

Submicron Particle Mass Concentrations and Sources in the Amazonian Wet Season (AMAZE-08)

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1 **Abstract**

2 Real-time mass spectra of the non-refractory species in submicron aerosol particles were
3 recorded in a tropical rainforest in the central Amazon basin during the wet season from
4 February to March 2008, as a part of the Amazonian Aerosol Characterization Experiment
5 (AMAZE-08). Organic material accounted on average for more than 80% of the non-refractory
6 submicron particle mass concentrations during the period of measurements. There was
7 insufficient ammonium to neutralize sulfate. In this acidic, isoprene-rich, HO₂-dominant
8 environment positive-matrix factorization of the time series of particle mass spectra identified
9 four statistical factors to account for the 99% variance of the signal intensities of the organic
10 constituents. The first factor was identified as associated with regional and local pollution and
11 labeled as “HOA” for its hydrocarbon-like characteristics. A second factor was associated with
12 long-range transport and labeled as “OOA-1” for its oxygenated characteristics. A third factor,
13 labeled “OOA-2,” was implicated as associated with the reactive uptake of isoprene oxidation
14 products, especially of epoxydiols to acidic haze, fog or cloud droplets. A fourth factor, labeled
15 as “OOA-3,” was consistent with an association to the fresh production of secondary organic
16 material (SOM) by a mechanism of gas-phase oxidation of biogenic volatile organic precursors
17 followed by gas-to-particle conversion of the oxidation products. The suffixes 1, 2, and 3 on the
18 OOA labels signify ordinal ranking with respect to the extent of oxidation represented by the
19 factor. The process of aqueous-phase oxidation of water-soluble products of gas-phase
20 photochemistry might also have been associated to some extent with the OOA-2 factor. The
21 campaign-average factor loadings were in a ratio of 1.4:1 for OOA-2:OOA-3, suggesting the
22 comparable importance of particle-phase compared to gas-phase pathways for the production of
23 SOM during the study period.

24 **1. Introduction**

25 Aerosol particles in the atmosphere make an important contribution to the Earth's
26 radiation budget (IPCC, 2013). They can directly scatter and absorb shortwave and longwave
27 radiation, and they can indirectly affect radiative forcing and precipitation by modifying cloud
28 properties. The assessment of the impact of human perturbations on climate requires an
29 understanding of the natural functioning of the aerosol-cloud-climate system. During the wet
30 season, the pristine Amazon basin provides a unique environment for studying the sources and
31 atmospheric evolution of natural aerosol particles and hence understanding the role of aerosol
32 particles in biosphere-atmosphere interactions (Andreae, 2007; Martin et al., 2010a).

33 Tropical forest emissions and long-range transport from outside of the basin are major
34 contributors to the number and mass budgets of Amazonian aerosol particles during the wet
35 season because regional biomass burning emission is largely suppressed by heavy rainfall
36 (Martin et al., 2010a). The forest ecosystem emits biogenic volatile organic compounds (BVOC)
37 that can be oxidized in the atmosphere, principally by reaction with photochemically produced
38 hydroxyl radical and ozone molecules. Some of the oxidized products have sufficiently low
39 vapor pressures to condense and produce SOM in the particle phase. Moreover, in haze, fog, and
40 cloud droplets, the production of organic acids and oligomers can occur from the OH-initiated
41 aqueous-phase oxidation of the photooxidation products of isoprene, e.g., glyoxal, methacrolein
42 (MACR), and methylvinyl ketone (MVK) (Lim et al., 2010), as well as from the acid-catalyzed
43 reactive uptake of epoxydiol isomers (IEPOX) (Surratt et al., 2010; Lin et al., 2012). For SOM
44 produced by these aqueous-phase pathways, a fraction of the mass can remain in the particle
45 phase after dehumidification. In addition, the forest also directly emits primary biological
46 particles containing potassium, phosphorus, sugars, sugar alcohols, and fatty acids, including an

47 upper limit of a 20% contribution to the submicron organic mass concentration (Graham et al.,
48 2003a; Elbert et al., 2007; Schneider et al., 2011; Pöhlker et al., 2012). The forest also emits
49 gases important to the particle mass concentrations of inorganic ions. For example, ammonia
50 partitions from the gas phase to acidic particles (Trebs et al., 2005). Reduced sulfur gases
51 undergo atmospheric oxidation to produce sulfuric acid that condenses to the particle phase
52 (Andreae et al., 1990).

