

Response to Report #2

Reviewer comments are in **bold**. Author responses are in plain text. Excerpts from the manuscript are in *italics*. Modifications to the manuscript are in *blue italics*.

I thank the authors for updating the manuscript, I think it has improved a lot and I only have a few additional comments.

Thank you.

In line 67, the authors state: A separate publication is planned for IOP2, 67 corresponding to the dry season period of August 15 to October 15, when biomass burning 68 emissions were prevalent (de Sá et al., in preparation). I think that this sentence here is not needed as it doesn't add any additional valuable information to the presented manuscript.

This sentence was removed.

The Figures are really nice and the presentation of the results is very well done. I am missing a proper description of Figure 5 in the text though. Even a few sentences with the key points of what we see in Figure 5 would be very useful already.

To address this comment, the following adjustments were made to the text:

Line 224:

The scientific interpretation of each factor was based on a combination of (i) the characteristics of the factor profile (i.e., “mass spectrum”), as referenced to a worldwide database of AMS spectra and PMF analyses (Ulbrich et al., 2009c; Ulbrich et al., 2009b, 2009a), and (ii) the temporal correlations between the factor loading and other co-located measurements (Figure 5).

Line 233:

Figure 5 shows that the correlations of factor loadings with external measurements of gas- and particle-phase species support this interpretation, as detailed in the following discussion for each factor.

My other comment is related to Figure 4: I agree with the other referee that it contains a lot of information and is hard to digest, but I think the authors are giving very good guidance through it in the text. I am not fully convinced that panel (c) in Figure 4 is really necessary. I am not sure how much it adds to the information already presented in the other panels and in Figure 5. I understand if the authors want to keep it as it is also.

We thank the referee for this comment. We agree that Figure 4c is not essential for the understanding of the paper. It does however add value to the presentation, and we therefore chose to keep it, specifically for the following two reasons: (A) completeness of the presentation of results from the PMF analysis, which consist of factor profiles (Figure 4a) and loading time series (Figure 4c), and (B) visualization of some important correlations, which in Figure 5 are represented only as numbers.

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 air mass 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., 2018). In the northeastern USA, de Gouw et
16 al. (2005) showed that concentrations of organic particulate matter (PM) correlated well with
17 anthropogenic tracers, yet the concentrations of the anthropogenic precursors were insufficient to
18 explain the observed PM concentrations. In the southeastern USA, radioisotope analysis of
19 organic PM determined that 70% to 80% of the carbon mass had a modern origin even as
20 correlations were observed between SOM mass concentrations and anthropogenic VOC and CO
21 concentrations (Weber et al., 2007). This finding and those of further field studies in the region
22 together suggested that the organic PM was produced mainly from biogenic VOCs (BVOCs) yet
23 modulated by anthropogenic emissions of NO_x and SO₂ (Hu et al., 2015; Xu et al., 2015a; Xu et

24 al., 2015b; Zhang et al., 2018). In the western USA, ground and aircraft measurements observed
25 the highest organic PM increases when air masses having high BVOC concentrations intercepted
26 anthropogenic emissions (Setyan et al., 2012; Shilling et al., 2013). A metastudy for several
27 locations in the USA concluded that air downwind of urban areas had increased organic PM
28 concentrations due to the photochemical production of SOM (De Gouw and Jimenez, 2009).
29 Models have estimated that 50% to 70% of the biogenic SOM mass concentration in several
30 locations is modulated by anthropogenic emissions (Carlton et al., 2010; Heald et al., 2011;
31 Spracklen et al., 2011). In addition, global-scale modeling studies have estimated an increase of
32 20% to 60% in the global annual mean SOM concentration relative to the pre-industrial period
33 (Tsigaridis et al., 2006; Hoyle et al., 2009).

34 Many possible mechanisms may contribute to the effects of anthropogenic emissions on
35 increased SOM production, including changes in gas-particle partitioning, new particle
36 production and growth, and particle acidity. Changes in the concentrations of nitrogen oxides,
37 however, should be regarded as a critical factor (Hoyle et al., 2011 and references therein).
38 Different NO_x regimes favor distinct gas-phase oxidation pathways, leading to different
39 oxidation products and particle yields, as evidenced in isoprene photo-oxidation (Kroll et al.,
40 2005, 2006; Hallquist et al., 2009; Worton et al., 2013; Liu et al., 2016b; Liu et al., 2016a).
41 Isoprene accounts for half of global BVOC mass emissions, and tropical forests are responsible
42 for about 80% of terpenoid emissions (Guenther et al., 2012). In the Amazon, isoprene is the
43 dominant BVOC emitted by vegetation and is estimated to contribute to about half of the organic
44 PM concentrations under background conditions (Kuhn et al., 2010; Chen et al., 2015; Yáñez-
45 Serrano et al., 2015). Under HO₂-dominant conditions (i.e., low NO_x), isoprene epoxydiols
46 (IEPOX) are produced in the gas phase and, through heterogenous reactions involving sulfate,

47 PM is produced (Paulot et al., 2009; Surratt et al., 2010). Depending on the relative importance
48 of increased concentrations of sulfate and NO_x associated with pollution in a given region, an
49 enhancement or suppression of IEPOX-derived PM production relative to background conditions
50 may occur (Xu et al., 2015a; de Sá et al., 2017). As part of GoAmazon2014/5, de Sá et al. (2017)
51 demonstrated that PM derived from IEPOX generally decreased under polluted compared to
52 background conditions downwind of Manaus. Nitrogen oxides in the pollution plume suppressed
53 the production of isoprene hydroxyhydroperoxides (Liu et al., 2016b), leading to a decrease in
54 the production of gas phase IEPOX and consequently of IEPOX-derived PM (de Sá et al., 2017).

55 Amazonia, the largest tropical forest in the world and a large global source of SOM, is
56 comparatively understudied relative to northern mid-latitude regions, especially with respect to
57 the influence of pollution on the SOM lifecycle (Martin et al., 2010b). Manaus, a city of over
58 two million people in the central Amazon, continuously releases an urban plume into an
59 otherwise mostly unperturbed region (Kuhn et al., 2010; Martin et al., 2017). The region
60 downwind of Manaus, especially in the wet season in the absence of regional fires (Artaxo et al.,
61 2013), offers a natural laboratory for the investigation of biogenic-anthropogenic interactions and
62 the resulting consequences for the amount and composition of PM in the region.

63 The present study investigates the influences of urban pollution on the concentration and
64 composition of fine particles in central Amazonia, focusing on organic PM and its several
65 component classes. The analysis employs data sets collected in the wet season from February 1
66 to March 31, 2014, corresponding to the first Intensive Operating Period (IOP1) of the
67 GoAmazon2014/5 experiment (Martin et al., 2016). ~~A separate publication is planned for IOP2,~~
68 ~~corresponding to the dry season period of August 15 to October 15, when biomass burning~~
69 ~~emissions were prevalent (de Sá et al., in preparation).~~ Herein, positive-matrix factorization

70 (PMF) of organic mass spectra measured by aerosol mass spectrometry (AMS) in conjunction
71 with a clustering analysis of pollution indicators by Fuzzy c-means are employed to investigate
72 the changes in particle concentration and composition associated with the influence of urban
73 pollution downwind of Manaus.

74 **2. Methodology**

75 **2.1 Site description**

76 The primary site of this study, named “T3” (3.2133 °S, 60.5987 °W), was located 70 km
77 to the west of Manaus, Brazil, in central Amazonia (Martin et al., 2016). The site was situated in
78 a pasture of 2.5 km × 2 km surrounded by forest. Based on modeled flow trajectories of the
79 pollution plume, the T3 site intercepted the plume about 40% of the time (Martin et al., 2017).
80 Auxiliary sites “T0a” and “T0t”, served as references for background conditions in relation to T3
81 (Figure S1). Site T0a (2.1466 °S, 59.0050 °W) refers to the Amazonian Tall Tower Observatory
82 (ATTO; Andreae et al., 2015), located 150 km to the northeast of Manaus. Site T0t (2.5946°S,
83 60.2093°W) was situated 60 km to the north-northwest of Manaus in the Cuieiras Biological
84 Reserve (“ZF2”) and refers to tower “TT34”, established in 2008 for the AMAZE-08 experiment
85 (Martin et al., 2010a). The T0 sites were typically upwind of Manaus, with only occasional
86 transport of pollution to these sites (Andreae et al., 2015; Chen et al., 2015). Auxiliary site “T2”
87 served as a reference for polluted conditions. This site was located just across the Rio Negro
88 (3.1392°S, 60.1315°W), 8 km from the southwestern edge of Manaus and typically downwind of
89 urban emissions during the daytime.

