhancement above background concentrations was statistically significant. Emission ratios (ER) and particle number to CO were then calculated for these selected species and converted to emission factors (EF).

The first 10 hours of Period A from BB2 (from 23:00 on the 23rd Feb to 09:00 on the 24th Feb) was selected to characterise the fresh plume composition. During this time, the air which brought the Robbins Island BB emissions to Cape Grim had previously passed over the ocean and so was free of terrestrial or urban influence (NOAA HYSPLIT Supp Fig. 2A). While fresh BB emissions were measured at Cape Grim beyond 10:00 on the 24th Feb, the air at this time had prior contact with the Australian mainland, including the Melbourne region and so was considered unsuitable for characterising the BB plume. During the selected time period, wind speeds of 16 m s^{-1} meant that the plume travelled the 20 km to Cape Grim over a period of about 20 minutes, which allows the plume to cool to ambient temperatures but ~~ensures~~ ensured minimum photochemical processing of the plume (Akagi et al., 2011). Advection of the plume to the site occurred primarily at night so minimal impact of photochemical reactions on the plume composition is expected (Vakkari et al., 2014). It is therefore assumed that the enhancement ratios measured at Cape Grim during this time are unaltered from the original emission ratios. ~~-~~Finally, photos indicate the Robbins Island fire plume was well mixed within the boundary layer and was not lofted into the FT, allowing representative 'fire-averaged' measurements to be collected (Akagi et al., 2014).

Background concentrations of gas and particle species were determined from fire-free periods in early March 2006 which had a very similar air back trajectory to trajectories during the fire (not shown). Concentrations of long lived urban tracers (not emitted from fires) including HFC-32, HFC-125a and HFC-134a were also used to match suitable background time periods with the fresh plume period.

Table 3 lists the gas and aerosol species measured, whether concentrations were statistically higher in the plume compared to background air, average background concentrations, average in-plume concentrations, emission ratios (ER) to CO and EF (g kg^{-1}). Details of ER and EF calculations are given below. Hourly average data were used for these calculations.

3.2.3 Species emitted in BB event 2 (BB2) –t tests

Hypothesis testing using the student t tests (one sided) were carried out to determine whether concentrations in the BB plume (x_1) were significantly higher than concentrations observed in the background periods (x_2), with a 95% level of significance. Table 3 shows which species were statistically enhanced in the BB plume, and hence assumed to be emitted from the fire (x_1-x_2>0) and those which were not statistically enhanced in the BB plume ($x1-x2=0$). While the vast majority of species measured were found to be significantly enhanced in the BB plume, there were a number of species including DMS, chloroform, methyl chloroform, dichloromethane, carbon tetrachloride, bromoform and the urban tracers HFC-032, HFC-125 and HFC-134a which were not significantly enhanced. DMS has consistently been found to be emitted from BB in many studies (as summarised by Akagi et al 2011). However, in this study due to close proximity to the ocean, the likely emission of DMS from the BB was likely obscured by the high variability in the background concentration. The absence of emission of chloroform, methyl chloroform, dichloromethane, carbon tetrachloride, tribromomethane and the HFCs are in agreement with a recent study of boreal forest emissions by Simpson et al (2011).

3.2.4 Calculation of Emission Ratios to CO

Excess mixing ratios (Δx) were calculated for species that were statistically higher in the plume compared to background air by subtracting background mixing ratios from the hourly in-plume mixing ratios. Emission ratios to CO were then calculated by plotting Δx versus ΔCO, fitting a least squares line to the slope and forcing the intercept to zero (Yokelson et al., 1999). Emission ratios (ER) to CO and the R^2 of the fit are reported in Table 3.

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The excess mixing ratios of all species significantly enhanced in the plume correlated with the excess mixing ratios of CO with an R^2 value of ≥0.4, with the exception of CO_2, HCHO, HCOOH, m/z 101, N_2O, and CCN number concentration (see discussion below and Fig. 3b). ER plots for BC, CN>3nm, H_2, CH_4, C_2H_6, C_6H_6, CH_3COOH, C_6H_6O and C_2H_3N are shown in Fig. 7. The ER of CO to particle number (38 cm^{-3} ppb^{-1}) agrees well with a literature averaged value of 34 ± 16 cm^{-3} ppb^{-1} (Janhall., et al 2010). The H_2 ER to CO (0.10) is lower than the range reported from BB emissions (0.15-0.45), as summarised by Vollmer et al., (2012). ~~The ER of BC to CO (2.8 ng m^{-3} ppb^{-1}) is similar to that derived for smouldering fires of 2.3 ± 2.2 ng m^{-3} $ppbv^{-1}$ (Kondo et al., 2011), where ppbv is approximately equal to molar ppb used here.~~

There is a low correlation between mixing ratios of CO and CO_2 (ER to CO R^2 = 0.15, see Table 3). This is in part ~~likely~~ because CO and CO_2 are emitted in different ratios from different combustion processes (smouldering and flaming respectively) and may also be influence by variability in background levels of CO_2 ~~the enhancement of CO_2 in BB plumes is very small compared to the variation of CO_2 in the background atmosphere, particularly when sampling at some distance from the fire~~ (Andreae et al., 2012). ~~The lack of correlation seen here between CO and CO_2 means that the CO_2 emissions from the fire cannot be reliably determined. For this reason, in Sect. 3.2.5., EFs are calculated using a published EF for CO.~~

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Of the other species with R^2 values of <0.4, HCHO and HCOOH are both emitted directly from BB, but are also oxidation products of other species co-emitted in BB. It is therefore possible that in the 20 minute period between plume generation and sampling, chemical processing has lead to generation of these compounds in the plume, which has changed the ER to CO. In addition, sampling losses of HCOOH down the inlet line are possible (Stockwell et al., 2014)~~ as observed by Christian et al (2004)~~. The lack of relationship between ΔCO and ΔN_2O is likely because N_2O is an intermediate oxidation product which is both formed and destroyed during combustion. Studies of emissions from Savanna burning in Northern Australia have found N_2O to be insensitive to changes in MCE (Meyer and Cook, 2015; Meyer et al., 2012; Volkova et al., 2014). A further reason for a lack of correlation with ΔCO for ΔN_2O is that as for CO_2, the plume enhancement of ΔN_2O is relatively small compared to the observed variability in background concentrations. Finally the lack of correlation between ΔCCN and ΔCO may be due interaction of plume aerosol with background sources of CCN, such as sea salt, and the change in particle properties and composition in the 20 minutes after emission.

