Aircraft Observations of Aerosol in the Manaus Urban Plume and Surrounding Tropical Forest during GoAmazon 2014/15

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Abstract. The Green Ocean Amazon (GoAmazon 2014/5) campaign, conducted from January 2014 – December 2015 in the vicinity of Manaus, Brazil, was designed to study the aerosol lifecycle and aerosol-cloud interactions in both pristine and anthropogenically-influenced conditions. As part of this campaign, the U.S. Department of Energy (DOE) G-1 research aircraft was deployed from February 17 – March 25, 2014 (wet season) and September 6 – October 5, 2014 (dry season) to investigate aerosol and cloud properties aloft. Here, we present results from the G-1 deployments focusing on measurements of the aerosol chemical composition and discussion of aerosol sources and secondary organic aerosol formation and aging.

In the first portion of the manuscript, we provide an overview of the data and compare and contrast the data from the wet and dry season. Organic aerosol (OA) dominates the deployment-averaged chemical composition, comprising 78% of the non-refractory PM_1 aerosol mass with sulfate comprising 13%, nitrate 5%, and ammonium 4%. This product distribution was unchanged between seasons, despite the fact that total aerosol loading was significantly higher in the dry season and that regional and local biomass burning was a significant source of OA mass in the dry, but not wet, season. However, the OA was more oxidized in the dry season, with the median of the mean carbon oxidation state increasing from -0.45 in the wet season to -0.02 in the dry season.

In the second portion of the manuscript, we discuss the evolution of the Manaus plume on March 13, 2014, one of the golden days in the wet season. On this flight, we observe a clear increase in OA concentrations in the Manaus plume relative to the background. As the plume is transported downwind and ages, we observe dynamic changes in the OA. The mean carbon oxidation state of the OA increases from -0.6 to -0.45 during the 4-5 hours of photochemical aging. Hydrocarbon-like organic aerosol (HOA) mass is lost with $\Delta HOA/\Delta CO$ values decreasing from 17.6 $\mu g/m^3$ $ppmv^{-1}$ over Manaus to 10.6 $\mu g/m^3$ $ppmv^{-1}$

95 km downwind. Loss of HOA is balanced out by formation of oxygenated organic aerosol (OOA) with ΔOOA/ΔCO increasing from 9.2 to 23.1 μg/m^3 ppmv^{-1}. Because HOA loss is balanced by OOA formation, we observe little change in the net Δorg/ΔCO values; Δorg/ΔCO averages 31 μg/m^3 ppmv^{-1} and does not increase with aging. Our observation of constant Δorg/ΔCO are in contrast to literature studies of the outflow of several North American cities, which report significant increases

5 in Δorg/ΔCO for the first day of plume aging. These observations suggest that SOA formation in the Manaus plume occurs, at least in part, by a different mechanism than observed in urban outflow plumes in most other literature studies. Constant Δorg/ΔCO with plume aging has been observed in many biomass burning plumes, but we are unaware of reports of fresh urban emissions aging in this manner. These observations show that urban pollution emitted from Manaus in the wet season forms much less particulate downwind than urban pollution emitted from North American cities.

10 **1 Introduction**

Aerosol particles have important impacts on visibility, human health, and the Earth's energy balance and water cycle. The impact of aerosol particles on radiation balance, in particular their impact on cloud properties and lifetimes, continues to be a significant source of uncertainty for global climate models (Intergovernmental Panel on Climate, 2014). An extensive series of field studies has shown that a large fraction of the total non-refractory aerosol mass is organic aerosol (OA) and that a large

15 fraction of this OA mass forms in the atmosphere when organic compounds in the gas phase are oxidized and subsequently condense as secondary organic aerosol (SOA) (Zhang et al., 2007;Jimenez et al., 2009). Because SOA is such a large fraction of the aerosol mass, condensation of SOA is critical to growing nucleation-mode particles, which are initially too small to serve as cloud condensation nuclei (CCN), to sizes that are capable of forming cloud droplets (Ehn et al., 2014;Riipinen et al., 2011;Pierce et al., 2012), though a recent study showed particles smaller than 50 nm acted as CCN during GoAmazon 2014/5

20 (Fan et al., 2018). Thus, accurate descriptions of SOA condensation and aerosol growth kinetics are crucial to accurately predicting aerosol size distributions and therefore CCN number concentrations and aerosol optical properties, both of which are required for accurately predicting the impact of aerosols on climate (Scott et al., 2015;Riipinen et al., 2012;Zaveri et al., 2014).

For several years, there has been an interest in studying the Lagrangian evolution of organic aerosol from the emissions of

25 urban centers. Field studies generally accomplish this by arranging fixed observation sites at different distances downwind of a city along the direction of the prevailing wind or by tracking the plume with a mobile platform, such as an aircraft. Larger campaigns may employ both strategies. To account for atmospheric dilution and spatial and temporal variability in emissions, studies often utilize the ratio of excess OA to that of an inert tracer as a metric for evaluating OA formation in a plume (Kleinman et al., 2008;Takegawa et al., 2006;de Gouw et al., 2005;Sullivan et al., 2006). CO is a common choice for the inert

30 tracer because it is emitted during combustion and other anthropogenic processes, is significantly enhanced in urban plumes relative to the background, and is routinely and robustly measured. Measurements of Δorg/ΔCO in aged urban outflow have spanned a range from 47 μg/m^3 ppmv^{-1} in the NE US (de Gouw et al., 2008), to 62-80 μg/m^3 ppmv^{-1}in Mexico City (DeCarlo

et al., 2008;Kleinman et al., 2008), to 100 μg/m^3 ppmv^{-1} in the Po Valley, Italy (Crosier et al., 2007), to 44 – 197 μg/m^3 ppmv^{-1} in Sacramento, CA (Shilling et al., 2013;Setyan et al., 2012), to 97-133 μg/m^3 ppmv^{-1} in Paris (Freney et al., 2014). The same studies have found that Δorg/ΔCO increases roughly linearly with airmass age for the first 1 day of aging and levels off after approximately 2 days (de Gouw and Jimenez, 2009;DeCarlo et al., 2010;Kleinman et al., 2008;Takegawa et al., 2006;Sullivan

5   et al., 2006;Freney et al., 2014). Observations suggest that changes in Δorg/ΔCO begin soon after emission. For example, measurements during the MILAGRO campaign showed that Δorg/ΔCO increased from 10-35 μg/m^3 ppmv^{-1} for fresh emissions to 70-80 μg/m^3 ppmv^{-1} after approximately one day of photochemical aging (DeCarlo et al., 2010;Kleinman et al., 2008). Changes of similar magnitude over similar aging times have been measure in the urban outflow of: Tokyo (Takegawa et al., 2006), the SE USA (Sullivan et al., 2006), Paris (Freney et al., 2014), and the NE USA (de Gouw et al., 2005).

10   Measurements have also suggested that organic aerosol production may be enhanced when urban emissions interact with biogenic emissions. Organic aerosol concentrations have shown strong correlation with CO and other tracers of anthropogenic emissions (de Gouw et al., 2005;Volkamer et al., 2006;Weber et al., 2007;Sullivan et al., 2006). Furthermore, satellite observations suggest that the spatial and seasonal patterns of aerosol optical depth coincide with biogenic emissions (Goldstein et al., 2009). At the same time, radiocarbon dating has shown that a large fraction of the carbon in the aerosol phase is modern

15   and that fraction of modern carbon increased with increasing distance from urban centers (Weber et al., 2007;Schichtel et al., 2008). During the CARES campaign near Sacramento, CA, aircraft observations showed that Δorg/ΔCO measurements were 35-44 μg/m^3 ppmv^{-1} when anthropogenic emissions evolved in the absence of strong biogenic emissions and 77-157 μg/m^3 ppmv^{-1} when the urban plume interacted with regions of strong biogenic emissions (Shilling et al., 2013). Measurements from a ground site during CARES report average Δorg/ΔCO values of 36 μg/m^3 ppmv^{-1} in the Sacramento plume during periods of

20   low biogenic emissions and 97 μg/m^3 ppmv^{-1} during periods of high biogenic emissions (Setyan et al., 2012). Several additional field studies report enhancements of SOA through interactions of anthropogenic and biogenic interactions, but may not employ the Δorg/ΔCO metric (Zhou et al., 2016;Xu et al., 2015;Ng et al., 2017;Bean et al., 2016). The potential mechanisms responsible for these enhancements are known in some cases but remain uncertain in others and have been outlined in recent review articles (Shrivastava et al., 2017;Ng et al., 2017;Glasius and Goldstein, 2016;Hoyle et al., 2011).

