Biomass burning at Cape Grim: exploring photochemistry using multi-scale modelling

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Abstract

We have tested the ability of a high resolution chemical transport model~~ling~~ (CTM) to reproduce biomass burning (BB) plume strikes and ozone (O_3) enhancements observed at Cape Grim in Tasmania Australia from the Robbins Island fire. The ~~model~~ CTM has also been used to explore the contribution of near-field BB emissions and background sources to O_3 observations under conditions of complex meteorology. Using atmospheric observations, we have tested model sensitivity to meteorology, BB emission factors (EF) corresponding to low, medium and high modified combustion efficiency (MCE) and spatial variability. The use of two different meteorological models (TAPM-CTM and CCAM-CTM) varied the first (BB1) plume strike time by up to 15 hours, and duration of impact between 12 and 36 hours, and varied the second (BB2) plume duration between 50 and 57 hours. ~~while the second plume strike (BB2) was simulated well using both meteorological models.~~ Meteorology also had a large impact on simulated O_3, with one model (TAPM-CTM) simulating 4 periods of O_3 enhancement, while the other model (CCAM) simulating only one period. Varying the BB EFs, which in turn varied the non~~-methanic~~methane ~~-~~organic compound (NMOC) / oxides of nitrogen (NO_x) ratio, had a strongly non-linear impact on simulated O_3 concentration, with either destruction or production of O_3 predicted in different simulations. As shown in ~~the~~ previous work (Lawson et al., 2015), minor rainfall events have the potential to significantly alter EF due to changes in combustion processes. Models which assume fixed EF for O_3 precursor species in an environment with temporally or spatially variable EF may be unable to simulate the behaviour of important species such as O_3.

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TAPM-CTM is used to further explore the contribution of the Robbins Island fire to the observed O_3 enhancements during BB1 and BB2. Overall, ~~the model~~TAPM-CTM suggests the dominant source of O_3 observed at Cape Grim was aged urban air (age = 2 days), with a contribution of O_3 formed from local BB emissions. ~~The model indicates that in an area surrounding Cape Grim, between 25 – 43% of O_3 enhancement during BB1 was formed from BB emissions while the fire led to a net depletion in O_3 during BB2.~~

This work shows the importance of assessing model sensitivity to meteorology and EF, and the large impact these variables can have in particular on simulated destruction or production of O_3 in regional atmospheric chemistry simulations. ~~This work also demonstrates how a model can be used to elucidate the degree of contribution from different sources to atmospheric composition, where this is difficult using observations alone.~~

1 Introduction

Biomass burning (BB) makes a major global contribution to atmospheric trace gases and particles with ramifications for human health, air quality and climate. Directly emitted species include carbon monoxide (CO), carbon dioxide (CO_2), oxides of nitrogen (NO_x), primary organic aerosol (POA), non-~~methanic~~ methane organic compounds (NMOC) and black carbon (BC), while chemical transformations occurring in the plume over time lead to formation of secondary species such as O_3, oxygenated NMOC and secondary aerosol. Depending on a number of factors, including magnitude and duration of fire, plume rise and meteorology, the impact of BB plumes ~~from a fire~~on human health, air quality and climate may be local, regional or global.

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BB plumes from wildfires, prescribed burning, agricultural and trash burning can have a major impact on air quality in both urban and rural centres (Keywood et al., 2015; Luhar et al., 2008; Reisen et al., 2011; Emmons et al., 2010; Yokelson et al., 2011) and regional scale climate impacts (Andreae et al., 2002; Keywood et al., 2011b; Artaxo et al., 2013; Anderson et al., 2016). In Australia, BB from wild and prescibed fires impacts air quality in both rural and urban areas (Keywood et al., 2015; Reisen et al., 2011; Luhar et al., 2008; Keywood et al., 2011a) as well as indoor air quality (Reisen et al., 2011). More generally, as human population density increases, and as wildfires become more frequent (Flannigan et al., 2009; Keywood et al., 2011b), assessing the impact of BB on air quality and human health becomes more urgent (Keywood et al., 2011b; Reisen et al., 2015). In particular, particles emitted from BB frequently

lead to exceedances of air quality standards, and exposure to BB particles has been linked to poor health outcomes including respiratory effects, cardiovascular disease and mortality (Reisen et al., 2015; Reid et al., 2016; Dennekamp et al., 2015). There is also increasing evidence that mixing of BB emissions with urban emissions results in enhanced photochemistry and production of secondary pollutants such as secondary aerosol and O_3 (Jaffe and Wigder, 2012; Akagi et al., 2013; Hecobian et al., 2012), which may result in more significant health impacts than exposure to unmixed BB or urban emissions.

To be able to accurately predict and assess the impact of BB on human health, air quality and climate, models must be able to realistically simulate the chemical and microphysical processes that occur in a plume as well as plume transport and dispersion. In the case of BB plumes close to an urban centre or other sensitive receptor, models can be used to mitigate risks on community by forecasting where and when a BB plume will impact, the concentrations of toxic trace gases and particles in the plume, and potential impact of the BB plume mixing with other sources. Models also allow investigation of the contributions from BB and other sources on observed air quality when multiple sources are contributing. Understanding the relative importance of different sources is required when formulating policy decisions to improve air quality.

Lagrangian parcel models are often used to investigate photochemical transformations in BB plumes as they are transported and diluted downwind (Jost et al., 2003; Trentmann et al., 2005; Mason et al., 2006; Alvarado and Prinn, 2009; Alvarado et al., 2015) while three-dimensional (3D) Eulerian grid models have been used to investigate transport and dispersion of plumes, plume age, as well as contributions from different sources. 3D Eulerian grid models vary from fine spatial resolution on order of a few kilometers~~kms~~ (Luhar et al., 2008; Keywood et al., 2015; Alvarado et al., 2009; Lei et al., 2013) to a resolution of up to hundreds of ~~km~~ kilometers in global models (Arnold et al., 2015; Parrington et al., 2012).

Sensitivity studies have allowed the influence of different model components (emissions, plume rise, transport, chemistry) on model output to be investigated. Such studies are particularly important in formation of secondary species such as O_3 which have a non-linear relationship with emissions. Studies have found that modelled O_3 concentration from BB emissions is highly dependant on a range of factors including a) meteorology (plume transport and dispersion) in global (Arnold et al., 2015) and high resolution (Lei et al., 2013) Eulerian grid models, b) absolute emissions/biomass burned (Pacifico et al., 2015; Parrington et al., 2012), c) model grid size resulting in different degrees of plume dilution (Alvarado et al.,

2009), and oxidative photochemical reaction mechanisms in Lagrangian parcel models (Mason et al., 2006).

Broadly speaking, models used for simulating BB plumes comprise a) description of the emissions source b) a determination of plume rise c) treatment of the vertical transport and dispersion and d) a mechanism for simulating chemical transformations in the plume (Goodrick et al., 2013). There are challenges associated with accurately representing each of these components in BB modelling. The description of emissions source includes a spatial and temporal description of the area burnt, the fuel load, combustion completeness, and trace gas and aerosol emission factors (mass of species emitted per mass of fuel burned). ~~per kg of fuel burned~~. The area burned is often determined by a combination of hotspot and fire scar data, determined from retrievals from satellite (Kaiser et al., 2012; Reid et al., 2009(Giglio et al., 2013)). Cloud cover may lead to difficulties in obtaining area burnt data, while scars from small fires may be difficult to discern against complex terrain, and low intensity fires may not correspond with a detectable hotspot (Meyer et al., 2008). Emission factors are determined experimentally either by field or laboratory measurements, and are typically grouped by biome type. In some regions, such as SE Australia, biomes have been sparsely characterised (Lawson et al., 2015). Furthermore, models use biome–averaged EF which do not account for complex intra-biome variation in EF as a result of temporal and spatial differences in environmental variables. This includes factors such as impact of vegetation structure, monthly average ~~monthly~~ rainfall (van Leeuwen and van der Werf, 2011) and the influence of short term rainfall events (Lawson et al., 2015). For example, EFs have been shown to vary significantly with fuel moisture which can vary seasonally (Korontzi et al., 2003;Urbanski, 2013). There may be significant spatial variability in emission factors within a biome (Castellanos et al., 2014); taken along with temporal variability, this has been shown to have a large impact on simulated concentrations of BB species in global-scale modelling (van Leeuwen et al., 2013).

Finally, the very complex mixture of trace gases and aerosols in BB plumes creates analytical challenges in quantifying EF, especially for semi and low volatility organics which are challenging to measure and identify but contribute significantly to secondary aerosol formation and photochemistry within the plume (Alvarado and Prinn, 2009; Alvarado et al., 2015; Ortega et al., 2013).

Plume rise is a description of how high the buoyant smoke plume rises above the fire, and consequently the initial vertical distribution of trace gases and aerosols in the plume (Freitas et al., 2007). This is still a large area of uncertainty in BB models, with a generalised plume

rise approach typically used which may include either homogenous mixing, prescribed fractions of emissions distributed according to mixing height, use of parametisations, and finally plume rise calculated according to atmospheric dynamics. A key driver of this uncertainty is the complexity of fire behaviour resulting in high spatial and temporal variability of pollutant and heat release, which drives variability in plume rise behaviour, such as multiple updraft cores (Goodrick et al., 2013).

Transport and dilution in models is driven by meteorology, particularly wind speed and direction, wind shear and atmospheric stability. Meteorology has a large impact on the ability of models to simulate the timing and magnitude and even composition of BB plume impacts in both local and regional scale models (Lei et al., 2013; Luhar et al., 2008; Arnold et al., 2015). For example, too-high wind speeds can lead to modelled pollutant levels which are lower than observed (e.g. Lei et al., ~~(~~2013~~)~~) while small deviations in wind direction lead to large concentration differences between modelled and observed, particularly when modelling emissions of multiple spatially diverse fires (Luhar et al., 2008). Dilution of BB emissions in large grid boxes in global models may also lead to discrepancies between modelled and observed NO_x, O_3 and aerosols (Alvarado et al., 2009).

Finally, models use a variety of gas-phase and aerosol-phase physical and chemical schemes, which vary in their ability to accurately represent chemical transformations, including formation of O_3 and organic aerosol (Alvarado and Prinn, 2009; Alvarado et al., 2015). Validating and constraining chemical transformations in models requires high quality, high time resolution BB observations of a wide range of trace gas and aerosol species, including important but infrequently measured species such as OH and semi volatile and low volatility NMOC. Field observations, whilst often temporally and spatially scarce, are particularly valuable because the processes and products of BB plume processing are dependent on long range transport, cloud processing, varying meteorological conditions and heterogeneous reactions.

~~Sensitivity studies have allowed the influence of different model components (emissions, plume rise, transport, chemistry) on model output to be investigated. Such studies are particularly important in formation of secondary species such as O_3 which have a non-linear relationship with emissions. Studies have found that modelled O_3 concentration from BB emissions is highly dependant on a range of factors including a) meteorology (plume transport and dispersion) in global (Arnold et al., 2015) and high resolution (Lei et al., 2013) Eulerian grid models, b) absolute emissions/biomass burned (Pacifico et al., 2015; Parrington et al.,~~

~~2012), c) model grid size resulting in different degrees of plume dilution (Alvarado et al., 2009), and oxidative photochemical reaction mechanisms in Lagrangian parcel models (Mason et al., 2006).~~

In this work we test the ability of ~~a~~ CSIRO's high resolution 3D Eulerian grid chemical transport model (CTM) to reproduce BB plume observations of the Robbins Island fire reported in Lawson et al., (2015) with a focus on CO, BC and O_3. We undertake sensitivity studies using varying emission factors associated with a low, medium and high Modified Combustion Efficiency (MCE), which in turn changes the NMOC / NO_x ratio, in contrast to other sensitivity studies which typically vary emissions linearly. We also test ~~the model~~ sensitivity to meteorology by ~~utilising~~coupling the CTM with two different meteorological models, TAPM and CCAM. The fire and fixed observation site (Cape Grim) were only 20 km apart, and so simulation of the plume strikes is a stringent test of ~~the model's~~TAPM and CCAM's ability to reproduce windspeed and direction. ~~We undertake sensitivity studies using varying emission factors associated with a low, medium and high Modified Combustion Efficiency (MCE), which in turn changes the NMOC / NO_x ratio, in contrast to other sensitivity studies which typically vary emissions linearly. We also test the model sensitivity to meteorology by utilising two different meteorological models.~~ Plume rise and chemical mechanism are held constant. Finally, we use ~~the~~ TAPM-CTM ~~model~~ to separate the contribution of the Robbins Island fire emissions and urban emissions to the observed O_3 enhancements at Cape Grim reported in Lawson et al., (2015), and ~~use the model~~ to determine the age of the O_3-enhanced air parcels.

2 Methods

2.1 Fire and measurement details

Details of the fire and measurements are given in Lawson et al (2015). Briefly, 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. Fire burned through native heathland and pasture grass on Robbins Island some 20 km to the east of Cape Grim for two weeks in February 2006. 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 in the range of 75-95 %. Under a northerly wind direction, urban air from the city of Melbourne (population 4.2 million) some 300 km away is transported across the ocean (Bass Strait) to Cape Grim.

A wide variety of trace gas and aerosol measurements were made during the fire event (Lawson et al., 2015). In this work, measurements of black carbon (BC), carbon monoxide (CO) and ozone (O_3) are compared with model output. BC measurements were made using an aethelometer (Gras, 2007). CO measurements were made using an AGAGE gas chromatography system with a multi-detector (Krummel et al., 2007) and O_3 measurements were made using a TECO analyser (Galbally et al., 2007). ~~Measurements made included non-methanic 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 monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), nitrous oxide (N_2O), halocarbons and meteorology.~~ For further details see Lawson et al., (2015).

2.2 Chemical transport models

Simulations were undertaken with ~~a~~ CSIRO's chemical transport model (CTM), coupled offline with two meteorological models (see below). The CSIRO CTM is a three-dimensional Eulerian chemical transport model with the capability of modelling the emission, transport, chemical transformation, wet and dry deposition of a coupled gas and aerosol phase atmospheric system. The CTM was initially developed for air quality forecasting (Cope et al., 2004) and has had extensive use with shipping emission simulations (Broome et al., 2016), urban air quality (Cope et al., 2014; Galbally et al., 2008), biogenic (Emmerson et al., 2016) and biomass burning studies (Keywood et al., 2015; Meyer et al., 2008; Luhar et al., 2008).

The chemical transformation of gas-phase species was modelled using an extended version of the Carbon Bond 5 mechanism (Sarwar et al., 2008) with updated toluene chemistry (Sarwar et al., 2011). The mechanism was also extended to include the gas phase precursors for secondary (gas and aqueous phase) inorganic and organic aerosols. Secondary inorganic aerosols were assumed to exist in thermodynamic equilibrium with gas phase precursors and were modelled using the ISORROPIA-II model (Fountoukis and Nenes, 2007). Secondary organic aerosol (SOA) was modelled using the Volatility Basis Set (VBS) approach (Donahue et al., 2006). The VBS configuration is similar to that described in Tsimpidi et al., (2010). The

production of S-VI in cloud water was modelled using the approach described in Seinfeld and Pandis (1998). The boundary concentrations in the models for different wind directions were informed by Cape Grim observations of atmospheric constituents during non BB periods (Lawson et al., 2015). In this work the modelled elemental carbon (EC) output was considered equivalent to the BC measured with aethalometer at Cape Grim.

Horizontal diffusion is simulated according to equations detailed in Cope et al (2009) according to principles of Smagorinsky et al., (1963) and Hess (1989). Vertical diffusion is simulated according to equations detailed in Cope et al., (2009) according to principles of Draxler and Hess (1997). Horizontal and vertical advection uses the approach of Walcek et al., (2000).

2.2.1 Meteorological models

Prognostic meteorological modelling was used for the prediction of meteorological fields including wind velocity, temperature, ~~and~~ water vapour mixing ratio ~~(including~~and clouds~~)~~, radiation and turbulence. The meteorological fields force key components of the emissions and the chemical transport model. Two meteorological models were used in this work. CSIRO's (The) Air Pollution Model (TAPM) (Hurley, 2008b), a limited area, nest-able, three-dimensional Eulerian numerical weather and air quality prediction system, and CSIRO's Conformal Cubic Atmospheric Model (CCAM) a global stretched grid atmospheric simulation model (McGregor, (2015) and references therein). The models represent two unique (and independent) approaches for generating the meteorological fields required by the chemical transport model.

For CCAM, 20 km spaced simulations over Australia were used by the CTM (with the same grid spacing) to model large scale processes on the continent including the emission and transport of windblown dust, sea salt aerosol and smoke from wildfires. Note that the governing equations for TAPM do not enable this model to simulate spatial scales greater than 1000 km in the horizontal and thus only the CCAM meteorology was available for the continental-scale simulations. TAPM and CCAM 12 km spaced simulations were then used to model the transport of the Melbourne plume to Cape Grim by the CTM (at 12 km grid spacing) with boundary conditions provided by the continental simulation. Nested grid simulations by the CTM at 3 km and 1 km grid spacing utilised TAPM and CCAM meteorology simulated at matching grid spacing. The 1 km spaced meteorological fields were also used to drive a 400 m spaced CTM domain which encompassed Robbin's Island and Cape Grim. This domain was

included in the nested grid system because we wanted to better numerically resolve the spatial extent of the fire and the process of plume advection between Robbin's Island and Cape Grim.

~~The model was run using five nested computational domains with cell spacings of 20 km, 12 km, 3 km, 1 km and 400 m (Figure 1). This multi-scale configuration was required in order to capture a) large scale processes such as windblown dust, sea salt aerosol and ambient fires; b) transport of the Melbourne urban plume to Cape Grim; c) transport of the Robbin's Island smoke plume between the point of emission and Cape Grim.~~

In this work the CTM coupled with CCAM meteorological model is referred to as CTM-CCAM, while the CTM coupled with the TAPM meteorological model is referred to as TAPM-CTM.

2.2.2 Emission inventories

Anthropogenic emissions

Anthropogenic emissions for Victoria were based on the work of Delaney et al., (2011). No anthropogenic emissions were included for Tasmania. The north-west section of Tasmania has limited habitation and is mainly farmland, and so the influence of Tasmanian anthropogenic emissions on Cape Grim are expected to be negligible.

Natural and Biogenic emissions

The modelling framework includes methodologies for estimating emissions of sea salt aerosol (Gong, 2003) emissions of windblown dust (Lu and Shao, 1999); gaseous and aerosol emissions from managed and unmanaged wild fires (Meyer et al., 2008); emissions of NMOC from vegetation (Azzi et al., 2012) and emissions of nitric oxide and ammonia from vegetation and soils. Emissions from all but the wildfires are calculated inline in the CTM at each time step using the current meteorological fields. There were no other major fires burning in Victoria and Tasmania during the study period.

Emissions – Robbins Island fire

~~An image of the~~The area burnt by the fire ~~fire scar on Robbins Island at the end of February 2006~~ was determined from hotspots from the Sentinel product (Geosciences Australia) which were derived from MODIS imagery. The hotspots were buffered to give polygon spots at a resolution of 400ha spot^{-1}, then merged into a single polgygon for each fire day (Meyer et al.,

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2008). ~~was the only information available about the area burned and t~~There ~~was no detailed information available about the direction of fire spread.~~ The fire burnt~~-~~ 2000 ha over the two week period, and the direction of fire spread was unknown. As such, the fire scar was divided up into 250m grids ~~area burnt was subdivided into~~ and the hourly ~~amounts~~ areas burnt calculated using a normalised version of the Macarthur Fire Danger Index (FDI) (Meyer et al., 2008). ~~Therefore area burnt was divided up into 250m grids, and t~~The models assumed that an equal proportion of each grid burned simultaneously over the two week period. The fuel density used was estimated to be 18.7 t C ha^{-1}, based on mean mass loads of coarse and fine fuels taken from the biogeochemical production model (VAST 1.2, Barrett 2002) and converted into carbon mass (Meyer et al., 2008).

