



Urban influence on the concentration and composition of submicron particulate matter in central Amazonia

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1 Abstract

2 Fundamental to quantifying the influence of human activities on climate and air quality is
3 an understanding of how anthropogenic emissions affect the concentrations and composition of
4 airborne particulate matter (PM). The central Amazon basin, especially around the city of
5 Manaus, Brazil, has experienced rapid changes in the past decades due to ongoing urbanization.
6 Herein, changes in the concentration and composition of submicron PM due to pollution
7 downwind of the Manaus metropolitan region are reported as part of the GoAmazon2014/5
8 experiment. A high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) and a
9 suite of other gas- and particle-phase instruments were deployed at the “T3” research site, 70 km
10 downwind of Manaus, during the wet season. At this site, organic components represented on
11 average $79 \pm 7\%$ of the non-refractory PM_{10} mass concentration, which was in the same range as
12 several upwind sites. The organic PM_{10} was, however, considerably more oxidized at T3
13 compared to upwind measurements. Positive-matrix factorization (PMF) was applied to the time
14 series of organic mass spectra collected at the T3 site, yielding three factors representing
15 secondary processes ($73 \pm 15\%$ of total organic mass concentration) and three factors
16 representing primary anthropogenic emissions ($27 \pm 15\%$). Fuzzy c-means clustering (FCM) was
17 applied to the afternoon time series of concentrations of NO_y , ozone, total particle number, black
18 carbon, and sulfate. Four clusters were identified and characterized by distinct airmass origins
19 and particle compositions. Two clusters, Bkgd-1 and Bkgd-2, were associated with background
20 conditions. Bkgd-1 appeared to represent near-field atmospheric PM production and oxidation of
21 a day or less. Bkgd-2 appeared to represent material transported and oxidized for two or more
22 days, often with out-of-basin contributions. Two other clusters, Pol-1 and Pol-2, represented the
23 Manaus influence, one apparently associated with the northern region of Manaus and the other



24 with the southern region of the city. A composite of the PMF and FCM analyses provided
25 insights into the anthropogenic effects on PM concentration and composition. The increase in
26 mass concentration of submicron PM ranged from 25% to 200% under polluted compared to
27 background conditions, including contributions from both primary and secondary PM.
28 Furthermore, a comparison of PMF factor loadings for different clusters suggested a shift in the
29 pathways of PM production under polluted conditions. Nitrogen oxides may have played a
30 critical role in these shifts. Increased concentrations of nitrogen oxides can shift pathways of PM
31 production from HO₂-dominant to NO-dominant as well as increase the concentrations of
32 oxidants in the atmosphere. Consequently, the oxidation of biogenic and anthropogenic precursor
33 gases as well as the oxidative processing of pre-existing atmospheric PM can be accelerated. The
34 combined set of results demonstrates the susceptibility of atmospheric chemistry, air quality, and
35 associated climate forcing to anthropogenic perturbations over tropical forests.



1 **1. Introduction**

2 Secondary organic material (SOM) constitutes a large fraction of the atmospheric particle
3 burden (Hallquist et al., 2009; Jimenez et al., 2009) and therefore has important effects on the
4 Earth's radiation balance, atmospheric visibility, and human health. SOM is a complex mixture
5 of compounds resulting from many chemical pathways, and the processes underlying the
6 production of SOM remain poorly understood. Models are especially challenged to accurately
7 represent production of SOM in regions where there is a mix of biogenic and anthropogenic
8 emissions (de Gouw et al., 2008; Glasius and Goldstein, 2016; Shrivastava et al., 2017). Possible
9 shifts in the contributing mechanisms of SOM production between background and polluted
10 conditions must be understood and quantified for distinct environments on the globe to test and
11 enable accurate modeling predictions.

12 Several field observations, mainly in mid-latitudes of the Northern Hemisphere, and
13 modeling efforts have suggested that the production of SOM from biogenic precursor
14 compounds becomes more efficient in polluted air (Weber et al., 2007; Goldstein et al., 2009;
15 Hoyle et al., 2011; Huang et al., 2014; Zhang et al., in press). In the northeastern USA, de Gouw
16 et al. (2005) showed that organic PM concentrations correlated well with anthropogenic tracers,
17 yet the concentrations of anthropogenic precursors were insufficient to explain the observed PM.
18 In the southeastern USA, observations suggested that organic PM was produced mainly from
19 BVOCs, however modulated by anthropogenic emissions of NO_x and SO₂ (Weber et al., 2007;
20 Goldstein et al., 2009). In the western USA, ground and aircraft measurements observed the
21 highest organic PM increases when air masses having high concentrations of biogenic VOCs
22 (BVOCs) intercepted anthropogenic emissions (Setyan et al., 2012; Shilling et al., 2013). A
23 metastudy for several locations in the USA concluded that downwind urban air had increased



24 organic PM concentrations due to the photochemical production of SOM (De Gouw and
25 Jimenez, 2009). Models have estimated that 50 to 70% of the biogenic SOM mass concentration
26 in several locations is modulated by anthropogenic emissions (Carlton et al., 2010; Heald et al.,
27 2011; Spracklen et al., 2011). In addition, global-scale modeling studies have estimated an
28 increase of 20% to 60% in the global annual mean SOM concentration relative to the pre-
29 industrial period (Tsigaridis et al., 2006; Hoyle et al., 2009).

30 Many possible mechanisms may contribute to the effects of anthropogenic emissions on
31 increased SOM production, including changes in gas-particle partitioning, new particle
32 production and growth, and particle acidity. Changes in the concentrations of nitrogen oxides,
33 however, should be regarded as a critical factor (Hoyle et al., 2011 and references therein).
34 Different NO_x regimes favor distinct gas-phase oxidation pathways, leading to different
35 oxidation products and particle yields, as evidenced in isoprene photo-oxidation (Kroll et al.,
36 2005, 2006; Hallquist et al., 2009; Worton et al., 2013; Liu et al., 2016b; Liu et al., 2016a). For
37 tropical forests, isoprene emissions are especially important in PM production (Martin et al.,
38 2010a; Chen et al., 2015). Under HO₂-dominant conditions (i.e., low NO_x), isoprene epoxydiols
39 (IEPOX) are produced in the gas phase and, through heterogenous reactions involving sulfate,
40 PM is produced (Paulot et al., 2009; Surratt et al., 2010). Depending on the relative importance
41 of increased concentrations of sulfate and NO_x associated with pollution in a given region, an
42 enhancement or suppression of IEPOX-derived PM production relative to background conditions
43 may occur (Xu et al., 2015a; de Sá et al., 2017).

44 Amazonia, the largest tropical forest in the world and a large global source of SOM, is
45 comparatively understudied relative to northern mid-latitude regions, especially with respect to
46 the influence of pollution on the SOM lifecycle (Martin et al., 2010a). Manaus, a city of over two



47 million people in the central Amazon, continuously releases an urban plume into an otherwise
48 mostly unperturbed region (Kuhn et al., 2010; Martin et al., 2017). The region downwind of
49 Manaus, especially in the wet season in the absence of regional fires (Artaxo et al., 2013), offers
50 a natural laboratory for the investigation of biogenic-anthropogenic interactions and the resulting
51 consequences for the amount and composition of PM in the region. As part of GoAmazon2014/5,
52 de Sá et al. (2017) demonstrated that PM derived from IEPOX generally decreased under
53 polluted compared to background conditions downwind of Manaus. Nitrogen oxides in the
54 pollution plume suppressed the production of isoprene hydroxyhydroperoxides (Liu et al.,
55 2016b), leading to a decrease in the production of gas phase IEPOX and consequently of IEPOX-
56 derived PM (de Sá et al., 2017). IEPOX-derived PM was the exclusive focus of de Sá et al.
57 (2017).

58 The present study investigates the influences of urban pollution on the concentration and
59 composition of fine particles in central Amazonia, focusing on organic PM and its several
60 component classes. The analysis employs data sets collected during the first Intensive Operating
61 Period (IOP1) of the GoAmazon2014/5 experiment (Martin et al., 2016), corresponding to the
62 wet season during the period of February 1 to March 31, 2014. A separate publication is planned
63 for IOP2, corresponding to the dry season period of August 15 to October 15, when biomass
64 burning emissions were prevalent (de Sá et al., in preparation). Herein, positive-matrix
65 factorization (PMF) of organic mass spectra measured by aerosol mass spectrometry (AMS) in
66 conjunction with a clustering analysis of pollution indicators by Fuzzy c-means are employed to
67 investigate the changes in particle concentration and composition associated with the influence
68 of urban pollution downwind of Manaus.



69 2. Methodology

70 2.1 Site description

71 The primary site of this study, named “T3” (3.2133 °S, 60.5987 °W), was located 70 km
72 to the west of Manaus, Brazil, in central Amazonia (Martin et al., 2016). The site was situated in
73 a pasture of 2.5 km × 2 km surrounded by forest. Auxiliary sites “T0a” and “T0t”, served as
74 references for background conditions in relation to T3 (Figure S1). Site T0a (2.1466 °S,
75 59.0050 °W) refers to the Amazonian Tall Tower Observatory (ATTO; Andreae et al., 2015),
76 located 150 km to the northeast of Manaus. Site T0t (2.5946°S, 60.2093°W) was situated 60 km
77 to the north-northwest of Manaus in the Cuieiras Biological Reserve (“ZF2”) and refers to tower
78 “TT34”, established in 2008 for the AMAZE-08 experiment (Martin et al., 2010b). The T0 sites
79 were typically upwind of Manaus, with only occasional transport of pollution to these sites
80 (Andreae et al., 2015; Chen et al., 2015). Auxiliary site “T2” served as a reference for polluted
81 conditions. This site was located just across the Rio Negro (3.1392°S, 60.1315°W), 8 km from
82 the southwestern edge of Manaus and typically downwind of urban emissions during the
83 daytime.

84 2.2 Aerosol Mass Spectrometry

85 Characterization of the atmospheric PM was obtained using a High-Resolution Time-of-
86 Flight Aerosol Mass Spectrometer (hereafter AMS; Aerodyne, Inc., Billerica, Massachusetts,
87 USA; DeCarlo et al., 2006; Canagaratna et al., 2007). Detailed aspects of the AMS operation in
88 GoAmazon2014/5 were presented in de Sá et al. (2017). In brief, the instrument was housed
89 within a temperature-controlled research container, and the inlet to the instrument sampled from
90 5 m above ground level. Ambient measurements for this study were obtained every other 4 min.