3.2.5 Calculation of MCE and EF and comparison with other studies

Combustion efficiency (CE) is a commonly used measure of the degree of oxidation of fuel carbon to CO_2. Combustion efficiency is commonly approximated as the modified combustion efficiency (MCE) (Yokelson et al., 1999), which is calculated using the following equation

$$MCE = \frac{\Delta CO_2}{\Delta CO_2 + \Delta CO} \qquad (1)$$

Field Code Changed

In this study the 10 hour integrated MCE was 0.88, which indicates predominantly smouldering combustion. The ER of BC to CO reported here is in good agreement with BC to CO ERs in smouldering fires (MCE <0.9) reported by Kondo et al., (2011) and May et al., (2014) which suggests that the excess CO_2, and MCE has been determined reliably.

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Whole of fire Emission factors were calculated according to the Carbon Mass Balance method (Ward and Radke, 1993). Emission factors were calculated relative to combusted fuel mass (Andreae and Merlet, 2001), assuming 50% fuel carbon content by dry weight according to the following equation.

$$EFx(g/kg) = \frac{[\Delta x]}{\sum([\Delta CO_2]+[\Delta CO]+[\Delta CH_4])} \times 0.5 \times 1000(g/kg) \times \frac{MW(x)}{12} \qquad (2)$$

Field Code Changed

The Carbon Mass Balance method assumes all volatilised carbon is detected, including CO_2, CO, hydrocarbons and particulate carbon. Here the major volatile carbon components of CO_2, CO and CH_4 were used in the EF calculation, so the resulting EF may be overestimated by 1-2 % (Andreae and Merlet, 2001).

For comparison with the carbon mass balance method, EF were also calculated using an average CO EF for temperate forests from Akagi et al (2011), which corresponds to an MCE of 0.92 (see Supplementary material for EF and method details). Trace gas EF calculated using an assumed CO EF were generally 50% lower than EF calculated using the carbon mass balance method.

~~EFs (g/kg fuel) were calculated using the equation detailed in Andreae et al., (2001), using CO as the reference gas:~~

~~$EF(X) = ER(X/CO)\times\frac{MW(X)}{MW(CO)}\times EF(CO)$ (1)~~

~~Where EF (X) is the calculated emission factor in g/kg fuel, ER (X/CO) is the molar emission ratio with respect to CO, MW(X) is the molecular weight of the trace species, MW (CO) is the molecular weight of CO, and EF(CO) is the emission factor of CO. The EF (CO) used was the temperate average EF from Akagi et al., (2011) of 89 ±32 g CO kg^{-1} fuel, which corresponds to MCE of 0.92.~~

~~EFs were calculated only for species which had an ER with CO with a fit of R^2 > 0.4 (which excludes HCHO, HCOOH and N$_2$O) and were statistically emitted from the fire according to the t test (see Table 3). As the EFs calculated were from a single fire, no variability (e.g. standard deviation) is given.~~

Table 4 shows EFs calculated from this study (Carbon Mass Balance Method) compared with other Australian BB studies both of eucalypt and schlerophyll forest fires in temperate south eastern Australia (Paton-Walsh et al., 2005; Paton-Walsh et al., 2008; Paton-Walsh et al., 2014), and tropical savanna fires in northern Australia (Paton-Walsh et al., 2010; Meyer et al., 2012; Hurst et al., 1994a; Hurst et al., 1994b; Shirai et al., 2003; Smith et al., 2014). The fire in this study (41ºS) is >1000 km south of the temperate forest fires used for comparison (33-35ºS), and some 2500 km South East of the tropical savannah fires in the comparison (12-14ºS). ~~The vegetation in this study (coastal scrub and grasses) is comparable in structure to the mid and lower story vegetation in the temperate forest and savannah woodland fires in the other Australian studies, though lacks the coarse woody debris and the dominant upper story of trees found particularly in temperate Australian forests.~~

EF from this study reported in Table 4 are within 50% of the EFs from the other South Eastern Australian studies except for acetic acid, which is 5 times lower than the EF reported by Paton-Walsh et al., (2014). EF from this study are also within 50% of temperate NH EF (temperate forests and chaparral) except for hydrogen, acetic acid and the methyl halides and within 80% of the average tropical savannah EF, with the exception of acetic acid and the methyl halides.

The acetic acid EF from this study is significantly lower than reported from Australian and NH temperate studies, though the variability reported elsewhere is large. Acetic acid may form rapidly in BB plumes (Akagi et al., 2012), which adds uncertainty to the EF in plumes which are sampled some distance downwind of emission. The lower EF reported in this work may be due to inlet losses, or another loss process such as nocturnal uptake of acetic acid on to wet aerosols (Stockwell et al., 2014).

The methyl halides EF from this study are in the same proportion as seen elsewhere (eg EF (CH_3Cl) > EF(CH_3Br) > EF(CH_3I) but the EF magnitudes are substantially higher. The CH_3Cl EF from this study is more than a factor of 4 higher than elsewhere in Australia and the NH, the CH_3Br EF between 5 and 11 times higher and CH_3I EF a factor of about 3 times higher than elsewhere. EF calculated by the alternative ER to CO method (Supplementary material) gives methyl halide EFs which are 30% lower but still much larger than those observed elsewhere. It is likely that the high methyl halide EFs reported here are due to high halogen content of soil and vegetation on the island, due to very close proximity to the ocean, and transfer of halogens to the soil via sea spray (McKenzie et al., 1996). Chlorine and bromine content in vegetation has been shown to increase with proximity to the coast (McKenzie et al., 1996; Stockwell et al., 2014) and methyl chloride and hydrochloric acid EF are impacted by the chlorine content of vegetation (Reinhardt and Ward, 1995; ~~)(~~Stockwell et al., 2014).

~~Two of the temperate Australian studies (Paton-Walsh et al., 2005; Paton-Walsh et al., 2008) use a published EF for CO (Andreae and Merlet (2001) extra tropical value of 107 g kg^{-1}), to convert ER to EF while the temperate study by Paton Walsh et al (2014) measured a CO emission factor of 118 g kg^{-1}. These CO EF from Paton-Walsh et al., (2005, 2008, 2014) correspond to MCEs ranging between 0.88-0.91, slightly lower than the MCE assumed here of 0.92. The Australian savanna studies used for comparison all measured CO and CO_2 EF corresponding to a MCE of 0.92. EFs from temperate vegetation in the NH are also included for comparison: Akagi et al., (2011) reports average EFs for temperate pine-oak, evergreen and coniferous forests (average MCE 0.92), and Yokelson et al., (2013) gives an average EF for temperate semi arid shrub land including coastal sage scrub and maritime chaparral (MCE 0.94). The vegetation burned in Yokelson et al., (2013) is expected to be more similar in structure to the Robbins Island coastal scrub than the temperate forests in Akagi et al., (2011).~~