90 **2.2 Aerosol Mass Spectrometry**

91 Characterization of the atmospheric PM was obtained using a High-Resolution Time-of-
92 Flight Aerosol Mass Spectrometer (hereafter AMS; Aerodyne, Inc., Billerica, Massachusetts,

93 USA; DeCarlo et al., 2006; Canagaratna et al., 2007). Detailed aspects of the AMS operation in
94 GoAmazon2014/5 were presented in de Sá et al. (2017). In brief, the instrument was housed
95 within a temperature-controlled research container, and the inlet to the instrument sampled from
96 5 m above ground level. Ambient measurements for this study were obtained every other 4 min.
97 The other 4 min were used for analysis of output from an oxidation flow reactor as presented in
98 Palm et al. (2018).

99 Data analysis was performed using *SQUIRREL* (1.56D) and *PIKA* (1.14G) of the AMS
100 software suite (Sueper and collaborators; DeCarlo et al., 2006). Organic, sulfate, ammonium,
101 nitrate, and chloride PM mass concentrations were quantified. “Sulfate” and “nitrate”
102 concentrations reported by the AMS may include contributions from both organic and inorganic
103 species (Farmer et al., 2010; Liao et al., 2015). Organic and inorganic nitrate concentrations were
104 estimated based on the ratio of NO_2^+ to NO^+ signal intensity, as described in Section S2 (Fry et
105 al., 2009; Farmer et al., 2010; Fry et al., 2013). The organic elemental ratios, O:C and H:C, were
106 calculated following the methods of Canagaratna et al. (2015).

107 **2.3 Auxiliary measurements and datasets**

108 In complement to the AMS data set, the analysis herein incorporated auxiliary gas and
109 particle measurements collected during IOP1 at T3 (Martin et al., 2016). Mass concentrations of
110 molecular and tracer organic species in the gas and particle phases were measured by a Semi-
111 Volatile Thermal Desorption Aerosol Gas Chromatograph (SV-TAG) at a time resolution of one
112 hour (Isaacman-VanWertz et al., 2016). Concentrations of volatile organic compounds (VOCs)
113 were measured by a Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-
114 MS; Liu et al., 2016b). In the Mobile Aerosol Observing System (MAOS) of the ARM Climate
115 Research Facility (ACRF; Martin et al., 2016), measurements of NO_y were made using a

116 chemiluminescence-based instrument (Air Quality Design). The raw NO_y measurements (10-s
117 resolution) were averaged across 30-min intervals to dampen the influence of brief local events.
118 In addition, ozone concentrations were measured by an ultraviolet photometric analyzer (Thermo
119 Fisher, model 49i, Ozone Analyzer). Particle number concentrations were measured by a
120 Condensation Particle Counter (TSI, model 3772). Black carbon (BC) concentrations were
121 measured both by a 7-wavelength aethalometer (Magee Scientific, model AE-31) and a Single
122 Particle Soot Photometer (SP2; Droplet Measurement Techniques). The two datasets differed by
123 a factor of up to three in absolute mass concentrations, as observed in other studies (Subramanian
124 et al., 2007; Cappa et al., 2008; Lack et al., 2008), but they agreed well in the temporal trend.
125 The analysis herein for BC is thus restricted to the temporal trends. Wind direction, solar
126 irradiance, and precipitation rate were measured by the ARM Mobile Facility (AMF-1), which
127 was also part of the ACRF.

128 Additional measurements from T0a, T0t, and T2 were also used in the analysis. At T2,
129 non-refractory particle composition and concentration were measured by an Aerosol Chemical
130 Speciation Monitor (ACSM) during the wet season from March 9 to April 30, 2014 (Cirino et al.,
131 submitted). ACSM measurements were made at T0a during the wet season of 2015, from
132 February 1 to March 31 (Andreae et al., 2015). Further AMS datasets collected at T0t during the
133 wet season of 2008 (February 6 to March 22; AMAZE-08 campaign) were used in the analysis
134 (Chen et al., 2009; Schneider et al., 2011).

135 **2.4 Air mass backtrajectories and precipitation rates**

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

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

140 Trajectory steps were calculated for every 12 min.

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

152 **3. Results and discussion**

153 **3.1 Fine-mode PM composition**

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

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

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

173 The diel trends of organic and sulfate mass concentrations as well as their variabilities
174 across the four sites are shown in Figure 2. Lines represent means, solid markers show medians,
175 and boxes span interquartile ranges. Organic mass concentrations and associated variability were
176 higher at the T3 site compared to the T0 sites, markedly so in the afternoon hours. The greater
177 variability at T3 is in line with a time-varying influence of Manaus emissions. This influence
178 waxes and wanes with small northerly or southerly shifts of the trade winds as well as other
179 changes in regional circulation tied to daily meteorology (dos Santos et al., 2014; Martin et al.,
180 2017). The higher afternoon mass concentrations at T3 can be attributed to a combination of (i)
181 an oxidant-rich, sunlight-fed plume that increases the production rate of secondary PM and (ii)
182 faster near-surface winds during the day that transport PM from Manaus to T3 with less loss by
183 deposition and dispersion compared to more-stagnant air at night. Among all sites, the T2
184 observations had both the highest average organic mass concentrations and the largest

185 variability. These characteristics of the T2 dataset can be explained by a combination of (i) the
186 proximity of the site to Manaus, (ii) the rapid and 180° changes in wind direction caused by the
187 intersection of the trade winds with a local river breeze (dos Santos et al., 2014), and (iii)
188 possible contributions of emissions from brick kilns, located mostly southwest of the site,
189 especially during night time (Martin et al., 2016; Cirino et al., submitted).

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

196 Overall, the organic PM₁ at T3 was highly oxidized, as indicated by the position of gray
197 markers in the plot of Figure 3. By contrast, the blue markers represent the dataset collected at
198 T2 during the same period. The datasets encompass all times of days and all conditions at both
199 sites. Datasets from background sites collected in different years are shown in Figure S2. Points
200 to the upper left represent more oxidized material, and points to the lower right represent less
201 oxidized material (Ng et al., 2011a). The comparison depicted in Figure 3 indicates the effects
202 of the plume over the 4 h of transport from T2 to T3, which were investigated in detail by Cirino
203 et al. (submitted). The plot suggests that the enhanced oxidative cycle associated with higher OH
204 and O₃ concentrations in the pollution plume might cause (i) the production of highly oxidized
205 SOM, from both biogenic and anthropogenic precursors including aromatic compounds
206 (Chhabra et al., 2011; Lambe et al., 2011), and (ii) the accelerated oxidative processing of pre-
207 existing organic PM by OH and O₃ (Martin et al., 2017). The implication is that the emissions

208 from Manaus can significantly affect the mechanisms that produce or modify fine-mode PM over
209 the tropical forest.

210 **3.2 Characterization of organic PM by positive-matrix factorization**

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

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

223 The scientific interpretation of each factor was based on a combination of (i) the
224 characteristics of the factor profile (i.e., “mass spectrum”), as referenced to a worldwide database
225 of AMS spectra and PMF analyses (Ulbrich et al., 2009c; Ulbrich et al., 2009b, 2009a), and (ii)
226 the temporal correlations between the factor loading and other co-located measurements ([Figure](#)
227 [5](#)). Three factors interpreted as primary emissions of organic PM were resolved: an
228 anthropogenic-dominated factor (hereafter, “ADOA”), a biomass burning factor (“BBOA”), and
229 a fossil-fuel hydrocarbon-like factor (“HOA”). Three factors interpreted as secondary production
230 and processing were resolved: a more-oxidized oxygenated factor (“MO-OOA”), a less-oxidized

231 oxygenated factor (“LO-OOA”), and an isoprene epoxydiols-derived factor (“IEPOX-SOA”).

232 Figure 5 shows that the correlations of factor loadings with external measurements of gas- and
233 particle-phase species support this interpretation, as detailed in the following discussion for each
234 factor.

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

254 The BBOA factor profile was characterized by distinct peaks of $C_2H_4O_2^+$ (m/z 60) and
255 $C_3H_5O_2^+$ (m/z 73), as shown in Figure 4a. These peaks can be attributed to levoglucosan and
256 other anhydrous sugars that result from biomass pyrolysis (Schneider et al., 2006; Cubison et al.,
257 2011). Correlations of the factor loadings with the mass concentrations of levoglucosan and
258 vanillin ($R > 0.8$) measured by SV-TAG corroborate the association with biomass burning
259 (Figure 4c; [Figure 5](#)). The BBOA factor of this study had an O:C ratio of 0.61 ± 0.08 (Table 1),
260 which is consistent with large contributions from levoglucosan (O:C of 0.83) and similar sugars.
261 The factor loading on average accounted for 9% of the organic PM_{10} mass concentration (Figure
262 4a, inset). This result is consistent with the low incidence of fires in the Amazon during the wet
263 season (Martin et al., 2016). The BBOA factor loading typically decreased during the day
264 (Figure 4b), which is suggestive of the dilution of local sources during the development of the
265 PBL rather than long-range transport. Emissions from local fires around T3, including trash and
266 tree burning, as well as from wood-fueled brick kilns along the road from Manaus to T3 might
267 have contributed to this factor.

