



# Contributions of biomass-burning, urban, and biogenic emissions to the concentrations and light-absorbing properties of particulate matter in central Amazonia during the dry season

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**Abstract.** Urbanization and deforestation have important impacts on atmospheric particulate matter (PM) over Amazonia. This study presents observations and analysis of PM<sub>1</sub> concentration, composition, and optical properties in central Amazonia during the dry season, focusing on the anthropogenic impacts. The primary study site was located 70 km downwind of Manaus, a city of over 2 million people in Brazil, as part of the GoAmazon2014/5 experiment. A high-resolution time-of-flight aerosol mass spectrometer (AMS) provided data on PM<sub>1</sub> composition, and aethalometer measurements were used to derive the absorption coefficient  $b_{\text{abs,BrC}}$  of brown carbon (BrC) at 370 nm. Non-refractory PM<sub>1</sub> mass concentrations averaged  $12.2 \mu\text{g m}^{-3}$  at the primary study site, dominated by organics (83%), followed

by sulfate (11%). A decrease in  $b_{\text{abs,BrC}}$  was observed as the mass concentration of nitrogen-containing organic compounds decreased and the organic PM<sub>1</sub> O : C ratio increased, suggesting atmospheric bleaching of the BrC components. The organic PM<sub>1</sub> was separated into six different classes by positive-matrix factorization (PMF), and the mass absorption efficiency  $E_{\text{abs}}$  associated with each factor was estimated through multivariate linear regression of  $b_{\text{abs,BrC}}$  on the factor loadings. The largest  $E_{\text{abs}}$  values were associated with urban ( $2.04 \pm 0.14 \text{ m}^2 \text{ g}^{-1}$ ) and biomass-burning ( $0.82 \pm 0.04$  to  $1.50 \pm 0.07 \text{ m}^2 \text{ g}^{-1}$ ) sources. Together, these sources contributed at least 80% of  $b_{\text{abs,BrC}}$  while accounting for 30% to 40% of the organic PM<sub>1</sub> mass concentration. In addition, a comparison of organic PM<sub>1</sub> composition between wet and

dry seasons revealed that only part of the 9-fold increase in mass concentration between the seasons can be attributed to biomass burning. Biomass-burning factor loadings increased by 30-fold, elevating its relative contribution to organic PM<sub>1</sub> from about 10 % in the wet season to 30 % in the dry season. However, most of the PM<sub>1</sub> mass (> 60 %) in both seasons was accounted for by biogenic secondary organic sources, which in turn showed an 8-fold seasonal increase in factor loadings. A combination of decreased wet deposition and increased emissions and oxidant concentrations, as well as a positive feedback on larger mass concentrations are thought to play a role in the observed increases. Furthermore, fuzzy *c*-means clustering identified three clusters, namely “baseline”, “event”, and “urban” to represent different pollution influences during the dry season. The baseline cluster, representing the dry season background, was associated with a mean mass concentration of  $9 \pm 3 \mu\text{g m}^{-3}$ . This concentration increased on average by  $3 \mu\text{g m}^{-3}$  for both the urban and the event clusters. The event cluster, representing an increased influence of biomass burning and long-range transport of African volcanic emissions, was characterized by remarkably high sulfate concentrations. The urban cluster, representing the influence of Manaus emissions on top of the baseline, was characterized by an organic PM<sub>1</sub> composition that differed from the other two clusters. The differences discussed suggest a shift in oxidation pathways as well as an accelerated oxidation cycle due to urban emissions, in agreement with findings for the wet season.

## 1 Introduction

The Amazon basin has undergone significant urbanization and deforestation in the past decades (Davidson et al., 2012; Martin et al., 2017; van Marle et al., 2017). An understanding of how the composition of atmospheric particulate matter (PM) changes due to anthropogenic activities and how these changes affect PM optical properties is essential for quantifying the global anthropogenic radiative forcing (IPCC, 2013; Sena et al., 2013). Light absorption coefficients,  $b_{\text{abs}}$ , and their spectral dependence, commonly referred to as the Ångström absorption exponent,  $\hat{a}_{\text{abs}}$ , are needed for accurate interpretation of satellite-retrieved aerosol optical depth (AOD) for climate modeling. Estimates of the mass absorption efficiency  $E_{\text{abs}}$  for PM subcomponents are useful for models to estimate optical effects based on PM composition and mass concentrations (Laskin et al., 2015).

Organic material that can efficiently absorb radiation in the near-ultraviolet through the blue end of the visible spectrum, with decreasing absorption efficiency as wavelength increases, is termed “brown carbon” (BrC) (Pöschl, 2003; Andreae and Gelencsér, 2006; Laskin et al., 2015). By comparison, black carbon (BC) absorbs light efficiently throughout the visible spectrum. Although global climate models

have typically treated organic PM as purely scattering, several studies have shown that brown carbon can contribute substantially to light absorption by PM, especially in regions affected by biomass-burning and urban emissions (Andreae and Gelencsér, 2006; Ramanathan et al., 2007; Bond et al., 2011; Bahadur et al., 2012; Ma and Thompson, 2012; Feng et al., 2013). In addition to primary emissions of BrC, secondary production of BrC can occur from the oxidation of non-methane volatile organic compounds (NMVOCs) present in biomass smoke (Saleh et al., 2014) and from atmospheric multiphase reactions involving a wide range of precursor NMVOCs (Nozière et al., 2007; De Haan et al., 2009; Nguyen et al., 2012; Lee et al., 2013; Lin et al., 2014; Powelson et al., 2014). The specific sources, chemical characteristics, and optical properties of BrC remain largely unconstrained.

Biomass-burning and urban pollution can affect the concentrations, composition, and properties of atmospheric PM. In Amazonia, urban pollution is significant downwind of large cities such as Manaus, Brazil (Kuhn et al., 2010; Martin et al., 2017; Cirino et al., 2018; de Sá et al., 2018). Martin et al. (2017) reported increased concentrations of particles, nitrogen oxides, carbon monoxide, and hydroxyl radicals for in-plume compared to out-of-plume conditions downwind of Manaus. Liu et al. (2016) and de Sá et al. (2017) demonstrated that the Manaus pollution plume shifted the oxidation pathway of isoprene, thereby significantly affecting gas- and particle-phase compositions. de Sá et al. (2018) determined that the submicron PM mass concentration increased by up to 3-fold for polluted compared to background conditions downwind of Manaus during the wet season.

Most biomass burning in Amazonia is related to human activities (Davidson et al., 2012; Artaxo et al., 2013; Aragão et al., 2014; van Marle et al., 2017). Among the main activities are the clearing of land and the burning of waste for several agricultural purposes as well as the burning of wood as fuel (Crutzen and Andreae, 1990; van Marle et al., 2017). Burning events are most frequent in the period of August through October, corresponding to the dry season (Setzer and Pereira, 1991; Artaxo et al., 2013; Martin et al., 2016). These activities can affect the biogeochemical cycles, atmospheric chemistry, precipitation, and climate throughout Amazonia (Crutzen and Andreae, 1990; Andreae et al., 2004; Lin et al., 2006). PM<sub>1</sub> mass concentrations typically increase by an order of magnitude between the wet and dry seasons in the Amazon, which has been commonly attributed to the increased biomass-burning emissions (Artaxo et al., 1994, 2013; Holben et al., 1996; Martin et al., 2010b, and references therein). Related increases in  $b_{\text{abs}}$  by 1 order of magnitude have also been attributed to biomass burning (Rizzo et al., 2011, 2013; Artaxo et al., 2013). Although black carbon is usually the main light-absorbing component for atmospheric particles smaller than  $1 \mu\text{m}$  (PM<sub>1</sub>), absorption by the organic BrC component of PM<sub>1</sub> could also be significant (Rizzo et al., 2013; Wang et al., 2016; Saturno et al.,

2017). Palm et al. (2018) showed that the formation potential of secondary organic PM<sub>1</sub> increased by a factor of 1.7 in the dry season compared to the wet season, although biomass-burning gases were not dominant precursors in either season. An understanding of the types and optical properties of organic components that may affect PM<sub>1</sub> light absorption in the Amazon and elsewhere is still emerging (Laskin et al., 2015).

The study herein investigates the contributions of biomass burning, urban emissions, and biogenic emissions to the composition and optical properties of organic PM<sub>1</sub> in central Amazonia during the dry season. Positive-matrix factorization (PMF) of organic mass spectra measured by an aerosol mass spectrometer (AMS) was used to identify component classes of the organic PM<sub>1</sub>. A fuzzy *c*-means clustering analysis of pollution indicators was employed to identify different conditions at the measurement site, as influenced by biomass-burning and urban emissions. Connections are made between the optical properties of organic PM<sub>1</sub>, including  $b_{\text{abs,BrC}}$  and  $E_{\text{abs}}$ , and its component classes. Taken together, these three pieces of analysis allow for insights into the changes in particle concentration, composition, and optical properties associated with the influences of biomass-burning and urban pollution downwind of Manaus.

## 2 Methodology

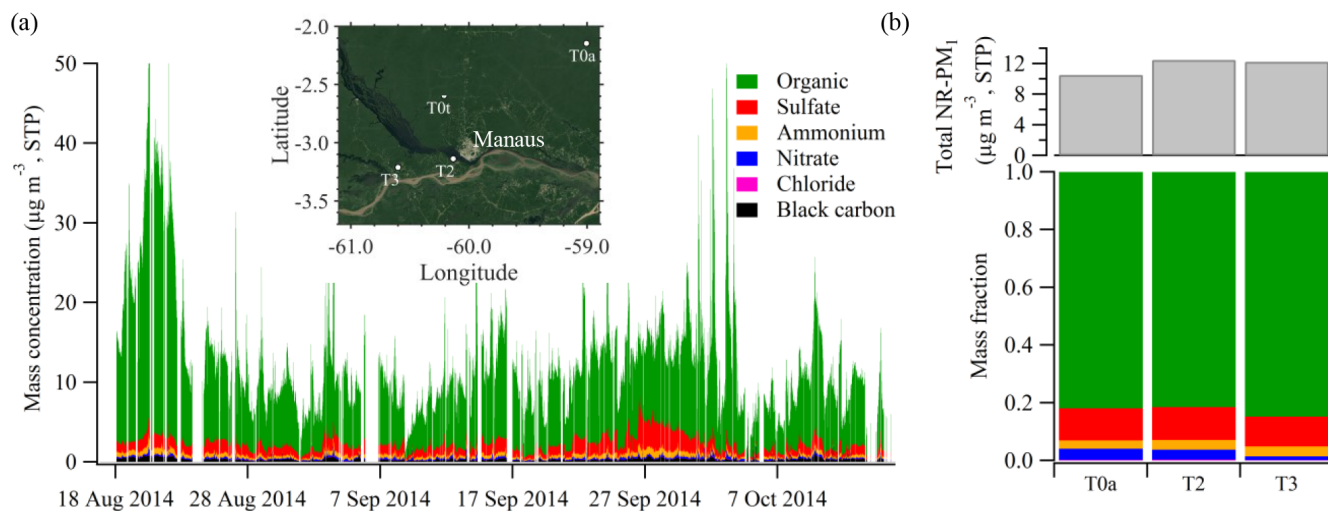
### 2.1 Research sites and measurements

The primary site of this study was called “T3”, located 70 km to the west of Manaus, Brazil, in central Amazonia (Martin et al., 2016; inset of Fig. 1a). The pollution plume from Manaus was primarily westerly in the dry season and was modeled to intercept the T3 site about 60 % of the time (Martin et al., 2017). Analyses of observational data sets have labeled pollution episodes for at least 15 to 30 % of the time (Thalman et al., 2017; Cirino et al., 2018). Auxiliary sites “T0a” and “T2” served as references for background and urban-polluted conditions, respectively, in relation to T3. The T0a site was located at the Amazon Tall Tower Observatory (Andreae et al., 2015), about 150 km to the northeast of Manaus, and the air masses were typically upwind of the urban region without the influence of Manaus pollution. The T2 site was located 8 km to the west of Manaus, directly downwind of the city, and air masses were therefore typically heavily polluted at this site. During the dry season, the three sites were also affected by both nearby and long-range-transported biomass-burning emissions. The study period from 15 August to 15 October 2014 corresponded to the second Intensive Operating Period (IOP2) of the GoAmazon2014/5 experiment (Martin et al., 2016).

At the T3 site, mass concentrations of non-refractory PM<sub>1</sub> components (organic, sulfate, ammonium, nitrate, and chloride) were measured by a high-resolution time-of-flight AMS (DeCarlo et al., 2006; Sueper, 2018). A detailed description of operation was provided in de Sá et al. (2017). In brief, the AMS was deployed inside a temperature-controlled research container, and ambient data were collected every other 4 min. Data analysis was performed using *SQUIRREL* (1.56D) and *PIKA* (1.14G) of the AMS software suite (DeCarlo et al., 2006). The mean composition-dependent collection efficiency was 0.51 (Sect. S1; Fig. S1 in the Supplement) (Middlebrook et al., 2012). Organic and inorganic nitrate concentrations were estimated from the AMS measurements based on the ratio of the signal intensity of NO<sub>2</sub><sup>+</sup> to that of NO<sup>+</sup> (Sect. S1, Fig. S2 in the Supplement) (Fry et al., 2009, 2013; Farmer et al., 2010). Sulfate measured by the AMS includes contributions from organosulfates (Farmer et al., 2010; Glasius et al., 2018). The oxygen-to-carbon (O : C) and hydrogen-to-carbon (H : C) ratios of the organic PM<sub>1</sub> were calculated following the methods of Canagaratna et al. (2015).

Several other instruments complemented the AMS measurements. Gas- and particle-phase semi-volatile tracers were obtained by a semi-volatile thermal desorption aerosol gas chromatograph (SV-TAG) (Isaacman-VanWertz et al., 2016; Yee et al., 2018), and NMVOCs were obtained by a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS) (Jordan et al., 2009; Liu et al., 2016). In addition, measurements of NO<sub>y</sub>, O<sub>3</sub>, particle number, and CO concentrations were employed in the analyses (Martin et al., 2016). Refractory black carbon (rBC) concentrations were measured by a single particle soot photometer (SP2). Meteorological variables, including temperature, relative humidity, and solar irradiance were also measured. Particle absorption coefficients,  $b_{\text{abs}}(\lambda)$ , were obtained by a seven-wavelength aethalometer (370, 430, 470, 520, 565, 700, and 880 nm; Magee Scientific, model AE-31) following the methods and corrections of Rizzo et al. (2011). Additional measurements of non-refractory particle composition and concentration from the T0a and T2 sites were made by an aerosol chemical speciation monitor (ACSM) at each site (Ng et al., 2011; Andreae et al., 2015; Martin et al., 2016).