25   To date, most studies of the evolution of urban plumes have been conducted in the Northern Hemisphere. Far fewer studies have been performed in the Southern Hemisphere where there is less landmass, lower population, and therefore lower background concentrations of anthropogenic pollutants (Andreae, 2007). The Amazon tropical forest, in particular, is an important ecosystem in which background levels of anthropogenic pollution may sometimes reach levels characteristic of pre-industrial conditions but is becoming increasingly impacted by industrialization and anthropogenic pollution (Martin et al.,

30   2017;Martin et al., 2010b;Andreae et al., 2015). Fuzzi et al. (2007) described chemical analysis of filter samples collected in Rondonia, Brazil (~825 km SW of Manaus, Brazil) from September to November 2002. They found that water-soluble organic species were the main contributors to submicron particles (90%) with the balance consisting of soluble inorganic ions (Fuzzi et al., 2007). The SAAMBA aircraft campaign, based out of Rondonia, Brazil, was focused primarily on biomass burning but Allen et al. (2014) discuss measurements from five flights investigating biogenic processes. They report that concentrations of

SOA derived from isoprene epoxydiols (IEPOX) were the highest in the presence of acidic seed, low NO$_x$ concentrations, and high RH (Allan et al., 2014). The AMAZE-08 campaign was conducted in February and March of 2008 and Chen et al. (2009, 2015) reported on chemical composition measurements made with an AMS from a tower site 60 km NNW of Manaus, Brazil (Martin et al., 2010a;Chen et al., 2009;Chen et al., 2015). They found that organics accounted for more than 80% of the non-

5   refractory aerosol mass, with the organic mass often dominated by SOA, and that the aerosol was acidic in composition (Chen et al., 2015). It is important to note that Chen et al. (2009, 2015) excluded data impacted by Manaus emissions from their analysis. de Sá et al. (2017) investigated the production of IEPOX SOA downwind of Manaus during GoAmazon2014/5 and found decreased concentrations of IEPOX-SOA in the plume relative to the background which they attribute to suppression of IEPOX formation by elevated NO concentrations in the plume. Kuhn et al. (2010) describe aircraft-based aerosol

10   measurements in the Manaus plume as it was transported downwind. They report increases in ΔCCN/ΔCO as the plume aged, which they attribute to condensation of both organic and inorganic mass, but did not measure the aerosol chemical composition (Kuhn et al., 2010). Additional aircraft campaigns conducted in the Amazon often focused on biomass burning and the impact of biomass burning on cloud properties (Morgan et al., 2013;Yokelson et al., 2007;Andreae et al., 2012).

To that end, the Green Ocean Amazon (GoAmazon 2014/5) campaign was conducted in the vicinity of Manaus, Brazil from

15   January 2014 – December 2015. The goal of GoAmazon 2014/5 was to investigate the interaction of Manaus urban emissions with the surrounding pristine Amazon basin and the subsequent impact of these emission on cloud formation and properties (Martin et al., 2017;Martin et al., 2016). Manaus's geography makes it ideal for this mission. Manaus, an industrial city and with a metropolitan population of more than 2 million people, is the largest city in the Amazon basin. The prevailing wind is from the east with the nearest major upwind city, Belem, approximately 1250 km away. The surrounding tropical forest emits

20   vast quantities of biogenic gases and aerosol. Few roads connect Manaus to the rest of Brazil and most freight and traffic from outside the city is via ship or plane. Thus, Manaus acts as a large point source of anthropogenic emissions which are transported to the surrounding and nearly pristine Amazon basin. As part of this campaign, the DOE Gulfstream-1 research aircraft conducted two, six-week-long missions in which it investigated the evolution of the Manaus plume as it was transported into the surrounding Amazon tropical rainforest. Here we report on measurements from instruments deployed on the G-1, focusing

25   on measurements of aerosol species and the evolution of organic aerosol particles in the plume.

2 Experimental

2.1 G-1 Flight Strategy

The GoAmazon 2014/5 campaign was conducted in the vicinity of Manaus, Brazil from January 1, 2014 through December 31, 2015 (Martin et al., 2016). During this period, DOE's Gulfstream-1 research aircraft, based out of the Manaus International

30   Airport, was deployed for two periods during which time it sampled the Manaus urban plume as it was transported downwind over the Amazon rainforest. The first aircraft deployment period occurred during the wet season from February 15 - March 26, 2014 while the second occurred in the dry season from September 1 - October 10, 2014. Sixteen research flights were

conducted in the wet season and 19 were conducted in the dry season. In general, flight plans were focused on successive perpendicular plume crossings spaced approximately equally at intervals of 24 km downwind of the city. A representative flight path for March 13, 2014, a golden day in the wet season with few clouds, is shown in Figure 1. The paths for all flights during the two deployments are shown in Martin et al. (2016) and therefore are not reproduced here. The first leg approximately

5   bisected the city along a NW/SE line, the second leg passed near a highly instrumented ground site directly across the Amazon river from Manaus (T2), the fourth leg passed over a second highly instrumented site located NE of Manacaparu (T3), with an additional leg between the T2 and T3 sites, and a final leg downwind of the T3 site. The first pass through the pattern was generally at an altitude of 500 m above ground level with a second pass at a higher altitude and often, though not always, focused on sampling clouds. The pattern was rotated to align with the prevailing wind direction. Most flights departed the

10   airport between 9:30 - 10:30 local time (13:30 - 14:30 UTC) and returned at between 13:00 – 14:30 local (17:30 – 18:30 UTC), lasting 3 – 3.5 hours, with a small number of flights occurring outside this window.

2.2 Instrumentation

An Aerodyne HR-ToF-AMS (abbreviated as AMS hereafter) was deployed on the G-1 to measure aerosol chemical composition (Jayne et al., 2000;DeCarlo et al., 2006). The AMS operated only in a higher-sensitivity, lower resolution "V"-

15   MS mode (the particle sizing mode was not used) with a 13s data sampling interval. Before, during, and after flights, the AMS-sampled air was periodically diverted through a HEPA filter to remove particulates and these filter periods were used to account for gas-phase interferences with isobaric particulate signals. All aerosol instruments, including the AMS, sampled from a common, double-diffuser isokinetic inlet. Flow for the AMS was sub-sampled from the center of the isokinetic inlet and dried to RH < 40% by passage through a 1/2" ID PermaPure Nafion membrane. A constant pressure inlet operating at approximately

20   620 hPa was used to maintain a constant volumetric flow to the AMS up to altitudes of approximately 3900 m (Bahreini et al., 2008). Because the AMS was powered off between flights, a correction based on the real-time N_2^+ signal was applied to all data to account for drifting sensitivity as the instrument warmed up during flights. The AMS was regularly calibrated in the field using monodisperse ammonium nitrate particles quantified with a TSI condensation particle counter (CPC). Data was analyzed using both the unit mass resolution analysis (Allan et al., 2003;Jimenez et al., 2003) and the high-resolution analysis

25   (Canagaratna et al., 2015;Kroll et al., 2011;Aiken et al., 2007) described in the literature. All AMS data are normalized to 23 °C 1013 hPa. Primary Matrix Factorization (PMF) analysis was performed on the wet-season dataset by combining all flight data into a single experiment (Ulbrich et al., 2009;Paatero, 1997;Paatero and Tapper, 1994).

An Ionicon quadrupole high-sensitivity PTR-MS was used to measure selected gas-phase volatile organic carbon (VOC) concentrations (Lindinger et al., 1998). The PTR-MS was used in the ion monitoring mode where it sequentially steps through

30   a series of m/z values with each cycle through the series taking 3.5 s. Averaging time at each m/z in the series varied depending on the sensitivity of the instrument to that species, the expected concentration, and the background, but generally varied between 0.2 and 0.5 s. Isoprene at m/z 69 was sampled multiple times during the cycle to enable flux analysis (Gu et al., 2017).

Drift tube temperature, pressure and voltage were held at 60 °C, 2.22 hPa, and 600 V, respectively resulting in an E/N value of 134 Td. The PTR-MS sampled air through a dedicated forward-facing inlet that consisted of approximately 6" of 1/4" OD stainless steel followed by approximately 46" of 1/4" Teflon tubing, and 36" of 1/16" OD PEEK tubing. The flow through the Teflon tubing was 600 ccm with 300 ccm subsampled through the PEEK tubing for introduction into the PTR-MS. To assess the PTR-MS background, air was periodically diverted through a stainless steel tube filled with Shimadzu Pt catalyst heated to 600 °C, which removes VOCs from the airstream without perturbing relative humidity. The catalyst efficiency was tested during the campaign by comparing signal from air containing VOCs passed through the catalyst with signal from VOC-free air. The PTR-MS was calibrated by introducing known concentrations of calibration gases into the instrument with variable dilution by VOC-free air. The calibration tank VOC concentrations were determined gravimetrically and verified using GC analysis by the manufacturer (AiR Environmental, Inc).