The hourly diurnal emissions of all gases and particles from the fire were calculated using the ~~Macarthur Fire Danger Index (FDI)~~ FDI ~~(Meyer et al., 2008)~~ in which the presence of strong winds will result in faster fire spread and enhanced emissions, compared to periods of lower wind speeds ~~(Figure 2)~~. The effect of wind speed on the fire behaviour and emissions i~~n~~s particularly important during the second BB event in which the winds ranged from 10 to15 m s^{-1}. This is evident from Figure 2 where hourly emission profiles based on an average diurnal FDI calculated by Meyer et al., (2008) (which peaks early afternoon) is compared with profiles based on hourly FDI generated by TAPM and CCAM meteorology. It can be seen that the use of the dynamic FDI approach during the BB2 period increases the Base emissions by 70% for TAPM meteorology and by 45% for the CCAM meteorology. It is also notable that the use of the dynamic approach with TAPM meteorology leads to the peak emissions occurring overnight on the 24th Feb which is when the Base emissions are at a minimum.

Savanna category EF were used as base case EFs in this work from Andreae and Merlet (2001). Three different sets of fire emission factors, corresponding to low, medium and high ~~modified combustion efficiency (~~MCE~~)~~ were used to test the sensitivity of the models, where MCE = $\Delta CO_2 / \Delta CO + \Delta CO_2$ (Ferek et al., 1998). We used ~~reported~~published EF of CO and CO_2 from temperate forests (Akagi et al., 2011), to calculate a typical range of MCEs for temperate fires, including an average (best estimate) of 0.92, a lower (0.89) and upper estimate (0.95). Fires with MCEs of approximately 0.90 consume biomass with approximately equal amounts of smouldering and flaming, while MCEs of 0.99 indicate complete flaming combustion (Akagi et al., 2011). Therefore the calculated range of MCEs (0.89 - 0.95) correspond to fires in which both smouldering and flaming is occurring, with a tendency for more flaming combustion in

the upper estimate (0.95) compared to a tendency of more smouldering in the lower estimate (0.89).

In previous smoke modelling work, CCAM-CTM and TAPM-CTM used savannah EF from Andreae and Merlet (2001). However, as Robbins Island is in a temperate region, the Andreae and Merlet (2001) savannah EF used in the models were adjusted to reflect temperate EF based on the following methodology. Minimum, mean and maximum CO EF for temperate forests from Agaki et al., (2011) were used for lower (0.89), best estimate (0.92) and upper MCE (0.95). For all other species, savannah EF (corresponding to MCE 0.94) were adjusted to EF for MCE=0.89, 0.92 and 0.95 using published relationships between MCE and EF (Meyer et al., 2012; Yokelson et al., 2007; Yokelson et al., 2003; Yokelson et al., 2011).

For example to adjust the Andreae and Merlet (2001) savannah EF (corresponding to an MCE of 0.94) to our temperate 'best estimate' EF (corresponding to MCE of 0.92) the Andreae and Merlet (2001) NO EF was reduced by 30%, the NMOC EFs were increased by 30%, the BC EF was reduced by 30% and the OC EF was increased by 20%. Table 1 gives emission factors for the original savannah EF (Andreae and Merlet, 2001) and the adjusted EF used in this work. The NO_x/NMOC ratios used are also shown, and vary by a factor of 3 between the low and high MCE scenarios, mainly driven by the variability in NO emissions with MCE. The EF calculated from observations for this fire are shown for comparison (Lawson et al., 2015).

~~The CO EF for lower, best estimate and upper MCE were taken as minimum, mean and maximum EF for temperate forests summarised by Agaki et al., (2011). For all other species, the savannah fuel EF (Andreae and Merlet, 2001) were adjusted according to published relationships between MCE and EF (Meyer et al., 2012; Yokelson et al., 2007; Yokelson et al., 2003; Yokelson et al., 2011). For example to adjust from the savannah EF (corresponding to an MCE of 0.94) to our temperate 'best estimate' EF (corresponding to MCE of 0.92), all NMOC EF's were increased by a factor of 1.3, as an approximate response based on relationships between MCE and EF for CH_4 (Meyer et al., 2012), methanol (Yokelson et al., 2007), HCN and formaldehyde (Yokelson et al., 2003). The savannah BC EF (Andreae and Merlet, 2001) was reduced by 30%, and the OC EF was increased by 20%, based on the relationship reported in Yokelson et al., (2011), in which smouldering results in lower EC and higher OC emission. The Andreae and Merlet (2001) savannah NO EF from was reduced by 30% according to the relationship in (Yokelson et al., 2007). Table 1 shows emission factors which correspond to the three MCEs.~~

Field Code Changed

We recognise calculating EF in this way is approximate, however the purpose of including a range of EF was to explore the model's sensitivity to EF. While EFs were calculated for the Robbins Island fire for several species (Lawson et al., 2015), ~~but these EF are~~these are only available for a subset of species required by the CB05 chemical mechanism. ~~and so EF currently used in the model for Savannah fires were adjusted as described above to better reflect the likely range of EF expected in temperate fires.~~ The adjustment of the Andreae and Merlet (2001) Savannah EF to a lower MCE (0.89) resulted in good (± 20%) agreement with the calculated EF for CO, BC and several NMOC from Lawson et al., (2015), in which the MCE was calculated as 0.88. This provides confidence in using published relationships between MCE and EF to estimate EF in this work.

With respect to plume rise, the Robbin's Island fire was a relatively low energy burn (Lawson et al., 2015), and as noted by Paugam et al., (2016) the smoke from such fires is largely contained within the planetary boundary layer (PBL). Given that ground-based images of the Robbin's Island smoke plume support this hypothesis, in this work we adopted a simple approach of mixing the emitted smoke uniformly into the model's layers contained within the PBL. The plume was well mixed between the maximum of the PBL height and 200 m above the ground, with the latter included to account for some vertical mixing of the buoyant smoke plume even under conditions of very low PBL height. The high wind speeds particularly during the second BB event, also suggest that the plume was not likely to be sufficiently buoyant to penetrate the PBL.

~~**Plume rise**~~

~~The chemical transport model calculates plume rise from buoyant sources and/or sources with appreciable vertical momentum within the computational time step loop. In the case of industrial sources (such as power stations) plume rise is calculated by numerically integrating state equations for the fluxes of moment and buoyancy according to the approach used in TAPM (Hurley, 2008a). In the case of landscape fires, there are a hierarchy of approaches which can be used (Paugam et al., 2016), including rule of thumb, simple empirical approaches, and deterministic models varying in complexity from analytic solutions to cloud resolving numerical models. The Robbin's Island fire was a relatively low energy burn (Lawson et al., 2015), and as noted by Paugam et al., (2016) the smoke from such fires is largely contained within the planetary boundary layer (PBL). Given that ground based images of the Robbin's Island smoke plume support this hypothesis, in this work we adopted a simple approach of mixing the emitted smoke uniformly into the model layers contained within the~~

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3 Results and Discussion

3.1 Modelling Sensitivity Study

The ability of the models to reproduce the two plume strikes (BB1 and BB2, described in Lawson et al (2015)) was tested. The period examined was the 13 February 2006 to the 28 February 2006. ~~-~~The sensitivity of the models to meteorology, emission factors and spatial variability was also investigated and is discussed below. Observation and model data shown are hourly averages. Table 2 summari~~s~~zes the main findings of the model sensitivity study. A MODIS Truecolour Aqua image of the Robbins Island fire plume is shown in Figure 3 from ~~the~~ 23 February 2006, with the modelled plume during the same period.

3.1.1 Sensitivity of modelled BB species to meteorology~~Sensitivity of model to meteorology~~

Qualitative and quantitative assessment of model performance for meteorological parameters were undertaken for both TAPM and CCAM. Hourly observed and modelled winds, temperature, humidity and PBL are compared and discussed in the Supplementary section (Figures S2-S8). Briefly, both TAPM and CCAM demonstrated reasonable skill in modelling the meteorological conditions, with the TAPM simulations slightly better than the CCAM with respect to the low level wind, temperatures and relative humidity and CCAM simulations slightly better in terms of PBL height.

~~Before investigating impact of different meteorology models on concentrations of chemical species, modelled wind speed and direction were compared with observations at Cape Grim. Briefly, throughout the study period wind direction simulated by TAPM and CCAM agreed very well with observed wind direction at Cape Grim, with the exception of some differences in timing between observed and modelled wind direction change from easterly to north north-westerly (discussed below) on the 16th February. Simulated and observed wind speeds agreed~~

~~in most cases, although both TAPM and CCAM tended to underestimate observed wind speeds by 2 - 2.5 m s^{-1} overall.~~

Primary species- CO and BC

Figure 4 and Figure 5 shows concentration isopleths generated by~~a typical output of spatial plots from~~ TAPM-CTM and CCAM-CTM respectively for BB1 with the models output every 12 hours shown. The narrow BB plume is simulated intermittently striking Cape Grim ~~(until 17 Feb 4:00)~~, and then the plume is swept away from Cape Grim after a wind direction change.

The simulated and observed time series concentrations of CO and BC for the two different models (TAPM-CTM and CCAM-CTM) and for 3 different sets of EF (discussed in Section 3.1.2) are shown in ~~Figure~~ Figure 6~~5~~. TAPM-CTM~~N~~ and CCAM-CTM- both reproduce the observed plume strikes (BB1 and BB2). The impact of meteorology on the plume strike timing and duration is discussed below.

Both models overestimate the duration of BB1 and are a few hours out in the timing of the plume strike. TAPM-CTM predicts the timing of BB1 ~~to be about~~is 3 hours later than occurred (BC data) and predicts that BB1 persists for 12 hours (~~actual~~ observed duration 5 hours) (Figure 4). CCAM-CTM predicts that BB1 occurs 12 hours prior to the observed plume strike and predicts that the plume intermittently sweeps across Cape Grim for up to 36 hours (Figure 5)~~(Figure 4)~~ ~~(5 hours actual)~~. Both models indicate that the plume is narrow and meandering.

Both models overestimate the duration of BB2 and simulate the plume strike occurring earlier than observed. TAPM-CTM predicts BB2 is 26 hours earlier than observed and that BB2 persists for 50 hours (observed duration 29 hours). CCAM-CTM predicts BB2 is 26 hours earlier than observed and that BB2 persists for 57 hours. It should be noted that there is a brief observed enhancement of BB species which correspond with the beginning of the modelled BB2 plume strike, some 24 hours prior to the prolonged observed event. This was likely due to the edge of the plume impacting the station briefly.

~~In contrast, both models successfully predict the timing and duration of BB2. TAPM-CTM correctly predicts the timing of the first enhancement of BC prior to BB2 (if the first BC enhancement on the 22 Feb at 20:00 is included) and predicts that BB2 persists for 50 hours (actual duration 57 hours). CCAM-CTM correctly predicts the timing and duration of BB2 (57 hours modelled and observed).~~

~~The difference between the TAPM and CCAM simulated wind direction is driving these differences.~~ In both observed BB1 and BB2~~,~~ the plume strike at Cape Grim occurred just prior

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to a wind direction change from easterly (fire direction), to ~~north-north~~south~~–~~westerly. The timing of the wind direction change in the models is therefore crucial to correctly predicting plume strike time and duration. In BB1 CCAM predicts an earlier wind direction change with higher windspeeds which advects the plume directly over Cape Grim while TAPM predicts a later wind change, lower windspeeds and advection of only the edge of the plume over Cape Grim. The higher concentrations CO and BC in BB1 by CCAM-CTM is are likely due to the direct advection of the plume over the site compared to only the plume edge in TAPM-CTM. ~~In BB2, both models predict similar wind speeds and directions, and a direct 'hit' of the plume over the station.~~

~~The magnitudes of the BC and CO peaks shown are also influenced by meteorology. Overall, CCAM-CTM predicts higher concentrations of CO and BC in BB1, and TAPM predicts higher concentrations in BB2. Assuming a constant EF, peak magnitudes are influenced by several factors including wind direction (directness of plume hit), wind speed (degree of dispersion and rate of fuel combustion, see Section 2.2.2) and PBL height (degree of dilution). In BB1, the larger BC and CO concentrations in CCAM are likely due to the direct advection of the plume over the site compared to only the plume edge in TAPM. I~~

In BB2, both TAPM-CTM and CCAM-CTM predict direct strikes of the Robbin's Island smoke plume on Cape Grim, because the wind direction is modelled to be predominantly easterly for the duration of the event (Fig S18). Both models simulate some backing and veering of the wind direction for the duration of BB2 due to gravity waves processes which lead to intermittent strikes on Cape Grim as the Robbin's Island smoke plume sweeps to the north and south of Cape Grim. The gravity wave oscillations are more pronounced in CCAM-CTM than TAPM-CTM (and thus the plume strikes are more pronounced from the former) due to differences in how the models are coupled to large scale synoptic forcing. The event is eventually curtailed by the passage of a south-westerly change.

Fig. S18 shows that TAPM-CTM predicts the onset of the change to occur about six hours ahead of the observed change and thus the BB2 event ends too early for this meteorological simulation. CCAM-CTM models the south-westerly change to occur one hour after the observed, leading to the modelled BB2 event extending beyond the observed duration for this meteorological simulation.

Differences in the magnitude of the modelled CO and BC peaks for TAPM-CTM and CCAM-CTM have two principal cause: a), the coupling of the smoke emissions to the TAPM and

CCAM meteorology via the FDI scaling leads to approximately 20% higher emissions in the case of the TAPM-CTM simulations; b), the CCAM wind speeds are 20-50% higher than the TAPM wind speeds during BB2, which in combination with the emission differences, leads to TAPM-CTM generating near-surface smoke concentrations which are up to 80% higher than CCAM-CTM. Mixing depth can also play an important role in plume dispersion, however the PBL heights generated by both models are similar and generally low during BB2 due to the easterly wind direction and the mainly maritime upwind fetch.~~n BB2, both CCAM and TAPM predict direct plume strikes, and the higher CO and BC peaks in TAPM are likely due to a lower PBL in TAPM which leads to lower levels of dilution and more concentrated plume.~~

Secondary species – O_3

Figure 6~~Figure 5~~ e-f shows the simulated and actual O_3 concentration time series for TAPM-CTM and CCAM-CTM for 3 different sets of EF (discussed in Section 3.1.2). The two observed O_3 peaks which followed BB1 and BB2 can clearly be seen in the time series of observations. Figure 7 shows the TAPM-CTM and CCAM-CTM concentration isopleths of O_3 enhancement downwind of the fire during BB1 at 11:00 and 13:00 on the 16 February.

~~The two observed O_3 peaks which followed BB1 and BB2 can clearly be seen in the time series.~~

Again the simulated meteorology has a major impact on the ability of the models to reproduce the magnitude and timing of the observed O_3 peaks. TAPM-CTM reproduces the major O_3 peak observed following BB2, and captures part of the O_3 peak following BB1. For the peak following BB1 it under predicts the peak duration and fails to capture the subsequent observed peaks on the 19th and 19th February. ~~TAPM reproduces both of the major O_3 peaks observed following BB1 and BB2, with the timing of the first peak within 5 hours of the observed peak and the second within 8 hours of the observed peak.~~ ~~The model~~TAPM-CTM also shows 2 additional O_3 peaks about 24 hours prior to the BB1 and BB2 peaks respectively, which were not observed~~ at the Cape Grim~~. The magnitude of these additional peaks shows a strong dependency on the EF suggesting an influence of fire emissions. This is discussed further below and in Section 3.2.1.

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Compared to TAPM-CTM, CCAM-CTM predicts fewer distinct peaks of ozone above the background (where background is 15-17 ppb) throughout the entire period. ~~Compared to TAPM, CCAM generally shows only minor enhancements of O_3 above background.~~ Both TAPM-CTM and CCAM-CTM show depletion of O_3 below background levels which was not observed, and this is discussed further in Section 3.1.2.

Figure 7 shows that there are differences in wind fields between TAPM-CTM and CCAM-CTM as well as different simulated concentrations of O_3 generated from the fire. This is discussed further in Section 3.1.2.

To summarise, the impact of using two different meteorological models for a primary species such as BC was to vary the modelled time of impact of the BB1 plume strike by up to 15 hours (CCAM-CTM -12 and TAPM-CTM +3 hours, where actual plume strike time = 0 hours) and to vary the plume duration between 12 and 36 hours (actual duration 5 hours). For BB2, different meteorological models predicted the same impact time (TAPM-CTM and CCAM-CTM both -26 hours where actual plume strike time = 0 hours and to vary the plume duration between 47 and 60 hours (actual duration 29 hours).

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For O_3, the use of different meteorological models lead to one model (TAPM-CTM) reproducing both observed peaks plus two additional peaks, while the other model (CCAM-CTM) captured only one defined O_3 peak over the time series of 2 weeks.

3.1.2 Sensitivity of modelled BB species to Emission Factors

Primary species – CO and BC

Figure 6~~Figure 5~~ a-d shows the simulated and observed concentrations of BC and CO for ~~combustion~~ MCE~~s of~~ =0.89, MCE= 0.92 and MCE=0.95 (see ~~Method~~ Section 2.2.2). Because CO has a negative relationship with MCE, and BC has a positive relationship with MCE, the modelled BC concentrations are highest for model runs using the highest MCE, while the modelled CO concentrations are highest for model runs using the lowest MCE (Figure 6~~Figure 5~~).

Changing the EF from low to high MCE varies the modelled BC concentrations during BB1 and BB2 by a factor of ~3 for BC and a factor of ~2 for CO, and increases the EF ratio of BC/CO by a factor of ~6, ~~and for these primary pollutants this is~~ in proportion to the difference in EF input to the models.

Quantile-quantile plots of observed and modelled ratios of BC/CO during BB1 and BB2 for the different EF scenarios are shown in Fig S11. The use of BC/CO ratios were used to minimise uncertainty resulting from errors in modelling transport, dilution (and mixing height), thus enabling a focus on the impact of EF variability. A period incorporating both the modelled and observed BB1 and BB2 was used for the analysis. The TAPM-CTM simulation with MCE=0.89 performed best with greater than 60% of the model percentiles falling within a

factor of two of the observed. The CCAM-CTM simulation with MCE = 0.89 was the second best performer with 50% of the modelled percentiles falling within a factor of two of the observed. Overestimates of the EC/CO ratio by up to a factor of 8 occur for some percentiles for the MCE=0.95 scenarios, while the scenarios with no fire significantly underestimated the observed ratio. Plots of mean fractional bias and mean fractional error (Fig. S12 and S13) show that TAPM-CTM simulation with MCE=0.89 has the smallest bias and error, followed by the CCAM-CTM simulation with MCE=0.89. As discussed previously there is uncertainty in the derivation of EF as a function of MCE, as these were based on relationships from a small number of studies. Nevertheless, the percentile, bias and error analysis indicates that using emission factors corresponding to an MCE of 0.89 gives the best agreement with the observations for the BC/CO ratio. This is in agreement with the calculated MCE of 0.88 for this fire (Lawson et al., 2015)~~As discussed previously there is also uncertainty in the derivation of EF as a function of MCE, as these were based on relationships from a small number of studies.~~

~~Observed CO and BC peaks were compared in magnitude to peaks simulated using different EF in CCAM-CTM and TAPM-CTM. In TAPM, the simulation with the lowest combustion efficiency EFs (MCE 0.89) gives closest agreement to the CO observations, while the run with the medium combustion efficiency EFs (MCE 0.92) gives best agreement with BC observations. For CCAM, the lowest MCE model run (0.89) provides the best agreement with observations for CO for BB and BB2, while for BC, model runs corresponding to the low MCE 0.89 (BB1) and high MCE 0.95 (BB2) provide the best agreement with observations.~~

~~As discussed in Section 3.1.1, the magnitude of the modelled concentration is a function of both the input EF, the wind speed (rate of fuel burning, dispersion) and the mixing height which controls the degree of dilution after plume injection. Hence a good agreement between the magnitude of the model and observed peaks is not necessarily indicative that a suitable set of EF has been used. As discussed previously there is also uncertainty in the derivation of EF as a function of MCE, as these were based on relationships from a small number of studies. However interestingly, in most cases, model simulations with EF corresponding to the low MCE 0.89 appear to best represent the observations, which is in agreement with the calculated MCE of 0.88 for this fire (Lawson et al., 2015).~~

Secondary species - O_3

For secondary species such as O_3 (Figure 6~~Figure 5~~e-f), the relationship between EF precursor gases and model output is more complex than for primary species such as CO and BC, because the balance between O_3 formation and destruction is dependent on the degree of dilution of the BB emissions and also factors such as the NMOC composition and the NMOC/NO_x ratio.