Air-mass back-trajectories were estimated using Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4; Draxler and Hess, 1998). Data sets of the S-band radar of the System for Amazon Protection (SIPAM) in Manaus (Machado et al., 2014) provided precipitation data, which allowed to filter out trajectories that intercepted precipitation. The HYSPLIT4 simulations started at 100 m above T3 and were calculated up to 2 d back in time for every 12 min to match with the radar data. Input meteorological data to the simulations were obtained on a grid of 0.5° × 0.5° from the Global Data Assimilation System (GDAS). Additional information on the back-trajectory calculations and on the radar were described in de Sá et al. (2018).



**Figure 1.** PM<sub>1</sub> composition during the dry season from 15 August to 15 October 2014, representing the second Intensive Operating Period (IOP2) of the GoAmazon2014/5 experiment. Results are shown for measurements at T3 in comparison to other sites. **(a)** PM<sub>1</sub> mass concentrations of non-refractory AMS organic, sulfate, ammonium, nitrate, and chloride. Mass concentrations of SP2 refractory black carbon (rBC) are also plotted. rBC refers to the carbon content of graphite-like components that are strongly light absorbing (Pöschl, 2003). **(b)** Summed mass concentrations (top) and segregated mass fractions (bottom) of the non-refractory species at the T0a, T2, and T3 sites. The inset of panel **(a)** shows the locations of the relevant research sites for this study. A larger map is shown in Fig. 3. T0a is the Amazon Tall Tower Observatory (Andreae et al., 2015). T2 is a site 8 km downwind of Manaus, just across the Black River (“Rio Negro”) (Cirino et al., 2018). Measurements at T0a and T2 were made by an aerosol chemical speciation monitor (ACSM). Concentrations in both panels were adjusted to standard temperature (273.15 K) and pressure (10<sup>5</sup> Pa) (STP).

## 2.2 Brown carbon light absorption

The analysis partitioned the total absorption  $b_{\text{abs}}(\lambda)$  measured by the aethalometer between BrC and BC contributions as follows:

$$b_{\text{abs}} = b_{\text{abs,BrC}} + b_{\text{abs,BC}}. \quad (1)$$

The dependence on wavelength was expressed by the absorption Ångström exponent ( $\hat{a}_{\text{abs}}$ ) as follows:

$$\hat{a}_{\text{abs}}(\lambda_1, \lambda_2) = -\frac{\log_{10}[b_{\text{abs}}(\lambda_1)/b_{\text{abs}}(\lambda_2)]}{\log_{10}(\lambda_1/\lambda_2)}. \quad (2)$$

For the characterization of BrC absorption, the value of  $\hat{a}_{\text{abs,BrC}}$  at 370 nm was sought. To calculate  $b_{\text{abs,BrC}}(370)$ , an assumption has to be made about the spectral dependency of BC light absorption. In this study,  $\hat{a}_{\text{abs,BC}}$  was assumed to be wavelength independent, and  $\hat{a}_{\text{abs,BC}}(700, 880)$  was calculated for each sample based on  $b_{\text{abs}}$  at the wavelengths 700 and 880 nm (Eq. 2), assuming absorption to be insignificant for BrC and dominated by BC in this spectral range. Calculations of  $b_{\text{abs,BrC}}(370)$  using alternative treatments to retrieve  $\hat{a}_{\text{abs,BC}}$  were also carried out. These treatments included the assumption that  $\hat{a}_{\text{abs,BC}}$  is equal to 1.0 and wavelength-independent (e.g., Yang et al., 2009), or the assumption that  $\hat{a}_{\text{abs,BC}}$  has a spectral dependency itself (Wang et al., 2016; Saturno et al., 2018a). The results from these different treatments correlated with one another ( $R^2 > 0.9$ ),

and the  $b_{\text{abs,BrC}}$  estimate used in this study and detailed in the steps below represented a lower bound among the differing assumptions (Sect. S4).

For each point in time,  $b_{\text{abs,BrC}}(370)$  was estimated by the following steps: (1)  $b_{\text{abs,BC}}(700) = b_{\text{abs}}(700)$  and  $b_{\text{abs,BC}}(880) = b_{\text{abs}}(880)$  assuming that  $b_{\text{abs,BrC}} = 0$  at red wavelengths (e.g., Andreae and Gelencsér, 2006; Wang et al., 2016); (2)  $\hat{a}_{\text{abs,BC}}(700, 880)$  was calculated from Eq. (2) using  $b_{\text{abs,BC}}(700)$  and  $b_{\text{abs,BC}}(880)$ ; (3)  $b_{\text{abs,BC}}(370)$  was calculated from Eq. (2), using  $b_{\text{abs,BC}}(880)$  and  $\hat{a}_{\text{abs,BC}}(370, 880) = \hat{a}_{\text{abs,BC}}(700, 880)$  under the assumption that  $\hat{a}_{\text{abs,BC}}$  was independent of wavelength (e.g., Andreae and Gelencsér, 2006; Moosmüller et al., 2009); and finally (4)  $b_{\text{abs,BrC}}(370)$  was obtained by Eq. (1) using  $b_{\text{abs,BC}}(370)$  and  $b_{\text{abs}}(370)$ . The value of  $b_{\text{abs,BrC}}$  at 430 nm was also obtained by the same process. Based on  $b_{\text{abs}}(370)$  and  $b_{\text{abs}}(430)$ ,  $\hat{a}_{\text{abs}}(370, 430)$  was estimated. Hereafter,  $b_{\text{abs}}$  and  $b_{\text{abs,BrC}}$  refer to 370 nm, and  $\hat{a}_{\text{abs}}$  refers to the range of 370 to 430 nm.

The aethalometer, like other filter-based measurement schemes (e.g., PSAP, TAP, or MAA), is prone to artifacts. These artifacts may originate from light scattering by the filter media itself, the influence of the filter media on the microphysical properties of the collected particle (e.g., potential change in hygroscopic particle size), and the impact of the multiple scattered photons on the measured optical extinction (e.g., enhanced particle absorption as discussed by Nakayama et al., 2010). While several correction schemes

have been developed to address these artifacts, the individual schemes do not approach these problems in the same way, which may lead to different results among them (Weingartner et al., 2003; Schmid et al., 2006; Collaud Coen et al., 2010; Rizzo et al., 2011; Ammerlaan et al., 2017). For the present analysis, the correction scheme used was described by Rizzo et al. (2011). The potential impact of the different correction schemes on the analysis interpretation was not examined.

### 3 Results and discussion

#### 3.1 Contributions of biomass-burning and urban emissions to fine-mode PM

##### 3.1.1 Comparison of PM concentration and composition across sites

A comparison between the T3 site and the upwind sites can provide a first-order estimate of the effects of Manaus urban pollution on PM<sub>1</sub> concentration and composition (de Sá et al., 2018). During the dry season of 2014, organic compounds dominated the composition at T3, contributing  $83 \pm 6\%$  (mean  $\pm 1$  standard deviation) of the non-refractory PM<sub>1</sub> (NR-PM<sub>1</sub>), followed by sulfate ( $11 \pm 5\%$ ) (Fig. 1a). Mean NR-PM<sub>1</sub> mass concentrations and relative compositions at T3 and at T0a and T2 are represented in Fig. 1b for comparison. Organic material consistently constituted 80% to 85% of NR-PM<sub>1</sub> across all three sites. By comparison, the contribution of organic material to NR-PM<sub>1</sub> typically ranged from 70% to 80% during the wet season (de Sá et al., 2018).

The NR-PM<sub>1</sub> mass concentrations across the three sites differed slightly (Fig. 1b, top panel). The mean concentration at the T0a site upwind of Manaus was  $10.5 \mu\text{g m}^{-3}$ . The mean concentrations at the T2 site just downwind of Manaus and at the T3 site further downwind were 12.5 and  $12.2 \mu\text{g m}^{-3}$ , respectively, representing an increase of about 20% relative to the upwind site. By comparison, increases of 200% to 300% relative to the upwind site were observed during the wet season (de Sá et al., 2018). In absolute mass concentration, however, the difference between upwind and downwind sites of 1 to  $2 \mu\text{g m}^{-3}$  was similar between seasons, suggesting contributions from urban pollution of the same order of magnitude in both seasons. The larger percent increase for the wet season is explained by background concentrations of  $1 \mu\text{g m}^{-3}$ , which are an order of magnitude lower compared to the dry season.

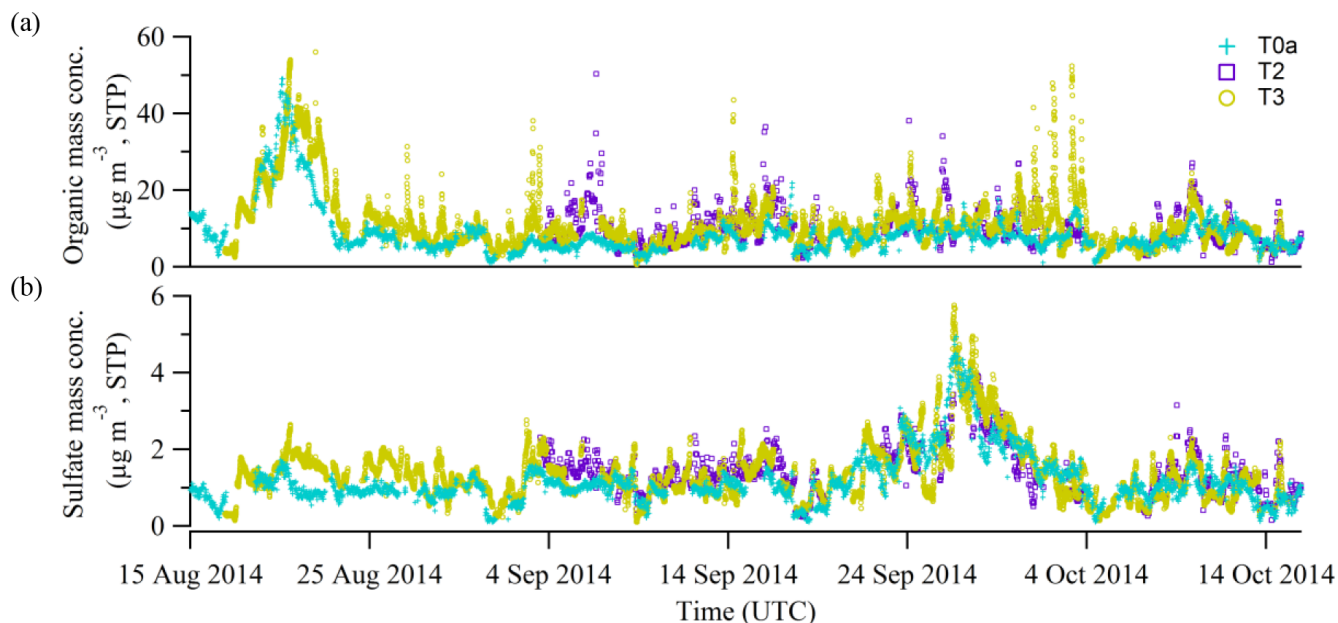
The time series of organic mass concentrations across the three sites were well correlated across the 2 months when considering the timescale of a day (Fig. 2a;  $0.55 < R < 0.85$ ). Similar behavior was observed for sulfate mass concentrations (Fig. 2b;  $0.86 < R < 0.93$ ). The T0a and T3 sites were separated by 215 km. This result shows that sources and processes of PM<sub>1</sub> production at a regional scale were important during the dry season. The data also show that for

timescales of an hour the sites were less correlated ( $0.70 < R < 0.80$  for sulfate, and  $0.38 < R < 0.75$  for organic mass concentrations). The large spikes in organic mass concentrations observed at T3 but generally smaller at T2 and absent at T0a could be explained by episodic fires along the Solimões River, especially during nighttime (Fig. 3).

In addition to the widespread and frequent occurrence of fires in the Amazon basin during the dry season (Fig. 3), meteorological conditions may also favor a regional reach of events (Sect. S3). For example, high organic concentrations were observed during the period of 17 to 23 August. During that week, widespread biomass-burning activity in the basin (beyond the scale of Fig. 3), in conjunction with a lack of precipitation events, clear skies, and temperatures of  $35^\circ\text{C}$  during daytime, allowed for intense photochemical activity and buildup of PM<sub>1</sub>. There appeared to be an offset in PM<sub>1</sub> concentrations by 1 d between T0a and T3 during that time, which would be consistent with the transport across 215 km from T0a to T3 for typical easterlies averaging  $3 \text{ m s}^{-1}$  over the course of a day. In short, a combination of regional-scale biomass-burning activity and meteorological conditions greatly influenced the mass concentration of PM<sub>1</sub> at the three sites.

The diel variability of organic and sulfate mass concentrations for the three sites is shown in Fig. 4. Organic mass concentrations were slightly higher at the T2 and T3 sites compared to the T0a site, as expected. The variability was larger at the T2 and T3 sites, especially at night. These two sites are closer to populated areas along the path of the Solimões River and thus are also closer to local biomass-burning sources. Activities include burning of crops and trash in houses and farms as well burning of wood in brick kilns (Martin et al., 2016; Cirino et al., 2018). Stagnant air and a shallow boundary layer during the night might explain how variable biomass-burning emissions lead to larger organic mass concentrations and variability at night compared to the day.

The influence of anthropogenic emissions on daytime chemistry is apparent in the diel trends of the sulfate mass concentrations. Sulfate concentrations had low variability throughout the day at T0a, indicating a prevalence of diffuse regional sources that had variations dampened after many hours or days of transport. Possible sources include the atmospheric oxidation of biogenic emissions (DMS, H<sub>2</sub>S) from the upwind forest and ocean, as well as long-range transport of fossil fuel combustion emissions from cities in northeastern Brazil and of biomass burning and volcanic emissions from Africa (Andreae et al., 1990; Martin et al., 2010a; Saturno et al., 2018b). Biomass burning can be an important source of sulfate and its precursors (Andreae and Merlet, 2001; Fiedler et al., 2011). For the T2 and T3 sites, sulfate concentrations increased in the morning hours and peaked in the afternoon. The Manaus sulfate source consists of the burning of heavy fuel oil for electricity production, refinery operations, and more diffuse traffic sources, and these emis-



**Figure 2.** Time series of (a) organic and (b) sulfate mass concentrations at the T0a, T2, and T3 sites. Concentrations were adjusted to standard temperature (273.15 K) and pressure ( $10^5$  Pa).

sions reach the T3 site in the afternoon, when OH levels are also the highest (de Sá et al., 2017). In addition, biomass-burning emissions around T2 and T3 might also have contributed to the increase in sulfate concentrations during the afternoons.