Ozone was measured with a Thermo Scientific Model 49i ozone analyzer based on measurement of UV absorption at 254 nm. The instrument was regularly calibrated in-flight by displacement of known quantities of ozone and zeroed in flight using ozone-scrubbed ambient air. CO was measured using a Los Gatos Research $CO/N_2O/H_2O$ analyzer that is based on cavity-enhanced near-IR absorption and was also calibrated regularly in-flight.

3 Results and Discussion

3.1 Overview of G-1 Aerosol Data and Comparison of Wet and Dry Season

Figure 2 and Table 1 summarize the AMS results for data collected on the G-1 flights in both the wet and the dry season. The top panel of Figure 2 shows box-and-whisker plots summarizing AMS data for organics, sulfate, nitrate, and ammonium particulate concentrations, with one data point representing each flight (note the scale change between the wet and dry season plot). The middle panel shows the relative distribution of the chemical species on each flight. The bottom panel shows the distribution of the chemical species averaged across the entire wet and dry season. Several trends are readily apparent in the data. First, it is clear that aerosol loadings were significantly higher in the dry season than in the wet season. Median organic loadings for the all wet and dry season data were 0.72 and 4.06 $\mu g/m^3$, respectively. Median sulfate, nitrate and ammonium loadings increased from 0.11, 0.04, and 0.03 $\mu g/m^3$ in the wet season to 0.67, 0.17, and 0.25 $\mu g/m^3$ in the dry season. Mean loadings of all species were somewhat higher than the median. Mean organic, sulfate, nitrate, and ammonium loadings were 0.85, 0.14, 0.05, and 0.05 $\mu g/m^3$ in the wet season and 4.23, 0.73, 0.23, and 0.27 $\mu g/m^3$ in the dry season. In the wet season, the mass loading of all species are lower than typically observed over continental regions in the Northern Hemisphere (Zhang et al., 2007).

The aerosol mass loadings we measure in the dry season are consistent with aircraft-based AMS measurements made during the SAMBBA campaign at the same time of year, though several hundred kilometers to the SW in the state of Rondonia (Allan et al., 2014). Chen et al. reported AMS-measured wet-season campaign average organic and sulfate loadings of 0.7 and 0.15

μg/m^3 from a ground site that was within the GoAmazon 2014/5 flight domain, though they excluded data impacted by Manaus emissions from their analysis (Chen et al., 2009). When comparing aircraft to ground site data, it is important to acknowledge differences in the datasets. First, the aircraft samples a different spatial domain in all three dimensions (latitude, longitude, and altitude) than a ground site. In addition, the G-1 typically sampled the boundary layer in the late morning (approximately 10:00 – 11:30 local time), and thus may miss peak concentrations of secondary species. Finally, the goal of the flights was often to sample the Manaus plume for the first half of the flight and clouds for the second half. The mean aerosol loadings reported here agree well with those reported by Chen et al. (2009), considering the inherent differences in datasets discussed above. We also found good agreement when comparing the G-1 measured aerosol loadings to those measured at the T3 site when the aircraft passed overhead and at an altitude within the boundary layer (de Sá et al., 2018). Our loadings are at the low end of the range (1- 2 μg/m^3) reported from a ground site in Rondonia, approximately 825 km to the southwest of Manaus, though those data were more heavily influenced by biomass burning and relied on a combination of offline techniques to speciate the aerosol (Fuzzi et al., 2007). To understand potential bias in the dataset due to altitude, we calculated statistics for data collected below 700 m, which roughly corresponds to data collected within the boundary layer. In the wet season, the low altitude loading statistics are generally either slightly higher or unchanged relative to the full dataset. In the dry season, the low altitude loading statistics are slightly lower relative to the full dataset, likely due to transport of biomass burning from the south in elevated layers.

The fractional contribution of each species to the total loading is nearly identical when comparing seasons, despite the large differences in aerosol absolute mass concentrations and sources. Organics dominate the chemical composition, comprising 78 % of the total with sulfate 12%, nitrate 5%, and ammonium 4%, regardless of the season. The relative distribution of the products changes only modestly among flights. Organics were the largest fraction of the total aerosol mass on each flight, varying between 72 – 83%. Sulfate was the second largest fraction of the total mass (7-20%) and the sum of sulfate and organic were nearly constant. The aircraft product distribution is nearly identical to the previous reports from Chen et al. (2009, 2015). The aircraft product distributions are also nearly identical to those measured at the T3 ground site (de Sá et al., 2018). The agreement between the T3 and G-1 product distributions suggest that the T3 ground site is sampling air that is representative of the regional air and is not unduly biased by local emissions, at least in the aggregate.

The observation that the total concentrations of all aerosol components significantly increases yet remain in the same proportions when comparing the wet and the dry season is unexpected. The more frequent and widespread precipitation events in the wet season contribute to the lower aerosol concentrations in the wet season. If the aerosol particles are internally mixed, it would be reasonable to assume that rainfall would remove aerosol in approximately equal proportions. However, there was a much larger biomass burning influence in the dry season, which is a known and significant source of OA (e.g., (Jolleys et al., 2012;Bond et al., 2004;Yokelson et al., 2009;Ferek et al., 1998). Biomass burning was previously shown to emit particulate sulfate and nitrate directly, and NOx, sulfuric acid, and MSA, precursors of particulate nitrate and sulfate, but not in the same ratio as OA and its precursors (Yokelson et al., 2009). Thus, given the significant influence of biomass burning in the dry season, it is surprising that the chemical composition of the aerosol does not change. Passage through fresh biomass burning

plumes was characterized by increased concentrations of organics and nitrate, with much smaller increases in sulfate, suggesting that sulfate formation occurs on a slower timescale. More aged biomass burning emissions originating from the southern and eastern edges of the Amazon basin also exerts an influence on the Manaus region, increasing the background aerosol concentrations significantly (Martin et al., 2016).

5   Despite the similarity of the distribution of organic, sulfate and nitrate in the aerosol particles between the wet and dry seasons, the chemical composition of the organic aerosol is quite different between seasons. Figure 3 shows normalized probability distributions for three metrics of the organic aerosol composition, the hydrogen to carbon ratio (H:C), the oxygen to carbon ratio (O:C), and the mean carbon oxidation state ($\bar{O}S_c$) segregated by season. It is clear that the organic particles are more oxidized in the dry season than the wet season. The median O:C, H:C, and $\bar{O}S_c$ in the dry season were, 0.78, 1.58, and -0.02

10   respectively, while they were 0.6, 1.65, and -0.45 in the wet season. While the H:C ratios change only slightly between season, the O:C and $\bar{O}S_c$ both show significant increases in the dry season. Thus, the aerosol in the dry season is significantly more aged, consistent with aged biomass burning aerosol dominating the organic aerosol mass in the dry season and relatively fresh, locally generated organic aerosol dominating in the wet season (Martin et al., 2010b). The probability distributions during the wet season are also wider than in the dry season. We postulate that small contributions from a wider range of sources are able

15   to influence the data to a larger degree in the wet season, when the total organic aerosol concentrations were much smaller. In contrast, during the dry season, small sources of organic mass would have a smaller impact on the organic composition due to the significant biomass burning background.

3.2 Case Study, March 13, 2014 Flight

Figure 1 shows the flight path on March 13 2014, which is a golden day for observing the evolution of the Manaus plume in

20   the wet season. Flight legs were perpendicular to the prevailing wind direction and spaced approximately 24 km apart at successively increasing distance from Manaus. The length of the legs was chosen such that measurements (e.g., CO concentration) returned to near background levels at the ends of the leg. Due to dispersion of the plume, the length of the legs generally increased downwind of Manaus, ranging from 56 km close to the city to 80 km downwind of the T3 site. The pattern was flown first at an altitude of 500 m with a second pass at 1000 m overlapping the first. This flight was marked by mostly

25   sunny skies with no clouds intercepted by the G-1 at 500 m and only brief passage through spatially small clouds at 1000 m. There was little local or regional biomass burning during this time period. Thus, this flight represents a case with coherent transport of the Manaus plume downwind into regions of high biogenic emissions with few complicating factors, such as biomass burning or cloud processing.

