Transformation and aging of biomass burning carbonaceous aerosol over tropical South America from aircraft in-situ measurements during SAMBBA

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Abstract.

We present a range of airborne in-situ observations of biomass burning carbonaceous aerosol over tropical South America, including a case study of a large tropical forest wildfire and a series of regional survey flights across the Brazilian Amazon and Cerrado. The study forms part of the South American Biomass Burning Analysis (SAMBBA) Project, which was conducted during September and October 2012. We find limited evidence for net increases in aerosol mass through atmospheric aging combined with substantial changes in the chemical properties of organic aerosol (OA). Oxidation of the OA increases significantly and rapidly on the scale of 2.5-3 hours based on our case study analysis and is consistent with secondary organic aerosol production. The observations of limited net enhancement in OA coupled with such changes in chemical composition, imply that evaporation of OA is also occurring to balance these changes. We observe significant coatings on black carbon particles at source, but with limited changes with aging in both particle core size and coating thickness.

We quantify variability in the ratio of OA to carbon monoxide across our study as a key parameter representing both initial fire conditions and an indicator of net aerosol production with atmospheric aging. We observe ratios of 0.075-0.13 $\mu g\,sm^{-3}\,ppbv^{-1}$ in the west of our study region over the Amazon tropical forest in air masses less influenced by precipitation and a value of 0.095 $\mu g\,sm^{-3}\,ppbv^{-1}$ over the Cerrado environment in the east. Such values are consistent with emission factors used by numerical models to represent biomass burning OA emissions. Black carbon particle core sizes typically range from mean mass diameters of 250-290 nm, while coating thicknesses range from 40-110 nm in air masses less influenced by precipitation. The primary driver of the variability we observe appears to be related to changes at the initial fire source. A key lesson from our study is that simply aggregating our observations as a function of atmospheric aging would have been

misleading due to the complex nature of the regional aerosol and its drivers, due to the many conflating and competing factors that are present.

Our study explores and quantifies key uncertainties in the evolution of biomass burning aerosol at both near-field and regional scales. Our results suggest that the initial conditions of the fire are the primary driver of carbonaceous aerosol physical and chemical properties over tropical South America, aside from significant oxidation of OA during atmospheric aging. Such findings imply that uncertainties in the magnitude of the aerosol burden and its impact on weather, climate, health and natural ecosystems most likely lie in quantifying emission sources, alongside atmospheric dispersion, transport and removal rather than chemical enhancements in mass.

1 Introduction

Biomass burning represents a significant source of aerosol particles on the global scale and thus has a substantial impact on the Earth System. At the regional level, where large-scale and seasonal burning practices are conducted annually, significant anthropogenic perturbations may occur. The Brazilian Amazon Rainforest and Cerrado are such regions, where an annual burning season typically running from August to October results in the build-up of a large atmospheric aerosol burden that can affect climate (e.g. Andreae, 2004), weather (e.g. Kolusu et al., 2015), human health (e.g. Reddington et al., 2015) and the regional ecosystem (e.g. Crutzen and Andreae, 1990; Pacifico et al., 2015). The co-emission of large amounts of both gas and particle phase pollutants from biomass burning complicates assessments of its impact as they undergo physical and chemical processes downwind.

Biomass burning is the largest source of black carbon (BC) particles when considering the global scale (Bond et al., 2013). One of the key complicating factors in relation to BC is the co-emission and subsequent mixing with other chemical components (e.g. Bond et al., 2013); aerosol components that predominantly scatter solar radiation can increase the absorption by BC (e.g. Bond et al., 2006) with the mixing state of the particles being vital (Liu et al., 2017). Furthermore, the relative abundance of BC compared to other (scattering) components in the aerosol will strongly govern the radiative impact from a specific emission source (Haywood and Shine, 1995). Koren et al. (2004, 2008) illustrated that absorption by biomass burning smoke over the Amazon can inhibit cloud formation or even induce so-called cloud "burn-off". Darbyshire et al. (2018) presented average vertical profiles of BC coating thickness across Brazil with significantly thinner coatings in the east than the west of the Amazon Basin.

As well as BC, biomass burning produces abundant emissions of organic carbon species in the gas and particle phase (e.g. van der Werf et al., 2017). As well as direct emissions of primary organic aerosol (POA), biomass burning produces significant emissions of semi-volatile or intermediate-volatility non-methane organic carbon species that may potentially play a role in secondary organic aerosol (SOA) formation (Yokelson et al., 2013b; Stockwell et al., 2015; Shrivastava et al., 2017). A number of field studies have attempted to quantify changes in organic aerosol (OA) production downwind of fire sources, which is a key parameter for global models (Reid et al., 2005; Shrivastava et al., 2017). Reid et al. (2005) reviewed a large body of work, including the chemistry of fresh smoke and particle evolution, with large variability in terms of composition and the time scale

of growth rates and the complexity of the "photochemical soup" that embodies aged smoke plumes. Furthermore they note the difficulty in comparing regional smoke with individual fires, as the former is subject to a vast array of complex drivers, while the latter is often relatively better constrained in terms of their specific burn characteristics and evolution. Many such studies have used carbon monoxide as a largely inert chemical tracer on the scale of anticipated changes in biomass burning emissions through aging and then compared this with OA mass concentrations downwind to investigate any net changes. Previous airborne studies have reported both an increase in OA mass (DeCarlo et al., 2008; Yokelson et al., 2009) and a decrease (Hobbs, 2003; Akagi et al., 2012; Jolleys et al., 2012), with the majority of studies reporting no detectable net addition of OA mass (Capes et al., 2008; Cubison et al., 2011; Hecobian et al., 2011; Forrister et al., 2015; Jolleys et al., 2015; May et al., 2015; Liu et al., 2016). Ground-based studies have also reported conflicting results with Lee et al. (2008) reporting enhancements in plumes from two prescribed fires in the US, Zhou et al. (2017) reporting no net enhancement for wildfire emissions in the US, while southern African biomass burning plumes have shown net enhancements with aging (Vakkari et al., 2014, 2018). One consistent trend within such studies is the increasing oxidation of the organic aerosol with atmospheric aging (Shrivastava et al., 2017, and references therein). Such observations imply that SOA is being produced and a number of studies (e.g. Capes et al., 2008; Cubison et al., 2011; Jolleys et al., 2012, 2015; May et al., 2015; Zhou et al., 2017) have hypothesised that this is frequently balanced by the dilution and evaporation of POA mass to explain the limited net changes observed in the field. Furthermore, in studies where net enhancements are observed, the magnitude of the enhancements are smaller than those observed in urban or biogenic emissions (Shrivastava et al., 2017).

The goal of this paper is to characterise the transformation and aging of biomass burning aerosol over the Amazon Basin with a focus on the carbonaceous component. The experimental study was conducted during the airborne component of the South American Biomass Burning Analysis (SAMBBA) during September/October 2012. SAMBBA aimed to investigate the impact of biomass burning in the region on the Earth System and on human health. SAMBBA represented the first airborne deployment of an Aerosol Mass Spectrometer and Single Particle Soot Photometer in Brazil, providing previously unobtainable characterisation of non-refractory aerosol species and BC-containing particles and their microphysical properties with high time-resolution and sensitivity. Such measurements allow us to investigate the composition of OA and mixing state of BC as a function of atmospheric aging for a case study analysis of a large fire plume as well as regional-scale measurements across the Amazon Basin. The analysis presented here serves as the bridge between near-source fire emissions characterised by Hodgson et al. (2018) and a regional-scale synthesis by Darbyshire et al. (2018). Compared to previous and subsequent biomass burning seasons, 2012 was a relatively 'normal' year when compared to the past decade (Darbyshire et al., 2018), which has seen reduced deforestation compared to the historical record albeit with less significant reductions in fire count (e.g. Aragão et al., 2018). As such, the observations presented here provide a characterisation of biomass burning aerosol under relatively 'typical' conditions.

2 Method

2.1 Instrumentation

All measurements presented here were conducted on the UK Facility for Airborne Atmospheric Measurement (FAAM) British Aerospace 146 (BAe-146) Atmospheric Research Aircraft. As a whole, SAMBBA (Facility for Airborne Atmospheric Measurements, Natural Environment Research Council, Met Office and Coe, 2014) was composed of eighteen science flights conducted between 14 September and 3 October 2012. For the purposes of our regional analysis, we investigate nine of these flights, which focussed on boundary-layer sampling of the regional biomass burning haze (see Darbyshire et al. (2018) for a broader discussion and context for SAMBBA). The flights and their operating regions are summarised in Table 1. The primary base of operations was Porto Velho in Rondônia state.

The aerosol instrumentation used in this study sampled via Rosemount inlets (Foltescu et al., 1995). These inlets have been shown to be satisfactory for sub-micron aerosol measurements (Trembath et al., 2012), which is typical of the SAMBBA dataset as a whole based on size distribution measurements. Nafion driers were used to dry the aerosol sample, which in combination with ram heating as the sampled air enters the aircraft and decelerates, reduced the measured sample relative humidity to a range from 20-60%. Losses associated with the nafion driers represent an additional uncertainty in our measurements, which we do not account for. All concentrations are reported at standard temperature and pressure (STP, 273.15 K and 1013.25 hPa respectively) and are denoted with an 's' in their unit where appropriate.

A Droplet Measurement Technologies (DMT, Boulder, CO, USA) Single Particle Soot Photometer (SP2, Stephens et al., 2003) measured BC physical properties during this study. The SP2 measures what is generally referred to as refractory BC or rBC, as defined by Petzold et al. (2013). Details of the instrument setup on the FAAM research aircraft and data processing relevant to this study have been detailed elsewhere (Liu et al., 2010; McMeeking et al., 2010). The incandescence signal of the instrument was calibrated using Aquadag BC particle standards (Aqueous Deflocculated Acheson Graphite, manufactured by Acheson Inc., USA) to calculate BC mass using a scaling factor of 0.75 (Baumgardner et al., 2012) to account for differences between the reference BC standard and ambient BC. As in previous studies, we assume a 30% uncertainty in the SP2 BC mass (e.g. McMeeking et al., 2010, 2012). Following the method presented by Liu et al. (2014) and Taylor et al. (2015) a rBC spherical equivalent core diameter, D_c, is derived and related to the particle diameter, D_p, which represents both the rBC core and its associated coating. By assuming a full concentric encapsulation of the spherical core, the coating thickness of single rBC particles are estimated using a core refractive index of 2.26-1.26i and coating refractive index of 1.50+0i.

An Aerodyne Research Inc. (ARI, Billerica, MA, USA) compact Time-of-Flight Aerosol Mass Spectrometer (AMS, Drewnick et al., 2005; Canagaratna et al., 2007) measured non-refractory OA and inorganic component mass (sulfate, nitrate, chloride and ammonium). In terms of OA, the AMS measures all non-refractory organic matter (OM) rather than just organic carbon (OC) and we thus refer to OM when discussing the AMS data specifically, while using OA when referring to the organic component more broadly. Details on the instrument setup on the FAAM research aircraft and calibration protocols have been detailed elsewhere (Crosier et al., 2007; Morgan et al., 2009, 2010). Measured mass concentrations are subject to an uncertainty of approximately 30% (Bahreini et al., 2009). In addition to the standard operating procedure of the AMS, we collected data at

1 s time resolution during discrete fire plume sampling by employing the 'fast mass spectrum' mode of the instrument (Kimmel et al., 2011).

Additional information regarding quality assurance procedures for the SP2 and AMS during SAMBBA can be found in Hodgson et al. (2018).

Carbon monoxide mixing ratios were measured using a vacuum ultraviolet (VUV) fast fluorescence CO analyser, with measurement uncertainties of approximately 2% (Hopkins et al., 2006; O'Shea et al., 2013).

2.2 Background concentration calculations

Excess mixing ratios and concentrations of individual species x, denoted as Δx, are necessary in order to investigate chemically-driven changes as well as other processes such as dilution and wet-removal. For the following regional-scale analysis, we use the fifth percentile for each species during a straight-and-level-run (SLR) as the ambient background values of species x to determine Δx. For the case-study analysis, we identified the smoke plumes manually based on the time series of CO, OM and rBC and then determined the ambient background values while sampling outside the smoke plumes for each cross-plume SLR using the same method as the regional-scale analysis. Tropospheric mixing can lead to changes in the background air composition, which can lead in uncertainties in the determination of Δx (Yokelson et al., 2013a); our sampling and method aims to mitigate for such changes as our SLRs are relatively short (10-30 minutes) and within the atmospheric boundary layer, typically sampling a fairly homogenous haze burden over a single SLR or flight. This limits large changes in mixing plus we manually inspect our time series and background values to identify clear shifts due to changing air masses e.g. large-scale spatial gradients (B734) or wet-scavening (B739) and recalculate background values over shorter flight segments if necessary. For the case-study analysis, our measurements are very close to source and we observed constant background concentrations throughout our plume intercepts. As a result, we expect uncertainties in the determination of Δx to be small.

3 Tropical forest fire case study

The following section presents a case study of a tropical forest fire sampled on flight B737 on 20 September 2012 in Rondônia state. Take-off was at 14:45 UTC (10:45 local-time), lasting 3 hours 45 minutes. The state is characterised by tropical moist broadleaf forest, as well as extensive deforestation. A large smouldering tropical forest fire was sampled and is shown in Fig. 1 alongside the flight track of the aircraft during the low-level sampling of the fire and smoke plume. Hodgson et al. (2018) reported near-source measurements of the fire, concluding that the fire was likely natural in origin as it was located well away from deforestation areas and was in a national park many kilometres from the nearest road. They reported a modified combustion efficiency (MCE, Ward and Radke, 1993) of 0.79 ± 0.02, which is relatively low compared to typical deforestation fires, Ferek et al. (e.g. 1998) reported a value of 0.87 for such fires in Brazil. The fire was characterised by substantial emissions of carbon monoxide and very low emissions of rBC compared to prior literature on Brazilian deforestation fires and global tropical forest fires, as well as being largely composed of OM (97.1% of the sub-micron mass, Hodgson et al., 2018).