### 3.1.2 Comparison of PM concentration and composition across clusters for the T3 site

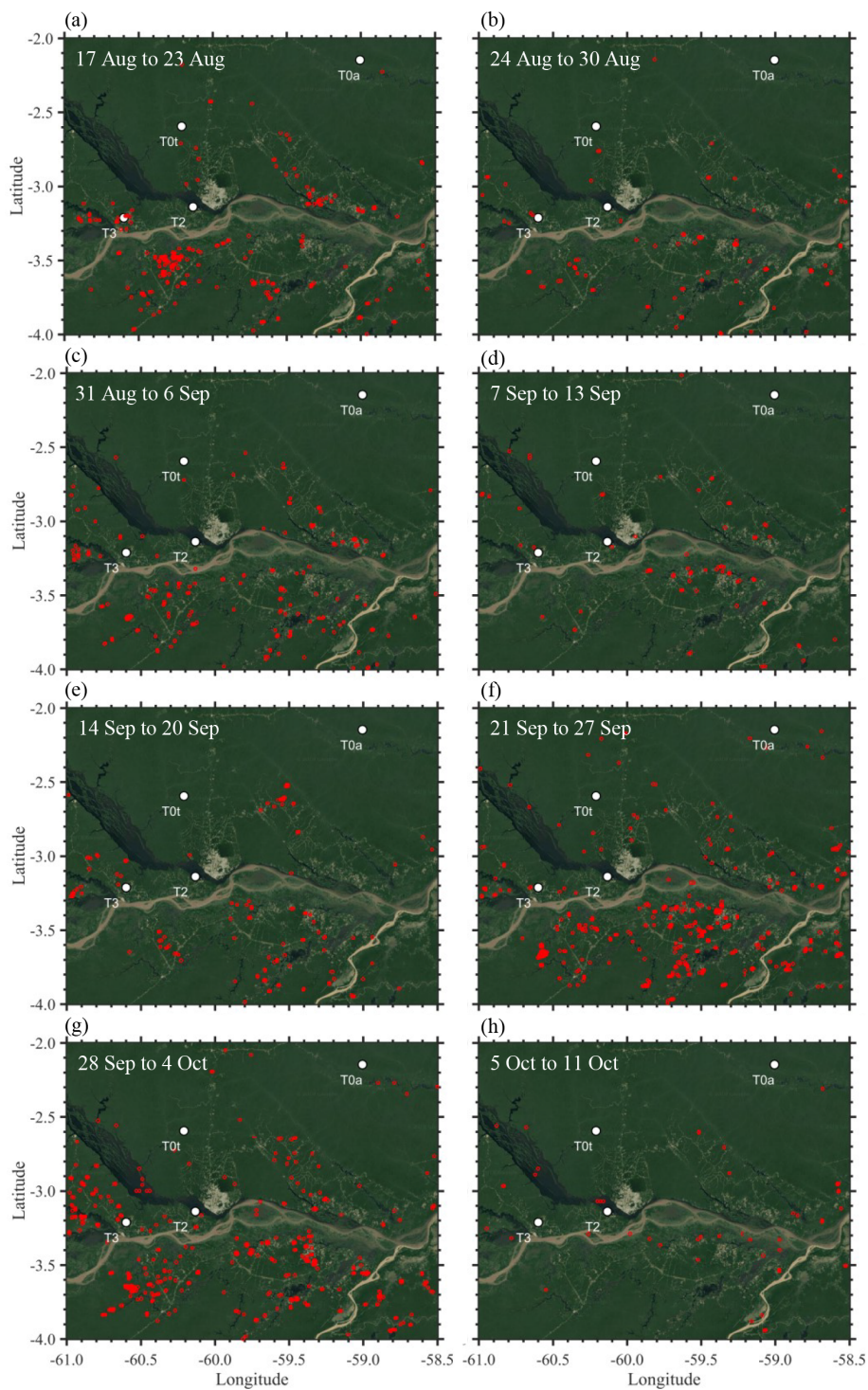
A second approach to investigate the changes in concentrations and compositions of the PM with pollution influences employed a combination of PMF and fuzzy *c*-means (FCM) clustering. The PMF analysis was applied to the organic mass spectra to separate the organic PM<sub>1</sub> into representative component classes (Sect. “Classification of organic PM<sub>1</sub> by positive-matrix factorization”). The FCM clustering algorithm was applied to auxiliary measurements to identify times of urban and biomass-burning influences at the T3 site (Sect. “Cluster analysis”). The results of the FCM analysis were crossed with the findings of the PMF analysis for further insights into pollution-related variability of PM concentration and composition (Sect. “Comparison of PM<sub>1</sub> composition among clusters”).

#### Classification of organic PM<sub>1</sub> by positive-matrix factorization

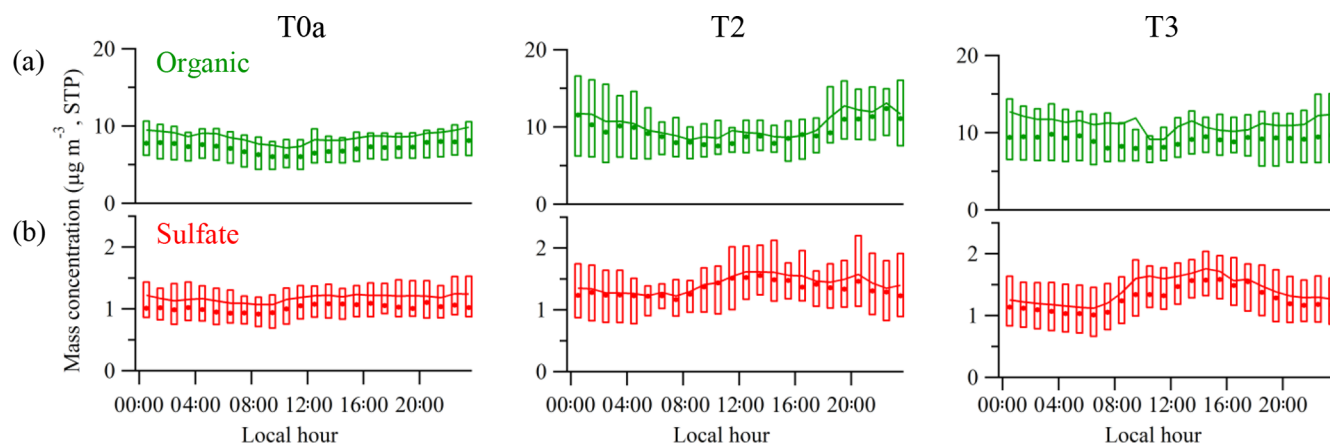
The organic mass spectra recorded by the AMS at the T3 site were analyzed by PMF (Ulbrich et al., 2009). Details and diagnostics of the PMF analysis are presented in the Supplement (Sect. S1). Following the nomenclature used in de

Sá et al. (2018), “mass spectrum” and “mass concentration” refer to the direct AMS measurements, while “factor profile” and “factor loading” are their counterpart mathematical products obtained from the PMF analysis. A six-factor solution was obtained, and the factor profiles, diel trends of the factor loadings, and the time series of the factor loadings and other related measurements are plotted in Fig. 5. The correlations of factor loadings with co-located measurements of gas- and particle-phase species are presented in Fig. 6.

The factors were interpreted considering the mass spectral characteristics of the factor profiles and the correlations between factor loading and mass concentrations of co-located measurements. Three resolved factors interpreted as secondary production and processing closely matched the counterpart profiles of the wet season ( $R \geq 0.99$ ; Table 1) (de Sá et al., 2018). These three factors consisted of a more-oxidized oxygenated factor (“MO-OOA”), a less-oxidized oxygenated factor (“LO-OOA”), and an isoprene epoxydiols-derived factor (“IEPOX-SOA”). Temporal correlations with external tracers and oxidation characteristics were also similar to those of the wet season, corresponding to the first Intensive Operating Period (IOP1) (Fig. 6; Table 1; de Sá et al., 2018). Although a hydrocarbon-like factor (“HOA”) was analogous to its counterpart in IOP1 ( $R = 0.94$ ), it also had characteristics of an IOP1 anthropogenic-dominated factor (“ADOA”) tied to other urban sources including cooking. The HOA factor of IOP2 therefore represented a mix of the HOA and ADOA factors of IOP1, which could not be separated by PMF in IOP2 due to their lower relative contributions. The interpretation of the HOA, IEPOX-SOA, LO-OOA, and MO-OOA factors follows that of IOP1, as pre-



**Figure 3.** Fire locations in the upwind region of the T3 site for each week of IOP2. Transport times from the fires to the T3 site represent up to 15 h at the scale of this figure and typical wind speeds. The plotted data were obtained from the fire database of the Brazilian National Institute of Spatial Research (INPE, 2018). Underlying image: Google Maps.



**Figure 4.** Diel trends of (a) organic and (b) sulfate mass concentrations at the T0a, T2, and T3 sites. Lines represent means, solid markers show medians, and boxes span interquartile ranges. Local time is UTC minus 4 h. Concentrations were adjusted to standard temperature (273.15 K) and pressure ( $10^5$  Pa).

sented in de Sá et al. (2018). The following discussion focuses on the two biomass-burning factors of IOP2.

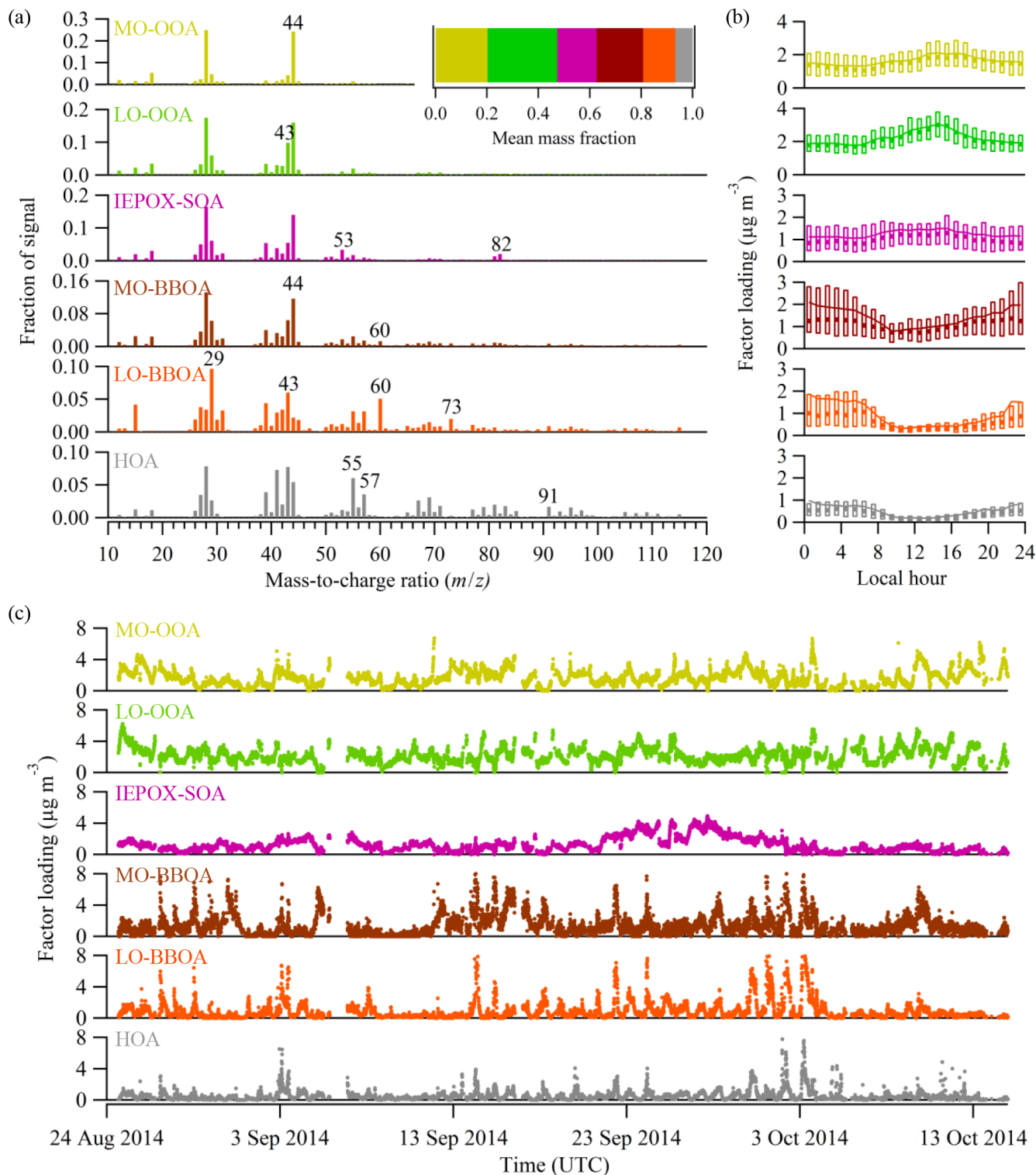
A less-oxidized factor (“LO-BBOA”) and a more-oxidized factor (“MO-BBOA”) were resolved for IOP2. For IOP1, a single “BBOA” factor was resolved, and it accounted for 9 % of the organic  $\text{PM}_{10}$  mass concentration. For IOP2, there were enough differences in mass spectral features and temporal contributions, as well as larger overall contributions of biomass burning, that the PMF analysis identified two different factors. The MO-BBOA and LO-BBOA factors, respectively, accounted for 18 % and 12 % of the mean organic  $\text{PM}_{10}$  mass concentration. Therefore, the relative contribution of biomass burning to organic  $\text{PM}_{10}$  during the dry season was at least a factor of 3 higher compared to the wet season (a more detailed discussion is presented at the end of this section).

The LO-BBOA and MO-BBOA factor profiles had a distinct peak at nominal  $m/z$  60 ( $\text{C}_2\text{H}_4\text{O}_2^+$ ) (Fig. 5a). The fractional intensity  $f_{60}$  at  $m/z$  60 was larger for LO-BBOA (0.051) than for MO-BBOA (0.013). A peak at  $m/z$  73 ( $\text{C}_3\text{H}_5\text{O}_2^+$ ) was also present in both profiles, although its intensity was 3–4 times smaller than that at  $m/z$  60. The peaks at  $m/z$  60 and 73 are attributed to fragments of levoglucosan and other anhydrous sugars that are produced by the pyrolysis of biomass (Schneider et al., 2006; Cubison et al., 2011). Accordingly, the loadings of both factors correlated with the concentrations of several biomass-burning tracers in the particle phase, including levoglucosan, vanillin, 4-nitrocatechol, syringol, mannosan, syringaldehyde, sinapaldehyde, and long-chain alkanolic acids ( $\text{C}_{20}$ ,  $\text{C}_{22}$ ,  $\text{C}_{24}$ ) and of tracers in the gas phase (acetonitrile) (Fig. 6). The loadings also correlated with less-specific tracers, including CO concentration and particle number concentration. The Pearson  $R$  correlations were typically higher for the LO-BBOA factor than for the MO-BBOA factor.