91 The other 4 min were used for analysis of output from an oxidation flow reactor as presented in
92 Palm et al. (2018).

93 Data analysis was performed using *SQUIRREL* (1.56D) and *PIKA* (1.14G) of the AMS
94 software suite (Sueper and collaborators; DeCarlo et al., 2006). Organic, sulfate, ammonium,
95 nitrate, and chloride PM mass concentrations were obtained from “V-mode” data. The choice of
96 ions to fit was aided by “W-mode” data, which were collected for one of every five days.
97 “Sulfate” and “nitrate” concentrations reported by the AMS may include contributions from both
98 organic and inorganic species (Farmer et al., 2010; Liao et al., 2015). Organic and inorganic
99 nitrate concentrations were estimated based on the ratio of NO_2^+ to NO^+ signal intensity, as
100 described in Section S2 (Fry et al., 2009; Farmer et al., 2010; Fry et al., 2013). The organic
101 elemental ratios, O:C and H:C, were calculated following the methods of Canagaratna et al.
102 (2015).

103 **2.3 Auxiliary measurements and datasets**

104 In complement to the AMS data set, the analysis herein incorporated auxiliary gas and
105 particle measurements from T3 (Martin et al., 2016). Mass concentrations of molecular and
106 tracer organic species in the gas and particle phases were measured by a Semi-Volatile Thermal
107 Desorption Aerosol Gas Chromatograph (SV-TAG) at a time resolution of one hour (Isaacman-
108 VanWertz et al., 2016). Concentrations of volatile organic compounds (VOCs) were measured
109 by a Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS; Liu et al.,
110 2016b). In the Mobile Aerosol Observing System (MAOS) of the ARM Climate Research
111 Facility (ACRF; Martin et al., 2016), measurements of NO_y were made using a
112 chemiluminescence-based instrument (Air Quality Design). The raw NO_y measurements (10-s
113 resolution) were averaged across 30-min intervals to dampen the influence of brief local events.



114 In addition, ozone concentrations were measured by an ultraviolet photometric analyzer (Thermo
115 Fisher, model 49i, Ozone Analyzer). Particle number concentrations were measured by a
116 Condensation Particle Counter (TSI, model 3772). Black carbon (BC) concentrations were
117 measured both by a 7-wavelength aethalometer (Magee Scientific, model AE-31) and a Single
118 Particle Soot Photometer (SP2; Droplet Measurement Techniques). The two datasets differed by
119 a factor of up to three in absolute mass concentrations, as observed in other studies (Subramanian
120 et al., 2007; Cappa et al., 2008; Lack et al., 2008), but they agreed well in the temporal trend.
121 The analysis herein for BC is thus restricted to the temporal trends. Wind direction, solar
122 irradiance, and precipitation rate were measured by the ARM Mobile Facility (AMF-1), which
123 was also part of the ACRF.

124 Additional measurements from T0a, T0t, and T2 were also used in the analysis. At T2,
125 non-refractory particle composition and concentration were measured by an Aerosol Chemical
126 Speciation Monitor (ACSM; Brito et al., in preparation). ACSM measurements were also made
127 at T0a during the wet season of 2015 (Carbone et al., in preparation). Further datasets collected
128 by AMS at T0t during the wet season of 2008 (AMAZE-08 campaign) were used in the analysis
129 (Chen et al., 2009; Schneider et al., 2011). AMS measurements made onboard the G-1 aircraft of
130 the ARM Aerial Facility (AAF) during IOP1 also supported the analysis herein (Shilling et al., in
131 preparation).

132 **2.4 Air mass backtrajectories and precipitation rates**

133 Simulations of two-day backward air mass trajectories, starting at 100 m above T3, were
134 made using HYSPLIT4 (Draxler and Hess, 1998). Input meteorological data were obtained
135 from the Global Data Assimilation System (GDAS), provided by the NOAA Air Resources



136 Laboratory (ARL), on a regular grid of $0.5^\circ \times 0.5^\circ$, 18 pressure levels, and 3-h intervals.

137 Trajectory steps were calculated for every 12 min.

138 Information on precipitation along the trajectories was obtained from the S-band radar of
139 the System for Amazon Protection (SIPAM) in Manaus (Machado et al., 2014). The radar had a
140 beam width of 1.8° , and it scanned 17 elevation angles every 12 min. Data were recorded to a
141 range of 240 km at 500-m gate spacing. The reflectivity fields were quality controlled to remove
142 non-meteorological echo and calibrated against the satellite precipitation radar of the Tropical
143 Rainfall Measuring Mission and Global Precipitation Measurement (TRMM-GPM; Kummerow
144 et al., 1998; Hou et al., 2014). Ground clutter was used to analyze the stability of the calibration.
145 The data were gridded at $2 \text{ km} \times 2 \text{ km}$ in the horizontal and 0.5 km in the vertical using the
146 NCAR *Radx* software. The reflectivity at 2.5 km in altitude was converted to rain rates based on
147 the data sets of a Joss-Waldvogel disdrometer (Joss and Waldvogel, 1967), located at T3, 70 km
148 downwind of the radar.

149 **3. Results and discussion**

150 **3.1 Fine-mode PM composition**

151 The time series of mass concentrations of PM_{10} species at T3 during the wet season of
152 2014 are plotted in Figure 1a. Organic material dominated the composition, contributing $79 \pm 7\%$
153 (average \pm one standard deviation), followed by sulfate ($13 \pm 5\%$). The standard deviation
154 quantifies the variability across the time series. Average non-refractory (NR) PM_{10} mass
155 concentrations and compositions at T3 as well as at three other sites in the region are represented
156 in Figure 1b. The two T0 sites corresponded to predominantly background conditions. By
157 contrast, the T2 site represented conditions just downwind of Manaus, and depending on wind
158 direction experienced fresh Manaus pollution or background air. The comparison in Figure 1b



159 demonstrates that the organic component consistently constituted 70% to 80% of NR-PM₁ across
160 sites in this region in the wet season, for both background and polluted conditions, in line with
161 previous observations (Chen et al., 2009; Martin et al., 2010a).

162 Even as the relative composition was similar across all sites, there were differences in the
163 absolute mass concentrations (Figure 1b, top panel). The NR-PM₁ mass concentrations at the T0
164 sites upwind of Manaus were approximately 1 µg m⁻³. The concentrations at the T2 site just
165 downwind of Manaus were more than three times higher on average (3.3 µg m⁻³). Average
166 concentrations at the T3 site (1.7 µg m⁻³), several hours downwind of Manaus, were lower
167 compared to those at T2. This relative progression from T0, to T2, and then to T3 can be
168 understood as a first-order quantification of the overall effect of Manaus emissions in increasing
169 the airborne PM burden in the downwind region.

170 The diel trends of organic and sulfate mass concentrations across the four sites are shown
171 in Figure 2. Lines represent means, solid markers show medians, and boxes span interquartile
172 ranges. Organic mass concentrations and associated variability were higher at the T3 site
173 compared to the T0 sites, markedly so in the afternoon hours. The greater variability at T3 is in
174 line with a time-varying influence of Manaus emissions. This influence waxes and wanes with
175 small northerly or southerly shifts of the trade winds as well as other changes in regional
176 circulation tied to daily meteorology (Cirino et al., submitted). The higher afternoon mass
177 concentrations at T3 can be attributed to a combination of (i) an oxidant-rich, sunlight-fed plume
178 that increases the production rate of secondary PM and (ii) faster near-surface winds during the
179 day that transport PM from Manaus to T3 with less loss by deposition and dispersion compared
180 to more-stagnant air at night. Among all sites, the T2 observations had both the highest average
181 organic mass concentrations and the largest variability. These characteristics of the T2 dataset



182 can be explained by a combination of (i) the proximity of the site to Manaus, (ii) the rapid and
183 180° changes in wind direction caused by the intersection of the trade winds with a local river
184 breeze (dos Santos et al., 2014), and (iii) possible contributions of emissions from brick kilns,
185 located mostly southwest of the site, especially during night time (Martin et al., 2016; Cirino et
186 al., submitted).

187 The diel trends of the sulfate mass concentrations were in large part similar to those of
188 the organic mass concentrations. One distinction in the case of sulfate, however, is that the
189 variability at the T0 sites is similar to that at the T3 site. The explanation is that the background
190 sources of sulfate, including not only in-basin emissions but also out-of-basin long-range
191 transport, are variable and significant enough to make the variability at the background sites
192 similar to that at the T3 site (de Sá et al., 2017).

193 Overall, the organic PM₁ at T3 was highly oxidized, as indicated by the position of gray
194 markers in the plot of Figure 3. By contrast, the blue markers represent the dataset collected at
195 T2 during the same period. The datasets encompass all times of days and all conditions at both
196 sites. Datasets from background sites collected in different years are shown in Figure S2. Points
197 to the upper left represent more oxidized material, and points to the lower right represent less
198 oxidized material (Ng et al., 2011a). The comparison depicted in Figure 3 illustrates the effects
199 of the plume over the 4 h of transport from T2 to T3 (Cirino et al., submitted). The plot suggests
200 that the enhanced oxidative cycle associated with higher OH and O₃ concentrations in the
201 pollution plume might cause (i) the production of highly oxidized SOM, from both biogenic and
202 anthropogenic precursors including aromatic compounds (Chhabra et al., 2011; Lambe et al.,
203 2011), and (ii) the accelerated oxidative processing of pre-existing organic PM by OH and O₃



204 (Martin et al., 2017). The implication is that the emissions from Manaus can significantly affect
205 the mechanisms that produce or modify fine-mode PM over the tropical forest.

206 **3.2 Characterization of organic PM by positive-matrix factorization**

207 Positive-matrix factorization was applied to the time series of the organic component of
208 the high-resolution “V mode” mass spectra (Ulbrich et al., 2009b). Diagnostics of the PMF
209 analysis are presented in the Supplement (Section S1; Figures S3 and S4). Herein, “factor
210 profile” and “factor loading” refer to the mathematical products of the multivariate statistical
211 analysis, whereas “mass spectrum” and “mass concentration” refer to direct measurements.