TAPM-CTM (Figure 6~~Figure 5~~e) reproduces the magnitude of both observed peaks following BB1 and BB2 (BB1 max observed = 33 ppb, modelled = 31 ppb, BB2 max observed = 34 ppb, modelled = 30ppb). Interestingly the magnitude of O_3 for these two peaks is the same for different EF inputs of O_3 precursors from the Robbins Island fire, suggesting that the BB emissions are not responsible for these enhancements as demonstrated in Section 3.2. In contrast, the two additional peaks modelled but not seen in the observations are heavily dependent on the input EF. For the first additional modelled peak which was ~~modelled~~ predicted at the time of ~~prior to~~ BB1observations on the 16th February, all EF ~~runs~~ scenarios result in an O_3 peak, with the ~~medium~~ MCE=0.92 model scenario resulting in highest predicted O_3. For the second additional modelled peak just prior to the BB2 observations on the 23rd February, only the ~~lowest~~ MCE=0.89 ~~model run~~scenario results in a net O_3 production, while MCE=0.92 and MCE=0.95 ~~medium and high MCE runs~~ scenarios lead to net O_3 destruction.

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This differing response to EF for the TAPM-CTM runs suggests the importance of the NO EF on O_3 production in BB plumes. Unfortunately there were no oxides of nitrogen measurements made during the fire to test the models. For the first simulated additional peak prior to BB1, while the medium NO EF (~~MCE 0.92~~MCE=0.92) resulted in the highest O_3 peak (with corresponding NO of 3.7 ppb, NO_2 4.5 ppb) the lower NO EF in the 0.89 MCE run perhaps indicates insufficient NO was present to drive O_3 production (corresponding NO 0.5 ppb, NO_2 1.5 ppb), which is in line with studies which have shown that BB plumes are generally NO_x limited (Akagi et al., 2013; Jaffe and Wigder, 2012; Wigder et al., 2013). Conversely the highest input NO EF (~~MCE 0.95~~MCE=0.95) lead to net destruction of O_3 (NO 9 ppb, NO_2 7 ppb), which is due to titration of O_3 with the larger amounts of NO emitted from the fire in these runs as indicated by excess NO (NO/NO_2 ratio > 1) at Cape Grim (where NO has a positive relationship with MCE). For the second additional peak prior to BB2, only the lowest NO EF run (~~MCE 0.89~~MCE=0.89) resulted in net production of O_3 (NO 1.5 ppb NO_2 2.6 ppb)– in the medium and high MCE runs the background O_3 concentration is completely titrated (0 ppb) with NO concentrations of 10 and 20 ppb and NO/NO_2 ratios of 1.3 and 2.6 respectively.

In contrast, the CCAM-CTM model (Figure 6~~Figure 5~~f) simulations reproduce only the first observed O_3 peak associated with BB1 (modelled = 27 ppb, measured = 34 ppb). This modelled O_3 peak does not show an influence of MCE on O_3 concentration, in agreement with TAPM, again suggesting no influence from fire emissions as later demonstrated in Section 3.2.~~.~~ The CCAM model runs also show significant titration of O_3 during BB1 and BB2 for the medium and high MCE model runs, with ~24 and ~48 hours of significant O_3 depletion below background concentrations being modelled for each event, which was not observed

Quantile-quantile plots of modelled and observed concentrations of O_3 for all EF scenarios are shown in Fig. S14 and S15. Model performance was assessed for both the BB and the background periods in order to test the ability of the models to reproduce O_3 from both the fire and other sources, including urban sources. The modelled O_3 concentrations from the TAPM-CTM simulation with MCE=0.89 are close to the 1:1 line with observations for all of the sampled percentiles, and demonstrates that this scenario is in best agreement with observations, and as stated previously, in agreement with the calculated MCE of 0.88 for BB2 (Lawson et al., 2015). Ozone titration in the MCE=0.92 and MCE=0.95 scenarios, which was not observed, is visible as a significant deviation from the 1:1 line in Fig S14. With the exception of these titration events, all of the sampled model concentration percentiles fall well within a factor of two of the observations. Plots of mean fractional error and mean fractional bias (Supp Figs 16 and 17) show that the error and bias are very low for all runs and fall within performance guidelines. ~~Unlike the simulation, the observations do not show significant reduction of O_3 below background levels. The lower MCE (0.89) TAPM-CTM model simulation predicts no O_3 titration and is in best agreement with the observations. This suggests that EF corresponding to lower MCE (0.89) are most representative of the combustion conditions during the Robbins Island fire, and as stated previously is in agreement with the calculated MCE of 0.88 for BB2 (Lawson et al., 2015). Again however it should be recognised that the absolute concentrations of NO in the plume, which determines O_3 production or destruction, are not only driven by EF but also dependent on the degree of dilution, which is driven by meteorology and mixing height.~~

.

~~To summarise, the impact of EF on primary species such as BC and CO was that the modelled peak concentrations varied in proportion with the variation in the input EFs, (factor of ~3 BC and ~2 CO). For the secondary species O_3, the EF of precursor gases, particularly NOx, had a~~

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~~major influence (along with meteorology) on whether the model predicted net production of O_3, or destruction of background O_3, as was particularly evident in TAPM.~~

The different EF scenarios presented here suggest that varying model EF has a major impact on whether the models simulate production or destruction of O_3, particularly important at a receptor site in close proximity to the BB emissions. ~~As shown i~~In the previous work (Lawson et al., 2015), the MCE for the first 10 hours of BB2 was calculated as 0.88, however later in BB2, a rainfall event led to changes in the NMOC/CO and BC/CO ratios. This suggests that during the course of BB2 the MCE decreased and thus EFs changed. As such, the used of fixed BB EF in this work and in other models, may lead to incorrect prediction of important species such as O_3.~~"minor rainfall events have the potential to significantly alter EF due to changes in combustion processes. This work suggests that varying model EF has a major impact on whether the model predicts production or destruction of O_3, particularly important at a receptor site in close proximity to the BB emissions. Models which assume a fixed EF for O_3 precursor species in an environment with temporally variable EF may therefore be challenged to correctly predict the behaviour of an important species such as O_3~~.~~

~~Given that TAPM-CTM meteorological model with EF corresponding to the low combustion efficiency (MCE 0.89) provides an overall better representation of the timing and magnitude of both primary and secondary species during the fire, this configuration has been used to further explore the spatial variability in the next section, as well as drivers of O_3 production and plume age in Section 3.2 and 3.3.~~

3.1.3 Sensitivity of modelled concentrations to spatial variability

The near-field proximity of the Robbins Island fire (20 km) to Cape Grim, the narrowness of the BB plume and the spatial complexity of the modelled wind fields around north Tasmania are likely to result in strong heterogeneity in the modelled concentrations surrounding Cape Grim. We investigated how much model spatial gradients vary by sampling ~~the~~ TAPM-CTM ~~model~~ output with MCE=0.89 at 4 grid points sited 1 km to the north, east, south and west of Cape Grim. ~~The TAPM-CTM model runs with EF corresponding to the MCE of 0.89 were used for the spatial analysis.~~

Primary species - CO

Figure 8~~Figure 6~~a shows a time series of the modelled CO output of the difference between Cape Grim and each grid point 1km either side.

Where plotted CO concentration is other location [CO] (N,S,E,W) –Cape Grim [CO].

The figure clearly shows that there are some large differences in the modelled concentrations of CO between grid points for both BB1 and BB2. Particularly large differences were seen for BB2 with the north gridpoint modelled concentrations in BB2 over 500 ppb lower than at Cape Grim grid point, while at the Southerly grid point the modelled CO was up to 350 ppb higher. Smaller differences of up to 250 ppb between the east and Cape Grim grid points were observed for BB1. This indicates the plume from the fire was narrow and had a highly variably impact on the area immediately surrounding Cape Grim.

Figure 8~~Figure 6~~b shows the observed cumulative concentration of CO over the ~~56~~ 29 hour duration of BB2 at Cape Grim, as well as the modelled cumulative concentration at Cape Grim and at the four gridpoints either side. This figure shows both the variability in concentration with location, but also with time. TAPM-CTM's underestimation of the observed CO by is visible by hour 20. ~~Beyond the 10 hour mark, the model~~TAPM-CTM begins to show~~s major~~ differences in modelled cumulative CO concentrations between the 5 gridpoints (including Cape Grim)~~,~~ by hour 10. ~~highlighting significant spatial variability. For example a~~At the end of BB2 ~~(hour 56), the model~~TAPM-CTM predicts that there are differences of 5 - 30% between the ~~-~~cumulative modelled CO concentration ~~at~~ at Cape Grim ~~is 24% lower than the cumulative concentration 1 km south~~and the gridpoints to the north, east, south and west. ~~and 47% higher than the cumulative concentration 1 km north. The modelled cumulative CO concentrations at the South gridpoint at hour 56 is almost twice as high as the north modelled concentration 2 km away (82% difference). T~~This ~~high~~ variability modelled between sites which are closely located highlights the challenges with modelling the impact of a near field fire at a fixed single point location. This also highlights the high spatial variability which may be missed in similar situations by using a coarser resolution model which would dilute emissions in a larger gridbox.

Ozone (O_3)

Figure 8~~Figure 6~~c shows a time series of the modelled O_3 output of the difference between Cape Grim and each gridpoint 1km either side, where plotted O_3 concentration is other location [O_3] (N,S,E,W) – Cape Grim [O_3].

The modelled TAPM-CTM concentrations are very similar at all grid points when BB emissions are not impacting. The variability increases at the time of BB1 and BB2, with differences mostly within 2-3 ppb, but up to 15 and 10 ppb at east and west sites for BB1. This largest difference corresponds to the additional modelled O_3 peak which was not observed

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which showed strong dependency on EF (see Section 3.1.2), and provides further evidence that local BB emissions are driving this enhancement.

The ~~model~~ TAPM-CTM output for O_3 for BB1 (Figure 7) shows O_3 enhancement downwind of the fire at 11:00 and 13:00 on the 16 February. The very localised and narrow O_3 plume is dispersed by the light (2 m s^{-1}) and variable winds, and Cape Grim is on the edge of the O_3 plume for much of this period, explaining the high variability seen in Figure 6c.

In summary there is a large amount of spatial variability ~~is the model~~ in TAPM-CTM for primary species such as CO during the BB events, with differences of > 500 ppb in grid points 1 km apart. This is due to the close proximity of the fire to the observation site and narrow plume non-stationary meteorology. For O_3, there is up to 15 ppb difference between grid points for a narrow O_3 plume which is formed downwind of the fire.

The highly localised nature of the primary and in some cases secondary species seen here highlights the benefits of assessing spatial variability in situations with a close proximity point source and a fixed receptor (measurement) site. ~~Due to the spatial variability shown for O_3 in BB1, model data from all 5 grid points are reported in Section 3.2.~~

3.2 Exploring plume chemistry and contribution from different sources

3.2.1 Drivers of O_3 production

In previous work on the Robbins Island fire, it was noted that the increases in O_3 observed after both BB1 and BB2 were correlated with increased concentration of HFC134a (Lawson et al., 2015). This indicated that transport of photochemically processed air from urban areas to Cape Grim was likely the main driver of the O_3 observed, rather than BB emissions (Lawson et al., 2015). However, during BB1 in a calm sunny period with minimal urban influence, ~~-~~an increase in O_3 ~~increase~~ was observed alongside a period of ~~during~~ particle growth and elevated BC, suggesting possible biomass burning influnce. ~~(BB1) when urban influence was minimal which suggested O_3 growth may also have been driven by emissions from local fire.~~ Normalised Excess Mixing Ratios (NEMR) observed during BB2 were also in the range of those observed elsewhere in young BB plumes (Lawson et al., 2015) (where NEMR is an excess mixing ratio normalised to a non-reactive co-emitted tracer, in this case CO, see Akagi et al., 2011).

~~In this section, we report on how~~ To explore this further, TAPM-CTM was used to determine the degree to which the local fire emissions, and urban emissions from mainland

Australia~~emissions~~, were driving the observed O_3 enhancements ~~observed~~. The scenario with EF corresponding to MCE=0.89 was used, as discussed previously

~~The model was run using TAPM-CTM with EF corresponding to the lowest MCE of 0.89, as discussioned previously.~~ Figure 9 shows the simulated ozone for all sources (With BB) and all sources excluding the Robbins Island fire (No BB). ~~Three different emission configurations were run to allow identification of BB-driven O_3 formation; a) with all emission sources (E_{all}); b) all emission sources excluding the Robbins Island fire ($E_{exRIfire}$); and c) all emission sources excluding anthropogenic emissions from Melbourne (E_{exMelb}).~~

~~The enhancement of O_3 due to emissions from the Robbins Island fire was calculated by~~

~~$E_{RIfire} = E_{all} - E_{exRIfire}$ (1)~~

~~The enhancement of O_3 due to emissions from anthropogenic emissions in Melbourne was calculated by~~

~~$E_{Melb} = E_{all} - E_{exMelb}$ (2)~~

~~In this way the contribution was estimated from the two most likely sources (emissions from the Robbins Island fire and transported emissions from Melbourne on the Australian mainland).~~

~~Due to the high spatial variability of O_3 for BB1 discussed in the previous section, E_{RIfire} and E_{Melb} was calculated for all 5 locations (Cape Grim and 1 km north, south, east and west).~~

There are two additional distinct ozone peaks in the 'With BB' simulation (Figure 9). These occured~~2 peaks attributed to the fire occur~~ during, or close to the plume strikes, and are short lived (3 and 5 hour) events. These same two peaks showed a strong dependance on model EF in Section 3.1.2. In contrast, the two peaks attributed to transport of air from mainland Australia are of longer duration, and occur after the plume strikes.

~~The O_3 modelled times series for the $E_{exRIfire}$ and the E_{exMelb} runs shows distinct O_3 peaks driven by the Robbins Island fire emissions and distict peaks from the Melbourne anthropogenic emissions (Figure 8). The 2 peaks attributed to the fire occur during, or close to the plume strikes, and are short lived (3 and 5 hour) events. These same two peaks showed a strong dependance on model EF in Section 3.1.2. In contrast, the two peaks attributed to transport of air from mainland Australia are of longer duration, and occur after the plume strikes.~~

~~The O_3 peaks which were observed following BB1 and BB2 correspond with the modelled O_3 peak in which the Robbins Island fire emissions were switched off, confirming that the origin of the two observed O_3 peaks is transport from mainland Australia, as suggested by the~~

~~observed HFC-134a.~~ Of the 2 modelled ~~Robbins Island~~ fire-derived O_3 peaks, the first modelled peak (33 ppb) corresponds with a small (21 ppb) observed peak during BB1 (Period B in Lawson et al., 2015), but the second modelled fire-derived O_3 peak is not observed. As shown in Figure 7 and discussed in Section 3.1.3, according to ~~the model~~TAPM-CTM the O_3 plumes generated from fire emissions were narrow and showed a strong spatial variability. Given this, it is challenging for TAPM-CTM~~the the model~~ to predict the exact timing and magnitude of these highly variable BB generated O_3 peaks impacting Cape Grim. This is likely why there is good agreement in timing and magnitude between model and observations for the large scale, spatially homogeneous O_3 plumes transported from mainland Australia, but a lesser agreement for the locally formed, spatially variable O_3 formed from local fire emissions.

In summary, TAPM-CTM suggests that the the two largest observed O_3 peaks followng BB1 and BB2 were urban air transported from mainland Australia, and suggests some O_3 formation was driven by emissions from the local fire event. TAPM-CTM captures the magnitude and timing of the larger scale urban-derived peaks well, but is challenged by the timing and magnitude of O_3 from local BB emissions.

~~Given the challenges in modelling narrow locally formed O_3 plumes and the dependence on meteorology in particular, we analysed a longer period surrouding BB1 and BB2 (32 and 71 hours) to remove this temporal variability. We calculated the overall contribution of the Robbins Island fire to total excess (excess to background) O_3 (including anthropogenic O_3) for these periods. To capture some of the spatial variability, model output at the 4 locations around Cape Grim was included in the calculation.~~

~~The contribution of the Robbins Island fire emissions to the excess O_3 was calculated by:~~

~~$E_{Rifire} / (E_{Rifire} + E_{Melb}) \times 100$ (3)~~

~~Where the contribution can be positive (O_3 enhanced above background levels) or negative (O_3 depleted below background levels).~~

~~Figure 8 shows the modelled contribution of the Robbins Island fire emissions to excess O_3 for the period surrounding BB1 and BB2, where the box and whisker values are the % contributions at each of the 5 sites (Cape Grim and 1 km either side). The model indicates that for an area 4 km^2 surrounding Cape Grim, the Robbins Island fire emissions contributed between 25 to 43% of the total excess O_3 during BB1 and contributed ~4 to ~6 % to the excess O_3 during BB2. In other words, during BB1, the fire emissions had a net positive contribution to the O_3 in excess of background, while during BB2 the fire emissions had a net destructive~~

~~effect on the excess O_3. The higher variability in the contribution for BB1 reflects the high spatial variability discussed previously.~~

~~In summary, running the model with and without the Robbins Island fire emissions allowed clear separation of the fire-derived O_3 peaks from the anthropogenic-derived O_3 peaks, and allowed estimation of the fire contribution to total excess O_3 during BB1 and BB2. While the contributions of BB emissions to O_3 are only estimates due to the issues discussed previously, this work demonstrates how a model can be used to elucidate the degree of contribution from different sources, where this is not possible using observations alone.~~

3.2.2 Plume age

~~The model~~TAPM-CTM was used to estimate the physical age of air parcels reaching Cape Grim over the two week period of the Robbins Island fire. The method is similar to the Eulerian effective physical age of emissions metric, accounting for mixing and chemical decay from Finch et al (2014) and ~~-~~has been described previously in Keywood et al., (2015). Briefly, two model simulations were run for scenarios which included all sources of nitric oxide (NO) in Australia ; the first treated NO as an unreactive tracer, the second with NO decaying at a constant first order rate. The relative fraction of the emitted NO molecules remaining after 96 hours was then inverted to give a molar-weighted plume age. As urban emissions are a larger NO source than BB, this approach would weight the age in the favour of the urban emissions if air masses from these two sources were mixed. However as shown in Figure 9, there are distinct periods where BB or urban sources dominate. As there is little mixing of air from the two sources, there are unlikely to be issues with the calculated age being weighted towards one source.