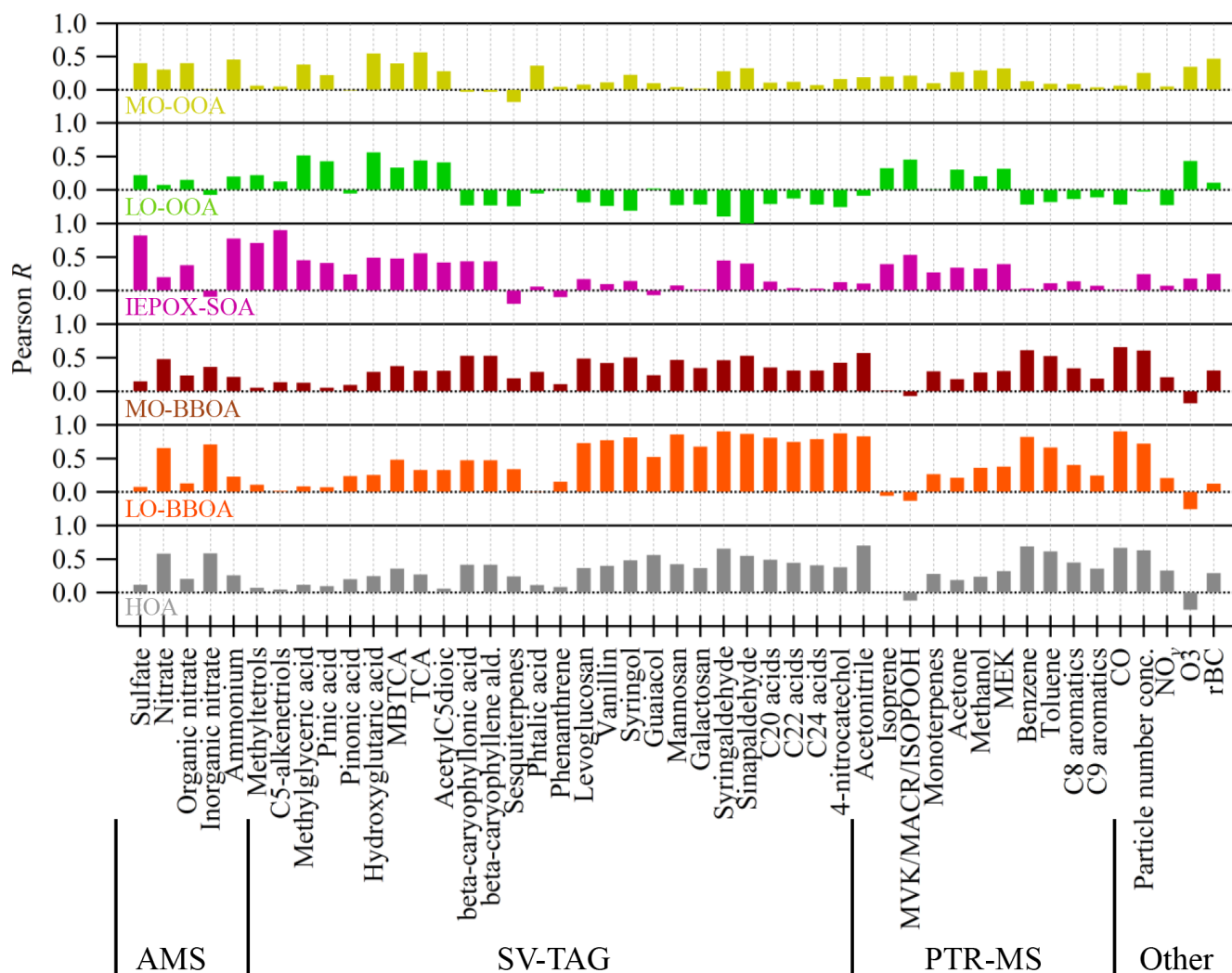
The LO-BBOA profile had the greatest ratio of signal intensity of the  $\text{C}_2\text{H}_3\text{O}^+$  ion ( $m/z$  43) to that of the  $\text{CO}_2^+$  ion ( $m/z$  44) compared to all other factors (Fig. 5a). In comparison, the MO-BBOA profile had a high intensity for the  $\text{CO}_2^+$  ion and a low intensity for the  $\text{C}_2\text{H}_3\text{O}^+$  ion. The MO-BBOA and LO-BBOA factors had O : C ratios of  $0.70 \pm 0.07$  and  $0.53 \pm 0.04$ , respectively. In addition, the LO-BBOA factor loading had higher correlation with the estimated inorganic nitrate concentrations than with the total nitrate concentrations, whereas the MO-BBOA factor did not (Fig. 6; Sect. S1 in the Supplement describes the nitrate estimates). Taken together, these results point to a less-oxidized, higher-volatility character of the LO-BBOA factor and a more-oxidized, lower-volatility character of the MO-BBOA factor, both with biomass-burning characteristics (Jimenez et al., 2009; Cubison et al., 2011; Gilardoni et al., 2016; Zhou et al., 2017).

The extent of the biomass-burning influence and atmospheric oxidation on the composition of organic  $\text{PM}_{10}$  can be visualized in a scatter plot of  $f_{44}$  and  $f_{60}$  (Fig. 7a) (Cubison et al., 2011). A background  $f_{60}$  value of  $0.3 \% \pm 0.06 \%$  (vertical black dashed line) indicates a threshold for negligible or completely oxidized biomass-burning  $\text{PM}_{10}$ . Points in the lower right of the  $f_{44}$ – $f_{60}$  representation usually characterize  $\text{PM}_{10}$  tied to recent biomass-burning emissions. For IOP1 (blue markers), all points lie on or close to the background value suggested by Cubison et al. (2011), indicating the absence of a strong influence from biomass burning. During the wet season, biomass burning was limited to local sources or to sources far enough away such as Africa that the  $\text{PM}_{10}$  was extensively oxidized by arrival in central Amazonia (de Sá et al., 2018). For IOP2 (red markers), the  $f_{60}$  values are greater for most observations, showing that for most times T3 was influenced to some extent by biomass burning (see Sect. “Comparison of  $\text{PM}_{10}$  composition among clusters”). This finding is in line with the widespread occur-





**Figure 5.** PMF analysis of the time series of AMS organic mass spectra collected at the T3 site. (a) Mass spectral profile of each factor represented at unit mass resolution. The inset shows the mean fractional loading of each factor. The factor profiles are shown in more detail, colored by ion families, in Fig. S5. (b) Diel trends for the loadings of each PMF factor. Local time is UTC minus 4 h. Lines represent means, solid markers show medians, and boxes span interquartile ranges. (c) Time series of the factor loadings.



**Figure 6.** Pearson  $R$  correlations between the loading of each PMF factor and concentrations of selected measurements at the T3 site. Abbreviations include tricarballic acid (TCA), methyl-butyl-tricarboxylic acid (MBTCA), methyl vinyl ketone (MVK), methacrolein (MACR), isoprene hydroxyhydroperoxides (ISOPOOH), and rBC. SV-TAG measurements refer to particle-phase concentrations, except for sesquiterpenes which refer to total concentrations and mostly occurred in the gas phase. The  $C_8$  and  $C_9$  aromatics include the xylene and trimethylbenzene isomers, respectively. The  $C_{20}$ ,  $C_{22}$ , and  $C_{24}$  acids include eicosanoic, docosanoic, and tetracosanoic acids, respectively.

rence of fires during the dry season (Fig. 3). As suggested by the robust trend in Fig. 7a, the  $f_{44}$  value increases and the  $f_{60}$  value decreases from the bottom right to the upper left as the organic  $PM_{10}$  emitted by biomass burning is oxidized in the atmosphere. The  $f_{60}$  and  $f_{44}$  values of the LO-BBOA and MO-BBOA profiles, plotted as diamonds, lie on the linear trend.

The LO-BBOA factor of high  $f_{60}/f_{44}$  and low O : C thus appears associated with primary  $PM_{10}$  emitted by biomass burning. The MO-BBOA factor, characterized by low  $f_{60}/f_{44}$  and high O : C, may represent a combination of primary  $PM_{10}$  of higher oxygen content as well as secondary  $PM_{10}$  tied to biomass burning in its early stages of atmospheric processing (Cubison et al., 2011; Gilardoni et

al., 2016). These secondary pathways could include (i) the heterogeneous oxidation of primary  $PM_{10}$ , such as that represented by the LO-BBOA factor, and (ii) the oxidation of gas-phase biomass-burning emissions or of species evaporated from primary  $PM_{10}$ , followed by the condensation of the gas-phase products onto the  $PM_{10}$ .

The LO-BBOA and MO-BBOA factor loadings had greater magnitude and variability at night compared to during the day (Fig. 5b). Their summed loading, represented as “BBOA<sub>T</sub>”, accounted for 40 % and 13 % of the organic  $PM_{10}$  during night and day, respectively. Overall, they accounted for 30 % of the organic  $PM_{10}$ . This result reflects the importance of fire activity during all times of day and during the entirety of IOP2 (Fig. 3). The surface concentrations were

**Table 1.** Characteristics of the PMF factor profiles. Listed are  $f_{44}$  and  $f_{60}$ , corresponding to the organic signal fraction at  $m/z$  44 and 60, respectively, as well as the oxygen-to-carbon (O : C) and hydrogen-to-carbon (H : C) ratios. Values and uncertainties were calculated by running the PMF analysis in “bootstrap mode” (Ulbrich et al., 2009). The Pearson  $R$  correlations between the factor profiles of IOP2 and their counterparts in IOP1 are also listed (i.e., dry season compared to wet season). “n/a” means “not applicable”. Elemental ratios were calibrated by the “improved-ambient” method, which has an estimated uncertainty of 12 % for O : C and 4% for H : C (Canagaratna et al., 2015).

PMF factor	$f_{44}$	$f_{60}$	O : C	H : C	Pearson $R$ against IOP1 counterpart
MO-OOA	$0.24 \pm 0.01$	$< 0.001$	$1.20 \pm 0.10$	$1.25 \pm 0.08$	1.00
LO-OOA	$0.15 \pm 0.01$	$0.001 \pm 0.001$	$0.86 \pm 0.08$	$1.51 \pm 0.06$	0.99
IEPOX-SOA	$0.14 \pm 0.01$	$< 0.001$	$0.74 \pm 0.02$	$1.51 \pm 0.01$	0.99
MO-BBOA	$0.13 \pm 0.01$	$0.011 \pm 0.003$	$0.70 \pm 0.07$	$1.59 \pm 0.11$	n/a
LO-BBOA	$0.02 \pm 0.01$	$0.05 \pm 0.01$	$0.53 \pm 0.04$	$1.79 \pm 0.06$	n/a
HOA	$0.05 \pm 0.01$	$0.001 \pm 0.001$	$0.22 \pm 0.03$	$1.82 \pm 0.03$	0.94

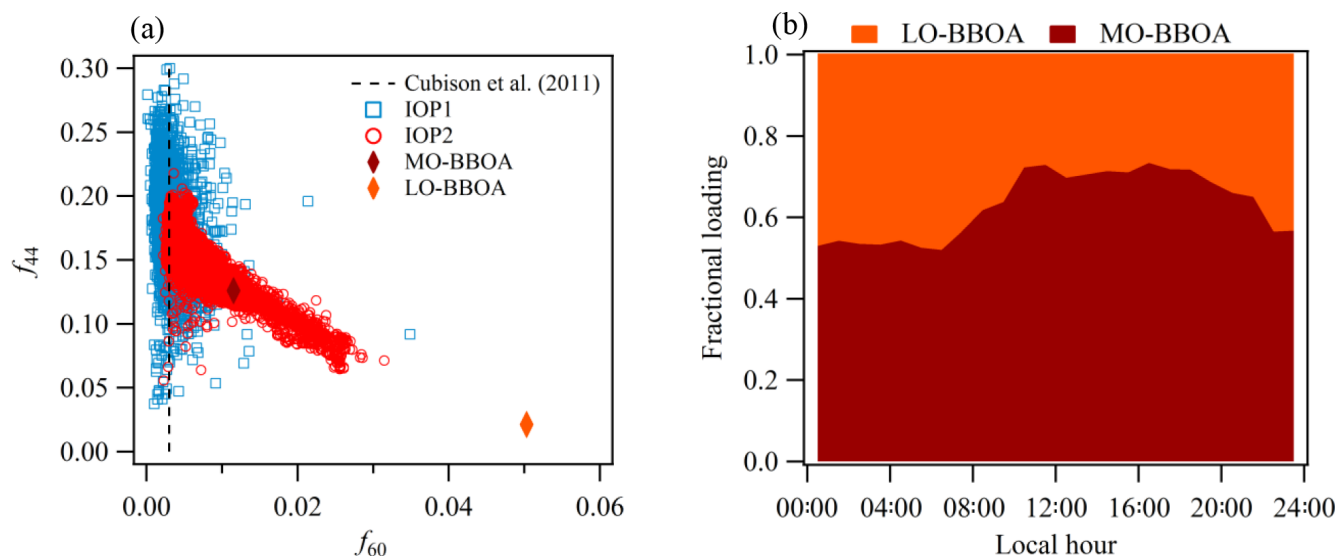
lower during the day because biomass-burning emissions are diluted with the development of the planetary boundary layer (PBL) and with the increased wind speeds as compared to the stagnant air and shallower PBL at night. The occurrence of significant dilution indicates that the emission sources were at least in part within a day of transport, meaning a distance on the order of a few hundred kilometers. The fractional contribution of the MO-BBOA factor to  $BBOA_T$  shifted from 0.7 to 0.5 from day to night, while that of LO-BBOA correspondingly shifted from 0.3 to 0.5 (Fig. 7b). This result is consistent with an additional secondary contribution to the MO-BBOA loading during daytime, including from LO-BBOA oxidation and possibly tied to photochemical processing, on top of a primary source from biomass burning.

Although the footprint of biomass burning is geographically more widespread throughout the basin compared to the urban footprint of nearby Manaus, fire incidence and large-scale emissions have historically concentrated in a region known as the arc of deforestation along the southern rim of the forest (Fuzzi et al., 2007; Artaxo et al., 2013). Several campaigns have focused on the effects of biomass burning during the dry season at locations that are highly affected by fires, usually in the states of Rondônia or Mato Grosso, within the arc of deforestation (SCAR-B, Kaufman et al., 1998; LBA-SMOCC, Fuzzi et al., 2007; LBA-EUSTACH, Andreae et al., 2002; TROFEE, Yokelson et al., 2007; SAMBBA, Morgan et al., 2013). At a ground site in Porto Velho, Rondônia, a PMF analysis of ACSM data showed that 70 % of the organic  $PM_{10}$  could be attributed to biomass burning (Brito et al., 2014). Compared to the present study, in which at least 30 % of the organic  $PM_{10}$  can be directly attributed to biomass burning, the contributions of fires to  $PM_{10}$  in the arc of deforestation region are considerably larger.

The combined contribution of 30 % by MO-BBOA and LO-BBOA at T3 represents a lower bound of biomass-burning influence because more-oxidized material from

biomass burning could be accounted for by the MO-OOA factor. In the limiting assumption that all MO-OOA loadings originated from BBOA loadings, an upper limit of 50 % can be established for the mean contribution of biomass burning to organic  $PM_{10}$  concentrations at T3. Considering that all organic  $PM_{10}$  components have been observed to age into MO-OOA at similar rates (Jimenez et al., 2009), a more likely estimate of 38 % can be derived by assuming that all factors contribute to MO-OOA proportionally to their ambient concentrations.

