An Assessment of Biomass Burning

Emissions over Amazonia Using Airborne Measurements

A dissertation submitted to the University of Manchester for the degree of Master of Science by Research in the Faculty of Engineering and Physical Sciences

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Abstract

Biomass burning activities occur around the globe, throughout the year and are a huge source of atmospheric trace gases and particulate matter. Emissions of aerosol species from biomass burning include organic aerosol, inorganic aerosol and black carbon and the associated effects on weather, climate and human health are poorly understood and quantified. Aerosols have a direct effect on climate by reflecting and absorbing solar radiation, a semi-direct effect of increasing atmospheric stability and reducing convective cloud formation and an indirect effect by acting as cloud condensation nuclei (CCN). The emission of these species from biomass burning needs to be more fully understood in order for climate models to accurately represent and predict future emissions.

The vast majority of biomass burning occurs in the tropics and this research presents data collected during the aircraft campaign of the South American Biomass Burning Analysis (SAMBBA), 2012. Biomass burning emissions from a smouldering rainforest fire and flaming cerrado fires were analysed and compared. Fire integrated emission ratios and emission factors for trace gas and particulate species for these two fire types were determined. Trace gas emissions differed substantially between the fire types and were highly dependent on the combustion efficiency of the fire, characterised by the integrated modified combustion efficiency (MCE) and are in agreement
with previous studies values. Organic aerosol and black carbon emissions also differ between the fire types, with an order of magnitude more black carbon emitted from the flaming cerrado fires and more than double the amount of organic aerosol per kg fuel burnt emitted from the smouldering rainforest fire. Particulate phase species emitted from both fire types sampled are generally within the range or lower than those reported in previous studies. A possible cause of the lower black carbon emissions compared to literature is due to the different measurement techniques used. Organic aerosol emission was found to be dependent on combustion efficiency, but for black carbon there is no significant dependence. Inorganic aerosols vary between fire types and are more dependent on fuel type and composition. The smouldering rainforest fire sampled was likely initiated due to lightning but results indicated that this fire is representative of smouldering deforestation fires. Recent studies show a shift from deforestation to cerrado fires in Brazil, which could lead to significant increases in CO\textsubscript{2} and BC concentrations in the region and have effects on future climate. The results presented in this dissertation provide up to date trace gas and particulate emission ratios and emission factors for fire type specific biomass burning in Brazil which are significant in terms of future climate change and can be used to challenge atmospheric weather and climate models.
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Finally, thanks to my parents for their continued belief, encouragement and patience.
Abbreviations

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<th>Description</th>
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<tr>
<td>AMS</td>
<td>Aerosol Mass Spectrometer</td>
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<td>AOD</td>
<td>Aerosol optical depth</td>
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<tr>
<td>ARCTAS</td>
<td>Arctic Research of the Composition of the Troposphere from Aircraft and Satellites</td>
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<tr>
<td>BASE-A</td>
<td>Biomass Burning Airborne and Space borne Experiment Amazon</td>
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<td>BASE-B</td>
<td>Biomass Burning Airborne and Space borne Experiment Brazil</td>
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<tr>
<td>BBA</td>
<td>Biomass Burning Aerosol</td>
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<td>BC</td>
<td>Black Carbon</td>
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<td>CCN</td>
<td>Cloud Condensation Nuclei</td>
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<td>CDNC</td>
<td>Cloud Droplet Number Concentration</td>
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<td>CE</td>
<td>Combustion Efficiency</td>
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<td>C-ToF-AMS</td>
<td>Compact Time of Flight Aerosol Mass Spectrometer</td>
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<td>EF</td>
<td>Emission Factor</td>
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<td>ER</td>
<td>Emission Ratio</td>
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<td>FAAM</td>
<td>Facility for Airborne Atmospheric Measurements</td>
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<td>FGGA</td>
<td>Fast Greenhouse Gas Analyser</td>
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<td>FLAME</td>
<td>Fire Laboratory at Missoula Experiments</td>
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<td>FRP</td>
<td>Fire radiative power</td>
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<td>GHG</td>
<td>Greenhouse gas</td>
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<td>GOES</td>
<td>Geostationary Operational Environmental Satellite</td>
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<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>LWC</td>
<td>Liquid Water Content</td>
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<td>MAC</td>
<td>Mass Absorption Coefficient</td>
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<td>MCE</td>
<td>Modified Combustion Efficiency</td>
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<tr>
<td>MILAGRO</td>
<td>Megacity Initiative Local and Global Research Observations</td>
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<tr>
<td>MODIS</td>
<td>Moderate Resolution Imaging Spectroradiometer</td>
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<td>NCAS</td>
<td>National Centre for Atmospheric Science</td>
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<td>NERC</td>
<td>Natural Environment Research Council</td>
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<tr>
<td>OA</td>
<td>Organic Aerosol</td>
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<td>OC</td>
<td>Organic Carbon</td>
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<td>POA</td>
<td>Primary Organic Aerosol</td>
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<td>PSAP</td>
<td>Particle soot absorption photometer</td>
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<td>SAFARI-2000</td>
<td>Southern African Regional Science Initiative</td>
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<td>SAMBBA</td>
<td>South American Biomass Burning Analysis</td>
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<td>SCAR-B</td>
<td>Smoke, Clouds, and Radiation-Brazil</td>
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<td>SOA</td>
<td>Secondary Organic Aerosol</td>
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<td>SP2</td>
<td>Single Particle Soot Photometer</td>
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<tr>
<td>SSA</td>
<td>Single Scattering albedo</td>
</tr>
<tr>
<td>TOR</td>
<td>Thermal/optical reflectance</td>
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<tr>
<td>TOT</td>
<td>Thermal/optical transmission</td>
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<tr>
<td>TROFFEE</td>
<td>Tropical Forest Fire and Emissions Experiment</td>
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<tr>
<td>Q-AMS</td>
<td>Quadrupole Aerosol Mass Spectrometer</td>
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<td>Δ</td>
<td>Excess</td>
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Chapter 1: Introduction, motivation and scope

Human induced global climate change has been well documented since the industrial revolution in the mid-18th century led to an increase in atmospheric greenhouse gas (GHG) concentrations. Human activities such as fossil fuel burning, land use and agricultural changes and biomass burning have led to increased atmospheric concentrations of CO₂, CH₄ and N₂O, with the IPCC stating with ‘very high confidence’ that these increases have led to a combined radiative forcing of +2.3 ± 0.2 W m⁻² (Forster and G. Raga, 2007). The forcing due to greenhouse gases is relatively well understood with only a small uncertainty. Aerosol species are also emitted directly into the atmosphere through human activities (Haywood and Boucher, 2000), however the scientific understanding of these species in relation to radiative forcing is not well understood and there are large uncertainties. Radiative forcing due to aerosol species, primarily sulphate, organic carbon, black carbon, nitrate and dust overall acts in the opposite direction to that of greenhouse gas species. The direct effect of aerosol forcing is estimated to be between -0.1 to -0.9 W m⁻², with an indirect forcing of between -0.3 and -1.8 W m⁻² (Forster et al., 2007). Therefore, an increase in atmospheric aerosol concentrations could offset the warming due to greenhouse gases, however due to the large uncertainties in aerosol forcing this needs to be more fully understood. Absorbing atmospheric aerosols can also lead to a warming of the atmosphere. This warming can
cause cloud burn off, known as the semi-direct effect (Ackerman et al., 2000; Forster et al., 2007) and can increase atmospheric stability, leading to pollutants being trapped near the surface. Both of these effects act to inhibit convection which is highly significant in highly convective regions such as Amazonia.

Aerosol species are short lived compared to greenhouse gas species and therefore are spatial and temporally heterogeneous. Aerosols subsequently have a large impact regionally due to directly scattering incoming solar radiation or through interactions with clouds. This can in turn; along with long range transport and aging of aerosols have an impact globally. The complexity of aerosols and difficulties in measuring these species has led to this area of research being a focus of the scientific community, with numerous field campaigns taking place to study these species. Biomass burning emissions have been a particular focus over recent years due to the large amounts of aerosols emitted during this burning.

1.1 Dissertation Overview

This dissertation examines trace gas and aerosol species emitted during biomass burning. Firstly, a review of biomass burning, it’s temporal and spatial variation, species emitted and drivers in the variability of emissions are examined in chapter 2. A description of the effect that these emissions have on weather and climate, visibility and human health is given in chapter
3. Chapter 4 explains the main quantitative descriptions of emissions from biomass burning including the modified combustion efficiency, emission ratios and emission factors. Chapter 5 provides information about early measurements of biomass burning, the methods by which they were measured and any limitations in the measurements. A review of biomass burning campaigns that have taken place around the world and in Brazil is given, with the major achievements and outcomes of these campaigns described. The South American Biomass Burning Analysis (SAMBBA) campaign provides the observational data analysed in the dissertation. The details of the campaign and the main instrumentation on board the aircraft campaign are detailed in chapter 6. A comparison of biomass burning emissions emitted from two different fires types (a smouldering rainforest fire and flaming cerrado fires) observed during SAMBBA are presented in chapter 7 in the form of a paper to be submitted to the Atmospheric Chemistry and Physics journal. Finally, the dissertation will conclude with a summary of the findings that biomass burning emissions differ between fire types, the importance of these results and what implications these findings have.
Chapter 2: Biomass Burning

This chapter describes what biomass burning is, where and when biomass burning occurs and the species emitted during burning. The final section of this chapter explains the processes and drivers that cause variability in biomass burning species emitted.

2.1 What is Biomass Burning

Biomass burning (BB) is defined as the burning of dead or living vegetation, which can burn by a range of combustion processes (flaming to smouldering) and these fires can be natural (e.g. lightning induced wildfires) or human induced (e.g. deforestation fires). Natural grass and forest wildfires usually occur by a lightning strike and are prevalent in boreal and temperature ecosystems. These natural wildfires must have existed since the evolution of plants and a natural fire frequency was established (Andreae, 1991; Bowman et al., 2009). Next came the evolution of humans which since then have played an important role in the global fire regime (Schule, 1990), with an estimated 90% of biomass burning fires being human induced (Koppmann et al., 2005). Human induced fires include deforestation fires, clearance fires for agricultural expansion and harvesting practices, burning of biofuel for energy and the combustion of biomass waste products (Koppmann et al., 2005).
Biomass burning fires produce a wide range of gaseous compounds such as CO, CO$_2$ and CH$_4$ (Koppmann et al., 2005) and particle compounds including organic and inorganic aerosol and black carbon (Reid et al., 2005; Forster et al., 2007). These BB emissions are highly dependent on the fire combustion stage (smouldering or flaming), vegetation type and chemical composition (e.g. forest or savannah) and the local environmental conditions such as relative humidity and temperature (Yokelson et al., 1996; Ward et al., 1996; Hoffa et al., 1999; Bond et al., 2004). These emissions have effects on weather, climate, visibility and human health, which will be discussed in detail in chapter 3.

2.2 Temporal and Spatial Patterns

Biomass burning fires, both natural and human induced occur throughout the year around the globe. It is estimated that approximately 8700 Tg of dry matter is burnt each year (Andreae 1991), with over 80% of all emissions from biomass burning globally originating in the tropics (Ward et al., 1992; Hao et al., 1990; Crutzen and Andreae, 1990). Hao and Liu (1994) estimate that 50% of biomass burning is savannah fires with 24% and 10% due to shifting cultivation fires and deforestation fires respectively. Koppmann et al. (2005) estimates that 66% of biomass burning is due to savannah and agriculture fires and 15% is due to biofuel and tropical forest fires. The large percentage of fires being savannah fires is due to the large
biomass produced during the wet season which then turns to highly flammable fuel during the dry season. Geographically, 40% of biomass burning fires occur in Africa, 25% in South America and 35% occur in the rest of the world (Koppmann et al., 2005). Biomass burning not only occurs in the tropics but also in other regions around the globe. Although its contribution to global biomass burning is low, Boreal forest fires in places such as China, Siberia, Canada and Alaska are increasing (Levine, 1996; Turetsky et al., 2011).

As figure 1 shows and Hao and Liu (1994) conclude, most biomass burning North of 5°N occurs from March to June. South of the equator most of the biomass burning occurs from September to December. Fire activity can also vary year to year due to other factors such as El Nino/La Nina (van der Werf et al., 2004; Westerling et al., 2006) and increasing global temperatures (Westerling et al., 2006).

![Figure 1](image)

**Figure 1.** The month of maximum climatological fire activity (November 2000 to October 2005) from Terra MODIS observations (Giglio et al., 2006)
2.3 Trace Gas Emissions

Numerous trace gases are emitted during biomass burning, however I will focus on three trace gases, carbon dioxide, carbon monoxide and methane. These three gases are the main contributors to the atmospheric carbon budget and account for the majority of carbon emitted through burning. Their emissions are well characterised and their relationship to combustion state well established and this allows comparison of other, less characterised species.

2.3.1 Carbon Dioxide

$\text{CO}_2$ is the most abundant compound emitted during combustion of organic material (Keene et al., 2006), is long lived and chemically stable (Forster et al., 2007). Emissions of $\text{CO}_2$ from biomass burning are highly dependent on combustion conditions (Reid et al., 2005). Since the industrial revolution, atmospheric $\text{CO}_2$ concentrations have been increasing due to fossil fuel burning (Forster et al., 2007). The enhanced greenhouse effect caused by increases in gases such as $\text{CO}_2$ has caused more outgoing long wave radiation emitted by the Earth’s surface to become trapped in the Earth system and therefore warms the planet (Ramanathan, 1988). The effect that biomass $\text{CO}_2$ emissions have on weather and climate will be discussed in more detail in Chapter 3.1.1. In May 2013 levels reached the 400ppmv mark.
for the first time since records began at the Mauna Loa observatory (BBC, 2013).

Combining both landscape and biomass fires, Bowman et al. (2009) estimates that CO₂ emissions from these fires equals 50% (4 Pg C year⁻¹) of emissions from burning fossil fuels, with deforestation burning contributing 0.65 Pg C year⁻¹. Westerling et al. (2006) has shown that wildfire activity has increased substantially in the Western US since the mid 1980’s, with a longer wildfire season. This will therefore produce more CO₂ emissions and likely to cause further warming due to increased CO₂ concentrations (Marston et al., 1991). CO₂ emissions from biomass burning during El Nino years may exceed the emissions from fossil fuel burning (Page et al., 2002).

2.3.2 Carbon Monoxide

CO is released through incomplete combustion and smouldering fires (Ward and Radke, 1993; Keene et al., 2006). Biomass burning emissions of CO have been estimated to be 495 Tg C year⁻¹ between 1997 and 2001 (van der Werf et al., 2004), which although is significantly less than the CO₂ emissions, CO is a very important gas. It has a relatively short atmospheric lifetime of 10 days in summer continental regions (Holloway et al., 2000) compared to CO₂ (Forster et al., 2007) but reacts with OH radicals which can lead to ozone formation, another important greenhouse gas. Although radiatively CO is not an important greenhouse gas, its indirect effects of
altering atmospheric chemistry are important (Ramanathan et al., 1985). Increases in CO emissions can lower the oxidative efficiency of the atmosphere through its reaction with OH radicals. This can then lead to increases in other greenhouse gases such as CH$_4$ (Hameed et al., 1980; Crutzen and Andreae, 1990).

2.3.3 Methane

CH$_4$ is a relatively stable, long lived greenhouse gas with an atmospheric lifetime of ~12 years (Forster et al., 2007) and is second only to CO$_2$ in terms of radiative forcing (Ramaswamy et al., 2001; Forster et al., 2007). CH$_4$ also affects atmospheric chemistry through its reaction with OH, leading to ozone and water vapour increases, further increasing greenhouse gas concentrations (Ramaswamy et al., 2001; Ramanathan et al., 1985; Hameed et al., 1980). There are year to year variations in emissions of CH$_4$ which has partly been attributed to variations in biomass burning (Dlugokencky et al., 2001; Koppmann et al., 2005). Biomass burning emits approximately 40 Tg C year$^{-1}$ of CH$_4$ into the atmosphere and is the third largest source of atmospheric CH$_4$ (Koppmann et al., 2005).

2.4 Particulate Emissions

Aerosols are defined as a suspension of liquid or solid matter within a gaseous medium and can be manmade or from natural sources. The main
particulate species emitted during biomass burning in terms of the importance in the effect on radiative forcing are organic species and black carbon. Inorganic species such as nitrates and sulphates are also emitted (Lioussse et al., 1996). Approximately 50-60% of smoke particles are composed of organic carbon and 5-10% are composed of black carbon particles by mass (Reid et al., 2005). Variations in the emissions of the species due to factors such as combustion stage, vegetation type and environmental conditions will be discussed in chapter 2.4.4.

2.4.1 Organic Aerosol

Organic aerosol consist of molecules containing a chain of carbon atoms along with hydrogen and other functional groups (Reid et al., 2005). Aerosol particles are short lived with lifetimes of a few minutes to a few weeks (Haywood and Boucher, 2000) and are therefore both spatially and temporally inhomogeneous, with peak concentrations near to the sources (Ramanathan et al., 2001). Sources of organic aerosol are numerous including fossil fuel burning, domestic burning and burning of vegetation (Kanakidou et al., 2005). These organic aerosols emitted directly from source are known as primary organic aerosol (POA). Secondary organic aerosol (SOA) can arise from condensation from the gas phase to the particle phase (Kanakidou et al., 2005). Approximately 90% of total biomass burning POA mass is emitted from wildfires, prescribed burns and
biofuel combustion (Bond et al., 2004) with 80% of global POA emitted in the tropics (Hobbs et al., 1997).

2.4.2 Inorganic Aerosol

Inorganic aerosol, including (Cl\(^{-}\)), sulphate (SO\(_4^{2-}\)), nitrate (NO\(_3^{-}\)) and ammonium (NH\(_4^{+}\)) are also emitted by biomass burning. Fuzzi et al. (2007) found that during the dry season in Brazil approximately 10% of biomass burning aerosol consisted of soluble inorganic species with the dominant inorganic species being SO\(_4^{2-}\), NO\(_3^{-}\) and NH\(_4^{+}\) (Trebs et al., 2008). These inorganic aerosols emitted during biomass burning can scatter and reflect incoming solar radiation, therefore reducing the downward flux and cause a cooling of the Earth surface (Sinha et al., 2003). Atmospheric sulphate and nitrate can either be directly emitted through biomass burning or can form through oxidation of SO\(_2\) and NO\(_X\). These species can then acidify rain water and affect soil acidity. Ammonium can also be emitted directly by biomass burning or can form from NH\(_3\), NH\(_4^{+}\) can then act to neutralise soils (Sinha et al., 2003).

2.4.3 Black Carbon

Black carbon is defined as a highly light absorbing carbon material such as soot that has a graphitic-like structure (Novakov, 1982; Petzold et al., 2013).
It is formed in the flames of fires, directly emitted into the atmosphere and is highly dependent on the combustion process (Bond et al., 2004; Bond et al., 2013). Sources of black carbon include fossil fuel burning (Novakov et al., 2003), biofuel cooking (Bond et al., 2007) and biomass burning (Bond et al., 2013). Black carbon emitted from open biomass burning (agricultural, forest, grass and woodland fires) is estimated to contribute 40% to global black carbon emissions (Bond et al., 2013). However, black carbon emissions from biomass burning are very uncertain, partly due to biases in instrument measurements (Ramanathan and Carmichael, 2008; Bond et al., 2013). Approximately 3.3 Tg C year\(^{-1}\) is emitted as black carbon in open biomass burning (Forster et al., 2007), with Kuhlbusch et al. (1996) estimating that 1-2 Tg of black carbon is emitted into the atmosphere per year in smoke from savannah fires alone. Haywood and Ramaswamy (1998) estimate a +0.4 Wm\(^{-2}\) radiative forcing due to fossil fuel and biomass burning black carbon, with each source contributing equally. After CO\(_2\), black carbon is the second largest contributor to the increase in global temperatures due to its high absorption of visible solar radiation (Ramanathan and Carmichael, 2008). However, the black carbon mass absorption coefficient (MAC) can vary depending on the species co-emitted that can coat the black carbon particles and alter the particles absorption of radiation (Bond et al., 2013). Black carbon can also be transported long distances and mix with other aerosol species forming ‘Brown clouds’ and
can also be deposited on the surface of snow and ice, both processes altering the Earth’s radiative balance (Ramanathan and Carmichael, 2008; Bond et al., 2013).

2.4.4 Drivers of variability in Biomass Burning Emissions

Particulate and trace gas emissions from biomass burning fires can vary due to numerous different factors relating to combustion stage, vegetation type and environmental conditions. Firstly, the combustion state of the fire is an important factor with intense flaming fires having a much higher temperature than smouldering fires. When the combustion process starts, flaming combustion dominates with rapid oxidation of the fuel material and pyrolysis of the organic material. Hydrocarbons are then vaporised and produce the fuel gas to sustain the visibly flaming stage (Ward, 1990). As the fuel is depleted, the lower temperature smouldering stage begins. The char formed during the flaming stage is oxidised, which is dependent on the supply of oxygen to the smouldering region (Ward, 1990).

If the temperature of the fire is high enough (usually during the flaming stage), approximately 910-980K, then CO can be converted to CO$_2$ (Reid et al., 2005). This leads to flaming fires emitting more CO$_2$ relative to CO than smouldering fires and the reverse of more CO emitted during smouldering combustion (Ward and Radke, 1993; Andreae and Merlet, 2001; Sinha et al., 2003). Methane has also been found to be preferentially
emitted during smouldering combustion (Ward, 1990; Sinha et al., 2003; McMeeking et al., 2009). Particulate emissions are also affected by the temperature of combustion (Ward, 1990). The smouldering stage of combustion releases larger amounts of particulate matter than the flaming stage (Ward, 1990) and are formed through the condensation of volatized organics (Reid et al., 2005). Black carbon forms during flaming combustion with temperatures between 1300-1600K and is therefore preferentially emitted during the flaming rather than smouldering stage (Reid and Hobbs, 1998). The inorganic aerosols as a function of particulate matter are usually relatively higher for flaming fires due to the higher combustion consuming more carbon and thereby increasing the inorganic matter percentage relative to total particulate matter (Ward, 1990).