212 A six-factor solution was obtained based both on the numerical diagnostics of the PMF
213 algorithm and the judged scientific meaningfulness of the resolved factors (Section S1). The
214 factor profiles, diel trends of the factor loadings, and the time series of the factor loadings and
215 other related measurements are plotted in Figures 4a, 4b, and 4c, respectively. The inset of
216 Figure 4a shows the mean fractional loading contribution of each factor during the analysis
217 period. The correlations of factor loadings with co-located measurements of gas- and particle-
218 phase species are shown in Figure 5.

219 The scientific interpretation of each factor was based on a combination of (i) the
220 characteristics of the factor profile (i.e., “mass spectrum”), as referenced to a worldwide database
221 of AMS spectra and PMF analyses (Ulbrich et al., 2009b; Ulbrich et al., 2009a, 2009c), and (ii)
222 the temporal correlations between the factor loading and other co-located measurements. Three
223 factors interpreted as primary emissions of organic PM were resolved: an anthropogenic-
224 dominated factor (hereafter, “ADOA”), a biomass burning factor (“BBOA”), and a fossil-fuel
225 hydrocarbon-like factor (“HOA”). Three factors interpreted as secondary production and



226 processing were resolved: a more-oxidized oxygenated factor (“MO-OOA”), a less-oxidized
227 oxygenated factor (“LO-OOA”), and an isoprene epoxydiols-derived factor (“IEPOX-SOA”).

228 The HOA factor profile had characteristic ions of $C_4H_7^+$ and $C_4H_9^+$ at nominal values of
229 m/z 55 and 57, respectively (Figure 4a). It had an oxygen-to-carbon (O:C) ratio of 0.18 ± 0.02 ,
230 the lowest among the six factors (Table 1). In line with the AMS PMF literature, the HOA factor
231 represents a class of primary hydrocarbon-like organic compounds that are typically associated
232 with traffic emissions (Zhang et al., 2005). In the present study, the HOA factor loadings
233 accounted for 6% of the organic mass concentrations on average (Figure 4a, inset). As a point of
234 comparison, the average in the southeastern USA typically varies from 9% to 15% (Xu et al.,
235 2015b). The lower relative contribution of 6% in this study might in part be due to a larger
236 relative role of secondary production in the environment of a tropical forest. In addition, the
237 distance from Manaus to the T3 site might allow time for substantial vertical mixing, dilution,
238 and subsequent evaporation of primary emissions into entrained background air (Robinson et al.,
239 2007; Liu et al., accepted; Shilling et al., in preparation). Finally, the possible differences in
240 emission profiles associated with different types of regional economic development between the
241 Brazilian Amazon and USA (e.g., fleet density, fuel matrix, industry, and so forth) should also be
242 considered. The HOA factor loading decreased during the day, which can be explained by the
243 growth of the planetary boundary layer (PBL) and the subsequent dilution of the concentrations
244 of primary emissions (Figure 4b). The time series of HOA factor loading did not correlate well
245 ($R < 0.5$) with any of the co-located measurements at T3 (Figure 5). It is plotted alongside the
246 time series of NO_y concentration in Figure 4c.

247 The BBOA factor profile was characterized by distinct peaks of $C_2H_4O_2^+$ (m/z 60) and
248 $C_3H_5O_2^+$ (m/z 73), as shown in Figure 4a. These peaks can be attributed to levoglucosan and



249 other anhydrous sugars that result from biomass pyrolysis (Schneider et al., 2006; Cubison et al.,
250 2011). Correlations of the factor loadings with the mass concentrations of levoglucosan and
251 vanillin ($R > 0.8$) measured by SV-TAG corroborate the association with biomass burning
252 (Figure 4c). The BBOA factor of this study had an O:C ratio of 0.61 ± 0.08 (Table 1), which is
253 consistent with large contributions from levoglucosan (O:C of 0.83) and similar sugars. The
254 factor loading on average accounted for 9% of the organic PM₁ mass concentration (Figure 4a,
255 inset). This result is consistent with the low incidence of fires in the Amazon during the wet
256 season (Martin et al., 2016). The BBOA factor loading typically decreased during the day
257 (Figure 4b), which is suggestive of the dilution of local sources during the development of the
258 PBL rather than long-range transport. Emissions from local fires around T3, including trash and
259 tree burning, as well as from wood-fueled brick kilns along the road from Manaus to T3 might
260 have contributed to this factor.

261 The ADOA factor profile, distinguished prominently by the $C_7H_7^+$ ion at m/z 91, also had
262 characteristic ions of $C_4H_7^+$ at m/z 55 and $C_3H_5^+$ at m/z 41 (Figure 4a). A peak at m/z 91 can arise
263 from many sources, including biogenic and anthropogenic emissions (Ng et al., 2011b). In itself,
264 m/z 91 therefore does not serve as a tracer for a specific source or process without consideration
265 of the atmospheric context. Factors having a characteristic m/z 91 peak (usually labeled “91fac”)
266 typically have been associated with biogenic emissions (Robinson et al., 2011; Budisulistiorini et
267 al., 2015; Chen et al., 2015; Riva et al., 2016). The ADOA factor profile of this study, however,
268 more strongly resembles the mass spectra previously reported for PM emissions from cooking
269 activities (Lanz et al., 2007; Mohr et al., 2012) than those from “91fac” (Section S1; Figure S5).
270 The ratio of m/z 55 to m/z 57 of the ADOA factor was 4.1. This ratio lies in the range of 2 to 10
271 reported for several factors representing primary cooking emissions and is well above the range



272 of 0.8 to 1.4 reported for factors associated with traffic emissions, i.e., HOA (Mohr et al., 2012
273 and references therein; Hu et al., 2016). Even though the ADOA factor profile has a large
274 contribution from non-oxygenated ions, similar to HOA and consistent with a dominance by
275 primary emissions, it also contains considerable signal from oxygenated ions, resulting in a
276 relatively higher O:C of 0.40 ± 0.05 (Table 1). The factor loading on average accounted for 13%
277 of the organic PM₁ mass concentration (Figure 4a, inset). The factor loading decreased as the
278 PBL developed during the day, consistent with dominant non-photochemical, primary sources
279 (Figure 4b). Furthermore, there were increases, albeit small, in factor loading at 12:00 and 18:00
280 (local time), suggestive of breakfast-time and lunch-time cooking activities in Manaus based on a
281 transport time of 4 to 6 h between the city and the T3 site (Martin et al., 2016; Cirino et al.,
282 submitted). Manaus typically has four rush-hour periods each day from 6:30 to 8:00, 12:00 to
283 13:30, 16:30 to 18:30, and 21:00 to 22:00. Traffic peaking at these hours may therefore also have
284 contributed to the ADOA factor. Correlations between factor loading and external measurements
285 exceeded $R = 0.5$ for many anthropogenic markers, including concentrations of aromatics (e.g.,
286 benzene, toluene, and C₈ and C₉ species), carbon monoxide, particle count, and NO_y (Figure 4c,
287 Figure 5). Contributions from secondary processes cannot be ruled out, and it is possible that PM
288 production from anthropogenic VOCs might have also been captured in this factor. Overall, the
289 ADOA factor was interpreted in the present study as an indicator of anthropogenic influence
290 associated with several sources in Manaus, most importantly cooking and possibly traffic
291 emissions.

292 The IEPOX-SOA factor profile had marker ions of C₄H₅⁺ (m/z 53) and C₅H₆O⁺ (m/z 82)
293 (Figure 4a; Lin et al., 2012; Hu et al., 2015; de Sá et al., 2017). It had an O:C ratio of 0.9 ± 0.10
294 (Table 1). The factor loading on average accounted for 17% of the organic PM₁ mass



295 concentration (Figure 4a, inset). There were high correlations ($R > 0.8$) between factor loadings
296 and concentrations of C₅-alkenetriols and 2-methyltetrols, which are markers of IEPOX-derived
297 PM, produced by the photo-oxidation of isoprene under HO₂-dominant conditions (Surratt et al.,
298 2010; Lin et al., 2012; Figure 4c). The increase in factor loading during daytime was consistent
299 with a photochemical source (Figure 4b). There were also correlations between factor loadings
300 and concentrations of sulfate and some acids, such as tricarballic acid (TCA; Figure 5), in
301 agreement with the association of IEPOX-derived PM and sulfate/acidity observed in other
302 studies (Budisulistiorini et al., 2013; Nguyen et al., 2014; Kuwata et al., 2015). Overall, this
303 factor was therefore interpreted as representative of PM produced from isoprene photo-oxidation
304 under HO₂-dominant conditions. The effects of urban pollution on the loadings of this factor
305 were the focus of a previous publication (de Sá et al., 2017).

306 The two remaining factors, LO-OOA and MO-OOA, were also associated with secondary
307 atmospheric processes. The LO-OOA and MO-OOA factors had O:C ratios of 0.72 ± 0.10 and
308 1.09 ± 0.17 , respectively. The LO-OOA factor was characterized by the greatest ratio of signal
309 intensity of the C₂H₃O⁺ ion (m/z 43) to that of the CO₂⁺ ion (m/z 44) (Figure 4a) compared to all
310 other factors. This factor is usually attributed to lower-generation, less-oxidized, higher-volatility
311 secondary organic PM (Jimenez et al., 2009). By comparison, the MO-OOA factor profile had
312 the strongest CO₂⁺ (m/z 44) peak among all factors (Figure 4a). This factor is usually attributed
313 to higher-generation, more-oxidized, less-volatile secondary organic PM or extensively oxidized
314 primary PM of any type that has resided in the atmosphere for several days or more (Jimenez et
315 al., 2009).