An important implication of these results, together with those of the wet season, is that although  $PM_{10}$  concentrations increase on average by a factor of 8.5 between seasons, not all of the increase is due to biomass burning, which has been a common assumption in previous studies (Artaxo et al., 1994, 2002, 2013; Holben et al., 1996; Echalar et al., 1998; Maenhaut et al., 1999; Andreae et al., 2002; Mace et al., 2003; Martin et al., 2010b; Rizzo et al., 2013; Brito et al., 2014; Pöhlker et al., 2016). In absolute mass concentrations, the contribution from biomass burning increased from  $0.12 \mu\text{g m}^{-3}$  in the wet season to  $3.4 \mu\text{g m}^{-3}$  in the dry season, which represents a 30-fold increase. This result corresponds to a change in percentage contribution to organic  $PM_{10}$  from 9 % to 30 % (not counting with the mass presumably present in MO-OOA). Nevertheless, the contribution from secondary biogenic sources (and their anthropogenically affected processes), as represented by the LO-OOA and IEPOX-SOA factors, also increased by around 8-fold from 0.6 to  $4.8 \mu\text{g m}^{-3}$ . In absolute terms, this mass increase (of  $4.2 \mu\text{g m}^{-3}$ ) is comparable to the one associated with biomass burning ( $3.3 \mu\text{g m}^{-3}$ ). Because the 8-fold mass increase of LO-OOA and IEPOX-SOA was similar to the 8.5-fold increase in total organic  $PM_{10}$ , these factors show a similar mass percentage contribution of 42 % to organic  $PM_{10}$  for both seasons. The MO-OOA factor loadings increased by 6-fold from 0.4 to  $2.3 \mu\text{g m}^{-3}$ . Because this relative increase was smaller than that of the total organic  $PM_{10}$ , the MO-OOA factor had a



**Figure 7.** Analysis of the organic PM<sub>1</sub> sampled at the T3 site in relation to biomass burning. **(a)** Scatter plot of the AMS signal fraction at  $m/z$  44 ( $f_{44}$ ) against that at  $m/z$  60 ( $f_{60}$ ). Red circles represent measurements during the dry season (IOP2), and blue squares represent measurements at the same site during the wet season (IOP1) (de Sá et al., 2018). Diamonds represent the MO-BBOA and LO-BBOA factors of IOP2. The dashed line represents a reference for negligible influence by biomass burning based on several field studies (Cubison et al., 2011). **(b)** Diel trends of the fractional loadings of the MO-BBOA and LO-BBOA factors relative to their sum BBOA<sub>T</sub>. Local time is UTC minus 4 h.

decrease from 30 % to 20 % of contribution to organic PM<sub>1</sub>. The contribution from urban sources, as represented by the HOA and ADOA factors, increased by 3-fold between seasons, from 0.24 to 0.76  $\mu\text{g m}^{-3}$ , representing a decrease in mass percentage contribution from 18 % to 7 %.

Therefore, reasons other than increased biomass burning in the dry season must have played a role in increasing organic PM<sub>1</sub> concentrations. Importantly, the mass concentrations of sulfate and ammonium also increased by 6-fold between seasons (Fig. S10), indicating that atmospheric physical processes governing particle mass concentrations possibly played an important role. In this context, reduced wet deposition due to reduced convection in the dry season may be one important contributor to the organic PM<sub>1</sub> increases (Machado et al., 2004; Nunes et al., 2016; Chakraborty et al., 2018). Another aspect is that biogenic NMVOC (BVOC) emissions are typically higher in the dry season (Yáñez-Serrano et al., 2015; Alves et al., 2016), which might partly explain the increases in LO-OOA, IEPOX-SOA, and MO-OOA factors. In addition, the directly measured biogenic (total) secondary organic PM<sub>1</sub> formation potential of ambient air increased by a factor of 2.4 (1.7) between seasons (Palm et al., 2018). Increased organic mass available for partitioning may account for another factor of 2 (Palm et al., 2018). As a consequence of increased PM<sub>1</sub> mass concentrations, the lifetime of semi-volatile gases may also be increased, since lifetime against dry deposition is much larger for particles than for gases (Knote et al., 2015). Increased oxidant levels during the dry season could also be a contributing factor

(Rummel et al., 2007; Artaxo et al., 2013; Andreae et al., 2015; Yáñez-Serrano et al., 2015; Fuentes et al., 2016).

### Cluster analysis

The time series of the afternoon concentrations of particle number, NO<sub>y</sub>, ozone, rBC, carbon monoxide, and sulfate were analyzed by fuzzy *c*-means clustering at the time resolution of the AMS measurements. The algorithm attributed degrees of cluster membership to each data point based on similarity in the sets of input concentrations (Sect. S2). The scope was restricted to data sets for which 10 h air-mass back-trajectories did not intersect precipitation. The scope also excluded data sets tied to the lowest 10 % of solar irradiance averaged over the previous 4 h at T3 (Sect. S2 in the Supplement). This approach aimed to capture fair-weather conditions and thereby minimize the role of otherwise confounding processes that influence mass concentrations, such as boundary layer dynamics and wet deposition.

Three clusters, labeled “baseline,” “event,” and “urban,” were identified based on a combination of minimization of the FCM objective function and an assessment of meaningfulness of the resolved set of clusters. Illustrative examples of the obtained degrees of membership (0 to 1) are plotted in Fig. 8a for several time windows. The concentrations of the input and additional species are plotted in Fig. 8b and c. The PMF results of Sect. “Classification of organic PM by positive-matrix factorization” are plotted for comparison in Fig. 8d. Air-mass back-trajectories are plotted in Fig. 9 for

time windows predominantly associated with only one cluster.

All three clusters reflected, albeit to different degrees, some influence of biomass burning. For the wet season, de Sá et al. (2018) identified clusters representing background conditions, which were characterized by low concentrations of particle number,  $\text{NO}_y$ , and  $\text{O}_3$ . For the dry season, no similar cluster was identified. As shown in Fig. 3, there were fires in the region at all times (cf. Martin et al., 2017).

The baseline cluster had the lowest concentrations of pollutant indicators, representing influences of far-field biomass burning on top of natural (i.e., biogenic) emissions and atmospheric processing. The cluster centroid corresponded to 1.3 ppb  $\text{NO}_y$ , 30 ppb ozone, and 2000 particles  $\text{cm}^{-3}$  (Table S1 in the Supplement). Results for 27 August, 28 August, and 9 September illustrate these lower concentrations compared to the other days (Fig. 8). The back-trajectories associated with the baseline cluster did not intersect the urban area of Manaus, especially the southern region of presumed higher emissions (Fig. 9a; de Sá et al., 2018).

The event cluster referred to conditions of increased influence from biomass burning and long-range transport of volcanic emissions from Africa. The cluster corresponded to a 10 d period from 22 September to 1 October in which biomass burning intensified in the surroundings of T3 as well as more broadly in the Amazon basin (Fig. 3f and g). Coincidentally, plumes carrying emissions from the Nyamuragira–Nyiragongo volcanoes in Africa were also observed to reach central Amazonia during that time period, as demonstrated by Saturno et al. (2018b). This cluster was characterized by higher concentrations of all species in relation to the baseline cluster (Table S1). In particular, the sulfate concentrations ( $2.3 \mu\text{g m}^{-3}$  at the centroid) were the highest among the three clusters. Results for 23, 27, and 28 September illustrate these findings for T3, with sulfate concentrations reaching  $4 \mu\text{g m}^{-3}$  (Fig. 8). This trend in sulfate concentrations was consistent across all three sites (Fig. 2). The back-trajectories associated with the event cluster were variable, passing to the north, directly over, and to the south of Manaus, although always with an east component (Fig. 9b). The long-range transport and increased regional fire count during the event period thus appeared more important in defining this cluster than did the directions of the back-trajectories in a smaller scale, making Manaus emissions of secondary importance.

The urban cluster had the highest centroid concentrations of  $\text{NO}_y$  (2.6 ppb), ozone (56.4 ppb), and particle number ( $4600 \text{ cm}^{-3}$ ) among the three clusters (Table S1). It represented conditions for which both biomass-burning and urban emissions were relevant, and these emissions may have interacted before reaching the T3 site. The results for 24 August, 11 September, 14 September, and 8 October illustrate the high pollutant concentrations (Fig. 8). The back-trajectories associated with the urban cluster consistently passed over Manaus and, more specifically, over the southern region where human activities were more concentrated (Fig. 9c).

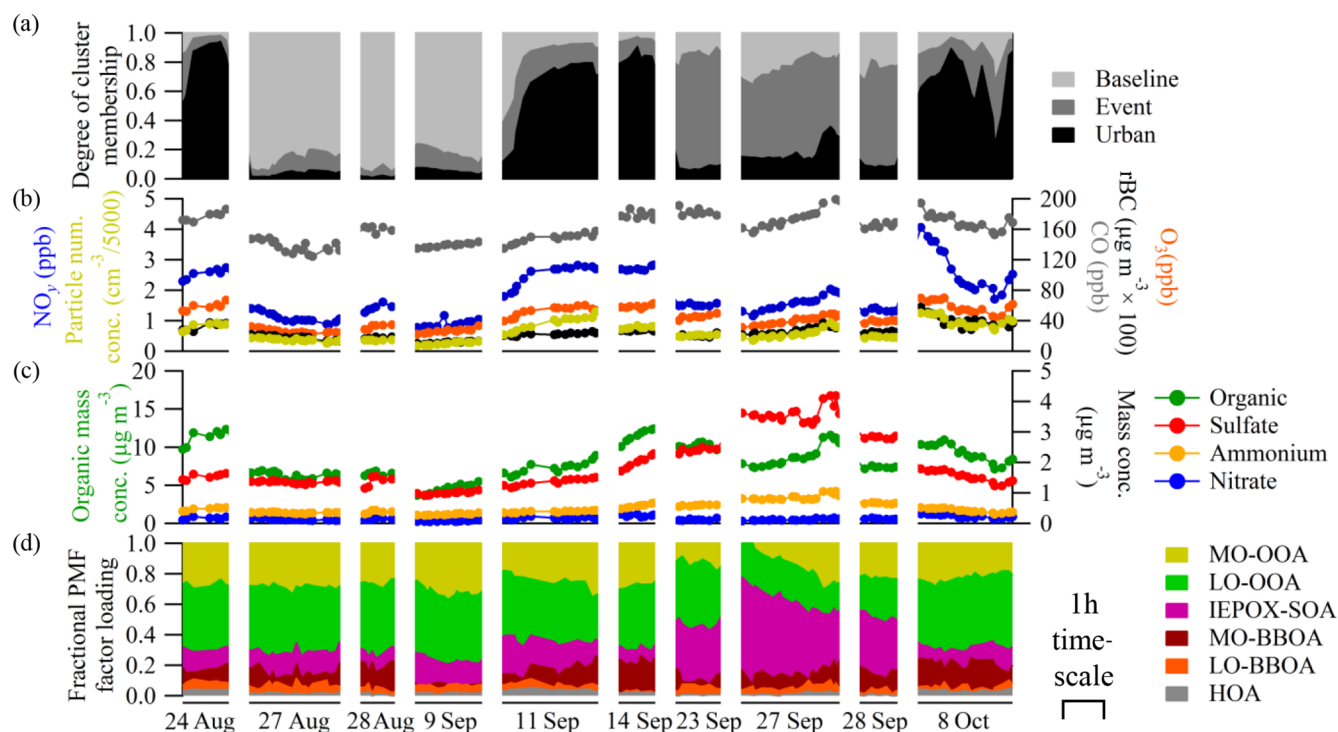
## Comparison of $\text{PM}_{10}$ composition among clusters

Species mass concentrations and PMF factor loadings associated with the cluster centroids were determined (Sect. S2). The resulting organic, sulfate, ammonium, nitrate, and chloride mass concentrations associated with each cluster are represented in Fig. 10a. The PMF factor loadings associated with each cluster are likewise represented in Fig. 10b.

The summed NR- $\text{PM}_{10}$  mass concentrations for the centroids of the event and urban clusters were both  $12.3 \mu\text{g m}^{-3}$ . This concentration was 33 % higher than that representing the baseline cluster ( $9.2 \mu\text{g m}^{-3}$ ). This result thus agrees with that based on direct comparison of  $\text{PM}_{10}$  mass concentrations between the T3 and the T0a sites (Sect. 3.1.1). Therefore, the overall effect of Manaus pollution was to add 1 to  $3 \mu\text{g m}^{-3}$  on top of the upwind concentrations. Increases in the organic mass concentration dominated the overall increase in  $\text{PM}_{10}$  mass concentration because organic species dominated the composition for all three clusters. The increases in organic mass concentration for the event and urban clusters relative to the baseline cluster were 26 % and 33 %, respectively (Fig. 10a).

Sulfate concentrations also increased relative to the baseline cluster, corresponding to 65 % for the event cluster and 31 % for the urban cluster. This result indicates that strong biomass-burning emissions reaching areas downwind of Manaus as well as long-range transport of volcanic emissions from as far away as Africa may increase sulfate concentrations in those areas beyond the sulfate values driven by the anthropogenic activities in the city. In other words, there were several other in-basin as well as out-of-basin sources of sulfate besides Manaus that could sustain relatively high sulfate concentrations (Chen et al., 2009; de Sá et al., 2017; Saturno et al., 2018b).

The relationship between clusters and PMF factors is represented in Fig. 10b. All three clusters were associated with an organic  $\text{PM}_{10}$  composition dominated by secondary production. The baseline cluster was largely dominated by the LO-OOA factor (40 %). By comparison, the event cluster had significant increases in the LO-BBOA, MO-BBOA, and IEPOX-SOA factor loadings. The increase in LO-BBOA and MO-BBOA loadings (40 %) can be associated with the increased contributions of primary and secondary particle components from biomass burning, respectively. The LO-BBOA factor had the highest loading ( $0.5 \mu\text{g m}^{-3}$ ) for the event cluster, consistent with the high incidence of fires during the period represented by this cluster. The increase of 65 % in IEPOX-SOA loading can be explained by the disproportionately higher increase of 65 % in the sulfate concentration (which favors higher IEPOX-SOA loadings), accompanied by the relatively moderate increase of 34 % in  $\text{NO}_y$  concentration (which suppresses IEPOX-SOA loadings), leading to a net increase in IEPOX-SOA loadings (Table S1; de Sá et al., 2017).



**Figure 8.** Results of the cluster analysis by FCM clustering for afternoon periods (12:00 to 16:00 LT) presented by several case studies. The shown case studies represent 30 % of the FCM results. (a) Degree of membership in each of the three clusters. The sum of degrees of membership across all clusters is unity. (b) Pollution indicators: concentrations of  $\text{NO}_y$ ,  $\text{O}_3$ , CO, rBC, and particle number count are plotted. (c)  $\text{PM}_{10}$  mass concentrations for organic, sulfate, nitrate, and ammonium species. (d) Fractional contribution of each factor to the  $\text{PM}_{10}$  organic mass concentration.