The vegetation type and fuel chemical composition can also effect biomass burning emissions. Studies such as McMeeking et al. (2009), Akagi et al. (2011) and Andreae and Merlet (2001) have shown that different vegetation types differ in emissions due to varying chemical compositions of fuel being burnt. These variations in fuel composition greatly affect the inorganic aerosols that are released and this has been found to be the dominant control in inorganic emissions (McMeeking et al., 2009; Sinha et al., 2003). The location of biomass being burnt relative to the coast can also influence the amount of chloride emitted as marine sea salt has been found to alter the chlorine content of the fuel (McKenzie et al., 1996; Yamasoe et al., 2000).
The moisture content of the vegetation or whether it is dead or alive are also determining factors of emissions (Ward et al., 1996). Hoffa et al. (1999) found that decreasing moisture content in Zambian savanna led to an increase in combustion efficiency, which will therefore affect emissions as discussed earlier.

Environmental factors such as local relative humidity, wind conditions and fire direction can all influence the combustion efficiency of the fire therefore altering the emissions (Reid and Hobbs, 1998; Ward and Hardy, 1991; Bond et al., 2013).
Chapter 3: Implications of Biomass Burning Emissions

Biomass burning emits large quantities of trace gas and particulates into the atmosphere throughout the year and around the globe. These emissions have local, regional and global implications on weather, climate, visibility and impacts on human health. These effects are discussed in detail in this chapter.

3.1 Effects on weather and climate

Both greenhouse gases and aerosol emissions from biomass burning have a substantial effect on the radiative balance of the Earth. Anthropogenic greenhouse gases are long lived and have increased since the industrial revolution. They have received particular attention in recent decades due to the warming effect that they have on the Earth’s climate. Aerosols have a much shorter lifetime but also impact radiative forcing causing a net negative, cooling effect on climate. However, there are large uncertainties in aerosol forcing through the direct effect, semi-direct effect and indirect cloud albedo effect, which will be discussed in the following sections.

3.1.1 Trace Gas Emission Implications

Both CO₂ and CH₄ are greenhouse gases. It is the increase in these greenhouse gas emissions by human activity that has perturbed the radiation
balance of the Earth. This increase in greenhouse gas concentrations makes the atmosphere more opaque and reduces the radiation emitted to space.

Radiative forcing is defined as the change in net irradiance at the tropopause i.e. the net change in downward radiation and upwards radiation, due to the presence of a human induced change in an atmospheric component (Forster et al., 2007). Between 1999 and 2005 the radiative forcing due to CO\textsubscript{2} increased by 20% with a radiative forcing value of $+1.66 \pm 0.17$ W m\textsuperscript{-2} in 2005, with levels of CH\textsubscript{4} over the same period decreasing with a net radiative forcing of $+0.48 \pm 0.05$ W m\textsuperscript{-2} in 2005. The reason for this decrease is not well understood (Forster et al., 2007). Figure 2 shows the radiative forcing of CO\textsubscript{2} and CH\textsubscript{4} between 1750 and 2005. Overall the IPCC states with very high confidence that human activity has caused a net positive forcing (Solomon et al., 2007) and has therefore caused a substantial warming of the Earth’s climate since preindustrial times.

**Figure 2.** Components of radiative forcing with the thin black lines representing the range of uncertainty for the respective value (Forster et al., 2007)
3.1.2 Direct Aerosol effect

The direct aerosol effect concerns the scattering and absorption of shortwave solar radiation by the aerosols in the atmosphere, thereby perturbing the planetary albedo, as shown in diagram 1 of figure 3 (Charlson et al., 1992; Horvath, 1993). Biomass burning organic carbon and inorganic aerosol emissions generally scatter solar radiation leading to a -0.4 W m$^{-2}$ radiative forcing whereas the emitted biomass burning black carbon tend to absorb solar radiation leading to a +0.2 W m$^{-2}$ radiative forcing (Forster et al., 2007; Haywood and Ramaswamy, 1998; Bond et al., 2013). The current estimate of the total direct aerosol radiative forcing due to anthropogenic emissions is -0.5 ± 0.4 W m$^{-2}$ (Forster et al., 2007), however this has medium to low scientific confidence, which is defined in the Intergovernmental Panel on Climate Change (IPCC) 2007 report as having between a 5 out of 10 chance (medium understanding) to a 2 out of 10 chance (low confidence) of being correct (Le Treut and Somerville, 2007). Due to the short atmospheric lifetime of aerosols they are spatially and temporally non uniform which leads to non-uniform effects on radiative forcing. Unlike the greenhouse gas forcing which is uniform year round across the globe, direct aerosol forcing is most prominent during the daytime in summer due to its effect of scattering solar radiation (Charlson et al., 1992). The parameter used to define the amount of relative scattering and absorption by an aerosol is the single scattering albedo (SSA)
SSA is defined as the ratio of scattering to the sum of scattering and absorption. When aerosols have a SSA greater than 0.95 they have a negative radiative forcing at the top of the atmosphere due to the particles being highly scattering compared to aerosols with a SSA less than 0.85 having a positive forcing due to the particles being more absorbing (Ramanathan et al., 2001). The critical value to determine whether an aerosol warms or cools the atmosphere is also a function of the surface albedo. A higher surface albedo makes the aerosol forcing more susceptible to changes in the critical SSA (Haywood and Shine, 1995). Black carbon has been found to have a SSA of 0.2 compared to a value of ~1 for sulphate which shows the importance of the particular aerosols physical and chemical properties in determining the effect it has on the radiative forcing (Haywood and Boucher, 2000;Forster et al., 2007;Solomon et al., 2007;Haywood and Ramaswamy, 1998). Sulphate aerosols are the main contributor to direct radiative forcing from fossil fuel burning with the smoke particles being the main contributor to the forcing from biomass burning (Hobbs et al., 1997). Penner et al. (1992) estimated a value of -0.8 W m$^{-2}$ due to the overall direct radiative forcing from biomass burning smoke aerosols, Hobbs et al. (1997) estimated a value of -0.3 W m$^{-2}$ for global mean direct radiative forcing due to biomass burning and most recently, Forster et al. (2007) estimated a value of -0.2 W m$^{-2}$ with a factor of three uncertainty.
Strongly absorbing aerosol species, such as black carbon, can have a significant effect on atmospheric column stability. Black carbon is the dominant absorber of visible solar radiation in the atmosphere and thus direct absorption of incoming solar radiation can cause atmospheric warming, with a +15 W m\(^{-2}\) warming of the lower atmosphere in regional hotspots (Ramanathan and Carmichael, 2008). The overall climate forcing by the black carbon direct effect is estimated to be between +0.09 to +1.26 W m\(^{-2}\) (Bond et al., 2013). This warming of the lower atmosphere through black carbon absorption can act to increase atmospheric stability, through the heating of the atmosphere and the reduction in solar radiation reaching the Earth’s surface. This increased atmospheric stability can therefore inhibit atmospheric convection (Ramanathan et al., 2005), with the heating of the atmosphere causing cloud burn off. In turn, this leads to a reduction in cloud cover and a reduction in cloud formation due to convective inhibition (Johnson et al., 2004; McFarquhar and Wang, 2006). This is known as the semi-direct effect (figure 3) and is a significant effect in highly convective regions such as the tropics.

Black carbon deposited on snow and ice can also produce warming due to the decrease in reflectivity of the surface causing more solar radiation to be absorbed and thus causes warming (Bond et al., 2013; Ramanathan and Carmichael, 2008).
3.1.3 Indirect Aerosol Effect

The indirect effects that aerosols have on the climate system are summarized in figure 3 to show how they perturb cloud microphysics. In biomass burning emissions between 45-75% of the total carbon mass emitted is highly water soluble (Asa-Awuku et al., 2008; Mayol-Bracero et al., 2002), with the rest of the mass being soluble inorganic salts NH$_4^+$, SO$_4^{2-}$, NO$_3^-$, K (Andreae et al., 2004). These highly water soluble aerosols increase cloud condensation nuclei (CCN) numbers and once activated increase the number of cloud droplets (Dusek et al., 2006). The ability of these CCN to activate depends upon their size and chemical composition (Broekhuizen et al., 2004) and is described by the Kohler theory which combines the Kelvin effect and Raoult’s law in order to explain the process.

**Figure 3.** Aerosol effects with CDNC meaning cloud droplet number concentration and LWC meaning liquid water content (Forster et al., 2007)
by which water vapour condenses and forms liquid cloud droplets (Giebl et al., 2002).

The second diagram in figure 3 shows the first indirect effect. The aerosols present have caused there to be an increase in the number of smaller droplets with constant liquid water content due to an increase in cloud droplet number therefore, the cloud droplet radius has to decrease. This leads to a more reflective cloud (Twomey et al., 1984) and a negative radiative forcing of between 0 to -2 Wm\(^{-2}\) (Forster et al., 2007). Drizzle suppression occurs where CCN are low such as a marine environment. Aerosols present will increase CCN, therefore reducing droplet radius which suppresses drizzle which may lead to an increase in fractional cloudiness and an increase in cloud lifetime (Albrecht, 1989). Aerosols may also increase cloud thickness and albedo (Pincus and Baker, 1994) and cause a semi-direct effect of causing cloud burn off through heating (Ackerman et al., 2000; Johnson et al., 2004). This effect is particularly significant in the tropics where the atmosphere is highly convective, therefore a significant change in cloud cover due to increased aerosol concentrations from biomass burning has the potential to change the climate.

3.2 Visibility

Haze layers over regions of biomass burning have been found to substantially reduce visibility. Andreae et al., (1988) observed haze layers
over the Amazonian basin at altitudes of between 1000-4000m, were 100-300m thick but extended horizontally over 100km. The reduction in visibility of these haze layers is due to the light extinction and chemical composition of the aerosols (White and Roberts, 1977). It has been found that the main components of aerosols that scatter light most efficiently are sulphate and nitrate particles (Watson, 2002; White and Roberts, 1977). Aerosols that contain nitrate and sulphate grow by water vapour absorption therefore increase in size and scatter more incident light, further reducing visibility (Watson, 2002). Studies by Phuleria et al. (2005), Muhle et al. (2007) and McMeeking et al. (2006) have shown a link between an increase in biomass burning and reductions in atmospheric visibility. Biomass burning emissions are dominated by organics with high concentrations of light absorbing carbon (LAC) particles, which are associated with reductions in visibility (Malm et al., 2004; McMeeking et al., 2006).

3.3 Health impacts

Particles emitted by biomass burning fires have found to be detrimental on human health (Cancado et al., 2006; Arbex et al., 2007; do Carmo et al., 2013). Increases in biomass burning have been linked to increased hospital admissions and increased mortality rates (Lohman et al., 2007). Particulate matter exposure causes cardiac and respiratory problems (Nel, 2005), with particulate matter in polluted air estimated to cause the deaths of 500,000
people each year (Nel, 2005). Studies by Arbex et al. (2007), Cancado et al. (2006) and do Carmo et al. (2013) found that during periods of increased biomass burning in Brazil there were increases in hospital admissions due to respiratory problems. Ultrafine particulate matter can diffuse into the lungs and enter the body through alveoli of the lungs leading to health problems, with organic compounds being irritants, allergens and carcinogens (Pope et al., 2002). Black carbon can also cause tissue irritation and release toxic chemicals (Lighty et al., 2000; Bond et al., 2004).
Chapter 4: Quantifying Biomass Burning Emissions

In order for biomass burning emissions to be uniformly quantified across all fire types, three different derived quantities are usually used to describe the emissions. These quantities are the modified combustion efficiency (MCE), the emission ration (ER) and the emission factor (EF). In this chapter each of the quantities are described.

4.1 Modified Combustion Efficiency

The modified combustion efficiency (MCE) of a fire gives an indication of the relative amount of flaming or smouldering combustion and is defined by

$$MCE = \frac{\Delta CO_2}{\Delta CO_2 + \Delta CO}$$  \hspace{1cm} (Ward and Radke, 1993)

Where $\Delta$ indicates the excess mixing ratio of the species.

The discussion by Yokelson et al. (2013) examines the limitations of defining the excess mixing ratios due to changes in background air composition through tropospheric mixing. Therefore, this should be taken into account when defining excess mixing ratios.

A MCE greater than 90% is a fire in the flaming stage, whereas a MCE less than 90% is defined as being in the smouldering phase (Ward and Radke, 1993).
4.2 Emission Ratio

When measuring the emission of trace gases and particulates from fires the absolute concentration of these species has little significance due to the dilution of the species with the ambient background air. This is particularly important when sampling smoke from aircraft. Therefore emission ratios are calculated to give the relative emission of species x to a simultaneously measured reference gas, usually CO or CO₂ as these gases are non-reactive and conserved (Andreae and Merlet, 2001; Sinha et al., 2003). The ER of species x using CO as the reference gas is defined below:

\[ ER_x = \frac{\Delta x}{\Delta CO} \]

Where \( \Delta \) indicates the excess mixing ratio of the species.

For gas species \( ER_x \) is usually given as the molar ratio and for aerosol species \( ER \) is stated as the mass ratio at 1 atm, 273K. When only one pass is made through a BB plume the calculation of \( ER_x \) is trivial using the equation above. The \( ER_x \) can also be derived when multiple passes are made through the BB plume by using the regression slope of the excess species concentration of x versus the reference species with the line forced through 0 (Yokelson et al., 1999). If however, a direct regression between two species is not possible due to the different instrument response times an
integration method can be used as discussed by LeCanut et al. (1996), Yokelson et al. (2009) and Akagi et al. (2012).

The use of either CO₂ or CO as the reference species depends on the purpose of the analysis as well as the combustion stage of the fire, either flaming or smouldering. CO is the dominate trace gas emitted during smouldering combustion and is therefore suitable to use for species emitted during smouldering combustion whereas CO₂ is the dominant trace gas emitted during flaming combustion and is therefore used as the reference species for species emitted during flaming combustion (Andreae and Merlet, 2001; Sinha et al., 2003).

4.3 Emission Factor

Emission factors (EF) are another parameter used to define the emission of a particulate species from fires. It is defined as the mass of compound x released to the atmosphere to the total mass of carbon species released in the form of CO, CO₂, CH₄, non-methane hydrocarbons (NMOC), particulate carbon etc. EFs are calculated using the carbon mass balance method (Ward and Radke, 1993; Yokelson et al., 1996). EF is reported as the mass of species x emitted per kg of dry fuel burnt. The EF can be calculated from a number of ERs with CO₂ as the reference species using a total carbon balance (e.g. Wooster et al. (2011), Yokelson et al. (2009), Goode et al. (2000)). The EF for species x (g kg⁻¹) is defined below:
\[ EF_x = F_c \, 1000 \, \frac{MM_x}{MM_{\text{carbon}}} \, \frac{C_x}{C_T} \]

(Wooster et al., 2011)

Where \( F_c \) is the carbon content of the fuel, \( MM \) is the molecular mass of species \( x \), \( 1000 \, \text{g kg}^{-1} \) is a unit conversion factor, \( MM_{\text{carbon}} \) if the molecular mass of carbon (12), and \( C_x/C_T \) is the ratio of the number of moles of carbon.

\[ \frac{C_x}{C_T} = \frac{ER_x/CO_2}{\sum_{j=1}^{n} (NC_j \, ER_j/CO_2)} \]

(Wooster et al., 2011)

Where \( ER_x/CO_2 \) is the ER of species \( x \) to \( CO_2 \), \( NC_j \) is the number of carbon atoms in compound \( j \), and the sum is over all carbon species including \( CO_2 \).

(Wooster et al., 2011; Delmas et al., 1995)
Chapter 5: Previous Biomass Burning Studies

There have been numerous studies of biomass burning emissions taking place around the globe for many decades now since Crutzen et al. (1979) and Seiler and Crutzen (1980) reported about the importance of these emissions on the Earth system. The following chapter summarizes some of the main campaigns outcomes, ranging from laboratory based burning to ground based and aircraft measurements and the associated uncertainties of particular instrumentation.

5.1 Laboratory, ground, airborne and satellite based measurements

In order to fully understand and compare the results presented from different research campaigns it is important to recognise the different measurement methods and how these may alter the main conclusions drawn. The three main methods used in biomass burning studies are laboratory burns, ground based measurements or airborne measurements, each having different advantages depending on desired outputs or burn conditions. For example, laboratory based measurements of biomass burning are conducted in a very clean environment without any external factors to be considered such as ambient biogenic or urban anthropogenic emissions. These laboratory burns also allow measurements to be taken at the source of combustion, reducing
the probability of secondary reactions such as secondary organic aerosol formation taking place between the fresh emission and measurement location. Measurements can also be taken to sample the whole fire and combustion stages. The main disadvantage however is that the laboratory fires may be very different than if it were to burn in the natural environment. Examples of laboratory studies include those by McMeeking et al. (2009), Yokelson et al. (2008), Chen et al. (2007) and Yokelson et al. (1997).

Measurements of biomass burning taken in the field have the advantage of emissions being taken from the actual fires in their natural environment. However, one main disadvantage is that measurements are usually not taken for the entirety of the burn, therefore missing measurements during the different combustion stages. This is not the case for controlled burns where all the different combustions stages can be sampled. The number of different species measured may also be reduced due to limited instrumentation available in the field. In terms of ground based or airborne measurements the advantages depend upon the desired output. Ground based sampling allows emissions to be measured close to the source, reducing the probability of aerosol ageing when fresh biomass burning emissions are required. However ground based sampling is unable to measure how aerosols age in the atmosphere. Airborne measurements allow emissions to be measured in the location where they are most likely to have an effect on solar radiation or interaction with clouds, therefore maybe more
useful for modelling studies. However, airborne measurements depend upon the combustion stage of the fire and targets more flaming combustion that is lofted upwards. Smouldering emissions are generally underestimated by airborne measurements due to these emissions not being lofted due to low fire intensity. Airborne measurements also have the advantage of being able to measure the aging of the different species emitted into the atmosphere.

Satellites such as NASA’s polar orbiting Terra and Aqua satellites allow global observations of fires, while the GOES (Geostationary Operational Environmental Satellite) geostationary satellites have high temporal resolution. On board NASA’S Terra and Aqua satellites is a Moderate Resolution Imaging Spectroradiometer (MODIS) which gives fire hotspot information such as the fire radiative power (FRP), the area being burnt and the temperature of the fire (Kaufman et al., 1998b; Kaufman et al., 2003; Giglio et al., 2006; Schroeder et al., 2010; Lentile et al., 2006). NASA’s geostationary operational environmental satellites (GOES) use on-board imagery and fire algorithms to determine fire size, temperature and fire radiative power (Prins et al., 1998; Schroeder et al., 2008, Xu et al., 2010).

5.2 Early measurements of biomass burning

Early estimates of global biomass burning emissions used a combination of demographic, statistical data and inventory data (e.g. (Seiler and Crutzen, 1980; Hao et al., 1990)). These first datasets are highly uncertain, are
generally incomplete and are only available for certain time periods. Since these early estimates, the use of remote sensing techniques from satellites (as discussed above) has vastly improved these estimates of global biomass burning estimates (Zhang et al., 2012; Wooster et al., 2003). For example Kaufman et al. (1992) used satellite measurements calibrated to ground based measurements of biomass burning in Brazil to improve upon biomass burning emission estimates, which can then be utilised in emission inventories.

Advances in instrument development for in-situ sampling of biomass burning emissions have also led to improved estimates. The early measurements of organic matter and black carbon techniques and their subsequent limitations are discussed in the following two sections.

5.2.1 Measurement methods used for organic matter

A review of numerous measurement techniques used to analyse organic atmospheric aerosols is presented by Jacobson et al. (2000). A filter sampling technique is one of the more simple techniques and a basic analysis run by heating the filter gives total organic and elemental carbon (Cadle et al., 1983; Chow et al., 2004). This thermal analysis technique uses the principle that different amounts of carbon leave the filter at different temperatures. Thermal/optical reflectance (TOR) or thermal/optical transmission (TOT) techniques are then used to monitor the conversion of
organic carbon to elemental carbon (Watson et al., 2005). However, this thermal filter technique and the material of the filter used (e.g. quartz or Teflon) can cause inaccuracies in these measurements (McDow and Huntzicker, 1990; Turpin et al., 1994; Kirchstetter, 2001). McDow and Huntzicker (1990) estimate that a 20-50% correction is needed for organic carbon concentrations collected on quartz filters due to organic vapour adsorption onto the filters that leads to a positive artifact. The thermal techniques used to determine organic and elemental carbon can lead to an underestimation of organic carbon and an overestimation of elemental carbon due to charring of the organic carbon during heating (Cheng et al., 2010). Cheng et al., (2010) found the bias due to a thermal analysis technique used to determine organic carbon on a quartz filter led to a positive sampling artefact of between 10-23%. Currie et al., (2002) conducted a study on elemental carbon analysis techniques. Simulated ambient filter samples were sent to different laboratories for analysis and a factor of 7 difference between elemental carbon concentrations due to the different techniques used was found. Other techniques and chemical analysis of filters such as extraction using solvents or carbon isotope analysis can also be used to measure the organic aerosol content on the filter (Jacobson et al., 2000). All of these offline measurement techniques of organic aerosol have associated uncertainties during analysis but other issues such as the need for time integration and sample storage can also lead
to biases (e.g. a 20% decrease in carbon concentrations due to organic aerosol losses over a 3 year period during which the samples had been stored (Chow et al., 1993)).