316 The LO-OOA factor loading on average accounted for 25% of the organic PM₁ mass
317 concentration (Figure 4a, inset). The factor loading correlated better with the estimated



318 concentrations of inorganic nitrate than with organic or total nitrate (Figure 5; Section S2 and
319 Figure S6), which is consistent with the interpretation of the higher volatility associated with this
320 factor (Jimenez et al., 2009; Zhang et al., 2011). The factor loading also correlated ($R > 0.7$) with
321 the concentrations of 2-methylglyceric acid and methyl-butyl-tricarboxylic acid (MBTCA),
322 which are products of isoprene and monoterpene oxidation, respectively, under NO-dominant
323 conditions (Figure 4c; Figure 5). The factor loading increased starting at 9:00 (local time) and
324 peaked in the afternoon hours (Figure 4b). This diel trend, tied to the sunlight cycle, tracked the
325 typical daily emission patterns of isoprene and monoterpenes from the surrounding forest
326 (Yáñez-Serrano et al., 2015). The absence of a sharp decline at sunset and the higher variability
327 at nighttime may also indicate a contribution by terpene ozonolysis. For these several reasons,
328 the LO-OOA factor was interpreted herein as secondary organic PM produced mostly within
329 several hours of observations by many possible pathways, including (i) the photo-oxidation of
330 isoprene along non-IEPOX pathways, (ii) the photo-oxidation of terpenes and other biogenic
331 VOCs along both HO₂- and NO-dominant reaction pathways, (iii) the ozonolysis of terpenes, and
332 (iv) the possible production of SOM from anthropogenic emissions from Manaus.

333 The MO-OOA factor loading on average accounted for 30% of the organic PM₁ mass
334 concentration (Figure 4a, inset). The factor loading correlated ($R > 0.7$) with the mass
335 concentrations of several particle-phase carboxylic acids as well as the concentrations of sulfate,
336 ammonium, and ozone (Figure 5). The time series of malic acid and ozone concentrations are
337 shown alongside the MO-OOA factor loadings in Figure 4c. Malic acid is a highly oxidized
338 compound (O:C of 1.25), which may have many different sources (Röhrh and Lammel, 2002; van
339 Pinxteren et al., 2014). The MO-OOA factor loading increased starting at 8:00 (local time;
340 sunrise was at 6:00) and peaked between 10:00 and 16:00, with a large variability in the factor



341 loadings in the afternoon hours among different days (Figure 4b). The afternoon increase and
342 day-to-day variability were consistent with strong but variable photochemical processing leading
343 to further oxidation of organic PM during the day, depending on daily weather. The high O:C of
344 1.09 ± 0.17 could also be indicative of production of PM from aromatic compounds emitted from
345 Manaus (Chhabra et al., 2011; Lambe et al., 2011). Overall, this factor was interpreted to
346 represent highly oxidized PM from multiple processes. Species initially associated with HOA,
347 BBOA, ADOA, IEPOX-SOA, and LO-OOA factors may converge after sufficient atmospheric
348 oxidation to become represented by the MO-OOA factor (Jimenez et al., 2009; Palm et al.,
349 2018).

350 **3.3 Shifts in PM with anthropogenic influences**

351 **3.3.1 Cluster Analysis**

352 To further investigate changes in the concentration and composition of PM associated
353 with anthropogenic influences, a Fuzzy c-means (FCM) algorithm was applied to the time series
354 of concentrations of particle number, NO_x , ozone, black carbon, and sulfate measurements at the
355 T3 site (Bezdek et al., 1984). The analysis was fully independent of the PMF results. For each
356 point in time, these concentrations represented the spatial coordinates of the data point. As
357 discussed below, four clusters were identified. Based on measures of spatial similarity, the
358 clustering algorithm attributed to each data point a degree of membership relative to each of the
359 four clusters (Section S3; Figure S7 and Figure S8).

360 The scope of the clustering analysis was restricted to afternoon time points for which ten-
361 hour air mass backtrajectories did not intersect significant precipitation and for which solar
362 irradiance at T3 averaged over the previous 4 h was higher than 200 W m^{-2} (Section S3). This
363 scope aimed at capturing fair-weather conditions and thereby minimizing the role of otherwise



364 confounding processes, such as boundary layer dynamics and wet deposition. The elimination of
365 trajectories having precipitation, however, should not be regarded as fully accurate given the
366 uncertainties in the HYSPLIT trajectories. The scoped dataset spanned 24 afternoons.

367 Four clusters were identified based on minimization of the FCM objective function as
368 well as a subjective assessment of meaningful interpretation of the set of clusters (Section S3).
369 The FCM algorithm returned a matrix containing the degrees of membership (ranging from 0 to
370 1) to each of the four clusters (columns) for each point in time (rows). For any given time point
371 (i.e., row), the sum of its degrees of membership to clusters (i.e., sum across columns) was
372 always unity, by definition. A collection of examples, representing 37% of the analyzed data
373 points by FCM, is shown in Figure 6a. For times predominantly associated with only one cluster
374 (e.g., Feb 9 and Feb 10), the corresponding air mass backtrajectories are plotted in Figure 7. The
375 FCM algorithm also returned the coordinates of cluster centroids, which are listed in Table 2.

376 Two clusters of data were interpreted as “background” and labeled “Bkgd-1” and “Bkgd-
377 2”. They were characterized by $\text{NO}_y < 1$ ppb, ozone < 20 ppb, and particle number $< 1200 \text{ cm}^{-3}$
378 (Table 2; Figure 6). The two clusters differed especially in that Bkgd-2 had significantly larger
379 concentrations of sulfate and black carbon. A comparison of the datasets of Feb 13
380 (predominantly Bkgd-1) and Feb 16 (predominantly Bkgd-2) in Figure 6 highlights these
381 differences. Concentrations of sulfate and black carbon were 0.15 and $0.10 \mu\text{g m}^{-3}$, respectively,
382 on Feb 13, compared to 0.40 and $0.15 \mu\text{g m}^{-3}$ on Feb 16. The backtrajectories associated with
383 Bkgd-1 had both northeasterly and southeasterly components. The wind fields, out of line with
384 the trade winds, may suggest passage through recent weather systems and may imply wet
385 deposition, which in turn might explain lower gas and particle concentrations (Table 2). These
386 recent weather systems might not have been excluded from the scoped dataset because of



387 inaccuracies in the intersections of the backtrajectories with precipitation data, as discussed
388 above, or because they were more distant than captured by the 10-h backtrajectories. Consistent
389 with this hypothesis, the centroid value calculated for the 4-h averaged solar irradiance at T3
390 (Section 3.3.2) was lower for Bkgd-1 (400 W m^{-2}) compared to the other clusters (600 W m^{-2}),
391 suggesting an association of Bkgd-1 with overcast conditions. By comparison, the
392 backtrajectories associated with Bkgd-2 were predominantly from the northeast, coming from the
393 direction of the T0t and T0a sites (Figure 7), in line with the dominant trade winds of the wet
394 season. The air masses of Bkgd-2 may have experienced less wet deposition and may represent
395 more extensive atmospheric oxidation than those of Bkgd-1. They may also have carried PM
396 contributions from out-of-basin sources, which would be consistent with the higher sulfate and
397 black carbon concentrations of Bkgd-2 compared to Bkgd-1 (Chen et al., 2009; Pöhlker et al.,
398 2017).

399 Two other clusters were interpreted as “polluted” and labeled “Pol-1” and “Pol-2”. They
400 were characterized by concentrations of $\text{NO}_y > 1 \text{ ppb}$, ozone $> 20 \text{ ppb}$, and particle number $>$
401 1200 cm^{-3} (Table 2; Figure 6). The dataset of the afternoon of Mar 9 illustrates a shift in
402 dominance from Pol-2 to Pol-1 (Figure 6). Although Pol-1 and Pol-2 both have high
403 concentrations of sulfate and other pollutants, they differ in the extent of those high
404 concentrations. The explanation may be that these clusters represent different source regions.
405 Pol-1 may be associated with emissions from the northern region of Manaus, and Pol-2 may be
406 associated with emissions from the southern region of Manaus. Industry, power production, and
407 oil refineries are concentrated in the southeastern region of Manaus (Figure S9; Medeiros et al.,
408 2017). Population density and commercial activity is concentrated in the southwestern portion of
409 the city where downtown is located (Figure S10). Aircraft observations show that concentrations



410 of sulfate as well as other pollutants are higher in the urban outflow from the southern compared
411 to the northern region of Manaus (Figure S10). Directional plots of SO₂ and particle number
412 concentrations observed at the T2 site further demonstrate the heterogeneity in Manaus
413 emissions (Figure S10). This hypothesis of a geographical difference in source regions
414 qualitatively aligns with the differences in backtrajectories characteristic of times dominated by
415 Pol-1 and Pol-2 (Figure 7). This interpretation does imply, however, that the backtrajectories
416 may have a 20° inaccuracy. Such inaccuracy is reasonable for the application of HYSPLIT
417 modeling in this region given (i) the absence of surface weather stations and (ii) the relatively
418 large scale of input wind fields (i.e., 50 km) compared to the scale of modeling (i.e., 70 km from
419 T3 to Manaus and a city cross section of 20 km).

420 **3.3.2 Comparison of PM among clusters**

421 The characteristic PM composition associated with each cluster was determined by
422 calculating the centroid coordinates of the clusters for the AMS species and PMF factors
423 (Section S3). The centroid coordinate of a cluster for a given variable is defined as a weighted
424 mean of that variable across all points in time, where the weight is the degree of membership of
425 each data point to that cluster. A comparison of PM₁ concentrations and compositions for the
426 four clusters is shown in Figure 8. Values are listed in Table 2.

427 The NR-PM₁ mass concentrations increased by 25% to 200% in clusters Pol-1 and Pol-2
428 compared to clusters Bkgd-1 and Bkgd-2 (Figure 8a). Increases in sulfate and associated
429 ammonium concentrations had a smaller yet non-negligible role in the increased PM₁ mass
430 concentrations. Sources of sulfate other than Manaus sustain relatively high concentrations in the
431 Amazon basin, as represented by the Bkgd-2 cluster (Chen et al., 2009; de Sá et al., 2017).
432 Compared to these regional background concentrations (i.e., Bkgd-2 cluster), the increases in



433 sulfate concentrations were significant only for air masses associated with the heavily
434 industrialized and densely populated southern region of Manaus (i.e., Pol-2 cluster).