The composition of the organic  $\text{PM}_{10}$  associated with the urban cluster differed from that of the two other clusters, as indicated by the factor contributions (Fig. 10). Compared to the baseline cluster, the loadings of all factors except IEPOX-SOA increased. An increase in HOA loading is consistent with emissions in the city, including from vehicles and power plants. An increase in the loadings associated with secondary processes, as represented by the MO-OOA, LO-OOA, and MO-BBOA factors, can be explained by the accelerated oxidation cycle in the plume. In brief, an increase in the concentrations of both precursors and oxidants provided by urban emissions accelerates the production of secondary  $\text{PM}_{10}$  and thereby increases the  $\text{PM}_{10}$  concentrations downwind of the city (Martin et al., 2017; de Sá et al., 2018).

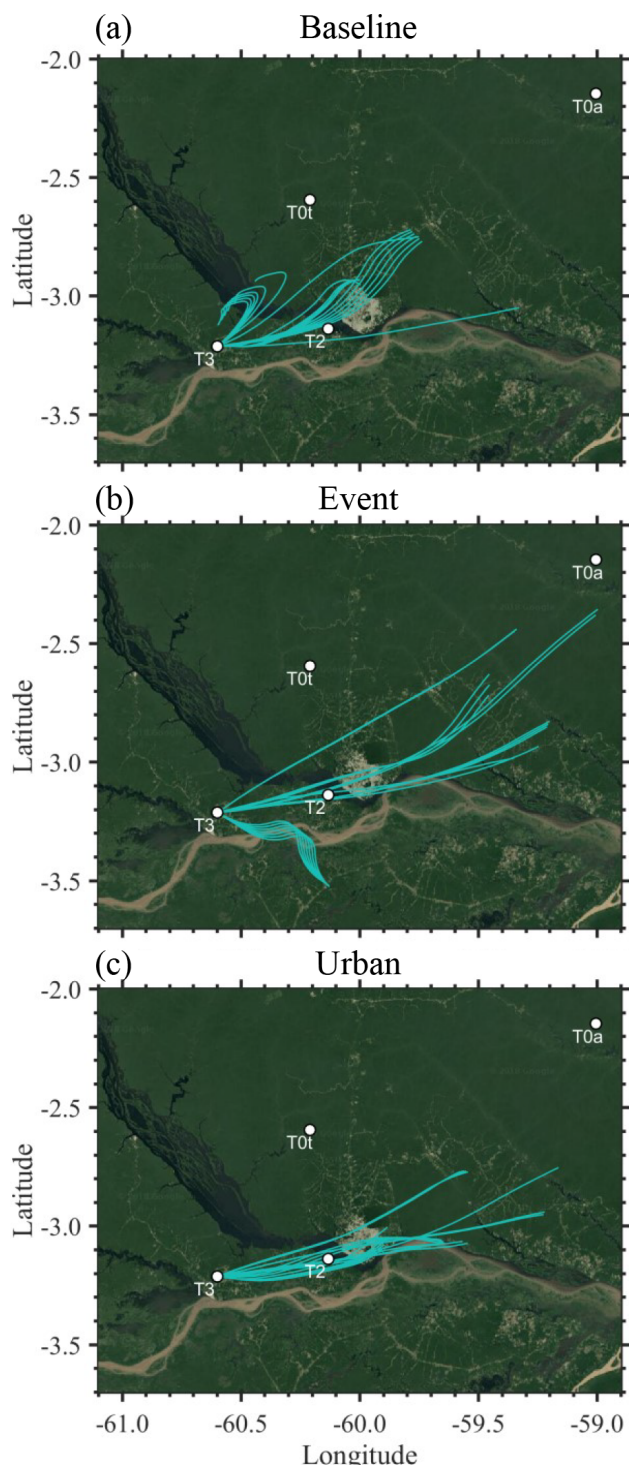
The similarity in IEPOX-SOA factor loading for the baseline and the urban clusters may be explained by the following aspects. First, the lifetime of IEPOX-derived PM in the boundary layer is thought to be around 2 weeks (Hu et al., 2016). Therefore, a substantial fraction of this component observed at T3 will be formed upwind of the Manaus plume. Second, favored conditions for IEPOX production and uptake are low NO concentrations (i.e.,  $\text{HO}_2$ -dominant pathway for the ISOPPO radical) and high sulfate concentrations (de Sá et al., 2017). Sulfate concentrations increased by 31 %,

and  $\text{NO}_y$  concentrations, used as an indicator for exposure of the air mass to NO concentrations, increased by 100 % for the urban compared to the baseline cluster. These two changes work against one another with respect to IEPOX production and uptake. For the wet season, de Sá et al. (2017) reported that the IEPOX-SOA factor loading was more sensitive to changes in  $\text{NO}_y$  concentration for 1 ppb and less. By comparison,  $\text{NO}_y$  concentrations in the dry season were consistently greater than this value. Due to this lower sensitivity, large increases in  $\text{NO}_y$  may not be tied to large decreases in IEPOX-SOA factor loading in the dry season. In sum, the opposite roles of sulfate and  $\text{NO}_y$  concentrations can explain the net zero change in IEPOX-SOA factor loadings between baseline and urban clusters. Because all of the loadings for other factors increased, the fractional loading of IEPOX-SOA decreased from 26 % to 15 %.

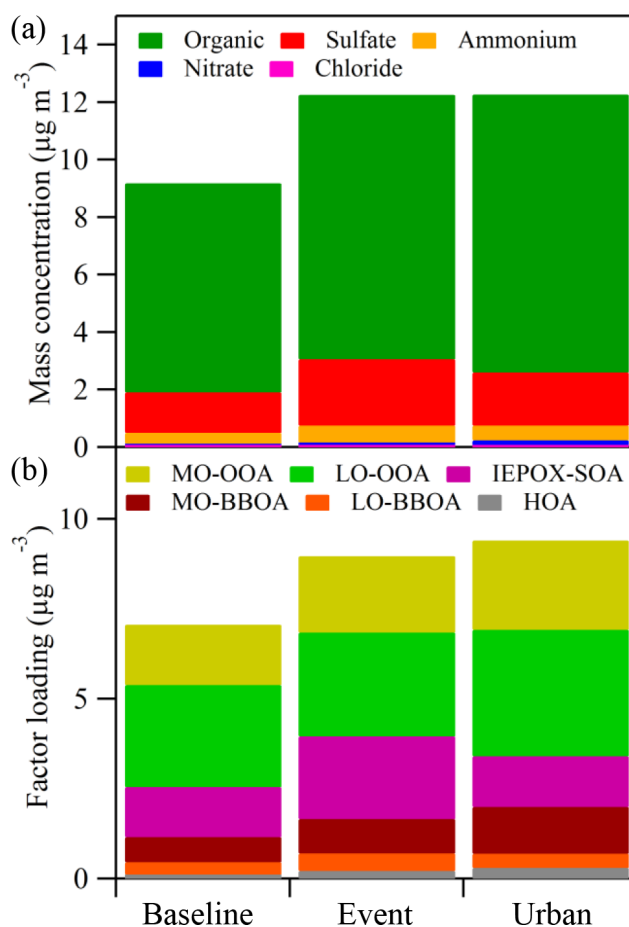
### 3.2 Contributions of biomass-burning and urban emissions to brown carbon

#### 3.2.1 Brown carbon light absorption

The diel trends of  $b_{\text{abs}}$ ,  $b_{\text{abs,BrC}}$ ,  $b_{\text{abs,BrC}}/b_{\text{abs}}$ , and  $\hat{a}_{\text{abs}}$  are shown in Fig. 11. Both  $b_{\text{abs}}$  and  $b_{\text{abs,BrC}}$  were larger and had greater variability at night compared to day. The variability



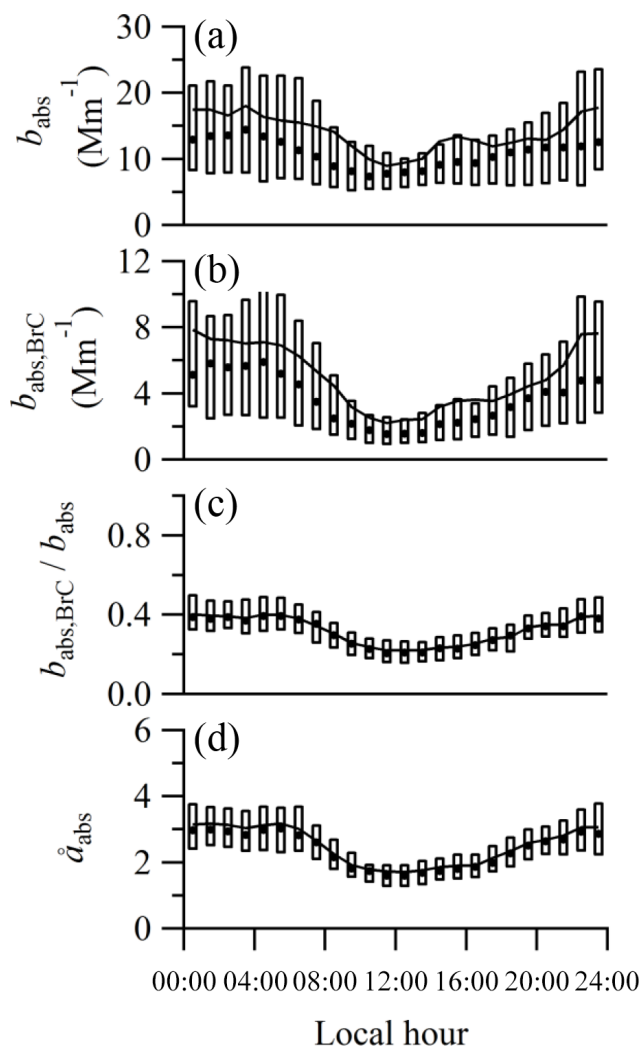
**Figure 9.** Air-mass back-trajectories associated with the three clusters of the FCM analysis. Trajectories were calculated using HYSPLIT4 in steps of 12 min and are shown for 10 h (Draxler and Hess, 1998). A total of 20 trajectories are plotted for each cluster, corresponding to the times of highest degree of membership to that cluster.



**Figure 10.** PM<sub>1</sub> characterization represented by the centroids of the FCM clusters. (a) Mass concentrations of AMS species. (b) PMF factor loadings. Results are for afternoon time periods. Table S1 lists the values presented in this figure.

of the fractional contribution of BrC to the total absorption, represented by  $b_{\text{abs,BrC}}/b_{\text{abs}}$ , was smaller than the variability of its components  $b_{\text{abs}}$  and  $b_{\text{abs,BrC}}$  (i.e., Fig. 11c compared to Fig. 11a–b). The absorptive contributions of BC and BrC thus co-varied to some extent, suggesting a partial overlap in sources, which is consistent with previous studies (Collier et al., 2016; Jen et al., 2019). Furthermore, the fractional contribution  $b_{\text{abs,BrC}}/b_{\text{abs}}$  increased from 0.2 in the day to 0.4 at night. The absorption Ångström exponent  $\hat{a}_{\text{abs}}$  followed a similar diel trend, on average ranging from 2 during the day to 3 during the night (Fig. 11d). Compared to the diel trends of the six PMF factor loadings, the diel trends of the absorption properties were most similar to those of the MO-BBOA, LO-BBOA, and HOA factors (Fig. 5b).

Figure 12 illustrates connections between  $b_{\text{abs,BrC}}$  and the organic PM<sub>1</sub> chemical composition. BrC light absorption decreases for increases in the O : C ratio (Fig. 12a). Conversely, light absorption increases for decreases in the concentration of nitrogen-containing species, as represented by the



**Figure 11.** Diel trends of PM<sub>1</sub> optical properties. (a) Total absorption coefficient  $b_{\text{abs}}$  (370 nm). (b) Absorption coefficient  $b_{\text{abs,BrC}}$  of brown carbon (370 nm). (c) Fractional contribution of  $b_{\text{abs,BrC}}$  to  $b_{\text{abs}}$ . (d) Absorption Ångström exponent  $\hat{a}_{\text{abs}}$  from 370 to 430 nm. Local time is UTC minus 4 h.

$\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$  family (Fig. 12b). In addition, light absorption increases as the fractional contribution of the  $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$  family to organic PM<sub>1</sub> increases and that of the  $\text{C}_x\text{H}_y\text{O}_z^+$  family decreases (Fig. S14). The diel trends of Fig. 11 and the O : C ratios of Fig. 12a support an association of BrC light absorption with HOA and LO-BBOA factor loadings. These factors had the lowest O : C values (Table 1), and they are associated with recent urban and biomass-burning emissions, which are typically important sources of brown carbon (Laskin et al., 2015, and references therein).

The decrease in  $b_{\text{abs,BrC}}$  as O : C increases suggests that the atmospheric processing of organic material bleaches the BrC components under the conditions of central Amazonia. This behavior has been observed in several laboratory studies: BrC species and thus their optical properties can be mod-

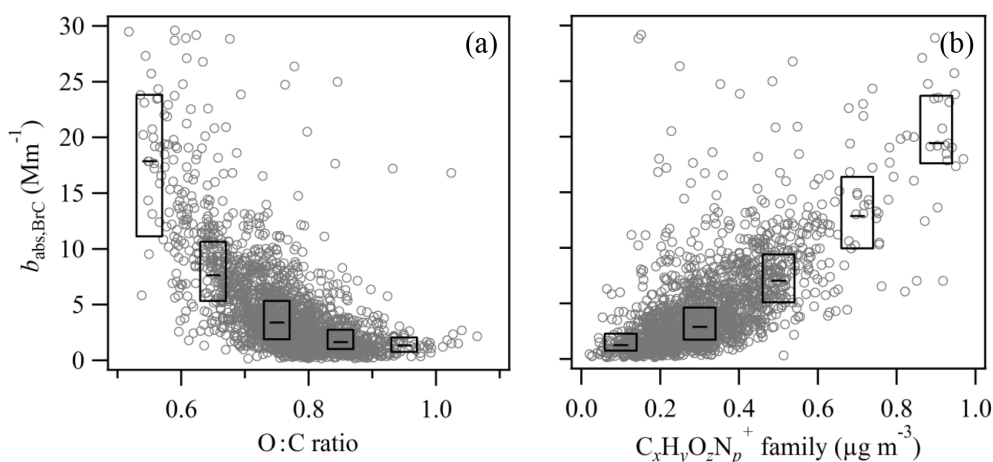
ified through atmospheric processing, which may involve reactions at the gas–particle interface, reactions in the aqueous phase of particle and cloud droplets, and photolysis driven by sunlight (Laskin et al., 2015; Zhao et al., 2015; Sunlin et al., 2017; Lee et al., 2014; Romonosky et al., 2015). In addition, Saleh et al. (2014) provided evidence that both primary and secondary material from biomass burning may absorb light, and that the secondary component may be less absorptive than the primary component in the visible spectral range. Lin et al. (2016) found that the absorbance at 300 nm by biomass-burning particles decayed with a half-life of approximately 16 h against photolysis under typical atmospheric conditions. Forrister et al. (2015) followed plumes from wildfires aboard an aircraft during the 2013 NASA SEAC4RS mission over the continental US and estimated a half-life of 9 to 15 h for the decay of BrC light absorption in the plumes.