Figure 10~~Figure 9~~ shows a time series of the modelled NO tracer (decayed version), modelled plume age (hours) and the observed O_3. Direct BB1 and BB2 plume strikes can be clearly seen with increases in NO corresponding with a plume age of 0-2 hours. The plume age then gradually increases over 24 hours in both cases, peaking at 15:00 on the 17th February during BB1 (aged of plume 40 hours) and peaking at 17:00 on the 25th February during BB2 (age of plume 49 hours). The peak observed O_3 enhancements correspond with the simulated plume age in both BB1 and BB2 (with an offset of 2 hours for BB1), and the observed HFC-134a, suggesting that the plume which transported O_3 from Mebourne to Cape Grim was approximately 2 days old. ~~The model~~TAPM-CTM also simulates a smaller NO peak alongside the maximum plume age, indicating transport of decayed NO from the mainland to Cape Grim.

As reported in Lawson et al., (2015), during BB2 NEMRs of $\Delta O_3/\Delta CO$ ranged from 0.001-0.074, in agreement with O_3 enhancements observed in young BB plumes elsewhere (Yokelson et al., 2003; Yokelson et al., 2009). However, the modelling reported here suggests that almost all of the O_3 observed during BB2 was of urban, not BB origin. This suggests NEMRs should not be used in isolation to identify the source of observed O_3 enhancements, and highlights the value of utilising air mass back trajectories and modelling to interpret the source of O_3 enhancements where there are multiple emission sources.

~~3.~~3~~4~~ Summary and conclusions

In this work we have used a unique set of opportunistic BB observations at Cape Grim Baseline Air Pollution Station to test the ability of CSIRO's ~~a~~ high resolution (400m grid cell) ~~chemical transport model~~CTM to reproduce primary (CO, BC) and secondary (O_3) BB species in challenging non-stationary, inhomogeneous, and near field conditions. We tested the sensitivity of the ~~model~~ CTM to three different parameters (meteorology, MCE and spatial variability) while holding the plume rise and the chemical mechanisms constant.

We found meteorology, EF and spatial variability have a large influence on the modelled output mainly due to the close proximity of the fire to the receptor site (Cape Grim). The lower MCE (MCE=0.89) TAPM-CTM model simulation provided the best agreement with the observed concentrations, in agreement with the MCE calculated from observations of 0.88 (Lawson et al., 2015). The changing EFs, in particular NO dependency on MCE, had a major influence on ~~the ability of the model to predict~~ the simulated O_3 concentrations, with a tendency of the models in some configurations to both fail to simulate observed O_3 peaks, and to simulate complete titration of O_3 which was not observed. As shown in the previous work (Lawson et al., 2015), minor rainfall events have the potential to significantly alter EF due to changes in combustion processes. This work suggests that varying model EF has a major impact on whether the models predict~~s~~ production or destruction of O_3, particularly important at a receptor site in close proximity to the BB emissions. Models which assume a fixed EF for O_3 precursor species in an environment with temporally and spatially variable EF may therefore be challenged to correctly predict the behaviour of important species such as O_3.

There were significant differences in model output between Cape Grim and grid points 1 km away highlighting the narrowness of the plume and the challenge of predicting when the plume would impact the station. This also highlights the high spatial variability which may be missed

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in similar situations by using a coarser resolution model which would dilute emissions in a larger gridbox.

~~The model~~TAPM-CTM was used to distinguish the influence of the two sources on the observed O_3 enhancements which followed BB1 and BB2. Transport of a 2 day old urban plume some 300km away from Melbourne was the main source of the O_3 enhancement observed at Cape Grim over the two week period of the fire. ~~The model suggests the Robbins Island fire contributed approximately 25-43% of observed O_3 to the BB1 O_3 enhancement, but for BB2 the fire caused a net O_3 depletion below background levels.~~ Despite NEMRs of $\Delta O_3/\Delta CO$ during BB2 being similar to that observed in young BB plumes elsewhere, this work suggests NEMRs should not be used in isolation to identify the source of observed O_3 enhancements, and highlights the value of utilising air mass back trajectories and modelling to interpret the source of O_3 enhancements where there are multiple emission sources.

Acknowledgements

The Cape Grim program, established by the Australian Government to monitor and study global atmospheric composition, is a joint responsibility of the Bureau of Meteorology (BOM) and the Commonwealth Scientific and Industrial Research Organisation (CSIRO). We thank the staff at Cape Grim and staff at CSIRO Oceans and Atmosphere for providing observation data for this work. Thank you to Nada Derek for producing figures, Mick Meyer for providing fire scar information, and Suzie Molloy for providing advice on ozone observation data. Finally we thank the three anonymous reviewers for their helpful suggestions and comments~~.~~

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Table 1. EF used in model sensitivity studies, corresponding to low (MCE=0.89), medium (MCE=0.92) and high (MCE = 0.95) MCEs. A subset of the total species included in the CB05 lumped chemical mechanism are shown. Also shown are savannah EF from Andreae and Merlet (2001) (A&M) and EF calculated from BB2 in previous work (Lawson et al., 2015). NO = nitric oxide, CO =carbon monoxide, PAR=paraffin carbon bond, OLE= terminal olefin carbon bond, TOL=toluene and other monoalkyl aromatics, XYL=xylene and other polyalkyl aromatics, BNZ =benzene, FORM=formaldehyde, ALD2=acetaldehyde, EC25=elemental carbon <2.510 µm, OC=primary organic carbon < 2.510 µm

	EF g kg $^{-1}$		
	MCE 0.89	MCE 0.92	MCE 0.95
NO	0.8	2.7	4.7
CO	121	89	57
PAR	2.33	2.02	1.40
OLE	0.81	0.7	0.49
TOL	0.3	0.26	0.18
XYL	0.07	0.06	0.04
BNZ	0.35	0.3	0.21
FORM	0.63	0.55	0.38
ALD2	0.75	0.65	0.45
EC25	0.16	0.29	0.45
OC25	4.34	3.47	2.60

	EF g kg $^{-1}$				
	A&M (2001)	Lawson et al., (2015)	Used in this work		
	MCE 0.94	MCE 0.88	MCE 0.89	MCE 0.92	MCE 0.95
NO	3.9	n/a	0.8	2.7	4.7
CO	65	127	121	89	57
PAR	1.55	n/a	2.33	2.02	1.40
OLE	0.54	n/a	0.81	0.7	0.49
TOL	0.2	0.30	0.3	0.26	0.18
XYL	0.045	0.26	0.07	0.06	0.04
BNZ	0.23	0.69	0.35	0.3	0.21
FORM	0.42	1.64	0.63	0.55	0.38
ALD2	0.5	0.92	0.75	0.65	0.45
EC	0.48	0.16	0.19	0.34	0.53
OC	3.40	n/a	5.10	4.08	3.06
NMOC/NO_x	1.60	n/a	11.99	2.97	1.20

Table 2. Summary of sensitivity study results, including Meteorology, Emission Factors and Spatial Variability.

Sensitivity study	Species	TAPM-CTM simulation	CCAM-CTM simulation	Comments/drivers of model outputs
Meteorology (Section 3.1.1)	BC and CO	BB1 plume strike +3 hr Duration 12 hr (actual 5 hr)	BB1 plume strike -12 hr Duration 36 hr intermittent (actual 5 hr)	Narrow BB plume. Differences in plume strike due to timing and duration driven by timing of wind direction change, windspeeds
		BB2 plume strike 0 hr Duration 50 hr (actual 57 hr)	BB2 plume strike 0 hr Duration 57 hr (actual 57 hr)	Concentrations driven by directness of plume hit and PBL height
	O_3	4 O_3 peaks simulated (2 observed, 2 not)	1 O_3 peak simulated (observed)	Dilution of precursors due to dispersion and PBL height (and EF – see below)
Emission Factors (Section 3.1.2)	BC and CO	BC peak magnitude varies by factor 3, CO factor 2 with different EF runs	As for TAPM -CTM	Concentrations vary according to EF input ratios.
	O_3	2 peaks with high EF sensitivity, 2 peaks with no EF sensitivity	1 peak with no EF sensitivity	NO EF (varies with MCE) drives destruction or production of O_3 in fire related peaks. MCE 0.89 TAPM-CTM simulation gives best agreement with observations
Spatial Variability (Section 3.1.3)	CO	Differences of up to > 500 ppb in grid points 1 km apart (BB2)	n/a	Narrow BB plume
	O_3	Differences of up to 15 ppb in grid points 1 km apart (BB1)	n/a	Narrow ozone plume generated downwind of fire

Sensitivity study	Species	TAPM-CTM simulation	CCAM-CTM simulation	Comments/drivers of model outp
Meteorology (Section 3.1.1)	BC and CO	BB1 plume strike +3 hr Duration 12 hr (actual 5 hr)	BB1 plume strike -12 hr Duration 36 hr intermittent (actual 5 hr)	Narrow BB plume. Differences in plume to timing of wind direction change; windspeeds; direct or indirect advection of plume over Cape Grim
		BB2 plume strike -26 hr Duration 50 hr (actual 29 hr)	BB2 plume strike -26 hr Duration 57 hr (actual 29 hr)	Wind direction differences driven by gravity wave oscillations;timing of wind direction change; different wind speeds driving absolute BB emissions and plume dispersion
	O_3	4 O_3 peaks simulated (2 observed, 2 not)	1 O_3 peak simulated (observed)	Differences in simulated wind speed and direction (and EF – see below)
Emission Factors (Section 3.1.2)	BC and CO	BC peak magnitude varies by factor 3, CO factor 2 with different EF runs	As for TAPM -CTM	Concentrations vary according to EF input ratios.
	O_3	2 peaks with high EF sensitivity, 2 peaks with no EF sensitivity	1 peak with no EF sensitivity	Different NMOC/NO_x emission ratios (varies with MCE) drives destruction or production of O_3 in fire related peaks. MCE 0.89 TAPM-CTM simulation gives best agreement with observations
Spatial Variability (Section 3.1.3)	CO	Differences of up to > 500 ppb in grid points 1 km apart (BB2)	n/a	Narrow BB plume
	O_3	Differences of up to 15 ppb in grid points 1 km apart (BB1)	n/a	Narrow ozone plume generated downwind of fire

Commented [LS(A1]: Note that the comments/drivers text has been changed for Meteorology sensitivity study in accordance with changes to the text in the manuscript

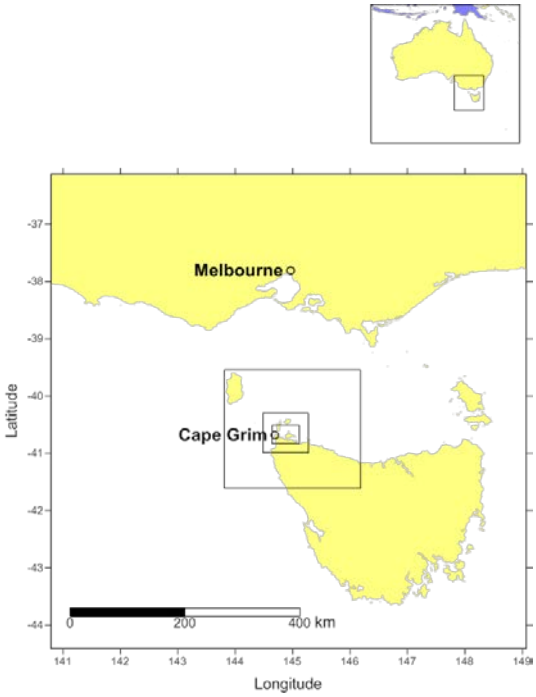

Figure 1. The five nested computational domains used in TAPM-CTM and CCAM-CTM~~this work~~, showing cell spacings of 20 km, 12 km, 3 km, 1 km and 400 m.

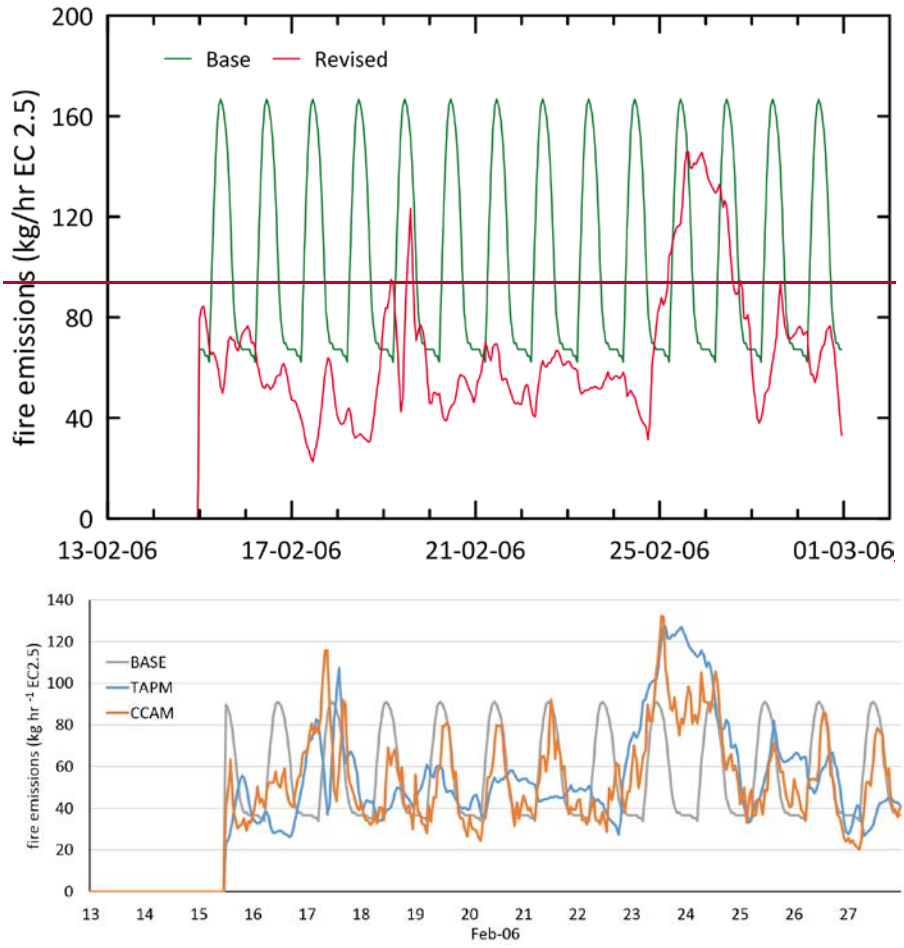

Figure 2 Base hourly diurnal emissions and revised Macarthur Fire Danger Index (FDI)-scale emissions generated using TAPM and CCAM meteorology. ~~emissions calculated using the Macarthur Fire Danger Index (FDI), in which the presence of strong winds results in faster fire spread and enhanced emissions. Revised emissions were used in all simulations.~~

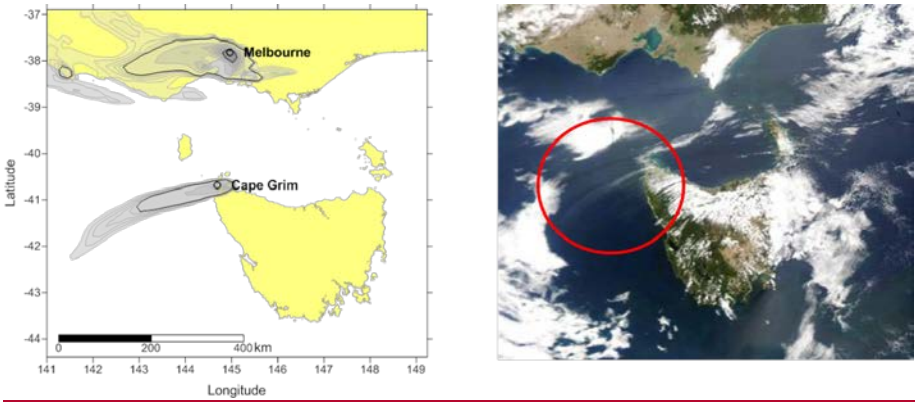

Figure 3. Model output of BC (left) on the 23rd February, with a MODIS Truecolour image of the same period.

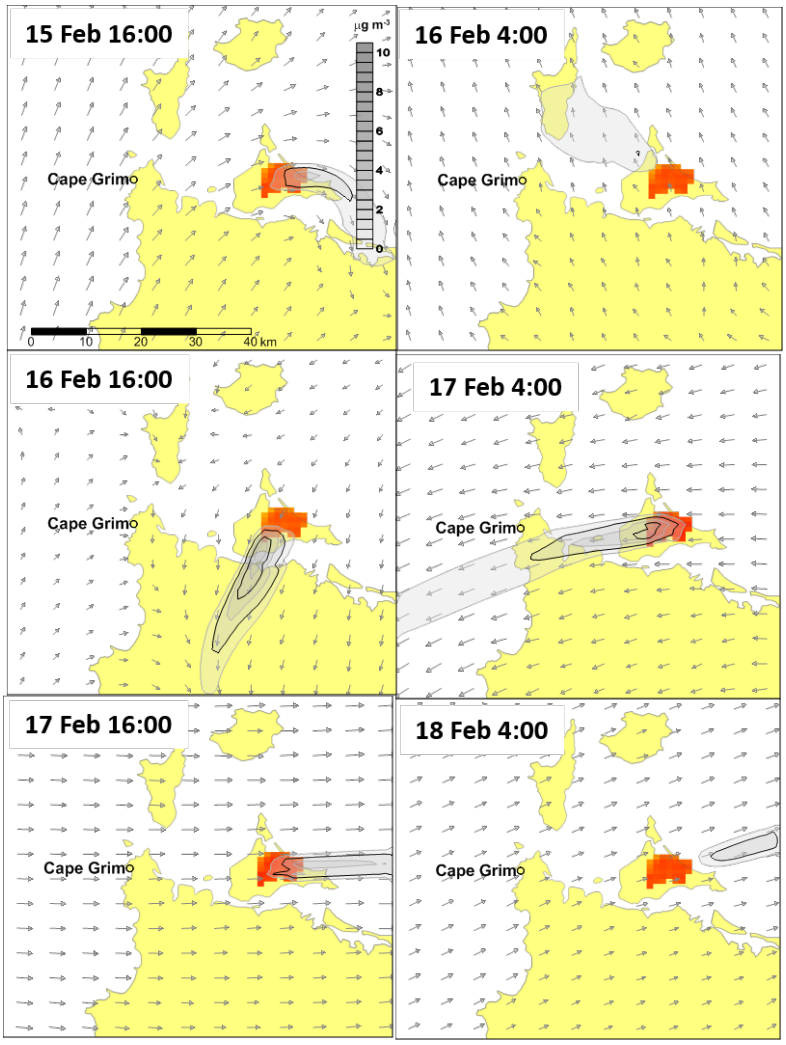

Figure 4. Model output of BC for TAPM-CTM at 12 hour time intervals during BB1, showing the Robbins Island BB plume ~~strike~~ intermittently striking Cape Grim, and then the change in plume direction with wind direction change. Arrows are wind vectors.