435 With respect to the composition of the organic PM, Figure 8b shows that the Bkgd-1
436 cluster had large contribution from the LO-OOA factor. By comparison, the Bkgd-2 cluster had
437 larger contributions from the MO-OOA and IEPOX-SOA factors. A comparison of 13 Feb and
438 16 Feb of 2014 (Figure 6d) illustrates these findings. The low mass concentrations and the
439 dominant contribution by the LO-OOA factor suggest that the Bkgd-1 cluster may represent
440 conditions under which secondary organic PM was produced within recent hours through photo-
441 oxidation of VOCs emitted by the forest and subsequent condensation of secondary organic
442 material. The low sulfate concentrations for Bkgd-1 may rationalize the absence of a significant
443 contribution by the IEPOX-SOA factor. Isoprene photo-oxidation may have contributed to PM
444 production by pathways other than IEPOX uptake (Krechmer et al., 2015; Riva et al., 2016). By
445 comparison, for Bkgd-2, the higher mass concentrations and the greater contributions by IEPOX-
446 SOA and MO-OOA factors suggest that this cluster may represent conditions under which
447 secondary organic PM was a combination of material produced both on that day as well as on
448 previous days. During transport, the organic PM may have undergone extensive atmospheric
449 oxidation by a combination of surface and condensed-phase chemistry, including cloud water
450 processes (Carlton et al., 2006; Ervens et al., 2011; Hoyle et al., 2011; Perraud et al., 2012).
451 Concentrations and composition of the Bkgd-2 cluster may therefore represent an extensive
452 geographical footprint.

453 The organic PM concentration and composition associated with the Pol-1 and Pol-2
454 clusters were distinct from those of the Bkgd-1 and Bkgd-2 clusters (Figure 8). The mass
455 concentrations of organic PM were greater by 25% to 150% for Pol-1 and Pol-2. According to



456 the PMF factors (Figure 8b), the larger part of this increase in organic PM between the
457 background and polluted clusters was tied to the production of secondary organic PM, although
458 primary emissions also contributed significantly. By comparison, for both Bkgd-1 and Bkgd-2
459 clusters, contributions by primary emissions were negligible, as indicated by the low summed
460 contribution of factors of primary origin (i.e., ADOA, BBOA, and HOA) to the organic PM₁ (<
461 10%). For Pol-1 and Pol-2, the ADOA factor loading on average accounted for 10% of the
462 organic mass concentration at T3, serving as a strong marker of Manaus pollution. A comparison
463 of 9 Feb and 9 Mar with 13 Feb and 16 Feb illustrates these findings (Figure 6d).

464 In regard to secondary organic PM, the IEPOX-SOA factor loading decreased by almost
465 50% under polluted compared to background conditions. de Sá et al. (2017) attributed this
466 decrease to the suppression of IEPOX production by elevated NO concentrations. This
467 suppression typically outweighed possible enhancements in IEPOX uptake and subsequent PM
468 production because of elevated sulfate concentrations. By contrast, the LO-OOA and MO-OOA
469 factor loadings increased by 50% to 100% under polluted conditions. These increases exceeded
470 the decrease in IEPOX-SOA factor loadings, resulting in a net increase of around 100% in mass
471 concentration of secondary organic PM (Figure 8).

472 The shifts in the processes governing the production of secondary organic PM because of
473 increased NO_x, OH, and O₃ concentrations characteristic of the pollution plume were complex
474 and non-linear (Figure 9a). Overall, the oxidation pathways were driven faster. The relatively
475 high $f_{\text{CO}_2^+}$ values and O:C ratios of all factors (Table 1), including those associated with primary
476 emissions, compared to typical values at other locations worldwide (Canagaratna et al., 2015),
477 corroborate this interpretation. Ozone concentrations in the plume increase by 200 to 300 %, and
478 hydroxyl radical concentrations increased by 250% or more (Liu et al., accepted). As HO₂-



479 dominant pathways were inhibited, NO-dominant pathways became active. Increased oxidant
480 concentrations may also have promoted additional multigenerational chemistry of semi- or
481 intermediate-volatility species (Robinson et al., 2007). Oxidation of VOCs by aqueous-phase
482 reactions, including in-cloud processing, and oxidation of biomass burning emissions may also
483 have played roles to varying degrees on different days (Carlton et al., 2006; Ervens et al., 2011;
484 Hoyle et al., 2011; Perraud et al., 2012). In addition, when primary and secondary PM mass
485 concentrations increased, further uptake of oxidized semi-volatile molecules could have been
486 thermodynamically favored according to partitioning theory, representing a positive feedback on
487 the increase of mass concentrations (Pankow, 1994; Odum et al., 1996; Carlton et al., 2010).

488 The increase in the LO-OOA and MO-OOA factor loadings associated with Pol-1 and
489 Pol-2 indicates that the net effect of this accelerated and modified chemistry was the quick
490 production and further oxidation of secondary organic PM. Precursors may have included both
491 the wide range of biogenic VOCs as well as contributions from anthropogenic precursors, such
492 as gas-phase species from vehicle emissions or evaporated primary material (Nordin et al., 2013;
493 Presto et al., 2014). The LO-OOA factor loading was important for the polluted conditions of
494 Pol-1 and Pol-2 as well as for the clean conditions of Bkgd-1. This result is not necessarily
495 because of an in-common molecular composition but rather because of an in-common process,
496 i.e., fresh production of secondary organic PM (Figure 9b). Likewise, the MO-OOA factor
497 loading was important for Pol-1, Pol-2, and Bkgd-2 because this factor represented an in-
498 common process, i.e., extensive oxidation (Figure 9b). In the case of the MO-OOA factor, there
499 is also an overall in-common composition characterized by highly oxidized species even as
500 precursor species and subsequent oxidation pathways differed (Jimenez et al., 2009).



501 The complexity of the real atmospheric processes, as illustrated in Figure 9, is to some
502 extent captured by the instrumental and analytical tools herein employed. Positive-matrix
503 factorization identified several broad classes of organic PM. Some PMF factors had sufficiently
504 unique signatures that they could be associated to one specific source and/or process (e.g., HOA
505 and IEPOX-SOA). Other factors, in contrast, represented a wide range of sources that shared in-
506 common processes (e.g., LO-OOA and MO-OOA). The clustering analysis contextualized the
507 PMF results and demonstrated that the effects of the urban pollution were neither limited to nor
508 captured by a single PMF factor. Instead, the urban plume influenced several PMF factors in
509 different ways and to different extents. The implication is that changes in the AMS spectral
510 signature of the organic PM caused by polluted conditions may not be sufficiently unique to
511 allow for its complete separation by PMF analysis alone, especially in respect to the production
512 of secondary organic PM. In this context, the Fuzzy c-means analysis served herein as a useful
513 tool to incorporate auxiliary datasets and thereby to further understand anthropogenic influences
514 on PM production and characteristics.

515 **4. Summary and conclusions**

516 Changes in the concentrations and the composition of fine-mode PM due to the influence
517 of anthropogenic emissions were investigated for the Amazonian wet season. Organic material
518 dominated the submicron composition, consistently representing between 70% and 80% of the
519 PM₁ mean mass concentration across measurement sites upwind and downwind of Manaus and
520 across different levels of pollution. Absolute mass concentrations, however, varied significantly
521 among sites. Average concentrations downwind of Manaus were 100% to 200% higher than
522 those upwind. Furthest downwind at T3, the organic component was more oxidized compared to
523 that at the T2 site.



524 Positive-matrix factorization and Fuzzy c-means clustering were applied to the datasets to
525 obtain a composite analysis of the shifts in PM₁ concentrations and composition under polluted
526 conditions. Based on the FCM clustering, every point in time at T3 was interpreted as being
527 affected by a combination of four influences, as represented by four clusters. Two background
528 (Bkgd-1 and Bkgd-2) and two polluted (Pol-1 and Pol-2) clusters were identified. Particle mass
529 concentrations were double for polluted compared to background conditions. Contributions from
530 secondary processes dominated (> 80%) for both background and polluted conditions.

531 In terms of primary emissions, absolute contributions increased by a factor of five or
532 more under polluted conditions, corresponding to an increase from < 10% to 15% of total PM₁.
533 The ADOA factor loading increased over five-fold for the polluted compared to the background
534 clusters, and this factor thus served as a strong tracer of Manaus pollution. BBOA and HOA
535 factor loadings, associated with biomass burning and fossil fuels, respectively, increased by two-
536 fold with pollution. The ADOA factor loading represented 61% to 76% of the total primary
537 factor loadings for the Pol-1 and Pol-2 clusters.

538 As for the secondary processes, the analysis further finds that the pollution plume acted
539 both to shift pathways of secondary organic PM production and to accelerate the atmospheric
540 oxidation of pre-existing organic PM. The oxidation of biogenic PM precursors shifted from
541 HO₂- to NO-dominant pathways, and the oxidation of anthropogenic precursors possibly
542 contributed to increased PM concentrations. The IEPOX-SOA factor loadings were highest for
543 the Bkgd-2 cluster, associated with long-range transport under background conditions, and
544 decreased by almost 50% for the polluted clusters, in line with a shift of isoprene oxidation from
545 HO₂- to NO-dominant pathways. Concomitantly, the LO-OOA factor loading increased by more
546 than 50% for these clusters, suggesting rapid in-plume production of secondary organic PM



547 through several pathways. The LO-OOA factor was also important for the Bkgd-1 cluster,
548 associated with fresh background conditions, which is suggestive of recent biogenic organic PM
549 production. The MO-OOA factor had large relative contributions in the Bkgd-2, Pol-1, and Pol-2
550 clusters, suggestive of significant oxidative processing associated with these clusters. Increases
551 of up to 300% in the MO-OOA factor loadings for Pol-1 and Pol-2 relative to background
552 conditions of Bkgd-1 showed the effects of an accelerated oxidation cycle, leading to highly
553 oxidized PM downwind of Manaus. Based on this and related studies (Liu et al., 2016b; de Sá et
554 al., 2017; Martin et al., 2017), the critical lever seems to be increased concentrations of nitrogen
555 oxides in the pollution plume for both directly shifting and indirectly accelerating mechanisms of
556 secondary organic PM production in central Amazonia during the wet season.

557 The altered composition under anthropogenic influences also affects the physical
558 properties of the PM₁. Bateman et al. (2017), using the results of the PMF analysis presented
559 herein, reported a shift from predominantly liquid PM under background conditions to a
560 considerable presence of non-liquid PM above 50% RH under polluted conditions. Non-liquid
561 PM can have different reactive chemistry from liquid PM (Li et al., 2015; Liu et al., 2018). A
562 linear relationship between the increase in particle rebound fraction and the sum of ADOA,
563 BBOA, and HOA factor loadings had an R^2 of 0.7. The highest individual correlation was with
564 the ADOA factor loading (Bateman, personal communication). In addition, Thalman et al.
565 (2017), also using the PMF results reported herein, concluded that the larger relative contribution
566 of secondary organic material during the daytime compared to the nighttime was the primary
567 driver of the diel trend of higher particle hygroscopicity during the day compared to the night, as
568 tied to cloud condensation nuclei (CCN) properties.