53 The Amazonian Aerosol Characterization Experiment 2008 (AMAZE-08) investigated
54 the sources and properties of Amazonian particles (Martin et al., 2010b). Evidence from
55 AMAZE-08 led to the conclusion that there is a large-scale contribution of biogenic SOM to the
56 mass concentration of submicron aerosol particles during the wet season (Chen et al., 2009;
57 Martin et al., 2010b; Pöschl et al., 2010; Schneider et al., 2011). In particular, Chen et al. (2009)
58 demonstrated that on order of 90% of the organic material of submicron Amazonian particles
59 arises from the in-Basin production of biogenic SOM. Primary biogenic particles enriched in
60 potassium salts and emitted by fungal spores as 10 to 20 nm dried particles possibly provide
61 surfaces for the condensation of SOM from the gas phase (Pöhlker et al., 2012). These bio-
62 related particles participate in the regulation of the hydrological cycle of the forest by serving as
63 nuclei for cloud formation and subsequent precipitation (Gunthe et al., 2009; Prenni et al., 2009).
64 In addition to particle production tied to the forest ecosystem, lidar and satellite observations
65 provide evidence of episodic long-range advection of African smoke and Saharan dust (Ben-Ami
66 et al., 2010; Baars et al., 2011). These intrusions are temporally consistent with increases of
67 heavily oxidized organic particles observed by Chen et al. (2009), indicative of long atmospheric
68 residence times, as well as increases in the concentrations of ice nuclei observed by Prenni et al.
69 (2009).

70 The present study analyzes multiple data sets collected during AMAZE-08 in relation to
71 one another and in the context of the chemistry and properties of submicron particles in the
72 Amazon basin during the wet season. A focus topic is the relative importance of aqueous-phase
73 reactions compared to gas-phase oxidation followed by condensation to the production of SOM
74 mass concentration. The relative importance of these two pathways remains poorly understood
75 (Martin et al., 2010a; Ervens et al., 2011). On the one hand, condensational growth has been
76 reported as an important pathway of the biogenic SOM production (Graham et al., 2003a). On
77 the other hand, a significant role of liquid-phase processing for Amazonian aerosol particles is
78 proposed (Pöhlker et al., 2012). In the current study, positive-matrix factorization of the time
79 series of particle mass spectra is used to identify statistical factors that differ in mass spectral
80 patterns (Zhang et al., 2011). The properties of these factors, in conjunction with the auxiliary
81 data sets, are used to investigate the relative importance of different possible sources of
82 submicron organic material in Amazonia during the wet season.

83 **2. Site and Instrument Description**

84 Ground-based measurements were carried out at a rainforest site during the wet season
85 from 7 February to 13 March 2008 (Martin et al., 2010b). The site ($02^{\circ}35.68' \text{S}$, $60^{\circ}12.56' \text{W}$,
86 110 m above sea level) located 60 km NNW of Manaus and faced 1600 km of nearly pristine
87 forest to the east to the Atlantic Ocean. The site was accessed by a 34-km unpaved road from
88 Highway 174 (Fig. S1). The ten-day back trajectories indicated that during the measurement
89 period the air masses mainly originated from the northeast over the Atlantic Ocean in the
90 direction of Cape Verde and the Canary Islands. Air was sampled at the top of a tower (“TT34”;
91 38.75 m) above the forest canopy (33 m). Instrumentation deployed during AMAZE-08 is
92 described in Martin et al. (2010b).

93 The present study focuses mostly on the statistical analysis of the data sets of an
94 Aerodyne high-resolution Aerosol Mass Spectrometer (HR-AMS) in the context of
95 complementary data sets of other instruments. Mass concentrations were adjusted to standard
96 temperature and pressure (noted as STP; 273.15 K and 10^5 Pa), which were approximately 10%
97 greater than those at calibration conditions (299.3 K and 100591.7 Pa). Details on sampling by
98 the AMS and data analysis are provided in Chen et al. (2009) and Sect. A of the Supplement.
99 The description of other concurrent measurements and the comparisons among the
100 measurements are provided in Sect. B of the Supplement. Table S1 lists the regression
101 coefficients for the multi-instrument data comparison. For a collection efficiency of unity, the
102 AMS data agreed within measurement uncertainty with the other data sets, which is consistent
103 with the understanding that liquid particles do not bounce from the AMS vaporizer (Matthew et
104 al., 2008). Images of filter samples showed that spherical organic particles, appearing as like-
105 liquid droplets, were the main population in the submicron fraction of the ambient particle
106 population for AMAZE-08 (Pöschl et al., 2010).