~~For most species, there is a good agreement between EFs from this study and EFs previously published from Australia and elsewhere. The H_2 EF from this study (0.64 g kg^{-1}) is approximately one third the EF from Akagi et al., (2011) (2.03 g kg^{-1}), however there is a large variability reported in the Akagi et al., (2011) average value. There are no previously reported H_2 EFs for Australia. The CH_4 EF from this study (2.49 g kg^{-1}) is slightly higher than EF for the tropical savanna studies (2.03-2.33 g kg^{-1}). The C_2H_6 EF reported here of~~

~~0.30 g kg^{-1} agrees very closely with the SE Australian EF by Paton-Walsh et al., 2005 (0.26 g kg^{-1}), and is lower than (but within variability of) the value reported by Paton-Walsh et al., 2014 of 0.5 g kg^{-1}. The ethane EF reported here (0.3 g kg^{-1}) is within the wide range reported from Australian savanna burns (0.08-0.6 g kg^{-1}), and a factor of almost a factor of 4 lower than the NH temperate forests average (Akagi et al., 2011) although comparable to coastal scrub and chaparral (Yokelson et al., 2013).~~

~~The HCN EF (0.49 g kg^{-1}) agrees well with the temperate SE Australian value of 0.43 g kg^{-1} (Paton-Walsh et al., 2005) and is at the higher end of the wide range reported for tropical Australian savanna (0.11-0.53 g kg^{-1}). The HCN EF reported here is lower than values from the NH temperate forests (0.73 g kg^{-1}) and coastal scrub and chaparral (0.75 g kg^{-1}). There are no temperate Australian acetonitrile EFs available for comparison, but the EF from this study (0.17 g kg^{-1}) agrees well with that from the Australian savanna (0.11 g kg^{-1}) and temperate coastal scrub and chaparral (0.15 g kg^{-1}). No Australian EF for phenol is available for comparison but the EF from this study (0.24 g kg^{-1}) is somewhat lower to those reported in the temperate NH by Akagi et al., (2011) (0.33 g kg^{-1}) and Yokelson (0.45 g kg^{-1}). Acetic acid EF from this study (0.52 g kg^{-1}) is a factor of 7 lower than temperate value by Paton-Walsh et al., 2014 (3.8 g kg^{-1}), and a factor of 4 lower than those reported in the temperate NH by Akagi et al., (2011) (1.97 g kg^{-1}) and Yokelson et al., (2013) (1.91 g kg^{-1}) though the variability in these values is large. The methanol EF (1.37 g kg^{-1}) is somewhat lower than temperate EF of 2.03 g kg^{-1} and 2.4 g kg^{-1} (Paton-Walsh et al., 2005;Paton-Walsh et al., 2014) and 1.93 g kg^{-1},(Akagi et al., 2011) though agrees very well with Yokelson et al (2013) EF of 1.35 g kg^{-1}. The EF for benzene (0.47 g kg^{-1}) is in the upper range reported for Australian savanna burning by Hurst et al., (1994a; 1994b) (0.29-0.42 g kg^{-1}), is higher than Shirai et al., (2003) savanna (0.21 g kg^{-1}) and agrees closely with the Yokelson et al., (2013) temperate value of 0.45 g kg^{-1}. The toluene EF (0.17 g kg^{-1}) has no Australian EF for comparison but is similar to the temperate value reported by Yokelson et al., (2013) (0.20 g kg^{-1}).~~

~~While the EF for the methyl halides here are in the same proportion as other studies (eg EF (CH_3Cl) > EF(CH_3Br) > EF(CH_3I), the magnitude of the EF are substantially higher than other studies. The CH_3Cl EF from this study (0.208 g kg^{-1}) is more than a factor of 3 higher than elsewhere in Australia and the NH, the EF of CH_3Br between 4 and 9 times higher and CH_3I a factor of about 2 times higher than elsewhere. The ER to CO correlation for the methyl halides on which these EF are based consists of only a few observations. However,~~

~~the ethane (C_2H_6) ER to CO and EF in this study was derived from the same number of data points and same measurement system (the AGAGE CGMS Medusa), and the resulting EF for C_2H_6 is very consistent with other EF from Australian temperate and savanna regions, as discussed above. It is therefore possible that the high methyl halide EFs reported here are due to high halogen content of soil and vegetation on the island, due to very close proximity to the ocean, and transfer of halogens to the soil via sea spray. Chlorine content in vegetation does vary substantially as reported by Lobert et al., (1999) and Christian et al., (2003) but whether a high halogen content in vegetation is the reason for these high EF remains unknown. A further reason could be a contribution from another local source; while the methyl halide emission ratios were calculated using background mixing ratios similar to multi-annual average Cape Grim mixing ratios in air from NW Tasmania, elevated methyl halide 'events' have been previously linked to coastal wetlands around and to the east of Robbins Island (Cox et al., 2005; Cox et al., 2003).~~

~~In summary, the EF reported for this study agree well with other EF from temperate Australia with the exception of acetic acid. These temperate EF (with the exception of acetic acid and methyl halides) are higher than or in the upper range of Tropical Australian savannah EF. Compared to NH temperate EF, most species in this study have EF lower than reported in Akagi et al., (2011) NH temperate forests, despite the fact that EF in this study were calculated using the CO EF from Akagi et al., (2011) and therefore assumes the same MCE. The values from this study are in many cases in very good agreement with the NH coastal scrub and chaparral values reported by Yokelson et al., (2013), particularly for ethane, HCN, acetaldehyde, methanol, benzene and toluene.~~

4 ~~Conclusions~~ Summary and future work

The opportunistic measurement of BB plumes at Cape Grim Baseline Air Pollution Station in February 2006 has allowed characterisation of BB plumes in a region with few BB measurements. Plumes were measured on two occasions (events BB1 and BB2) when the plume was advected to Cape Grim from a fire on Robbins Island some 20 km to the east.

The fresh plume had a large impact on the number of particles at Cape Grim, with absolute numbers of particles > 3 nm increasing from 600 cm^{-3} in background air up to 25,000 cm^{-3} during the fresh plume in BB2 (hourly average) and CCN increasing from 160 cm^{-3} in background air up to 5500 cm^{-3} (hourly average). The dominant particle diameter mode measured in BB1 was 120 nm~~ during the fresh plume~~.

After a slight wind direction change, BB tracers BC and CO decreased dramatically and the dominant particle mode decreased to 50nm. ~~During BB1,~~ A gradual increase in particle size to 80nm was observed over 5 hours, in calm sunny conditions, alongside a modest increase in ozone. BC was present above background levels during particle growth but CO was not significantly elevated, so the presence of the fire emissions during particle growth cannot be determined. ~~dilution of the plume in the morning via a wind direction change resulted in a drop in the dominant particle mode to 50 nm, and a particle growth event in which particles grew to 80 nm over 5 hours. Particle growth was accompanied by an increase in O_3 from 12 to 20 ppb, suggesting photochemical processing of air and condensation of low volatility oxidation products may be driving the particle growth.~~. During BB1, the ability of particles > 80nm to act as CCN at 0.5% supersaturation was investigated, including during the fresh BB, particle growth and background terrestrial/marine periods. The ΔCCN/ΔCN80 ratio was lowest during the fresh BB plume strike (5~~7~~6±8%), higher during the particle growth event (77±4%) and is higher still (104±3%) in background marine air.