The need for more accurate real-time measurements lead to further analytical development techniques. One such development was the Aerosol Mass Spectrometer (AMS) which provides real-time measurements of size resolved aerosol mass and chemical composition. The first iteration of the AMS was the Quadrupole AMS (Q-AMS) as described by Jayne et al. (2000). A detailed description of an AMS can be found in chapter 6.2.2.1. A further development to the AMS was the use of a time of flight spectrometer in place of the quadrupole spectrometer and this development improved the sensitivity and time resolution of the AMS (Drewnick et al., 2005). A more recent iteration of the AMS is the compact time of flight AMS (C-TOF-AMS) (Canagaratna et al., 2007; Drewnick et al., 2005) as described in chapter 6.2.2.1. The AMS instrument has the advantage of providing real time measurements of aerosol species rather than the offline measurements of previous instruments discussed above. However, the particle detection by the AMS is size and composition dependent which can be affected by environmental conditions such as temperature, relative humidity or particle inlet characteristics (Kane and Johnston, 2000). The collection efficiency (CE) of the AMS (which is the mass or number of particles detected relative
to the mass or number of particles sampled) used can also effect the mass concentrations obtained (Middlebrook et al., 2012).

5.2.2 Measurement methods used for black carbon

There are numerous techniques that have been used to measure black carbon, with each having known biases. A filter based technique uses the optical absorption by particles collected on a filter to derive black carbon mass. The Particle Soot Absorption Photometer (PSAP) instrument uses this technique and has been used in many biomass burning campaigns e.g. Haywood et al. (2003), Capes et al. (2008) and Yokelson et al. (2009). This technique however is known to have a positive bias in black carbon mass due to the presence of other absorbers such as organics (Lack et al., 2008; Bond et al., 2013; Cappa et al., 2008). When the organic aerosol to black carbon ratio is high (15-20 as in biomass burning plumes) the PSAP absorption coefficient can be biased by 50-80% too high due to the coating of black carbon with volatile compounds (Bond et al., 2013). There may also be interactions between the particles and filter matrix which may cause a further positive bias. With the use of empirical corrections to overcome these artifacts the PSAP accuracy is estimated to be ~30% (Bond et al., 2013). A photoacoustic –based technique which also uses optical absorption to determine black carbon mass can also be subjected to this positive bias and can also be affected by the mass absorption coefficient (MAC) which
may also be source dependant and can change with aerosol aging (Lack et al., 2008; Bond et al., 2013). This photoacoustic-based technique has an overall uncertainty of ~5% with respect to aerosol absorption (Lack et al., 2006). These techniques use absorption to derive black carbon mass rather than measuring black carbon mass directly.

Thermal heating techniques are also used to determine black carbon mass. These methods are based on volatility, with the filter firstly heated with inert gas to burn off the organic carbon. After the organic fraction is oxidised, the temperature is raised to oxidise the elemental carbon and the CO$_2$ evolved is measured (Birch and Cary, 1996). This technique can lead to both positive and negative biases in black carbon mass. The presence of charred organic carbon and the detection of less volatile organic carbon can lead to a positive bias, while the oxidation of black carbon in the presence of metals can lead to a negative bias (Bond et al., 2013). Schmid et al., (2001) found that derived elemental carbon concentrations can differ by over an order of magnitude when different thermal and optical techniques are used.

Finally, the most recent development in black carbon measurements use laser induced incandescence to measure in real time refractory black carbon. This technique, which the single part soot photometer (SP2) uses is discussed in detail in chapter 6.2.2.2. This technique may have a negative bias due to the lack of detection of small particle of less than ~80nm in diameter (Bond et al., 2013), with an accuracy of ~30% (McMeeking et al.,
2010; McMeeking at al., 2012). This technique provides high accuracy black carbon mass due to the greater discrimination of black carbon. The SP2 also has the ability to measure black carbon number and mass size distributions and derives quantitative information about the black carbon mixing state (Baumgardner et al., 2004; Moteki and Kondo., 2007).

5.3 Studies and Campaigns around the World

The Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) campaign took place in North America in three different stages. ARCTAS-A took place out of Alaska during spring 2008, ARCTAS-B took place out of Cold Lake, Alberta during summer 2008 and ARCTAS-CARB was based in Palmdale, California during summer 2008 (Jacob et al., 2010). The campaigns main overall aim was to better understand and quantify the changing atmospheric composition in the Arctic. In order to undertake this ARCTAS-A and –B aircraft campaigns took place, with one of the main scientific themes being to focus on measuring Boreal forest fire emissions in Canada, Alaska and Asia. The ARCTAS-CARB aircraft campaign took place to improve understanding of air quality problems in California, with one of the focuses being on wildfire emissions. These results will improve biomass burning estimates in the Arctic.
Kondo et al. (2011) found that the majority of particles emitted from biomass burning during ARCTAS –A and –B in North America and Asia did not contain black carbon and that the emission ratios of black carbon were dependent on the MCEs of the fires (BC to CO ratio increased with increasing MCE but BC to CO$_2$ ratio decreased with increasing MCE). Kondo et al. (2011) also found that the black carbon size distribution shapes were similar for both North American and Asian fire emissions. However, differences in organic aerosol and sulphate emissions were evident between the two fire types. Hecobian et al. (2011) analysed data from the three different phases of the campaign and found that Boreal forest fire emissions had a higher concentration of organic aerosol and nitrate relative to CO compared to California fires. Sulphate, chloride and ammonium concentrations relative to CO were similar for Boreal and Californian fires. Singh et al. (2010) also found that Boreal and Canadian fires emissions had very similar characteristics and optical properties. Sahu et al. (2012) investigated emissions during ARCTAS-CARB and found that organic aerosol emissions varied with MCE for Californian wildfires. A fire with a MCE of 0.87 emitted 95.4% organic aerosol by mass to total particulate mass compared to 78.9% organic aerosol for a fire with a MCE of 0.92.

The Fire Laboratory at Missoula Experiments (FLAME) took place to characterize trace gas and particulate species emissions from different plant species ranging from grass and chaparral species to spruce and mixed
woods. Emission factors for all species were calculated and results showed that carbonaceous gas and particulate species emissions depend more strongly on the combustion efficiency whereas inorganic species emissions depend more on the composition of the fuel being burnt (McMeeking et al., 2009; Levin et al., 2010).

The Megacity Initiative Local and Global Research Observations (MILAGRO) campaign took place to study atmospheric pollution from mega cities and the impacts this has both locally and globally. Part of this study was aimed at quantifying emissions forest fires near to Mexico City and biomass burning in the Yucatan Peninsula and in March 2006 these aircraft campaigns took place (Yokelson et al., 2007b; Yokelson et al., 2009). It was found that the pine-dominated forests surrounding Mexico City emit higher levels of Nitrogen (2-4 times high NOx concentrations) during biomass burning than previous literature values. These high values may be due to the close distance to urban areas and these interactions between biomass burning and urban areas need be further investigated. Other regions such as the tropics where biomass burning and urban areas are in close proximity could have these same effects. The introduction of smoke management to regional biomass burning in Mexico could help improve air quality in Mexico City (Yokelson et al., 2007b). During the Yucatan campaign over 20 deforestation and crop residue fires were sampled and 49 trace gas and particulate species were measured. Yokelson et al. (2009)
found differences in emissions of NH$_4^+$ and organic acid emissions with crop residue fires emitting more of these species than deforestation fires, however other species measured were similar. Results also showed that Yucatan fires emit higher concentrations of SO$_2$ and particulate Cl$^-$ which is likely due to the close location to the marine environment.

The Southern African Regional Science Initiative (SAFARI-2000) campaign took place with one of the objectives to measure and characterise atmospheric emissions from savannah and other biomass burning in Africa. Sinha et al. (2003) used aircraft measurements from plume penetrations of savannah fires in Southern Africa to derive emission factors and emission ratios for trace gases and particulates, some of which had not been measured before in African savannah fires. Yokelson et al. (2003) also measured fresh emission from savannah during this campaign and derived initial emission ratios. Post emission processing and aging of these species were also investigated, however this is beyond the scope of this dissertation. These emission ratios and emission factors can be used in emission inventories and used to calculate annual emissions from savannah fires in Africa and worldwide.

The Dust and Biomass-burning Experiment (DABEX) took place in January and February 2006 to study the impact of biomass burning aerosol and dust over West Africa (Haywood et al., 2008). A total of thirteen research flights investigated biomass burning emissions from intense agricultural fires and
their subsequent transformation. Organic aerosol mass and CO were linearly correlated during the dry season which indicated that there was a lack of secondary organic aerosol (SOA) formation. Emission ratios of black carbon and organic carbon to CO were derived and found to be in agreement with literature values (Capes et al., 2008; Jolley et al., 2012). The data provided by DABEX has also been utilised in models to determine the impact that biomass burning aerosols have on radiative forcing over West Africa and to compare model outputs to observational data (Myhre et al., 2008).

5.4 Studies and Campaigns in Brazil

Numerous campaigns have taken place in Brazil to study biomass burning emissions as summarized by Kaufman et al. (1998a) and Martin et al. (2010). This section describes a few of these campaigns and the major scientific outcomes.

The first campaigns that took place to investigate biomass burning emissions in Brazil focused on the trace gas emissions. The Brushfire-80 campaign was conducted during the Amazonian dry seasons (August and September) in 1979 and 1980 (Crutzen et al., 1985) to study the emissions of trace gases and hydrocarbons and the importance of these species in atmospheric chemistry. Through an aircraft campaign and ground based sampling, it was found that CO concentrations from biomass burning in
Brazil were comparable to industrial CO emissions at mid-latitudes in the Northern Hemisphere. The authors state the importance that these agricultural biomass burning emissions have on atmospheric photochemical reactions and air pollution, both locally and globally (Crutzen et al., 1985).

The BASE-A and –B (Biomass Burning Airborne and Space borne Experiment Amazon and Brazil) was conducted in 1989 and 1990 in the Amazon and Brazil respectively. The BASE-A campaign utilised aircraft measurements of biomass burning plume concentrations and physical and optical particle properties, satellite imagery of the fires and extensive ground based measurements of smoke characteristics to better understand environmental impacts of biomass burning. The increase in trace gas and particulate emissions was found to contribute significantly to increased ozone concentrations. Combustion efficiency and emission factors were calculated for forest and cerrado fires in Brazil. It was found that cerrado fires have a higher combustion efficiency (97%) than forest fires (90%) but emission factors for Brazilian fires were similar to emissions factors for North American fires with similar combustion efficiencies. The BASE-B campaign took place a year later, August and September, 1990 in Brazil. The two different fire types as in BASE-A were investigated, forest and cerrado fires. Average cerrado fires combustion efficiencies were 0.94 and decreased from 0.88 for flaming deforestation fires to less than 0.80 for smouldering fires (Ward et al., 1992). Emission factors were also calculated
and compared for cerrado and deforestation fires in Brazil. Average $\text{EF}_{\text{CO2}}$ for deforestation and cerrado fires were 1614 g kg$^{-1}$ and 1722 g kg$^{-1}$ respectively and for $\text{EF}_{\text{CO}}$ were 110 g kg$^{-1}$ and 58 g kg$^{-1}$ respectively. These differences signify the importance of considering the different combustion efficiencies, ecosystems and weather patterns when estimating emissions from biomass burning on both regional and global scales. Emission factors for particulate organic matter, inorganics and black carbon however were not determined.

The Smoke, Clouds, and Radiation-Brazil (SCAR-B) was the next major biomass burning campaign to take place in Brazil. It took place in the rainforest and cerrado regions of Brazil during August and September 1995 and included aircraft and ground based in-situ measurements. Measurements of smoke emission factors, compositions, size and optical properties of the smoke particles were studied as well as the transport and aging of the biomass burning plume (Kaufman et al., 1998a). These results were then used to quantify the direct and indirect forcing due to biomass burning emissions (Hobbs et al., 1997). It was estimated that smoke exerts a global direct radiative forcing of -0.1 to -0.3 W m$^{-2}$ (Kaufman et al., 1998a; Hobbs et al., 1997). Correlation was found between smoke concentrations and cloud condensation nuclei, indicating a relationship between biomass burning smoke emission and cloud properties (Kaufman et al., 1998a).
Results from SCAR-B have also been used to validate remote sensing measurements of fire emissions from satellites (Kaufman et al., 1998a).

The Tropical Forest Fire and Emissions Experiment (TROFFEE) was the next campaign to take place during the Amazonian dry season in 2004 with the aim to quantify emissions from both pristine tropical rainforest and biomass burning in Brazil (Yokelson et al., 2007a; Yokelson et al., 2008). The campaign firstly consisted of a laboratory experiment and then ground based and airborne based measurements were made in the field. The laboratory campaign took place first and allowed inter-comparison of instruments for 26 different burns, the calculation of emission factors and helped plan the sampling method for the field campaign (Karl et al., 2007; Yokelson et al., 2008). The intensive TROFFEE aircraft campaign took place between 27th August and 8th October 2004, with nineteen tropical deforestation fires sampled by the aircraft (Yokelson et al., 2007a) and a ground based Fourier transform infrared spectrometer (FTIR) measuring residual smouldering combustion (RSC) from logs (Christian et al., 2007). A two week period of intense burning and low humidity led to a ‘mega plume’ greater than 500km wide across Brazil, Bolivia and Paraguay for one month (Yokelson et al., 2007a). This ‘mega plume’ was found to have a large impact on air quality in Sao Paulo with a 3 to 4 increase in atmospheric aerosol concentrations and highlights the importance of
understanding biomass burning emissions with relation to the effect it has on air quality and human health in the region.

All of these previous campaigns show that the species emitted from biomass burning are dependent on numerous factors, including the combustion efficiency of the fire, the fuel composition and vegetation being burnt, and environmental conditions such as proximity to the marine or urban environment and wind conditions. The importance of these measurements in terms of use in emission inventories and for accurate predictions of future air quality, weather and climate are also underlined. Particulate species need further investigations as these are poorly understood and as the most recent study of Amazonian biomass burning emissions took place almost a decade ago, more accurate and up to date measurements are needed. Many of these previous studies do not provide particulate emission factors of organics, inorganics and black carbon which are vital when considering the implications that biomass burning has on the atmosphere.

Instrumentation such as the ToF-AMS (Canagaratna et al., 2007) and SP2 (Moteki and Kondo, 2007) have been developed since these campaigns and provide more accurate measurements of particulate species. As recent studies in Brazil have found a shift from forest to savannah burning (Ten Hoeve et al., 2012) these new, accurate and up to date measurements of biomass burning emissions will provide data in order to assess what effect
this shift in vegetation burning will have on atmospheric trace gas and particulate species in the region.
Chapter 6: The South American Biomass Burning Analysis Project

The South American Biomass Burning Analysis Project (SAMBBA) is an international research project between seven UK University partners, the University of Sao Paolo and the UK and Brazilian Operational Forecasting Centres (Met Office and INPE). The project took place during September and October 2012 and used ground based measurements, satellite retrievals and an aircraft campaign to collect atmospheric data over the Amazon Basin during the dry season. This dissertation and subsequent data analysis focuses on the FAAM BAe-146 aircraft campaign data.

6.1 Campaign overview and objectives

The aims of SAMBBA were to improve knowledge of BB emissions, improve upon aerosol process models, improve satellite retrievals; test next generation models on the effect BB aerosols have on regional weather and climate and finally assess the effects BB has on the Amazonian biosphere. The key objectives of SAMBBA included assessing the impact of Amazonia biomass burning aerosol on the radiation budget and the effects this has on the local energy budget, atmospheric dynamics and hydrological cycle. And to assess the regional and global impact of the forcing and feedbacks arising
from biomass burning aerosol and the impact biomass burning emissions have on the carbon cycle. In order for these key objectives to be met, an intensive airborne and ground based measurement campaign took place. The enabling objectives include determining the emission rates of aerosol species, quantify the aging rates of biomass burning aerosols and assessing the vertical distribution of these aerosols.

6.2 Aircraft campaign

A total of 20 flights took place during SAMBBA between 14th September 2012 and the 3rd October 2012. Each flight during the aircraft campaign had a specific science objective that included direct sampling of fresh biomass burning emissions, transformations in biomass burning plumes, sampling of regional pollution haze, sampling in pristine biogenic environments or high altitude remote sensing. These objectives were met through three different types of flight including single plume penetrations and cross plume raster scans to allow measurements of fresh biomass burning emissions and ageing of these emissions in the plume to be made; closure studies of the direct radiative effect by flying over the biomass burning pollution and under it to quantify radiative flues; and survey flights from polluted to clean air regions. In total ~70 hours of flight were completed throughout the campaign. Four different airports across Brazil were utilised for the
campaign: Porto Velho, Palmas, Manaus and Rio Branco. The two biomass burning flights described in the subsequent sections were B737 which took off and landed at Porto Velho and B742 which took off and landed at Palmas.

6.2.1 FAAM BAe-146 aircraft

The Facility for Airborne Atmospheric Measurements (FAAM) is a partnership between the Met Office and the Natural Environment Research Council (NERC) and is part of the National Centre for Atmospheric Science (NCAS) which provides the BAe-146 (British Aerospace-146) aircraft for atmospheric research use for the UK scientific community. This aircraft was utilised in the SAMBBA campaign. The aircraft has the ability to fly up to 1800 nautical miles up to an altitude of 35,000 feet and has a maximum flight duration of 5 hours. These capabilities mean the aircraft can be used for a variety of atmospheric campaigns both in the UK and abroad.

6.2.2 Instrumentation

The BAe-146 aircraft houses a comprehensive suite of instruments. These instruments are mounted on racks in the cabin of the aircraft, with the core instruments provide by FAAM. The instruments are capable of measuring aerosols, dynamics, cloud physics, chemistry and radiation. The following
section will focus on the instruments that provided data for use in this
dissertation which include the aerosol mass spectrometer (AMS), single
particle soot photometer (SP2), fast greenhouse gas analyser (FGGA) and
the VUV (vacuum ultraviolet) fast fluorescence CO analyser.

6.2.2.1 Aerosol Mass Spectrometer

The Aerosol Mass Spectrometer provides quantitative real time
measurements of size resolved non-refractory (NR) aerosol mass and
composition. Jayne et al. (2000) describes the development of the first
AMS. This first AMS, known as Quadrupole AMS (Q-AMS) was
developed due to the demand for time resolved measurements of aerosol
mass and composition and used quadrupole mass spectrometry compared
later versions using time of flight (tof) mass spectrometry or high resolution
tof mass spectrometry (HR-tof) (Drewnick et al., 2005; Canagaratna et al.,
2007; DeCarlo et al., 2006). An Aerodyne Compact Time Of Flight Aerosol
Mass Spectrometer (C-ToF-AMS) was used on board the BAe-146 during
SAMBBA and provided real time size-resolved mass measurements of non-
refractory (NR) organic aerosol (OA) and inorganics: sulphate, nitrate,
chloride and ammonium (µg/sm³, where ‘sm³’ refers to standard cubic metre
at 1 atm, 273.15K) (Drewnick et al., 2005; Canagaratna et al., 2007). The
detection limit for nitrate and sulphate is 0.003 µg/sm³ and for ammonium
and organics is 0.03 µg/sm³ (Drewnick et al., 2009). These detection limits
are also a function of altitude. The basic operating principles of the instrument are the same for all aerosol mass spectrometers apart from the slight changes to the mass spectrometry detection methods. The schematic in figure 4 of a C-ToF-AMS shows the three main sections of an AMS. The first section is the aerosol inlet where sub-micron aerosols enter the instrument and are focused through an aerodynamic lens into a narrow particle beam of ~1mm diameter (Jayne et al., 2000; Canagaratna et al., 2007; Liu et al., 1995a, b). The narrow beam is then transmitted into the detection chamber. This section of the AMS utilises the velocity or ‘time of flight’ of the aerosols to infer the aerosols size. The ‘chopper’ as shown in figure 4 can be operated in three different positions. The closed position blocks the beam completely, the open position continuously transmits the beam and the ‘chopped’ position allows the time of flight of the aerosol particles to be measured and
consequently for the size to be determined (Canagaratna et al., 2007; Drewnick et al., 2005; Jayne et al., 2000). The final section of the AMS is the particle composition stage and where the numerous versions of the AMS differ. The detection method used in the C-ToF-AMS is described here as this was the instrument used during SAMBBA. In this final stage the aerosols impact onto a heated tungsten surface (usually ~600°C), the non-refractory components are flash vaporised and ionised by electron impact at 70eV and then transferred to an orthogonal time of flight extractor and extracted by a pulsed high voltage. (Drewnick et al., 2005; Canagaratna et al., 2007; Kimmel et al., 2011). The mass concentration is then derived from the data using the detected ion signals from the mass spectrometer to give the mass loading in µg/sm³. This is achieved by combining the relative molecular weight of the species, the flow rate entering the instrument, the ionization efficiency and the detected ion rate. The C-ToF-AMS provides quantitative high time resolution data with high precision and accuracy making it ideal for use on aircraft campaigns.

6.2.2.2 Single Particle Soot Photometer

The Single Particle Soot Photometer (SP2) characterises single particle mass, number and size of particles containing refractory black carbon (rBC) species in µg/sm³ (Stephens et al., 2003; Schwarz et al., 2006). The SP2 uses laser-induced incandescence to detect the individual black carbon particles.
Particles enter a laser cavity where the light absorbing particles are then heated (to ~4000K) and begin to incandesce and emit thermal radiation. The light absorbing particles are then vaporized due to this heating. These interactions are measured by two optical detectors and the intensity of the detected radiation is related to the mass of refractory black carbon (Moteki and Kondo, 2010; McMeeking et al., 2010). The SP2 usually has a black carbon particle diameter measurement range of ~90-400nm (Reddington et al., 2013) but the instrument was upgraded for SAMBBA and measured down to 60 nm. It has an accuracy of ~30% (McMeeking at al., 2010; McMeeking at al., 2012).