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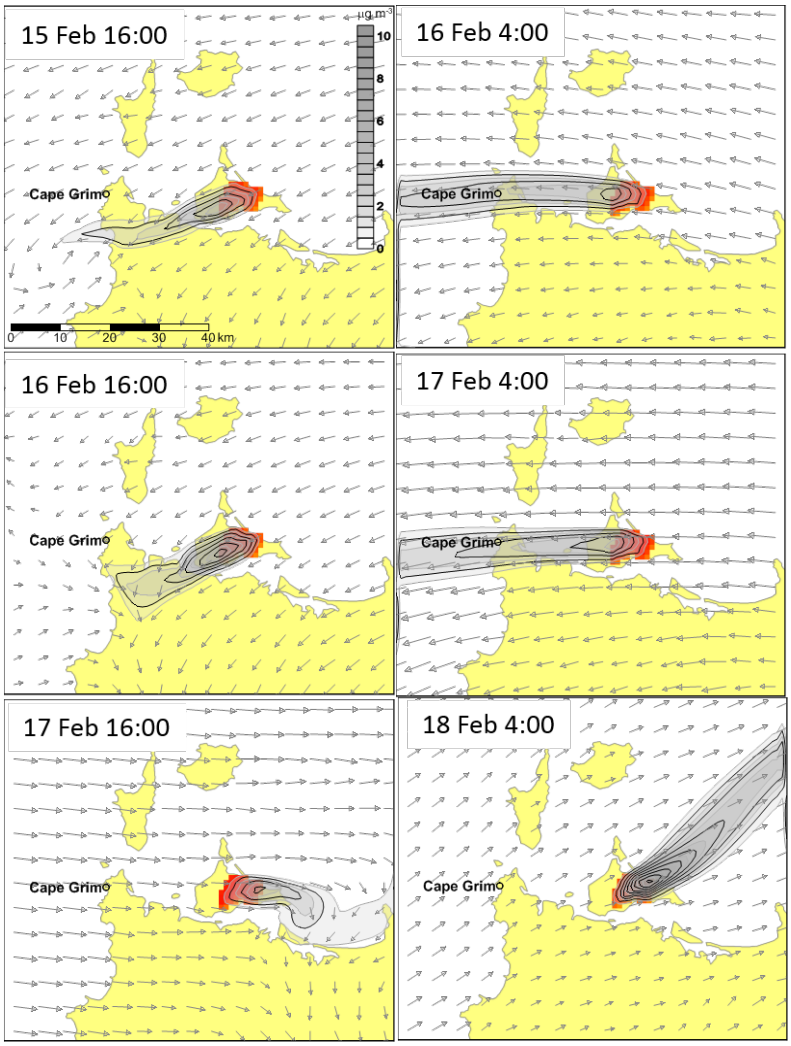

Figure 5. Model output of BC for CCAM-CTM at 12 hour time intervals during BB1, showing the Robbins Island BB plume ~~strike~~ intermittently striking Cape Grim ~~(until 17 Feb 4:00)~~, and then the change in plume direction with wind direction change. Arrows are wind vectors.

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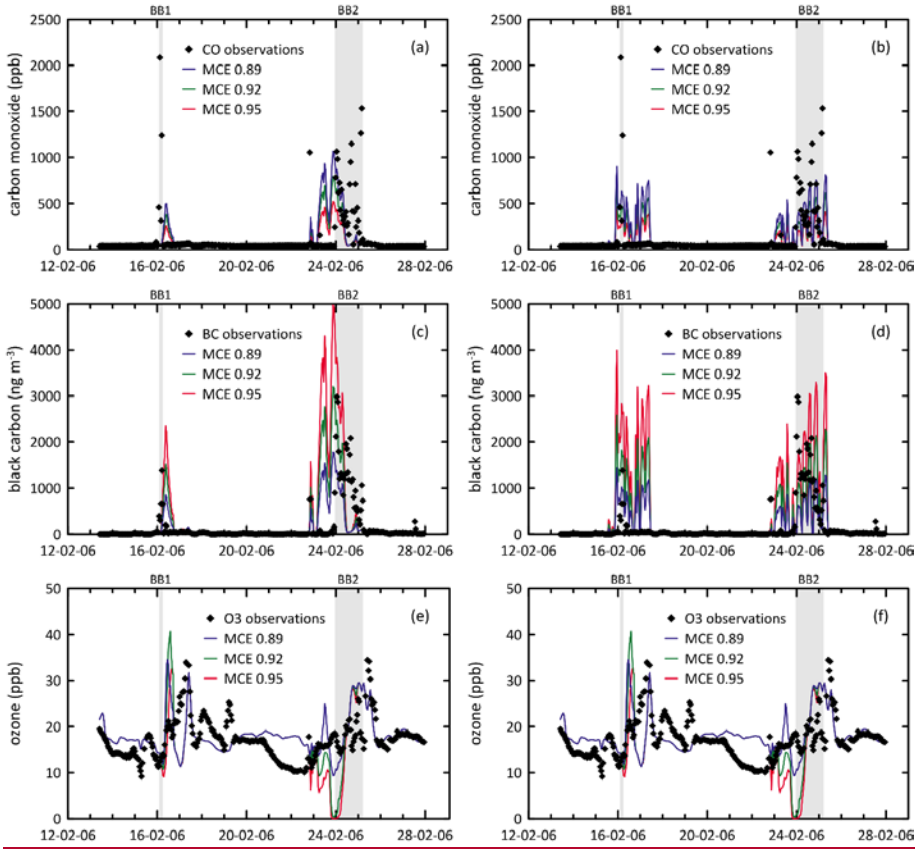
BB1
BB2
(a)
CO observations
MCE 0.89
MCE 0.92
MCE 0.95
carbon monoxide (ppb)
(b)
(c)
BC observations
black carbon (ng m-3)
(d)
(e)
O3 observations
ozone (ppb)
(f)
12-02-06
16-02-06
20-02-06
24-02-06
28-02-06

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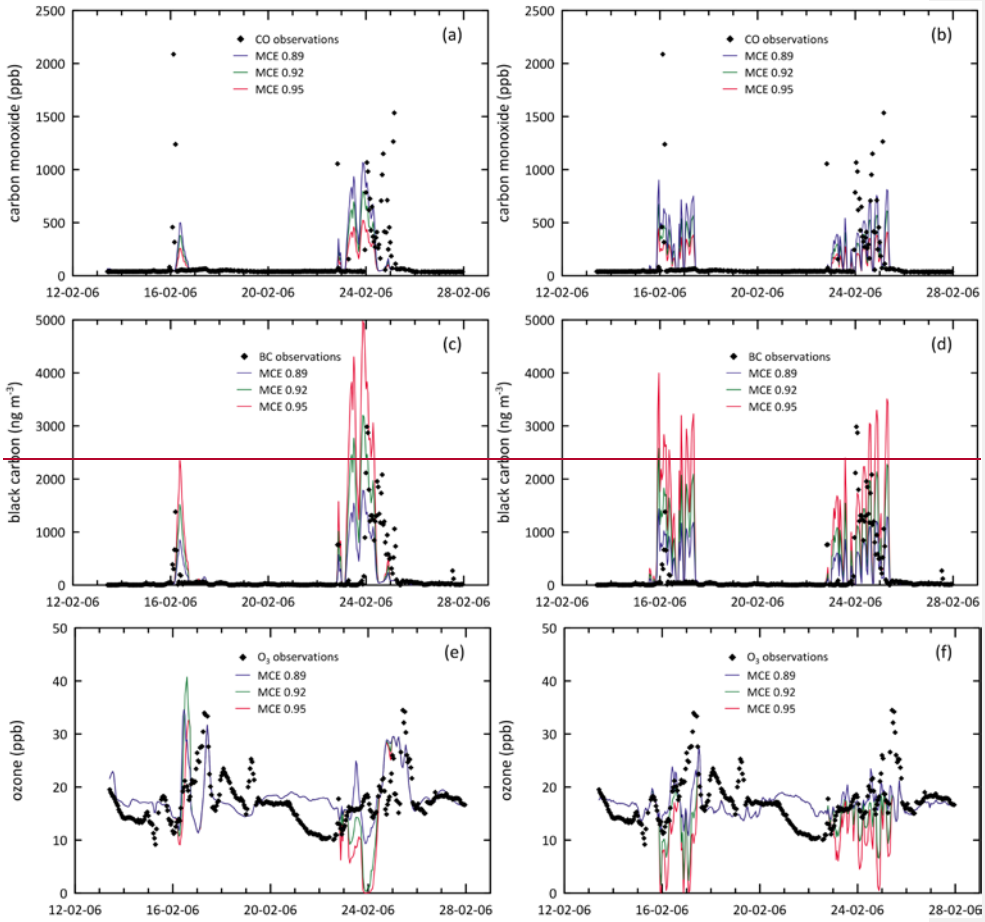

Figure 6. Simulated CO using a) TAPM-CTM and b) CCAM-CTM, simulated BC using c) TAPM-CTM and d) CCAM-CTM, and simulated O_3 using e) TAPM-CTM and f) CCAM-CTM. Coloured lines represent different MCE EF simulations, black symbols are observations

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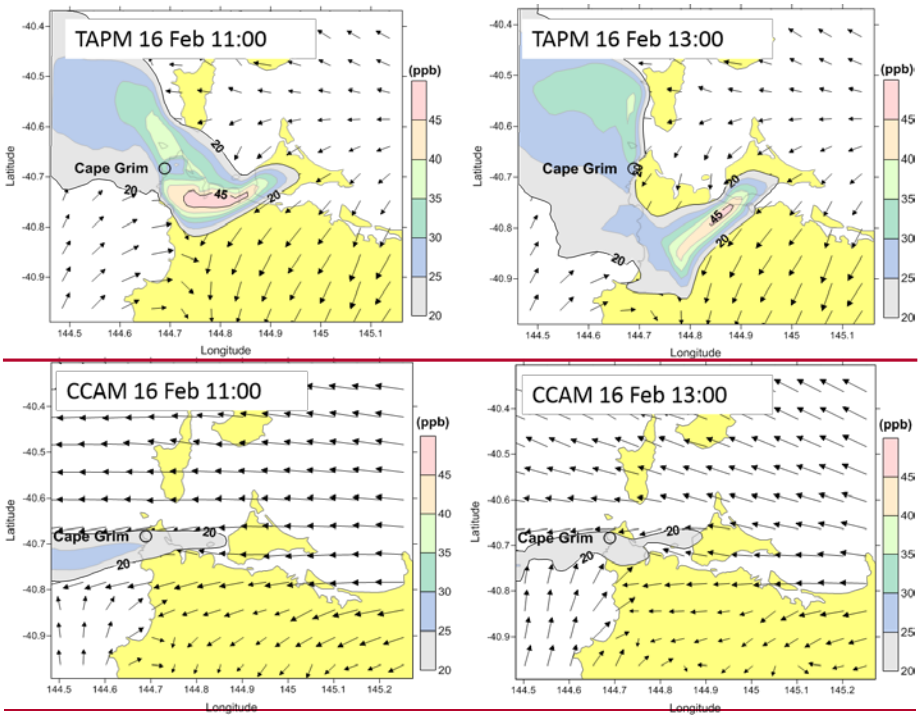

TAPM 16 Feb 11:00
TAPM 16 Feb 13:00
CCAM 16 Feb 11:00
CCAM 16 Feb 13:00
Cape Grim
(ppb)
Latitude
Longitude

37

45

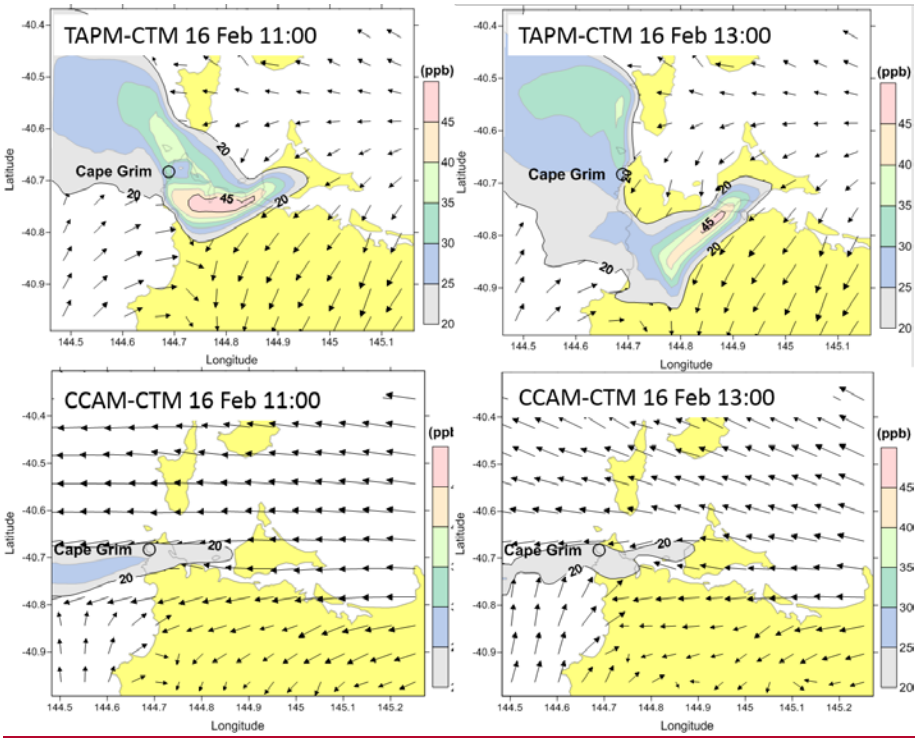
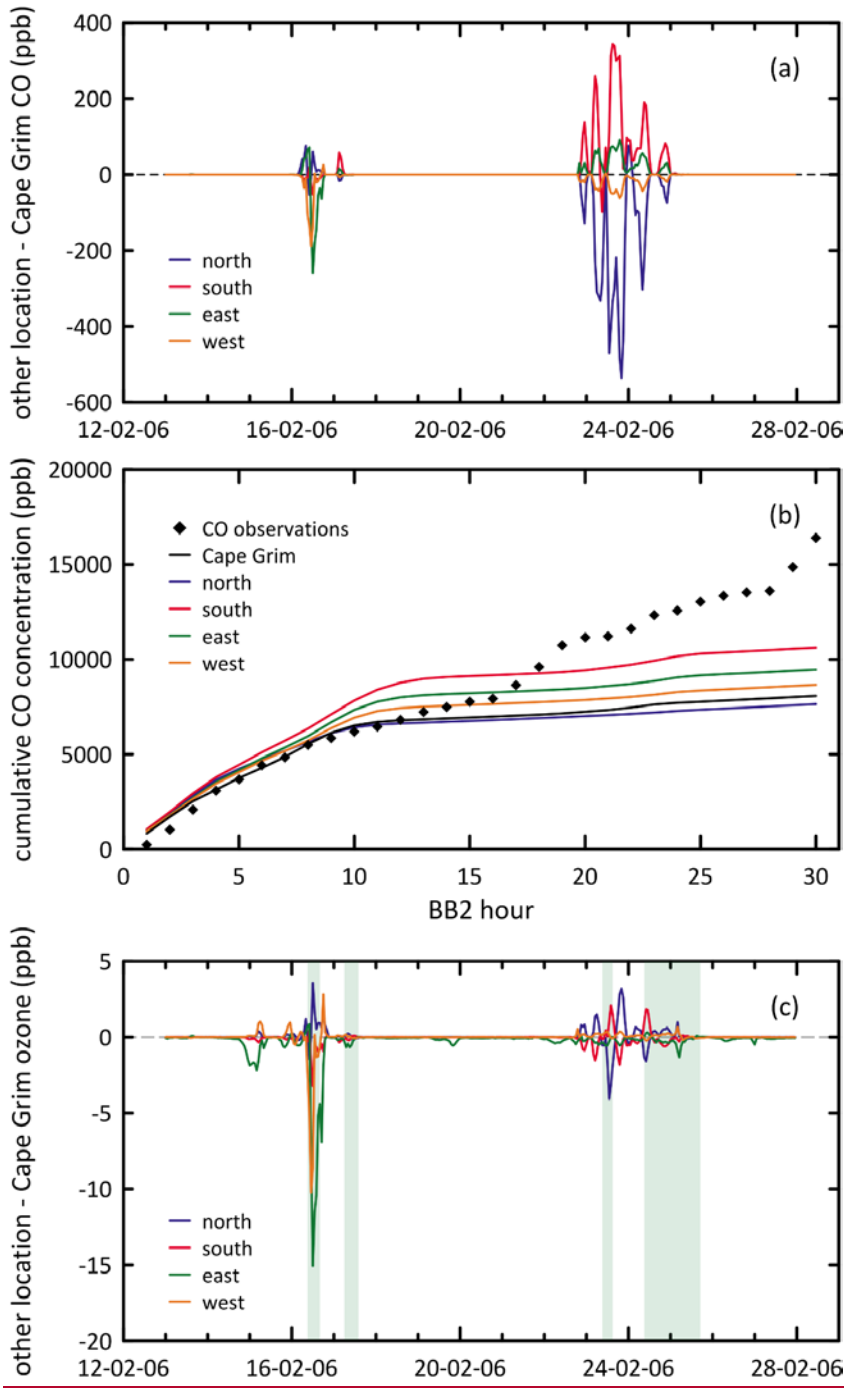


Figure 7 Model output showing O_3 enhancement downwind of the fire during BB1 at 11:00 and 13:00 on the 16 February for TAPM-CTM (top) and CCAM-CTM (bottom). The spatially variable plume and complex wind fields are shown. Arrows are wind vectors.


(a)
other location - Cape Grim CO (ppb)
400
200
0
-200
-400
-600
north
south
east
west
12-02-06
16-02-06
20-02-06
24-02-06
28-02-06
(b)
cumulative CO concentration (ppb)
20000
15000
10000
5000
0
CO observations
Cape Grim
north
south
east
west
0
5
10
15
20
25
30
BB2 hour
(c)
other location - Cape Grim ozone (ppb)
5
0
-5
-10
-15
-20
north
south
east
west
12-02-06
16-02-06
20-02-06
24-02-06
28-02-06

43

47

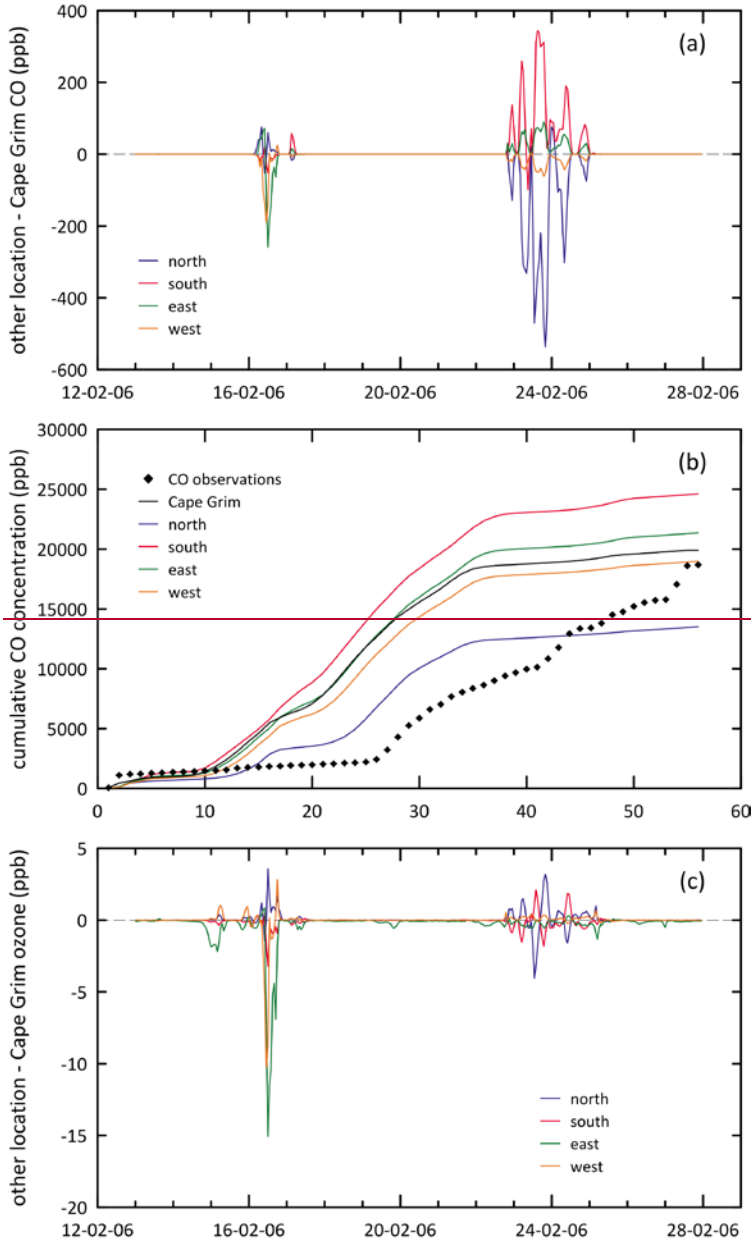


Figure 8 Simulated spatial variability using TAPM-CTM with MCE=0.89 showing a) time series of CO over two weeks of fire (BB1 and BB2 shown), b) the observed and modelled cumulative concentration of CO over the 29 hour duration of BB2 and c) time series of O_3 over the two weeks of fire. The four modelled

O_3 peaks in the Cape Grim gridpoint are shaded. ~~All p~~Figs~~lots~~ a and c show the difference between simulated concentrations at Cape Grim and at 4 surrounding grid points 1km north, south, east and west of Cape Grim. Fig b shows simulated cumulative CO at Cape Grim and at 4 surrounding grid points. ~~4 grid points surrounding Cape Grim over two weeks of fire (BB1 and BB2 shown)~~. Observations are black symbols.