~~Without chemical composition measurements, it is difficult to determine the sources, and the chemical species responsible for the particle growth event, and the increase in CCN/CN80 ratio observed during BB1. The implied increase in hygroscopicity during the particle growth period, along with an increase in particle diameter is suggestive of condensation of a hygroscopic coating, such as inorganics or highly oxidised organics, on primary particles of low hygroscopicity. However, identities of the condensing species, and the source of trace gases and aerosols during this period are difficult to determine with observations alone.~~

Enhancements in O_3 concentration above background were observed following the direct plume strikes in BB1 and during the direct plume strike in BB2, with NEMRs ($\Delta O_3/\Delta CO$) of 0.001-0.074. It is likely that some of the O_3 enhancement that occured during the particle growth event in BB1 was driven by fire emissions. However on other occasions enhancement of O_3 which occured at night, corresponding with enhancements of urban tracer HFC-134a was most likely due to air being transported from mainland Australia. Chemical transport modelling will be used in a follow up paper to elucidate the sources, and where possible the species responsible for the O_3 enhancement~~, particle growth~~ and change in particle hygroscopicity observed, as well as the age of the urban emissions transported from Melbourne.

The more prolonged BB2 allowed determination of emission ratios (ER) to CO and Emission Factors (EF) for a range of trace gas species, CN and BC using the carbon mass balance method. These EF, which were calculated from nocturnal measurements of the BB plume, provide a unique set of emission estimates for a wide range of trace gases from burning of coastal heathland in temperate Australia. ~~, and these have been used to determine emission factors in g kg^{-1} of fuel. While these EF are based on only one fire and were calculated using a published EF for CO (an average temperate value), this work provides new estimates of EFs for a number of trace gas species for burning of coastal scrubland in temperate Australia.~~

A very large increase in emissions of NMOCs (factor of 16) and CO (factor of 21), and a more modest increase in BC (factor of 5) occurred during BB2. The ratio of acetonitrile to CO increased by a factor of 2-3 and the ratio of BC to CO halved during this period. This change in emission~~s and~~ ratios is attributed to decreased combustion efficiency during this time, due to rainfall over Robbins Island. Given that air quality and climate models typically use a fixed EF for trace gas and aerosol species, the impact of varying emissions due to meteorology may not be captured by models.

More broadly, given the high variability in reported EF for trace gas and aerosol species in the literature, the impact of EF variability on modelled outputs of both primary BB species (i.e. CO, BC, NMOCs) and secondary BB species (i.e. O_3, oxygenated NMOCs, secondary aerosol) is likely to be significant. ~~However, few studies have systematically examined the impact of EF variability on model outputs.~~ In the next phase of this work, in addition to exploring the chemistry described above with chemical transport modelling, we will also systematically explore the sensitivity of these models to EF variability, as well as spatial and meteorological variability.

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Tab01

Measurement	Instrument	Air intake height	Time resolution	Reference
NMOCs	PTR-MS	10m	10 min	(Galbally et al., 2007a)
Particle size distribution and number 14-700 nm	SMPS	10m	1 min	(Cravigan et al., 2015)
Condensation nuclei (particle number > 3 nm)	TSI particle counters	10m	1 min	(Gras, 2007)
black carbon concentration	aethelometer	10m	integrated 30 min	(Gras, 2007)
CCN number at 0.5% SS	CCN counter	10m	1 min	(Gras, 2007)
ozone (O_3)	TECO analyser	10m	1 min	(Galbally et al., 2007b)
methane (CH_4)	AGAGE GC-FID	10m/70m/75m	40 min (discrete air sample every 40 minutes)	(Prinn et al., 2000; Krummel et al., 2007)
carbon monoxide (CO) and hydrogen (H_2)	AGAGE GC-MRD	10m/70m/75m	40 min (discrete air sample every 40 minutes)	(Prinn et al., 2000; Krummel et al., 2007)
carbon dioxide (CO_2)	CSIRO LoFlo NDIR	70m	1 min (continuous analyser)	(Steele et al., 2007)
nitrous oxide (N_2O), major CFCs, $CHCl_3$, CH_3CCl_3, CCl_4	AGAGE GC-ECD system	10m/70m/75m	40 min (discrete air sample every 40 minutes)	(Prinn et al., 2000; Krummel et al., 2007)
minor CFCs, HCFCs, HFCs, PFCs, methylhalides, chlorinated solvents, halons, ethane	AGAGE GC-MS-Medusa	75m	2 hour (20 minute integrated air sample every 2 hours)	(Miller et al., 2008; Prinn et al., 2000; Krummel et al., 2007)

Tab02

Event	Date and Time	Period	Air Mass Origin	Marker Species	Comments
BB 1	16/02/2006 2:00	A	Ocean & NW Tasmania	CO, BC, low O_3, particles (uni modal)	Fresh Plume
	16/02/2006 6:00	B	Ocean & NW Tasmania	BC, O_3, particle growth	Particle growth ~~Plume processing & dilution~~
	16/02/2006 12:00	C	mainland Australia	O_3 (overnight enhancement)	Background terrestrial
	17/02/2006 6:00	D	Melbourne	O_3, particles, HFC-134a	Urban
	17/02/2006 1~~6~~5:00	E	Ocean	Particles (bi-modal)	Clean Marine
	18/02/2006 0:00	F	Ocean & mainland Australia	O_3, HFC-134a	Marine with minor terrestrial
BB2	23/02/2006 23:00	A	Ocean & NW Tasmania	CO, BC, Acetonitrile, particles	Fresh Plume
	24/02/2006 23:00	B	mainland Australia	CO, NMOC (Acetonitrile)	Fresh plume + precipitation
	25/02/2006 5:00	C	Melbourne	HFC-134a, O_3	Urban
	25/02/2006 23:00	D	Ocean	Low particles, HFC-134a	Clean Marine