The in-situ plume sampling was conducted as a sequence of cross-wind intercepts downwind of the fire at approximately 2500 m above sea level, an along-plume SLR at the same altitude and a series of overpass intercepts directly above the fire at an altitude of approximately 1800 m above sea level. As the fire was located on a 900 m high plateau, the near-source sampling was conducted approximately 900 m above ground-level. These flight sections are illustrated in Figs. 1 and 2.

We do not have a quantitative estimate of fire size for the B737 case study, although based on MODIS hotspot data corresponding to our sample location, the maximum fire size is approximately 5 km^2 and was likely smaller during our sampling. Furthermore, based on the velocity of the aircraft and the width of cross-plume intercepts, we estimate that the plume was approximately 3-4 km wide in the near-field before expanding to approximately 21 km when 56 km downwind of the fire. The atmospheric stability profile tends towards instability in the flight conditions during our case study, with absolutely unstable air below approximately 2 km where the lapse rate is 10.9 $\mathrm{K\,km^{-1}}$ and conditionally unstable air from 2-3 km where the lapse rate is 7.44 $\mathrm{K\,km^{-1}}$.

The time series of gas and particle-phase species shown in Fig. 2 illustrates the significant enhancements in their concentrations during plume intercepts, as well as the gradual increase in their concentrations as the aircraft approached the fire. CO mixing ratios were in excess of 5000 ppb on the approach to the fire, climbing to over 15000 ppb when directly above it during the overpass intercepts. OM mass concentrations reached almost 800 $\mu\mathrm{gsm}^{-3}$ on the along-plume SLR and over 3500 $\mu\mathrm{gsm}^{-3}$ during the above-fire intercepts.

Measurements from the along-plume SLR are shown in Fig. 3 relative to the distance from the fire, as well as the approximate age of the plume at the point of sampling. The distance from the fire is calculated as the great circle distance of the aircraft from the latitude and longitude of the fire (approximately 11.0° S, 63.6° W). The age of the plume is calculated using the average wind speed, which was 6.2 $\pm$ 1.7 ms^{-1}. We note there was a small gradient in wind speed along the length of the plume of 0.02 $\mathrm{ms}^{-1}\mathrm{km}^{-1}$, corresponding to an average increase of 1.2 ms^{-1} along the length of the plume. We omit this from our calculations due to the variability in wind speed also observed, while noting that the latter plume ages reported are potentially biased towards higher values. The plume extended approximately 65 km downwind based on the concentrations reaching regional background values, which equates to approximately 3 hours in terms of plume age.

The evolution of ΔOM:ΔCO ratio along the length of the plume indicates negligible net change in OM mass downwind of the fire, with the ratio exhibiting a small net decline over the course of the measurements and a low correlation coefficient of -0.16. Compared to the near-source measurements directly above the fire, the ΔOM:ΔCO ratio is slightly enhanced in the near-field, although the variability in the above-fire ratio is large relative to the difference. Small net enhancements in sulfate and nitrate relative to CO are observed along the length of the plume, with correlation coefficients of 0.36 and 0.48 respectively. In addition, the along-plume measurements are enhanced relative to the above-fire intercepts. The relative intensity of the organic signal at $\mathrm{m/z}$ 44 to the total organic mass, which corresponds to the CO_2^+ ion and is denoted as f_{44}, is used as an indicator for the level of oxidation of the organic aerosol. We observed a substantial increase in f_{44} along the length of the plume from approximately 0.05 to 0.15, with a correlation coefficient of 0.90. This equates to an increase in O:C of approximately 0.29 to 0.73 over the course of the sampling, which is calculated using the equation from Canagaratna et al. (2015). We observe a small reduction in coating thickness of the rBC-containing particles of -4.9 $\pm$ 1.4 $\mathrm{nm\,hr}^{-1}$ with a correlation coefficient of -0.28.

The coating thickness observed during the along-plume sampling is lower than that from the above-fire intercepts, although the variability is large in the latter. We do not observe any change in the ΔrBC:ΔCO ratio along the length of the plume sampling; based on the cross-plume intercepts, the mean ratio was 0.098 ± 0.013 $\mu g\,sm^{-3}\,ppmv^{-1}$, which was lower than the above-fire intercept value of 0.37 ± 0.22 $\mu g\,sm^{-3}\,ppmv^{-1}$ reported in Hodgson et al. (2018). We observe a minor absolute decrease in rBC core diameter along the plume (-4.4 $\pm$ 2.3 $nm\,hr^{-1}$), with a correlation coefficient of -0.16; the geometric mean mass diameter along the plume was 249 ± 49 nm, compared to 270 ± 30 nm from the above-fire intercepts. The lower values in the plume-run compared to the above-fire intercepts for these rBC parameters may point towards a small shift in the fire conditions, although the variability in the plume is large.

Fig. 4 shows examples of average OM mass spectra at different stages of the plume's evolution, with approximately one order of magnitude decreases in concentration. Consistent with the f_{44} evolution above, the organic aerosol becomes increasingly oxidised downwind of the fire and closely resembles the background regional aerosol after approximately 2.5 hours of aging. Above the fire, m/z 43 dominates (7.6%) corresponding to CH and CHO ions, with further enhancements from other hydrocarbon peaks, especially m/z 29, 41, 55 and 57. m/z 60, which is associated with levoglucosan and other anhydrous sugars, is also elevated (3.9% of the organic signal); levoglucosan is often reported as a tracer for biomass burning aerosol. To illustrate the evolution of the mass spectra, we calculate the mean absolute difference between the plume spectra and the background as the square root of the sum of the square differences between their organic peak intensities. We also calculate the linear correlation coefficient between them. The mean absolute difference and correlation between the mass spectrum and the background is 0.0023 and 0.66 respectively, illustrating their similarity. Approximately 1 hour downwind, a similar pattern is observed but now with increased signal at m/z 44 (6.2%), while maintaining the signal at m/z 43 (7.5%) and reduced signal at the hydrocarbon peaks noted above. The contribution of m/z 60 has reduced to 2.7% at this point. The mean absolute difference and correlation between the mass spectrum and the background is 0.0016 and 0.87 respectively, illustrating their similarity. After 2.5 hours, the contribution from the hydrocarbon peaks has reduced substantially and m/z 44 dominates the organic mass spectrum (13.3%). The contribution of m/z 44 increases further in the background organic aerosol (15.7%). The mean absolute difference and correlation between the mass spectrum and the background is 0.00064 and 0.99 respectively, illustrating their similarity. The contribution of m/z 60 has diminished further after 2.5 hours (1.0%), while being close to zero in the background (0.4%).

The evolution in the organic mass spectra is further illustrated in Fig. 5, where f_{44} is compared with f_{43} and f_{60} for the plume run and regional background aerosol. Relative to the increase in f_{44} along the plume and its eventually comparable magnitude to the regional background, f_{43} initially decreases within approximately the first 45 minutes of the plume's evolution, before a partial increase and stable magnitude up to the 2 hour mark. f_{43} then increases over the rest of the plume run until reaching the regional background value. The points fall within the f_{44} and f_{43} 'triangle' space reported by prior studies focussed on organic aerosol less influenced by biomass burning (Morgan et al., 2010; Ng et al., 2010). Comparing f_{44} and f_{60} illustrates a gradual reduction in f_{60} as the plume ages and becomes increasingly oxidised downwind, falling within the space reported by Cubison et al. (2011) and Lack et al. (2013) who reported a similar linear progression.

4 Regional biomass burning haze analysis

The following section examines regional biomass burning flights during SAMBBA to investigate the aging and evolution of the carbonaceous aerosol on the regional scale. Following the case study in Section 3, we relate the evolution of the regional OM based on changes in f_{44} as an indicator of the age of the biomass burning smoke sampled. We couple this with the ratio of rBC to CO as an indicator of the air mass history based on the assumption that both are relatively inert tracers that are strongly controlled by the initial conditions at source; the ratio also provides an indication for the influence of precipitation, which would reduce the rBC mass concentration to a larger extent than CO. Including this ratio in our analysis framework provides a means of isolating net changes in OM mass concentration during aging from changes driven by air mass history.

We focus on boundary layer regional haze, which is determined based on the procedure outlined in Darbyshire et al. (2018) where near-source plumes were identified based on a series of threshold concentrations for multiple pollutants and then flagged separately. This allows us to exclude such plumes from the wider regional haze that we are interested in here.

Fig. 6 illustrates the geographical scope of the flight campaign, with the majority of flights sampling within Rondônia state, as well as western Mato Grosso and Tocantins. Deforestation and degradation fires in tropical forest environments are the primary source within Rondônia and Mato Grosso, while Cerrado fires dominate in Tocantins. As well as the geographical regions identified, the analysis can be split into distinct meteorological phases following Brito et al. (2014) and Darbyshire et al. (2018). From 14-22 September (flights B731-B737), relatively dry conditions were prevalent and were characteristic of the 'dry season'. Following this period, the monsoonal transition was being established and was characterised by increased precipitation across the western and southern Amazon Basin. The number of fires was consequently reduced during this transition phase. Further details and analysis of the meteorological fields are available in Darbyshire et al. (2018).

Fig. 7 summarises the aerosol chemical composition for each flight using data from SLRs in boundary layer regional haze. Flight B731 in Rondônia state was the most polluted with total sub-micron mass concentrations of 46 $\mu\mathrm{gsm}^{-3}$. Lower average concentrations are observed across the remainder of the flights, with B734 in Rondônia and B742 in Tocantins being the next greatest in terms of total sub-micron mass concentrations of 18 and 17 $\mu\mathrm{gsm}^{-3}$ respectively. OM dominates the sub-micron chemical composition, ranging from 75% of the total on flight B746 to 86% of the total on flight B739. Sulphate mass fractions ranged from 3.2-9.7% and are typically larger than nitrate mass fractions, which generally fell between 1.7-3.9% with flight B740 as an outlier with 7.7%. Chloride mass fractions were low, ranging from 0.2-0.6%. Based on ion balance calculations of the inorganic aerosol species, the aerosol was typically neutralised. rBC mass concentrations varied from 2.0-6.1% on flights within Rondônia state, with the largest concentrations on flights B731 and B734. Note the data coverage for the SP2 was more limited on flight B731 than the other flights. Average rBC mass concentrations (1.5 $\mu\mathrm{gsm}^{-3}$) were greatest on flight B742 in Tocantins, contributing 8.7% of the total sub-micron mass concentration. The largest contribution by rBC was 12.4% on flight B746, which sampled within both western Mato Grosso and Rondônia.

Fig. 8 illustrates the relationship between excess concentrations of OM and CO for each flight. For additional context, the points are coloured by the ratio of rBC to CO. Broadly speaking, there is a strong linear relationship between OM and CO, with correlation coefficients ranging from 0.57-0.98. However, the ratio varies both between and within flights. Variability

within individual flights e.g. B734, B737, B739 and B746 is coincident with differences in the ratio of rBC to CO, which likely reflects differences in air mass history across the region(s) sampled on the flight.

Fig. 9 shows the relationship between the ratio of OM and CO compared with f_{44} to examine whether the ratio changes with variability in OM oxidation and aging. Within an individual flight, we observe a limited relationship between the ratio and the level of oxidation of the OM, with predominantly low correlation coefficients ranging from -0.09-0.09, except for B734 (0.51) and B740 (-0.26). On some flights (B731, B734, B745) there are enhancements for f_{44} greater than approximately 0.16, although in the case of B734 and B745 they appear at least partially related to a change in the ratio of rBC and CO; the limited SP2 data coverage for B731 precludes analysis, although we note that there is also a reduction in the ratio at greater f_{44} values. In addition, the uncertainty in the ratio of ΔOM to ΔCO will tend to be larger for low concentrations of either or both, leading to more extreme values; this predominantly occurs for the most aged air masses in terms of f_{44}. Comparing across all flights, changes in the ratio of OM and CO compared to the level of oxidation appear related to changes in the ratio of rBC and CO, which suggests a link with air mass history and any perceived change in net condensation or evaporation of OM.

Figs. 10 and 11 examine f_{44} compared with f_{43} and f_{60} in a similar manner to Fig. 5 in Section 3. The majority of the regional haze data shown in Fig. 10 fall within the 'triangle' space reported by prior studies focussed on OM less influenced by biomass burning (Morgan et al., 2010; Ng et al., 2010). Some flights display a broader range of values suggesting that the flights sampled a more diverse range of air masses in terms of their chemistry and aging. The behaviour described in Section 3 in relation to the evolution during the early stages of the plume's age are present in flights B731, B742 and B745, which suggests sampling of fresher biomass burning smoke on those flights; on flights B742 and B745, such features are distinct in terms of the ratio of rBC and CO as well. In terms of the f_{44} and f_{60} space shown in Fig. 11, the regional sampling is predominantly confined to lower f_{60} values, as well as displaying the linear tendency noted for the case study in Section 3 and previous work (e.g. Cubison et al., 2011; Lack et al., 2013).

Fig. 12 presents histograms of the median rBC coating thickness across the individual flights, which appears to vary appreciably from flight-to-flight, as well as within some individual flights. We found no clear and consistent relationship between coating thickness and f_{44} across the dataset. The broad bimodal-like structure in coating thickness in flight B737 could be linked with differences in the ratio of rBC and CO, with the thicker coatings of 80-100 nm associated with a larger ratio; conversely, the thinner coatings of less than 60 nm are coincident with the smaller ratios observed. However, there was no clear pattern in this linkage in flights B740 and B744, which also had a bimodal-like structure in coating thickness. Regional-scale variability in rBC coating thickness appears to be predominantly driven by fire-source and/or air mass differences, rather than aging of the aerosol population after emission. We also observed no clear link between the physical size of the rBC core and f_{44}, with geometric mean mass diameters typically between 250-290 nm.