268 The ADOA factor profile, distinguished prominently by the $C_7H_7^+$ ion at m/z 91, also had
269 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
270 from many sources, including biogenic and anthropogenic emissions (Ng et al., 2011b). In itself,
271 m/z 91 therefore does not serve as a tracer for a specific source or process without consideration
272 of the atmospheric context. Factors having a characteristic m/z 91 peak (usually labeled “91 fac”)
273 typically have been associated with biogenic emissions (Robinson et al., 2011; Budisulistiorini et
274 al., 2015; Chen et al., 2015; Riva et al., 2016). The ADOA factor profile of this study, however,
275 more strongly resembles the mass spectra previously reported for PM emissions from cooking
276 activities (Lanz et al., 2007; Mohr et al., 2012) than those from “91 fac” (Section S1; Figure S5).

277 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
278 reported for several factors representing primary cooking emissions and is well above the range
279 of 0.8 to 1.4 reported for factors associated with traffic emissions, i.e., HOA (Mohr et al., 2012
280 and references therein; Hu et al., 2016). Even though the ADOA factor profile has a large
281 contribution from non-oxygenated ions, similar to the HOA factor and consistent with a
282 dominance by primary emissions, it also contains considerable signal from oxygenated ions,
283 resulting in a relatively higher O:C of 0.40 ± 0.05 (Table 1). The factor loading on average
284 accounted for 13% of the organic PM_{10} mass concentration (Figure 4a, inset). The factor loading
285 decreased as the PBL developed during the day, consistent with dominant non-photochemical,
286 primary sources (Figure 4b). Furthermore, there were increases, albeit small, in factor loading at
287 12:00 and 18:00 (local time), suggestive of breakfast-time and lunch-time cooking activities in
288 Manaus based on a transport time of 4 to 6 h between the city and the T3 site (Martin et al.,
289 2016; Cirino et al., submitted). Manaus typically has four rush-hour periods each day from 6:30
290 to 8:00, 12:00 to 13:30, 16:30 to 18:30, and 21:00 to 22:00. Traffic peaking at these hours may
291 therefore also have contributed to the ADOA factor. Correlations between factor loading and
292 external measurements exceeded $R = 0.5$ for many anthropogenic markers, including
293 concentrations of aromatics (e.g., benzene, toluene, and C_8 and C_9 species), carbon monoxide,
294 particle count, and NO_y (Figure 4c, Figure 5). Contributions from secondary processes cannot be
295 ruled out, and it is possible that PM production from anthropogenic VOCs might have also been
296 captured in this factor. Overall, the ADOA factor was interpreted in the present study as an
297 indicator of anthropogenic influence associated with several sources in Manaus, most
298 importantly cooking and possibly traffic emissions.

299 The IEPOX-SOA factor profile had marker ions of $C_4H_5^+$ (m/z 53) and $C_5H_6O^+$ (m/z 82)
300 (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
301 (Table 1). The factor loading on average accounted for 17% of the organic PM_1 mass
302 concentration (Figure 4a, inset). There were high correlations ($R > 0.8$) between factor loadings
303 and concentrations of C_5 -alkenetriols and 2-methyltetrols, which are markers of IEPOX-derived
304 PM, produced by the photo-oxidation of isoprene under HO_2 -dominant conditions (Surratt et al.,
305 2010; Lin et al., 2012; Figure 4c). The increase in factor loading during daytime was consistent
306 with a photochemical source (Figure 4b). There were also correlations between factor loadings
307 and concentrations of sulfate and some acids, such as tricarballic acid (TCA; Figure 5), in
308 agreement with the association of IEPOX-derived PM and sulfate/acidity observed in other
309 studies (Budisulistiorini et al., 2013; Nguyen et al., 2014; Kuwata et al., 2015). Overall, this
310 factor was therefore interpreted as representative of PM produced from isoprene photo-oxidation
311 under HO_2 -dominant conditions. The effects of urban pollution on the loadings of this factor
312 were the focus of a previous publication (de Sá et al., 2017).

313 The two remaining factors, LO-OOA and MO-OOA, were also associated with secondary
314 atmospheric processes. The LO-OOA and MO-OOA factors had O:C ratios of 0.72 ± 0.10 and
315 1.09 ± 0.17 , respectively. The LO-OOA factor was characterized by the greatest ratio of signal
316 intensity of the $C_2H_3O^+$ ion (m/z 43) to that of the CO_2^+ ion (m/z 44) (Figure 4a) compared to all
317 other factors. This factor is usually attributed to lower-generation, less-oxidized, higher-volatility
318 secondary organic PM (Jimenez et al., 2009). By comparison, the MO-OOA factor profile had
319 the strongest CO_2^+ (m/z 44) peak among all factors (Figure 4a). This factor is usually attributed
320 to higher-generation, more-oxidized, less-volatile secondary organic PM or extensively oxidized

321 primary PM of any type that has resided in the atmosphere for several days or more (Jimenez et
322 al., 2009).

323 The LO-OOA factor loading on average accounted for 25% of the organic PM₁ mass
324 concentration (Figure 4a, inset). The factor loading correlated better with the estimated
325 concentrations of inorganic nitrate than with organic or total nitrate (Figure 5; Section S2 and
326 Figure S6), which is consistent with the interpretation of the higher volatility associated with this
327 factor (Jimenez et al., 2009; Zhang et al., 2011). The factor loading also correlated ($R > 0.7$) with
328 the concentrations of 2-methylglyceric acid and methyl-butyl-tricarboxylic acid (MBTCA),
329 which are products of isoprene and monoterpene oxidation, respectively, under NO-dominant
330 conditions (Figure 4c; Figure 5). The factor loading increased starting at 9:00 (local time) and
331 peaked in the afternoon hours (Figure 4b). This diel trend, tied to the sunlight cycle, tracked the
332 typical daily emission patterns of isoprene and monoterpenes from the surrounding forest
333 (Yáñez-Serrano et al., 2015). The absence of a sharp decline at sunset and the higher variability
334 at nighttime may also indicate a contribution by terpene ozonolysis. For these several reasons,
335 the LO-OOA factor was interpreted herein as secondary organic PM produced mostly within
336 several hours of observations by many possible pathways, including (i) the photo-oxidation of
337 isoprene along non-IEPOX pathways, (ii) the photo-oxidation of terpenes and other biogenic
338 VOCs along both HO₂- and NO-dominant reaction pathways, (iii) the ozonolysis of terpenes, and
339 (iv) the possible production of SOM from anthropogenic emissions from Manaus.

340 The MO-OOA factor loading on average accounted for 30% of the organic PM₁ mass
341 concentration (Figure 4a, inset). The factor loading correlated ($R > 0.7$) with the mass
342 concentrations of several particle-phase carboxylic acids as well as the concentrations of sulfate,
343 ammonium, and ozone (Figure 5). The time series of malic acid and ozone concentrations are

344 shown alongside the MO-OOA factor loadings in Figure 4c. Malic acid is a highly oxidized
345 compound (O:C of 1.25), which may have many different sources (Röhrl and Lammel, 2002; van
346 Pinxteren et al., 2014). The MO-OOA factor loading increased starting at 8:00 (local time;
347 sunrise was at 6:00) and peaked between 10:00 and 16:00, with a large variability in the factor
348 loadings in the afternoon hours among different days (Figure 4b). The afternoon increase and
349 day-to-day variability were consistent with strong but variable photochemical processing leading
350 to further oxidation of organic PM during the day, depending on daily weather. The high O:C of
351 1.09 ± 0.17 could also be indicative of production of PM from aromatic compounds emitted from
352 Manaus (Chhabra et al., 2011; Lambe et al., 2011). Overall, this factor was interpreted to
353 represent highly oxidized PM from multiple processes. Species initially associated with HOA,
354 BBOA, ADOA, IEPOX-SOA, and LO-OOA factors may converge after sufficient atmospheric
355 oxidation to become represented by the MO-OOA factor (Jimenez et al., 2009; Palm et al.,
356 2018).

357 **3.3 Shifts in PM with anthropogenic influences**

358 **3.3.1 Cluster Analysis**

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

367 The scope of the clustering analysis was restricted to afternoon time points for which ten-
368 hour air mass backtrajectories did not intersect significant precipitation and for which solar
369 irradiance at T3 averaged over the previous 4 h was higher than 200 W m^{-2} (Section S3). This
370 scope aimed at capturing fair-weather conditions and thereby minimizing the role of otherwise
371 confounding processes, such as boundary layer dynamics and wet deposition. The elimination of
372 trajectories having precipitation, however, should not be regarded as fully accurate given the
373 uncertainties in the HYSPLIT trajectories. The scoped dataset spanned 24 afternoons.