Tab03

Compound	formula	Background concentration[a]	BB plume concentration[a]	ER CO[b]	CO ER R^2	EF (g kg $^{-1}$)[c]
Species statistically enhanced in plume		mean (stdev)	mean (stdev)			
carbon dioxide	CO_2	378.1 (0.7)	382.9 (1.2)	1620	0.15	1621~~n/a~~
carbon monoxide	CO	42 (6)	618 (279)	n/a	n/a	127~~89[c]~~
methane	CH_4	1713 (2)	1743 (10)	49	0.48	3.8~~2.5~~
nitrous oxide	N_2O	319.0 (0.2)	319.1 (0.2)	0.27	0.01	0.06~~n/a~~
hydrogen	H_2	551 (3)	6010 (28)	100	0.87	0.93~~0.64~~
ethane	C_2H_6	1845 (146)	1765 (1008)	3.2	0.79	0.41~~0.30~~
hydrogen cyanide (m/z 28)	HCN	122 (4)	903 (292)	5.7	0.42	0.73~~0.49~~
formaldehyde (m/z 31)	HCHO	541 (339)	1895 (561)	11	0.08	1.64~~n/a~~
methanol (m/z 33)	CH_3OH	721 (413)	8603 (2521)	14	0.43	2.07~~1.4~~
acetonitrile (m/z 42)	C_2H_3N	35 (4)	983 (324)	1.3	0.58	0.25~~0.17~~
acetaldehyde (m/z 45)	CH_3CHO	48 (27)	2608 (807)	4.4	0.53	0.92~~0.62~~
unknown (m/z 46)	unknown	105 (72)	279 (74)	0.27	-0.9	0.06~~n/a~~

Comment [law208 2]: Now calculated using carbon mass balance method

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Comment [law208 1]: All ER to CO are now given (including those with R^2<0.4)

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formic acid (m/z 47)	CH_2O_2	19 (7)	141 (63)	0.20	-0.09	0.05~~n/a~~
acetone/propanal (m/z 59)	C_3H_6O	170 (31)	1315 (372)	2.0	0.40	0.54~~0.36~~
acetic acid (m/z 61)	CH_3COOH	75 (32)	2054 (971)	3.6	0.64	0.75~~0.52~~
furan/isoprene (m/z 69)	C_4H_4O	78 (39)	3113 (1139)	5.3	0.72	1.69~~1.15~~
MVK/MAK (m/z 71)	C_4H6O	14 (10)	673 (234)	1.2	0.76	0.38~~0.26~~
methylglyoxal/methyl ethyl ketone (m/z 73)	C_4H_8O	21 (12)	618 (209)	1.0	0.69	0.35~~0.24~~
benzene (m/z 79)	C_6H_6	7 (6)	1093 (390)	1.9	0.78	0.69~~0.47~~
2-furanone (m/z 85)~~unknown (m/z 85)~~	$C_4H_4O_2$~~unknown~~	15 (5)	847 (276)	1.5	0.51	0.57~~0.39~~
2,3-butanedione (m/z 87)~~unknown (m/z 87)~~	$C_4H_6O_2$	16 (5)	576 (186)	0.97	0.67	0.39~~0.27~~
toluene (m/z 93)	C_7H_8	8 (5)	409 (113)	0.69	0.51	0.30~~0.20~~
phenol (m/z 95)	C_6H_5OH	12 (9)	472 (149)	0.80	0.73	0.35~~0.24~~
unknown (m/z 101)	Unknown	15 (4)	124 (33)	0.19	0.32	0.09~~n/a~~
xylenes (m/z 107)	C_8H_{10}	15 (0)	319 (100)	0.53	0.70	0.26~~0.18~~
unknown (m/z 113)	unknown	9 (0)	279 (87)	0.47	0.60	0.25~~0.17~~
C_3-benzenes (m/z 121)	C_9H_{12}	20 (12)	290 (89)	0.47	0.73	0.27~~0.18~~
monoterpenes + unknowns (m/z 137) ~~monoterpenes (m/z 137)~~	$C_{10}H_{16}$/$C_8H_8O_2$~~$C_{10}H_{16}$~~	17 (9)	219 (79)	0.18	0.51	0.11~~0.08~~
unknown (m/z 153)	unknown	45 (135)	91 (29)	0.09	0.61	0.06~~n/a~~

methyl chloride	CH_3Cl	594~~5~~ (79)	1251 (458)	1.30	0.74	0.28~~0.21~~
methyl bromide	CH_3Br	9 (2)	34 (18)	0.05	0.74	0.02~~0.015~~
methyl iodide	CH_3I	1.3 (0.2)	3.7 (1.5)	0.004	0.75	0.002~~0.0019~~
black carbon	n/a	1.6 (0.3)	1657 (769)	0.003	0.81	0.16~~0.22~~
CN > 3 nm	n/a	625 (2078)	24902 (8031)	38.4	0.7	n/a~~n/a~~
CCN 0.5%	n/a	160 (31)	5501 (1355)	8.3	-0.4	n/a~~n/a~~
Species not statistically enhanced in plume						
dimethyl sulphide (m/z 63)	C_2H_6S	158 (57)	172 (15)	n/a	n/a	n/a~~n/a~~
chloroform	$CHCl_3$	6.6 (0.5)	8.8 (1.4)	n/a	n/a	n/a~~n/a~~
methyl chloroform	CH_3CCl_3	16.1 (0.2)	16.0 (0.2)	n/a	n/a	n/a~~n/a~~
dichloromethane	CH_2Cl_2	7.5 (0.04)	7.6 (0.1)	n/a	n/a	n/a~~n/a~~
carbon tetrachloride	CCl_4	90.2 (0.7)	90.3 (0.2)	n/a	n/a	n/a~~n/a~~
bromoform	$CHBr_3$	4.2 (0.8)	4.7 (0.4)	n/a	n/a	n/a~~n/a~~
HFC-32	CH_2F_2	1.02 (0.03)	1.04 (0.03)	n/a	n/a	n/a~~n/a~~
HFC-125	C_2HF_5	3.57 (0.04)	3.63 (0.05)	n/a	n/a	n/a~~n/a~~
HFC-134a	CH_2FCF_3	33.20 (0.22)	33.28 (0.17)	n/a	n/a	n/a~~n/a~~
ozone	O_3	15.1 (1.1)	15.8 (1.5)	n/a	n/a	n/a~~n/a~~

Tab04

	This study g kg^{-1} (~~calculated using Akagi et al., (2011) CO EF of 89 g kg~~coastal heath~~-$^{-1}$~~)	Temperate south eastern Australia	Tropical savannah Australia	Temperate Northern Hemisphere
Hydrogen (H_2)	0.93~~0.64~~	n/a	n/a	2.03 (1.79) [j]
Methane (CH_4)	3.8~~2.49~~	3.5 (1.1) [c]	2.26 (1.27) [d] 2.33 (0.80) [e] 2.20 (0.32) [f] 2.03 (0.13) [h] 2.10 (1.16) [i]	3.92 (2.39) [j] 3.69 (1.36) [l]
Ethane (C_2H_6)	0.41~~0.30~~	0.26 (0.11) [a] 0.5 (0.2) [c]	0.60 (0.225) [d] 0.11 (0.09) [e] 0.53 (0.02) [f] 0.13 (0.04) [g] 0.08 (0.05) [i]	1.12 (0.67) [j] 0.48 (0.61) [l]
Hydrogen cyanide (HCN)	0.73~~0.49~~	0.43 (0.22)[a]	0.036 (0.002) [d] 0.025 (0.024) [e] 0.11 (0.04) [g] 0.53 (0.31) [i]	0.73 (0.19) [j] 0.75 (0.26) [l]
Acetonitrile (CH_3CN)	0.25~~0.17~~	n/a	0.11 (0.06) [f]	0.15 (0.07) [l]
Acetaldehyde (C_2H_4O)	0.92~~0.62~~	n/a	0.55 (0.26) [d] 1.0 (0.62) [e]	0.56 (0.40)[l]