5 Discussion

Whether considering the case study analysis in Section 3 or regional analysis in Section 4, we observe either limited or no net enhancement in the ratio of OM to CO. However, we do observe substantial increases in f_{44}, which is interpreted as an

indicator for the O:C content of the OM. Such a trend with atmospheric aging is consistent with SOA being produced downwind of source following dilution but that this is approximately balanced by the loss of POA emitted at source. A number of studies have observed such features in other biomass burning environments and hypothesised such a process (e.g. Cubison et al., 2011; Jolleys et al., 2012, 2015; May et al., 2015; Zhou et al., 2017). An additional feature of our observations of the single plume case study is the apparent plateau in f_{44} approximately 2.5 hours downwind of source; we also observe a similar plateau in net ozone production and reduction in nitrogen dioxide downwind. After reaching this plateau, the level of oxidation is comparable to the regional background with highly similar organic mass spectra as well. Such observations suggest that whatever chemical process drives the aging of OM, it is relatively fast under the environmental conditions of our measurements. We note that our case study is likely of a natural fire and that it is highly-smouldering compared to previous fires sampled in Brazil (Hodgson et al., 2018), which may have a bearing on our observations. While we cannot directly ascertain the regional evolution of f_{44} with atmospheric aging, our results imply similar phenomena are present as f_{44} increases with decreasing OM concentrations as well as reaching a defined 'end-point' at approximately 0.20 in the f_{44} vs f_{43} and f_{60} spaces.

Bian et al. (2017) examined the role of a number of factors that could control SOA production in ambient plumes, including fire area as a driver of dilution rate, mass emission flux and atmospheric stability. Based on Bian et al. (2017), our estimated initial fire size and atmospheric stability conditions would lead to some evaporation of OM in the near-field but with significant SOA production downwind that could balance the initial loss of particulate, which would be consistent with our observations of limited net enhancement in OM. Based on thermodynamic analysis of the SAMBBA experiment by Darbyshire et al. (2018), our regional sampling was typically conducted in unstable air, which is consistent with our observed limited net enhancement in OM.

Aqueous processing of biomass burning emissions has been identified as a potential source of SOA (e.g. Gilardoni et al., 2016; Tomaz et al., 2018), which is likely an important component in Amazonia. However, we are not in a position to assess the role of such processes through our observations. More oxidised OM is thought to be more hygroscopic (e.g. Jimenez et al., 2009), so such processes have implications for the lifetime and radiative impact of biomass burning smoke.

Our regional analysis illustrates the importance of evaluating changes in the aging of regional OM within a framework that also accounts for differences in air mass history. Differences in vegetation, fire dynamics and environmental conditions can result in significant diversity in the absolute and relative emissions of different pollutants from biomass burning that will manifest in the regional aerosol burden. We also observe significant variability from flight-to-flight, even within the same region that is likely a consequence of differing meteorological conditions e.g. the influence of precipitation, as well as changes in fire dynamics. Were we to interpret our observed changes in the ratio of OM to CO as a function of f_{44}, we would see enhancements of 2-3 in some instances that are most likely driven by differences in air mass history and fire dynamics rather than chemical processing - ΔrBC:ΔCO was key in illustrating such differences where enhancements in OM to CO were often easily distinguished by large changes in rBC to CO.

Our results indicate that uncertainties in the magnitude of the aerosol burden most likely lie in quantifying emission sources, alongside atmospheric dispersion, transport and removal rather than chemical enhancements in mass. Across our study, ΔOM:ΔCO ratios range from 0.029-0.13 $\mu g\,sm^{-3}\,ppbv^{-1}$ in the west of the Amazon Basin, with a value of 0.095

$\mu g\,sm^{-3}\,ppbv^{-1}$ in the Cerrado-environment sampled on flight B742. Numerical models that attempt to represent the magnitude of the atmospheric aerosol burden typically use fixed emission factors for distinct ecosystems e.g. those used in the fourth version of the Global Fire Emissions Database (GFED4, van der Werf et al., 2017) report ΔOM:ΔCO ratios of 0.10 $\mu g\,sm^{-3}\,ppbv^{-1}$ and 0.09 $\mu g\,sm^{-3}\,ppbv^{-1}$ for tropical forest and savannah fires respectively (assuming an OM:OC ratio of 1.6 for biomass burning OA following Yokelson et al. (2009) and Akagi et al. (2012)). In the western Amazon Basin, our central estimate for the ΔOM:ΔCO ratio when considering all flights together is 0.09-0.10 $\mu g\,sm^{-3}\,ppbv^{-1}$, closely matching the value for tropical forests in GFED4. Based on the local and synoptic scale situations during flights B739 and B746, we suspect that the lower observed ratios on these flights are a consequence of wet removal; the lower ratio associated with limited rBC in B734 is less clear based on the large-scale synoptic situation, so we do not speculate on a cause in this case. If these three flights with lowered observed ΔOM:ΔCO ratios are excluded from the analysis then our regional values range from 0.075-0.13 $\mu g\,sm^{-3}\,ppbv^{-1}$ in the west of the Amazon Basin, indicating significant variability compared to any assumed fixed emission factor. However, we note that variability of 25-30% is much lower than the discrepancy reported between measurements and models quantifying the aerosol burden over tropical South America where factors ranging from 1.5-6 are required to match satellite and ground-based observations of aerosol optical depth (Reddington et al., 2016, and references therein).

In terms of inorganic species, we observe small net enhancements in sulfate and nitrate relative to CO in the case study analysis. We do not observe clear enhancements in nitrate at the regional scale, while we do observe minor absolute increases in sulfate on some flights.

Aside from the comparison between the above-fire intercepts and the along-plume sampling in the case study, we do not observe clear changes in rBC coating thickness with plume age. Our observations indicate that rBC is rapidly coated in the near-field based on our case study, as well as other near-field sampling during SAMBBA, in contrast to many urban sources and environments (e.g. Liu et al., 2017). This is consistent with previous measurements of North American wildfire emissions, which also showed significant coatings on near-field rBC particles (Schwarz et al., 2008; Sedlacek et al., 2012). On the regional scale, we observe no clear link between coating thickness and f_{44}, with variability in coating thickness appearing to be driven by fire-source and/or air mass differences. Prior measurements of biomass burning emissions over Boreal Canada by Taylor et al. (2014) reported that scavenging of rBC via wet deposition preferentially removed the largest and most coated particles. Such processes may explain some of our observed variability in coating thickness on the regional scale, although we observe limited variability in rBC core size across the dataset. Our measurements indicate that the vast majority of rBC-containing particles within the boundary layer are at least partially coated, with the lowest coating thicknesses of 10-20 nm observed in our case study flight and the majority of our regional measurements indicating thicknesses of 40-120 nm. Such coatings will lead to a lowering of rBC lifetime as rather than being hydrophobic, the rBC containing-particles will be at least mildly hygroscopic, making them more susceptible to cloud-activation and wet removal. Furthermore, such coatings have implications for the radiative impact of black carbon containing particles via enhanced absorption (Liu et al., 2017). The lack of change in coating thickness appears consistent with the limited enhancement in OM, although given that our results imply a process of both evaporation and condensation of OA-related species there are potentially complex particle dynamics occurring within the rBC-containing fraction that warrant further investigation.

6 Conclusions

We observe limited to no enhancement in OM mass production during atmospheric aging of biomass burning over Brazil for both a case study of a likely natural tropical forest fire and regional sampling over the Amazon and Cerrado. Variability in the ratio of OM to CO is predominantly driven by regional differences likely related to changes at the initial fire source, as well as air mass differences likely as a consequence of wet scavenging of the aerosol. What enhancements we do observe are small in absolute terms compared to regional-scale variability across our study. Such variability at the regional-scale can be significant, with flight-averaged ΔOM:ΔCO ratios ranging from 0.075-0.13 $\mu g\,sm^{-3}\,ppbv^{-1}$ across our study region in cases where we suspect the influence of precipitation to be minor. We did not observe a systematic difference between the west of our study region and the Cerrado in terms of ΔOM:ΔCO, although we only have one flight in the latter region. While significant, we note that the scale of the variability is much smaller than typical factors required to match satellite and ground-based observations of aerosol optical depth to numerical model estimates of the aerosol burden. We do observe substantial changes in the chemical composition of OM, with significantly increased oxidation downwind, implying SOA formation that is being balanced by evaporation of OM. During our case study, we observed an increase in O:C of approximately $0.25 \pm 0.09\ hr^{-1}$, reaching a plateau after approximately 2.5-3.0 hours of atmospheric aging and a comparable magnitude to the background regional aerosol. Such changes may enhance the hygroscopicity of the OA and given its dominance of the aerosol burden (75-86% of the sub-micron mass in our study), this will have implications for the life cycle and radiative impact of biomass burning aerosol in the region.

We observe limited changes in the microphysical properties of rBC subsequent to emission, with neither significant changes in particle core size or coating thickness. We observe substantial coatings on rBC-containing particles at source. Given the limited changes with aging, our results suggest that any absorption enhancements will be dictated by the initial conditions in the near-field and precipitation-influences, rather than aging, although we have not investigated particle morphology changes that may occur. Such coatings likely reduce the lifetime of rBC as they are likely to be at least mildly hygroscopic, especially compared to un-coated hydrophobic rBC particles.

The complex nature of the regional aerosol and its drivers implies that aggregating our observations from the entire study as a function of atmospheric aging is unwise due to the many conflating and competing factors present. The continuing puzzle over the contrasting observations of the evolution of OM:OC ratios with atmospheric aging remains, although our results appear consistent with the framework presented by Bian et al. (2017). Further detailed quantification of the processes driving these should be further explored in the literature, as well as chamber and ambient studies specifically designed to probe such processes.

Overall, our results suggest that the initial conditions are the biggest driver of carbonaceous aerosol composition and physical properties in the region, aside from significant oxidation of OA during atmospheric aging. Uncertainties in the magnitude of the aerosol burden and its impact most likely lie in quantifying emission sources, alongside atmospheric dispersion, transport and removal rather than chemical enhancements in mass.

Data availability

All raw time series data from the FAAM research aircraft are publically available from the Centre for Environmental Data Analysis website, where the entire SAMBBA dataset may be accessed. AMS mass spectral features, SP2 size distribution and coating thickness data is available on request. Data masks for categorising flight patterns into plume-sampling and other sampling types (vertical profiles and SLRs) are currently available on request. Active fire data used in the manuscript is available publically from NASA (see acknowledgements for further details).

Author contributions. W. T. Morgan analysed the data and wrote the manuscript. J. D. Allan, E. Darbyshire, J. Lee and D. Liu provided additional data analysis support, including data processing and quality assurance. S. Bauguitte and J. Lee operated the gas-phase instruments, while J. D. Allan and M. J. Flynn operated the aerosol instruments during the field campaign. B. Johnson, J. M. Haywood, K. M. Longo, P. E. Artaxo and H. Coe led the planning of the field campaign and were co-principal investigators on the SAMBBA project.

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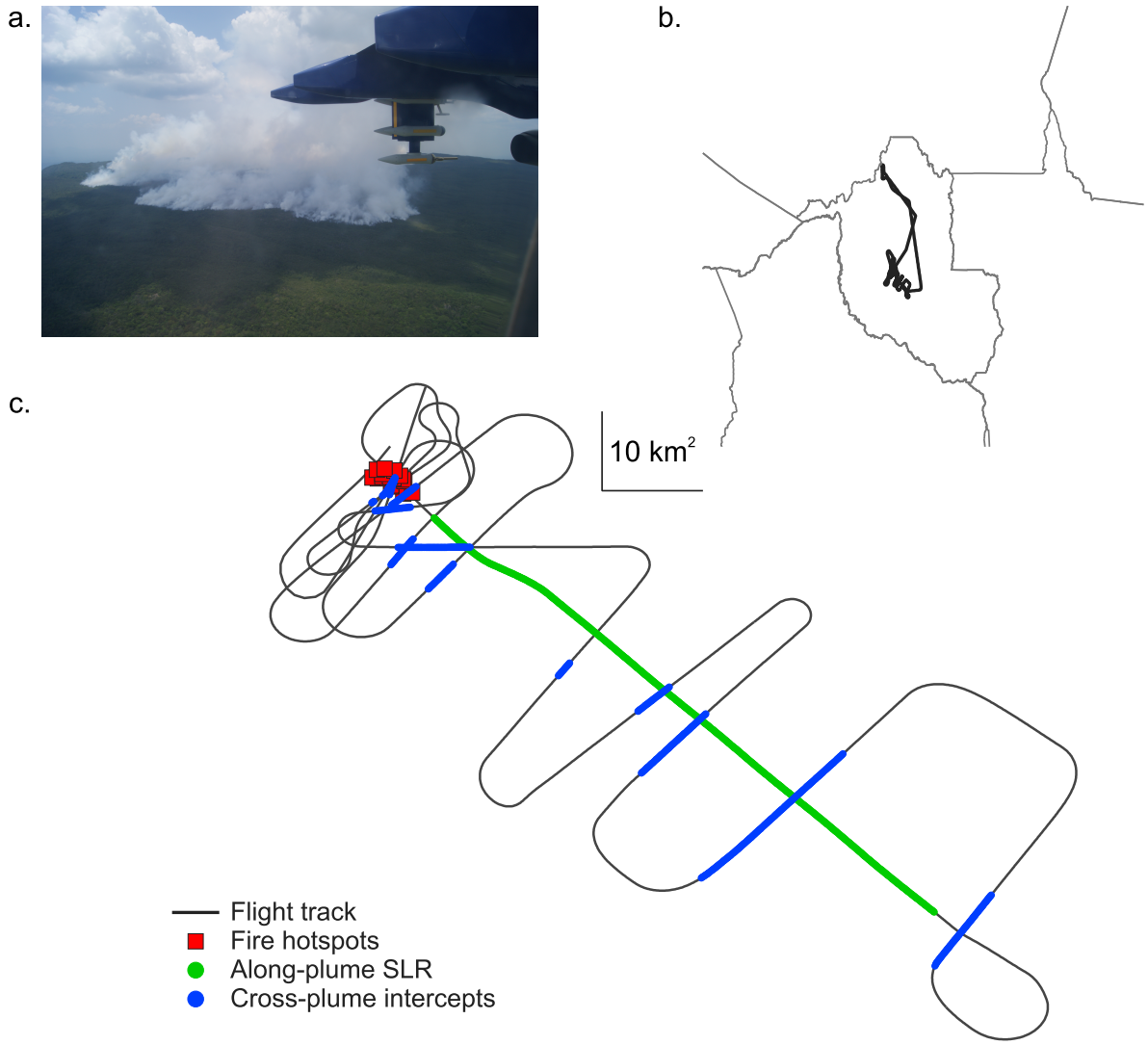

Figure 1. Spatial overview of case study analysis for flight B737. (a) Photograph taken from the aircraft of the fire courtesy of William T. Morgan. (b) Flight track of B737 in relation to the wider study region. (c) Low-level flight track of the case study, indicating both cross-plume intercepts and the along-plume straight-and-level run (SLR). Also shown are Moderate Resolution Imaging Spectroradiometer (MODIS) hotspot data from the Terra overpass coincident with our flight sampling. 10 km^2 box represents the scale for the flight track.