6.2.2.3 Fast Greenhouse Gas Analyser

The Fast Greenhouse Gas Analyser (FGGA) provides high accuracy, fast measurements of carbon dioxide and methane mixing ratios. The technique used for these measurements is based on an infrared spectrometer using cavity-enhanced absorption spectroscopy (O'Shea et al., 2013). The instrument uses an optical cavity and an off-axis trajectory of a laser beam to achieve an effective path length of several kilometres (Paul et al., 2001; Baer et al., 2002). Briefly, this technique uses the principle that the change in the laser beam light intensity entering the cavity is related to the absorption of the molecular species. The molar fraction of the absorbing species can then be determined taking into account the cavity temperature.
and pressure (O’Shea et al., 2013). The FGGA has a 0.1% uncertainty in CO₂ and CH₄ mixing ratios (O’Shea et al., 2013).

6.2.2.4 VUV Fast Fluorescence CO Analyser

The VUV (vacuum ultraviolet) fast fluorescence CO analyser is a fast response instrument that measures carbon monoxide mixing ratios. The principle technique that this instrument employs is that when carbon monoxide is exposed to UV light at 150nm it fluoresces. This fluorescence is then detected and is proportional to the carbon monoxide mixing ratio, with an uncertainty of 2% (Gerbig et al., 1996; Gerbig et al., 1999).
Chapter 7: Paper

Comparison of biomass burning emissions from different fire types in Brazil during SAMBBA 2012.


Status:

To be submitted to Atmospheric Chemistry and Physics following the outcome of this dissertation. The analysis of the auxiliary data in order to determine the collection efficiency value for the AMS data is ongoing (and the paper will be updated with this before it is submitted), but initial comparisons suggest that a CE of 1 appears appropriate for the AMS within instrumental uncertainties. This agrees with previous AMS measurements of similar particles previously. By using a value of 1 this gives the lower limit for the ERs and EFs rather than introducing an estimate that is biased high without having sufficient supporting information.

Overview:

Calculated modified combustion efficiencies, emission ratios and emission factors are presented for a smouldering rainforest fire in Rondonia, Brazil and flaming cerrado fires in Tocantins, Brazil observed during the
SAMBBA campaign. Large differences in both trace gas and particulate species emitted between the two fires was seen. The Rondonia fire was found to be highly smouldering with a modified combustion efficiency of 0.79 compared to the flaming Tocantins fires with a MCE of 0.94. The Tocantins fires emitted a magnitude more black carbon and ~20% more CO$_2$ than the Rondonia fire. However, the Rondonia fire emitted more than double the mass of organic aerosol than the Tocantins fires. As first author, I lead the manuscript preparation and data analysis.

Contributions from co-authors:

Morgan participated in field work, processed SP2 and AMS data, assisted with data analysis and manuscript preparation. O'Shea and Baguitte processed CO$_2$ and CH$_4$ data. Allan operated the SP2 and AMS during the fieldwork. Darbyshire assisted in data analysis. Flynn operated the SP2 and AMS during the fieldwork. Liu assisted with processing the SP2 data. Lee processed CO data. Johnson participated in the fieldwork and led the UK consortium. Haywood, Longo and Artaxo were SAMBBA PIs. Coe was also a PI, participated in fieldwork and assisted in manuscript preparation.
Comparison of biomass burning emissions from different fire types in Brazil during SAMBBA 2012.

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Abstract

The airborne campaign of the South American Biomass Burning Analysis Project (SAMBBA) provided trace gas and particulate species measurements from biomass burning fires in Brazil during September and October 2012. This unique data of Amazonian biomass burning emissions included measurements from the C-ToF-AMS and SP2, with SAMBBA
being the first campaign to use these high accuracy instruments in a tropical environment to study biomass burning emissions. Emissions from a smouldering rainforest fire in Rondonia State and numerous smaller flaming cerrado fires in Tocantins state are presented. We determined fire integrated emission ratios and emission factors for trace gas and particulate components for these two fire types. Trace gas species included CO, CO$_2$ and CH$_4$ and particulate species included organic aerosol, inorganic aerosol (chloride, nitrate, sulphate and ammonium) and size resolved black carbon. Trace gas emissions differed substantially between the fire types and were highly dependent on the combustion efficiency of the fire, characterised by the integrated modified combustion efficiency (MCE). The trace gas emission factors for these fires are generally in agreement with these other studies for biomass burning in Brazil. Organic aerosol and black carbon emissions also differ between the fire types, with an order of magnitude more black carbon emitted from the flaming cerrado fires in Tocantins, EF$_{BC}$ of 0.018 g kg$^{-1}$ for the Rondonia fire compared to EF$_{BC}$ of 0.13 g kg$^{-1}$ for the Tocantins fires. More than double the amount of organic aerosol per kg fuel burnt was emitted during the smouldering rainforest fire compared to the flaming cerrado fires, EF$_{OA}$ of 5.67 g kg$^{-1}$ compared to 2.31 g kg$^{-1}$ for Rondonia and Tocantins fires respectively. Particulate phase species emitted from the fires sampled are generally lower than those reported in previous studies for different locations. We find that organic aerosol emission is
dependent on combustion efficiency, however for black carbon we do not find significant dependence on combustion efficiency. Inorganic aerosols vary between fire types and are more dependent on fuel type and composition rather than combustion efficiency. The extent to which representative of the Rondonia rainforest fires as indicative of deforestation fires is investigated by comparing with previous deforestation fire emission values. The results show that the Rondonia fire is indicative of a highly smouldering deforestation fire, with EF\(_{CO_2}\), EF\(_{CH_4}\) and EF\(_{OC}\) in agreement with other deforestation values but EF\(_{BC}\) and inorganics lower than reported deforestation fire values. With recent studies showing a shift from deforestation to savannah fires in Brazil, this could lead to significant increases in CO\(_2\) and BC concentrations in the region and have significant effects on regional climate. The EF values for particulate matter are generally within range or lower than values used in emission inventories, and therefore we do not see evidence for a discrepancy in the EFs that could explain the underestimation of biomass burning AODs in models, both globally and over South America. These findings provide up to date trace gas and particulate emission ratios and emission factors for fire type specific biomass burning in Brazil which are significant in terms of future climate change and can be utilised in atmospheric weather and climate models.
1. Introduction

Biomass burning (BB) emissions represent a significant source of trace gas and atmospheric aerosol in the global troposphere (Crutzen and Andreae, 1990; Crutzen et al., 1979; Penner et al., 1992). Although the predominate trace gas emitted during BB is carbon dioxide, other gases such as carbon monoxide and methane are also emitted in significant quantities (Ferek et al., 1998; Andreae, 1991). These gases have been well documented in relation to the effect that they have on radiative forcing and global climate change (Forster et al., 2007). Atmospheric aerosols represent the largest uncertainty in the current understanding of radiative forcing of climate (Forster et al., 2007), with biomass burning aerosol (BBA) estimated to have a net warming of 0.03 Wm\(^{-2}\) with a very large uncertainty of ± 0.12 Wm\(^{-2}\) (Forster et al., 2007). BBA have both a global and regional effect on weather and climate (Andreae et al., 2004; Ramanathan et al., 2001) and visibility (Andreae et al., 1988) but can also affect human health. Studies by Arbex et al. (2007), Cancado et al. (2006) and do Carmo et al. (2013) found an increase in hospital emissions due to respiratory problems during biomass burning events in Brazil. Black carbon is also an important species emitted by BB due to its light absorbing properties and interactions with clouds, thereby altering the radiation balance (Cooke and Wilson, 1996; Bond et al., 2004; Haywood and Boucher, 2000; Bond et al., 2013). It is estimated that black carbon emissions from open biomass burning
(agricultural, forest, grass and woodland fires) contribute 40% to global black carbon emissions (Bond et al., 2013). Organic aerosols are the dominant particulate phase species emitted during biomass burning (e.g. (Ferek et al., 1998; Yokelson et al., 2009)) which can significantly perturb the Earth’s radiation balance directly by scattering and absorbing solar radiation or indirectly by acting as CCN (Charlson et al., 1992; Penner et al., 1992).

Emissions from BB are quantified either by emission ratios (ERs) (ER$_{x/y}$, the relative excess amounts of two smoke species, $x$ and $y$) or emission factors (EFs) (grams of species released per kg of dry fuel burnt) and these are vital in order to compute trace gas and particulates released from biomass burning fires. Numerous scientific studies have taken place to study smoke from biomass burning both in the field (for example Reid and Hobbs (1998)) and in the laboratory (for example McMeeking et al. (2009)). These studies have taken place in different locations around the globe ranging from Boreal forest in Canada (Cofer et al., 1990) to Savannah fires in Africa (LeCanut et al., 1996). Every fire is unique, differing in vegetation type and combustion stage (Gao et al., 2003) e.g. flaming or smouldering (represented by the Modified Combustion Efficiency, MCE). Other factors such as moisture content of the fuel, the environmental conditions and whether the vegetation is dead or alive can alter the emissions of certain BB species (Yokelson et al., 1996; Ward et al., 1996). Korontzi et al. (2003)
found a seasonal influence on trace gas emission factors from grassland fires in Southern Africa due to the fuel moisture content. Previous studies showing large variations in emissions from different vegetation types include those by Akagi et al. (2011), Andreae and Merlet (2001), Koppmann et al. (1997) and McMeeking et al. (2009). All of these previous studies provide data for emission inventories which can then be directly used in atmospheric models. However, due to the large uncertainties and factors influencing BB emissions, further understanding of these emission variations are needed.

Biomass burning in the tropics contributes to more than 80% of all the emissions produced from total biomass burning globally (Ward et al., 1992), with most of these fires being deforestation fires (Yokelson et al., 2007). The Amazon Basin in Brazil contains approximately $4 \times 10^6 \text{km}^2$ of evergreen tropical forest (Christian et al., 2007) and during the dry season (August-October) intense widespread burning occurs leading to high levels of atmospheric particulate matter (Chand et al., 2006). Between 2004 and 2010 deforestation rates in the Brazilian Amazon decreased from $27,000 \text{km}^2/\text{year}$ to $7000 \text{km}^2/\text{year}$ (Malingreau et al., 2012; de Souza et al., 2013) due to governance actions (Nepstad et al., 2009). Both tropical rainforest fires and savannah-like fires occur in Brazil (Yamasoe et al., 2000) for land clearing and pasture maintenance (Martin et al., 2010) which leads to high levels of black carbon, organic matter and gas phase species in the atmosphere. The
high levels of BBA can lead to regional haze which affects the regional radiation budget directly by scattering and absorbing radiation and indirectly by acting as cloud condensation nuclei (CCN) and altering cloud properties (Forster et al., 2007; Haywood and Boucher, 2000; Ramanathan et al., 2001). The emissions of gas and particulate phase species from BB in Brazil therefore need to be accurately represented in global climate models for the model outputs to be accurate and reliable (Bowman et al., 2009).

Previous field experiments to study biomass burning smoke emissions in Brazil are summarized in Kaufman et al. (1998a) and Martin et al. (2010) and include Brushfire-80 in 1980 (Crutzen et al., 1985), BASE-A and –B (Biomass Burning Airborne and Space borne Experiment- Amazon and Brazil) (Kaufman et al., 1992; Ward et al., 1992) in 1989 – 1990 and SCAR-B (Smoke, Clouds, and Radiation – Brazil) in 1995 (Kaufman et al., 1998a; Ferek et al., 1998). The CLAIRE 98 (Large-Scale Biosphere-Atmosphere Experiment in Amazonia – Cooperative LBA Airborne Regional Experiment ‘98) (Andreae et al., 2001) and CLAIRE 2001 (Graham et al., 2003) took place in Brazil in 1998 and 2001 to investigate biomass emissions. A more recent study took place in 2004 during the Amazon dry season, TROFFEE (Tropical Forest and Fire Emissions Experiment) (Yokelson et al., 2007; Christian et al., 2007; Karl et al., 2007). These studies have allowed trace gas emissions from BB in Brazil to be relatively well understood and quantified, varying with fire type. However
particulate species need further investigations as these are poorly understood and as most of these campaigns took place over a decade ago, more accurate and up to date measurements are needed. Instrumentation such as the ToF-AMS (Canagaratna et al., 2007) and a DMT (Droplet Measurement Technologies) SP2 (Moteki and Kondo, 2007) have been developed since these campaigns and provide more accurate measurements of particulate species (see section 2.1 for further details). SAMBBA is the first campaign to utilise both of these instruments in a tropical environment for studies of biomass burning. These fire type specific measurements are vital as recent biomass burning studies in Brazil have found a shift from forest to savannah burning, which will impact trace gas and particulate emissions in the region (Ten Hoeve et al., 2012). This led to a major scientific project to take place, The South American Biomass Burning Analysis Project (SAMBBA). The campaign took place in the Brazilian dry season between September and October, 2012 with the aim to improve knowledge of biomass burning emissions which affects air quality, numerical weather prediction and climate in the region. Results presented here were collected during the aircraft campaign on the UK Facility for Airborne Atmospheric Measurement (FAAM) Airborne Research Aircraft, BAe-146. This research compares two different fire regimes: a large smouldering rainforest fire in Rondonia (RO) and numerous smaller flaming cerrado fires in Tocantins (TO). The chemical characteristics, emission ratios (ER), emission factors
(EF) and the Modified Combustion Efficiency (MCE) of the smoke plumes are presented.

1.1 Campaign details and aims of the study

During the airborne campaign of SAMBBA a wide range of instrumentation was utilised (described in detail in section 2.1) to make these measurements. Twenty flights were conducted from 13th September to 4th October 2012 in the Brazilian dry season, with each flight having a specific objective ranging from characterising regional haze to investigating biogenic emissions in pristine conditions to measuring fresh biomass burning emissions. In this research two very different vegetation and fires types were selected to compare and contrast the biomass burning emissions. The first fire selected was a large smouldering rainforest fire in Rondonia State, a suspected wildfire. During a second flight emissions from numerous smaller flaming cerrado fires in Tocantins State were measured. These flights were chosen due to their very different emission characteristics and with recent studies showing a shift from deforestation to cerrado fires in Brazil (Ten Hoeve et al., 2012), this research is important in understanding future atmospheric species from biomass burning. We present up to date emissions ratios and emission factors for the two different fire types for use in emission inventories that can be utilised in models.
2. Experimental Details

2.1 Instruments onboard the BAe 146 aircraft

The BAe 146 aircraft has a wide range of instruments on board, but only those relevant to the analysis are discussed below. An Aerodyne Compact Time Of Flight Aerosol Mass Spectrometer (C-ToF-AMS) provided real time size-resolved mass measurements of non-refractory (NR) organic aerosol (OA) and inorganics: sulphate, nitrate, chloride and ammonium (µg/sm³, where ‘sm³’ refers to standard cubic metre at 1 atm, 273.15K) (Canagaratna et al., 2007; Drewnick et al., 2005). This instrument provides quantitative high time resolution data with high precision and accuracy making it ideal for use on aircraft campaigns. Measured mass concentrations for the C-ToF-AMS have an uncertainty of ~ 30% (Bahreini et al., 2009).

Previous studies by (Crosier et al., 2007) and (Morgan et al., 2010) have detailed the sampling strategy and calibration protocols for the AMS on the BAe 146. Plume interceptions utilised the ‘fast mass spectrum’ mode of the AMS (Kimmel et al., 2011), which provided data a 1 second time resolution. The data was processed using the ToF-AMS Analysis Toolkit in Igor Pro, with a collection efficiency of 1.0 applied to the data. The collection efficiency of one was determined from analysis of data from instruments on another flight which indicated a collection efficiency of one.

The Single Particle Soot Photometer (SP2) provides physical property measurements of individual refractory black carbon particles by measuring
the single particle mass, number and size of particles containing refractory black carbon (rBC) species in µg/sm³ (Baumgardner et al., 2004; Schwarz et al., 2006). We define the term refractive black carbon as the incandescent material measured by the SP2 (Moteki and Kondo, 2010; McMeeking et al., 2010). The SP2 instrument operation and subsequent data interpretation have been described elsewhere e.g. (Liu et al., 2010; McMeeking et al., 2010). Briefly, the particles enter a laser cavity and an intra-cavity Nd:YAG laser at 1064 nm determines the optical size of a single particle through the light scattered. If material within the particle absorbs at the specific laser wavelength, the resultant laser induced incandescence radiation will be detected and the refractory mass of the particle can then be quantified (Stephens et al., 2003; Moteki and Kondo, 2010) Calibration of the SP2 incandescence signal to the single particle rBC mass used the Aquadag samples standard, with further details of this calibration described in (Liu et al., 2013). A 30% uncertainty in the SP2 black carbon mass is used as in previous studies e.g. (McMeeking et al., 2010; McMeeking et al., 2012). SAMBBA is the first campaign to use both the C-ToF-AMS and the SP2 instruments, in a tropical environment.

The Fast Greenhouse Gas Analyzer (FGGA) provides high accuracy, fast measurements of carbon dioxide and methane mixing ratios with a ~0.1% uncertainty (O’Shea et al., 2013) and the VUV Fast Fluorescence CO Analyser measures carbon monoxide mixing ratios with a ~2% uncertainty.
2.2 Fire Selection

The two contrasting fire types selected for this study are detailed below.

2.2.1 Rondonia flight

The first flight in this study took place in Rondonia State in the West of Brazil on 20th September 2012, with take-off at 1445 UTC (1045 local time) and a flight duration of ~3 hours 45 minutes. The natural vegetation in Rondonia is characterised by dense Amazonian rainforest, but the region has become one of the most deforested areas of the Amazon. As Fig. 1 shows there was a large smouldering rainforest fire with a BB plume extending 50 miles downwind. It should be noted that this fire is suspected to be a natural wildfire, likely initiated by lightning, compared to the many human induced deforestation fires studied in many previous campaigns. The fire was located many kilometres from the nearest road, in a region well away from any deforestation and located in a National Park. It is therefore unlikely the fire was a deforestation fire. MODIS hotspot data from the TERRA overpass at 1426 UTC on 19/09/12 indicated that this fire was likely started the day before we sampled the smouldering plume. The flight track is shown in Fig 2 with the fire location shown by the MODIS hotspot data red markers. The near field plume interceptions took place at an altitude of 1800m with far field interceptions at an altitude of 2500m. The fire was
located on a 900m high plateau, therefore the plume was intercepted at 900m above the fire, with smoke estimated to be ~6 minutes old. This paper only focuses on the near field measurements to understand initial emissions. A future publication (Morgan et al., in prep) will characterise the ageing and transformation of the plume downwind. Initial results however show no net change in organic mass concentrations in the plume when accounting for dilution effects but there is an increase in inorganic species, which is important in understanding how biomass burning aerosols age and the effect they have on weather and climate.

Figure 1. Aircraft photograph of Rondonia BB plume. Courtesy of Axel Wellpott
Some mid-level cloud was present in central Rondonia and a large pyrocumulus cloud was observed over the BB plume. Winds were from the North-North-West and relative humidity outside of plume interceptions was high with values ~70% at 900m.

During this flight 9 separate plume interceptions took place, each lasting approximately 15 seconds, shown in Fig. 3. Fig. 3 just shows the intercepts of the plume in the near field with the large increase in CO, rBC and OA clearly visible. Background concentrations of CO, OA and BC were 213 ppbv, 7 µg/sm³ and 0.14 µg/sm³ respectively. Plume maximums ranged

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**Figure 2.** Flight track of the Rondonia flight coloured by altitude. Plume interceptions shown by black markers with MODIS hotspot from the TERRA overpass at 0241 and 1509 UTC and Aqua overpass at 0543 UTC on 20/09/12 shown in red.
between 1261–29554 ppbv for CO, 94–2685 µg/sm$^3$ for OA and 1–9 µg/sm$^3$ for BC.

**Figure 3.** Time series of CO, rBC and OA concentrations during the Rondonia flight with plume interceptions clearly visible as large increases in concentrations.

### 2.2.2 Tocantins flight

The second flight selected took place in the Tocantins State of Brazil (Fig. 4) on the 27th September 2012, with take-off at 1300 UTC (1000 local) and a flight duration of ~3 hours 15 minutes. Tocantins State is characterized by a cerrado landscape which consists of a variety of vegetation from open savannah grasslands to forest. Fig. 4 shows an example of one of the fires sampled during the Tocantins flight. The vegetation consists mainly of grassland with some trees. During the flight numerous new fires were starting, these were likely the result of man-made agricultural burning. The BB smoke plumes were sampled at an altitude of 600m above the fires (Fig. 5), with smoke sampled being ~4 minutes old, which we define as initial
smoke. The flight track is shown in Fig. 5, with the Moderate Resolution Imaging Spectroradiometer (MODIS) hotspot data from NASA’s Terra satellite (Giglio et al., 2006; Kaufman et al., 1998b; Kaufman et al., 2003), shown by the red markers to indicate the fire locations and the plume interceptions shown by the black crosses.

Figure 4. Aircraft photograph of Tocantins BB plume. Courtesy of Axel Wellpott.