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

383 Two clusters of data were interpreted as “background” and labeled “Bkgd-1” and “Bkgd-
384 2”. They were characterized by $\text{NO}_y < 1 \text{ ppb}$, ozone $< 20 \text{ ppb}$, and particle number $< 1200 \text{ cm}^{-3}$
385 (Table 2; Figure 6). The two clusters differed especially in that Bkgd-2 had significantly larger
386 concentrations of sulfate and black carbon. A comparison of the datasets of Feb 13
387 (predominantly Bkgd-1) and Feb 16 (predominantly Bkgd-2) in Figure 6 highlights these
388 differences. Concentrations of sulfate and black carbon were 0.15 and $0.10 \mu\text{g m}^{-3}$, respectively,
389 on Feb 13, compared to 0.40 and $0.15 \mu\text{g m}^{-3}$ on Feb 16. The backtrajectories associated with

390 Bkgd-1 had both northeasterly and southeasterly components. The wind fields, out of line with
391 the trade winds, may suggest passage through recent weather systems and may imply wet
392 deposition, which in turn might explain lower gas and particle concentrations (Table 2). These
393 recent weather systems might not have been excluded from the scoped dataset because of
394 inaccuracies in the intersections of the backtrajectories with precipitation data, as discussed
395 above, or because they were more distant than captured by the 10-h backtrajectories. Consistent
396 with this hypothesis, the centroid value calculated for the 4-h averaged solar irradiance at T3
397 (Section 3.3.2) was lower for Bkgd-1 (400 W m^{-2}) compared to the other clusters (600 W m^{-2}),
398 suggesting an association of Bkgd-1 with overcast conditions. By comparison, the
399 backtrajectories associated with Bkgd-2 were predominantly from the northeast, coming from the
400 direction of the T0t and T0a sites (Figure 7), in line with the dominant trade winds of the wet
401 season. The air masses of Bkgd-2 may have experienced less wet deposition and may represent
402 more extensive atmospheric oxidation than those of Bkgd-1. They may also have carried PM
403 contributions from out-of-basin sources, which would be consistent with the higher sulfate and
404 black carbon concentrations of Bkgd-2 compared to Bkgd-1 (Chen et al., 2009; Pöhlker et al.,
405 2017).

406 Two other clusters were interpreted as “polluted” and labeled “Pol-1” and “Pol-2”. They
407 were characterized by concentrations of $\text{NO}_y > 1 \text{ ppb}$, ozone $> 20 \text{ ppb}$, and particle number $>$
408 1200 cm^{-3} (Table 2; Figure 6). The dataset of the afternoon of Mar 9 illustrates a shift in
409 dominance from Pol-2 to Pol-1 (Figure 6). Although Pol-1 and Pol-2 both have high
410 concentrations of sulfate and other pollutants, they differ in the extent of those high
411 concentrations. The explanation may be that these clusters represent different source regions.
412 Pol-1 may be associated with emissions from the northern region of Manaus, and Pol-2 may be

413 associated with emissions from the southern region of Manaus. Industry, power production, and
414 oil refineries are concentrated in the southeastern region of Manaus (Figure S9; Medeiros et al.,
415 2017). Population density and commercial activity is concentrated in the southwestern portion of
416 the city where downtown is located (Figure S10). Aircraft observations show that concentrations
417 of sulfate as well as other pollutants are higher in the urban outflow from the southern compared
418 to the northern region of Manaus (Figure S10). Directional plots of SO₂ and particle number
419 concentrations observed at the T2 site further demonstrate the heterogeneity in Manaus
420 emissions (Figure S10). This hypothesis of a geographical difference in source regions
421 qualitatively aligns with the differences in backtrajectories characteristic of times dominated by
422 Pol-1 and Pol-2 (Figure 7). This interpretation does imply, however, that the backtrajectories
423 may have a 20° inaccuracy. Such inaccuracy is reasonable for the application of HYSPLIT
424 modeling in this region given (i) the absence of surface weather stations and (ii) the relatively
425 large scale of input wind fields (i.e., 50 km) compared to the scale of modeling (i.e., 70 km from
426 T3 to Manaus and a city cross section of 20 km).

427 **3.3.2 Comparison of PM among clusters**

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

434 The NR-PM₁ mass concentrations increased by 25% to 200% in clusters Pol-1 and Pol-2
435 compared to clusters Bkgd-1 and Bkgd-2 (Figure 8a). Increases in sulfate and associated

436 ammonium concentrations had a smaller yet non-negligible role in the increased PM₁ mass
437 concentrations. Sources of sulfate other than Manaus sustain relatively high concentrations in the
438 Amazon basin, as represented by the Bkgd-2 cluster (Chen et al., 2009; de Sá et al., 2017).
439 Compared to these regional background concentrations (i.e., Bkgd-2 cluster), the increases in
440 sulfate concentrations were significant only for air masses associated with the heavily
441 industrialized and densely populated southern region of Manaus (i.e., Pol-2 cluster).

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

458 Concentrations and composition of the Bkgd-2 cluster may therefore represent an extensive
459 geographical footprint.

460 The organic PM concentration and composition associated with the Pol-1 and Pol-2
461 clusters were distinct from those of the Bkgd-1 and Bkgd-2 clusters (Figure 8). The mass
462 concentrations of organic PM were greater by 25% to 150% for Pol-1 and Pol-2. According to
463 the PMF factors (Figure 8b), the larger part of this increase in organic PM between the
464 background and polluted clusters was tied to the production of secondary organic PM, although
465 primary emissions also contributed significantly. By comparison, for both Bkgd-1 and Bkgd-2
466 clusters, contributions by primary emissions were negligible, as indicated by the low summed
467 contribution of factors of primary origin (i.e., ADOA, BBOA, and HOA) to the organic PM₁ (<
468 10%). For Pol-1 and Pol-2, the ADOA factor loading on average accounted for 10% of the
469 organic mass concentration at T3, serving as a strong marker of Manaus pollution. A comparison
470 of February 9 and March 9 with February 13 and 16 illustrates these findings (Figure 6d).

471 In regard to secondary organic PM, the IEPOX-SOA factor loading decreased by almost
472 50% under polluted compared to background conditions. de Sá et al. (2017) attributed this
473 decrease to the suppression of IEPOX production by elevated NO concentrations. This
474 suppression typically outweighed possible enhancements in IEPOX uptake and subsequent PM
475 production because of elevated sulfate concentrations. By contrast, the LO-OOA and MO-OOA
476 factor loadings increased by 50% to 100% under polluted conditions. These increases exceeded
477 the decrease in IEPOX-SOA factor loadings, resulting in a net increase of around 100% in mass
478 concentration of secondary organic PM (Figure 8).

479 The shifts in the processes governing the production of secondary organic PM because of
480 increased NO_x, OH, and O₃ concentrations characteristic of the pollution plume were complex

481 and non-linear (Figure 9a). Overall, the oxidation pathways were driven faster. The relatively
482 high $f_{\text{CO}_2^+}$ values and O:C ratios of all factors (Table 1), including those associated with primary
483 emissions, compared to typical values at other locations worldwide (Canagaratna et al., 2015),
484 corroborate this interpretation. Ozone concentrations in the plume increase by 200% to 300%,
485 and hydroxyl radical concentrations increased by 250% or more (Liu et al., accepted). As HO₂-
486 dominant pathways were inhibited, NO-dominant pathways became active. Increased oxidant
487 concentrations may also have promoted additional multigenerational chemistry of semi- or
488 intermediate-volatility species (Robinson et al., 2007). Oxidation of VOCs by aqueous-phase
489 reactions, including in-cloud processing, and oxidation of biomass burning emissions may also
490 have played roles to varying degrees on different days (Carlton et al., 2006; Ervens et al., 2011;
491 Hoyle et al., 2011; Perraud et al., 2012). In addition, when primary and secondary PM mass
492 concentrations increased, further uptake of oxidized semi-volatile molecules could have been
493 thermodynamically favored according to partitioning theory, representing a positive feedback on
494 the increase of mass concentrations (Pankow, 1994; Odum et al., 1996; Carlton et al., 2010).

495 The increase in the LO-OOA and MO-OOA factor loadings associated with Pol-1 and
496 Pol-2 indicates that the net effect of this accelerated and modified chemistry was the quick
497 production and further oxidation of secondary organic PM. Precursors may have included both
498 the wide range of biogenic VOCs as well as contributions from anthropogenic precursors, such
499 as gas-phase species from vehicle emissions or evaporated primary material (Nordin et al., 2013;
500 Presto et al., 2014). The LO-OOA factor loading was important for the polluted conditions of
501 Pol-1 and Pol-2 as well as for the clean conditions of Bkgd-1. This result is not necessarily
502 because of an in-common molecular composition but rather because of an in-common process,
503 i.e., fresh production of secondary organic PM (Figure 9b). Likewise, the MO-OOA factor

504 loading was important for Pol-1, Pol-2, and Bkgd-2 because this factor represented an in-
505 common process, i.e., extensive oxidation (Figure 9b). In the case of the MO-OOA factor, there
506 is also an overall in-common composition characterized by highly oxidized species even as
507 precursor species and subsequent oxidation pathways differed (Jimenez et al., 2009).