569 This study communicates a snapshot of the changes that occur in the atmospheric
570 composition over a tropical forest because of regional urbanization. In the context of a forest in
571 transition (Davidson et al., 2012), the findings herein provide a quantitative assessment of the
572 effects of urban pollution on the forested surroundings of Manaus. The studied region and the
573 observed changes in atmospheric composition represent a microcosm that might become more
574 widespread through Amazonia as urbanization trends continue in the future. Further
575 investigations of the specific chemical pathways and physical mechanisms that enhance PM
576 production in the urban plume are warranted to understand what other pollutants are critical for
577 control in the context of ongoing and future air quality regulation in the study region as well as
578 for other tropical forested environments worldwide.



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List of Figures

Figure 1. (a) Mass concentrations of PM₁ species at T3 during the wet season of 2014 (IOP1).

Non-refractory (NR) PM₁ species of organic, sulfate, ammonium, nitrate, and chloride were measured by the AMS. Mass concentrations of black carbon were obtained by scaling aethalometer measurements by a factor of 2 based on the range of 1 to 3 for the comparison of SP2 to aethalometer measurements. The temporal trend of the two instruments agreed well. (b) Comparison of the summed mass concentrations of non-refractory PM₁ species (top) and the mass fractions of these species (bottom) at T3 and three other regional sites. T0a-2015 refers to measurements in the wet season of 2015 at the ATTO location (Carbone et al., in preparation). T0t-2008 refers to the AMAZE-08 experiment, which took place in the wet season of 2008 at the TT34 location (Chen et al., 2015). T2-2014 refers to measurements made during IOP1 at a site 8 km downwind of Manaus, just across the Black River (“Rio Negro) (Brito et al., in preparation). Measurements at T0a in 2015 and at T2 in 2014 were made by an ACSM, and measurements at T0t in 2008 and at T3 in 2014 were made by an AMS. Concentrations were adjusted to standard temperature (273.15 K) and pressure (10⁵ Pa). Bars represent means and whiskers represent the standard deviation of measurements.

Figure 2. Diel patterns of the mass concentrations of organic (top, green) and sulfate (bottom, red) species during the wet season at four different sites (cf. Fig. 1 and Fig. **Error! Reference source not found.**). Mass concentrations were corrected to standard temperature and pressure (273.15 K and 10⁵ Pa). Local time is (UTC - 4 h). Lines represent means, solid markers show medians, and boxes span interquartile ranges.



The ordinate scale for the T2 panel differs from the other three panels. Concentrations were adjusted to standard temperature (273.15 K) and pressure (10^5 Pa).

Figure 3. Scatter plot of the AMS signal fraction at m/z 44 (f_{44}) against that at m/z 43 (f_{43}). Gray and blue circles correspond, respectively, to measurements at T3 and T2 during IOP1, in the wet season of 2014. Solid squares represent median values, and whiskers represent 10 and 90 percentiles. Dashed lines delineate the region where worldwide measurements of ambient organic PM_{10} commonly lie (Ng et al., 2011a).

Figure 4. Results of the PMF analysis on the time series of AMS organic mass spectra collected at T3. (a) Mass spectral profile of each factor represented at unit mass resolution. The inset shows the mean fractional loading of each factor. (b) Diel trends for the loadings of each PMF factor. Local time is (UTC - 4 h). Lines represent means, solid markers show medians, and boxes span interquartile ranges. (c) Time series of the factor loadings (left axis) and other related measurements at T3 (right axis). Methyl-butyl-tricarboxylic acid is abbreviated as MBTCA.

Figure 5. Column plot of Pearson R correlations between the loading of each PMF factor and values of selected measurements at T3. Abbreviations include tricarballic acid (TCA), methyl-butyl-tricarboxylic acid (MBTCA), methyl vinyl ketone (MVK), methacrolein (MACR), and isoprene hydroxyhydroperoxides (ISOPOOH). SV-TAG measurements refer to particle-phase concentrations. Isomers could not be distinguished by PTR-ToF-MS measurements; C_8 and C_9 aromatics include the xylene and trimethylbenzene isomers, respectively.

Figure 6. Results of the cluster analysis by Fuzzy c-means (FCM) for afternoon periods (12:00 to 16:00 h) are presented by several case studies. (a) Degree of membership in each of



the four clusters. The sum of degrees of membership across all clusters is unity. Background conditions are abbreviated as “Bkgd”, and polluted conditions are abbreviated as “Pol”. (b) Pollution indicators: concentrations of NO_y , O_3 , black carbon (BC), and particle number count are plotted. (c) PM_{10} mass concentrations for organic, sulfate, nitrate, and ammonium species. (d) Fractional contribution of each factor to total organic PM_{10} .

Figure 7. Air mass backtrajectories associated with the four clusters of the FCM analysis for the case studies of Figure 6. Trajectories were calculated using HYSPLIT 4 in steps of 12 min for ten hours (Draxler and Hess, 1998). Image data: Google earth.

Figure 8. Characteristic PM composition of the FCM clusters as represented by coordinates of cluster centroids. (a) Mass concentrations of AMS species characteristic of each cluster. (b) PMF factor loadings characteristic of each cluster. Calculations are presented in more detail in the Supplementary Material (Section S3). Values plotted are shown in Table 2.

Figure 9. Schematic representation of (a) atmospheric processes, illustrated in a simplified manner, associated with the production of organic PM_{10} and (b) observables of these processes as captured by the datasets and analytical approach employed in this study. In panel (a), the left side depicts the emissions of biogenic volatile organic compounds (VOCs), their atmospheric oxidation, and the production of biogenic secondary organic PM_{10} . The right side depicts anthropogenic emissions of gas species and particulate matter that can alter natural atmospheric concentrations and processes. There are primary organic PM_{10} emissions from traffic, cooking, and industrial



activities. Anthropogenic VOCs can be precursors for the production of secondary organic PM₁ and can affect the production of ozone and hydroxyl radical. NO_x emissions directly and indirectly alter the natural pathways of PM₁ production in the atmosphere. NO_x and SO_x can also directly contribute to the formation of secondary inorganic PM₁ (not shown), which can in turn play a role in changing pathways of secondary organic PM₁ production. In panel (b), different PMF factors represent distinct sources and/or processes. The IEPOX-SOA factor is at the intersection of the two, as it represents both a source (i.e., isoprene emissions from the forest) and a process (i.e., photo-oxidation under HO₂ dominant conditions, influenced by sulfate concentrations). The dashed black line represents the natural and anthropogenic oxidative processes that transform the chemical signature of the HOA, ADOA, BBOA, IEPOX-SOA, and LO-OOA factors after sufficient atmospheric residence time into the MO-OOA factor. The clusters represent different conditions at the receptor site (i.e., T3) and therefore incorporate the meteorological and geographical histories of the air masses that reach the site and affect the observed concentrations. The different PMF factors are associated to the different clusters (solid lines) to various extents (not detailed here for simplification purposes; cf. Figure 8).



Table 1. Characteristics of the PMF factors derived from the AMS datasets. Listed are signal fractions $f_{\text{CO}_2^+}$ at nominal m/z 44 and oxygen-to-carbon (O:C) and hydrogen-to-carbon (H:C) ratios. Values and associated uncertainties were calculated by running PMF in “bootstrap mode” (Ulbrich et al., 2009b). 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	$f_{\text{CO}_2^+}$	O:C	H:C
MO-OOA	0.25 ± 0.01	1.09 ± 0.17	1.27 ± 0.12
LO-OOA	0.14 ± 0.02	0.72 ± 0.10	1.49 ± 0.07
IEPOX-SOA	0.17 ± 0.01	0.93 ± 0.10	1.39 ± 0.07
ADOA	0.11 ± 0.01	0.40 ± 0.05	1.63 ± 0.02
BBOA	0.123 ± 0.004	0.61 ± 0.08	1.57 ± 0.04
HOA	0.048 ± 0.006	0.18 ± 0.02	1.94 ± 0.02



Table 2. Coordinates of cluster centroids for input variables, AMS species concentrations, and PMF factor loadings. Table entries for AMS species and PMF factors are plotted in Figure 8. The AMS species concentrations (except for sulfate) and PMF factor loadings were not used as input variables in the FCM clustering analysis.

Species	Cluster Centroid			
	Bkgd-1	Bkgd-2	Pol-1	Pol-2
Input variables				
Particle number (cm ⁻³)	714	1117	2636	6697
NO _y (ppb)	0.64	0.95	1.2	2.2
O ₃ (ppb)	14	17	26	36
Black carbon (μg m ⁻³)	0.05	0.16	0.21	0.18
Sulfate (μg m ⁻³)	0.15	0.36	0.44	0.57
AMS species concentrations (μg m⁻³)				
Organic	0.96	2.0	2.5	2.6
Ammonium	0.05	0.12	0.15	0.21
Nitrate	0.03	0.07	0.10	0.12
Chloride	0.007	0.011	0.009	0.007
PMF factor loadings (μg m⁻³)				
MO-OOA	0.29	0.83	1.13	1.13
LO-OOA	0.38	0.41	0.62	0.77
IEPOX-SOA	0.18	0.49	0.43	0.29
ADOA	0.044	0.086	0.19	0.32
BBOA	0.028	0.054	0.081	0.063
HOA	0.017	0.027	0.039	0.040