Figure 4 shows a time-series of several important gas- and particle-phase species for the March 13, 2014 flight. Passage through

30   the Manaus plume is indicated by clear and significant increases in CO, ozone, and PTR-MS m/z 79 (benzene) above the background levels. While CO may be produced from the oxidation of biogenic VOCs (Slowik et al., 2010), the intense peaks are primarily from urban emissions, given the proximity to Manaus and the correlation of CO with other known anthropogenic species, such as ozone, benzene, and toluene (not shown). Concentrations of CO (80 ppbv) and ozone (10 ppbv) are lowest at

the edges of the flight legs and, although we did not sample extensively in regions that were far removed from Manaus, these concentrations are consistent with the background concentrations that have been previously reported in the region (Andreae et al., 2015;Martin et al., 2010b;Harriss et al., 1990). Isoprene concentrations (PTR-MS m/z 69) typically reach their highest levels outside of the plume and are lower inside, though isoprene concentrations of approximately 1 ppbv are still observed in

5   the plume. As seen in Figure 1, much of the land cover outside of Manaus is tropical forest, with some pasture land interspersed. Significant isoprene emissions are expected and indeed measured from the forest (Guenther et al., 2006;Gu et al., 2017). Significant concentrations of methacrolein, methyl vinyl ketone, and isoprene hydroxyhydroperoxides (PTR-MS m/z 71), all oxidation products of isoprene, are also observed and have a more complicated structure (Liu et al., 2016). Concentrations of these products tend to be highest near the edges of the plume and they do not correlate strongly with either isoprene (r^2= 0.24)

10   or with anthropogenic plume markers such as CO (r^2= 0.24). Production of these oxidation products requires OH, the concentration of which depends on NO_x, to oxidize isoprene and thus they are expected to have a more complex relationship with the urban plume and the surrounding biogenic emissions. Taken together, the observations of both isoprene and its oxidation products suggest that photooxidation of BVOCs is enhanced in the plume relative to the background, as would be expected (Martin et al., 2017). Monoterpene concentrations (not shown) on this flight are approximately a factor of ten lower

15   than isoprene concentrations, consistent with previous measurements (Kesselmeier et al., 2000), and are often near or below the instrument limit of detection (~200 pptv). Monoterpene concentrations correlate with isoprene concentrations during the flight, when they are above the instrument detection limit.

Organic aerosol (OA) mass increases from background values of 0.5 μg/m³ to as high as 3.1 μg/m³ in the Manaus plume and on this day it is correlated relatively well with both ozone (r^2= 0.65) and CO (r^2=0.76). While OA concentrations do not reach

20   the levels that are typically seen in the outflow of large North American cities, they are significantly larger than background concentrations (up to 6x), indicating a clear impact of the plume on OA concentrations. Sulfate also clearly increases in the plume, though its peak concentrations occur toward the southern edge of the plume, relative to organics, CO, and ozone, suggesting sulfur emissions may not be co-located with other anthropogenic emissions. However, there are also occasional peaks in the sulfate concentration (for example at 10:47) that coincide with minima in other plume indicators, such as CO and

25   ozone. Nitrate concentrations are significantly lower than sulfate concentrations, but tend to correlate more strongly with organic concentrations than sulfate concentrations. There are indications that a portion of the nitrate mass exists as organic nitrates, consistent with measurements at the T3 site and with aircraft measurements (Allan et al., 2014;de Sá et al., 2018;Schulz et al., 2018). The NO^+:NO_2^+ ion ratio is 5-7 in the plume, compared to a NO^+:NO_2^+ ion ratio of 1.2-1.5 measured during the campaign for ammonium nitrate calibration aerosol. NO^+:NO_2^+ ion ratios significantly above that of ammonium

30   nitrate are indicative of the presence of organic nitrates, though quantifying the organic fraction is challenging (Farmer et al., 2010). Ammonium concentrations tend to closely mirror sulfate concentrations. The bottom panel of Figure 4 shows the fractional composition of the aerosol, which helps to illustrate the relative differences among the aerosol species. Organic species clearly dominate at all points, with sulfate the next most important species.

At 1000 m altitude, the plume can still be observed in the G-1 data, though the concentrations of plume markers such as CO, ozone, and benzene are lower. Increases in organic concentration are less sharp and defined than observed at 500 m, though enhancements are still clear. The organic mass fraction is somewhat smaller at 1000 m and sulfate and ammonium mass fractions are larger. Based on radiosonde measurements, the boundary layer grew from 900 to 1200 m between the beginning and end of the flight on this dat. Data from the G-1 suggest that the 1000-m flight path was near the top of the boundary layer. Thus, at 1000-m altitude, the data are influenced by both the local conditions and from air that has been transported over longer distances.

Figure 5 shows a PMF analysis of the organic species, for the March 13th flight along with independently measured species that might be expected to correlate with the PMF factors. We were able to resolve the organic aerosol into three factors; an OOA factor that is a proxy for SOA, an HOA factor that is a proxy for primary organic particulate emissions, and a IEPOX SOA factor, which forms from the heterogeneous uptake of IEPOX, a product of isoprene oxidation under low-NO_x conditions (Hu et al., 2015;Robinson et al., 2011;Lin et al., 2012;Zhang et al., 2011;Zhang et al., 2005;de Sá et al., 2017). Details of the PMF analysis, including mass spectra of the factors, can be found in the supporting information. As expected, both the OOA and HOA factor mass loadings are significantly higher in the plume relative to the background. The HOA factor correlates strongly with CO while the OOA factor correlates strongly with ozone, though we will show below that the slope of the correlation changes with plume age. The HOA factor is a larger fraction of the organic mass on the legs nearest to Manaus and becomes a smaller fraction on the downwind legs. The OOA mass fraction displays the opposite behavior, increasing downwind as the plume ages. The transformation of HOA to SOA/OOA has been observed previously, both in laboratory experiments and in the field (Sage et al., 2008;Robinson et al., 2007;DeCarlo et al., 2008;Zhang et al., 2007;Ng et al., 2010). Taken together, these observations are consistent with the literature assignment of HOA as a marker of primary organic emissions and OOA as a marker of secondary organic aerosol. Outside of the plume, HOA concentrations approach zero. OOA concentrations on the other hand, remain significant and approach the organic aerosol background concentrations. The IEPOX SOA factor does not appear to change with passage through the plume and does not correlate with sulfate aerosol on this day as may be expected based on the chemical mechanism (Hu et al., 2015;Surratt et al., 2010). We note that the IEPOX SOA factor is noisy, is near or below the limit of detection for much of this flight, and is shown largely for the sake of completeness. Because of the low concentrations, it is difficult to draw definitive conclusions about IEPOX SOA formation on this flight. However, given the focus of this flight was on tracking the Manaus plume which contains significant NO_x, our findings are consistent with de Sa et al. (2017) who report that NO_x from the Manaus plume suppresses IEPOX SOA formation in the plume and that the IEPOX-SOA factor was less than 5% of the total OA at T_3 at the time of G1 overflight.

Figure 6 summarizes several relevant plume quantities at 500 m altitude as a function of the approximate distance downwind from Manaus, which serves as a proxy for the photochemical age of the airmass. The ratio of excess organic aerosol to excess CO (Δorg/ΔCO) is a metric that is often used to quantify organic aerosol formation in a source plume as it ages. The utility of the Δorg/ΔCO metric rests mainly the assumptions that CO is conserved on the timescale of the measurements and that urban emissions scale linearly with CO. Using this ratio rather than absolute concentrations of organic aerosol can normalize for

dilution due to mixing of the plume with background air. Two aspects of the Δorg/ΔCO distinguish these measurements from most previous measurements in the literature. First, Δorg/ΔCO is ~31 μg/m^3 ppmv^{-1}, a value that is lower than the value of 70 ± 20 μg/m^3 ppmv^{-1} observed in the outflow of cities in North America e.g., (de Gouw and Jimenez, 2009) and references therein. The Δorg/ΔCO values observed here are also significantly smaller than the values of 77 – 157 μg/m^3 ppmv^{-1} we

5   previously observed when fresh urban anthropogenic emissions evolved in the presence of strong biogenic emissions, as is the case in the present data set (Shilling et al., 2013;Setyan et al., 2012). We measure a ΔHOA/ΔCO value of 17.6 μg/m^3 ppmv^{-1} near Manaus (Figure 6) which should represent fresh emissions. This value is at the upper end of what is reported in the literature for North American cities, indicating that lower primary particulate emissions from Manaus are not responsible for the lower Δorg/ΔCO values (DeCarlo et al., 2010;de Gouw and Jimenez, 2009).