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

522 **4. Summary and conclusions**

523 Changes in the concentrations and the composition of fine-mode PM due to the influence
524 of anthropogenic emissions were investigated for the Amazonian wet season. Organic material
525 dominated the submicron composition, consistently representing between 70% and 80% of the
526 PM_{10} mean mass concentration across measurement sites upwind and downwind of Manaus and

527 across different levels of pollution. Absolute mass concentrations, however, varied significantly
528 among sites. Average concentrations downwind of Manaus were 100% to 200% higher than
529 those upwind. Furthest downwind at T3, the organic component was more oxidized compared to
530 that at the T2 site.

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

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

545 As for the secondary processes, the analysis further finds that the pollution plume acted
546 both to shift pathways of secondary organic PM production and to accelerate the atmospheric
547 oxidation of pre-existing organic PM. The oxidation of biogenic PM precursors shifted from
548 HO₂- to NO-dominant pathways, and the oxidation of anthropogenic precursors possibly
549 contributed to increased PM concentrations. The IEPOX-SOA factor loadings were highest for

550 the Bkgd-2 cluster, associated with long-range transport under background conditions, and
551 decreased by almost 50% for the polluted clusters, in line with a shift of isoprene oxidation from
552 HO₂- to NO-dominant pathways. Concomitantly, the LO-OOA factor loading increased by more
553 than 50% for these clusters, suggesting rapid in-plume production of secondary organic PM
554 through several pathways. The LO-OOA factor was also important for the Bkgd-1 cluster,
555 associated with fresh background conditions, which is suggestive of recent biogenic organic PM
556 production. The MO-OOA factor had large relative contributions in the Bkgd-2, Pol-1, and Pol-2
557 clusters, suggestive of significant oxidative processing associated with these clusters. Increases
558 of up to 300% in the MO-OOA factor loadings for Pol-1 and Pol-2 relative to background
559 conditions of Bkgd-1 showed the effects of an accelerated oxidation cycle, leading to highly
560 oxidized PM downwind of Manaus. Based on this and related studies (Liu et al., 2016b; de Sá et
561 al., 2017; Martin et al., 2017), the critical lever seems to be increased concentrations of nitrogen
562 oxides in the pollution plume for both directly shifting and indirectly accelerating mechanisms of
563 secondary organic PM production in central Amazonia during the wet season.

564 The altered composition under anthropogenic influences also affects the physical
565 properties of the PM₁. Bateman et al. (2017), using the results of the PMF analysis presented
566 herein, reported a shift from predominantly liquid PM under background conditions to a
567 considerable presence of non-liquid PM above 50% RH under polluted conditions. Non-liquid
568 PM can have different reactive chemistry from liquid PM (Li et al., 2015; Liu et al., 2018). A
569 linear relationship between the increase in particle rebound fraction and the sum of ADOA,
570 BBOA, and HOA factor loadings had an R^2 of 0.7. The highest individual correlation was with
571 the ADOA factor loading (Bateman, personal communication). In addition, Thalman et al.
572 (2017), also using the PMF results reported herein, concluded that the larger relative contribution

573 of secondary organic material during the daytime compared to the nighttime was the primary
574 driver of the diel trend of higher particle hygroscopicity during the day compared to the night, as
575 tied to cloud condensation nuclei (CCN) properties.

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

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List of Tables

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., 2009c). 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

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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 (Andreae et al., 2015). 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”) (Cirino et al., submitted). 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). The variability of measurements across sites is evaluated in Figure 2.

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. S1). The ordinate scale for the T2-2014 panel is twice that of the other panels. 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.

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. For visualization purposes, the two datasets are plotted separately in panels a and b. 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 PM_{10} 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).