Phenol (C_6H_5OH)	0.35~~0.24~~	n/a	n/a	0.33 (0.38) ^{j} 0.45 (0.19) ^{l}
Acetic acid (CH_3COOH)	0.75~~0.52~~	3.8 (1.3)^{c}	1.54 (0.64) ^{i}	1.97 (1.66) ^{j} 1.91 (0.93) ^{l}
Methanol (CH_3OH)	2.07~~1.37~~	2.3 (0.8)^{b} 2.4 (1.2)^{c}	1.06 (0.87) ^{i}	1.93 (1.38)^{j} 1.35 (0.4) ^{l}
Benzene (C_6H_6)	0.69~~0.47~~	n/a	0.42 (0.23) ^{d} 0.29 (0.24) ^{e} 0.21 (0.02) ^{f}	0.45 (0.29) ^{l}
Toluene (C_7H_8)	0.30~~0.20~~	n/a	n/a	0.17 (0.13)^{l}
Methyl chloride (CH_3Cl)	0.28~~0.2082~~	n/a	0.0605 (0.0072) ^{f}	0.059^{k}
Methyl bromide (CH_3Br)	0.02~~0.0148~~	n/a	0.0018 (0.0003)f	0.0036^{k}
Methyl iodide(CH_3I)	0.002~~0.0019~~	n/a	n/a	0.0008^{k}

Table 1. Measurement summary

Table 2. Summary of Periods described in the text for BB1 and BB2 (as shown in Figs 3 and 6)

Table 3. Summary of species measured in BB2 coastal heathland fire including background concentration, plume concentration, ER to CO and EF. [a] Units – all in ppt except for CO, CH_4, N_2O in ppb, CO_2 in ppm, CN and CCN in particles cm^{-3}, BC in ng m^{-3} [b]Trace gas emission ratios are molar ratios, BC is mass ratio, particle number is # particles ppb^{-1} [c] ~~EF for CO taken from temperate forest (Akagi et al., 2011)~~calculated using carbon mass balance method n/a = not applicable

Table 4. Comparison of emission factors with other studies

[a] Paton-Walsh et al., 2005, [b] Paton-Walsh et al., 2008, [c] Paton-Walsh et al., 2014, [d]Hurst et al., 1994a [e]Hurst et al., 1994b [f] Shirai et al., 2003 [g] Paton-Walsh et al., 2010 [h] Meyer et al., 2012 [i] Smith et al., 2014 [j]Akagi et al., 2011 temperate updated May 2014 [k]Akagi et al., 2011 extratropical [l]Yokelson et al., 2013 semi arid shrubland