Figure 5. Flight track of the Tocantins flight coloured by altitude. Plume interceptions shown by black markers with MODIS hotspot from the TERRA overpass at 1336 UTC on 27/09/12 shown in red.
There was little cloud cover in the area with low relative humidity at an altitude of 600m outside of plume interceptions of ~30% and winds were light coming from the South East at 950hPa. During this flight 23, plume interceptions took place each lasting between 5 to 10 seconds. The plume interceptions can clearly be seen in the time series of CO, BC and organics shown in Fig. 6. Background concentrations at 600m altitude were 228 ppbv for CO, 0.8 µg/sm³ for BC and 15.5 µg/sm³ for OA. Maximum concentrations in the plume interceptions are show in Fig 6 and ranged between 750-17732 ppbv for CO, 9-113 µg/sm³ for BC and 128-3297 µg/sm³ for OA.

Figure 6. Time series of CO, rBC and OA concentrations during the Tocantins flight with plume interceptions clearly visible as large increases in concentrations.
3. Methodology

3.1 Background ambient and in-plume measurements

Excess mixing ratios of species (Δx) are needed in order to calculate MCE, ER and EF of a species (as described in sections 3.2, 3.3 and 3.4). In order to calculate Δx, the ambient background mixing ratios of species x must be subtracted from the values measured in the smoke plume. Percentile calculations of the species mixing ratio were conducted in order to find background mixing ratios. The fifth percentile value was the value taken as the ambient background mixing ratio as this should reflect background levels and have been used previously. As Fig. 3 and Fig.6 show, it is highly evident from CO, OA and rBC time series concentrations when the aircraft entered a BB plume, therefore this was done by eye. We note the discussion by Yokelson et al. (2013) that examines the limitations of the excess mixing ratios due to changes in background air composition through tropospheric mixing. As our measurements were made close to initial source through numerous plume intercepts on both flights and background concentrations were constant throughout we do not consider this mixing of background to be a significant effect in this study.

The numerous instruments onboard the BAe 146 each had different response times and inlet lag leading to difficulties when comparing data from different instruments (see supplementary figure S1). Therefore, an integral based approach was used which helps to compensate for these
different response times (Karl et al., 2007; Yokelson et al., 2009; Yokelson et al., 2011; Yokelson et al., 1996). Integrated methods have been found to be more robust and decrease uncertainty compared to the direct point by point method (Karl et al., 2007).

### 3.2 Modified Combustion Efficiency

The combustion efficiency (CE) and modified combustion efficiency (MCE) define the relative amount of flaming or smouldering combustion taking place. The CE is defined as the ratio of carbon emitted as CO\(_2\) to the total carbon emitted. Total carbon emitted includes CO\(_2\), CO, CH\(_4\), hydrocarbons and carbon containing particulates (Ward and Radke, 1993; Ward and Hardy, 1991; Radke et al., 1991). All of these carbon emissions can be difficult to measure in field campaigns, meaning the CE cannot be calculated, therefore we use the MCE which is defined below:

\[
MCE = \frac{\Delta CO_2}{\Delta CO_2 + \Delta CO} \quad (\text{Ward and Radke, 1993})
\]  

Where \(\Delta\) indicates the excess mixing ratio of the species.

CE and MCE are closely related with a difference of only a few percent, as CO and CO\(_2\) represent the majority of the carbon species emitted (Ward and Radke, 1993; Ferek et al., 1998). A MCE greater than 90\% is a fire in the flaming stage, whereas a MCE less than 90\% is defined as being in the smouldering phase (Ward and Radke, 1993). The fire integrated MCE was calculated for this study as used in many previous studies such as
McMeeking et al. (2009) due to the different instrument response times as discussed in section 3.1 and shown in supplementary figure S1. The excess concentrations of CO and CO$_2$ were integrated over the plume interception time to give integrated excess values. These values for each plume interception were then plotted with intercept forced to 0 to give the fire average MCE (see supplementary figure S2 for MCE plots).

### 3.3 Emission Ratio

The absolute concentration of trace gases and particulates in fire plumes cannot directly be used to interpret emissions due to the dilution of the species with the ambient background air. This is particularly important when sampling smoke from aircrafts. Therefore emission ratios (ERs) are calculated to give the relative emission of species $x$ to a simultaneously measured reference gas, usually CO or CO$_2$ as these gases are non-reactive and conserved (Andreae and Merlet, 2001; Sinha et al., 2003). The ER of species $x$ using CO as the reference gas is defined below:

$$ ER_x = \frac{\Delta_x}{\Delta_{CO}} $$ (2)

Where $\Delta$ indicates the excess mixing ratio of the species.

For gas species ER$_x$ is usually given as the molar ratio and for aerosol species ER is stated as the mass ratio at 1 atm, 273K. When only one pass is made through a BB plume the calculation of ER$_x$ is trivial using the equation above. The ER$_x$ can also be derived when multiple passes are made
through the BB plume by using the regression slope of the excess species concentration of x versus the reference species with the line forced through 0 (Yokelson et al., 1999). If however, a direct regression between two species is not possible due to the different instrument response times an integration method can be used as discussed by LeCanut et al. (1996), Yokelson et al. (2009) and Akagi et al. (2012). This is the method chosen in this study, where the excess concentrations of species x and the reference species concentration are integrated over the plume intercept, with the regression slope of these species giving ER_x as shown in fig 7.

The use of either CO_2 or CO as the reference species depends on the purpose of the analysis as well as the combustion stage of the fire, either flaming or smouldering. CO is the reference gas used for smouldering combustion whereas CO_2 is the reference gas used for more flaming combustion (Andreae and Merlet, 2001; Sinha et al., 2003). We present ER of species using both CO and CO_2 as references in section 3.4.

### 3.4 Emission Factor

Emission factors (EFs) are another parameter used to define the emission of a particulate species from fires. It is defined as the mass of compound x released to the atmosphere to the total mass of carbon species released in the form of CO, CO_2, CH_4, non-methane hydrocarbons (NMOC), particulate carbon etc. EFs were calculated using the carbon mass balance method (Ward and Radke, 1993; Yokelson et al., 1996). EF is reported as the mass
of species x emitted per kg of dry fuel burnt. The EF can be calculated from a number of ERs with CO$_2$ as the reference species using a total carbon balance (e.g. Wooster et al. (2011), Yokelson et al. (2009), Goode et al. (2000)). The carbon content of the vegetation is needed for EF calculation and as this quantity was not measured during the campaign we used a value of 0.5 ± 0.05 (Susott et al., 1996). Susott et al. (1996) presented data that shows the carbon content of Brazilian vegetation ranges from 45-55%. As we only used CO, CO$_2$ and CH$_4$ as the carbon containing species in the EF calculations our EFs are likely to be overestimated by 1-2% (Andreae and Merlet, 2001; Susott et al., 1996). The particulate phase carbon is usually only a small fraction of the carbon emitted (Lipsky and Robinson, 2006; McMeeking et al., 2009). Keene et al (2006) and Delmas et al. (1995) show that CO, CO$_2$ and CH$_4$ represent the vast majority of carbon emissions from BB. The EF for species x (g kg$^{-1}$) is defined below:

$$EF_x = \frac{F_c}{C_x/C_T} \frac{MM_x}{MM_{carbon}} \times 1000$$

(Wooster et al., 2011; Yokelson et al., 1999)

Where $F_c$ is the carbon content of the fuel, $MM$ is the molecular mass of species x(g), 1000g kg$^{-1}$ is a unit conversion factor, $MM_{carbon}$ is the molecular mass of carbon (12), and $C_x/C_T$ is the ratio of the number of moles of carbon.
\[
\frac{C_x}{C_T} = \frac{ER_{x/CO_2}}{\sum_{j=1}^{n}(NC_j ER_{j/CO_2})}
\]  

(4)

(Wooster et al., 2011; Yokelson et al., 1999)

Where \(ER_{x/CO_2}\) is the ER of species \(x\) to \(CO_2\), \(NC_j\) is the number of carbon atoms in compound \(j\), and the sum is over all carbon species including \(CO_2\) (Wooster et al., 2011; Delmas et al., 1995).

4. Results

4.1 MCE

The modified combustion efficiency of the two fires, the associated uncertainties and previous literature values are presented in table 1. The Rondonia fire MCE of 0.79 is in good agreement with Christian et al. (2007) MCE of 0.788 for residual smouldering combustion (RSC) of logs in Brazil. Christian et al. (2007) took ground based measurements of the RSC as these emissions are not lofted by the fire induced convection so cannot be measured from the air, whereas our measurements were taken from the air which can underestimate smouldering emissions. Ferek et al. (1998) reported a value of 0.87 for smouldering forest fires in Brazil measured by aircraft, and Bertschi et al. (2003) reported a value of 0.854 for RSC of smouldering cotton wood and Zambian logs as measured in a laboratory study, both of which are above our MCE. As our measurements are for just one fire in Rondonia, the uncertainty is the ability to replicate the same measurement rather than fire to fire variability as in the Tocantins fires.
Although our measurements were taken at altitude by an aircraft which may underestimate smouldering emissions, we see very large concentrations of CO relative to CO$_2$, with our MCE for Rondonia lower than many other reported values. This is likely to be caused by the very wet conditions of the rainforest vegetation which will increase incomplete combustion emissions such as CO (Reid and Hobbs, 1998).

The Tocantins fires MCE of 0.94 agrees with the Ferek et al. (1998) value of 0.94 for cerrado in Brazil measured by an aircraft campaign. Yokelson et al. (2007) provided an MCE of 0.91 for the average of Brazilian forest, pasture and grass fires measured by aircraft which when taking into account uncertainties is comparable to our value. Kaufman et al. (1992) reported a higher value of 0.97 for cerrado fires in Brazil measured by aircraft. African savannah fires (Yokelson et al., 2003) and California chaparral fires (Akagi et al., 2012) have similar MCE values of 0.94 and 0.93 (to two significant figures) respectively and compare well to value the MCE of 0.94 for Brazilian cerrado fires.
Table 1. Modified Combustion Efficiency (MCE) with the uncertainty derived in quadrature from the measurement uncertainties for the Rondonia fire and the Tocantins fires. Calculation methods as described in section 3.2 and shown in supplementary figure S2. Also included are other studies MCE’s from Brazil and from other locations with the specific fuel type quoted.

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>MCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rondonia: Smouldering Rainforest</td>
<td>0.79 ± 0.02</td>
</tr>
<tr>
<td>Tocantins: Flaming cerrado</td>
<td>0.94 ± 0.03</td>
</tr>
<tr>
<td>Yokelson et al. (2007) Brazil: forest, pasture, grass average</td>
<td>0.91 ± 0.021</td>
</tr>
<tr>
<td>Christian et al. (2007) Brazil: Residual smouldering combustion of logs</td>
<td>0.788 ± 0.059</td>
</tr>
<tr>
<td>Ferek et al. (1998) Brazil: Forest residual smouldering (FS) and cerrado (C)</td>
<td>FS = 0.87 C = 0.94</td>
</tr>
<tr>
<td>Kaufman et al. (1992) Brazil: Deforestation (DF) and cerrado (C)</td>
<td>DF = 0.91 C = 0.97</td>
</tr>
<tr>
<td>Yokelson et al. (2009) Yucatan: Crop residue(CR) and deforestation (DF)</td>
<td>CR = 0.934 ± 0.023 DF = 0.927 ± 0.013</td>
</tr>
<tr>
<td>Yokelson et al. (2003) African Savannah</td>
<td>0.938 ± 0.019</td>
</tr>
<tr>
<td>Bertschi et al. (2003) Laboratory study of smouldering cotton wood and Zambian logs</td>
<td>0.854</td>
</tr>
<tr>
<td>Akagi et al. (2012) California chaparral</td>
<td>0.933</td>
</tr>
<tr>
<td>McMeeking et al. (2009) Laboratory study, range of fuel types</td>
<td>0.857 - 0.977</td>
</tr>
</tbody>
</table>

4.2 Trace gas emissions

This section compares the emission values derived for the trace gas species for the two fire types and to values in literature. Detailed discussion into the processes involved and the differences in values are described in section 5. Fig. 7 shows the scatter plots used for derivation of the trace gas ERs as explained in section 3.3. High $R^2$ values for trace gas species of between 0.93 and 0.99 indicate good agreement between the two data sets. The different points in the Tocantins plots come from measurements from
different fires and the lack of variability from the regression indicates that this approach is valid. The trace gas ER values are stated in table 2, with an uncertainty of one standard deviation in the line of best fit.

EFs were calculated as described in section 3.4. Table 3 show these calculated values for trace gas species with the associated uncertainties derived in quadrature from the uncertainty in the carbon content of the fuel (0.05) and the uncertainty in the ERx/CO2 values used to calculate the EFs. Also presented are reported values from other types of vegetation.

The ER CO:CO2 for Rondonia of 25.8 x 10^{-2} is in good agreement with the value of 27.5 x 10^{-2} for residual smouldering logs in Brazil derived by Christian et al. (2007). Christian et al. (2007) used ground based sampling which preferentially samples products from more smouldering combustion compared to our result for airborne sampling which preferentially targets more flaming combustion which is lofted upwards by high combustion intensity (Yokelson et al., 2008). We would therefore expect our values measured by airborne sampling to be lower than that measured at ground for smouldering emissions however this is not the case, likely to be due to the large size of the fire and the high moisture content of the vegetation producing large amounts of smouldering emissions. Our ER CO:CO2 value is 53% higher than Bertschi et al. (2003) value of 16.85 x 10^{-2} for smouldering cotton wood and Zambian logs, however this is within experimental uncertainties. For the Tocantins fires the ER CO:CO2 value of
6.2 \times 10^{-2} for flaming cerrado in Brazil is in good agreement to the values reported for African savannah of 6.64 \times 10^{-2} measured by aircraft sampling (Yokelson et al., 2003) and 9.6 \times 10^{-2} measured by ground sampling (Wooster et al., 2011) when including experimental uncertainties. Californian chaparral fires sampled from aircraft also have a comparable CO:CO\textsubscript{2} ER of 7.13\times 10^{-2} (Akagi et al., 2012). Finally, Crutzen et al. (1985) value of 15.4\times 10^{-2} measured by aircraft for a mix of fire types in Brazil is within the range our calculated CO:CO\textsubscript{2} ER for smouldering rainforest, 25.8\times 10^{-2} and flaming cerrado 6.2\times 10^{-2}.

### 4.2.1 Carbon Dioxide

The Rondonia fire EF\textsubscript{CO\textsubscript{2}} of 1447 g kg\textsuperscript{-1} is in good agreement with previous values of 1346 g kg\textsuperscript{-1} for smouldering Brazilian logs (Christian et al., 2007) and a value of 1461.5 g kg\textsuperscript{-1} for smouldering cotton wood and Zambian logs (Bertschi et al., 2003) and is within the experimental uncertainties. Ferek et al. (1998) reports an EF\textsubscript{CO\textsubscript{2}} value of 831 g kg\textsuperscript{-1} for smouldering Brazilian forest, which is just over half the value that we report. Ward et al. (1992) reports a value of 1614 g kg\textsuperscript{-1}, slightly higher than our value, likely due to the combustion of the fire being a mix of smouldering and flaming compared to our fire being predominantly smouldering. Kaufman et al. (1992) also reported a slightly higher value for deforestation fires in Brazil of 1664 g kg\textsuperscript{-1}. Our value of 1447 +/- 145 g kg\textsuperscript{-1} is within Andreae and Merlet (2001) global average value for tropical forests of 1613 +/- 95 g kg\textsuperscript{-1} and
Akagi et al. (2011) tropical forest global average of 1643 +/- 58 gkg\(^{-1}\). The EF\(_{\text{CO2}}\) value of 1626 gkg\(^{-1}\) for deforestation fires used in the GFEDv3 and GFASv1.0 emission inventories (van der Werf et al., 2010; Kaiser et al., 2012) is 12% higher than the EF\(_{\text{CO2}}\) calculated for the Rondonia smouldering tropical forest fire and is consistent with our measurements.

The Tocantins fires EF\(_{\text{CO2}}\) of 1720 gkg\(^{-1}\) is in good agreement with Ward et al. (1992) value of 1722 gkg\(^{-1}\) and Kaufman et al. (1992) value of 1783 gkg\(^{-1}\), both for cerrado fires in Brazil when including experimental uncertainties. Again, as before, Ferek et al. (1998) report a much lower value of 928 gkg\(^{-1}\) for cerrado fires in Brazil. Our value of 1720 +/- 172 gkg\(^{-1}\) lies within the values of 1686 +/- 38 gkg\(^{-1}\) for global average savannah (Akagi et al., 2011) and the value of 1613 +/- 95 gkg\(^{-1}\) for global average savannah and grassland (Andreae and Merlet, 2001). Our value for cerrado fires in Brazil is similar to values of African savannah fire reported by Yokelson et al. (2003), Sinha et al. (2003) and Wooster et al. (2011). Yokelson et al. (2007) value of 1651 gkg\(^{-1}\) for Brazilian forest, pasture and grass average lies between our two reported values for rainforest and cerrado fires. Our EF\(_{\text{CO2}}\) value for Brazilian cerrado fires is ~5% higher than the EF\(_{\text{CO2}}\) value of 1646 gkg\(^{-1}\) used in the GFEDv3 and GFASv1.0 emission inventories for savannah fires and again supports the use of savannah EF\(_{\text{CO2}}\) in the global model.

Comparing our two EF\(_{\text{CO2}}\), the flaming cerrado fires in Tocantins emitted 19% more CO\(_2\) per kg of fuel burnt than the Rondonia smouldering
rainforest fire, whereas Ferek et al. (1998), Kaufman et al. (1992) and Ward et al. (1992) cerrado EF$_{	ext{CO}_2}$ were 12%, 7% and 7% higher than rainforest fires in Brazil. The GFEDv3 and GFASv1.0 emission inventories values have a 1.2% increase in CO$_2$ emissions per kg of fuel burnt for savannah fires compared to deforestation fires. The likely reason for the larger difference on CO$_2$ emission for the two fires in this study is due to the highly smouldering state of the Rondonia fire compared to the highly flaming state of the Tocantins fires.

4.2.2 Carbon Monoxide

The Rondonia fire EF$_{\text{CO}}$ of 237 gkg$^{-1}$ is again in good agreement with Christian et al. (2007) value of 229 gkg$^{-1}$ for smouldering logs in Brazil. Other reported values of smouldering rainforest type fires such as Ferek et al. (1998) and Bertschi et al. (2003) have values less than our EF$_{\text{CO}}$, 120 gkg$^{-1}$ and 156.5 gkg$^{-1}$ respectively. This is likely due to the large highly smouldering fire that we measured with a low MCE and high moisture content vegetation producing large concentrations of CO. Global average tropical forest EF$_{\text{CO}}$ are less than half than our value with Akagi et al. (2011) reporting a value of 93 ± 27 gkg$^{-1}$ and Andreae and Merlet (2001) reporting a value of 104 ± 20 gkg$^{-1}$, both of which even when including uncertainties are below our value of smouldering rainforest in Brazil. The EF$_{\text{CO}}$ value of 101gkg$^{-1}$ used in the GFEDv3 and GFASv1.0 emission inventories for deforestation fires is ~57% lower than our value for
smouldering tropical forest fires in Brazil, which again is likely due to the highly smouldering nature of the fire being measured. The Tocantins fires EF\textsubscript{CO} of 68 gkg\textsuperscript{-1} is agrees within the uncertainties to the Ward et al. (1992) value of 57 ± 28 gkg\textsuperscript{-1} for cerrado in Brazil. Our value is also comparable to reported values of savannah fires in Africa, 68 ± 30 gkg\textsuperscript{-1} reported by Sinha et al. (2003), 101 ± 30 gkg\textsuperscript{-1} reported by Wooster et al. (2011) and the global average savannah EF\textsubscript{CO} of 63 ± 17 gkg\textsuperscript{-1} (Akagi et al., 2011). Our value is ~10% higher but in good agreement for savannah fires value used in the GFEDv3 and GFASv1.0 emission inventories. Again, Yokelson et al. (2007) value of 101 gkg\textsuperscript{-1} for Brazilian forest, pasture and grass average lies between our two reported values for smouldering rainforest and flaming cerrado fires. Comparing the two fire types of flaming cerrado and smouldering rainforest fires in Brazil, the smouldering rainforest emits 249% more CO per kg of fuel burnt, whereas Ferek et al. (1998) found a lower increase of 110% between the two fire types and the GFEDv3 and GFASv1.0 emission inventories values have a 66% increase in CO emissions per kg of fuel burnt for deforestation fires compared to savannah fires. This again is likely due to the two fires measured being highly smouldering and highly flaming in nature, leading to large differences in CO emissions.
4.2.3 Methane

The ER for CH$_4$:CO for the Rondonia fire is $38.3 \times 10^{-3}$, over twice the value reported by Christian et al. (2007) of $14.3 \times 10^{-3}$ for smouldering Brazilian logs but ~6 times lower than the ER of $219 \times 10^{-3}$ reported by Bertschi et al. (2003) for smouldering cotton wood and Zambian logs. Bertschi et al. (2003) states this high CH$_4$ is due to emissions from downed woody material. The Tocantins fires CH$_4$:CO ER of $52.6 \times 10^{-3}$ agrees well with the reported value of $53.1 \times 10^{-3}$ for African savannah fires (Yokelson et al., 2003). Overall, ER CH$_4$:CO for Rondonia and Tocantins fires fall within the range of other reported literature values.