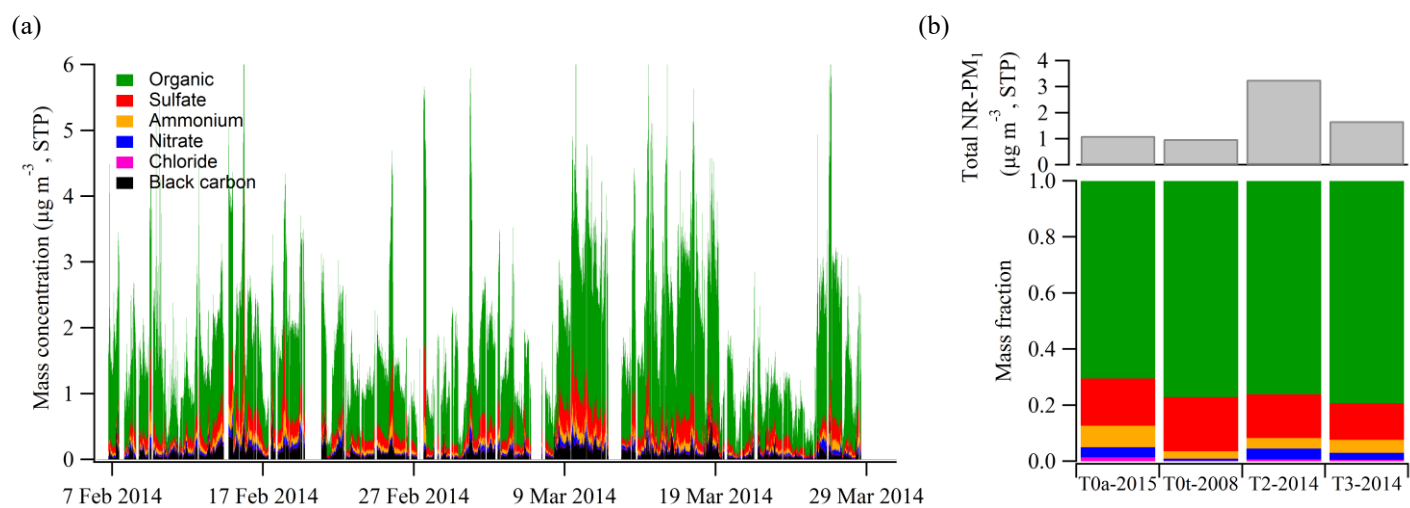


Figure 1

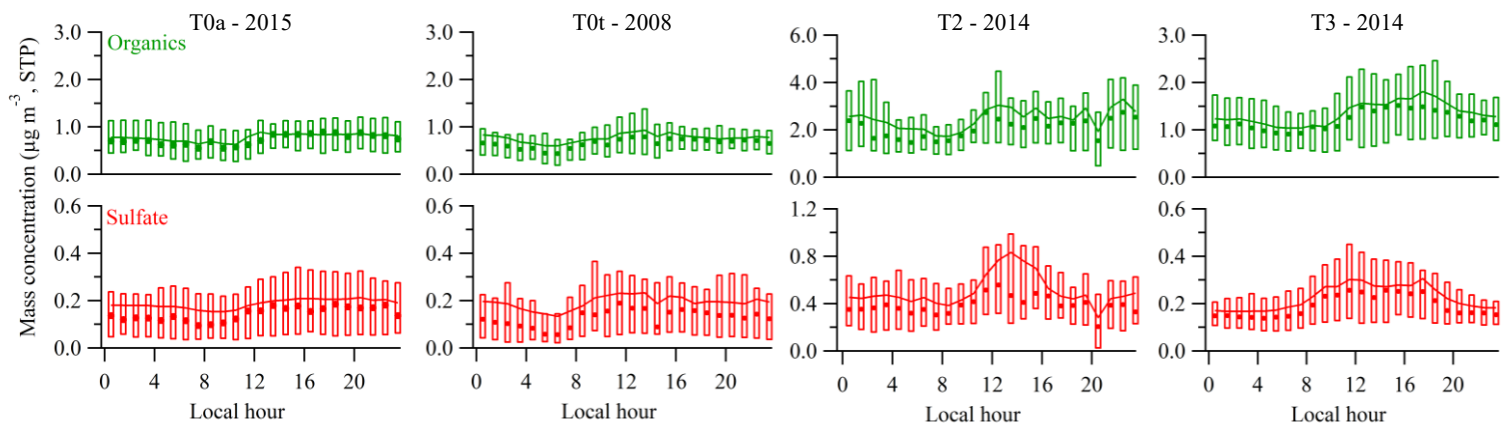


Figure 2

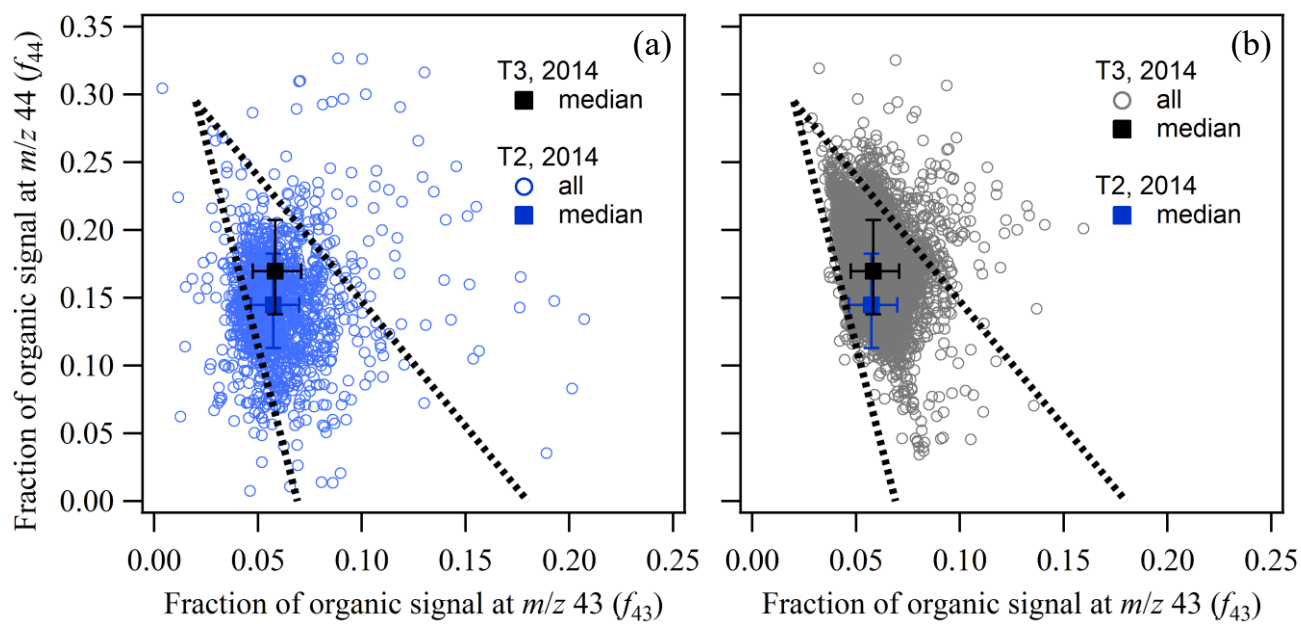


Figure 3