107 Atomic ratios of oxygen-to-carbon (O:C), hydrogen-to-carbon (H:C), nitrogen-to-carbon
108 (N:C), and sulfur-to-carbon (S:C), as well as the organic-mass-to-organic-carbon (OM:OC)
109 ratios, were calculated from the high-resolution “W-mode” data (Aiken et al., 2008). The ratios
110 were corrected by the method of Canagaratna et al. (2015). The contributions of organonitrates
111 and organosulfates, detected as inorganic nitrate or sulfate ions by the AMS, to the elemental
112 ratios were negligible because their low mass concentrations (cf. Sect. A of the Supplement).
113 Positive-matrix factorization (PMF; (Paatero and Tapper, 1994)) was conducted on the organic
114 mass spectra of the medium-resolution “V-mode” data (m/z 12 to 220) taken to unit-mass
115 resolution. The analysis used the PMF evaluation panel of Ulbrich et al. (2009) (version 4.2;

116 “robust mode”). Further aspects of the analysis and output evaluation are provided in Sect. C of
117 the Supplement. Because of the low mass concentrations, the signal-to-noise ratios were
118 insufficient for satisfactory PMF analysis of the high-resolution data. PMF results are reported
119 herein for unit mass resolution.

120 The AMS mass spectra of SOM produced in the Harvard Environmental Chamber (HEC)
121 by (i) the photooxidation of isoprene (C_5H_8), (ii) the dark ozonolysis of the monoterpene α -
122 pinene ($C_{10}H_{16}$) (adapted from Shilling et al. (2009)), and (iii) the dark ozonolysis of the
123 sesquiterpene β -caryophyllene ($C_{15}H_{24}$) are reported herein for the purpose of comparison to the
124 AMAZE-08 data. Experimental details are described elsewhere (Shilling et al., 2009; King et al.,
125 2010; Chen et al., 2011 and 2012). A library of spectra was collected at different SOM mass
126 concentrations.

127 **3. Results and Discussion**

128 **3.1 Mass concentrations**

129 Figure 1 shows a time series of measurements by the AMS and other instruments during
130 AMAZE-08. The AMS detects the non-refractory chemical components of the submicron
131 fraction of the ambient particle population (NR-PM₁) (Fig. 1a-1c). As described in Chen et al.
132 (2009), organic material and sulfate were the two major components identified by the AMS,
133 with correspondingly low concentrations of ammonium and negligible concentrations of nitrate
134 and chloride. The campaign-average organic particle mass concentration was $0.76 \pm 0.23 \mu\text{g m}^{-3}$,
135 corresponding to $0.45 \pm 0.13 \mu\text{g C m}^{-3}$ of organic carbon and an OM:OC ratio of 1.7. The
136 campaign-average sulfate mass concentration of $0.19 \pm 0.06 \mu\text{g m}^{-3}$ agreed well with the average
137 value of $0.21 \pm 0.06 \mu\text{g m}^{-3}$ measured by ion chromatography (IC) and the value of 0.24 ± 0.05
138 $\mu\text{g m}^{-3}$ measured by particle-induced X-ray emission (PIXE) for the fine-mode (PM₂) filters.

139 Ammonium accounted for 2% of the submicron particle mass concentration. The campaign-
140 average mass concentration was $0.03 \pm 0.01 \mu\text{g m}^{-3}$, in agreement with the average value of 0.04
141 $\pm 0.01 \mu\text{g m}^{-3}$ obtained for the fine-mode filters by the IC analysis. Chloride concentrations, had
142 a campaign-average concentration of 2 ng m^{-3} , which was consistent with the filter average,
143 though there were transiently larger (up to 26 ng m^{-3}) during some periods. Nitrate had a
144 campaign-average concentration of $7 \pm 2 \text{ ng m}^{-3}$. This value was greater than the average fine-
145 mode concentration of $4 \pm 1 \text{ ng m}^{-3}$ measured by IC, perhaps because of increased instrument
146 uncertainties at low concentrations. Another possibility, meaning substantial evaporative losses
147 of nitrate during filter sampling, is not anticipated for the hygroscopic, acidic particles present
148 during the measurement periods for the prevailing relative humidity. The AMS-measured nitrate
149 accounted for 0.6% of the total submicron particle mass concentration.