10   The second new aspect of these observations is that we do not observe a corresponding increase in Δorg/ΔCO as the plume photochemically ages, contrary to our expectations. We note that, as described above, organic aerosol concentrations are significantly higher in the plume than in the background and the Δorg/ΔCO analysis that follows focuses on understanding the aging of the Manaus plume. Based on existing literature (de Gouw and Jimenez, 2009;Kleinman et al., 2008;DeCarlo et al., 2010;Takegawa et al., 2006;Sullivan et al., 2006;Freney et al., 2014), we hypothesized that Δorg/ΔCO would rapidly increase

15   in the Manaus plume due to OA formation from sources not associated with urban CO emissions (Setyan et al., 2012;Shilling et al., 2013). Specifically, we expected that enhanced OH concentrations in the plume would lead to rapid oxidation of BVOCs from the surrounding forest, which would produce OA with little concomitant production of CO. As seen in Figure 6, the data did not support this hypothesis. We acknowledge that calculation of Δorg/ΔCO values can be sensitive to the calculation method and choice of background values for both OA and CO; therefore, we performed calculations using different methods

20   and assuming different background concentrations for both OA and CO (see SI for more details). We did not find significant increases in Δorg/ΔCO in any of these calculations. Furthermore, though we focus on Δorg values based on the AMS data, we also calculated Δvolume/ΔCO using aerosol size distribution data from two independent instruments, the Ultra-High Sensitivity Aerosol Spectrometer (UHSAS) and the Fast Integrated Mobility Spectrometer (FIMS) that were also onboard the G-1. Neither of these calculations indicates an increase in Δvolume/ΔCO with plume age. The median Δorg/ΔCO values for

25   the plume as measured at the T2 and T3 sites are also nearly identical to one another in the wet season, suggesting the March 13, 2014 G-1 observations are representative of the Manaus plume behavior across longer timescales in the wet season (Cirino et al., 2018).

Previous studies have observed increases in Δorg/ΔCO with plume age, with the largest increases occurring for the first ~1 day of aging and changes in Δorg/ΔCO gradually leveling off beyond approximately 1-2 days (DeCarlo et al., 2010;de Gouw

30   and Jimenez, 2009;Kleinman et al., 2008;Freney et al., 2014). Based on the mean wind speeds observed along the flight track (7.3 m s^{-1}) and the transport distance (up to 100 km), we estimate that the plume was 4-5 hours old at the farthest leg and freshly emitted over the city. Unfortunately, photochemical clocks could not be used to more precisely calculate the photochemical age of the plume. NO$_y$ measurements were not available on this flight. Benzene and toluene concentrations were low and noisy, particularly at increasingly downwind distances from Manaus, so we were unable to use this clock to

reliably estimate the plume age, though they do appear to indicate some degree of aging. Though our observations are limited to shorter aging timescales (4-5 hours) than many literature studies (1-2 days), the literature studies report measurable changes in Δorg/ΔCO at short aging timescales (Kleinman et al., 2008;DeCarlo et al., 2010). Furthermore, we clearly observe other indicators of photochemical aging in the plume. Ozone concentrations are 30 – 50 ppbv in the plume, compared to background

5   levels of 10-15 ppbv, indicating active photochemistry. The mean particle oxidation state ($\bar{O}S_c$) of plume OA increases from -0.6 to -0.44 as it ages. It is expected that photochemical aging would produce progressively more oxygenated species downwind of Manaus that subsequently partition to the aerosol phase, increasing the mean carbon oxidation state. Other studies have observed a similar phenomenon as particles were transported downwind of urban centers (DeCarlo et al., 2010). The particles size distributions measured by both the FIMS and the UHSAS also indicate that particles size increases downwind of

10   Manaus. As discussed in the previous section, we also observe that the mass fraction of HOA decreases and simultaneously the mass fraction of OOA increases as the plume ages. As seen in Figure 6, ΔHOA/ΔCO is 17.6 μg/m^3 ppmv^{-1} on the leg nearest to the city and decreases to 10.6 μg/m^3 ppmv^{-1}. At the same time, ΔOOA/ΔCO increases from 9.2 μg/m^3 ppmv^{-1} to 23.1 μg/m^3 ppmv^{-1}. Thus, some fraction of HOA appears to be lost, either through volatilization or deposition, with the lost HOA mass balanced by an increase in OOA mass. All of these factors indicate that active photochemistry occurring and is

15   transforming VOC's into SOA and aging the particles. Thus, we would expect to see significant increases in Δorg/ΔCO for these aging times, if similar observations of outflow from North American cities were representative of the Manaus plume.

The sum of the HOA and OOA factors explains >95% of the total OA mass within the plume, as the IEPOX SOA mass is small. Though calculating the ΔHOA/ΔCO and ΔOOA/ΔCO ratios introduces some noise (particularly ΔOOA/ΔCO close to Manaus), the sum of these ratios is approximately constant with aging and equal to the Δorg/ΔCO values. Thus, the total OA

20   mass is conserved with loss and volatilization of HOA balanced out by formation of OOA. This process appears to explain the lack of an increase in Δorg/ΔCO with aging. It is difficult to determine whether the OOA carbon mass is anthropogenic, biogenic, or (most likely) a combination of both. Volatilized HOA and co-emitted anthropogenic VOCs would undergo oxidation in the plume and the products may condense as OOA (Sage et al., 2008;Robinson et al., 2007). In addition, we see evidence that biogenic VOCs are oxidized in the plume, likely more rapidly than in the background due to enhanced in-plume

25   OH concentrations, and these oxidation products may also condense as OOA. Either mechanism or a combination of both would explain the observed increase in the carbon oxidation state. It is surprising that the volatilized HOA mass is compensated by oxidation and re-condensation of SOA for these relatively fresh particles. As previously discussed, most studies examining outflow of North American cities have shown changes in Δorg/ΔCO that are largest at the shortest aging times and we are unaware of reports of constant Δorg/ΔCO in an aging urban plume. Both the identity and the distribution of Manaus's emissions

30   may very well be distinct from that of a typical North American city. In addition, background concentrations of anthropogenic pollutants are lower and biogenic VOC emissions are higher downwind of Manaus relative to most North American cities. Finally, background OA concentrations near Manaus are lower than in most other continental regions and SOA yield is known to increase with OA mass loading (Odum et al., 1996). All of these factors may contribute of the difference in the Δorg/ΔCO observations.

A similar phenomenon, clear chemical aging with little change of Δorg/ΔCO, has been observed in biomass burning plumes by several researchers (Jolleys et al., 2012;Cubison et al., 2011;Hecobian et al., 2011;Akagi et al., 2012;Forrister et al., 2015). Clearly, the mix of organic compounds emitted from a forest fire and from the Manaus urban region will be significantly different and this is not to imply that the detailed chemical mechanisms are the same. However, the similarity of the observations is suggestive that a similar process could occur in both types of plumes.

3.3 Sources of Sulfate in the Manaus Region

Sulfate was the second largest contributor to the non-refractory aerosol mass during the GoAmazon 2014/5 campaign (accounting for 13% of the PM_1 mass in both the wet and dry season), so it is also instructive to examine the source of sulfate in the area. In 2014 Manaus generated much of its power from fuel oil and diesel, which are known to emit SO_2 that eventually oxidizes to form condensable sulfate (Medeiros et al., 2017). However, several observations suggest that the major source of sulfate in the plume may not come from local SO_2 emissions. First, on many flights, particulate SO_4 levels clearly increases in the plume (e.g., Figure 4), including on the legs closest to Manaus and thus very near the source. The lifetime of SO_2 with respect to homogeneous oxidation by OH is expected to be about one week and only small fraction (~5% on the farthest leg) of SO_2 emissions would have time to oxidize to H_2SO_4 in the gas phase. In addition, there is no indication of dramatically enhanced sulfate loading downwind of Manaus on the March 13 flight when $\Delta SO_4/\Delta CO$ ratio averages 2.6 μg/m^3 ppmv^{-1} and does not increase with plume age. On the March 13 flight, there was no precipitation and relatively few clouds along the flight track so heterogeneous oxidation of sulfate in cloud water cannot explain the sulfate enhancement seen in the plume.