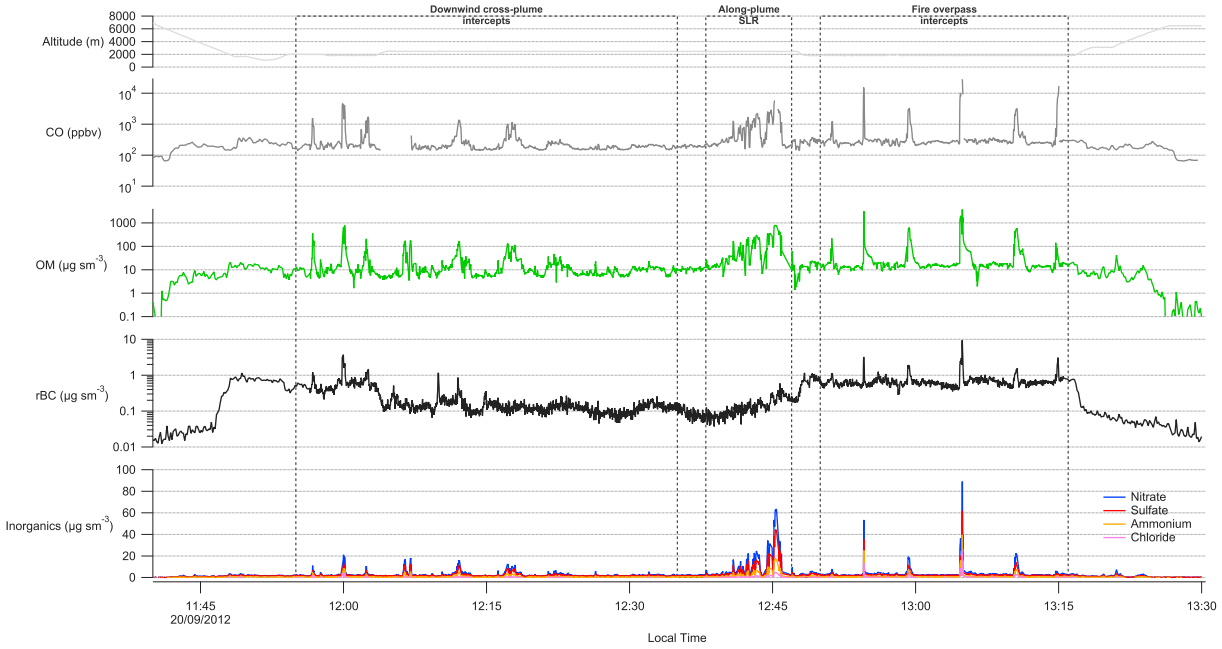

Figure 2. Time series of altitude, carbon monoxide (CO), organic matter (OM), refractory black carbon (rBC) and inorganic aerosol components during the case study analysis for flight B737. Downwind cross-plume intercepts, the along-plume straight-and-level run (SLR) and fire overpass intercepts across the plume are indicated by the dashed boxes. The fire itself was located on a 900 m high plateau.

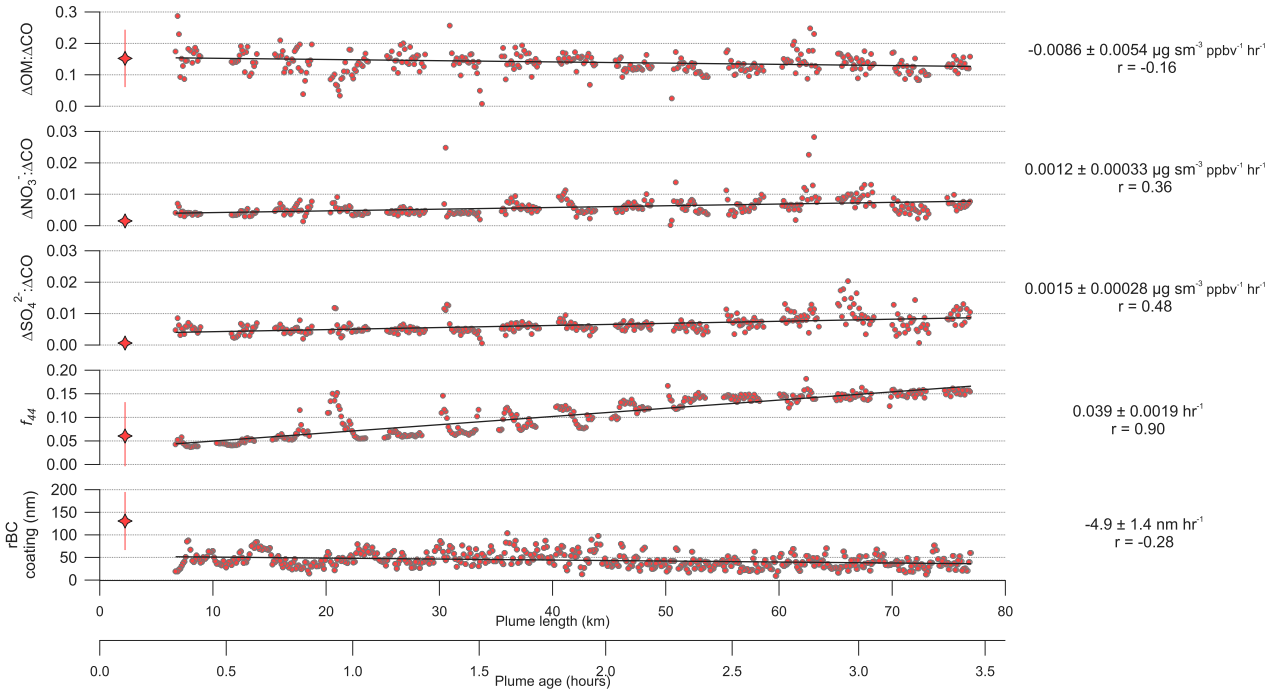

Figure 3. Various aerosol chemical and physical parameters as a function of plume length and age for the case study analysis from flight B737. Organic matter (OM), nitrate and sulfate are normalised by carbon monoxide (CO) to account for dilution of the smoke plume downwind. Further details on the calculations are provided in sections 2.2 and 3. Red star markers on the left-hand-side of the figure are averaged across the fire overpass intercepts across the plume with the bars denoting the 2σ standard deviation range around the mean value (OM, nitrate and sulfate ratios are taken from Hodgson et al. (2018)). Individual data points are shown as red circles from the along-plume straight-and-level run (SLR) with a linear regression slope included to illustrate any apparent trends. Slopes of the linear regression are given on the right-hand-side of the figure along with their 95% confidence interval. The correlation coefficient, r, is also provided.

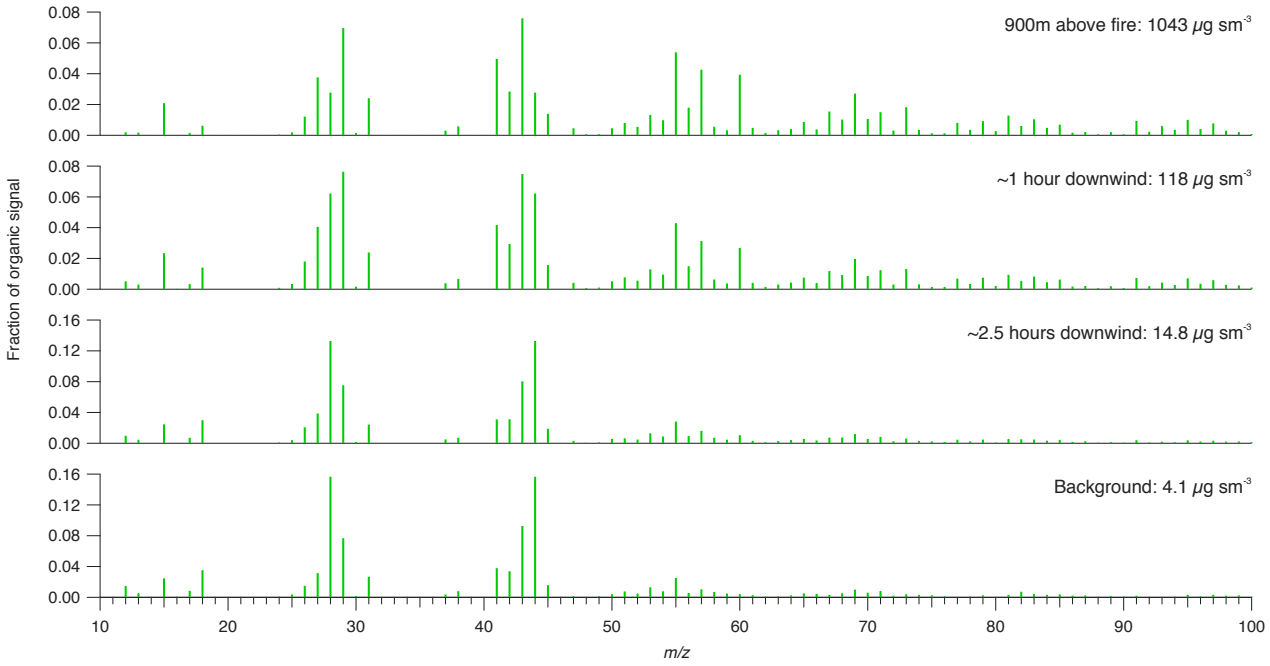

Figure 4. Aerosol mass spectrometer organic mass spectra from different segments of the case study analysis from flight B737. The above fire mass spectrum is from sampling directly above the fire during a cross-plume intercept, with the two downwind mass spectra measured during the along-plume straight-and-level run (SLR), while the background mass spectum is in the regional aerosol haze away from the main fire plume study region.

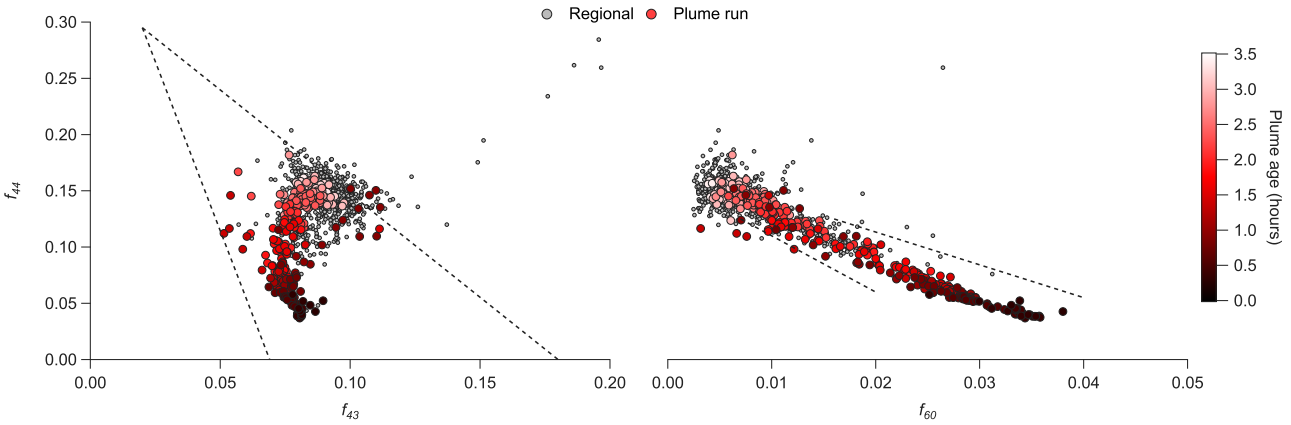

Figure 5. Comparison of f_{44} vs f_{43} and f_{60} during the case study analysis for B737, where f_x refers to the fraction of the organic aerosol mass signal at a given mass-to-charge ratio measured by the aerosol mass spectrometer. Also shown is regional haze data during the same flight. Points from the along-plume straight-and-level run (SLR) are coloured according to the approximate plume age. Dashed lines in the f_{44} vs f_{43} show the 'triangle' space reported by prior studies focussed on organic aerosol less influenced by biomass burning (Morgan et al., 2010; Ng et al., 2010). Dashed lines in the f_{44} vs f_{60} are from previous studies on biomass burning organic aerosol aging, with the upper line from Cubison et al. (2011) and the lower line from Lack et al. (2013).

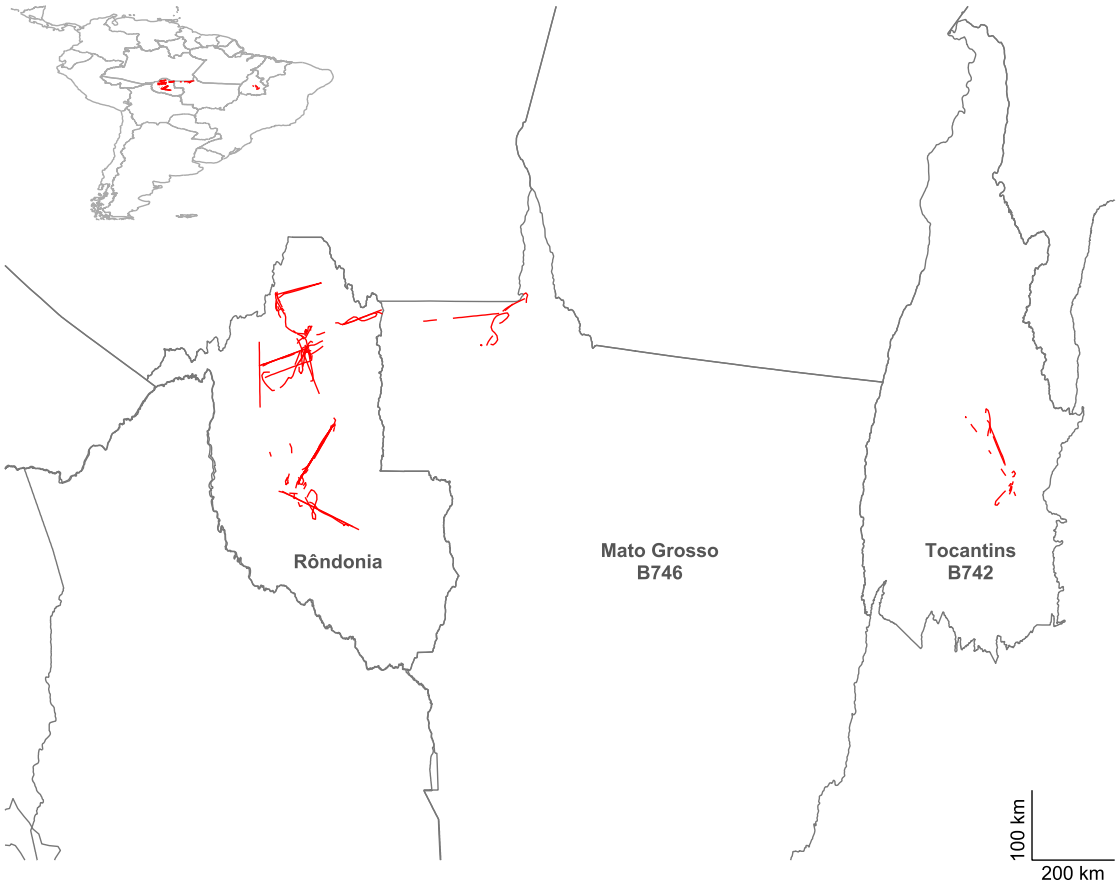

Figure 6. Flight tracks of the aircraft while sampling within regional haze that are included in our regional analysis. Scale in lower right-hand corner pertains to the enlarged map focussed on our study region. See section 4 and table 1 for further details.