150 Black carbon, mineral dust, and sea salt are common refractory components that are not
151 quantified by the AMS. The multiangle absorption photometer (MAAP) instrument provides an
152 optically based measurement of the black-carbon-equivalent (BCe) mass concentration, without
153 size resolution (Petzold et al., 2002). The campaign-average concentration was $0.13 \mu\text{g m}^{-3}$ (Fig.
154 1d). Under a limiting assumption that all black carbon occurred in the submicron fraction of the
155 atmospheric particle population, this concentration corresponded to 11% of the submicron mass
156 concentration (inset of Fig. 1e). The relative contribution of black carbon varied significantly
157 during the course of AMAZE-08 (Fig. 1e), perhaps corresponding to the occasional advection of
158 urban pollution from Manaus or biomass burning from Africa (Kuhn et al., 2010; Martin et al.,
159 2010b; Rizzo et al., 2013). This interpretation is supported by the covariance of BCe with
160 sulfate. Major fine-mode (PM_2) trace elements of mineral dust, including Si, Al, Fe, and Ca, had
161 campaign-average mass concentrations of 0.12, 0.05, 0.04, and $0.01 \mu\text{g m}^{-3}$, respectively, as

162 analyzed for fine-mode filter samples by PIXE. An important source of the mineral dust was
163 long-range transport from Africa. Previous campaigns in the Amazon found that about 20% of
164 the mineral dust occurred in the submicron domain (Fuzzi et al., 2007). Using this result for
165 AMAZE-08 implies that mineral dust contributed about $0.1 \mu\text{g m}^{-3}$ to the average mass
166 concentration of the submicron particle population (Malm et al., 1994). The modified pie chart is
167 shown in Fig. S2. Moreover, the campaign-average mass concentrations of fine-mode metallic
168 elements (V, Cr, Mn, Ni, Cu, Zn, Pb, and Mg in total of 2 ng m^{-3}) measured by PIXE were
169 sufficiently low during AMAZE-08 to confirm the absence in the submicron particle mass
170 concentration of significant metals from anthropogenic sources. The campaign-average mass
171 concentration of fine-mode Na^+ measured by IC was $0.02 \mu\text{g m}^{-3}$. This result suggests a minimal
172 contribution of sea salt from Atlantic Ocean, at least to the submicron particle population (Fuzzi
173 et al., 2007).

174 Figure 1f shows the time series of the particle light scattering coefficient measured by
175 nephelometry at 550 nm for $\text{PM}_{7.5}$. The elevated scattering coefficients during 22 February to 3
176 March 2008 were driven by elevated mineral dust concentrations in the coarse mode, along with
177 elevated submicron sulfate, BCo, and organic material arising from the advection of the Manaus
178 pollution plume as well as long-range transport from Africa (Sect. B of the Supplement). Other
179 temporal maxima corresponded to increases of submicron particle mass concentration. Figure 1g
180 shows the elemental compositions of the submicron organic material measured by the AMS. The
181 O:C and H:C ratios, corrected as described in Canagaratna et al. (2015), were 0.58 ± 0.16 (one
182 standard deviation) and 1.60 ± 0.18 on average, respectively. The 10/90 quantiles were 0.40/0.74
183 and 1.42/1.80, respectively. The N:C ratios were 0.03 ± 0.01 .

184 Ammonium and sulfate mass concentrations had high correlation ($R^2 = 0.95$) during

185 AMAZE-08 (Fig. S3). The molar ratio of $\text{NH}_4^+ : \text{SO}_4^{2-}$ was 0.80 (Fig. 2), meaning that there was
186 insufficient ammonium to neutralize sulfate for the submicron particle population and suggesting
187 a composition close to that of ammonium bisulfate. Similar molar ratios have been reported in
188 several previous studies in the central and northeast Amazon basin (Talbot et al., 1988, 1990;
189 Gerab et al., 1998; Graham et al., 2003b). The AMS is unable to quantify refractory components
190 such as K^+ , Na^+ , Ca^{2+} , and Mg^{2+} . Mass-diameter distributions of these ions obtained by IC
191 analysis of samples collected by a Multi-Orifice Uniform Deposit Impactor (MOUDI) on 22
192 March 2008 suggest that 40% of the mass of these ions was distributed to the submicron particle
193 fraction. For comparison, Fuzzi et al. (2007) for the wet season reported 50-60% of K^+ and Ca^{2+}
194 in the submicron fraction, compared to the predominance of Na^+ and Mg^{2+} in the supermicron
195 fraction. The campaign-average fine-mode mass concentrations of K^+ , Ca^{2+} , Na^+ , and Mg^{2+}
196 measured by IC were 0.03, 0.01, 0.02, and 0.01 $\mu\text{g m}^{-3}$, respectively. The implication of the
197 relative concentrations (i.e., sulfate concentration of $0.19 \pm 0.06 \mu\text{g m}^{-3}$) is that the submicron
198 inorganic ion composition is reasonably approximated as ammonium bisulfate during AMAZE-
199 08.