The Rondonia fire EF$_{\text{CH}_4}$ value of 5.21 gkg$^{-1}$ is less than half the previously reported values for smouldering logs in Brazil with a value of 17.1 gkg$^{-1}$ reported by Christian et al. (2007), a value of 12.5 gkg$^{-1}$ reported by Ferek et al. (1998) for smouldering Brazilian forest and a value of 19.7 gkg$^{-1}$ for smouldering cotton wood and Zambian logs (Bertschi et al., 2003). Our value does however agree well with the Yokelson et al. (2007) value of 5.68 gkg$^{-1}$ for a mix of Brazilian vegetation and Kaufman et al. (1992) value of 5 gkg$^{-1}$ for Brazilian deforestation fires. The global averages for tropical forest also agree well, 5.07 ± 1.98 gkg$^{-1}$ (Akagi et al., 2011) and 6.8 ± 2 (Andreae and Merlet, 2001). The value of 6.6 gkg$^{-1}$ used in the GFEDv3 and GFASv1.0 emission inventories for deforestation fires is ~27% higher than our reported value for the Rondonia tropical forest fire. The Tocantins fires
EF$_{\text{CH}_4}$ value of 2.05 g kg$^{-1}$ is comparable to Ferek et al. (1998) value of $3.7 \pm 2.7$ g kg$^{-1}$ for Brazilian cerrado fires, with Ward et al. (1992) value of 1.3 g kg$^{-1}$ and Kaufman et al. (1992) value of 0.6 g kg$^{-1}$ slightly lower. Again, African savannah fires EF$_{\text{CH}_4}$ values agree well with Brazilian cerrado fires, 2.19 g kg$^{-1}$ (Yokelson et al., 2003) and 2.5 g kg$^{-1}$ (Wooster et al., 2011). Global average of savannah EF$_{\text{CH}_4}$ also agrees well with our value for Brazilian cerrado, 1.94 ± 0.85 g kg$^{-1}$ (Akagi et al., 2011) and 2.3 ± 0.9 g kg$^{-1}$ (Andreae and Merlet, 2001) for global savannah and grassland. The GFEDv3 and GFASv1.0 emission inventories for savannah fires use a value of 2.2 g kg$^{-1}$, which is ~7% higher than our value for cerrado fires in Brazil and is in good agreement with our value. An increase of 154% CH$_4$ emitted per kg fuel burnt was calculated for the smouldering rainforest fires compared to the cerrado fires, Ferek et al. (1998) found a 238% increase for the same fire types in Brazil and the values used in the GFEDv3 and GFASv1.0 emission inventories have a 200% increase in CH$_4$ emissions per kg of fuel burnt for deforestation fires compared to savannah fires. EF$_{\text{CH}_4}$ vs MCE plots (see supplementary material figure S3 for plots) for the two fires show that as MCE increases emissions of CH$_4$ decrease. R$^2$ values of 0.61 for the Tocantins fires and 0.39 for the Rondonia fire indicate a slight dependence of CH$_4$ emissions on combustion efficiency as was found by Sinha et al. (2003), Yokelson et al. (2007) and McMeeking et al. (2009).
Figure 7. Regressions of excess concentrations of trace gas species used to derive ERs in table 2.
<table>
<thead>
<tr>
<th>Location</th>
<th>CO ER&lt;sub&gt;x/CO2&lt;/sub&gt; (x100)</th>
<th>CH&lt;sub&gt;4&lt;/sub&gt; ER&lt;sub&gt;x/CO2&lt;/sub&gt; (x1000)</th>
<th>CO ER&lt;sub&gt;x/CO2&lt;/sub&gt; (x1000)</th>
<th>CH&lt;sub&gt;4&lt;/sub&gt; ER&lt;sub&gt;x/CO2&lt;/sub&gt; (x1000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rondonia</td>
<td>25.8 ± 0.7</td>
<td>9.9 ± 0.3</td>
<td>38.3 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>Tocantins</td>
<td>6.2 ± 0.3</td>
<td>3.3 ± 0.08</td>
<td>52.6 ± 1.6</td>
<td></td>
</tr>
<tr>
<td>Christian et al. (2007)</td>
<td>27.5 ± 9.3</td>
<td>-</td>
<td>14.3 ± 8.6</td>
<td></td>
</tr>
<tr>
<td>Crutzen et al. (1985)</td>
<td>15.4</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yokelson et al. (2009)</td>
<td>-</td>
<td>-</td>
<td>110.4</td>
<td></td>
</tr>
<tr>
<td>Yokelson et al. (2003)</td>
<td>6.64 ± 2.14</td>
<td>-</td>
<td>53.1 ± 11.8</td>
<td></td>
</tr>
<tr>
<td>Bertschi et al. (2003)</td>
<td>16.85</td>
<td>-</td>
<td>219</td>
<td></td>
</tr>
<tr>
<td>Akagi et al. (2012)</td>
<td>7.13 ± 0.55</td>
<td>-</td>
<td>87.2 ± 2.4</td>
<td></td>
</tr>
<tr>
<td>Wooster et al. (2011)</td>
<td>9.6 ± 3.1</td>
<td>4.3 ± 1.7</td>
<td>4.6 ± 0.7</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.** Emission ratios and uncertainties for CO and CH<sub>4</sub> with respect to CO (ER<sub>x/CO</sub>) and CO<sub>2</sub> (ER<sub>x/CO2</sub>) for the Rondonia fire and the Tocantins fires. The ERs are presented as molar ratios. Uncertainties for the two fires shown are one standard deviation in the line of best fit, due to the uncertainty due to instrument measurements uncertainties being smaller than this value. Calculation methods are described in section 3.3 and figure 7. Also included are other ERs from other studies conducted in Brazil and other locations with the specific fuel type quoted.
<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
<th>CO</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rondonia</strong></td>
<td>1447 ± 156</td>
<td>237 ± 26</td>
<td>5.21 ± 0.58</td>
</tr>
<tr>
<td><strong>Tocantins</strong></td>
<td>1720 ± 196</td>
<td>68 ± 8</td>
<td>2.05 ± 0.24</td>
</tr>
<tr>
<td>(Yokelson et al., 2007) Brazil: forest, pasture, grass average</td>
<td>1651 ± 40</td>
<td>101.41 ± 23.78</td>
<td>5.68 ± 1.38</td>
</tr>
<tr>
<td>(Christian et al., 2007) Brazil: smouldering logs</td>
<td>1346 ± 123</td>
<td>229 ± 64.6</td>
<td>17.1 ± 10</td>
</tr>
<tr>
<td>(Ferek et al., 1998) Brazil: Forest smouldering (FS) and cerrado (C)</td>
<td>FS=831 ± 22, C=928 ± 30</td>
<td>FS= 120 ± 13, C= 57 ± 28</td>
<td>FS= 12.5 ± 2.7</td>
</tr>
<tr>
<td>(Ward et al., 1992) Brazil: Deforestation (DF) and Cerrado (C)</td>
<td>DF=1614, C=1722</td>
<td>DF=110, C=58</td>
<td>DF=6.6, C=1.3</td>
</tr>
<tr>
<td>(Kaufman et al., 1992) Brazil: Deforestation (DF) and cerrado (C)</td>
<td>DF=1664, C=1783</td>
<td>DF=89, C=24</td>
<td>DF=5 C=0.6</td>
</tr>
<tr>
<td>(Yokelson et al., 2009) Yucatan: Mix of crop residue and deforestation</td>
<td>1641 ± 40</td>
<td>80.18 ± 19.4</td>
<td>5.059 ± 2.369</td>
</tr>
<tr>
<td>(Akagi et al., 2011) Global average: Tropical forest (TF), Savannah(S)</td>
<td>TF= 1643 ± 58, S= 1686 ± 38</td>
<td>TF=93 ± 27, S= 63 ± 17</td>
<td>TF=5.07 ± 1.98, S= 1.94 ± 0.85</td>
</tr>
<tr>
<td>(Sinha et al., 2003) Africa: Savannah</td>
<td>1700 ± 60</td>
<td>68 ± 30</td>
<td>1.7 ± 0.98</td>
</tr>
<tr>
<td>(Andreae and Merlet, 2001) Global: Savannah and Grassland (S+GL) and Tropical Forest (TF)</td>
<td>S+GL=1613 ± 95, TF=1580 ± 90</td>
<td>S+GL=65 ± 20, TF=104 ± 20</td>
<td>S+GL=2.3 ± 0.9, TF=6.8 ± 2.0</td>
</tr>
<tr>
<td>(Yokelson et al., 2003) African savannah</td>
<td>1703 ± 39</td>
<td>71.5 ± 21.7</td>
<td>2.19 ± 1.00</td>
</tr>
<tr>
<td>(Bertschi et al., 2003) Laboratory study of smouldering cotton wood and Zambian logs</td>
<td>1461.5</td>
<td>156.5</td>
<td>19.7</td>
</tr>
<tr>
<td>(Wooster et al., 2011) African savannah</td>
<td>1665 ± 54</td>
<td>101 ± 30</td>
<td>2.5 ± 0.9</td>
</tr>
<tr>
<td>(McMeeking et al., 2009) Laboratory study, range of fuel types</td>
<td>1034 ± 175 to 1868 ± 5</td>
<td>43.0 ± 1.4 to 129.5 ± 4.9</td>
<td>0.2 to 5.9 ± 1.2</td>
</tr>
<tr>
<td>GFEDv3 and GFASv1.0 emission inventories Deforestation (DF), Savannah (S) (van der Werf et al., 2010; Kaiser et al., 2012)</td>
<td>DF = 1626, S= 1646</td>
<td>DF = 101</td>
<td>DF = 6.6, S = 61</td>
</tr>
<tr>
<td>GFEDv3 and GFASv1.0 emission inventories Deforestation (DF), Savannah (S) (van der Werf et al., 2010; Kaiser et al., 2012)</td>
<td>DF = 1626, S= 1646</td>
<td>DF = 101</td>
<td>DF = 6.6, S = 61</td>
</tr>
</tbody>
</table>

Table 3. Trace gas emission factors (g kg⁻¹ of dry fuel burned) for Rondonia and Tocantins fires determined using the calculations as shown in section 3.4. Uncertainties were derived in quadrature from the uncertainty in the emission ratios used and the 10% uncertainty in the fuel carbon content used. EF values from previous studies in Brazil are included for comparison with the specific fuel type stated. Also included are EF’s from different geographical locations around the world and values used in GFEDv3 and GFASv1.0 emission inventories.
4.2.4 How representative is the Rondonia fire as a deforestation fire?

Comparing the trace gas EFs from the Rondonia rainforest fire to literature values of trace gas EFs for deforestation fires in Brazil will give an indication of how representative the Rondonia fire is for deforestation fires. Both Ward et al. (1992) and Kaufman et al. (1992) provide $EF_{CO_2}$, $EF_{CO}$ and $EF_{CH_4}$ for deforestation fires in Brazil. The $EF_{CO_2}$ values for Brazilian deforestation fires are between 12-15% higher than the EF value for the Rondonia fire, however when including the associated uncertainty value for the Rondonia fire the deforestation values are only 0.7-3.8% higher. The Rondonia fire emitted much higher amounts of CO compared to Brazilian deforestation fire values (Ward et al., 1992; Kaufman et al., 1992), between 92-137% more CO per kg dry fuel burnt is emitted compared to deforestation fires even when taking into account associated uncertainties. The $EF_{CH_4}$ value of 5.21 g kg$^{-1}$ is within the range of values for Brazilian deforestation fires of 5 g kg$^{-1}$ and 6.6 g kg$^{-1}$ as reported by Kaufman et al. (1992) and Ward et al. (1992) respectively.

4.3 Particulate Emissions

This section compares the emission values derived for the particulate species for the two fire types and to values in literature. Detailed discussion into the processes involved and the differences in values is described in section 5. Fig. 8 shows the scatter plots used for derivation of the particulate
species ERs as explained in section 3.3. Uncertainty values were derived in quadrature using the uncertainties in the instrument measurements, as stated in section 2.1. \( R^2 \) values of between 0.79 and 0.98 indicate good agreement between the two data sets. The particulate species ER values are listed in table 4.

EFs were calculated as described in section 3.4. Table 5 shows these calculated values for particulate species with the associated uncertainties derived in quadrature from the uncertainty in the carbon content of the fuel (0.05) and the uncertainty in the \( ER_{x/CO2} \) values used to calculate the EFs. Also presented are reported values from other types of vegetation.

### 4.3.1 Organic Aerosol

Due to the lack of OA ERs in literature for Brazil we compare our values to those by Jolleys et al. (2012) measured in Northern Australia, SE Mexico City and West Africa (see table 4). Our values for OA:CO ER of 87.5 \( \times 10^{-3} \) for the Rondonia fire and 128.2 \( \times 10^{-3} \) for the Tocantins fires lie within the range of values (51 \( \times 10^{-3} \) to 329 \( \times 10^{-3} \)) reported by Jolleys et al. (2012).

Jolleys et al. (2012) ER values show that OA:CO ER can vary substantially from region to region. The OA/CO\(_2\) value of 4.8 \( \times 10^{-3} \) for the Tocantins fires is comparable to the value of 3.55 \( \times 10^{-3} \) for Californian chaparral fires as presented by Akagi et al. (2012). Our results show that more OA is produced relative to CO\(_2\) in smouldering rainforest fires but more OA to CO is produced during flaming cerrado combustion.
Our results show EF$_{OA}$ value of 5.67 g kg$^{-1}$ for smouldering rainforest fires in Brazil and a value of 2.31 g kg$^{-1}$ for flaming cerrado fires. Yokelson et al. (2009) derived a value of 3.254 ± 0.69 g kg$^{-1}$ for crop residue and deforestation fires in the Yucatan which is within the range of our two reported values. We found a 126% increase in emissions of OA per kg fuel burnt for smouldering rainforest fires in Brazil compared to flaming cerrado fires. When the EF$_{OA}$ was plotted against the MCE (see supplementary material figure S3 for EF vs MCE plots) for each plume intercept of the two fires we found different relationships. The Rondonia plume interception MCEs ranged between 0.77 and 0.82 and when plotted against EF$_{OA}$ a positive correlation was found. EF$_{OA}$ increased with MCE with a gradient of 0.59 and $R^2$ value of 0.59. For the Tocantins plume interceptions MCEs ranged from 0.91 to 0.95 and a negative correlation to EF$_{OA}$ was found with a gradient of -0.78 and an $R^2$ value of 0.41.

### 4.3.2 Organic Carbon

The organic carbon (OC) emission was not directly measured in the campaign; therefore in order to compare with other reported values we estimate this using OA/OC ratio of 1.6 using the conversion of Yokelson et al. (2009) and Akagi et al. (2012) for fresh biomass burning. The OA/OC ratio value is composition, source and age dependent, with values ranging from 1.4 for fresh urban aerosol to 2.2 for aged non-urban aerosol (Turpin and Lim, 2001), therefore this adds another source of uncertainty to the
calculated OC emissions. We use a ratio of 1.6 for the fresh OA measured, which is the value used by Akagi et al. (2012). For Rondonia we estimate the OC:CO ER to be $54.7 \times 10^{-3}$, $28.8 \times 10^{-3}$ higher than Yokelson et al. (2009) reported value of $26.4 \times 10^{-3}$ for a mix of crop residue and deforestation fires in the Yucatan. For the Tocantins fires an OC/CO$_2$ ER value of $3 \times 10^{-3}$ was estimated which is comparable to Californian chaparral fires value of $2.22 \times 10^{-3}$ (Akagi et al., 2012) when including experimental uncertainties. Capes et al. (2008) estimated a OC/CO ER value of $41 \times 10^{-3}$ (using an OA/OC conversions factor of 1.4) for West African Sahel, which is $13.7 \times 10^{-3}$ and $39.1 \times 10^{-3}$ lower than our values for the Rondonia and Tocantins fires respectively.

As many previous studies report EFs for organic carbon (OC) rather than organic aerosol we also estimate this, which will add additional uncertainty into the values. The Rondonia fire EF$_{OC}$ value of $3.54 \pm 0.38$ gkg$^{-1}$ agrees within the uncertainties for average global tropical forests of $4.71 \pm 2.73$ gkg$^{-1}$ (Akagi et al., 2011) and $5.2 \pm 1.5$ gkg$^{-1}$ (Andreae and Merlet, 2001). The EF$_{OC}$ value of $4.3$ gkg$^{-1}$ is used for deforestation fires in the GFEDv3 and GFASv1.0 emission inventories, which is ~22% higher than the value we calculated for tropical forest fire in Rondonia. The Tocantins fires EF$_{OC}$ value of $1.44 \pm 0.26$ gkg$^{-1}$ also agrees well with global averaged savannah values of $2.62 \pm 1.24$ gkg$^{-1}$ (Akagi et al., 2011) and $3.4 \pm 1.4$ (Andreae and Merlet, 2001) when taking into account the associated uncertainties.
Yokelson et al. (2009) value of 2.117 gkg\textsuperscript{-1} for a mix of crop residue and deforestation fires in the Yucatan lies between our two values for rainforest and cerrado values in Brazil. The GFEDv3 and GFASv1.0 emission inventories value of 3.2 gkg\textsuperscript{-1} for savannah fires is over two times higher than the value we calculated for cerrado fires in Brazil. The Rondonia smouldering rainforest fire emitted approximately 145% more OC per kg dry fuel than the flaming cerrado fires in Tocantins.

4.3.3 Black Carbon

There is also a lack of reported BC ERs in literature. Our values show that the BC/CO ER is over an order of magnitude greater for the Tocantins fires compared to the Rondonia fire, 6.5 x10\textsuperscript{-3} compared to 0.29 x10\textsuperscript{-3} respectively. Yokelson et al. (2009) reports a value of 6.3 x10\textsuperscript{-3} for Yucatan fires which is comparable to the value for Tocantins. Capes et al. (2008) reports a BC/CO ER of 7.2 x10\textsuperscript{-3} for West African Sahel which when including measurement uncertainties is also comparable to our value for the Tocantins fires of 6.5 x10\textsuperscript{-3}. Both Capes et al. (2008) and Yokelson et al. (2009) used PSAP (Particle soot absorption photometer) measurements based on an optical absorption technique which may have a positive bias due to the presence of organics, compared to the laser-induced incandescence technique of the SP2 used in this study and by Akagi et al. (2012) which is not affected by non BC containing aerosol (Lack et al., 2008; Bond et al., 2013). The BC/CO\textsubscript{2} ER value for Tocantins is 0.27 x10\textsuperscript{-3}.
which is \(0.51 \times 10^{-3}\) lower than the value of \(0.783 \times 10^{-3}\) reported by Akagi et al. (2012) for Californian chaparral fires. BC ERs to both CO\(_2\) and CO show an order of magnitude more BC is emitted during flaming cerrado combustion.

An \(\text{EF}_{\text{BC}}\) value of \(0.018 \text{ gkg}^{-1}\) was calculated for the Rondonia fire, which is two orders of magnitude smaller than that reported by Ferek et al. (1998), \(1.5 \text{ gkg}^{-1}\) for smouldering rainforest fires in Brazil. Our value is also an order of magnitude smaller than Yucatan fires, \(0.541 \text{ gkg}^{-1}\) (Yokelson et al., 2009) and the global average for tropical forest fires of \(0.52 \pm 0.28 \text{ gkg}^{-1}\) (Akagi et al., 2011) and \(0.66 \pm 0.31 \text{ gkg}^{-1}\) (Andreae and Merlet, 2001). The GFEDv3 and GFASv1.0 emission inventories use a value of \(0.57 \text{ gkg}^{-1}\) for deforestation fires which is over an order of magnitude greater than the value we present for smouldering Brazilian rainforest fires. For the Tocantins fires an \(\text{EF}_{\text{BC}}\) value of \(0.13 \text{ gkg}^{-1}\) was derived, which is a factor of 5 smaller than the value of \(0.7 \text{ gkg}^{-1}\) reported by Ferek et al. (1998) for cerrado fires in Brazil. \(\text{EF}_{\text{BC}}\) values for African savannah fires and global average savannah fires are also larger than our value, \(0.39 \text{ gkg}^{-1}\) (Sinha et al., 2003) and \(0.37 \text{ gkg}^{-1}\) (Akagi et al., 2011) respectively. Sinha et al. (2003) and Ferek et al. (1998) both used quartz filters to collect aerosol samples which were then subsequently heated and the BC content derived. This technique can lead to both positive and negative BC biases (Bond et al., 2013). The GFEDv3 and GFASv1.0 emission inventories use a value
0.46 g kg\(^{-1}\) which is ~3.5 times greater than the value we calculated for the Tocantins cerrado fires. When we plotted EF\(_{BC}\) against MCE for each plume interception (see supplementary figure S3) for the two fires we found little correlation. R\(^2\) values of 0.13 and 0.11 were found for the Rondonia and Tocantins fires respectively which indicates little dependence on combustion efficiency for BC emissions. Ferek et al. (1998) found black carbon emissions to also be independent of the combustion efficiency of Brazilian cerrado, grass and rainforest, with a very low R\(^2\) value of 0.07 when MCEs of between 0.85 and 0.98 were plotted against EF\(_{BC}\).

### 4.3.4 Chloride

For the ER of chloride (Cl\(^-\)) an order of magnitude more Cl\(^-\) was emitted by the flaming cerrado Tocantins fires than the Rondonia fire with ER relative to both CO and CO\(_2\). Our ERs for Cl/CO are 0.46 x10\(^{-3}\) and 7.2 x10\(^{-3}\) for Rondonia and Tocantins fires respectively, with Yokelson et al. (2009) reporting a value of 6.3 x10\(^{-3}\) for the Yucatan crop residue and deforestation which is comparable to our value for the cerrado Tocantins fires rather than the rainforest Rondonia fire. Akagi et al. (2012) value of 0.0497 x10\(^{-3}\) for ER Cl/CO\(_2\) for California chaparral fires is one order of magnitude and two orders of magnitude smaller than our values for rainforest and cerrado fires respectively in Brazil. Overall the Tocantins fires emitted an order of magnitude more Cl\(^-\) than the Rondonia fire.
The Rondonia fire EF\textsubscript{Cl} value of 0.03 gkg\textsuperscript{-1} is an order of magnitude smaller than the global average for tropical forest of 0.15 gkg\textsuperscript{-1} reported by Akagi et al. (2011). However, when including the uncertainty of ± 0.16 gkg\textsuperscript{-1} in this global average this value lies within our reported value. McMeeking et al. (2009) reported a value of 0.03 gkg\textsuperscript{-1} for laboratory burns of Alaskan duff from Boreal forests which is in good agreement to our EF\textsubscript{Cl} for smouldering Brazilian rainforest. The Tocantins fires EF\textsubscript{Cl} of 0.13 gkg\textsuperscript{-1} is an order of magnitude higher than the Rondonia fire EF\textsubscript{Cl}. This value is of the same order of magnitude as reported by Sinha et al. (2003) for African savannah fires, 0.97 gkg\textsuperscript{-1} and for global average savannah fires, 0.23 gkg\textsuperscript{-1} (Akagi et al., 2011), although our reported absolute value is slightly lower than these EFs. The Tocantins fires emitted 333\% more Cl\textsuperscript{-} per kg dry fuel burnt than the Rondonia fire. We found EF\textsubscript{Cl} was not related to MCE, as R\textsuperscript{2} values of 0.34 and 0.0001 for the Rondonia and Tocantins fires were found when EF\textsubscript{Cl} was plotted against MCE (see supplementary figure S3 for plots).