We can possibly attribute these observations to two mechanisms. First, it is possible that natural sulfur emissions such as DMS and H_2S originating downwind of Manaus undergo oxidation by enhanced concentrations of OH in the Manaus plume and subsequently condense (Andreae et al., 1990;Chen et al., 2009). Andrea et al. (1990) estimate that in-basin sulfur emissions are responsible for approximately 0.05 μg/m^3 of the total sulfate loading. Measurements during the AMAZE-08 campaign also suggested natural in-basin emissions and transport of natural out of basin emission were a significant source of particulate sulfate (Chen et al., 2009). A 0.05 μg/m^3 SO_4 loading is roughly consistent with our measured SO_4 concentrations outside of the plume and would account for 15 – 30% of the sulfate in the plume. Higher OH concentrations in the plume would speed oxidation of natural sulfur compounds and further increase the fraction of in-plume SO_4 originating from natural emissions. Second, power plant plumes may directly emit sulfuric acid, which then may condenses on pre-existing particles. A previous aircraft study of the Manaus outflow observed high concentrations of particles smaller than 40 nm in power plant plumes, which they attribute to sulfuric acid (Kuhn et al., 2010). Though particles in this size range are unlikely to be detected by the AMS, condensation of sulfuric acid on larger, pre-existing particles would also contribute to the in-plume sulfate observations.

4 Summary and Implications

In summary, we report on measurements of the aerosol chemical composition, sources, and evolution of the urban plume from 35 research flights conducted in both the wet and dry season in the vicinity of Manaus, Brazil. Median mass loading of organics, sulfate, nitrate, and ammonium were 0.72, 0.11, 0.04, and 0.03 $\mu g/m^3$ in the wet season and 4.06, 0.67, 0.17, and 0.25 $\mu g/m^3$ in the dry season. Despite the significant difference in mass loadings, the average fractional composition of the aerosol did not change between seasons. Organics dominate the aerosol chemical composition in both seasons, comprising 79% of the total non-refractory aerosol mass. The OA was significantly more oxidized in the dry season with a $\bar{O}S_c$ of -0.02 in the dry season and -0.45 in the wet season.

The flight on March 13, 2014 was a golden day to study the evolution of the Manaus plume as it advected to the surrounding Amazon tropical forest. The organic and sulfate aerosol concentrations were both significantly enhanced in the plume along with CO, ozone, and benzene. The spatial distribution of the sulfate aerosol was shifted toward the southern edge of the plume, relative to organics, CO, and benzene. As the plume is transported downwind of Manaus, we observe a change in the relative fraction of HOA and OOA mass. $\Delta HOA/\Delta CO$ values decreased from 17.6 $\mu g/m^3$ ppmv^{-1} over Manaus to 10.6 $\mu g/m^3$ ppmv^{-1} 95 km downwind of Manaus, indicating a substantial loss of HOA mass. This loss of HOA mass was balanced out by OOA formation, with $\Delta OOA/\Delta CO$ values increasing from 9.2 to 23.1 $\mu g/m^3$ ppmv^{-1} during the 4-5 hour aging timescale. Concomitantly, the mean carbon oxidation state of the OA increased from -0.6 to -0.44. Because the loss of HOA mass was balanced out by addition of OOA mass, net changes in $\Delta org/\Delta CO$ with plume age were not observed and averaged 31 $\mu g/m^3$ ppmv^{-1}. The observation of constant $\Delta org/\Delta CO$ with aging was in contrast to our hypothesis that $\Delta org/\Delta CO$ would increase rapidly due to plume-enhanced oxidation of BVOCs, emitted by the surrounding tropical forest and not associated with CO emissions, and subsequent conversion to OA mass. Our $\Delta org/\Delta CO$ observations are also in contrast to literature observations of the outflow of several different North American urban centers, which have shown increases in $\Delta org/\Delta CO$ for the first 1-2 days of plume aging (Kleinman et al., 2008;de Gouw and Jimenez, 2009;DeCarlo et al., 2010;Freney et al., 2014;Sullivan et al., 2006).

The dataset generated from the G-1 measurements during GoAmazon 2014/5 provide a set of observations for understanding aerosol chemistry in the Amazon region. Our preliminary analysis shows that outflow from the Manaus plume generates less OA in the wet season when compared to outflow of many North American cities. The differences are likely due to a combination of factor including differences in emissions from both Manaus and the surrounding tropical forest, lower levels of background anthropogenic pollution in the Amazon, and lower background OA concentrations into which semi-volatile organics can partition. These results have implications for modeling efforts and for understanding how urban pollution impacts the surrounding pristine Amazon.