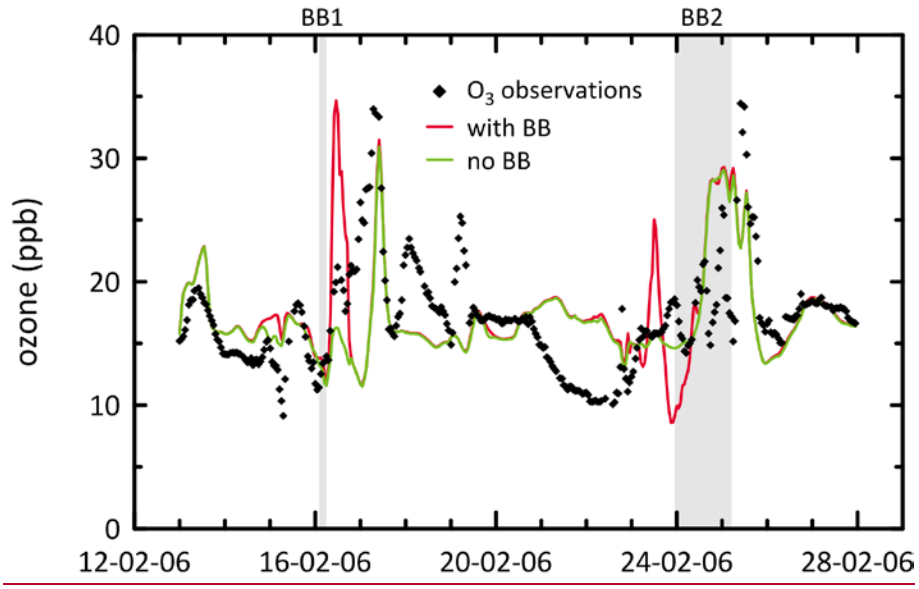


Figure 9 ~~a)~~ **Simulated** ~~contribution to~~ O_3 ~~formation~~ concentration **at Cape Grim** with the ~~from~~ **Robbins Island fire emissions (red line) and** ~~Melbourne emissions~~without the fire emissions **(green line). Observations are black symbols.** Model used was TAPM-CTM with EF corresponding to MCE=0.89. **The periods corresponding to** observed **BB1 and BB2 are shaded.** ~~; b) simulated contribution of the fire to excess O_3 for BB1 and BB2 at all 5 grid points surrounding Cape Grim, where upper and lower diamonds are minimum and maximum contribution.~~

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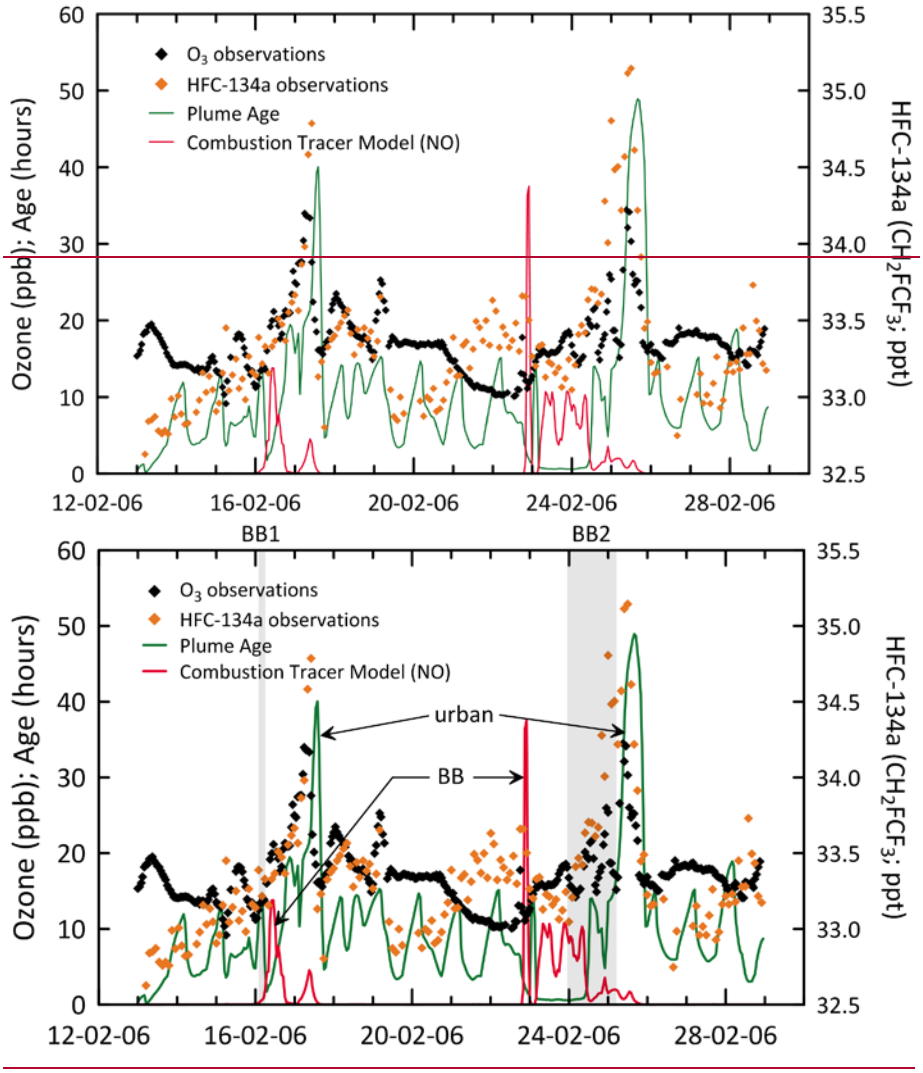

Figure 10 Simulated plume age (green line), simulated combustion tracer (NO) (red line), observed O_3 (black symbols) and observed HFC-134a (orange symbols) over 2 week duration of the fire. The modelled BB periods (red peaks) and impact of urban air from mainland Australia (green peaks) are labelled. The periods corresponding to observed BB1 and BB2 are shaded.

71
72
73 End

Biomass burning at Cape Grim: exploring photochemistry using multi-scale modelling

Sarah J. Lawson, Martin Cope, Sunhee Lee, Ian E. Galbally, Zoran Ristovski and Melita D. Keywood

Response to reviewers

We thank the reviewers for their very helpful suggestions which in almost all cases have been incorporated into the manuscript.

After encouragement from all three reviewers we have prepared a detailed Supplementary Section which provides a quantitative assessment of model performance for meteorology and simulated primary BB emissions (BC/CO ratio) and secondary pollutant (O3) concentrations, both in background conditions and during the fire. More detail is provided in response to specific reviewer comments below.

Our response to reviewer comments are prefixed with >

Changes to the manuscript are in inverted commas " "

Reviewer 1

Reviewer 1 This paper presents several sensitivity studies of high resolution chemical transport modeling (CTM) to reproduce biomass burning (BB) plume strikes observed at Cape Grim. Two meteorological models are used to explore the sensitivity of model predictions to meteorological inputs, while three sets of emission factors are used to explore the model sensitivity to adjustments to the modified combustion efficiency (MCE) of the fires. These results are compared to observations and used to estimate the impact of biomass burning on the enhancement of O3 observed at Cape Grim during both events.

In general, this is a well-written paper on an important topic, the impacts of biomass burning on surface O3 concentrations, using an interesting dataset from Cape Grim. The methods generally appear to be reasonable and the evidence presented supports the conclusions. The model sensitivity studies presented help to illustrate that the observed O3 peaks were generally due to anthropogenic pollution, rather than biomass burning emissions. However, in a few places the methods are not adequately explained, and I have some questions and concerns about the modeling studies. Thus I recommend publication after revision to address my comments as detailed below.

Major Comments:

P6, L14-16: We need more details on the measurements in the text, such as a reference for the measurement method, the measurement frequency and averaging, the precision and accuracy, any known biases or other interferences, etc.

>in response to similar comments from Reviewer 2, additional text has been added. Note that the O3, CO and BC measurements presented here are part of long term measurements at Cape Grim, a WMO GAW Global Site and as such the measurements methods are well characterised and well documented in the references cited.

“In this work, measurements of black carbon (BC), carbon monoxide (CO) and ozone (O3) are compared with model output. BC measurements were made using an aethelometer (Gras, 2007), CO measurements were made using an AGAGE gas chromatography system with a multi-detector (Krummel et al., 2007) and ozone measurements were made using a TECO analyser (Galbally et al., 2007). For further details

see Lawson et al., (2015).

P7, L20-21: At this horizontal scale, you are going to start to resolve some of the eddies in the boundary layer, which may cause problems if your meteorological model assumes that all turbulent eddies are sub-grid scale as part of its boundary layer parameterization. How did you avoid these issues in your models?

> the use of such a high resolution inner domain can run the risk of violating the firstorder closure assumptions used by the CTM to model horizontal dispersion. This can especially be the case when a point source geometry is modelled and the gradient transfer hypothesis breaks down in the near field where plume meandering is the dominant sub-grid scale transport process. Fortunately the Robbin's Island fire is a horizontally expansive area source and this source geometry will not lead to the same issues

(Csanady, 1973)
Csanady, G.T. Turbulent diffusion in the environment. Dordrecht, Bost, D. Reidel Pub. Co. 1973 248 pp. illus. 25 cm (Geophysics and Astrophysics Monographs, v. 3). ISBN 90-277-0260-8

P8, L24: You don't define how you arrived at the "base" emissions shown in Figure 2, or why the total emissions (integral under the curves) is not the same in the base and the FDI-scaled emissions. We need more detail on what you are doing to calculate the emissions

>Thank you for pointing out this issue with the description and Figure 2. We have now updated Figure 2 to correctly represent the emission profiles for the "base" scenario and have replaced the "Revised" profile with the FDI-scale emissions generated using TAPM and CCAM meteorology. We note that the integral of each emission profile (thus the total mass of EC2.5 emitted) is now consistent. The text has also been updated to include more detail on how the emissions were calculated.

"The effect of wind speed on the fire behaviour and emissions in particularly important during the second BB event in which the winds ranged from 10 to15 m s-1. This is evident from Figure 2 where hourly emission profiles based on an average diurnal FDI calculated by Meyer et al. (2008) (which peaks early afternoon) is compared with profiles based on hourly FDI generated by TAPM and CCAM meteorology. It can be seen that the use of the dynamic FDI approach during the BB2 period increases the BASE emissions by 70% for TAPM meteorology and by 45% for the CCAM meteorology. It is also notable that the use of the dynamic approach with TAPM meteorology leads to the peak emissions occurring overnight on the 24th Feb which is when the BASE emissions are at a minimum."

P8, L29-30: I assume you are using the temperate forest MCE range because savannas generally have a high MCE in these EF databases. However, this is seemingly inconsistent with using savanna EFs for most species. How do you reconcile this?

> Yes we used the temperate forest MCE range because Robbins Island is an a temperate region. We didn't use savanna EF for most species, rather we adjusted the savanna EF to correspond to the temperate MCE range using published relationships between MCE and EF. There was a similar query from Reviewer 2. As stated previously, we have endeavoured to make this clearer by rewriting the text in this section to:

"CCAM-CTM and TAPM-CTM models in previous work typically used savannah EF from Andreae and Merlet (2001). However, as Robbins Island is in a temperate region, the A&M savannah EF used in the models were adjusted to reflect temperate EF based on the following methodology. Minimum, mean and maximum CO EF for temperate forests from Agaki et al., (2011) were used for lower (0.89), best estimate (0.92) and upper MCE (0.95). For all other species, savannah EF (corresponding to MCE 0.94) were adjusted to EF for MCE 0.89, 0.92 and 0.95 using published relationships between MCE and EF (Meyer et al., 2012; Yokelson et al., 2007; Yokelson et al., 2003; Yokelson et al., 2011). For example to adjust the Andreae and Merlet (2001) savannah EF (corresponding to an MCE of 0.94) to our temperate 'best estimate' EF

(corresponding to MCE of 0.92) the Andreae and Merlet (2001) NO EF was reduced by 30%, the NMOC EFs were increased by 30%, the BC EF was reduced by 30% and the OC EF was increased by 20%. Table 1 gives emission factors for the original savannah EF (Andreae and Merlet 2001) and the adjusted EF used in this work. The NOx/NMOC ratios used are also shown, and vary by a factor of 3 between the low and high MCE scenarios, mainly driven by the variability in NO emissions with MCE. The EF calculated from observations are shown for comparison (Lawson et al., 2015)."

P13, L15-17: You need to make clear that this inconsistency between the best MCE values to use for CO and BC is due to errors in your assumed relationships of the emission factors of the two pollutants with MCE, rather than that you are suggesting that the fire had multiple MCEs or that the value is highly uncertain.

>As suggested by Reviewer 2, this section has been removed and rewritten so that BC/CO ratios (rather than absolute CO and BC concentrations) have been compared with different MCE scenarios.

P19, L6: You don't discuss how you estimated the background concentration, and thus the excess concentration, of O3. Since your results may be very sensitive to the choice of background, it's important to be clear on how you calculated it.

>background observations were taken from Lawson et al., 2015. However this section has now been removed due to concerns from Reviewer 3 and so no change has been made to the manuscript.

Minor Comments:

P1, L25-29: The first sentence here on the previous work seems out of place in the abstract, and the second sentence is true, but not really a conclusion of this study. Thus I recommend cutting both sentences.

>we have retained these sentences as they highlight an important implication of this work – that when BB EF change due to events such as rainfall, this may challenge a model's ability to simulate O3 when fixed EF are used. This is pertinent to this work, because we observed changes in trace gas and particle emission ratios (and likely MCE) with rainfall in the previous companion paper, and the modelling work in this paper highlights the potentially important implications of this. Therefore we have retained these two sentences.

P2, L7-11: This summary paragraph is not really necessary to include in the abstract, so I recommend cutting it.

>We agree that the second part of the paragraph is not necessary and have removed it. We have retained the first sentence of the paragraph because we think it is a key finding of this paper.

P2, L21: "impacts of BB plumes from a fire" – BB plumes are from fires by definition, correct? Also, you need to specify the impacts, e.g. impacts on human health, air quality, climate.

>as suggested this sentence has been changed to ". . ..the impact of BB plumes on human health, air quality and climate may be local, regional or global.

P7, L20: Were both models run at this resolution? If so, please correct that.
>this section has been rewritten in response to the same query by Reviewer 2 as follows:

"For CCAM, 20 km spaced simulations over Australia were used by the CTM (with the same grid spacing) to model large scale processes on the continent including the emission and transport of windblown dust, sea salt aerosol and smoke from wildfires. Note that the governing equations for TAPM do not enable this model to simulate spatial scales greater than 1000 km in the horizontal and thus only the CCAM meteorology was available for the continental-scale simulations. TAPM and CCAM 12 km spaced

simulations were then used to model the transport of the Melbourne plume to Cape Grim by the CTM (at 12 km grid spacing) with boundary conditions provided by the continental simulation. Nested grid simulations by the CTM at 3 km and 1 km grid spacing utilised TAPM and CCAM meteorology simulated at matching grid spacing. The 1 km spaced meteorological fields were also used to drive a 400 m spaced CTM domain which encompassed Robbin's Island and Cape Grim. This domain was included in the nested grid system because we wanted to better numerically resolve the spatial extent of the fire and the process of plume advection between Robbin's Island and Cape Grim."

P13, L24-26: This is only true for CO, not BC, right? So I think you need to make that clear.

>this section has been removed as the ratio of CO/BC model and observations has been compared rather than absolute concentrations of CO and BC, as described previously.

P14, L29-30: This is only true for BB2, right? If so, make that explicit.

>this section has been rewritten to incorporate quantitative comparison between modelled and observed O3 as requested by Reviewers 2 and 3 and as such this question does not apply to the new version of the text

P15, L11-22: I'd suggest cutting both of these paragraphs. The first just repeats statements you have already made, and thus belongs in the conclusions. The second is true, but except for the first sentence referring to the previous work, it is obvious and not really related to the study presented in this paper.

>as suggested the first paragraph has been removed. As for the second paragraph we believe it is an implication of this study, and so has been retained, but re-written so the implications are clearer:

"The different EF scenarios presented here suggest that varying model EF has a major impact on whether the models simulate production or destruction of O3, particularly important at a receptor site in close proximity to the BB emissions. In the previous work (Lawson et al., 2015), the MCE for the first 10 hours of BB2 was calculated as 0.88, however later in BB2, a rainfall event led to changes in the NMOC/CO and BC/CO ratios. This suggests that during the course of BB2 the MCE decreased and thus EFs changed. As such, the used of fixed BB EF in this work and in other models, may lead to incorrect prediction of important species such as O3."

P17, L4: Make clear again that this additional modeled peak was not observed.

>'which was not observed' added to sentence

P17, L22-23: Need a reference for this work.

>reference has been added

P17, L22-29: This paragraph sounds like it would fit better in the introduction rather than in the results section.

>this paragraph introduces the context and motivation for the next section. To make this clearer, line 30 has been changed to 'to explore this further. . .."

P19, L15-18 and P21, L18: Please also give the change in absolute units (ppbv).

>this section has been removed in response to comments by Reviewer 3.

P20, L3: Please make clear that this is a photochemical age, not the actual age of the air mass.

>it is not actually the photochemical age, rather it is a physical age. NO is used as a tracer however any gas could have been used that was emitted from both urban and

BB sources. Reviewer 3 requested more details about this metric which have been added to the text – please see response to Reviewer 3.

Figure 1 caption: Since you use two models, saying “the model” is ambiguous.
>as suggested caption has been changed to ‘TAPM-CTM and CCAM-CTM” rather than the Model

Figure 5: I’d suggest increasing the font size of all the text in this plot. It is difficult to read right now.

>as suggested font size of (now Fig 6) has been increased. This was also requested by Reviewer 3.

Figure 6c: I’d suggest adding vertical lines or bands showing the four modeled O3 peaks on this figure, so we can see how the peaks are affected by the presented differences. >As suggested this figure (now Fig 8c) has been modified so that these four modelled O3 peaks are shaded.