McMeeking et al. (2009) also found no correlation for a range of fuel types. These results indicate that chloride emissions are controlled by the chlorine content of the fuel being burnt rather than the combustion efficiency.

4.3.5 Nitrate

The Tocantins ER NO\textsubscript{3}/CO value of 1.8 x10\textsuperscript{-3} is of the same order of magnitude as reported by Yokelson et al. (2009), 2.9 x10\textsuperscript{-3} in the Yucatan but the Rondonia ER of 0.9 x10\textsuperscript{-3} is an order of magnitude smaller. The ER
NO$_3$/CO$_2$ for Tocantins of 0.07 x10$^{-3}$ is similar to Akagi et al. (2012) value of 0.0961 x10$^{-3}$ for California chaparral.

The Rondonia fire EF$_{NO3}$ value of 0.06 gkg$^{-1}$ is again an order of magnitude smaller than the global average value of 0.11 gkg$^{-1}$ for tropical forests (Akagi et al., 2011) and Yokelson et al. (2009) value of 0.233 gkg$^{-1}$ for Yucatan crop residue and deforestation fires. Our reported value does lie within the range of EF$_{NO3}$ calculated by McMeeking et al. (2009) for a range of biomass fuel types. The Tocantins fires EF$_{NO3}$ value of 0.035 gkg$^{-1}$ is of the same order of magnitude reported by Akagi et al. (2011), 0.016 gkg$^{-1}$ for the average global savannah emissions and is within the range of values reported by McMeeking et al. (2009). Sinha et al. (2003) reported an order of magnitude greater EF$_{NO3}$ value of 0.16 gkg$^{-1}$ for savannah fires in Africa. The possible reasons for these differences are discussed in section 5.

### 4.3.6 Sulphate

The Rondonia ER SO$_4^{2-}$/CO value of 0.51 x10$^{-3}$ is similar to Yokelson et al. (2009) value of 0.6 x10$^{-3}$ for Yucatan crop residue and deforestation fires. The Tocantins ER SO$_4^{2-}$/CO$_2$ value of 0.003 x10$^{-3}$ is comparable to the value of 0.000358 x10$^{-3}$ for Californian chaparral fires (Akagi et al., 2012).

The Rondonia fire EF$_{SO4}$ value of 0.033 gkg$^{-1}$ is comparable to the value of 0.047 gkg$^{-1}$ from Yokelson et al. (2009) for crop residue and deforestation fires in the Yucatan when taking into account associated uncertainties.
However, our value is an order of magnitude less than Akagi et al. (2011) value of $0.133 \text{ gkg}^{-1}$ for tropical forest average globally. The Tocantins fire $E_{\text{SO}_4}$ value of $0.0015 \text{ gkg}^{-1}$ is an order of magnitude smaller than Akagi et al. (2011) value of $0.018 \text{ gkg}^{-1}$ for average global savannah fires and two orders of magnitude smaller than Sinha et al. (2003) value of $0.17 \text{ gkg}^{-1}$ for African savannah. The possible reasons for the $E_{\text{SO}_4}$ differences are discussed in section 5.

### 4.3.7 Ammonium

The ER $\text{NH}_4^+/\text{CO}$ value of $2.4 \times 10^{-3}$ for Yucatan fires Yokelson et al. (2009) is of the same order of magnitude of the Tocantins value of $1.4 \times 10^{-3}$ but an order of magnitude greater than the Rondonia fire value of $0.4 \times 10^{-3}$. Akagi et al. (2012) value for ER $\text{NH}_4^+/\text{CO}_2$ for Californian chaparral fires is within the range of our reported values for the Tocantins ($0.05 \times 10^{-3}$) and Rondonia ($0.07 \times 10^{-3}$) fires.

For both the Rondonia and Tocantins fires a value of $0.026 \text{ gkg}^{-1}$ was calculated for $E_{\text{NH}_4}$, which is an order of magnitude less than the value of $0.192 \text{ gkg}^{-1}$ reported by Yokelson et al. (2009) for Yucatan crop residue and deforestation fires. Our values are however an order of magnitude greater than reported by Akagi et al. (2011) of $0.0564 \text{ gkg}^{-1}$ and $0.0035 \text{ gkg}^{-1}$ for global averaged tropical forest and savannah fires respectively. Our values
also lie within the range of $\text{EF}_{\text{NH}_4}$ calculated by McMeeking et al. (2009) for various fuel types measured in the laboratory.

### 4.3.8 How representative is the Rondonia fire as a deforestation fire?

In order to assess how representative the Rondonia fire is for deforestation fires the particulate species EFs are compared to deforestation values from literature. Due to there being a lack of particulate species EFs from Brazilian deforestation fires we are unable to give a direct comparison unlike the trace gas species emitted. We therefore compare our values to the deforestation values used in the GFEDv3 and GFASv1.0 emission inventories (Kaiser et al., 2012; van der Werf et al., 2010) and to the values presented by Akagi et al. (2011) which under the tropical forest category includes deforestation fires. The estimated $\text{EF}_{\text{OC}}$ for the Rondonia fire when including associated uncertainties is within the range of values for the two deforestation EFs. The $\text{EF}_{\text{BC}}$ however is an order of magnitude below the EFs presented by Kaiser et al. (2012) and Akagi et al. (2011) for deforestation fires. The EF values presented by Akagi et al. (2011) for $\text{Cl}^-$, $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ for tropical forest fires (which under this category include deforestation fires) are an order of magnitude greater than the values for the Rondonia fire, however for $\text{NH}_4^+$ it is an order of magnitude smaller. How representative this fire is as a deforestation fire will be further discussed in section 5.
Figure 8. Example scatter plots of species used to derive ERs for the Rondonia and Tocantins fires as stated in table 4
Table 4. Emission ratios and uncertainties for particulate species with respect to CO (ER$_{\text{CO}}$) and CO$_2$ (ER$_{\text{CO}_2}$) for the Rondonia fire and the Tocantins fires. The ERs are presented as molar ratios. Calculation methods are described in section 3.3 and figure 7. Uncertainties were calculated in quadrature using the uncertainties in the instrument measurements. Also included are other ERs from other studies conducted in Brazil and other locations with the specific fuel type quoted. 1 OC estimated assuming OA/OC is 1.6 in fresh smoke (Akagi et al., 2012; Yokelson et al., 2009). 2 Derived using OA/OC ratio of 1.4 (Capes et al., 2008).
<table>
<thead>
<tr>
<th></th>
<th>OA</th>
<th>OC</th>
<th>BC</th>
<th>Cl</th>
<th>NO\textsubscript{2}</th>
<th>SO\textsubscript{4}\textsuperscript{2}</th>
<th>NH\textsubscript{4}\textsuperscript{+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rondonia</td>
<td>5.67 ± 1.81</td>
<td>3.54 ± 1.13*</td>
<td>0.018 ± 0.006</td>
<td>0.03 ± 0.01</td>
<td>0.060 ± 0.002</td>
<td>0.033 ± 0.011</td>
<td>0.026 ± 0.008</td>
</tr>
<tr>
<td>Tocantins</td>
<td>2.31 ± 0.74</td>
<td>1.44 ± 0.46*</td>
<td>0.13 ± 0.04</td>
<td>0.13 ± 0.04</td>
<td>0.035 ± 0.011</td>
<td>0.0015 ± 0.0005</td>
<td>0.026 ± 0.008</td>
</tr>
<tr>
<td>Ferek et al. (1998) Brazil:</td>
<td>-</td>
<td>FS= 17.9 ± 7.6</td>
<td>FS= 1.5 ± 0.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Forest smouldering (FS) and cerrado (C)</td>
<td></td>
<td>C= 5.9 ± 2.8</td>
<td>C= 0.7 ± 0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Yokelson et al. (2009) Yucatan: Mix of crop residue and deforestation</td>
<td>3.254 ± 0.690</td>
<td>2.117 ± 0.569</td>
<td>0.541 ± 0.163</td>
<td>0.509 ± 0.377</td>
<td>0.233 ± 0.056</td>
<td>0.047 ± 0.024</td>
<td>0.192 ± 0.136</td>
</tr>
<tr>
<td>Akagi et al. (2011) Global average: Tropical forest (TF), Savannah(S)</td>
<td>-</td>
<td>TF= 4.71 ± 2.73</td>
<td>TF= 0.52 ± 0.28</td>
<td>TF= 0.15 ± 0.16</td>
<td>TF= 0.11 ± 0.05</td>
<td>TF= 0.13 ± 0.088</td>
<td>TF= 0.00564 ± 0.0172</td>
</tr>
<tr>
<td></td>
<td>S= 2.62 ± 1.24</td>
<td>S= 0.37 ± 0.20</td>
<td>S= 0.23 ± 0.055</td>
<td>S= 0.016 ± 0.013</td>
<td>S= 0.018 ± 0.009</td>
<td>S= 0.0035 ± 0.0035</td>
<td></td>
</tr>
<tr>
<td>Sinha et al. (2003)Africa: Savannah</td>
<td>-</td>
<td>2.3 ± 1.2</td>
<td>0.39 ± 0.19</td>
<td>0.97 ± 1.4</td>
<td>0.16 ± 0.11</td>
<td>0.17 ± 0.18</td>
<td>-</td>
</tr>
<tr>
<td>Andreae and Merlet (2001) Global: Savannah and Grassland (S+GL) and Tropical Forest (TF)</td>
<td>-</td>
<td>S+GL= 3.4 ± 1.4</td>
<td>S+GL= 0.48 ± 0.18</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>TF= 5.2 ± 1.5</td>
<td>TF= 0.66 ± 0.31</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>McMeeking et al. (2009) Laboratory study, range of fuel types</td>
<td>-</td>
<td>0.5 to 44.2</td>
<td>-</td>
<td>0.03 ± 0.02 to 5.39</td>
<td>0.0 ± 0.0 to 0.84 ± 1.17</td>
<td>0.01 to 0.73 ± 0.34</td>
<td>0.0 ± 0.01 to 0.51</td>
</tr>
<tr>
<td>GFEDv3 and GFASv1.0 emission inventories Deforestation (DF), Savannah (S) (van der Werf et al., 2010; Kaiser et al., 2012)</td>
<td>-</td>
<td>DF = 4.3</td>
<td>DF = 0.57</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>S = 3.2</td>
<td>S = 0.46</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5. Particulate species emission factors (g kg\textsuperscript{-1} of dry fuel burned) for Rondonia and Tocantins fires determined using the calculations as shown in section 3.4. Uncertainties were derived in quadrature from the uncertainty in the emission ratios used and the 10\% uncertainty in the fuel carbon content used. EF values from previous studies in Brazil are included for comparison with the specific fuel type stated. Also included are EF’s from different geographical locations around the world and values used in GFEDv3 and GFASv1.0 emission inventories.*OC estimated assuming OA/OC is 1.6 in fresh smoke (Akagi et al., 2012) (Yokelson et al., 2009).
Fig. 9 shows the ratios of excess OA to excess BC for the two different fire types. The ratio of 253 for the Rondonia fire shows the preferential emission of OA to BC. Compare this to the Tocantins flaming cerrado fires with a ratio of 18, emitted much more BC relative to OA than the Rondonia fire.

**Figure 9.** Excess OA vs BC for the Tocantins and Rondonia fires. Gradient shown with uncertainty of one standard deviation. $R^2$ values shows OA and BC emissions are well correlated.

4.4 Chemical Characteristics of Aerosols

The total excess mass of aerosol species integrated over the plume interceptions as a percentage of the total mass of aerosols measured (BC, OA, chloride, ammonium, sulphate and nitrate) are presented in Fig. 10 and table 6. The aerosol in the Rondonia fire was composed of over 95% organic mass emitted which is comparable to Sahu et al. (2012) value of 95.4% for a Californian forest fire with a MCE of 0.869. Ferek et al. (1998)
reports a lower value of 86.55% (Estimated value based on OA/OC of 1.6 from Akagi et al. (2012)) for a smouldering Brazilian rainforest fire. Ferek et al. (1998) value of 7.75% for BC mass is over an order of magnitude greater than our value for smouldering rainforest BC mass of 0.44%.

The value of 88.12% for OA for cerrado fires in Brazil by Ferek et al. (1998) is in agreement with our value of 88.66% for the Tocantins cerrado fires. Ferek et al. (1998) values for BC (6.76%), chloride (2.98%) and nitrate (1.29%) for cerrado fires are also all comparable to our measurements for Brazilian cerrado of 4.22%, 4.86% and 1.26% respectively.

Comparing the Rondonia and Tocantins fire mass fractions we see that the smouldering rainforest fire emitted 7.08% more OA to total aerosol mass compared to the flaming cerrado fires. The flaming cerrado fires emitted almost ten times more BC by mass to the total particulate mass than the smouldering rainforest fire. Yamasoe et al. (2000) found the difference was only 3 times as much for the same fire types as we sampled in Brazil. Yamasoe et al. (2000) studied particulate emissions from both smouldering and flaming cerrado and rainforest fires in Brazil. It was found that in both vegetation types the flaming fires emitted twice as much BC by mass relative to the total mass of particulates emitted and the cerrado fires emitted more BC than the rainforest fires relative to particulate mass, which is in agreement with our results.
The Tocantins fires emitted almost 9 times more Cl⁻ by mass of total particulates than the Rondonia fire which is in agreement with Yamasoe et al. (2000) who found the difference was approximately eleven times more for the flaming cerrado fires compared to the smouldering rainforest fire.

![Mass fraction of aerosol components as a percentage of total aerosol mass, including black carbon, organic aerosol, chloride, ammonium, sulphate and nitrate for the Rondonia fire, Tocantins fires and values for previous studies from the Yucatan (Yokelson et al., 2009), Brazil (Ferek et al., 1998), California (Sahu et al., 2012) and North America (Kondo et al., 2011). Ferek et al. (1998) and Yokelson et al. (2009) reported a percentage total including other particulate matter that we do not have data for, therefore we recalculated the values presented just including BC, organics and inorganics in order to compare values.*OA for the two Brazilian values estimated assuming OA/OC is 1.6 in fresh smoke (Akagi et al., 2012; Yokelson et al., 2009).](image-url)
Table 6. Mass fraction of aerosol components as a percentage of total aerosol mass, including black carbon, organic aerosol, chloride, ammonium, sulphate and nitrate for the Rondonia fire, Tocantins fires and values for previous studies from the Yucatan (Yokelson et al., 2009), Brazil (Ferek et al., 1998) and California (Sahu et al., 2012). Ferek et al. (1998) and Yokelson et al. (2009) reported a percentage total including other particulate matter that we do not have data for, therefore we recalculated the values presented just including BC, organics and inorganics in order to compare values.*OA for the two Brazilian values estimated assuming OA/OC is 1.6 in fresh smoke (Akagi et al., 2012; Yokelson et al., 2009).

<table>
<thead>
<tr>
<th>Species</th>
<th>Rondonia</th>
<th>Tocantins</th>
<th>Yucatan: Mix of crop residue and deforestation (Yokelson et al., 2009)</th>
<th>Brazil: Forest smouldering (FS) and cerrado (C) (Ferek et al., 1998)</th>
<th>California Forest (Sahu et al., 2012)</th>
<th>North America (Kondo et al., 2011)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCE:</td>
<td>0.79</td>
<td>0.94</td>
<td>0.93</td>
<td>FS = 0.87</td>
<td>C = 0.94</td>
<td>0.869</td>
</tr>
<tr>
<td>OA</td>
<td>95.74</td>
<td>88.66</td>
<td>68.04</td>
<td>86.55*</td>
<td>88.12*</td>
<td>95.4 ± 31.2</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.99</td>
<td>0.06</td>
<td>1.02</td>
<td>3.07</td>
<td>0.9</td>
<td>1.2 ± 0.4</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>1.47</td>
<td>1.29</td>
<td>4.95</td>
<td>1.02</td>
<td>1.29</td>
<td>0.8 ± 0.3</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.80</td>
<td>0.90</td>
<td>4.14</td>
<td>0.15</td>
<td>0.05</td>
<td>1.2 ± 0.4</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.55</td>
<td>4.86</td>
<td>11.01</td>
<td>1.46</td>
<td>2.98</td>
<td>0.10 ± 0.03</td>
</tr>
<tr>
<td>BC</td>
<td>0.44</td>
<td>4.22</td>
<td>10.84</td>
<td>7.75</td>
<td>6.76</td>
<td>1.2 ± 0.5</td>
</tr>
</tbody>
</table>

Fig. 11 shows the black carbon mass and number size distributions for the Rondonia and Tocantins fires. The grey bound gives the minimum and maximum size distributions from the plume intercepts on each flight to show the plume to plume variations, with the solid black line giving the average. There is little difference in the BC size distributions of the two fires despite the large difference in MCE. Mass median diameters are 0.2 µm for both fires and number median diameters are 0.1 µm for both fires.
This is consistent with previous studies such as Kondo et al. (2011) and Sahu et al. (2012).

Figure 11. Black carbon number- size and mass-size distributions for in plume measurements of the Rondonia and Tocantins fires. The grey bound gives the minimum and maximum size distributions from the plume intercepts on each flight and the solid black line gives the average. Note the difference in scales between Rondonia and Tocantins size distributions.

5. Discussion

Comparing the MCE between the two fires gives an indication of the different combustion regimes of the Rondonia and Tocantins fires. As expected the smouldering rainforest fire in Rondonia produced much higher concentrations of CO relative to CO$_2$ compared to the flaming cerrado fires in Tocantins. The CH$_4$ ER results show flaming cerrado fires emit more CH$_4$ relative to CO than smouldering rainforest fires in Brazil, but relative to CO$_2$ smouldering rainforest fires emit more CH$_4$ than flaming cerrado fires. The EF$_{CH4}$ results show that CH$_4$ is preferentially emitted during
smouldering rainforest fires compared to flaming savannah fires, which is in agreement with previous studies. Overall the trace gas ERs and EFs are in good agreement with previous literature values of similar fire types in Brazil and emissions of trace gases are dependent on the combustion efficiency of the fire.

Overall, we found that flaming cerrado fires in Brazil emit an order of magnitude more BC, 622% more per kg dry fuel than smouldering rainforest fires, whereas Ferek et al. (1998) only found a 50% increase. BC emissions are also dependent on the fuel moisture content and local relative humidity (Hoffa et al., 1999; Bond et al., 2004), which was very high for the Rondonia fire. For the particulate phase species 96% of the total mass for the smouldering forest fires was composed of organic aerosol as opposed to 89% of the total mass for the flaming cerrado fires. These results, combined with the calculated ERs and EFs for OA and BC show that flaming cerrado fires tend to emit more BC mass, which is important as BC in smoke lowers the single scattering albedo (SSA) (Yokelson et al., 2009) thereby affecting radiative balance and climate change. Smouldering rainforest fires tend to preferentially emit OA compared to the cerrado fires (145% more OA per kg dry fuel burnt for the Rondonia fire compared to Tocantins fires) and this could significantly affect cloud droplet formation. With 45-75% of biomass burning organic aerosol being highly water soluble these species act as cloud condensation nuclei (CCN) and perturb the radiative balance (Asa-
Awuku et al., 2008; Reid et al., 2005). For the smouldering rainforest fire it was found that EF_{OA} increased with increasing MCE compared to the EF_{OA} for the flaming cerrado fires which decreased with increasing MCE. For the smouldering rainforest fire this is likely due to at low MCE the oxygen supply is low and the fire is cooler so OA doesn’t form but at higher MCE the fire is hotter more OA can form. For the flaming cerrado fire the decrease in EF_{OA} with increasing MCE is likely due to the organic matter turning into CO_{2} at the higher MCE. The optimum OA production is likely to be in the middle of the MCEs for the two fires.

The low ERs and EFs for Cl\(^-\) and MCE for the Rondonia fire indicates that either the fire was not hot enough to volatize the Cl\(^-\) or the chlorine fuel content of the vegetation was low. Fig. 8 shows that through some of the plume interceptions during the Tocantins flight excess Cl\(^-\) concentrations were very low and similar to excess Cl\(^-\) concentrations observed in the Rondonia rainforest flight. As was observed and can be seen in Fig. 4 the cerrado region of Brazil contains a variety of vegetation types each with different chemical compositions. These low Cl\(^-\) concentrations in the Tocantins fires may be as a result of the cerrado containing woody fuels such as young trees (Ferek et al., 1998) which will differ in chlorine content from grassy vegetation. These outlier values for Tocantins compare well with the values in the Rondonia rainforest fire (Fig. 8). The enhancement in Cl\(^-\) emissions for the Tocantins fires could also be due to the influence of
marine sea-salt aerosol, which Yamasoe et al. (2000) states could be one of a numerous of reasons for enhance Cl− emissions in the cerrado region (Martin et al., 2010). The cerrado region of Tocatins state is approximately 1000km from the coast of East Brazil whereas the fires measured in Rondonia state are approximately 3000km away from the coast. As the predominant wind direction in the Amazon region is from the East (Longo et al., 1999), this could play a part in the increased Cl− emissions in the cerrado fires as McKenzie et al. (1996) found, the chlorine content of fuel is influenced by the distance from the coast.