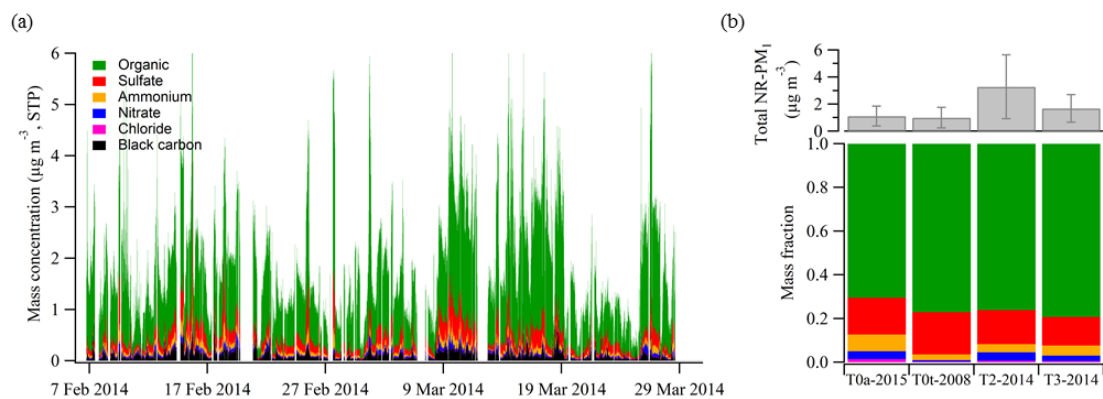


Figure 1

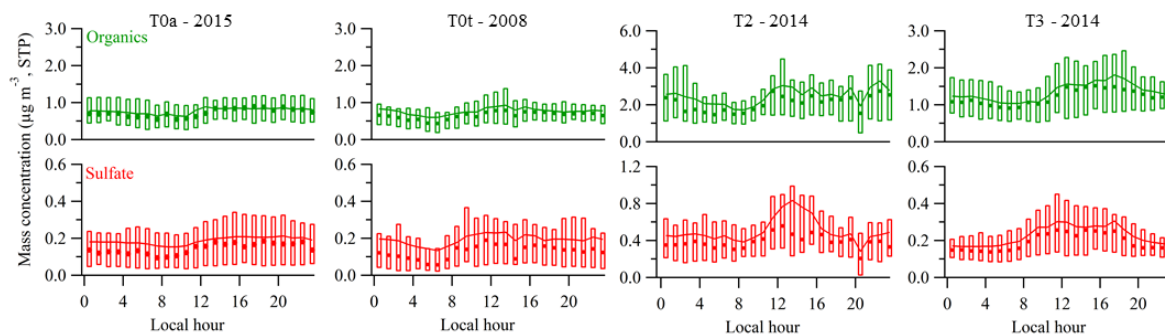


Figure 2

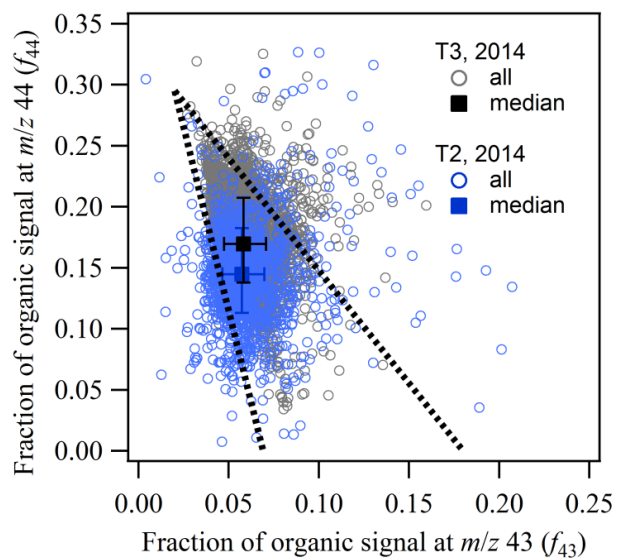


Figure 3

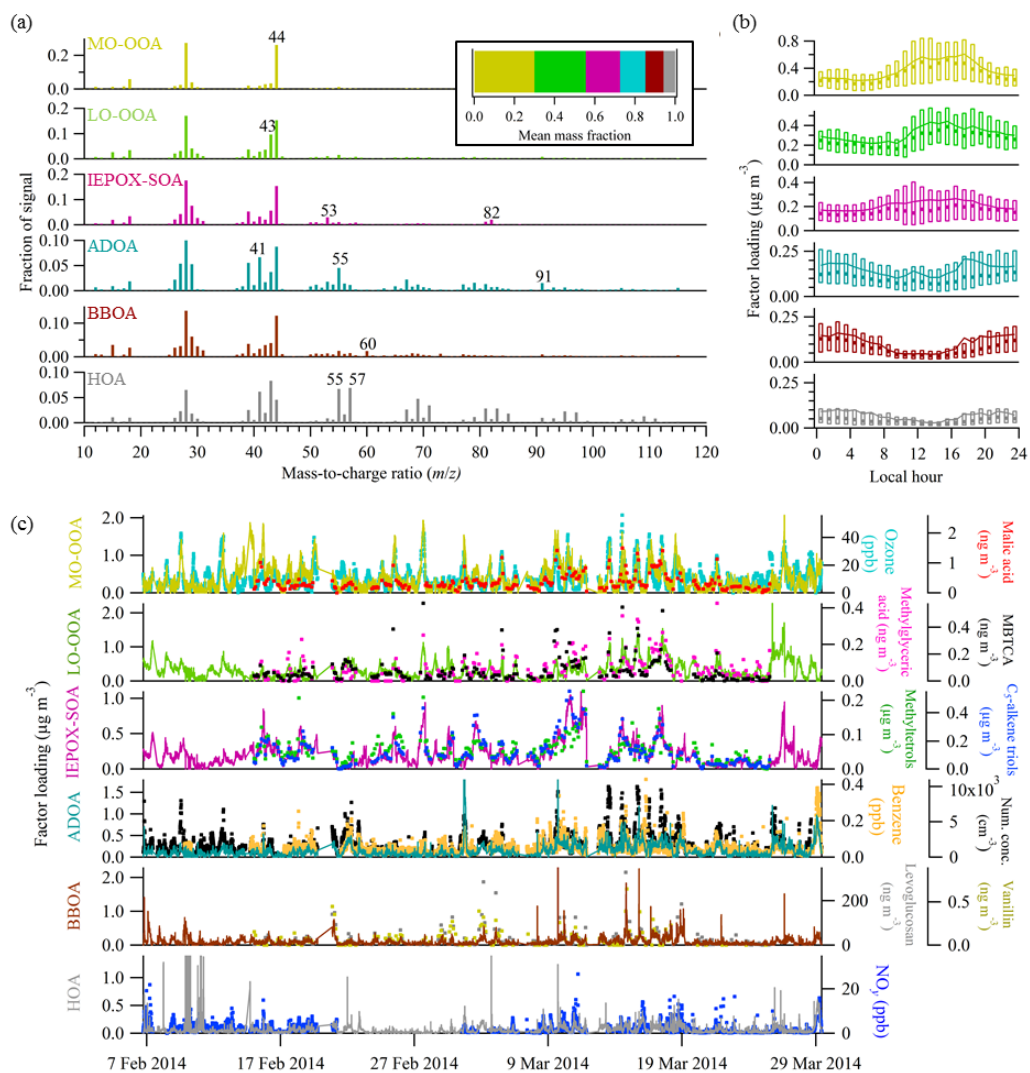


Figure 4

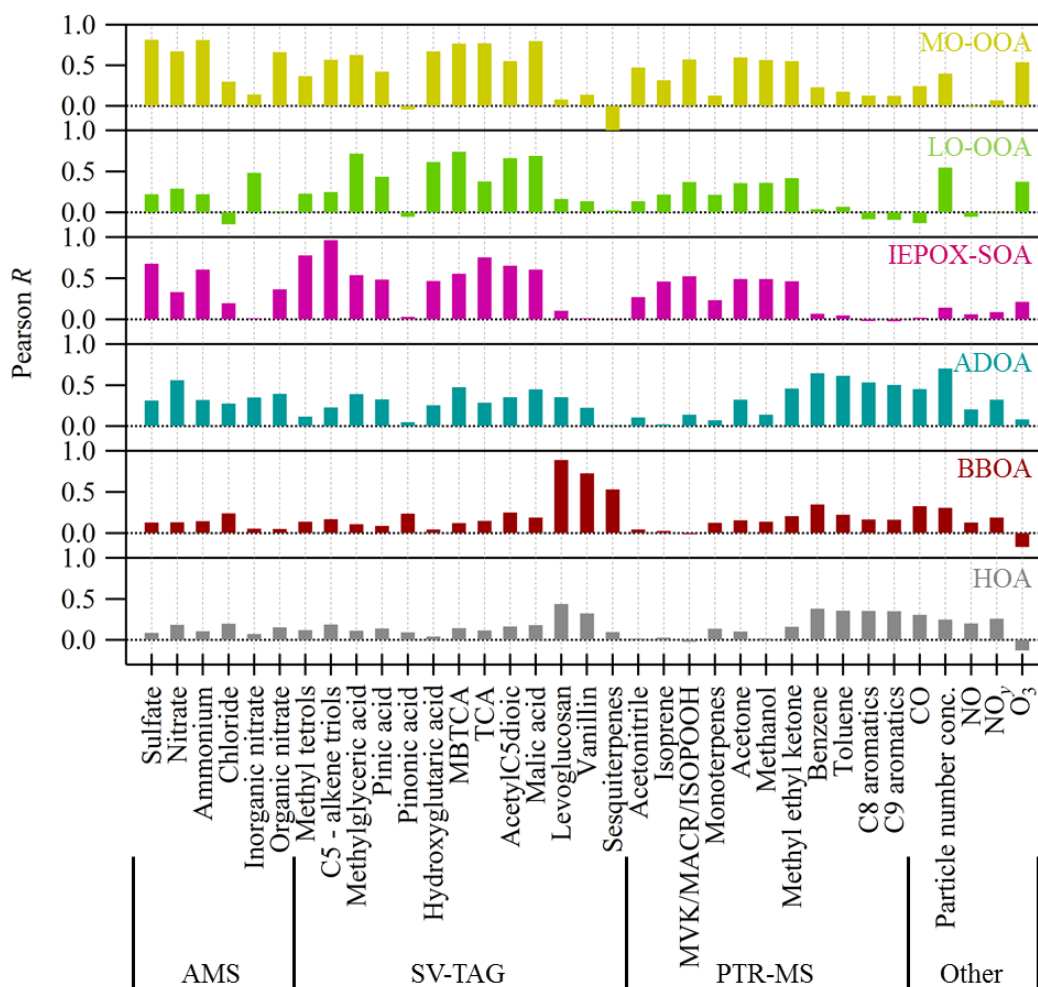