Fig 01

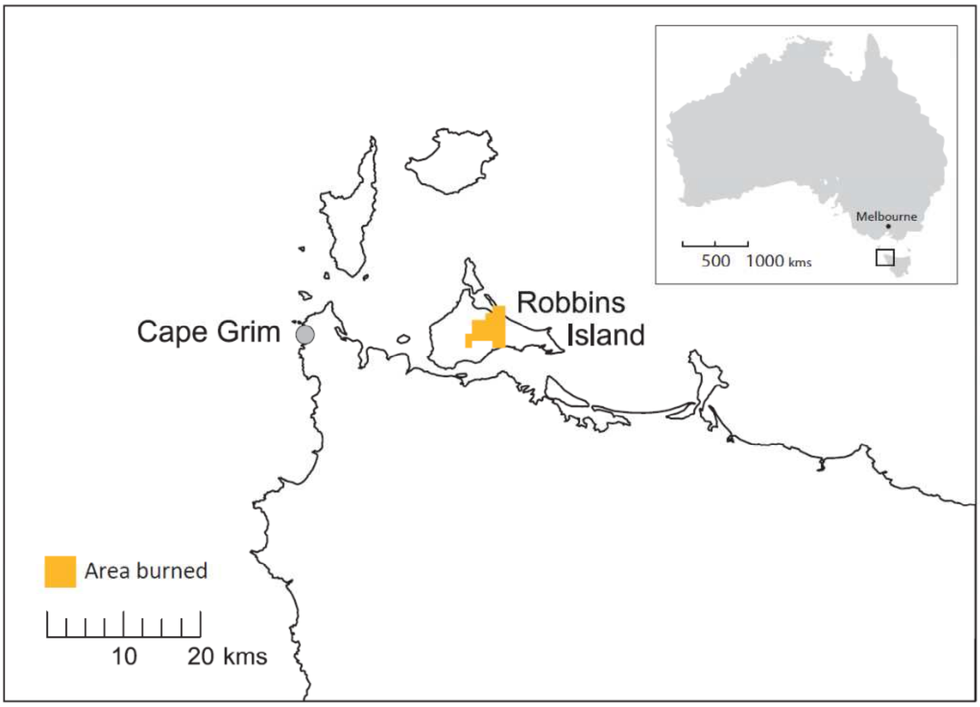

Fig 02

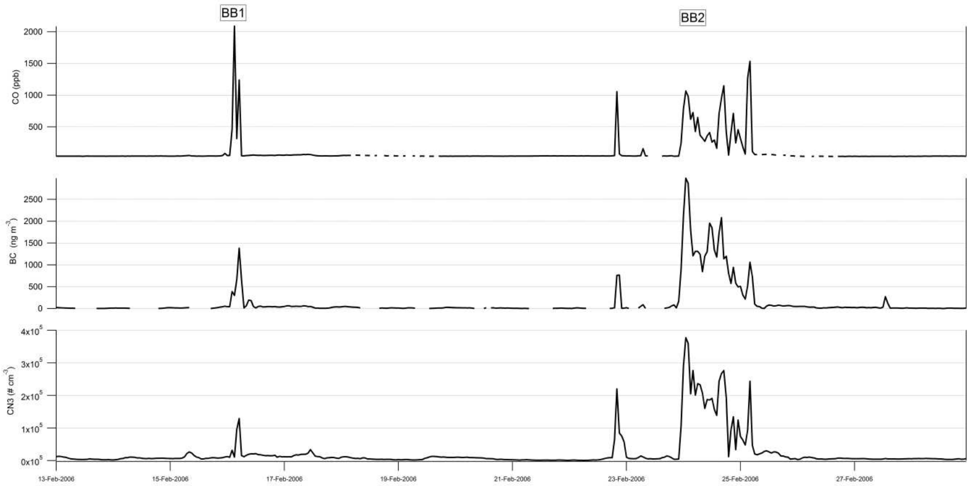

Fig 03

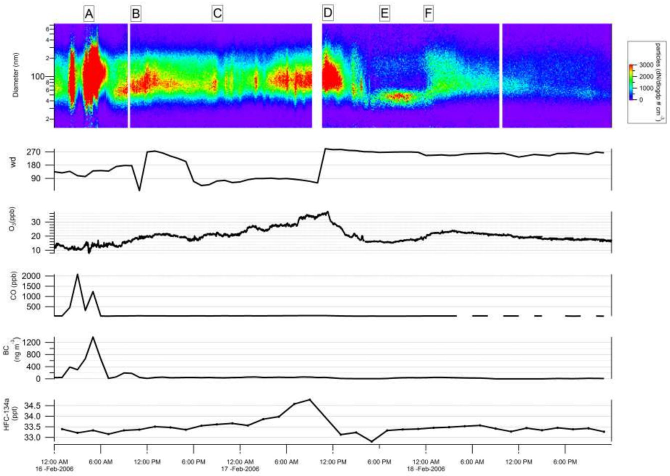

Fig 04

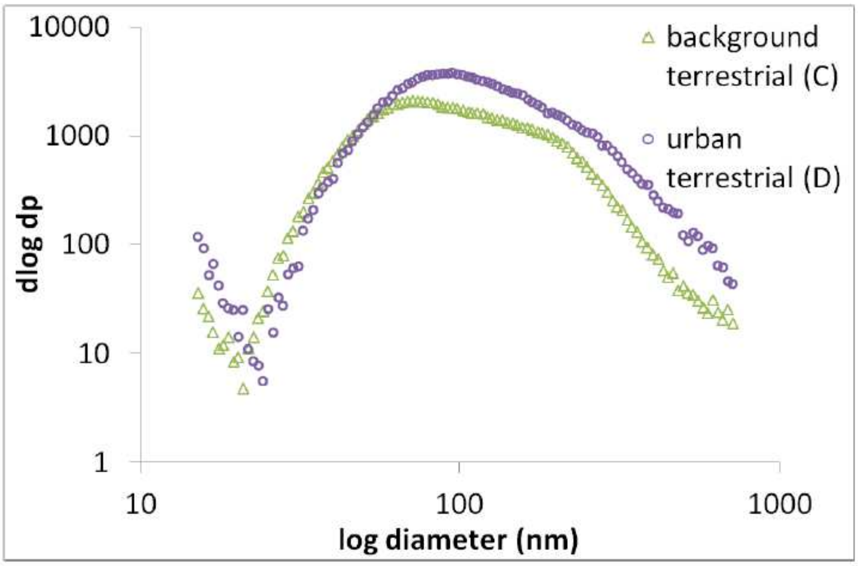

Fig04b

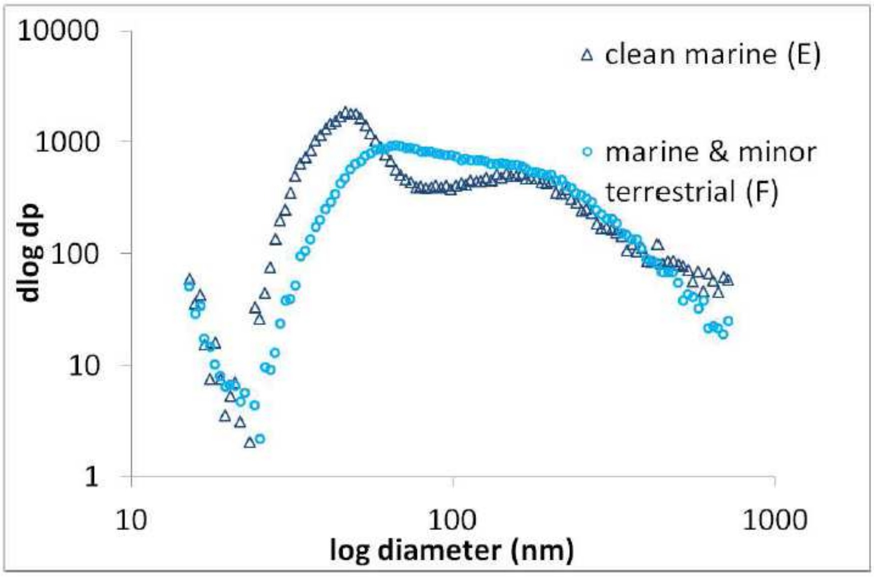

Fig 04c

Fig 05

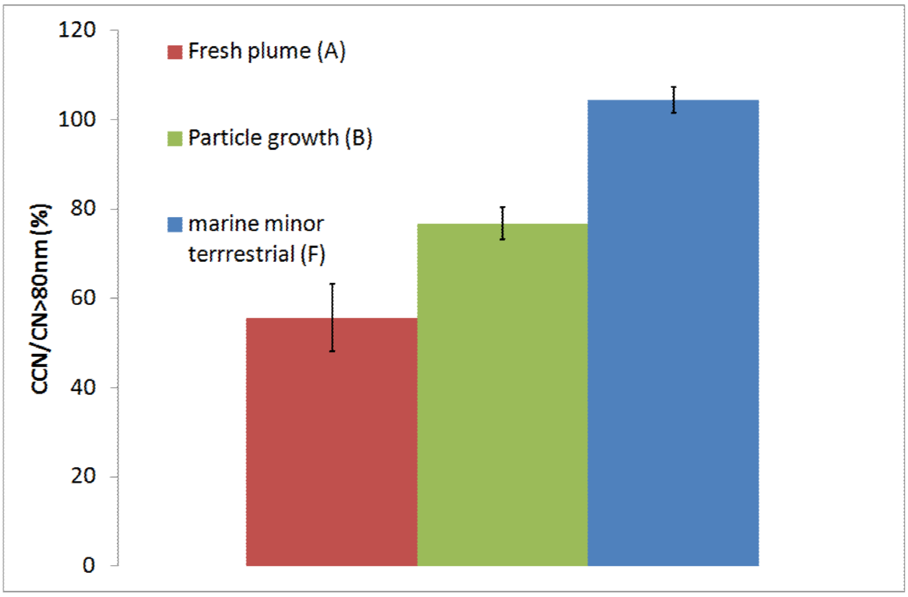

Fig05a

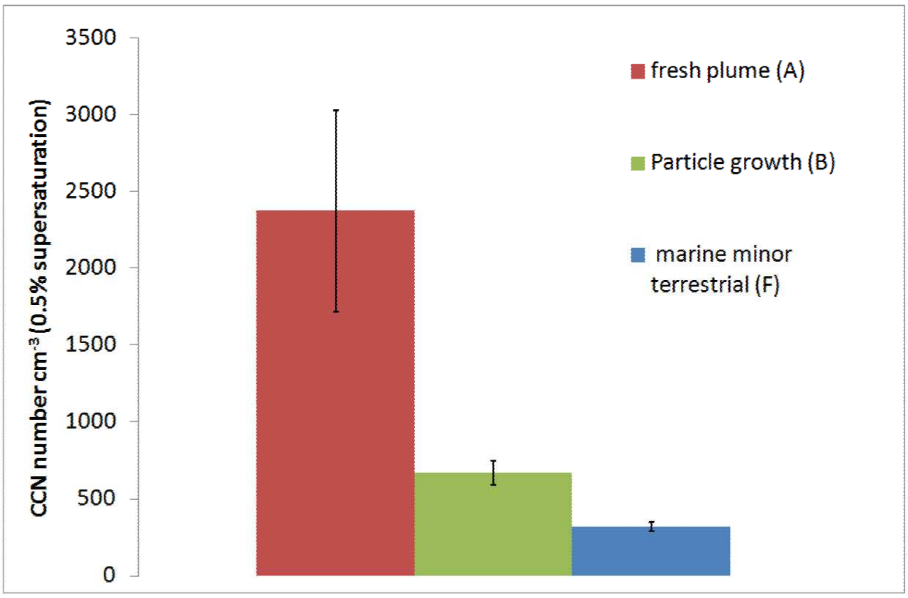

Fig05b

Fig 06

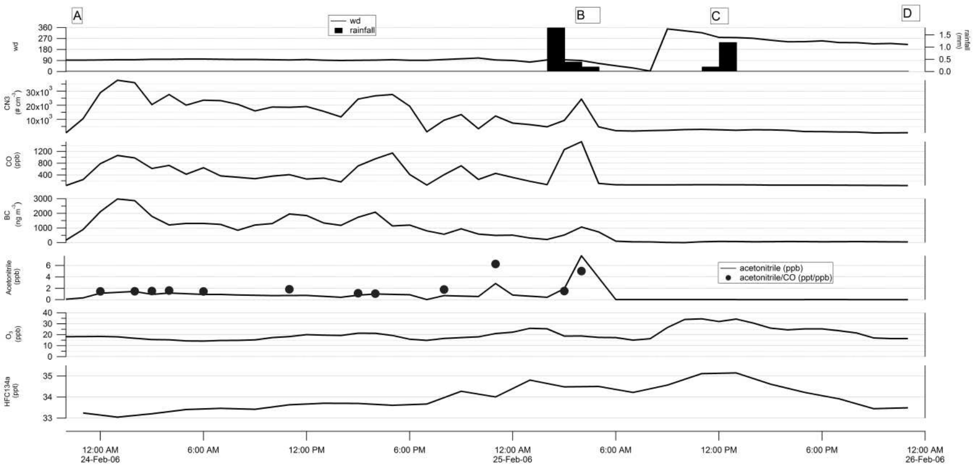

Fig 07

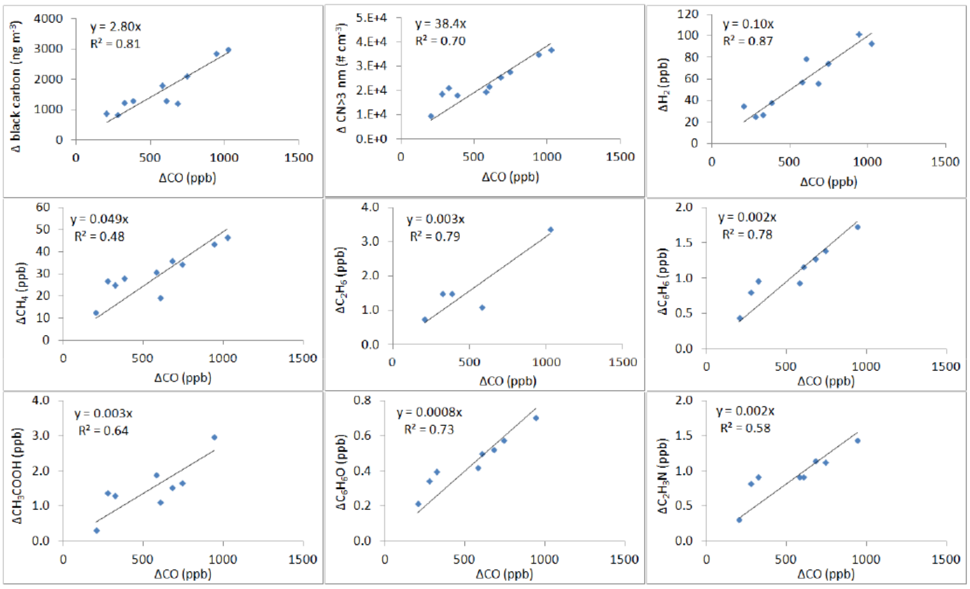

Figure 1. Location of Cape Grim and Robbins Island in North West Tasmania, Australia. Area burned is shown.

Figure 2. Time series of carbon monoxide (CO), black carbon (BC) and particles~~m~~>3 nm (CN3) for the study period (BB 1 and BB2 shown).

Figure 3. Time series from BB1 including a particle size and number contour plot, wind direction (degrees), ozone (O_3), carbon monoxide (CO), black carbon (BC) and HFC-134a. Periods A-F are discussed in the text.

Figure 4. Average particle size distributions (with log scale on both axes) from BB1 corresponding to periods shown in Fig 3 including (a) the fresh plume (Period A) and particle growth (Period B) (b) background terrestrial (Period C) and urban terrestrial (Period D) and (c) clean marine (Period E) and marine and minor terrestrial (Period F).

Figure 5 (a) Average ratios of CCN/CN>80 (hourly) in BB1 during fresh plume (Fig 3. Period A), particle growth event (Fig. 3 Period B), and in marine air with minor terrestrial influence (Fig 3. Period F). (b) average absolute number concentrations of CCN (hourly) during the same periods. Error bars are one standard error of the mean

Figure 6. Time series from BB2 including wind direction and rainfall, CN3 (particle number > 3 nm), CO (carbon monoxide), BC (black carbon), acetonitrile and ratio of acetonitrile to CO, O_3 and HFC-134a. Events corresponding to Periods A–D are discussed in the text.

Figure 7. Emission ratios (ER) of several trace gas and aerosol species to CO during Period A in BB2