An important contribution of nitrogen-containing organic molecules to  $b_{\text{abs,BrC}}$  is suggested by the relationship in Fig. 12b. The percent contribution of the  $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$  family to each PMF factor profile is listed in Table 2 and is highest for the HOA and LO-BBOA factors. The correlations of factor loadings with the  $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$  mass concentrations as well as with the  $b_{\text{abs,BrC}}$  values are highest for these two factors ( $R > 0.8$  and  $R > 0.6$ , respectively) (Table 2). The correlations of the MO-BBOA factor loading with these two parameters are lower but still significant. By comparison, the corresponding correlations for the IEPOX-SOA, LO-OOA, and MO-OOA factor loadings are all lower than 0.5. These results further support that the HOA and LO-BBOA factors to a larger extent and the MO-BBOA factor to a lesser extent were tightly associated with nitrogen-containing, light-absorbing organic molecules.

In contrast to the  $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$  family, the correlations between PMF factor loadings and mass concentrations of organic nitrates are low ( $R < 0.4$ , Table 2; Fig. S12). For the HOA, LO-OOA, and MO-OOA factors associated with BrC light absorption, the correlations are small ( $R < 0.25$ ). The implication could be that the  $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$  family is closely tied to PM<sub>1</sub> constituted by reduced nitrogen compounds and nitrogen–aromatic compounds. By comparison, organic nitrates are more strongly tied to photochemical production of secondary PM<sub>1</sub> and represent more-oxidized forms of nitrogen, including in aliphatic molecules.

Several studies have suggested that nitrogen-containing organic molecules are important absorbers in organic PM (Sun et al., 2007; Lin et al., 2016). Claeys et al. (2012) characterized humic-like substances (HULIS) present in PM collected during the biomass-burning season in Amazonia and identified nitro-aromatic catechols and aromatic carboxylic acids among the main constituents. Nitrophenol derivatives have been identified as major BrC components in several other urban and rural locations worldwide (Kitanovski et al., 2012; Desyaterik et al., 2013; Kahnt et al., 2013; Mohr et al., 2013). Importantly, Lin et al. (2016) further verified that compounds that are usually interpreted as secondary, such as





**Figure 12.** Relationships between the BrC absorption coefficient and the organic PM<sub>1</sub> composition. Scatter plots of  $b_{\text{abs,BrC}}$  against (a) the O : C ratio and (b) the mass concentration of the nitrogen-containing  $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$  family. For the  $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$  family, all ions contain at least one C atom and one N atom, meaning  $x > 0$ ,  $y \geq 0$ ,  $z \geq 0$ , and  $p > 0$ . Boxes indicate interquartile ranges, and horizontal lines within the boxes indicate medians. For panel (a), each bin width is 0.1, from 0.5 to 1.0, and for panel (b), each bin width is 0.2, from 0 to 1.0. In complement, Fig. S14 shows the relationships between the BrC absorption coefficient and the fractional contributions of the  $\text{C}_x\text{H}_y\text{O}_z^+$  and  $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$  families to organic PM<sub>1</sub>.

**Table 2.** Relationship of PMF factors to organonitrogen characteristics. Listed for each factor are the mean loading of the time series, the percent contribution of the  $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$  family to the factor profile, and the mean mass concentration of the  $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$  family (based on multiplication of columns 2 and 3), as well as the Pearson  $R$  correlation of factor loading against the mass concentration of  $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$ , the mass concentration of organic nitrates, and  $b_{\text{abs,BrC}}$ . The  $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$  family corresponds to the sum of all ions containing at least one C atom and one N atom, as measured by the AMS. Detailed family-colored spectra showing the nitrogen-containing ions for all PMF factors are presented in Fig. S6, and the most important ion fits are shown in Fig. S7. The AMS method characterizes organic nitrates through the  $\text{NO}^+$  and  $\text{NO}_2^+$  fragments, which remain distinct from the larger fragments of the  $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$  family (Sect. S1 and discussion therein).

PMF factor	Mean factor loading ( $\mu\text{g m}^{-3}$ )	Nitrogen characteristics of factor profile			Pearson $R$ of factor loading		
		$\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$ family contribution (%)	Mass concentration of the $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$ family ( $\mu\text{g m}^{-3}$ )		Against the mass concentration of $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$ family	Against the mass concentration of organic nitrates	Against $b_{\text{abs,BrC}}$
MO-OOA	1.6	5.7	0.09	0.33	0.38	0.17	
LO-OOA	2.2	3.7	0.08	0.10	0.15	-0.19	
IEPOX-SOA	1.2	6.6	0.08	0.39	0.40	0.17	
MO-BBOA	1.5	2.9	0.04	0.65	0.24	0.53	
LO-BBOA	1.0	10.4	0.11	0.89	0.13	0.69	
HOA	0.6	9.0	0.05	0.82	0.20	0.68	

nitro-phenols and derivatives, can be produced in the heat-laden, NMVOC-rich, high- $\text{NO}_x$  conditions of the biomass-burning process, being subsequently emitted as primary material. Furthermore, Yee et al. (2013) observed the quick conversion of guaiacol and syringol to nitro-guaiacol and nitro-syringol, respectively, in the presence of HONO even without heat or photo-oxidation. It is possible that BrC from other combustion sources could have similar characteristics based on this reasoning, helping to explain the association found in this study between BrC absorption and the LO-BBOA and HOA factors. Regarding the further atmospheric processing

of these nitrogen-containing organic compounds, laboratory studies have shown that hydroxy radical oxidation of nitro-aromatic species in aqueous solutions leads to fragmentation into smaller organic acids (e.g., oxalic, glycolic, malonic, and isocyanic) or, in general, reduces the size of the conjugated molecular systems, leading to a decrease in light absorption at visible wavelengths (Sumlin et al., 2017; Hems and Abbatt, 2018). These findings may help to explain the bleaching of BrC as the material becomes more oxidized. In the context of the PMF factors, these smaller later-generation prod-

ucts may then be associated with the MO-OOA factor or may partition to the gas phase depending on their volatility.

Scatter plots of  $\hat{a}_{\text{abs}}$  against markers of biomass burning are shown in Fig. 13. The Pearson  $R$  correlations against  $\log_{10}(f_{60}/f_{44})$  and  $(\text{BBOA}_{\text{T}}/\text{organic PM}_1)$  are 0.87 and 0.75, respectively. The  $f_{60}/f_{44}$  ratio is a tracer for the influence of fresh biomass burning, and an association of  $\hat{a}_{\text{abs}}$  and with this quantity was also reported for Boulder, Colorado, USA (Lack et al., 2013). These relationships could be useful parameterizations to estimate  $\hat{a}_{\text{abs}}$  when optical measurements are not available but AMS/ACSM measurements are, at least during times of biomass-burning influence in central Amazonia. Worldwide, observed values of  $\hat{a}_{\text{abs}}$  range from < 2 to 11 for particles tied to biomass burning (Chakrabarty et al., 2010; Saleh et al., 2014). The value of  $\hat{a}_{\text{abs}}$  reached 6 for the highest observed values of  $(f_{60}/f_{44})$ . It approached 1.0 in the limit of  $f_{60}/f_{44} < 0.02$ , which indicates little influence of proximate biomass burning (Fig. 13a; cf. upper left of Fig. 7a). Further observations elsewhere in the Amazon and on other regions are needed before the parameterizations suggested in Fig. 13 between  $\hat{a}_{\text{abs}}$  and markers of biomass burning can be generalized with confidence.

### 3.2.2 Contribution of organic PM components to BrC absorption

Herein, advantage is taken of the representation of the organic PM in its subcomponents provided by the PMF factors to estimate a mass absorption efficiency for each of them. The absorption coefficient is the sum of the absorption coefficient of the  $n$  parts of the organic PM (“Org”):

$$b_{\text{abs,BrC}} = b_{\text{abs,Org}_1} + b_{\text{abs,Org}_2} + \dots + b_{\text{abs,Org}_n}. \quad (3)$$

The treatment assumes the absence of cross-interactions among the parts and holds for a single wavelength. The absorption coefficient  $b_{\text{abs},i}$  of part  $i$  is defined as follows:

$$b_{\text{abs},i} = E_{\text{abs},i} \times C_i, \quad (4)$$

where  $E_{\text{abs},i}$  is the mass absorption efficiency and  $C_i$  is the mass concentration of part  $i$ . Based on Eqs. (3) and (4), the following model was constructed for  $b_{\text{abs,BrC}}$  by using the PMF factor loadings as a proxy for the mass concentrations of organic PM<sub>1</sub> components:

$$\begin{aligned} b_{\text{abs,BrC}} = & E_{\text{abs,MO-OOA}} G_{\text{MO-OOA}} + E_{\text{abs,LO-OOA}} G_{\text{LO-OOA}} + \\ & + E_{\text{abs,IEPOX-SOA}} G_{\text{IEPOX-SOA}} + \\ & + E_{\text{abs,MO-BBOA}} G_{\text{MO-BBOA}} + \\ & + E_{\text{abs,LO-BBOA}} G_{\text{LO-BBOA}} + \\ & + E_{\text{abs,HOA}} G_{\text{HOA}} + B, \end{aligned} \quad (5)$$

where  $G_i$  correspond to loadings of factor  $i$ , and the unknowns are the mass absorption efficiencies  $E_{\text{abs},i}$  associated with each PMF factor. An intercept  $B$  was added to account for the variability not explained by the PMF factors.

**Table 3.** Results of the constrained linear least-squares regression analysis for the BrC absorption coefficient (Eq. 5). **(a)** Mass absorption efficiency  $E_{\text{abs}}$  associated with each PMF factor. **(b)** Model intercept. The mean, standard error (SE), and 95 % confidence interval (CI) are listed in each panel. They were obtained through bootstrap of the regression analysis considering different samples (i.e., sets of points in time) for  $10^4$  runs. Unit of  $\text{Mm}^{-1}$  represents  $10^{-6} \text{ m}^{-1}$ . The coefficient of determination  $R^2$  between predicted  $b_{\text{abs,BrC,pred}}$  and observed  $b_{\text{abs,BrC}}$  was 0.66. The symbol “\*” indicates that the estimated value was statistically not higher than zero at the significance level of 5 %.

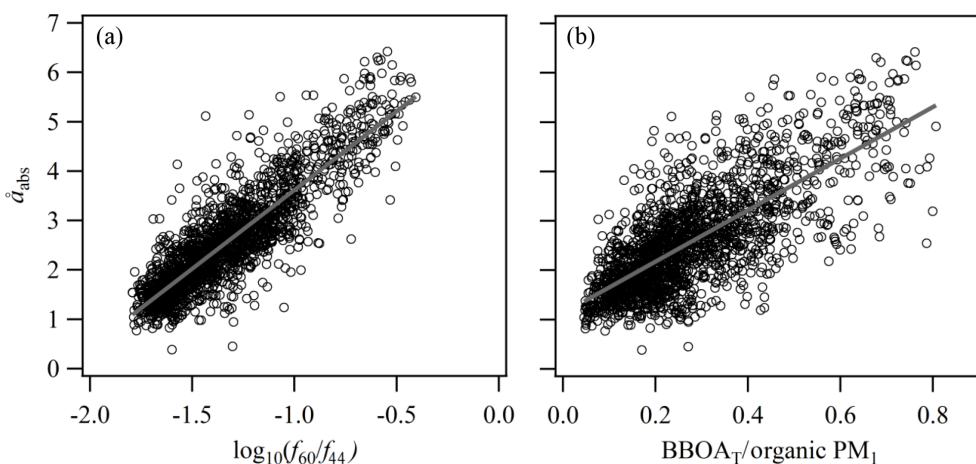
(a)	$E_{\text{abs}} (\text{m}^2 \text{ g}^{-1})$		
	PMF factors	Mean	SE
MO-OOA	0.01*	0.02	[0.00, 0.08]
LO-OOA	0.01*	0.02	[0.00, 0.08]
IEPOX-SOA	0.40	0.05	[0.31, 0.50]
MO-BBOA	0.82	0.04	[0.75, 0.90]
LO-BBOA	1.50	0.07	[1.37, 1.63]
HOA	2.04	0.14	[1.76, 2.31]
(b)	$b_{\text{abs}} (\text{Mm}^{-1})$		
Model intercept	Mean	SE	CI
$B$	0.13*	0.10	[0.00, 0.33]

Other studies have also made use of multivariate linear regression to retrieve mass absorption efficiencies (Hand and Malm, 2007; Washenfelder et al., 2015; Ealo et al., 2018).

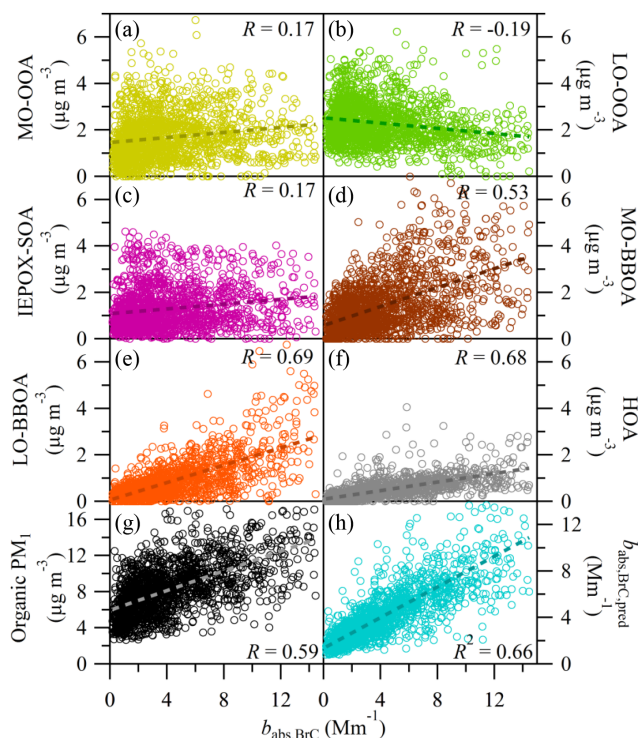
Estimates of  $E_{\text{abs},i}$  were obtained using a constrained linear least-squares algorithm applied to Eq. (5), where the inputs were the observed  $b_{\text{abs,BrC}}$  and the factor loadings for each point in time during IOP2. The input data are represented in the scatter plots of  $G_i$  against  $b_{\text{abs,BrC}}$  shown in Fig. 14a to f. A non-negative constraint on the model coefficients  $E_{\text{abs},i}$  was included for physical meaning. The algorithm was applied in bootstrap with replacement of residuals for  $10^4$  runs, and convergence of the bootstrap results was checked by varying the number of samples. The resulting estimates of mean and standard error of  $E_{\text{abs}}$  for all PMF factors are listed in Table 3.