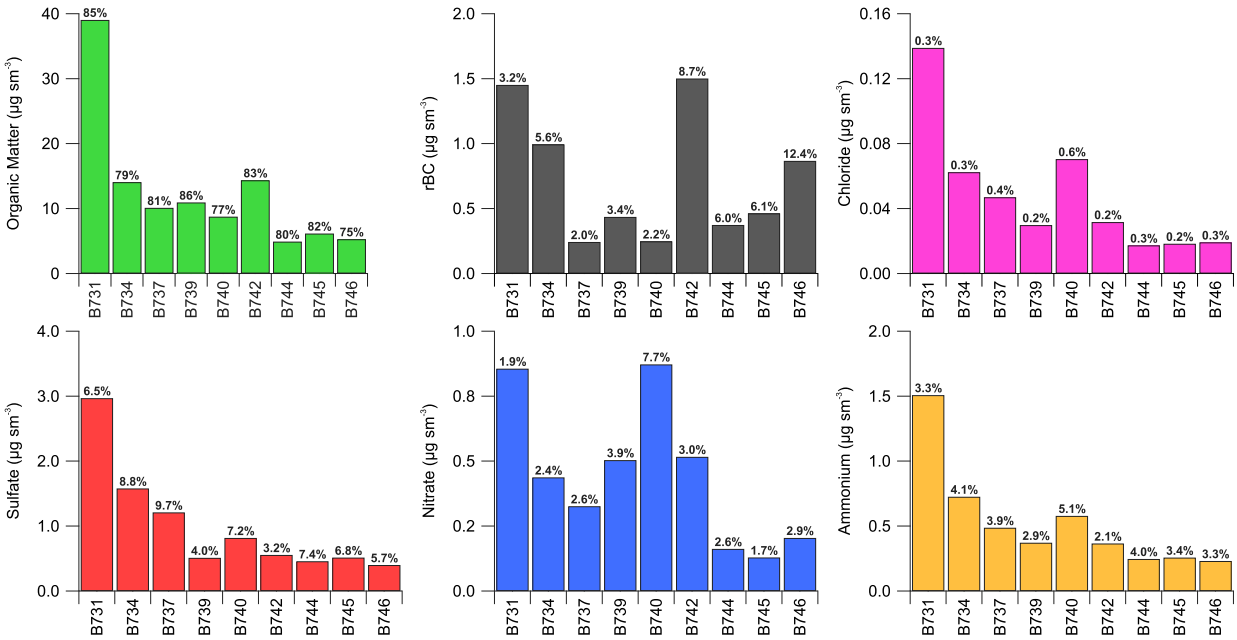

Figure 7. Sub-micron aerosol chemical composition overview for the regional analysis with the data split into individual flight operations in the regional boundary layer aerosol haze. Data is from straight-and-level runs (SLRs) only with the bars denoted mean concentrations and the text above each bar providing the mass fraction as a percentage. B742 took place over Tocantins, while B746 was primarily over Mato Grosso with some measurements over Rondônia. The rest of the flights were conducted over Rondônia.

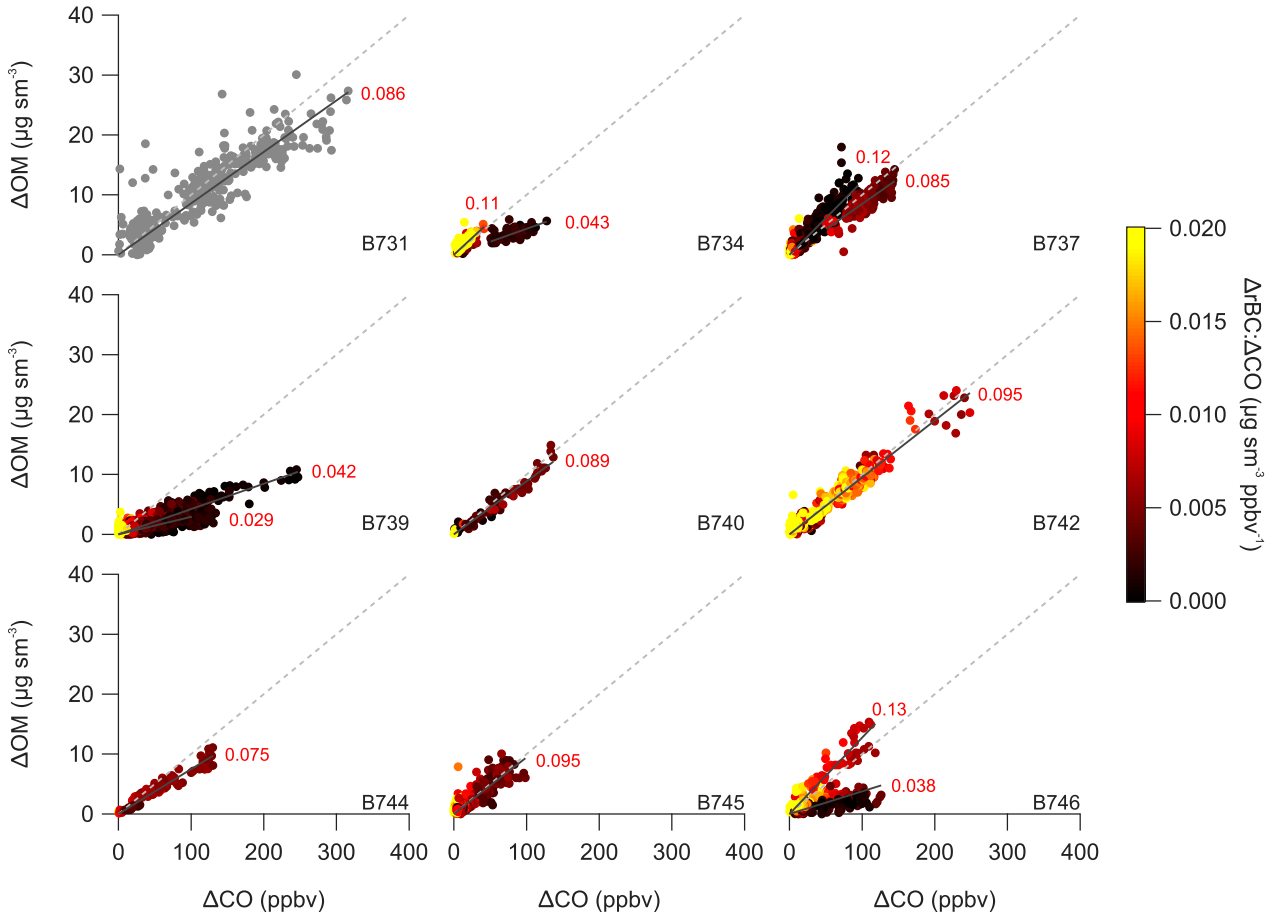

Figure 8. Comparison of organic matter (OM) with carbon monoxide (CO) across individual flights from the regional analysis. Points are coloured according to the ratio of refractory black carbon (rBC) to carbon monoxide (CO) except for B731 where limited rBC data was available. The black dashed line shows the 0.1 $\mu g\,sm^{-3}\,ppbv^{-1}$ as a consistent baseline for context across all flights, with the solid red lines showing the linear regression for either the whole flight or smaller segments where two lines are shown for a single flight. Red text next to the linear regression lines are the slope of the line-of-best fit in $\mu g\,sm^{-3}\,ppbv^{-1}$.

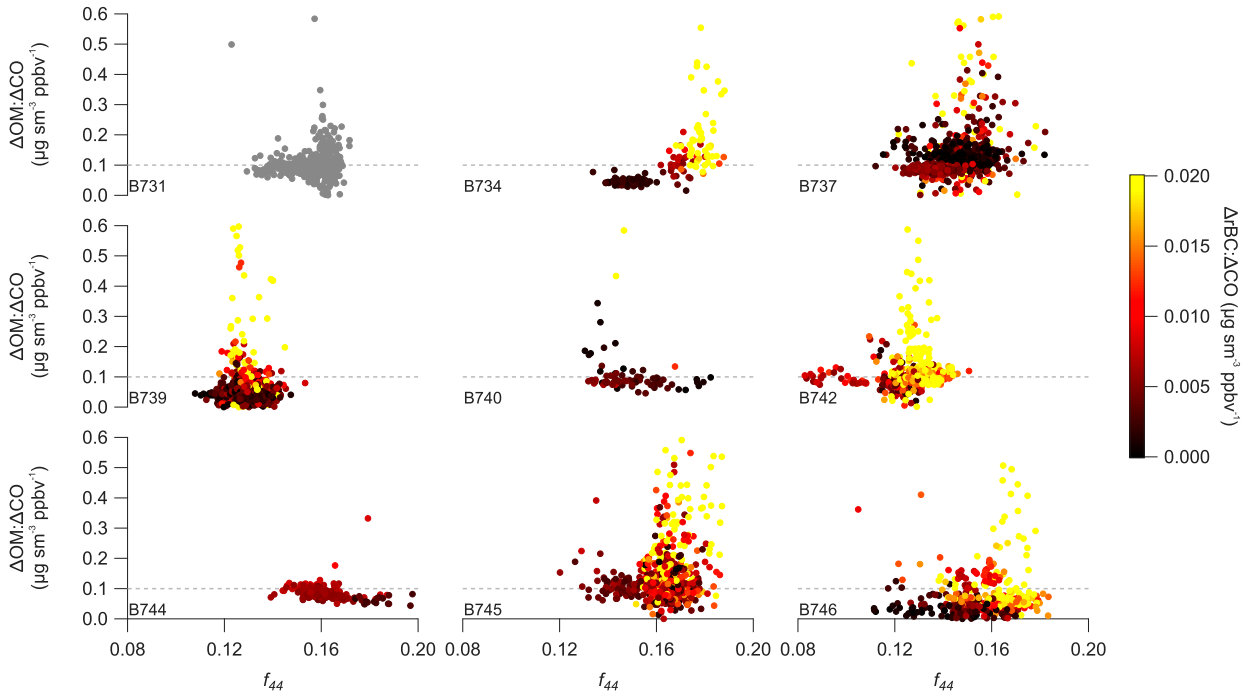

Figure 9. Comparison of the ratio organic matter (OM) to carbon monoxide (CO) vs f_{44} across individual flights from the regional analysis. f_{44} refers to the fraction of the organic aerosol mass signal at a mass-to-charge ratio of 44 measured by the aerosol mass spectrometer. Points are coloured according to the ratio of refractory black carbon (rBC) to carbon monoxide (CO) except for B731 where limited rBC data was available. The red dashed line shows the 0.1 $\mu g\,sm^{-3}\,ppbv^{-1}$ as a consistent baseline for context across all flights.

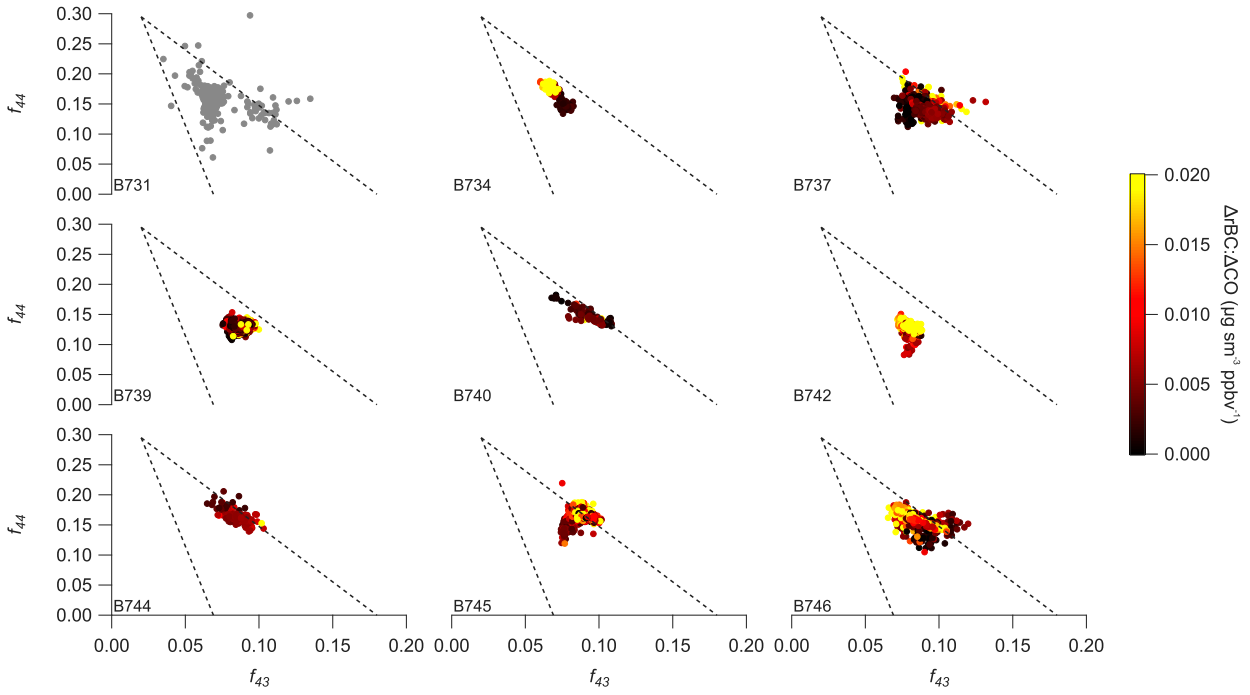

Figure 10. Comparison of f_{44} vs f_{43} from the regional analysis across individual flights, where f_x refers to the fraction of the organic aerosol mass signal at a given mass-to-charge ratio measured by the aerosol mass spectrometer. Points are coloured according to the ratio of refractory black carbon (rBC) to carbon monoxide (CO) except for B731 where limited rBC data was available. Dashed lines show the 'triangle' space reported by prior studies focussed on organic aerosol less influenced by biomass burning (Morgan et al., 2010; Ng et al., 2010).