We also found EFCl was not related to MCE, as R² values of 0.34 and 0.0001 for the Rondonia and Tocantins fires were found when EFCl was plotted against MCE. McMeeking et al. (2009) also found no correlation for a range of fuel types. These results indicate that chloride emissions are controlled by the chlorine content of the fuel being burnt rather than the combustion efficiency.

Overall, our results show that smouldering rainforest fires emit slightly more NO3−, 71% per kg fuel burnt than flaming cerrado fires in Brazil. We plotted the EFNO3 against the MCE for each plume intercept for the two fires and found no correlation between the two data sets (R² of 0.1 for the Rondonia fire and R² of 0.03 for the Tocantins fires) which indicates NO3− emission is not related to the combustion efficiency of the fire but may be due to the variability in nitrogen content of the fuel. Sinha et al. (2003) also
found a low $R^2$ value of 0.24 for initial smoke measured from African savannah fires. It should however be noted that transformations of NO$_x$ to gas phase HNO$_3$, which can then partition to the particle phase can occur even in initial smoke (Sinha et al., 2003).

Comparing our two sampled fire types, the Rondonia fire emitted over an order of magnitude more SO$_4^{2-}$ per kg fuel burnt than the flaming cerrado Tocantins fires. Again, this difference is likely due to the sulphur content of the fuel rather than the MCE. $R^2$ values of 0.01 and 0.02 for the Rondonia and Tocantins fires respectively were found when EF$_{SO4}$ was plotted against MCE for each plume intercept indicating little SO$_4^{2-}$ emission dependence on combustion efficiency. Sinha et al. (2003) found a $R^2$ value of 0.39 for African savannah fires which although higher than our values it shows weak correlation. McMeeking et al. (2009) also found that EF$_{SO4}$ were only weakly correlated with MCE. Oxidation of SO$_2$ to SO$_4^{2-}$ (which can then partition to the particle phase) also occurs in BB plumes however, due to our EF$_{SO4}$ being smaller than other reported values and our sampling being close to source, this is unlikely to have substantially occurred in the two fires we sampled.

We are unaware of particulate phase species EF values for fires in Brazil (apart from Ferek et al. (1998) EF$_{BC}$ value for smouldering Brazilian rainforest which is two orders of magnitude greater than our value for the Rondonia fire) and are therefore unable to investigate how representative
these values are for the Brazilian environment, however we are able to compare to EFs to other studies in numerous locations. We find that our $\text{EF}_{\text{OC}}$ values for Brazilian smouldering rainforest fires are of the same order of magnitude as averaged tropical forest $\text{EF}_{\text{OC}}$ values globally, but our value is on the low side. The EFs calculated for BC and inorganics for the smouldering Brazilian rainforest fires are generally an order of magnitude lower than other reported values for tropical forest. As stated earlier although the emission of these species is likely to be predominately due to the fuel type of the fires, if the fire is not hot enough to form these species then concentrations in the smoke plume will be low. This is a possible explanation for the very low EF values we present for BC and inorganics species for the smouldering rainforest fire and is related to the very low MCE of 0.79. The Brazilian cerrado fires EFs for OC, BC and inorganic species were generally of the same order of magnitude to values reported for average global savannah emissions, but the Tocantins $\text{EF}_{\text{BC}}$ was generally lower than previous values. It should be noted that SAMBBA was the first campaign to fly the C-ToF-AMS and SP2 instruments in a tropical biomass burning environment. BC mass concentrations in previous literature were measured using numerous techniques. Yokelson et al. (2009) used a particle soot absorption photometer (PSAP) and nephelometer to estimate BC mass using absorption efficiency and Sinha et al. (2003) and Ferek et al. (1998) used an optical absorption technique by collection on filter to determine BC
mass. These absorption based measurement techniques are prone to biases and may overestimate BC mass due to the presence of other absorbers such as OA and due to optical interactions between particles and the filter matrix (Lack et al., 2008; Bond et al., 2013). Therefore, in a biomass burning environment where there are high concentrations of organics, the SP2 data provides a better reflection of BC mass, as the SP2 is not prone to this bias. The SP2 however may not detect black carbon containing particles with a diameter less than ~60nm, which may also account for the smaller emission values. However, there would need to be a very large amount of black carbon particles below this size for there to be an appreciable difference in black carbon mass. Therefore this different measurement technique compared to previous studies may be the reason for the smaller emission measurements of BC compared to literature values. Kondo et al. (2011) studied black carbon emissions from biomass burning in North America and Asia using the SP2 instrument. Although the values Kondo et al. (2011) presented are not directly comparable to our values due the emissions being a few hours old rather than a few minutes old, Kondo et al. (2011) found these black carbon emission ratios to be 2-5 times lower than other literature values. This suggests that the likely reason for the low black carbon emissions measured during the two flights presented in this study compared to literature values was, at least in part due to instrument differences. The
emission values presented provide up to date ERs and EFs for different Brazilian biomass burning fire types.

To assess how representative the Rondonia rainforest fire is of deforestation fires the Rondonia fire emissions is compared to literature values of deforestation fire emissions in Brazil in Sec. 4. The comparable values of EF$_{\text{CO}_2}$ and EF$_{\text{CH}_4}$ but the much higher EF$_{\text{CO}}$ for the Rondonia fire compared to Brazilian deforestation fire emissions indicate that the Rondonia fire is representative of deforestation fires but is on the extreme smouldering side of deforestation fires. The estimated EF$_{\text{OC}}$ from the Rondonia fire is in agreement with global values of deforestation fires but EFs of BC and inorganics are lower than deforestation fire values. These lower values of organics and inorganics are likely due to the highly smouldering nature of the fire and again are on the more smouldering side of deforestation fires. The difference in black carbon emissions may be due to both the smouldering nature of the fire and due to the instrument measurements compared to previous studies. Kaufman et al. (1992) studied a deforestation fire in Brazil with combustion efficiency (CE) of 0.86, compared to the MCE for the Rondonia fire of 0.79 (CE and MCE are closely related and only differ within a few percent (Ferek et al., 1998)). The EF$_{\text{CO}_2}$ of 1586 g kg$^{-2}$ and EF$_{\text{CO}}$ of 121 g kg$^{-1}$ for the Brazilian deforestation fire in Kaufman et al. (1992) compare to the values of 1447 ± 156 g kg$^{-1}$ and 237 ± 26 g kg$^{-1}$ for Rondonia fire respectively. The EF$_{\text{CO}_2}$ values agree within the associated
uncertainties, with the EF\textsubscript{CO} 74% higher for the Rondonia fire. Kaufman et al. (1992) also presents deforestation emission values from Ward (1986) with a deforestation fire CE value of 0.77 ± 0.07 and a CO:CO\textsubscript{2} ER of 18 ± 7 compared to the Rondonia CO:CO\textsubscript{2} value of 25.8 ± 0.7, taking into account uncertainties these values are comparable. Ward et al. (1992) also observed a smouldering deforestation fire in Brazil with a combustion efficiency of <0.80, which is again comparable to the 0.79 MCE of the Rondonia fire. These results suggest that the Rondonia fire is representative of smouldering deforestation fires in Brazil.

Deforestation fires in Brazil have been shown to have a mix of flaming and smouldering combustion. For example Ward at al. (1992) observed deforestation fires in Brazil with combustion efficiencies ranging from 0.88 for flaming fires to less than 0.80 for smouldering deforestation fires. The contribution from these stages of combustion for deforestation fires is unknown and further investigations need to take place. Compare this to cerrado fires which are predominately flaming combustion due to the dry fine fuel which burns quickly and have high combustion efficiencies generally of 0.93 or greater (e.g. Ward et al. (1992), Ferek et al. (1998)).

Current global fires models e.g. the Global Fire Assimilation System (GFASv1.0) use a global particulate emission enhancement factor of 3.4 (with a discrepancy of 4.1 in South America) in order to reproduce global aerosol optical depths (AODs) (Kaiser et al., 2012). One of the possible
reasons for this underestimation in model AODs has been suggested to be
due to inaccuracies in the emission factors used in the models. The EF
values presented here for particulate matter are generally within range or
lower than previous reported EF values, which would lead to a larger
discrepancy between model AODs and observed AOD. Based on our
results, the emission factors presented are not able to account for this
discrepancy.

6. Conclusions

The SAMBBA 2013 aircraft campaign successfully provided biomass
burning emission measurements for a wide range of different fire types in
Brazil. The aerosol data presented was collected using the C-ToF-AMS and
SP2, which provided high accuracy chemical composition measurements
and it is the first time these instruments have been used together in a tropical
environment. We presented up to date fire integrated emission ratios and
emission factors from a large smouldering rainforest fire in Rondonia state
and numerous smaller man-made flaming cerrado fires in Tocantins state.
We also compared these emissions to those presented in previous studies.
These fires differ both in vegetation type (rainforest vs cerrado) and in
combustion phase (smouldering vs flaming). The two fires differed
substantially in emissions of CO and CO₂, resulting in MCEs of 0.79 and
0.94 for the Rondonia and Tocantins fires respectively. CH₄ emissions also
differed with the Rondonia fire having an EF_{CH₄} 154% higher per kg dry
fuel burnt than the Tocantins fires. We found that gas phase emissions of CO, CO$_2$ and CH$_4$ depend strongly on MCE, as has been found in previous studies such as McMeeking et al. (2009). Organic aerosol emissions also varied with the Rondonia smouldering rainforest fire having a higher emission factor for OA than the Tocantins flaming cerrado fires. EF$_{OA}$ vs MCE plots showed that for Rondonia emissions of OA increase with increasing MCE but decreased with MCE for the Tocantins fires over the MCE range. This is likely due to the fire being cool at lower MCE and oxygen supply is low so OA doesn’t form compared to more OA being converted to CO$_2$ at high MCE, therefore there is likely to be an optimum in OA emission between these two extremes. The BC emission per kg fuel burnt was an order of magnitude higher for the Tocantins fires than the Rondonia fire and we did not find a significant correlation of this to MCE. We also found similar BC mass-size distributions between the two fire types which is in agreement with other studies. Inorganic aerosols emitted also varied between the fire types. We found weak correlation of inorganics to MCE indicating that these emissions are more dependent on the fuel type and composition rather than combustion efficiency as was found by studies such as Ward and Hardy (1991) and McMeeking et al. (2009). Particulate species ERs and EFs were found these to be within range or lower than values reported in previous literature. EFs for black carbon were lower than previous reported literature values, which is possibly due to the previous
studies overestimating black carbon mass. These previous studies used optical techniques to derive black carbon mass which can be biased when high concentrations of organic aerosol are present. The SP2 however is unable to measure black carbon particles with a diameter less than ~60nm which may also account for the lower black carbon measurements. All of these reported emissions with respect to previous studies values are discussed in detail. The Rondonia wild fire was shown to be representative of more smouldering deforestation fires. The calculated ERs and EFs provide important fire type specific data for use in emission inventories. This can be used in numerical modelling to increase accuracy and reliability of model outputs. Current global models use a model enhancement factor of 3.4 for particulate emissions from fires to match global aerosol optical depth observations. Our results compare well with emission inventory values apart from black carbon and this contributes only around 10% or less to the total aerosol load from biomass burning, which indicates that the 3.4 enhancement used in models is not caused by issues in inventory values.
References


Chand, D., Guyon, P., Artaxo, P., Schmid, O., Frank, G. P., Rizzo, L. V., Mayol-Bracero, O. L., Gatti, L. V., and Andreae, M. O.: Optical and physical properties of aerosols in the boundary layer and free troposphere over the Amazon Basin during the biomass burning season, Atmospheric Chemistry and Physics, 6, 2911-2925, 2006.


do Carmo, C. N., Alves, M. B., and Hacon, S. D.: Impact of biomass burning and weather conditions on children's health in a city of Western Amazon region, Air Quality Atmosphere and Health, 6, 517-525, 10.1007/s11869-012-0191-6, 2013.


van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S., Morton, D. C., DeFries, R. S., Jin, Y., and van Leeuwen, T. T.: Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997-2009), Atmospheric Chemistry and Physics, 10, 11707-11735, 10.5194/acp-10-11707-2010, 2010.


Yokelson, R. J., Andreae, M. O., and Akagi, S. K.: Pitfalls with the use of enhancement ratios or normalized excess mixing ratios measured in plumes to characterize pollution sources and aging, Atmospheric Measurement Techniques, 6, 2155-2158, doi:10.5194/amt-6-2155-2013, 2013.
Chapter 8: Conclusions

8.1 Summary of Research Findings

This dissertation provides a quantitative comparison of biomass burning emissions from two fires in Brazil varying in combustion fuel type and combustion stage. Emission of trace gas species varied considerably between the two fire types with a 250% increase in CO emissions per kg dry fuel burnt for the smouldering rainforest fires in comparison to the flaming cerrado fires. Trace gas emission factors were found to be dependent on the modified combustion efficiency of the fire (MCE). Trace gas emission values were also found to be in agreement with previous reported values in literature.

Particulate species also varied between the two fires. The smouldering rainforest fire emitted double the mass of organic aerosol per kg dry fuel burnt than the flaming cerrado fires. The smouldering rainforest fires also emitted an order of magnitude less black carbon. Organic aerosol was found to be dependent on MCE whereas there was little dependence on MCE for black carbon emissions. Inorganic emissions also varied between fire types and emissions of these species were found to depend more on the fuel type being burnt than the MCE. In relation to previous reported particulate emission values it was found that the two fires studied were generally within
the range or lower than previous literature values. Black carbon emissions were lower than previous literature values and this is likely to be caused by the different instruments used to measure back carbon. The majority of previous studies of biomass burning studies used an optical absorption technique to determine black carbon mass. This technique is subjected to positive biases due to the high concentrations of organic aerosol present in biomass burning plumes. Further analysis comparing the SP2 and PSAP that were present on the aircraft during SAMBBA will indicate the bias involved in these measurements. The black carbon measurements used in SAMBBA and in this dissertation were made using a laser induced incandescent technique which is not affected by this bias but may have a slight negative bias due to the SP2’s inability to measure black carbon particles less than 60nm.

Although the rainforest fire observed during SAMBBA was likely to be caused by lightning rather than a human induced deforestation fire, the fire studied is a reasonable representation of the smouldering deforestation fires when the emissions are compared to literature values, indicated by the low MCE.
8.2 Implications

The ERs and EFs presented in this dissertation provide fire type specific values for use in emission inventories (e.g. GFEDv3 and GFASv1.0 (Kaiser et al., 2012; van der Werf et al., 2010)). These emission inventory values are then utilised in models, therefore it is imperative that up to date and accurate emission values used. Current fire and atmospheric models which assimilate the fire radiative power and combustion rate from satellite observations and the EFs from emission inventories struggle to correctly represent the observed global aerosol optical depths (AOD). Therefore a global emission enhancement factor of 3.4 is needed to correct for this discrepancy (Kaiser et al., 2012). This discrepancy is even larger, 4.1 for South America (Kaiser et al., 2012). Even though the EFs presented in this dissertation cannot account for this discrepancy, they do provide accurate emission values from state of the art instruments, with the emission values specific to the two predominant types of biomass burning in Brazil (rainforest and cerrado fires). One possible explanation for the discrepancy could be due to sub grid scale processes occurring such as the chemical and physical aging of aerosols downwind from the fire, which is not accurately represented in models. Initial results from SAMBBA however indicate for the smouldering rainforest fire plume that extended 50 miles there was no net change in organic aerosol mass concentrations but there was a change in inorganic mass concentrations. These processes along with sub grid scale aerosol
cloud interactions are not adequately represented in models. Therefore, future work should include better representation of these processes.

The large differences in emissions for different biomass burning fires in Brazil are particularly significant due to the effect they have on the weather, climate (Andreae et al., 2004; Ramanathan et al., 2001) and health impacts (Arbex et al., 2007; do Carmo et al., 2013). In particular the large difference in CO$_2$ and BC emissions between fire types is important in terms of future climate and policy. Black carbon also causes warming by absorbing solar radiation and therefore warms the atmosphere (Bond et al., 2004; Ramanathan and Carmichael, 2008). This atmospheric warming can cause cloud burn off (the semi-direct effect) (Ackerman et al., 2000), and an increase in atmospheric stability inhibits convection which will be significant in the highly convective Amazon basin. This warming of the atmosphere can also act to increase atmospheric stability which can lead to pollutants becoming trapped near the surface having a detrimental effect on human health (do Carmo et al., 2013).

Although, there has been a reduction in Amazonian deforestation fires in recent years (Ten Hoeve et al., 2012), there has been an increase in savannah fires in the Amazon basin, therefore it is likely that there will not be a reduction in regional aerosol optical depths (AOD). There has however been a decrease in the regional mean single scattering albedo over the last decade (Ten Hoeve et al., 2012). This supports the shift in vegetation type
burning and that cerrado fires emit more black carbon into the atmosphere, thereby reducing the scattered radiation and increasing absorbed radiation. The results presented in this dissertation indicate that this will cause the relative mass of atmospheric organic aerosols (as a percentage of total aerosol species) emitted in the region to decrease due to cerrado fires emitting half the mass of organic aerosol per kg dry fuel burnt compared to rainforest fires in Brazil. The relative mass of black carbon emitted into the atmosphere will increase due to cerrado fires emitting an order of magnitude more black carbon per kg dry fuel burnt than rainforest fires. Combining this increase in black carbon mass concentrations emitted with the increase in CO$_2$ emitted from cerrado fires compared to rainforest fires means that this could cause a large increase in atmospheric temperature. Model simulations using the results presented and the change in vegetation being burnt in the Amazon Basin should be used to assess the implications of these results. Future scientific campaigns in the region studying biomass burning emissions and atmospheric composition will also be able to verify these results.

The model improvements as discussed earlier along with the up to date emissions presented in this dissertation will lead to more accurate and reliable regional and global climate models that can better predict how changes in biomass burning (such as the shift from rainforest to savannah
fires in Brazil (Ten Hoeve et al., 2012)) will affect atmospheric composition and therefore global climate.

Further work to address unanswered questions include comparing the PSAP and SP2 measurements of black carbon on board the aircraft during SAMBBA in order to verify if the differences in black carbon emissions derived during SAMBBA compared to literature values are likely due to the different instrument techniques used. Further investigation into why the 3.4 enhancement factor in AOD is needed in models as the results presented in the dissertation indicate this issue is likely not due to the emission factors used. Finally further field campaigns into the effect that the change from deforestation to cerrado burning in the Amazon Basin has on atmospheric composition need to be conducted.
9. Appendix

9.1 Supplementary material for paper

**Figure S1.** Plots of CO mixing ratio and rBC mass to show the different response times of the VUV Fast Fluorescence CO Analyser and SP2. The slower response of the SP2 is due to the lag time in the inlet line predominately

**Figure S2.** MCE shown as the gradient of the regression line through zero for Tocantins and Rondonia
Figure S3. Emission factor and modified combustion efficiency plots to show how emissions vary with modified combustion efficiency.
References


impact of sugar cane-burning emissions on the respiratory system of children and the elderly, Environmental Health Perspectives, 114, 725-729, 10.1289/ehp.8485, 2006.


do Carmo, C. N., Alves, M. B., and Hacon, S. D.: Impact of biomass burning and weather conditions on children's health in a city of Western Amazon region, Air Quality Atmosphere and Health, 6, 517-525, 10.1007/s11869-012-0191-6, 2013.


Haywood, J. M., Osborne, S. R., Francis, P. N., Keil, A., Formenti, P., Andreae, M. O., and Kaye, P. H.: The mean physical and optical properties of regional haze dominated by biomass burning aerosol


McFarquhar, G. M., and Wang, H. L.: Effects of aerosols on trade wind cumuli over the Indian Ocean: Model simulations, Quarterly Journal of


Moteki, N., and Kondo, Y.: Dependence of Laser-Induced Incandescence on Physical Properties of Black Carbon Aerosols: Measurements and


Turetsky, M. R., Kane, E. S., Harden, J. W., Ottmar, R. D., Manies, K. L., Hoy, E., and Kasischke, E. S.: Recent acceleration of biomass burning
and carbon losses in Alaskan forests and peatlands, Nature Geoscience, 4, 27-31, 10.1038/ngeo1027, 2011.


van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S., Morton, D. C., DeFries, R. S., Jin, Y., and van Leeuwen, T. T.: Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997-2009), Atmospheric Chemistry and Physics, 10, 11707-11735, 10.5194/acp-10-11707-2010, 2010.


Wooster, M. J., Freeborn, P. H., Archibald, S., Oppenheimer, C., Roberts, G. J., Smith, T. E. L., Govender, N., Burton, M., and Palumbo, I.: Field determination of biomass burning emission ratios and factors via open-
path FTIR spectroscopy and fire radiative power assessment: headfire, backfire and residual smouldering combustion in African savannahs, Atmospheric Chemistry and Physics, 11, 11591-11615, 10.5194/acp-11-11591-2011, 2011.


Yokelson, R. J., Andreae, M. O., and Akagi, S. K.: Pitfalls with the use of enhancement ratios or normalized excess mixing ratios measured in plumes to characterize pollution sources and aging, Atmospheric Measurement Techniques, 6, 2155-2158, doi:10.5194/amt-6-2155-2013, 2013.