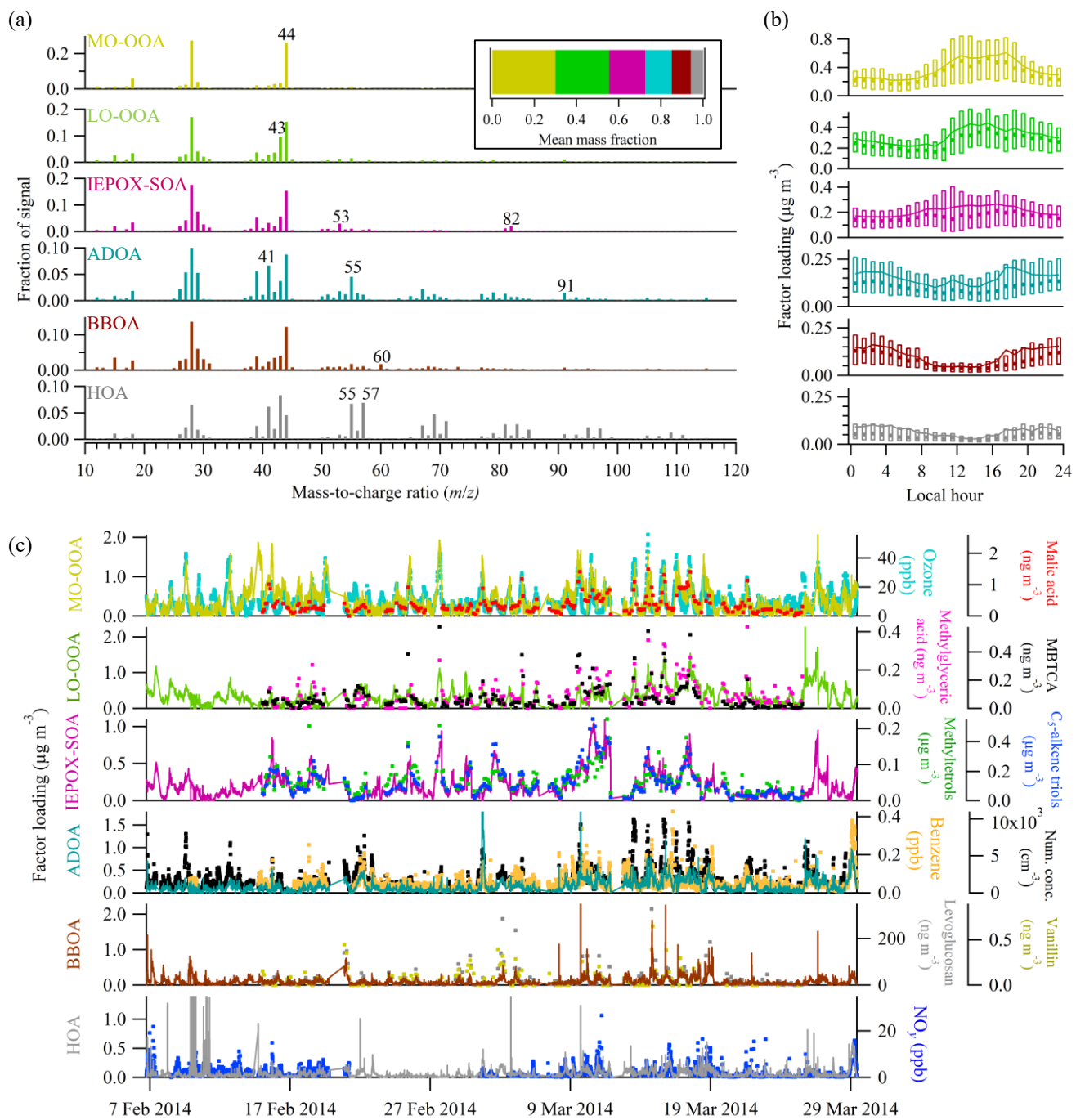


Figure 4

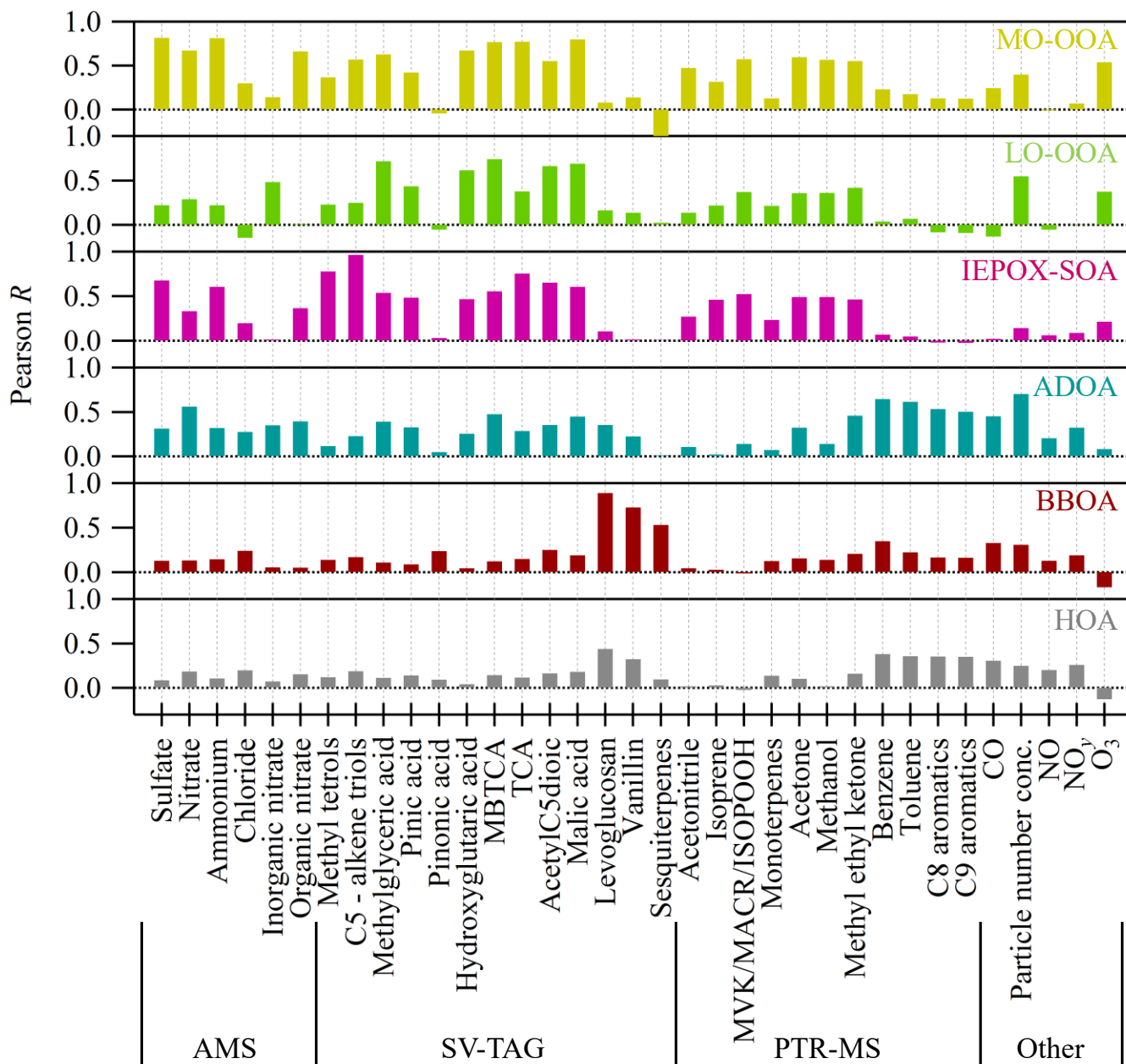


Figure 5

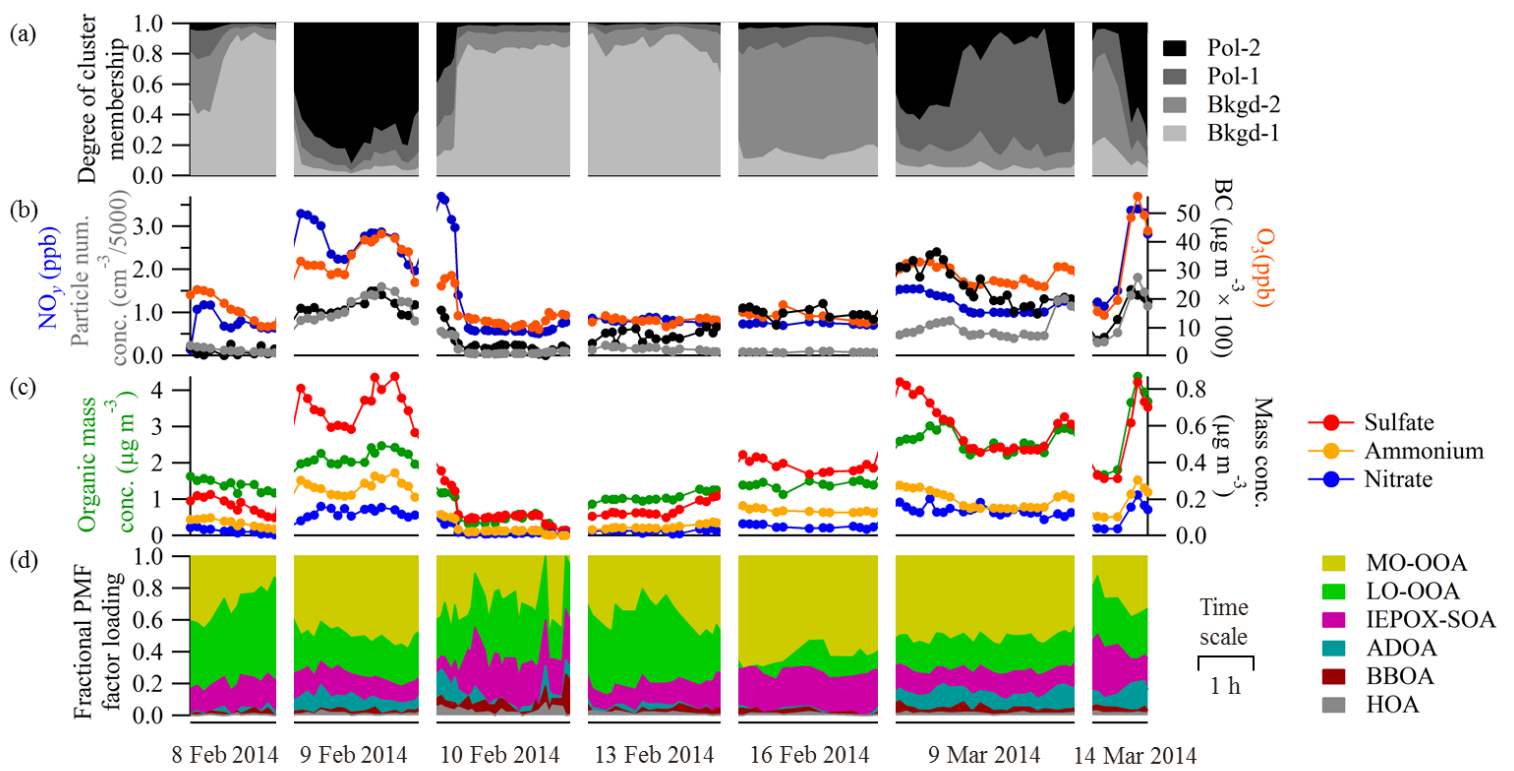


Figure 6

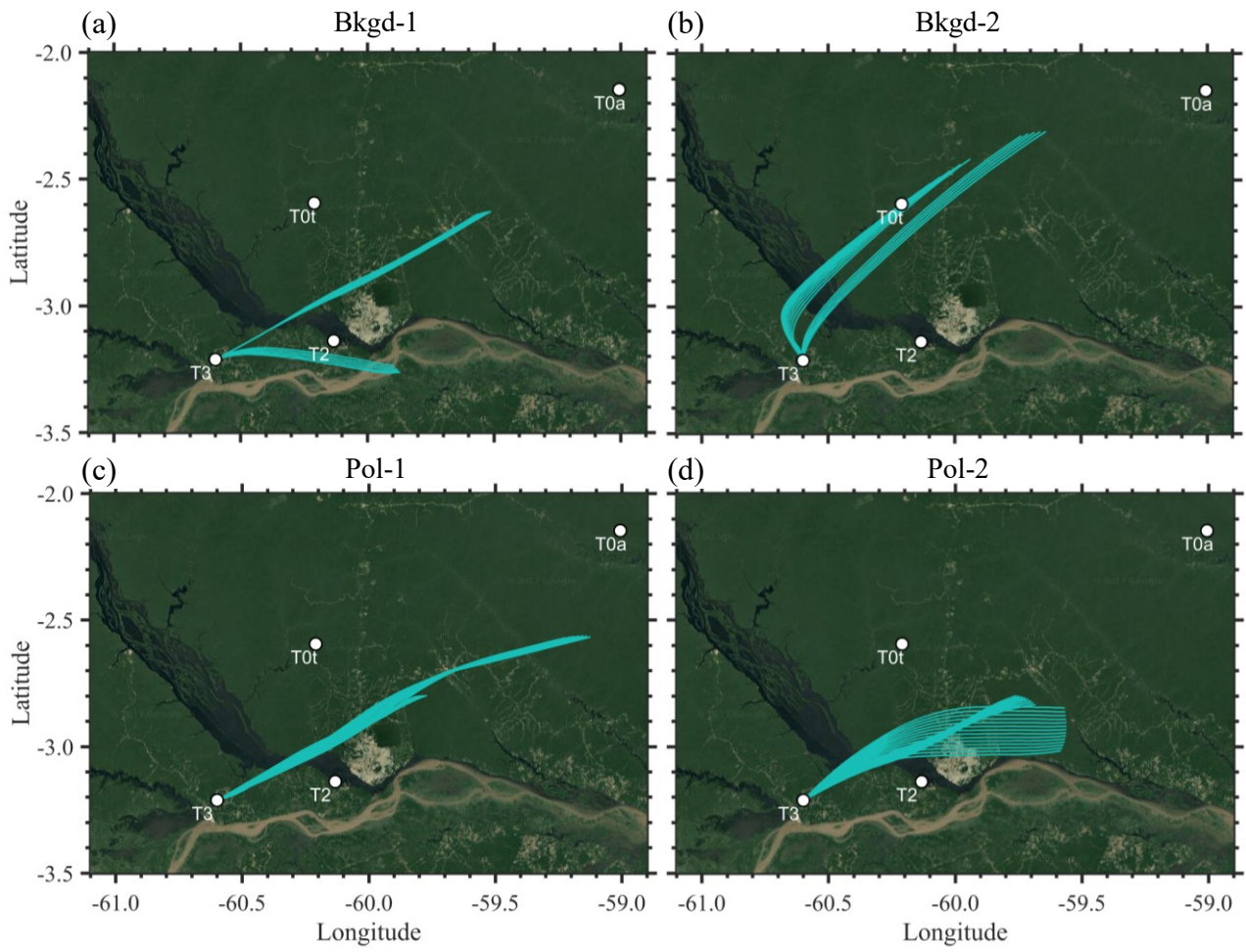