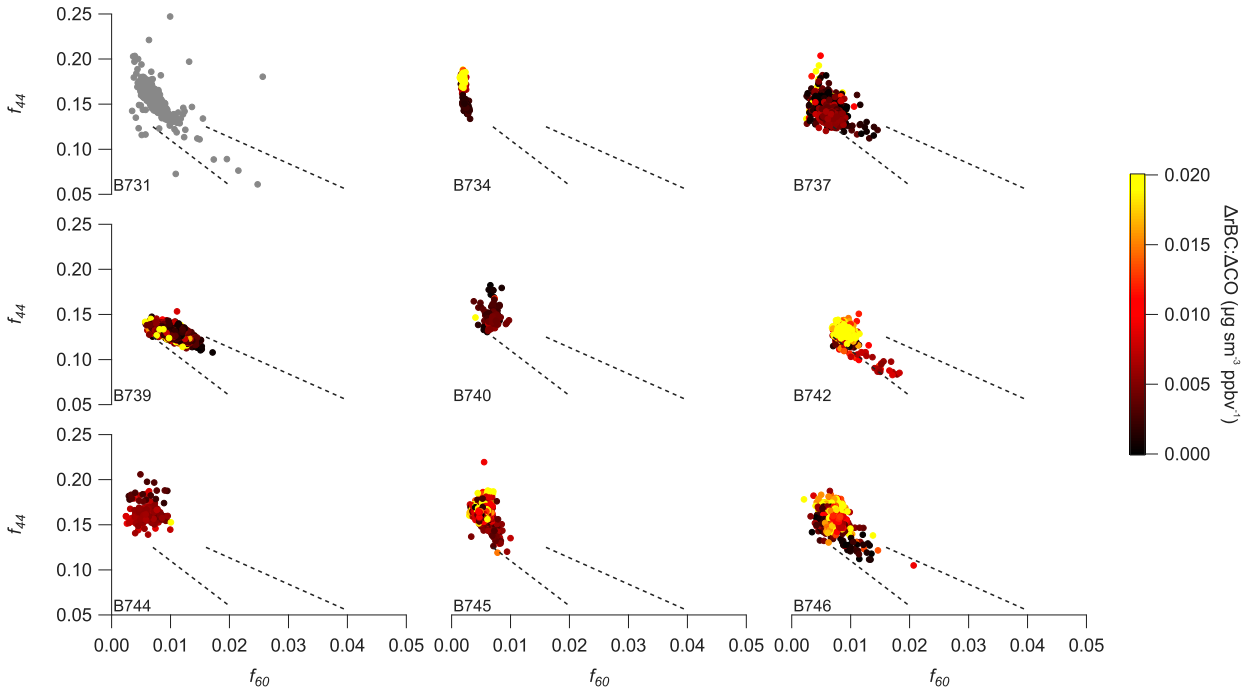

Figure 11. Comparison of f_{44} vs f_{60} from the regional analysis across individual flights, where f_x refers to the fraction of the organic aerosol mass signal at a given mass-to-charge ratio measured by the aerosol mass spectrometer. Points are coloured according to the ratio of refractory black carbon (rBC) to carbon monoxide (CO) except for B731 where limited rBC data was available. Dashed lines are from previous studies on biomass burning organic aerosol aging, with the upper line from Cubison et al. (2011) and the lower line from Lack et al. (2013).

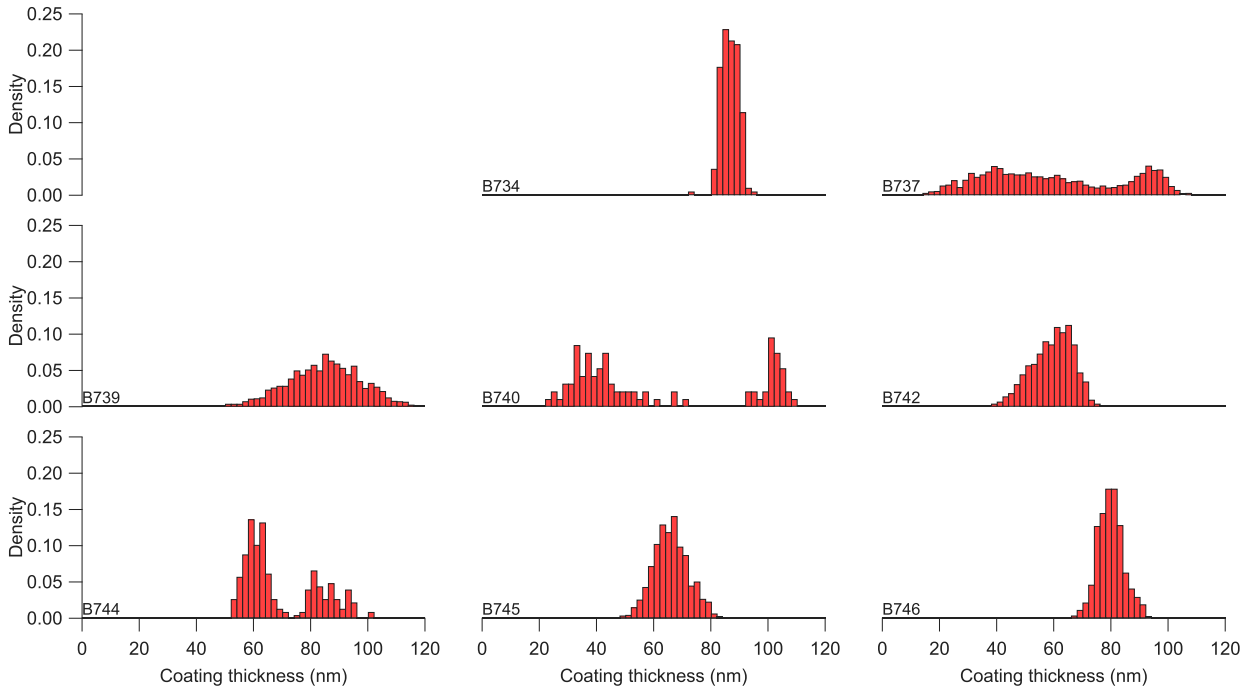

Figure 12. Histograms of refractory black carbon coating thickness from the regional analysis across individual flights.

Table 1. Flight summary of the operations included in this study. All flights were conducted during 2012. Local time is UTC-4. Take-off and land times include airport used: PVH - Porto Velho, PMW - Palmas. The phases correspond to the synoptic meteorological conditions during the study, where relatively dry conditions were prevalent in Phase 1 (P1), before the period when the monsoonal transition was being established in Phase 2 (P2).

Flight	Date	Take-off (L)	Land (L)	Phase	Operating region
B731	14 September	10:00 (PVH)	14:35 (PVH)	P1	Rondônia
B734	18 September	08:00 (PVH)	12:15 (PVH)	P1	Rondônia
B737	20 September	10:45 (PVH)	14:45 (PVH)	P1	Rondônia
B739	23 September	08:00 (PVH)	12:00 (PVH)	P2	Rondônia
B740	25 September	07:45 (PVH)	11:00 (PVH)	P2	Rondônia
B742	27 September	09:00 (PMW)	12:30 (PMW)	P2	Tocantins
B744	28 September	09:00 (PVH)	12:30 (PVH)	P2	Rondônia
B745	28 September	14:00 (PVH)	17:30 (PVH)	P2	Rondônia
B746	29 September	09:00 (PVH)	13:00 (PVH)	P2	Rondônia/Mato Grosso

Reviewer Comments

We thank the reviewers for their comments on our manuscript, which we have sought to answer and/or amend the revised submission. In the following we have included the reviewers' comments in bold text, with our responses beneath.

In the revised manuscript, significant additions are provided in red text.

Given that each of the referee's has questioned the reasoning for an apparent lack of additional measurements, namely total particle number concentrations, particle size distributions and optical properties, we provide a summary of our reasoning below.

Unfortunately these measurements either suffered from complete instrument failures on several flights, or did not pass quality assurance checks when analysed post-campaign. Instrument failures were particularly acute during our case study flight, so could not be included as an extended analysis for that flight alone.

In addition to the above instrument issues, in response to reviewer #2 regarding the absence of brown carbon measurements and the absorption Angstrom exponent, our PSAP measurements were single wavelength only.

Given our focus on the wide ranging conditions both within and between flights, we decided to base our study on the AMS and SP2 measurements given the data coverage was much greater and we had confidence in the robustness of the data. The alternative would have been to use a severely compromised dataset that would have made direct comparisons between flights impossible, while significantly lengthening the paper. Furthermore, the combination of the AMS and SP2 is the major novelty of our study, and provides valuable additions to the literature even with the absence of other measurements (most of which have been more extensively studied in the existing literature).

Modified combustion efficiency (MCE) estimates were also mentioned by the referees – based on our analysis and reading of the literature, we do not find that such estimates are robust for regional studies such as ours where the enhancements of CO2 above the background level are often minimal and/or impossible to quantitatively estimate. In fact, we did not have sufficient confidence to use such estimates for the plume-run portion of our study as the uncertainties were large and rendered the MCE values as effectively non-quantitative. Similarly to the discussion regarding inclusion of aerosol microphysical and optical measurements, we instead have focussed on the novel measurements where we are confident in their robustness. Given this, we use MCE for near-field situations only, where we have greater confidence in both the CO and CO2 measurements and determination of their background values.

In summary, the measurements presented in our study are what we have available and provide a valuable and unique addition to the literature, even without the additional measurements suggested by the reviewers. We cannot change what instruments and data are available – there are significant challenges to conducting airborne campaigns of this size

in a remote environment where heat and humidity present sizeable obstacles for instrument operations.

Anonymous Referee #1

This paper describes the analysis and interpretation of biomass burning carbonaceous aerosol emissions over Brazil from an individual plume case study and from regional haze. These emissions are thought to comprise a large fraction of the global aerosol budget and are important in their radiative effects. As these emissions age, there is a potential for changes of organic aerosol mass (OA or OM) relative to the standard inert tracer carbon monoxide (CO) due to evaporation (decrease) and secondary production (increase). The work presented here is from a unique dataset and is particularly relevant to current investigations into how biomass burning emissions are incorporated and treated in global models. Therefore, the paper is of interest to the readership of ACP. However, the conclusions could be made more strongly if a few more details about the observations were included as described below.

One of the main conclusions is that the observed regional differences in the relationships between OM and refractory black carbon (rBC) with CO are due to the initial emissions from the fire source. However, the data actually presented in this manuscript only partially support this conclusion. The manuscript presents a very clear aging case study of OM from only a single, tropical fire with an initial, low, modified combustion efficiency (MCE) of about 0.79. The ratio of OM to CO for this fire did not change significantly from the source emissions (Figure 3) and is quite similar to the average regional haze OM for the entire study (Figure 8). The near-fire emission paper using the same dataset (Hodgson et al., 2018) included fires from the Cerrado region that had higher average MCE (about 0.94) with roughly half of the OM/CO initially emitted compared to the tropical fires (Table 5 of that paper). The current manuscript shows that the ratio of OM to CO for haze from the same Cerrado region (flight B742) is similar to that observed for the tropical fire case study (Figure 8). While this implies that a Cerrado fire ages from a lower OM to CO ratio to a higher one, this case was not presented as a contrast to the low MCE, tropical fire. It is difficult to see that any regional haze OM to CO ratio differences are directly related to differences in fire source emissions. Hence, this conclusion of the manuscript would be stronger if it included an additional aging case study of a fire with a relatively-high MCE and how the aged aerosols from such a fire transformed into regional haze.

While we agree with the reviewer that the manuscript would be stronger if it included an additional aging case study of a fire with higher MCE, we simply do not have such measurements. The fires in the Cerrado were typically much smaller in size and the amount of smoke quickly dissipated to sub-visible plumes; we were able to sample the above-fire plumes in the near-field, which was the focus of Hodgson et al., 2018, but plume aging measurements examining the transition from the near-field to regional haze were impossible.

We would also add that directly comparing the regional and the near-field measurements over the Cerrado is complicated by the regional aerosol likely being from a range of sources that have been advected and mixed. This is particularly relevant in the Para/Mato Grosso/Tocantins borders as the vegetation and fire characteristics have larger gradients

than in the west. As such we do not focus on such comparisons as attempting to separate the sources e.g. via dispersion modelling, is beyond the scope of our measurement-focussed study.

While the analysis of the organic fraction of the biomass burning aerosols was fairly thorough, the analysis of rBC in this paper was surprisingly very limited. It was restricted mostly to coating thickness and some information on delta(rBC)/delta(CO) for the regional haze. rBC (number or mass median?) core sizes were mentioned in the abstract and some of the text, yet no data were presented. Furthermore, the sizes reported here were very different (250-290 nm) from those presented in the Hodgson work (number medians around 100 nm and mass medians around 200 nm). It looks like the mass of rBC in the fire overpass intercepts (and associated background) were significantly higher than in the along plume straight-and-level run (SLR) (Figure 2). There did not seem to be any explanation for this or how it might impact the derivation of a "background" rBC mass for the delta(rBC) calculations. More rBC data (not just in the text but in figures) and analysis should be included in this manuscript (e.g., mass of rBC, number fraction of rBC particles to the total number of particles, rBC-core size, and number fractions of rBC particles with coatings compared to all rBC particles as a function of plume age and similar values for the regional haze). Also, there was no data showing changes in the ratio of rBC to CO with wet scavenging. Such additional information about the rBC-containing carbonaceous aerosols should be included in this manuscript.