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Figure 1. Flight path for the March 13, 2014 flight colored by the CO concentration. Arrows indicate the direction of the flight. The first pass through the pattern was conducted at 500 m then repreated at 1000 m. The dots show the location of ground measurement sites. The color scale shows the CO concentration in ppm units. The underlying image is from Google Earth.
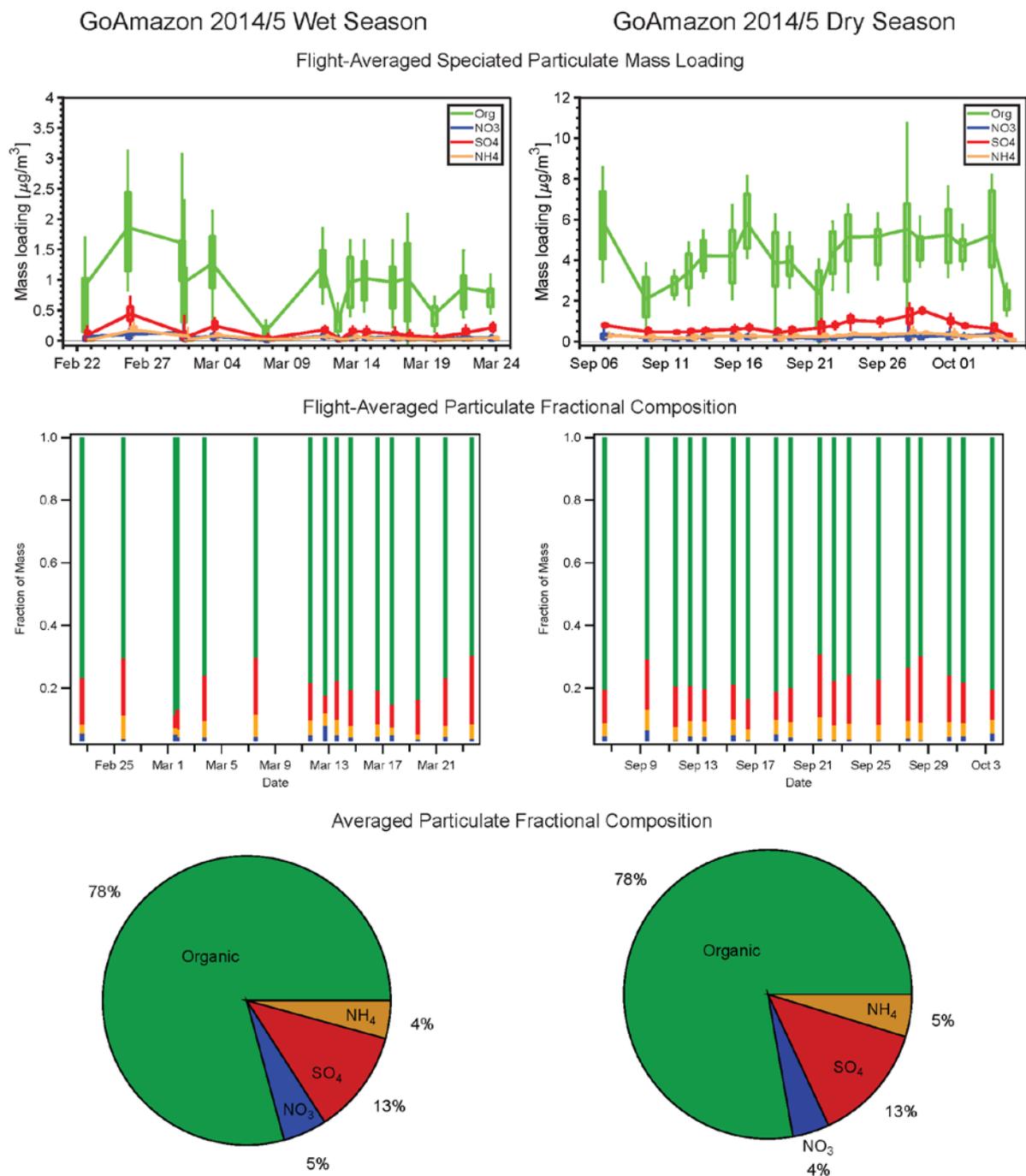
Figure 2: Box and whisker representations of the G-1 AMS data for both the wet and dry seasons (top panel), average particle chemical composition for each flight (middle panel), and average aerosol chemical composition for all flights (bottom). Boxes represent the quartiles, with whiskers extending to 10% and 90%. Lines between the boxes connect the mean and are drawn to guide the eye. Note the scale change between the wet and dry season box and whisker plots. Data presented here use the unit mass resolution analysis routine (e.g., Squirrel). AMS data are normalized to 23 °C and 1013 hPa.
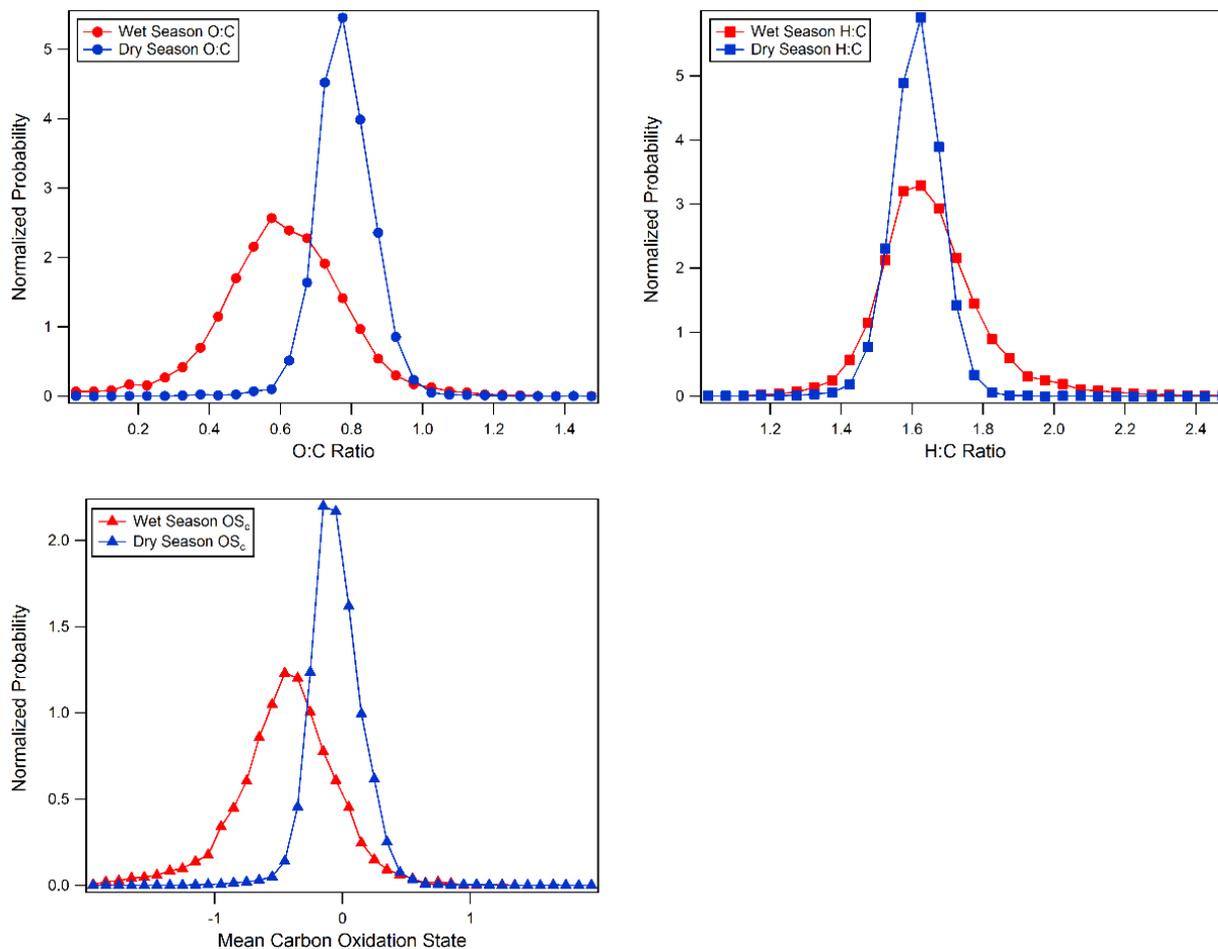
Figure 3. Normalized occurrence probability calculated from G-1 HR-AMS analysis of the organic aerosol during the wet (red) and dry (blue) seasons. O:C and H:C were binned into 0.05 unit wide bins and $\overline{OS}_c$ data were binned in 0.1 unit wide bins. O:C and H:C ratios were calculated using the updated methodology in Canagaratna et al. 2015. Mean carbon oxidation state is calculated according to Kroll et al. 2011. The same data were analyzed for this figure and for Figure 1 and as such cover a range of altitudes and to a lesser extent time of day.
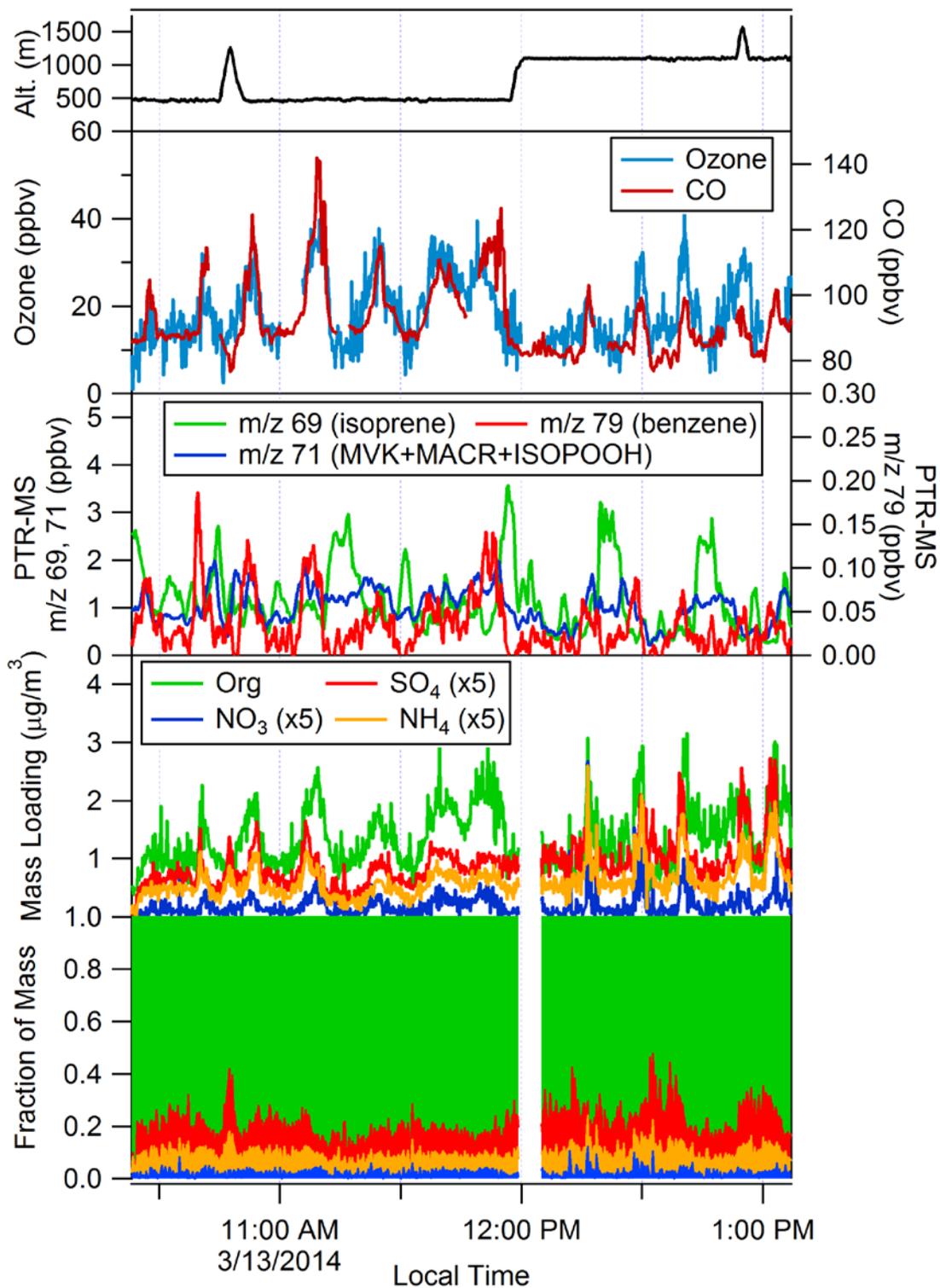