Figure 5

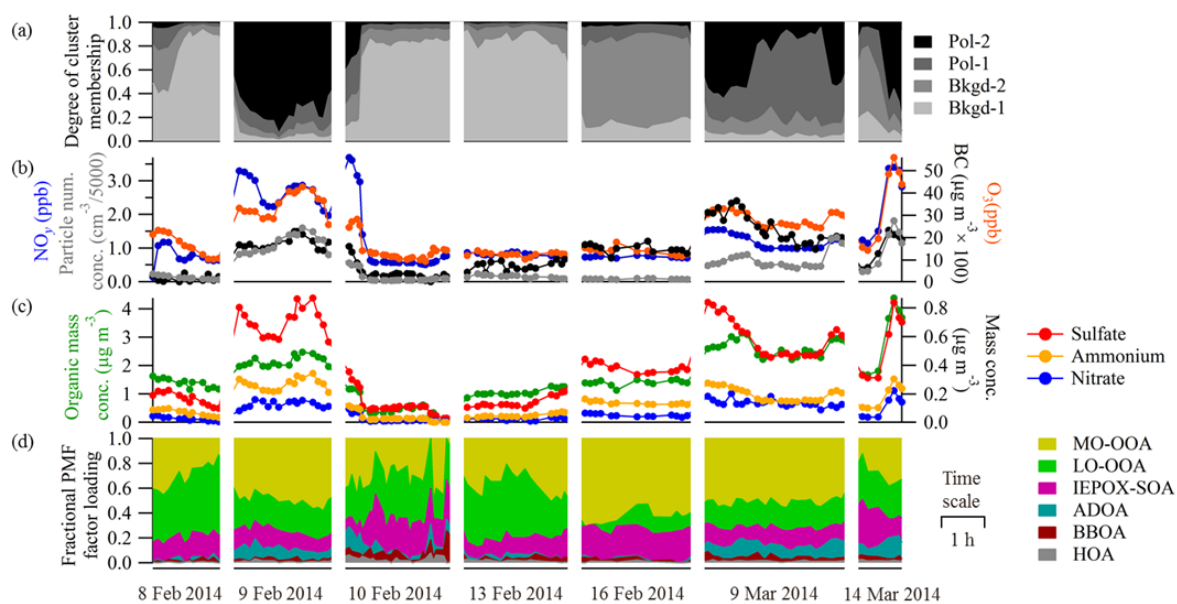


Figure 6

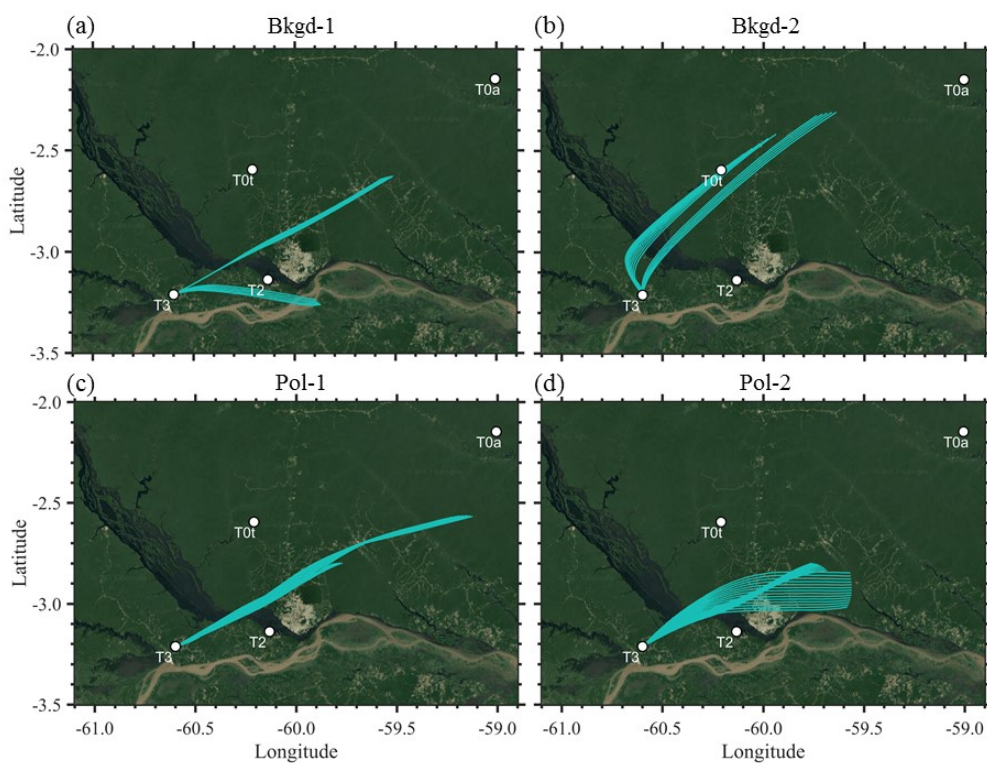


Figure 7

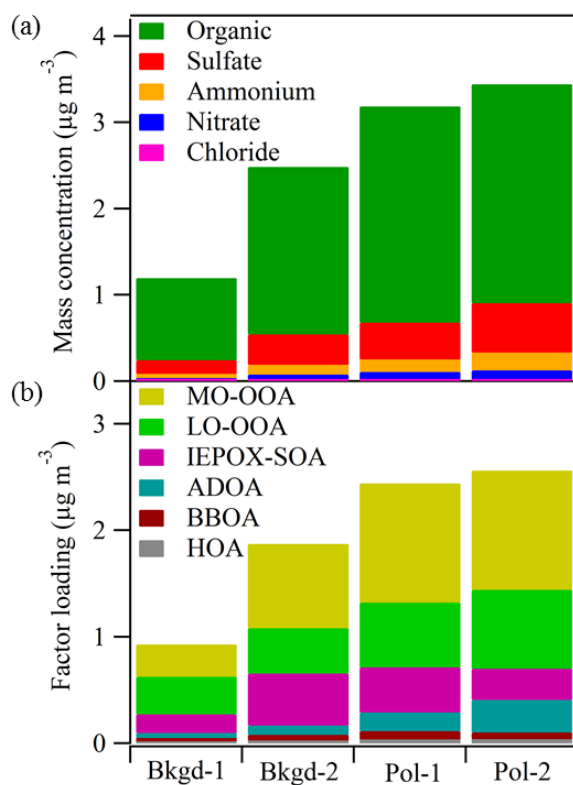


Figure 8

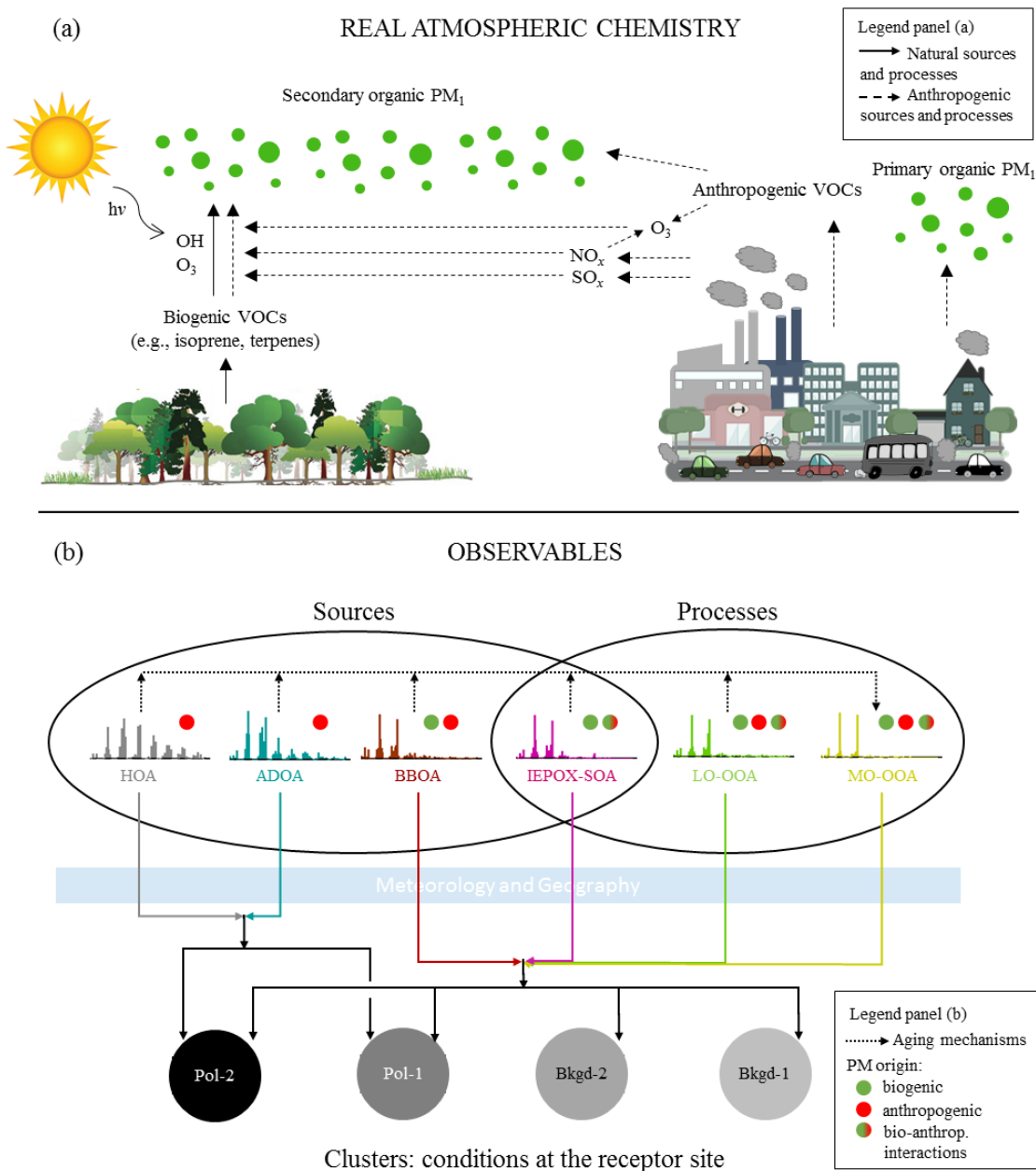


Figure 9