A scatter plot of the predicted  $b_{\text{abs,BrC,pred}}$  against the observed  $b_{\text{abs,BrC}}$  is shown in Fig. 14h. The model captured 66 % of the variance in  $b_{\text{abs,BrC}}$ , and the PMF factor loadings can be considered good predictors of the BrC absorption under the study conditions. Physical factors not directly represented in this statistical model, such as the effects of mixing state, size distribution, and so on for BrC absorption, either have low variability under the study conditions or alternatively have co-variability also captured in the PMF factor loadings.

The highest values of  $E_{\text{abs}}$  at 370 nm were associated with the HOA and LO-BBOA factors ( $2.04 \pm 0.14$  and  $1.50 \pm 0.07 \text{ m}^2 \text{ g}^{-1}$ , respectively). These results support the inter-



**Figure 13.** Relationships between the absorption Ångström exponent and indicators of biomass burning. Scatter plots of  $\hat{a}_{\text{abs}}$  against (a)  $\log_{10}(f_{60}/f_{44})$  of the AMS analysis ( $R = 0.87$ ), and (b) the ratio of the  $\text{BBOA}_T$  loading to the organic  $\text{PM}_{10}$  mass concentration ( $R = 0.75$ ).  $\text{BBOA}_T$  loading is the sum of the MO-BBOA and LO-BBOA factor loadings. The  $\hat{a}_{\text{abs}}$  value corresponds to 370 to 430 nm. In panel (a), the slope and intercept are  $3.2 \pm 0.1$  and  $6.8 \pm 0.1$ , respectively. In panel (b), they are  $5.2 \pm 0.1$  and  $1.1 \pm 0.1$ .



**Figure 14.** Scatter plots against  $b_{\text{abs,BrC}}$  of (a)–(f) PMF factor loadings, (g) organic  $\text{PM}_{10}$  mass concentration, and (h)  $b_{\text{abs,BrC,pred}}$  values predicted by a multivariate linear regression model using PMF factor loadings as parameters as described by Eq. (5).

pretation presented in the previous section about the association of the HOA and LO-BBOA factors with light absorption. As a point of comparison, Ealo et al. (2018) conducted a study in the northwestern Mediterranean and found

the highest mass absorption efficiencies, ranging from 0.9 to  $1.7 \text{ m}^2 \text{ g}^{-1}$  at 637 nm, for traffic and industrial sources. As another point of comparison,  $E_{\text{abs}}$  of 2 to  $3 \text{ m}^2 \text{ g}^{-1}$  at 300 nm was reported for HULIS extracts from  $\text{PM}_{2.5}$  filter samples collected under biomass-burning conditions during the Amazon dry season in Rondônia, Brazil (Hoffer et al., 2006). HULIS have been recognized as important components of BrC from biomass burning (Mukai and Ambe, 1986; Andreae and Gelencsér, 2006; Graber and Rudich, 2006). The  $E_{\text{abs}}$  value of the MO-BBOA factor was  $0.82 \pm 0.04 \text{ m}^2 \text{ g}^{-1}$ . The result of  $E_{\text{abs,MO-BBOA}} < E_{\text{abs,LO-BBOA}}$  is consistent with an interpretation of photochemically driven oxidation and bleaching during the atmospheric transport of biomass-burning emissions.

The  $E_{\text{abs}}$  value of the IEPOX-SOA factor was  $0.40 \pm 0.05 \text{ m}^2 \text{ g}^{-1}$ , and the  $E_{\text{abs}}$  values of the MO-OOA and LO-OOA factors ( $0.01 \pm 0.02 \text{ m}^2 \text{ g}^{-1}$ ) were not statistically different from zero. Laboratory studies suggest that biogenic PM does not appreciably absorb light in the near-UV and visible range, although this result may change with atmospheric exposure to ammonia and amines, changes in particle acidity, and other factors (Nakayama et al., 2012; Liu et al., 2013; Flores et al., 2014; Lin et al., 2014; Laskin et al., 2015). Biogenic PM is typically characterized by carbonyls, carboxyls, and hydroxyls without substantial conjugation; this composition does not have the low-energy electronic transitions relevant for BrC light absorption (Laskin et al., 2015). By contrast, PM produced by the photo-oxidation of aromatic NMVOCs, such as toluene, *m*-xylene, naphthalene, and trimethylbenzene, tends to absorb significantly, and the light absorption is greater for PM produced under conditions of higher  $\text{NO}_x$  concentrations because of the production of nitro-aromatic compounds (Zhong and Jang, 2011; Liu et al., 2012, 2015; Lee et al., 2014). This absorption, however,

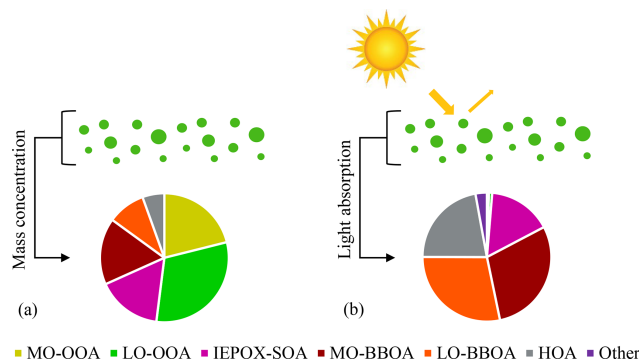
**Table 4.** Contribution of PM<sub>1</sub> components as represented by the PMF factors to organic mass concentrations and BrC light absorption. The contribution of the model intercept to BrC light absorption is also included. Values listed are resulting means and standard deviations of the contributions calculated throughout IOP2. Small differences between the values in the second column and the values represented in the inset of Fig. 5a are due to differences in data coverage by the aethalometer and AMS.

PMF factor	Contribution to organic mass concentration (%)	Contribution to BrC light absorption (%)
MO-OOA	21.1 ± 10.0	0.5 ± 0.4
LO-OOA	30.9 ± 11.4	0.8 ± 0.5
IEPOX-SOA	16.3 ± 9.8	15.7 ± 11.2
MO-BBOA	16.7 ± 12.0	28.9 ± 18.0
LO-BBOA	9.5 ± 7.5	27.8 ± 14.3
HOA	5.5 ± 3.9	21.7 ± 10.5
Model intercept	n/a	4.6 ± 2.6

may decrease with atmospheric processing as previously discussed for the case of biomass-burning emissions, which is also reflected in the negligible value of  $E_{\text{abs}}$  for MO-OOA. In central Amazonia, the organic PM is dominated by biogenic forest precursors even in the pollution plume of Manaus, which helps to explain the negligible  $E_{\text{abs}}$  value for LO-OOA. It may also be that some aromatic PM is associated with the HOA factor, which has a high  $E_{\text{abs}}$  value.

A comparison of the relative contributions of PMF factor loadings to organic PM<sub>1</sub> mass concentration and to light absorption is presented in Fig. 15 (a and b, respectively). The contribution of each class of organic compounds to total absorption by organic PM<sub>1</sub> was estimated for each point in time by multiplication of the  $E_{\text{abs}}$  value and the loading of each PMF factor during IOP2. The means and standard deviations of the resulting percentage contributions are listed in Table 4. Biomass-burning and urban emissions, as represented by the BBOA and HOA factors, appeared to contribute 80 % of  $b_{\text{abs,BrC}}$  while accounting for at least 30 % of the organic PM<sub>1</sub> mass concentration. The IEPOX-SOA factor was associated with the balance of  $b_{\text{abs,BrC}}$  while representing 16 % of the organic PM<sub>1</sub> mass concentration. Studies with further information on black carbon size distribution, particle mixing state, and the effect of RH on particle absorption are warranted to refine the estimates of  $E_{\text{abs}}$  for the components of organic PM<sub>1</sub> and therefore their contributions to BrC light absorption. A similar attribution analysis to the one in Fig. 15b was carried out for the baseline, event, and urban clusters separately and is discussed in the Supplement (Fig. S15).

The BrC light absorption can have direct and indirect effects on radiative forcing, which ought to be further investigated for the Amazon region. The inclusion of BrC absorption in models may result in a positive direct radiative forcing



**Figure 15.** Comparative relationship of the relative contributions of PMF factor loadings to (a) organic PM<sub>1</sub> mass concentration and (b) organic PM<sub>1</sub> light absorption. Results represent means for the full data sets of IOP2. The means and standard deviations are listed in Table 4. Results are for 370 nm. “Other” refers to the model intercept  $B$  (Eq. 5).

(DRF) in regions of high BrC concentrations, in contrast to models that assume organic PM as a purely scattering component (Ramanathan and Carmichael, 2008; Myhre et al., 2013). Recent models have estimated the global BrC contribution to DRF to be in the range of 0.1 to 0.25 W m<sup>-2</sup>, corresponding to 10 % to 25 % of the DRF by BC (Feng et al., 2013). In addition, BrC in cloud water can absorb light and thereby facilitate water evaporation and cloud dispersion (Hansen et al., 1997). This effect may compensate the cooling that aerosol particles offer by serving as seeds for cloud droplet formation and may also provide a positive feedback as increased fire activity may provoke more fire-prone conditions by suppressing precipitation (Nepstad et al., 1999; Bevan et al., 2009; Gonçalves et al., 2015; Laskin et al., 2015). Another implication is that light absorption by BrC in the ultraviolet may significantly decrease photolysis rates, thereby affecting the concentrations of precursors and oxidants such as ozone and OH radicals in the atmosphere (Li et al., 2011; Jiang et al., 2012; Laskin et al., 2015).

#### 4 Summary and conclusions

The influence of urban and biomass-burning emissions on the otherwise natural concentrations, composition, and optical properties of organic PM<sub>1</sub> in central Amazonia were investigated during the dry season. Positive-matrix factorization was used to classify the organic PM into subcomponents. The MO-OOA, LO-OOA, and IEPOX-SOA together accounted for about 62 % of the organic PM. The MO-BBOA and LO-BBOA factors together accounted for 31 %, and HOA for the remaining 7 %. An important conclusion is that the 8.5-fold increase in organic PM<sub>1</sub> concentrations between the wet and dry seasons is not all due to biomass burning but also to a concurrent increase of biogenic secondary organic PM<sub>1</sub> of 8-fold and smaller increases in urban PM<sub>1</sub>. Reasons that pos-

sibly played a role in such increases for the dry season are increased BVOC emissions, increased formation potential of biogenic secondary organic PM<sub>1</sub>, reduced wet and dry deposition and PBL ventilation of PM<sub>1</sub> particles, and increased partitioning due to larger organic PM<sub>1</sub> mass concentrations in the dry season.

The FCM clustering analysis identified the baseline, event, and urban clusters. Relative to the baseline cluster ( $9.2 \mu\text{g m}^{-3}$ ), both the event and the urban cluster had an increase of  $3 \mu\text{g m}^{-3}$ . For the event cluster, the increased sulfate concentrations together with only moderate increases in NO<sub>y</sub>, resulted in remarkable increases of almost  $1 \mu\text{g m}^{-3}$  (65 %) in IEPOX-SOA factor loadings relative to the baseline cluster. Regarding the urban cluster, increases in the factor loadings of MO-BBOA (40 % to 90 %) and LO-OOA (20 % to 25 %) were observed in comparison to the other two clusters. At the same time, the IEPOX-SOA contribution was either the same or lower (by 40 %) in absolute loadings and always lower in relative contribution to organic PM (15 % of organic PM compared to 20 %–30 % for the other clusters). These changes in the makeup of organic PM were consistent with the changes observed for the wet season (de Sá et al., 2017, 2018). They were attributed partly to (i) a shift in oxidation pathways from HO<sub>2</sub>- to NO-dominant, and partly to (ii) an accelerated oxidation cycle that increases the mass concentration of secondary organic PM.

Optical properties of the PM<sub>1</sub> were investigated, focusing on the organic component. The BrC absorption coefficient ( $b_{\text{abs,BrC}}$ ) had an inverse relationship with the O : C ratio and a positive relationship with the C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>N<sub>p</sub><sup>+</sup> family, indicating that BrC light in this region was associated with less-oxidized and N-containing organic compounds. The LO-BBOA and HOA factors had the lowest O : C ratios and highest relative contribution of C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>N<sub>p</sub><sup>+</sup> family ions, suggesting that these factors represent BrC components. In addition, a tight relationship between  $\hat{a}_{\text{abs}}$  and  $\log_{10}(f_{60}/f_{44})$  was found, corroborating the importance of BBOA factors for absorption properties of organic PM, and possibly providing a parameterization for  $\hat{a}_{\text{abs}}$  in the region. Further analysis determined the  $E_{\text{abs}}$  associated with each of the PMF factors. The results implied that the MO-OOA and LO-OOA factors were associated with non-absorbing components. The MO-BBOA ( $E_{\text{abs}} = 0.8 \text{ m}^2 \text{ g}^{-1}$ ), LO-BBOA ( $1.5 \text{ m}^2 \text{ g}^{-1}$ ), and HOA ( $2.0 \text{ m}^2 \text{ g}^{-1}$ ) factors were associated with 80 % of the light absorption by organic PM in the region. The remaining absorption (< 10 %) was attributed to IEPOX-SOA ( $E_{\text{abs}} = 0.4 \text{ m}^2 \text{ g}^{-1}$ ).

Given the importance of biomass burning and the increasing importance of urban pollution in the Amazon forest, light absorption by atmospheric particulate matter could become more prevalent in this region in the future. Further field, laboratory, and modeling studies are warranted to (i) more finely map the importance of both urban and biomass-burning emissions at different locations in the Amazon region, (ii) characterize BrC components at the molecular level

for structure–absorption relationships, and (iii) quantify the effects of BrC absorption on radiative forcing in the regional and global scales for current and future scenarios of increased human impacts.

*Data availability.* The data sets used in this publication are available at the ARM Climate Research Facility database for the GoAmazon2014/5 experiment (<https://www.arm.gov/research/campaigns/amf2014goamazon>, last access: 1 August 2018).

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*Author contributions.* SSdS, LVR, and STM defined the scientific questions and scope of this study. STM, JIJ, MLA, AHG, and PA designed, planned, and supervised the broader GoAmazon2014/5 field experiment. SSdS, BBP, PCJ, and DAD carried out the AMS measurements and data processing. AS collected and quality checked the aethalometer data. LVR performed the BrC calculations based on the aethalometer data. LDY, RW, GYV, JB, SC, YJL, SS, and HMJB performed auxiliary data collection/processing and simulations. SSdS carried out the scientific analysis involving PMF and FCM. SSdS prepared the paper with contributions from all co-authors.

*Competing interests.* The authors declare that they have no conflict of interest.

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