Figure 7

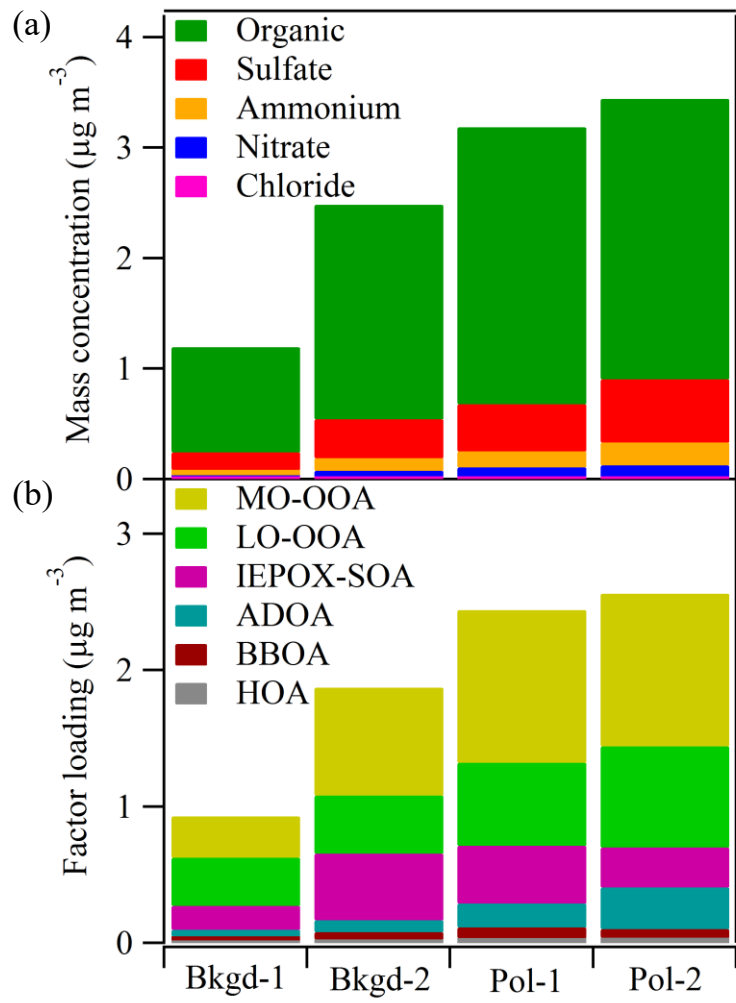


Figure 8

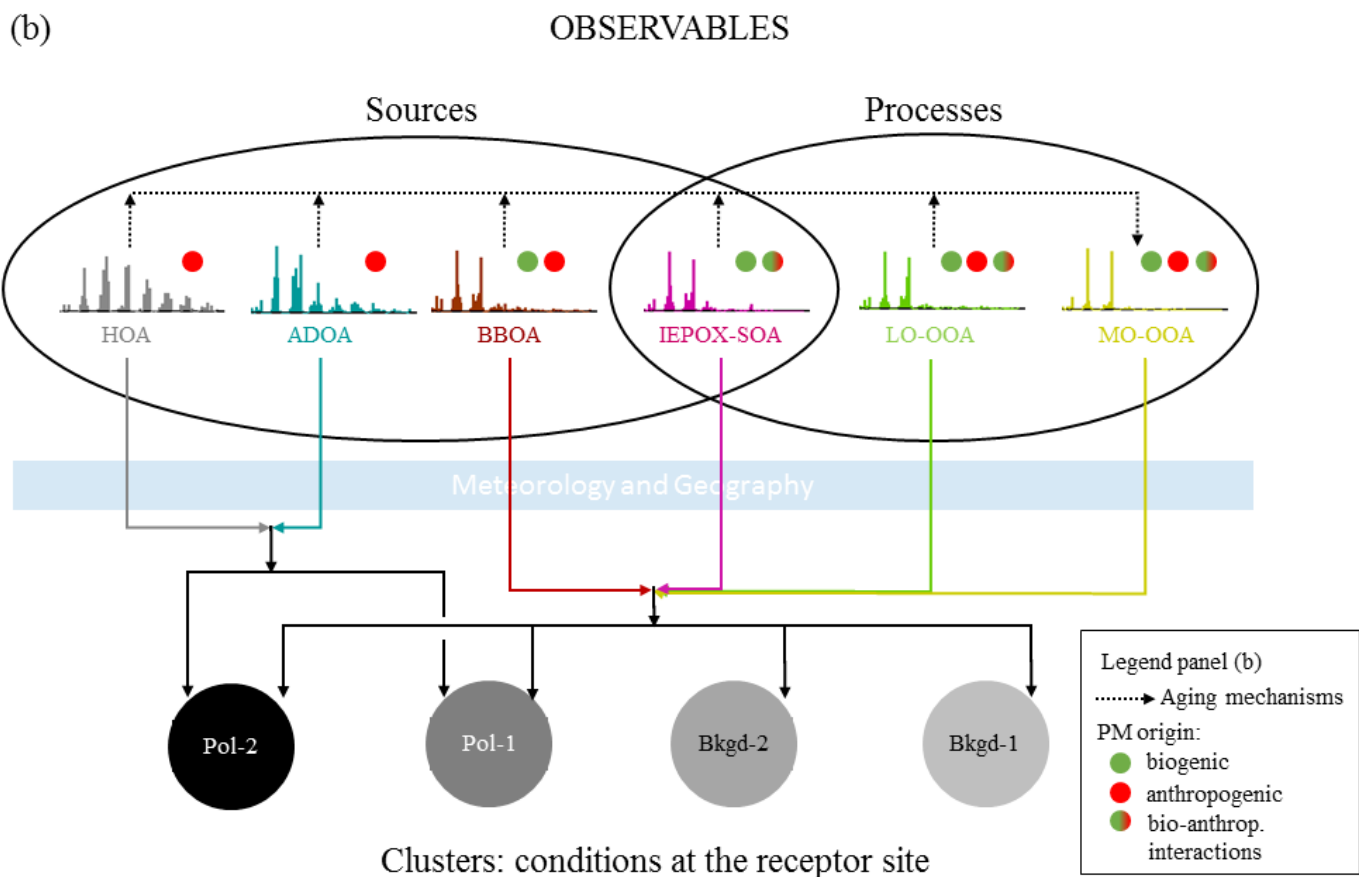
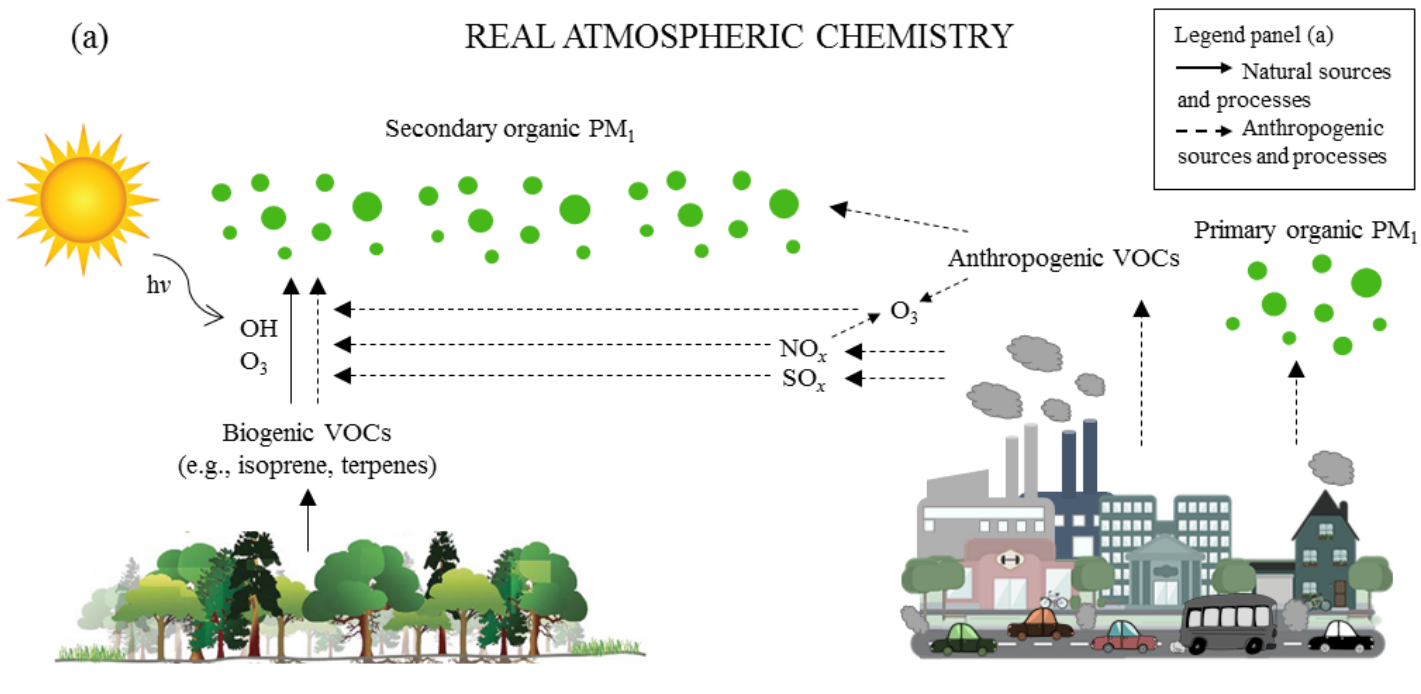


Figure 9