Typos:
P1, L23: I think “non-methane organic compound” is the more common phrase, so I’d suggest using this here and again at P2, L17
>as suggested has been changed to non-methane
P1, L23-24: I think you need commas before “which in turn” and after “ratio”
>commas added
P3, L25-28 and elsewhere: you need to use a consistent format for these lists of a), b), c) etc. Sometimes you separate them with commas, elsewhere with semi-colons, or here with nothing.
>this paragraph has been removed in response to another reviewer’s comments. For consistency in other parts of the paper we have consistently used commas as suggested
P4, L8: “monthly” is repeated.
>duplication removed
P4, L28 and elsewhere: The formatting of the references in the text is inconsistent with ACP style. Please double-check them all to save the copy-editor some time.
>formatted as suggested
P5, L24: Need a space between “20” and “km”
>space inserted
P8, L15-16: You should introduce the abbreviation FDI here along with the reference, rather than down at L22.
>changed as suggested
P9, L31: I suggest cutting “within the computational time step loop.”
>removed as suggested
P9, L33: “momentum”, not “moment”
>changed as suggested
P10, L20: “summarizes the main findings”
>changed as suggested
P10, L22: “from 23 February 2006,”
>changed as suggested
P10, L24: “Before investigating the impact”
>changed as suggested
P11, L15: “(5 hours actual)” is redundant and should be cut.
>removed as suggested
P12, L7: “and a more concentrated plume.”
>changed as suggested
P12, L16: Need commas before and after “respectively”
>changed as suggested
P13, L4: Cut “Method”
>removed as suggested
P13, L13 and elsewhere: I’d suggest adding an equals sign here, to give “(MCE = 0.89)” and do the same consistently through the paper.
>changed as suggested
P14, L25: Add units to the NO and NO2 mixing ratios.
»added as suggested
P17, L1: “The modeled concentrations are very similar”

>changed as suggested
P18, L11-12: The statement in parentheses is redundant, so I'd suggest cutting it, and then combining L13-14 with this paragraph.
>this section has been removed in response to comments from Reviewer 3
P20, L21: I'd make this Section 4.
>changed as suggested
P20, L30 and 31: You are missing a "the" at the beginning of each line.
>changed as suggested

Reviewer 2

This paper evaluates two different models against how they capture transport of chemical and formation of secondary O3 formation for two biomass burning events in Tasmania, for which the plume intersected with measurements taken at Cape Grimm. Different MCEs were used to drive emissions to test the sensitivity to uncertainty in this parameter. Further sensitivity simulations were run without fire emissions from Tasmania, and without emissions from Melbourne. The paper is reads well and covers an important topic, using interesting set of model experiments and source of data. However, more clarity is needed in describing the methodology and a more quantitative analysis of the data is required to draw the conclusions the authors have drawn. In addition, there are a few sections which seem long-winded and discuss nonessential information, and the paper would benefit from being made more succinct in these sections.

I think the other two reviewers have done a thorough job of picking up the main points of contention and so I have tried to avoid repeating them. I mostly add some minor points I think should also be picked up on. If the paper is revised appropriately, along with the comme
nts from the other reviewers, I think the paper would be suitable for publication.

Major corrections:

Section 3.3.1: Please provide some figures/tables showing evaluation of the model windspeed and other meterological parameters against observations.

> a comprehensive evaluation of TAPM and CCAM meteorology against observations has been provided in the Supplementary section (pages 1-8 and Fig S2-S8), including evaluation of wind speed, wind direction, temperature, humidity and PBL height. The following paragraph referring to the meteorological comparison has been included in manuscript

"Qualitative and quantitative assessment of model performance for meteorological parameters were undertaken for both TAPM and CCAM. Hourly observed and modelled winds, temperature, humidity and PBL are compared and discussed in the Supplementary section (Figures S2-S8). Briefly, both TAPM and CCAM demonstrated reasonable skill in modelling the meteorological conditions, with the TAPM simulations slightly better than the CCAM with respect to the low level wind, temperatures and relative humidity and CCAM simulations slightly better in terms of PBL height."

I would like to reemphasise Reviewer #3 in saying some kind of quantitative/statistical analysis of the data is required, particularly for the interpretation of Figure 5. I struggled to see which scenario supposedly matched the data better, please state exactly what metric you are using to make this decision (peak height etc.)

> A quantitative assessment of model performance in reproducing concentrations of BC/CO and O3 at the receptor has been undertaken and is presented in the Supplementary section. These measures follow the framework discussed in Dennis et al. (2010), and use the performance goals described in Boylan and Russell (2006) and provide quantitative evidence that the best overall agreement with the observations for both primary (EC/CO) and secondary (O3) species is for the TAPM-CTM run with MCE = 0.89. Further details about the analysis undertaken and resulting changes to the

manuscript have been provided in response to Reviewer 3, and in the Supplementary section.

Given that you later show such high spatial variability and missed plumes, I'm not convinced stating which MCE happened to give the best peak height is very illuminating. Perhaps discussing which gives the best ratios (OC:BC, CO:BC etc.) against measurements would be more useful.

>as suggested, the BC:CO ratio has been used to compare observed and modelled concentrations in the quantitative/statistical analysis in the Supplementary Material Pg 12. The differences between the two meteorological models in recording the O3 peaks must be due to differences in air-mass history, from differences in wind fields. However, the authors only present wind fields from CCAM in Figure 4. Please also present winds form the other model for comparison, and discuss in section 3.1.

>As requested the winds and BC from TAPM during BB1 have been presented in an additional figure in the manuscript (now Fig 4). As the reviewer is interested in the impact of meterorology on O3, the O3 generated from the fire for both CCAM-CTM and TAPM-CTM during BB1 is now also presented in Fig 7.While the differences in O3 from the fire are partly due to differences in wind fields, they are also due to the absolute concentration of O3 simulated from TAPM-CTM and CCAM-CTM, as demonstrated by Fig 7.

The following text has been added to the manuscript:

"Figure 7 shows the TAPM-CTM and CCAM-CTM concentration isopleths of O3 enhancement downwind of the fire during BB1 at 11:00 and 13:00 on the 16 February. Figure 7 shows that there are differences in wind fields between TAPM-CTM and CCAM-CTM as well as different simulated concentrations of O3 generated from the fire. This is discussed further in Section 3.1.2.".

Minor corrections: Pg1, ln12: insert "a" before 'High resolution".

>changed as suggested
Pg1, ln 18: As you use the acronyms for the two models later in the abstract, I think it would be best to introduce them here.

>changed as suggested

Pg 2., ln1. Add "further" as in "TAPM-CTM is further used to. . ." to make it clear you used one of the models for a further set of experiments.

>changed as suggested

Pg 3, ln 22: changes "kms" to "km".

>changed to 'a few kilometers'

Pg 5. ln 11-20. This paragraph repeats statements that were made earlier, but with more references to back it up. I think this paragraph should be moved earlier, replacing the paragraph on pg 3, ln 25-29. Doing this should condense the introduction a bit and make it read more smoothly.

> as suggested we have moved the paragraph discussing sensitivity studies on page 5 line 11-20 earlier, as we agree this makes the introduction read more smoothly. We have however retained the paragraph on pg 3 line 25-29 which discusses the different components of a BB model, because this is important context for the following discussion of challenges in representing each of these components.

Pg 6, ln 14-6. Please give details on the instruments (with appropriate references) for the BC, CO and O3 measurements.

>changed as suggested, text has been changed to:

435
436 “In this work, measurements of black carbon (BC), carbon monoxide (CO) and ozone
437 (O3) are compared with model output. BC measurements were made using an aethelometer
438 (Gras, 2007), CO measurements were made using an AGAGE gas chromatography
439 system with a multi-detector (Krummel et al., 2007) and ozone measurements
440 were made using a TECO analyser (Galbally et al., 2007).”
441
442 Pg. 6, ln 18: Does the CTM really not have a name? Just saying CTM seems too
443 general and ambiguous to me. Maybe refer to it as the CSIRO CTM as Emmerson et
444 al., (2016) do?
445
446 >changed to CSIRO CTM
447
448 Pg 7., ln 16-20. Its not clear whether you use the same resolution and nesting for both
449 models. On first reading, I thought you used one for modeling the globe and nested
450 the other inside.
451
452 >to clarify this, lines 20-24 have been replaced by the following text.
453
454 “The models represent two unique (and independent) approaches for generating the
455 meteorological fields required by the chemical transport model. For CCAM, 20 km
456 spaced simulations over Australia were used by the CTM (with the same grid spacing)
457 to model large scale processes on the continent including the emission and transport
458 of windblown dust, sea salt aerosol and smoke from wildfires. Note that the governing
459 equations for TAPM do not enable this model to simulate spatial scales greater than
460 1000 km in the horizontal and thus only the CCAM meteorology was available for the
461 continental-scale simulations. TAPM and CCAM 12 km spaced simulations were then
462 used to model the transport of the Melbourne plume to Cape Grim by the CTM (at
463 12 km grid spacing) with boundary conditions provided by the continental simulation.
464 Nested grid simulations by the CTM at 3 km and 1 km grid spacing utilised TAPM and
465 CCAM meteorology simulated at matching grid spacing. The 1 km spaced meteorological
466 fields were also used to drive a 400 m spaced CTM domain which encompassed
467 Robbin’s Island and Cape Grim. This domain was included in the nested grid system
468 because we wanted to better numerically resolve the spatial extent of the fire and the
469 process of plume advection between Robbin’s Island and Cape Grim.”
470
471 Please be consistent with plurals: if referring to both models, say models. If only
472 referring to one, please say which one. Never say “The Model”.
473
474 >as suggested this has been changed throughout text
475
476 Pg 9, ln 1-18. This paragraph is very dense and not very clear. I think it would work
477 better if you explain the methodology in the first couple of sentences, then describe
478 how all the key species change with increasing MCE in one sentence (referring to the
479 table). Please also discuss the net change in NOx:NMOC ratio, as this is key for O3
480 formation. I don’t understand why you use temperate biome emissions for CO, and
481 savannah for all the others.
482
483 >Paragraph has been condensed as suggested. As suggested the NOx/NMOC ratio
484 has been included in Table 1, and is discussed in text. Savannah EF for all other
485 species were adjusted to reflect MCEs typical of temperate areas (in line with the MCEs
486 corresponding to the CO emissions). We have clarified this in the modified text below.
487
488 “In previous smoke modelling work, CCAM-CTM and TAPM-CTM used savannah EF
489 from Andreae and Merlet (2001). However, as Robbins Island is in a temperate region,
490 the A&M savannah EF used in the models were adjusted to reflect temperate
491 EF based on the following methodology. Minimum, mean and maximum CO EF for
492 temperate forests from Agaki et al., (2011) were used for lower (0.89), best estimate
493 (0.92) and upper MCE (0.95). For all other species, savannah EF (corresponding to
494 MCE 0.94) were adjusted to EF for MCE 0.89, 0.92 and 0.95 using published relationships
495 between MCE and EF (Meyer et al., 2012; Yokelson et al., 2007; Yokelson et al.,
496 2003; Yokelson et al., 2011). For example to adjust the Andreae and Merlet (2001)
497 savannah EF (corresponding to an MCE of 0.94) to our temperate ‘best estimate’ EF

(corresponding to MCE of 0.92) the Andreae and Merlet (2001) NO EF was reduced by 30%, the NMOC EFs were increased by 30%, the BC EF was reduced by 30% and the OC EF was increased by 20%. Table 1 gives emission factors for the original savannah EF (Andreae and Merlet 2001) and the adjusted EF used in this work. The NOx/NMOC ratios used are also shown, and vary by a factor of 3 between the low and high MCE scenarios, mainly driven by the variability in NO emissions with MCE. The EF calculated from observations are shown for comparison (Lawson et al., 2015).

Pg 9. ln 24-8. Please also present the EFs you calculated from the previous work for comparison (perhaps in the table)?

>As suggested we have modified Table 1 to include EF calculated from Lawson et al., (2015). We have also included in Table 1 the MCE corresponding to the EF from Lawson et al., (2015) and Andreae and Merlet (2001).

Pg 9, ln 30-Pg 10. Ln 13. Given that you don't actually use a plume-rise parameterisation, I think this section is redundant. You can merge this section into the previous emissions section; just saying that low energy burn of the fire justified mixing in the PBL with a minimum height of 200m.

>We agree. As suggested, the plume rise section has been merged into the emissions section. The text now reads:

"With respect to plume rise, the Robbin's Island fire was a relatively low energy burn (Lawson et al., 2015), and as noted by Paugam et al., (2016) the smoke from such fires is largely contained within the planetary boundary layer (PBL). Given that groundbased images of the Robbin's Island smoke plume support this hypothesis, in this work we adopted a simple approach of mixing the emitted smoke uniformly into the model's layers contained within the PBL. The plume was well mixed between the maximum of the PBL height and 200 m above the ground, with the latter included to account for some vertical mixing of the buoyant smoke plume even under conditions of very low PBL height. The high wind speeds particularly during the second BB event, also suggest that the plume was not likely to be sufficiently buoyant to penetrate the PBL."

Pg 11. The section "Primary species – CO and BC' should be a new subsection (it is not part of meteorological evaluation).

>this section assesses the impact of meteorology on simulated pollutant concentrations. To make this clearer, the subheading 3.1.1 has been renamed "Sensitivity of modelled BB species to meteorology"

Pg 16, ln 26-28. This is an important point. The authors also have the perfect dataset to investigate it – presumably they also have data from the courser nests (1km, 3km etc.). Comparison between the finest nest and a few of the courser ones may be interesting.

>while we agree this would be an interesting investigation, we feel this is outside the scope of the current paper.

Tables and Figures:

Figure 6. I think there is a mistake on the labeling of the x-axis on panel b – should these be dates? The caption should be written clearer to say the locations are 1km North, South etc. of the Cape Grimm site.

>this is actually the hour of just BB2. The axis has been re- labelled to reflect this (now Figure 8). The caption has been rewritten to make the locations clearer.

Reviewer 3

Biomass burning at Cape Grim: exploring photochemistry using multi-scale modelling
Summary This paper present a chemical transport modeling study of the impacts of

the Robbins Island a biomass fire on CO, BC, and O3 at the nearby (20 km) Cape Grimm Baseline Air Pollution Station in February of 2006. The study goals included 1) testing the ability of an off-line high resolution chemical transport models (CTM) to reproduce Robbins Island fire plume strike observed at Cape Grimm, 2) test CTM sensitivity to meteorological model (TAPM and CCAM), biomass burning (BB) emission factors (EF), and spatial variability. The main findings reported are 1) the choice of meteorological model had a significant impact on the timing, duration, and intensity and O3 enhancement of two simulated BB plume impacts at the Cape Grimm Station during the study period and 2) varying EF profiles to represent different combustion regimes (i.e. different relative mix of flaming & smoldering represented by the modified combustion efficiency (MCE)) had a strong, non-linear impact on the simulated O3 concentration at Cape Grimm. The primary conclusion of this work is that CTMs employing BB emission estimates that assume a fixed EF may be unable to properly simulate the chemistry O3 or similar species that are highly sensitive to the NMOC/NOx ratio of emissions. The authors' stress the importance of considering the variability of BB EF, suggesting environmental conditions can be an important factor influencing EF.

The authors also conclude their study highlights the importance of assessing the CTM sensitivity to meteorology and the utility of using CTMs in conjunction with observations when attributing source contributions to atmospheric composition.
I found the paper suffers some significant deficiencies in the analysis methods and the presentation and interpretation of results. My general comments elaborating on these deficiencies are provided below. I agree with the authors' conclusion on the importance of EF variability.

However, they do little to identify and discuss the importance of environmental drivers and their potential variability. The authors also overlook previous studies that consider the importance of environmental effects (and vegetation type) on EF variability, for example: van Leeuwen et al. (2013, J. Geophys. Res. – Atmos., 118,6797-6815, doi:10.1002/jgrd.50478), Urbanski (Atmos. Chem. Phys., 13, 7241-7262, doi:10.5194/acp-13-7241-2013, 2013), Castellano et al. (Atmos. Chem. Phys., 14, 3929–3943, 2014), Korontzi et al. (Geophys. Res.,108(D24), 4758, doi:10.1029/2003JD003730).

>The following existing sentence discusses environmental drivers: Furthermore, models use biome–averaged EF which do not account for complex intra-biome variation in EF as a result of temporal and spatial differences in environmental variables. This includes factors such as impact of vegetation structure, monthly average monthly rainfall (van Leeuwen and van der Werf, 2011) and the influence of short term rainfall events (Lawson et al., 2015).

>As suggested to expand this we have added the following paragraph (which includes the 4 suggested references)

"For example, emission factors have been shown to vary significantly with fuel moisture which may vary seasonally (Korontzi et al., 2003; Urbanski, 2013). There may be significant spatial variability in emission factors within a biome (Castellanos et al., 2014); taken along with temporal variability, this has been shown to have a large impact on simulated concentrations of BB species in global-scale modelling (van Leeuwen et al., 2013)."

General Comments The assessment of the model performance in reproducing the observations is mostly qualitative. Assessing the model ability to simulate BB impacts of the Robbin Island fire on O3 at Cape Grimm requires some confidence in the model performance for background conditions (i.e. absent BB impacts). The model should be shown to reasonably reproduce the background O3 and likely factors for disagreement with observations identified (e.g. O3 boundary conditions). The authors have not convincingly done so. The authors note that TAPM-CTM captures two O3 peaks not associated with BB, but this is very qualitative. The TAPM-CTM completely misses the two extended periods of low O3. The model performance for these periods should be discussed. A systematic comparison of simulated O3 versus observed O3 for non-BB periods should be used to characterize and quantify the ability of the models to capture background O3. In the absence of such evidence it is difficult to accept interpretations

of the model performance for the far more complex situation of O3 chemistry in a fresh BB plume.

>The supplementary material includes two figures (S9 and S10) which compare the modelled and simulated O3 in background (non-BB) conditions. The model generally captures background O3 very well. The average modelled mean O3 during background (non BB) periods was 17.7 ppb versus 16.6 ppb observed, with a coefficient of determination of 0.4 . The scatter plot (S9) shows that all modelled concentrations are within a factor of 2 of observations (hourly data). Further, the campaign average diurnal 1 hour O3 (S10) (observed vs modelled) shown below indicates maximum differences of 2 ppb (< 15% of the hourly mean).

>To address the issue of low O3 periods raised by the reviewer: Both of the periods of low observed O3 concentrations mentioned by the reviewer correspond to an extended 'baseline' period of clean marine air from the south westerly direction. The modelled wind directions matched observed closely for both periods. During the first period of low O3 (13-15 Feb), the model overestimated the observed O3 by an average of 3 ppb (observed 14 ppb, modelled 17 ppb) with a maximum difference of 4 ppb. During the second period (20-22 Feb) the model overestimated the O3 by an average of 5 ppb (observed 13 modelled 18), with a maximum difference of 8 ppb (observed 10 ppb, modelled 18 ppb). The average observed baseline O3 concentrations for February from 1982 – 2015 are 17 ppb (S. Molloy, pers com) in good agreement with the model, and 95% of observed O3 baseline data in February falls into the range of 12.4 – 21.8 ppb (S.Molloy, pers com). Hence the minimum observed hourly O3 values during these periods are lower than is typical, with less than a 3% chance of baseline O3concentrations in February being less than 13 ppb.

>As such, these observations of low O3 in baseline air are anomalous, and the processes driving these low concentrations is unknown. Regardless, we believe that these unknown processes which occurred in the south-westerly Southern Ocean baseline sector are unlikely to be very important to the O3 concentration in a northerly or easterly wind direction (wind directions of the fire and urban periods), which have strong terrestrial influence and were was the focus of this work.

Biomass burning plume strikes at Cape Grimm Based on the observations presented in this paper (Figure 5) and through consultation of Lawson et al. (2015), I believe the authors have not properly identified the periods where the Cape Grimm observations show a BB influence. In Figure 5 it appears that after the initial few high BC (or CO) measurements for BB2, the BC and CO drop back to background for many hours before rebounding. It would seem the time period selected for BB2, 57 hours, includes many hours on the front end during which the site is not impacted by smoke. In Lawson et al. (2015) BB2 is described as 29 hour in duration. I believe that the BB2 period defined the current study (57 hours) is not appropriate for the analysis of smoke impacts and the model evaluation. This calls into question the validity the analysis, interpretation, and conclusions for key parts of this paper. I would suggest using the plume strike periods form Lawson et al. (2015).