We contest the reviewers' assertion that our rBC analysis was 'very limited' – rBC mass, coating thickness and rBC:CO ratios feature in every figure of the manuscript aside from the maps and the two AMS mass spectra-related figures from the plume case study. The ratio of rBC:CO in particular is a crucial aspect of our analysis and we provide far greater detail showing the range of values we observe, rather than bulk averages as has been common in the existing literature.

We did not include as much rBC size distribution data as the number of figures in the manuscript was already large (as noted by reviewer #2 who suggested reducing the number of figures) and we felt that we could sufficiently describe the results in the text body of the paper.

Several of the derived measurements suggested by the reviewer relating to comparing rBC number to total particles are not feasible from our dataset due to the instrument issues mentioned in our introductory response. We do not have direct measurements of wet scavenging and can only present our observed rBC:CO ratios and coating thickness across each flight – as we note in the manuscript, we use the changes in rBC:CO ratio to infer the presence of wet scavenging of the regional aerosol; without a different direct measurement, examining the rBC:CO ratio as suggested by the reviewer would be a circular endeavour.

In response to comment re. P6 L38-41 below, we have added a direct comparison of the rBC core sizes from both the above-fire intercepts and plume-run finding mean sizes of 270 nm and 249 nm respectively, with significant variability in each. In this paper we have reported the geometric mean diameter, whereas Hodgson et al. reported the diameters from log-

normal fits on the average distributions from the in-plume sampling, so the reviewer is not drawing an apples-to-apples comparison.

The reviewer notes that the rBC mass in the fire overpass intercepts were significantly higher than the along-plume sampling – given the distance and time since emission between the two, dilution and mixing with cleaner air away from the immediate vicinity of the fire are likely key in driving the observed peak and background mass values.

In summary, we feel that we have presented a great deal of detail on rBC-containing carbonaceous aerosol that is new to the literature both in this region and more generally. Had we had the additional measurements required to present the further suggestions from the reviewer, then we would have included them.

Minor comments:
P1 L6 and elsewhere: OA was used here and OM was used in other places. Consider using one or the other.

We have changed the majority of uses of OA to OM throughout the manuscript. We did retain OA in some cases where it was more appropriate e.g. for other studies that didn't specifically measure OM. We also retained the use of OA in the abstract as a more generic "catch-all" term.

P1 L17-19: If supported with additional analysis, this last sentence is confusing and should be re-written more clearly.

Rephrased.

P4 L17: change "refractory" to "non-refractory"

Amended.

P5 L32: should "cross-plume" be in front of "SLR" here?

Amended.

P5 L44 and elsewhere: The numbers for several figures are missing in the text.

This was a result of incorrectly referencing the Figures in our LaTeX file – we have amended the references to fix the issue.

P5 L51: Add citation to the Hodgson paper for the 97.1% value.

Added.

P6 L25: How does the time to reach background levels (3 hours) compare with calculated entrainment/mixing rates base on the boundary layer heights and the atmospheric (in)stability?

We have investigated whether we can reliably use the aircraft meteorological data to estimate the entrainment rate. However, due to the flight path followed and the limitations on aircraft duration the necessary information was not available.

P6 L38-41: What were the delta(rBC)/delta(CO) ratios and rBC core diameters referred to here? Suggest showing in SI.

We have added the values to the text, while noting that the somewhat lower values in the plume-run compared to the above-fire intercepts possibly point to a slight shift in fire conditions, although the variability is large in both cases making it likely unwise to draw definitive conclusions.

P7 L48 and others shortly afterward: "absolute difference and correlation between the mass spectrum and the background" – does this refer to deviation of the slope from one and r-value from a linear least squares correlation obtained by plotting the absolute peak intensities (instead of the "fraction of organic signal" peak intensities) of the top spectrum versus the bottom spectrum in Figure 4? Please clarify.

We have added a note to the paragraph to clarify what is being reported.

P8 L44 and after: Were there any flights where there was a clear distinction in delta(rBC)/delta(CO) before and after raining? This would be interesting to explore in light of the assertions made here about air mass history and fire burning conditions.

We agree that such an examination would be of interest but we do not unfortunately have observations to address this effect – our flight times were relatively short due to the operational restrictions that are unavoidable when working in such a remote location, as well as factoring in transit times that further cut down on low-level flying.

P9 L15 and earlier: The fraction of rBC particles that were coated is discussed in this paper, but the actual fraction is not shown in this paper. Should be included somewhere.

There appears to be some confusion on the nature of our measurements – we present coating thicknesses for rBC particles, not the fraction of rBC particles that were coated. The clearest example of this is Fig. 12 where we show the density of rBC particles with a given thickness – as discussed in the paper, we typically see coatings of greater than 40nm, with the lowest coatings being in the 10-20nm range during B737. Our measurements imply that the rBC is at the very least partially coated across our dataset i.e. the "fraction" is close to unity but the thickness of such coatings does vary.

P9 L22-23: Should include the rBC core-size data somewhere.

We did not include figures illustrating the data as there was little value in them due to the limited variability we note in the text, thus such figures would be fairly redundant and add little that could not be communicated in the main text.

P10 L43 & 44: "limited net enhancement of OA" seems to be inconsistent with "net OA production". Please clarify.

Amended.

P10 L54-56: This last sentence was confusing; suggest revising. Perhaps add a second statement (if observed) about how the rBC mass was useful for distinguishing differences in air mass history for two similar instances of OA/CO with the same f44.

We have added that rBC:CO was the key diagnostic for distinguishing differences in air mass history to make our statement clearer.

P11 L34-35: This statement is made without mentioning the actual fractions of coated rBC particles in the different locations studied.

We have added some additional commentary to the text detailing the observed thickness of the particles, that indicates that the majority of rBC particles are at least partially coated with the lowest observed thicknesses in the 10-20nm range. We also refer to the response above regarding P9 L15.

P11 L54: consider adding to the end of this sentence "to essentially background values."

Based on Figs. 4 and 5, we have amended the suggested statement as the data implies there is potentially scope for further aging to "essentially background levels" – in the prior analysis and discussion in the main text we referred to the values being "comparable/resembling" without going as far as to say they had reached background levels, which is not categorically supported by the observations.

We have added "…and a comparable magnitude to the background regional aerosol" to the main text.

Figure 1: It was unclear how the flight track matched up with the map. Suggest enlarging the map to show where the fire was.

We have enlarged the map to better illustrate the flight's location.

Figure 2: The values may be easier to obtain/visualize directly from the plots if they had horizontal lines across them. It would be good to see where the background CO, OM, and rBC values were chosen, especially for the along-plume SLR. Consider having plots of OM vs CO, rBC vs CO, and Inorganics vs CO in the SI. Add the fire altitude to the caption. Consider expanding the altitude axis and including the ground level height.

We have added horizontal lines to the plots to aid reading the figure. Adding the sections where the background values were determined would add significant clutter to the figure, so we have omitted these details. Regarding the along-plume SLR specifically, a short SLR in clear air from 1225-1230 was used prior to the aircraft repositioning to conduct the plume run.

Figure 3: This could be split into three separate figures: one of the top three plots, one of f44, f43, and f60 vs. plume age (instead of Figure 5), and one of the rBC data (delta(rBC)/delta(CO), rBC median number core size, fraction of rBC particles coated, and rBC coating thickness) vs. plume age. All three of these should have "background" values on the right hand side plus both horizontal and vertical grid lines for reference. Consider adding data from the cross-plume intersect points too.

We have added horizontal lines to the plots to aid reading the figure.

Adding cross-plume intersect points and "background" values would complicate the figure more than is really necessary – the aim is to show the plume-run data and compare it to the above-fire intercepts, not show every data-point. We did previously experiment with adding the background values but this was largely superfluous as the data beyond 70 km were essentially showing the same information.

As discussed below, we have not removed Figure 5 and the suggestions by the reviewer would swell the number of figures unnecessarily as we have captured the details of the additional parameters (where measured) in the text. Additionally, reviewer #2 noted that the paper is "heavy on the figures" – we agree and this motivated our decision to not include more of them.

N.B. While reviewing Fig. 3, we realised that we had made an error when transferring the Hodgson et al. OM, nitrate and sulfate ratios – we had failed to convert to the units we use in the figure, whereas in Hodgson et al., the molar ratios are reported. The corrected values are a factor of 1.23 larger as a result in the updated figure. We have also added that the values are from Hodgson et al. in the figure caption.

Figure 4: The background mass loading from "regional aerosol haze away from the main fire plume study region" is 4.1 here, but in Figure 7 the average background mass loading for this flight was about 10. Why were they so different?

Fig. 7 doesn't show the "average background mass loading" as stated by the reviewer – it shows the average regional loading across the flight which is subject to e.g. regional scale advection of the aerosol burden. The background mass loading referred to in Fig. 4 is just one portion of the study in the vicinity of the fire we studied, which was evidently a somewhat cleaner environment than the region to the north where the rest of the regional measurements were primarily conducted.

Figure 5: It is not clear why the dashed lines are important. How would these plots look if only mixing was occurring? Suggest omitting this figure or relegating to SI.

The dashed lines are from prior studies and are useful for understanding how our measurements relate to such work and are referred to in the text. Their addition is to illustrate that our measurements fall within the range of prior AMS observations, which is a useful comparison. Furthermore, having presented this exact figure at conferences attended

by others in the AMS community, we had valuable discussions as a result and strongly feel the figure is an important part of our work that belongs in the main manuscript.

Figure 6: Suggest enlarging the map showing only the portions of the flight tracks where the regional haze data were obtained and labeling the states with regional haze flight data. For the enlarged map it would be helpful to have an indication of scale.

We have enlarged the map and included an inset figure showing the whole of South America to illustrate the flight locations. We have also added a scale for the enlarged map and text labels for the different states.

Figure 7: Consider adding the location information from Table 1 to the caption, or at least mention which two flights were not only over Rondonia. Maybe point out the flight numbers on the map in Figure 6?

We have added the flight locations to the caption and added labels for B742 & B746 to Fig. 6.

Figure 8: It is difficult to distinguish variation in delta(rBC)/delta(CO) because the points are outlined in black. Suggest including the average value for each delta(OM)/delta(CO) value shown. Does B737 show the opposite trend (higher delta(OM)/delta(CO) with lower delta(rBC)/delta(CO)) than flights B734 and B746 (with lower delta(OM)/delta(CO) for lower delta(rBC)/delta(CO))? It's difficult to see either trend for flight B739 – are both those slopes for relatively low delta(rBC)/delta(CO)? Is there another indicator that could be used to distinguish low delta(rBC)/delta(CO) arising from precipitation rather than burn conditions? Perhaps the B737 flight was more/less impacted by precipitation than the other flights? Also, consider a table in the SI of background OM and CO (and rBC) for each correlation shown.

We have altered the colour scheme on the plot to make comparisons easier. The red text shows the slope of the line-of-best-fit for dOM vs dCO, which is essentially the average value, which was suggested for inclusion by the reviewer.

As discussed elsewhere, we do not have a clear and quantitative means of separating the influence of precipitation from burn conditions.

N.B. We have updated the colour scheme on Figs. 9-11 to match that used for Fig. 8.

Figure 9: How do low delta(CO) values contribute to the uncertainty in the high delta(OM)/delta(CO) ratios?

The reviewer raises a good point here – at least some of the extreme dOM/dCO values is likely driven by low concentrations of OM and/or CO. We have added a comment to the text to highlight this.

Figure 12: Suggest adding tick marks on the x-axis for the flights in the top and middle rows. Also consider coloring each bar with the average delta(rBC)/delta(CO) ratios for that coating thickness bin.

This is an aesthetic choice to cut-down on generally superfluous axis labelling (sometimes referred to as "chart-junk" in data visualisation discussions), so we have kept the tick marks as is.

As for colouring each coating thickness bin with the rBC:CO ratio, the data indicates that such averaging would be misleading as the ratio can vary significantly for a given coating thickness and vice-versa.

Table 1: (L) must mean Airport. What does Phase P1 or P2 mean?

These refer to the distinct meteorological phases following Brito et al. (2014) and Darbyshire et al. (2018) that are defined in Section 4.

We have added this additional information to the table caption.

Anonymous Referee #2

The present manuscript is a highly-focused piece of work that examines chemical and microphysical property changes of biomass burning aerosol emissions that were sampled during the SAMBBA field campaign in Brazil. By and large the manuscript is written reasonably clear (explicit areas where more clarity is needed are highlighted below). As biomass burning (BB) events represent a major source of particulate matter injected into the atmosphere, it is indeed important to characterize the emissions and to understand how the chemical, microphysical, and optical properties transform as the plume ages so that models can, in turn, improve upon there fidelity. Using the analysis tool of excess mixing ratios, the authors report on a negligible net increases in organic aerosol (OA) even though there is concomitant changes in chemical properties - namely the oxidation state of the OA. This finding is inline with that reported by others and the authors put forth the same argument as that put forth by others that the loss of primary organic aerosol (POA) due to plume dilution is offset by the production of secondary organic aerosol (SOA), hence the negligible change in net OA loading. The other reported findings centers on refractory black carbon and its mixing state. In summary, the present manuscript adds important findings to a growing body of data on biomass burn-generated carbonaceous aerosol production and evolution and as such should be published. That said, to this reviewer at least, this manuscript has a feel of being incomplete in some of its analyses and in other areas left this reviewer wondering why other datasets were not part of this manuscript. This feeling could be simply that the authors are parsing out various subject matter for other manuscripts (e.g., optical properties). If this is indeed the case, the authors should be explicit about that. Once this authors address this ad some other top-level items listed below along with several specific items (e.g., figure numbering and clarification text) the manuscript should be acceptable for publication.