Figure 4. Time traces of relevant quantities on March 13th, 2014 flight. AMS data uses the HR-analysis routine described in the literature to minimize interferences (Aiken et al., 2007). Note the mass of inorganic species (SO4, NO3, NH4) has been multiplied by a factor of five to improve the figure clarity. PTR-MS signal at m/z 69 corresponds to isoprene, m/z 71 corresponds to the sum of methylvinyl ketone (MVK), methacrolein (MACR), and isoprene hydroxyhydroperoxide (ISOPOOH), all oxidation products of isoprene, and m/z 79 corresponds to benzene.
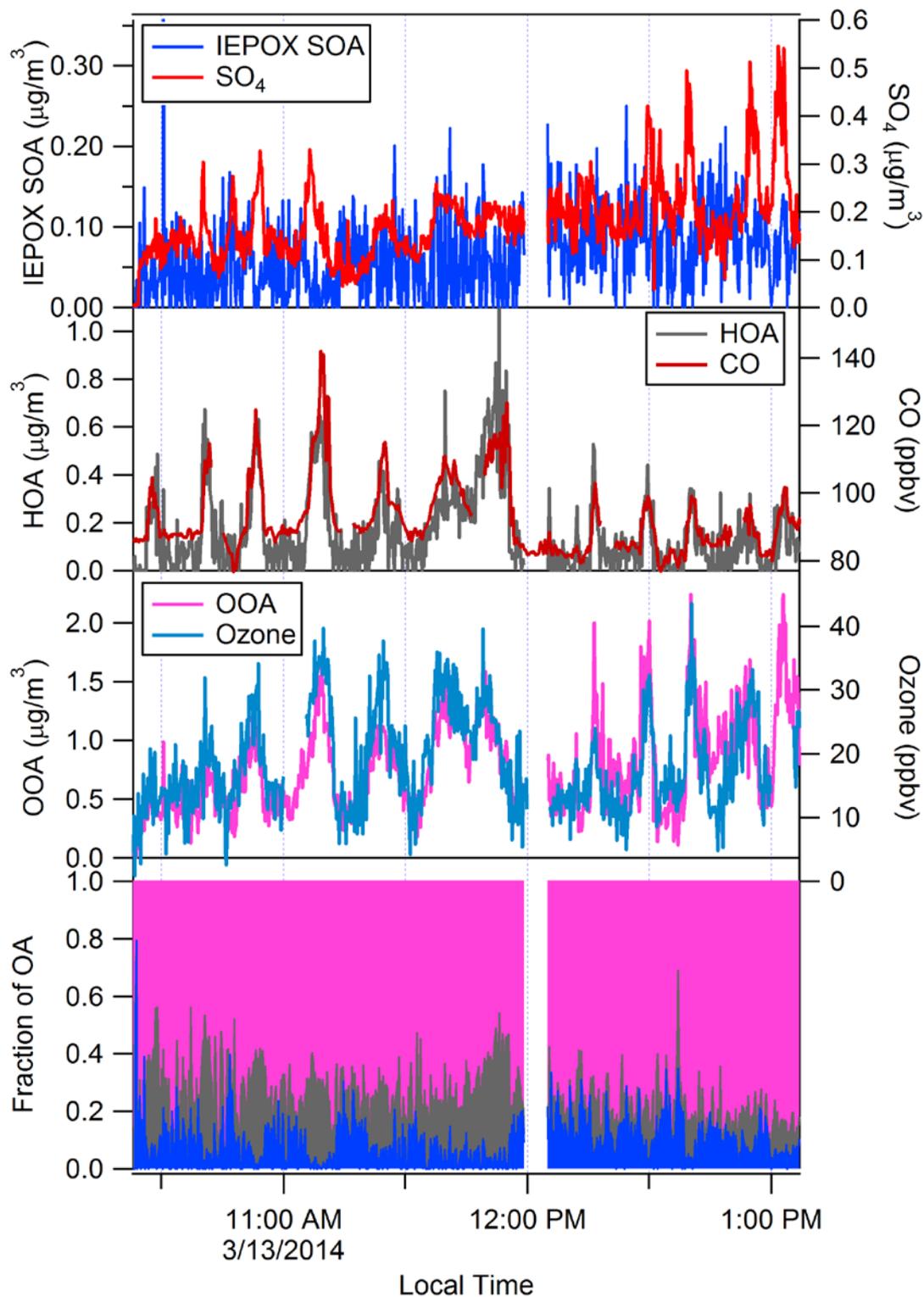
Figure 5. PMF analysis of the organic aerosol on the March 13th 2014 flight. The PMF analysis utilized the high resolution dataset. All data from the wet season were included in the analysis.
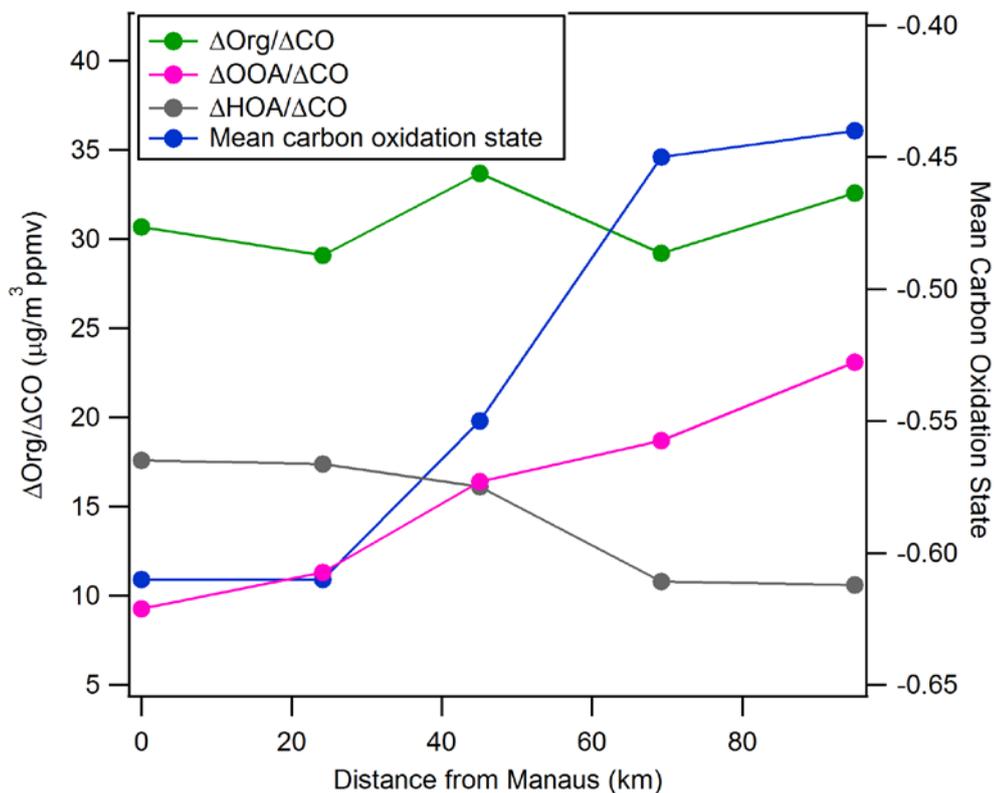
Figure 6. Key metrics describing the evolution of the Manaus urban plume on March 13. Each data point represents the average
5   **values for one pass through the plume. Mean wind speeds were 7 m/s on this flight, thus data capture approximately the first 4-5**
hours of the plume aging. Calculations of ΔOrg/ΔCO values use method one with details on the calculations and methods provided
in the SI. Spatial locations of each leg are labeled in Figure 1.

	Wet Season	Dry Season
Median Loading (All Data)		
Org	0.72	4.06
SO_4	0.11	0.67
NO_3	0.04	0.17
NH_4	0.03	0.25
Median Loading (Altitude < 700 m)		
Org	0.83	4.01
SO_4	0.13	0.61
NO_3	0.04	0.15
NH_4	0.03	0.21
Mean Loading (All data)		
Org	0.85	4.23
SO_4	0.14	0.73
NO_3	0.05	0.23
NH_4	0.05	0.27
Mean Loading (Altitude < 700 m)		
Org	0.96	4.16
SO_4	0.16	0.72
NO_3	0.05	0.28
NH_4	0.06	0.30

Table 1. Chemically resolved mass loading measured by the AMS onboard the G-1. Mass loadings are normalized to 23 °C and 1013 hPa. Units are µg/m³. The statistics for altitudes below 700 m approximate the boundary layer conditions at the time of the flights.