>it's true that BB2 was extended in this paper to include the initial brief plume strike before the more continuous plume strike period of BB2 reported in Lawson et al. 2015, as stated in the text 'if the first enhancement at 22:00 on the 23 Feb is included'. However for consistency between papers as suggested by the reviewer, the definition of the BB2 duration in this manuscript has been changed to 29 hours. The text has been modified to reflect this in the abstract, on page 11, 13, and in Table 2. The data in Figure 6C (now 8C) has also been changed to only include the 29 hours of revised BB2 definition. The discussion in section 3.1.3 has also been modified to reflect the changes to Figure 6C.

Regardless, the authors need to provide the criteria that were used to identify periods of BB smoke impact at the Cape Grim receptor. Specifically, what BC and CO levels were used as a threshold to identify periods when the plume was define impacting the measurement site? Lawson et al (2015) reports observations of BB tracers HCN and CH3CN, perhaps these should be used.

> For BB2, where NMOC including HCN and acetonitrile were available, the threshold used was a concentration of HCN of acetonitrile 5 times larger than background, corresponding to 0.6 ppb and 0.18 ppb. For BB1 where there were no NMOC data available, a threshold of CO of at least 300 ppb (approx 6 times background value) combined with BC of at least 300 ng m3 (approx 180 times larger than background value) was used. Background concentrations were taken from Lawson et al., (2015).

Figure 5 is the most important of the paper. However, it is difficult to view and interpret. The comparison of modelled CO/BC versus observed is difficult to assess from the Figure 5. The period of BB1 and BB2 are not delineated. Since the focus of the paper is BB impacts at Cape Grimm, I believe additional figures highlighting the periods BB1 and BB2 are needed so a reader can clearly discern the details. Also, the additional figures and Figure 5 should be plotted with the observations color coded to signify periods of smoke impact BB1 and BB2, at the receptor.

>BB1 and BB2 have been shaded and labelled on all relevant figures. An additional Figure (Fig S1) has been included in the supplementary section to highlight the periods of BB1 and BB2. Fig 5 (now Fig 6) has been modified to include thicker lines and larger font.

I found myself confused regarding the definition of BB1 and BB2. Are these periods defined by Cape Grimm observations which indicate the air mass was influenced by biomass burning OR periods when the models predict the biomass burning plume is impacting the Cape Grim site? It seems both definitions may be in use. This paper should clearly differentiate between the “observed” BB1 and BB2 and the model simulated BB1 and BB2, e.g. BB1obs and BB1model.

>we use both definitions, but in response to this comment we have made changes throughout the manuscript to clarify whether we are referring to model or observations.

Quantitative model assessment

The assessment of the model performance in reproducing the observations is mostly qualitative.The authors’ interpretation of the model meteorology influence on differences in the modelled CO and BC profiles at the receptor is not supported by the results, especially for BB2 (Sect 3.1.1). Because the study used the model meteorology to drive the fuel consumption and hence the emission rates, it is difficult to infer the contribution of the models’ transport and atmospheric structure to differences in the simulated concentrations at the receptor.

>Thank you for these suggestions. A quantitative assessment of model performance in reproducing both the concentrations of BC/CO and O3 at the receptor, as well as ability of the models to reproduce meteorology has been undertaken and is presented in the Supplementary section. The results of the assessments have been discussed in detail in response to individual reviewer comments (see below), and have been incorporated into the manuscript.

>The interpretation of the model meteorology influence on BC and CO concentrations at the receptor has been revisited, and the text revised accordingly in Sect 3.1.1. As this issue was raised in more detail by the same reviewer in a later comment, we have addressed the query there (please see response to Reviewer comment below beginning “P12, L6-7:”)

The presentation and discussion of modelled CO and BC sensitivity to EF is inadequate. The results presented, i.e. Figure 5, do not suitable support conclusion regarding the relative performance of the EF scenarios. In Figure 5 it appears that after the initial few high BC (or CO) measurements for BB2, the BC and CO drop back to background for many hours before rebounding. A direct comparison (e.g. plots and regression statistics) of simulated CO (and BC) vs. observed CO (and BC) for the periods when the receptor was impacted by smoke is needed to support the conclusions and provide a quantification of the differences.

>Following the request from all reviewers for additional information on the performance

of the models, a series of qualitative and quantitative performance measures have been provided in the Supplementary Section for the different EF scenarios. These measures follow the framework discussed in Dennis et al. (2010), and use the performance goals described in Boylan and Russell (2006). These measures provide quantitative evidence that the best overall agreement with the observations for both primary (EC/CO) and secondary (O3) species is for the TAPM-CTM run with MCE = 0.89.

>Based on the figures (Fig S11-S17) and text presented in the attached Supplementary material, the following paragraphs in Section 3.1.2 have been included in the manuscript to replace the previous qualitative discussion and to provide evidence that the TAPM-CTM simulation with MCE=0.89 is in best agreement with observations.
"Quantile-quantile plots of observed and modelled ratios of BC/CO during BB1 and BB2 for the different EF scenarios are shown in Fig S11. The use of BC/CO ratios were used to minimise uncertainty resulting from errors in modelling transport, dilution (and mixing height), thus enabling a focus on the impact of EF variability. A period incorporating both the modelled and observed BB1 and BB2 was used for the analysis.
The TAPM-CTM MCE=0.89 simulation performed best with greater than 60% of the model percentiles falling within a factor of two of the observed. CCAM-CTM;MCE = 0.89 was the second best performer with 50% of the modelled percentiles falling within a factor of two of the observed. Overestimates of the EC/CO ratio by up to a factor of 8 occur for some percentiles for the MCE=0.95 scenarios, while the scenarios with no fire significantly underestimated the observed ratio. Plots of mean fractional bias and mean fractional error (Figs S12 and S13) show that TAPM-CTM MCE=0.89 has the smallest bias and error, followed by the CCAM-CTM MCE=0.89 scenario. As discussed previously there is uncertainty in the derivation of EF as a function of MCE, as these were based on relationships from a small number of studies. Nevertheless, the percentile, bias and error analysis indicates that using emission factors corresponding to an MCE of 0.89 gives the best agreement with the observations for the BC/CO ratio. This is in agreement with the calculated MCE of 0.88 for this fire (Lawson et al., 2015)."

"Quantile-quantile plots of modelled and observed concentrations of O3 for all EF scenarios are shown in Fig S14 and S15. Model performance was assessed for both the BB and the background periods in order to test the ability of the models to reproduce O3 from both the fire as well as other significant sources, including urban sources. The TAPM-CTM;MCE=0.89 are close to the 1:1 line with observations for all of the sampled percentiles, and demonstrates that this scenario is in best agreement with observations, and as stated previously, in agreement with the calculated MCE of 0.88 for BB2 (Lawson et al 2015). Ozone titration in the MCE=0.92 and 0.95 scenarios, which was not observed, is visible as a significant deviation from the 1:1 line in Fig 12. With the exception of these titration events, all of the sampled model concentration percentiles fall well within a factor of two of the observations. Plots of mean fractional error and mean fractional bias (Figs S16 and S17) show that the error and bias are very low for all runs and fall within performance guidelines."

The presentation and discussion of O3 results is incomplete. Both models completely miss the two extended periods of low O3. The model performance for these periods should be discussed.

>this has been addressed previously in a response to this reviewer's comment

The discussion of Sect 3.2.1 (Drivers of O3 production) needs to recognize and discuss the considerable uncertainty in the approach used, eliminating emission sources individually in simulations, given the highly non-linear nature of O3 production and the very different emission profiles of biomass burning and urban air (BB plumes high in oxygenated VOC, terpenes, and typically lower in NOx compared with urban). The sum of O3 from the individual scenarios, EexRIfire and EexMelb, may be far off from Eall. For example, see Akagi et al. (Atmos. Chem. Phys., 13, 1141-1165, 2013) and the interaction of BB plume with urban emissions.

> we agree with the reviewer that the contribution of urban and BB emissions to the observed O3 is likely to be non-linear and that there are considerable uncertainties in our approach. To reflect this we have removed all text discussing quantifying the contribution of different sources to the observed O3, and have removed the box and

whisker plot. As such this section has been reduced significantly. We have replotted Figure 8 (now 9) as 'with BB' and 'no BB', so that the O3 peaks associated with the fire can be seen. This gives an indication of the main source of the observed ozone peaks (first order), without the highly uncertain step of quantifying the contributions.

Specific Comments

P3, L31: EF for X is: mass of X emitted per mass of fuel burned
> as suggested has been changed to "mass of species emitted per mass of fuel burned"

P3, L33: Should include Giglio et al. (JGR-Biogesciecnes, 118, 317-328, 2013)
>as suggested this has been included

P4, L7-9: Consdier also: van Leeuwen et al. (2013, J. Geophys. Res. – Atmos., 118, 6797-6815, doi:10.1002/jgrd.50478), Urbanski (Atmos. Chem. Phys., 13, 7241-7262, doi:10.5194/acp-13-7241-2013, 2013), Castellano et al. (Atmos. Chem. Phys., 14, 3929–3943, 2014), Korontzi et al. (Geophys. Res., 108(D24), 4758, doi:10.1029/2003JD003730).

> as suggested these have been included

P7, L17: Include formal name of TAPM
>now included

P7, L20-21: "The model was run using five nested computational domains with cell spacings of 20 km, 12 km, 3 km, 1 km and 400 m" Please clarify, by "The model" does this mean combinations TAPM-CTM and CCAM-CTM?

>yes – have clarified in text

P8, L12-14: Please confirm and clarify that the MODIS active fire product include and the MODIS MCD64A burn scarf product (nominal resolution = 1 day). (I'm guessing this may have been a cloudy stretch). Also, please note the final fire size somewhere in this paragraph.

>The fire scar was determined from hotspots from the Sentinel product (Geosciences Australia) which were derived from MODIS imagery. The hotspots were buffered to give polygon spots at a resolution of 400ha/spot. The buffered spots for each day were merged into a single polgygon for each fire day. The approach is described in Meyer et al., 2008.The following text has been added to the paper

"The fire burnt 2000 ha over the two week period. . .." "The area burnt by the fire was determined from hotspots from the Sentinel product (Geosciences Australia) which were derived from MODIS imagery. The hotspots were buffered to give polygon spots at a resolution of 400ha/spot, then merged into a single polgygon for each fire day (Meyer et al., 2008). "

P10 Section 3.1: Clarify the study period

>the following text has been added: "The period examined was the 13 February 2006 to the 28 February 2006."

P10, L26-27: Please quantify "agreed very well with observed wind direction at Cape Grim" in terms of error and bias for the study period.

>A detailed comparison of observed and modelled meteorology is now provided in the supplementary section, (Fig S2-S8) including error and bias, in response to a comment from Reviewer 2. Please see Supplementary section and response to Reviewer 2 for more details.

P11, L17-21: What BC / CO levels were used as a threshold to identify periods when the plume was define impacting the measurements site? In Figure 5 it appears that after the initial few high BC (or CO) measurements for BB2, the BC and CO drop back to

background for many hours before rebounding. During this period is the enhancement in BC / CO above background significant but it is not noticeable due to the y-axis scale?

>the thresholds have been stated above in response to a previous comment. It is true that in this Figure 5 there is an initial brief period of high BC and CO, followed by 24 hours of background levels, followed by the more prolonged period of BB2. The definition of BB2 has been changed just to include the prolonged period of impact, as suggested by this reviewer in a previous comment.

P12, L6-7: “In BB2, both CCAM and TAPM predict direct plume strikes, and the higher CO and BC peaks in TAPM are likely due to a lower PBL in TAPM which leads to lower levels of dilution and more concentrated plume.” This statement does not seem to be fully supported by the evidence presented, especially the concentration profiles in Figure 5. No evidence is provided of direct plume strikes for either model scenario for BB2. Even if wind directions were the same for both models different wind speed and turbulent processes could results in different degrees of horizontal diffusion leading to different surface concentration fields. Additionally, the wind speed impacts fuel consumption and hence emission rate as well. The differences in the models’ PBL for this period need to be quantified. Further, the shapes of the CO profiles of the two models are quite different. TAPM-CTM has two broad peaks and then drops off missing the later part of event while CCAM-CTM has many sharp peaks and valleys and it captures the duration of the event. These profiles suggest much more is at play in the modelled surface concentrations than simply different PBL heights.

>Thank you for highlighting the need to improve the clarity of the statements in P12 L6-7. In response we have re-examined this event and replaced the explanation on L6-7 with the following text, and included Fig S18 in the Supplementary material.

“In BB2, both TAPM and CCAM predict direct strikes of the Robbin’s Island smoke plume on Cape Grim, because the wind direction is modelled to be predominantly easterly for the duration of the event (see Supplementary Fig 18). Both models simulate some backing and veering of the wind direction for the duration of BB2 due to gravity waves processes which lead to intermittent strikes on Cape Grim as the Robbin’s Island smoke plume sweeps to the north and south of Cape Grim. The gravity wave oscillations are more pronounced in CCAM than TAPM (and thus the plume strikes are more pronounced from the former) due to differences in how the models are coupled to large scale synoptic forcing. The event is eventually curtailed by the passage of a south-westerly change."

"Fig S18 shows that TAPM predicts the onset of the change to occur about six hours ahead of the observed change and thus the BB2 event ends too early for this meteorological simulation. CCAM models the south-westerly change to occur one hour after the observed, leading to the modelled BB2 event extending beyond the observed duration for this meteorological simulation."

"Differences in the magnitude of the modelled CO and BC peaks for TAPM-CTM and CCAM-CTM have two principal causes. a), the coupling of the smoke emissions to the TAPM and CCAM meteorology via the FDI scaling leads to approximately 20% higher emissions in the case of the TAPM-CTM simulations; b), the CCAM wind speeds are 20-50% higher than the TAPM wind speeds during BB2, which in combination with the emission differences, leads to TAPM-CTM generating near-surface smoke concentrations which are up to 80% higher than CCAM-CTM. Mixing depth can also play an important role in plume dispersion, however the PBL heights generated by both models are similar and generally low during BB2 due to the easterly wind direction and the mainly maritime upwind fetch.”

P12, L1-7: Are any atmospheric soundings available during the period that could be used to evaluate the modelled PBLs?

>The reviewer’s suggestion to evaluation the modelled PBL is very helpful. Atmospheric soundings were undertaken at least once per day (000 UTC) for the majority of days in the period 8-21 February 2006. Sondes were released from the Cape Grim monitoring station and returned height, pressure, temperature, humidity, wind speed

and wind direction data at 10-20 m intervals between the surface and about 3000 m. We have used the data to calculate potential temperature and derived the potential temperature gradient using central differences over height intervals of 30-40 m (to include some smoothing of the raw radiosonde data). The observed boundary layer heights have been diagnosed by searching for positive gradients in the potential temperature profile.

>Fig S7 shows the modelled (TAPM and CCAM) hourly PBL time series with the spot hourly PBL observations superimposed on the plot. The figure is helpful because it shows the significantly hourly variability in the modelled PBL- which because Cape Grim is strongly influenced by maritime air, does not strongly follow the typical diurnal variation of PBL growth and collapse associated with sensible heating and long wave radiation cooling over land. Fig S7 suggests that both models has captured important features in the observed PBL heights, including the period of low boundary layer height between hours 168 and 264.

>Fig S8 shows a scatter plot of the observed and modelled PBL heights and indicates that 71% of the TAPM PBL heights lie within a factor of two of the observed and 79% of the CCAM PBL heights are within a factor of two. This is a good result given the complexity of the observed meteorological flows at the Cape Grim monitoring station.
P12, L13-14: TAPM-CTM does seem to capture O3 event starting around 00:00 on Feb 25 and the return to apparent background following this event. The model fails to capture the O3 event that begin around 06:00 on Feb 16 through early Feb 20.
> TAPM captures the peak on the 17th, but timing and duration are out, but as the reviewer says TAPM does not capture the ozone above background on the 18th and 19th. As such the text in the manuscript has been modified to

“TAPM reproduces well the major O3 peak observed following BB2, and captures part of the O3 peak following BB1. For the peak following BB1 it underpredicts the peak duration and fails to capture the subsequent observed peaks on the 19th and 19th February. “

P12, L20-22: “Compared to TAPM, CCAM generally shows only minor enhancements of O3 above background. Both TAPM and CCAM show depletion of O3 below background levels which was not observed, and this is discussed further in Section 3.1.2.”
Please define what is meant by background level. Clarify the period of “minor enhancements”. Does this refer to the observed O3 peaks following BB1 and BB2?

>This refers to the whole study period. For clarity, the text has been changed to "Compared to TAPM, CCAM predicts fewer distinct peaks of ozone above the background concentration of 15 ppb throughout the entire period.”

P14,L8-12: Please clarify “prior to BB1” and “prior to BB2”. Do the authors mean prior to smoke being observed?
>yes, prior to observations. The manuscript has been modified to reflect this.

P17, L26: “. . .O3 increase was observed during particle growth (BB1) when urban influence was minimal. . .” Please clarify / expand on this statement. Was in Lawson et al. (2015) was the particle growth attributed to biomass burning influence?

>the particle growth was tentatively attributed to biomass burning influence, due to accompanying elevated BC (but not CO). The text has been modified to clarify this:

“However, during BB1 in a calm sunny period with minimal urban influence, an increase in O3 was observed alongside a period of particle growth and elevated BC, suggesting possible biomass burning influence.”

P17, L28: define “normalized excess mixing ratio”
>The following has been added to the text – “where NEMR is an excess mixing ratio normalised to a non-reactive co-emitted tracer, in this case CO, see Akagi et al., 2011”.

Section 3.2.2 Plume age A more detailed explanation/description of the plume age metric employed in this analysis is needed. The metric is really a “mean plume age”

and should be referred to as such. Also, given that biomass burning tends to be a low NOx source compared to urban emissions, it would seem this approach weights the plume age in favor of urban emissions possibly leading to an underrate the contribution of the Robin's Island fire. Perhaps I am misinterpreting an aspect of this approach. Please comment and revise the 3.2.2 discussion as appropriate.

> The metric is similar to the Eulerian effective physical age of emissions metric, accounting for mixing and chemical decay from Finch et al., (2014). It is true that because urban sources are a larger NOx source than BB, the plume age would be weighted in favour of the urban emissions if air masses from these different sources were mixed. However what we see from the model is that there are distinct periods where the influence is predominantly from either BB emissions or urban emissions (eg Fig 9.) In this case, where there is limited or no mixing from different sources, the model calculates the mean plume age from each of these sources.The text has been modified to reflect this as follows.

"The method is similar to the Eulerian effective physical age of emissions metric, accounting for mixing and chemical decay from Finch et al (2014) and has been described previously in Keywood et al., (2015).". . ... "As urban emissions are a larger NO source than BB, this approach would weight the age in the favour of the urban emissions if air masses from these two sources were mixed. However as shown in Figure 9, there are distinct periods where BB or urban sources dominate and there appears to be little mixing of air from the two sources, and so there are unlikely to be issues with the calculation being weighted towards one source."

Conclusion I find the estimates of O3 enhancement / depletion due to biomass burning to be questionable. The model performed poorly in predicting O3 for periods when biomass burning appeared important (Fig 5e the periods of BB1 and BB2 where O3 shows dependence on EF scenario).

>we agree - due to the non linear response of ozone production we have removed all estimates of O3 enhancement/depletion due to biomass burning from the manuscript (please see previous comment)

Figure 4: Describe red squares (presumably these are the 250 m emission grid cells).

>we are unsure what is meant by red squares. Does reviewer mean wind vector arrows? Caption has been modified to include description of wind vectors.

Figure 6: The caption does not agree with the text description of Fig 6b given at P16, L15-17.

>caption has been revised to include more detail and is now in agreement with text description