While this manuscript is highly-focused, as highlighted above, it seems that the authors miss the opportunity to role in other data sets that could, potentially, elucidate all that is

going on in these complex emissions plumes. For example, the authors report that there are changes in the OA chemical properties and that they observe that the rBC coating thickness changes as a function of plume age, yet authors do not report on, nor reference any parallel paper, that looks at aerosol size distribution - arguably one of the most fundamental of measurements in our business. Doing so could tell us something about the roll of coagulation near the fire source as well as informing us about how the distribution evolves. Does the mode stay constant or grow? As hinted at above, perhaps the authors have the intention of publishing a separate aerosol size distribution-centric paper. If this is indeed the case they should make reference it, as the analysis of these dataset would easily complement what is being learned from the AMS. The absence of this dataset is even more puzzling given that the authors report on geometric mass mean diameter for rBC - along with estimates of the coating thicknesses. Why present microphysical properties of only one species (rBC) and not the primary particulate species (OA)?

Similarly, the authors say nothing about aerosol light scattering or light absorption. How does the scattering Angstrom exponent evolve with plume age in the near field? Does the mass scattering efficiency track what is observed with the AMS? In their rBC coating thickness analysis, the authors assume that the coating this transparent (coating refractive index of 1.5 +0i). What is the basis for this assumption? BB events are a known source of brown carbon. What does the absorption Angstrom exponent suggest? And, of course, what is the SSA doing in these first few hours where a lot of chemistry appears to be going on? As with the size distribution, perhaps the authors will report on this in a separate manuscript. It just seems to this reviewer that the absence of any reference to either the optical or size distribution datasets misses any opportunity to better examine what is going on.

In their examination of regional BB haze, the authors use the AMS tracer f44 and the ratio of rBC to CO. As the author state, rBC and CO are relative inert tracers that are strongly controlled by initial conditions, and that the ratio can provide some information about the influence of precipitation. But my question to the authors, especially when examining regional haze, is how do you know what the initial ratio was at the various sources that are contributing to the haze? Are all fires assumed to exhibit the same burning phase conditions (e.g., flaming versus smoldering)? Figure 7 indicates that the mass fraction of rBC ranged from 2% to 12.4%. Are the authors saying that the burn conditions are the same for these two bounding conditions? Here is where I would have expected some discussion of modified combustion efficiency (MCE) which might help answer this by telling us something about the initial burn conditions. Under active flaming conditions little CO is produced and more rBC while under smoldering conditions, more CO is produced and little rBC. Could this explain the variability observed in rBC mass fraction contributions or is the variability driven by differences in source fuel or subsequent cloud processing (e.g., rBC loss through precipitation)? While not listed in this paper, Darbyshire reports that a CO2 analyzer was deployed on the FAAM and thus is presumably available to use along with the CO data set, to estimate the MCE. It might b interesting to see if any of the variability in rBC mass fraction contributions can be explained by MCE. And if so, maybe the MCE can, in turn, improve the robustness of the rBC/CO ratio analysis. Finally, the authors might want to check out Collier et al., (figure 4; EST, 50, 8613, 2016) who

reported on the relationship between OA production and MCE - where OA production was favored under smoldering conditions.

We have not stated that rBC and CO provide a conclusive measure of the initial ratio when presented for our regional-scale observations. We have also not stated that all fires exhibit the same burning phase; past literature would suggest burn phase exists on a continuum rather than a simplified split between flaming and smouldering. We regularly state in the main text and present the detailed point-by-point measurements to illustrate the variability from flight-to-flight and within single flights/regions.

Our usage of the ratio of rBC to CO is very clear - we use it to reflect differences in air mass history that are most likely a function of both the initial fire conditions and the influence of precipitation. We feel this is a fair usage of such measurements as they do provide clues on processes that are relevant for the transformation of the aerosol burden on the regional scale.

As we noted in the introduction to our responses, we do not find that MCE is a robust measure on such scales.

The authors state that the fire used in their case study was likely a natural fire and one that is "highly-smoldering". Do we expect a highly-smoldering fire to generate a 12.4% mass fraction of rBC?

The reviewer appears to have confused our case study flight, B737 where the regional rBC mass fraction was 2%, with B746, which had the largest contribution of rBC with 12.4%. Regardless, Fig. 7 presents the regional boundary layer observations, which are not directly comparable with the in-plume measurements.

The manuscript seems heavy on the figures (12 figures). The authors are encouraged to try to reduce this number.

We are presenting a large body of observations in significant detail and feel that the manuscript benefits from the carefully chosen figures as is. Aside from Figs. 1 and 6 (the maps), each figure has at least a paragraph discussing the results and are thus central to the main manuscript text and not supplementary information.

Specific comments

We're unsure which exact lines the specific comments from Reviewer #2 refer to as they do not match up with the ACPD version of the manuscript – we have though identified and addressed the instances of missing figure number references. We have added our responses regarding the other aspects below.

Abstract: page 1, Line 32: Please add "mean mass diameter" in front of "250- 290 nm".

Amended.

Page 4. Line 11: Please add figure number. (“1”)

Amended.

Page 4, Line 22: Please add figure number (“1”). Also, not clear what comes after “and”

Amended.

Page 4, Line 30: Please add figure number (“2”)

Amended.

Page 4, Line 35: Please add figure number (“3”)

Amended.

Page 5, Line 4-5: How do the authors explain a slight decrease in rBC core diameter? This is a curious finding and this reviewer cannot help but wonder if the reported decrease is due to a measurement artifact as this was reported for the “case” study where the plume lifecycle could be well constrained (i.e., no cloud processing of coated rBC particles that could selectively wash out larger diameter rBC-containing particles). What were the highest number concentrations encountered near the source? Back-ofthe-envelope calculations assuming a size mode of 125 nm rBC particle and 1.5 ug/m3 suggests < 1000 particles/cc which should be low enough not to suffer from particle coincidence. Again, this is a very curious finding to simply close out a paragraph with, with no follow on statement or discussion.

The reviewer is correct that the rBC number concentrations were low enough for particle coincidence to be relatively limited. Peak concentrations were 600 particles/cc and the estimated coincident particle concentration determined by the SP2 data processing was below 50 particles/cc.

Regarding the actual change in size, the variability is large across the length of the plume and the change is relatively minor (on the order of 10-15nm total), so we did not over-interpret our observations.

We have added a note to the paragraph on the rBC measurements to highlight the small changes in rBC parameters that may imply some change in burn conditions (which is perfectly possible over a 3-3.5 hour period), while noting that the variability is large.

Page 5, Line 7: Please add figure number (“4”)

Amended.

Page 5, Line 23: Please add figure number (“5”) - Are both figures 4 and 5 necessary?

Amended missing figure number. As stated previously, we feel the figures are necessary as they complement each other – based on prior presentations of our findings and existing AMS literature, including both is useful for comparative purposes.

Page 5, Line 33: What is the useful "aging" range of the f44 marker as a tracer of age?

Based on prior work and our own observations of the case study fire (see Fig. 3 and discussion in Section 3), we use *f44* as an indicator of the aging of the organic aerosol component (rather than aging of all particulate and gas phase material per se). As a rule of thumb, the average value for such regional scale measurements in polluted environments tends to plateau at approximately 0.2 and are interpreted as being reflective of highly aged material – higher values have been observed in remote environments e.g. see Morgan et al. (2010).

For the purposes of our manuscript, it appears that the "useful" aging range is up to approximately 0.2 as based on Figs. 9, 10 & 11, the observed values do not pass beyond this point. Thus the most aged material we observe is in this range and reflects the regional background as far as the aging of organic aerosol is concerned. We refer to this as the "end-point" of the evolution in the discussion.

Page 6, Line 23: Please add Figure number ("5")

Amended.

Page 6, Lines 34-39 and page 21, Figure 8. As discussed above, perhaps examining the MCE might provide some useful insights. The delta rBC/delta CO scale in Figure 8 nominally ranges from ∼0.0025 to ∼ 0.02. Is this variability driven by cloud processing (i.e., precipitation) or MCE.

Addressed previously – as stated in the text we cannot infer whether such changes are a consequence of precipitation or initial fire conditions.

Page 25, Figure 12: Again, not to harp on the MCE theme, but it might prove interesting to examine whether the variability in coating thickness is driven by processing or MCE.

See prior comment and our overall commentary at the beginning of our author response.

Anonymous Referee #3

This paper provides an analysis of BC, OA, CO and OA oxidation state for a 2012 airborne field campaign of biomass burning emissions at Porto Velho Brazil. Data is presented in two parts, a case study of a single smoldering tropical plume and a regional analysis of 9 other regional flights. Some aspects of the paper were nicely put together, such as the observation of the evolution of smoke oxidation state. But the overall purpose of the paper on the evolution of aerosol mass is short on many important details. Trying to sort out mass evolution is quite tricky, especially for an individual plume. Accounting for the temporal evolution of the fire, controlling for combustion efficiency, linking source

plumes to the regional haze, all take a great deal of care. One also needs to demonstrate appropriate cross correlation between numerous parameter to ensure an apples to apples comparison to anything about temporal evolution. This is especially true in the present paper where it is clear from the regional survey work that the smoke particle properties show a lot of heterogeneity. While, I think the authors have spent a great deal of time on this paper, I found the narrative unconvincing. I think the paper probably needs significant revisions and resubmitted. At this point I think I can keep my comments to three main themes.

1. **The paper references a great deal of "Recent activity" but the whole line of scientific thought on particle evolution came out of the ABLE, ESPRESSO, SCAR-C, SCAR-B missions of the late 80's and 1990s. These studies were much more rigorous than anything that is presented here. Liousse demonstrated he issues with particle evaporation, and Martins, Reid and Hobbs evaluated secondary production and found in well documented Lagrangian plumes samples significant production. We know the authors of this paper are aware of this work because some of the co authors were actually on these papers. A summary of this work is in the 2005 biomass burning review papers by Reid. The conclusion "secondary production is complicated and varies by fire" is indeed true, but there has been a great deal of work done in the past and even currently (all un referenced) that actually narrows down processes. Reid and Martins points are that secondary production and basic condensation happen very rapidly. Secondary production of sulfate requires cloud processing. Going back to the late 1980s significant and rapid organic acid production has been observed (I think ABLE mission). This paper lacks any concrete linkage to past knowledge to move the field forward.**

   We certainly did not wish to exclude past work and relied on citations to review papers and their references in the interest of brevity. We thank the reviewer for the suggestions and have added a reference and discussion of the review paper from Reid et al. (2005) to summarise past findings.

   Where we did focus on individual studies, we highlighted predominantly AMS measurements and those conducted in Brazil as these were most relevant to our paper as we relate our observations to a key AMS mass spectral marker (*f44)* which was not measured in the prior studies in the 80s and 90s.

   Furthermore, past studies relied on either optical or mobility number concentration measurements that do not separate out the organic and inorganic components, thereby conflating the different processes these are subject to. Organic composition measurements were typically determined from thermal evolution techniques that are prone to biases and have far lower time-resolution than our AMS measurements. These are key aspects that differentiate our study from prior work.

   We also note that our measurements differ with many of the studies noted by the reviewer in that we were primarily presenting regional measurements i.e. not "well documented Lagrangian plumes" aside from our case study. We also had different instrumental payloads, which have their pros and cons – we focussed on discussion

of processes we could more directly infer while also outlining our measurements so that future work could use our observations e.g. plume modelling to constrain the likely processes.

We feel the reviewer is making an unfair criticism of our study in that we have not claimed, nor did we set out to, quantitatively explain all the relevant processes relating to secondary aerosol production in biomass burning plumes; ours is an observational study where we have explored the various potential drivers on the transformation and aging of carbonaceous aerosol.

2. **The single case study presented is for a low combustion efficiency plume without any presented evidence that downwind samples are of the same fire characteristics. During the observation of fires in SCAR-C and SCAR B it was found that fire properties change rapidly. Given that the test case had a MCE< 0.8, then black carbon production must have been at a minimum. Perhaps there was some flaming combustion along the periphery. Therefor the relationship of secondary production to rBC is probably pretty tenuous. At the same time, most of the cases observed for secondary production have been associated with flaming combustion. Smouldering combustion is essentially a surface reaction. So with the limited data provided, I am not sure what to make of this particular test case.**

   We're unsure exactly what the reviewer is referring to when they state that the "relationship of secondary production to rBC is probably pretty tenuous" – we do not focus on this as a part of our analysis of the case study – instead we relate our measurements to the distance of the smoke from the main fire and approximate age of the plume. We present the black carbon measurements as these are unique in terms of the existing literature on fire in Brazil and in general. Furthermore, they illustrate that the black carbon is rapidly coated at source, which in itself is a valuable contribution to the body of literature on black carbon in smoke plumes.

   While Reviewer #3 is unsure of what to make of our particular test case, Reviewers #1 and #2 have seen the value in our observations, as well as keen interest in our findings from the wider community when this work has been presented previously. Our case study is a presentation of the fire that we were able to observe during our flight campaign and serves as a useful addition to the literature with it being on the more extreme end of smouldering fire conditions – such observations are a valuable contribution as "edge cases" are a good test of our understanding of processes when e.g. recreated in laboratory or modelling studies.

3. **Both comments one and two then project onto overall issue of making an apples to apples comparison to evaluate particle evolution. The authors report an MCE value, so there must be CO2 data available. But no time series of MCE is provided, nor even a CO to rBC ratio plot. Rather the reader has to do an eyeball comparison of the two on a log plot. For the regional samples we are presented with a great deal of variability in particle properties (other than well known oxidation with time) but not the types of additional data that other studies have used to sort out**

what is going on. I think the authors need to spend more time on the data narrative.

As stated previously, we do not find that MCE is a robust measure downwind or on the regional scale, and thus do not present it as it is potentially misleading.

With regards to “additional data”, as discussed in the introductory commentary to our responses, we are constrained by the instrumental payload of the aircraft plus unavoidable instrument failures in what is a challenging environment to conduct measurements. There are unfortunately limits on what is possible in experimental campaigns such as these.

Given the above, the final suggestion from the reviewer that we need to “spend more time on the data narrative” is thus an invalid criticism of our study – we have spent a significant amount of time analysing the unique measurements that had good operational coverage in our study, presenting a large amount of detail and a synthesis of our findings.