200 Diel profiles of organic, sulfate, ammonium, nitrate, and chloride mass concentrations
201 measured by the AMS are shown in Fig. 3. The temporal trends of the four species were
202 correlated, with a minimum in mass concentrations near daybreak and a maximum in the
203 afternoon. Nighttime rainfall efficiently removed particle mass concentration after local midnight,
204 suggesting an absence of strong sources of submicron particles during the night. From the
205 morning to the afternoon, photochemical production of SOM, convective mixing of particles
206 from aloft, and regional advection sustained mass concentrations, with quick recovery after
207 daytime rainfall. Precipitation was typically local whereas advection was typically regional at a

208 larger scale than precipitation. The decrease and the recovery of species concentration during the
209 afternoon resulted from frequent rain events around that time of day (e.g., Fig. S4). The organic
210 particle mass concentration increased during the day even as temperature rose and relative
211 humidity dropped, both of which provide a thermodynamic driving force for the re-partitioning
212 of semivolatile species from the particle phase to the gas phase (Pankow, 1994). Possible
213 explanations include (1) sufficiently strong daytime production of SOM to outweigh evaporative
214 sinks, (2) significant production of low-volatility SOM (Ervens et al., 2011; Ehn et al., 2014), or
215 (3) a slow evaporation rate of SOM (Vaden et al., 2011).

216 3.2. Mass spectra of laboratory biogenic SOM

217 As a reference for interpreting the AMAZE-08 measurements, Figure 4 shows the mass
218 spectra of SOM produced in the HEC by the oxidation of isoprene, α -pinene, and β -
219 caryophyllene for three different mass concentrations. Signals at $m/z < 60$ account for 93-97%,
220 80-84%, and 71-79% of the total signal intensity for the three types of SOM. The fragmentation
221 pattern extends to higher m/z for the increasing carbon skeleton of precursor BVOC. For all three
222 types of SOM, the relative intensities of two prominent ions, $C_2H_3O^+$ at m/z 43 and CO_2^+ at m/z
223 44, show opposite trends as the mass concentration increases. The former increases for elevated
224 concentrations whereas the later decreases. Another ion at m/z 44, $C_2H_4O^+$, shows a trend
225 similar to that of $C_2H_3O^+$. This ion accounts for 10–25%, 3–5%, and 5–10% of the signal at m/z
226 44 for the isoprene, α -pinene, and β -caryophyllenethe SOMs, respectively. The relative
227 intensities of major $C_xH_y^+$ ions, such as CH_3^+ at m/z 15, $C_2H_3^+$ at m/z 27, $C_3H_3^+$ at m/z 39, and
228 $C_3H_5^+$ at m/z 41, typically increase as concentration increases. The most intense $C_xH_y^+$ ions at $m/z >$
229 80 for the three types of biogenic SOM is $C_7H_7^+$ at m/z 91, which does not occur in the spectra for
230 fresh emissions such as diesel exhaust, cooking, and biomass burning but is similar to the spectra

231 for aged primary emissions (Chirico et al., 2010; He et al., 2010; Ortega et al., 2013).

232 Compared to the spectra of the other types of biogenic SOM, isoprene-derived SOM
233 under HO₂-dominant conditions has a unique signature. “HO₂-dominant” refers to the fate of
234 peroxy radicals with respect to reaction with HO₂ or NO. The relative intensities of CHO⁺ at *m/z*
235 29, CH₂O⁺ at *m/z* 30, CH₃O⁺ at *m/z* 31, C₃H₆O₂⁺ at *m/z* 74, and C₃H₇O₂⁺ at *m/z* 75 in the spectra
236 of isoprene-derived SOM are much greater, and the contributions of C_xH_y⁺ ions are less,
237 especially for *m/z* > 65. Moreover, *m/z* 82 that mainly consists of C₃H₅O⁺ appears to be the most
238 intense peak for *m/z* ≥ 75. This fragment has been suggested as a characteristic fragment of
239 isoprene-derived SOM (Robinson et al., 2011). Isoprene-derived SOM also does not follow the
240 empirical linear relationship between O:C and *I*₄₄:*I*_{org} described by Aiken et al. (2008) (Fig. S5),
241 indicating that deriving O:C from *I*₄₄:*I*_{org} requires careful judgments on the contribution of
242 isoprene-derived SOM.

243 3.3 Multivariate factor analysis of the organic mass spectra

244 Multivariate analysis by PMF of the temporal series of the organic component of the
245 mass spectra was carried out for 12 ≤ *m/z* ≤ 220 at unit-mass resolution. In overview, four
246 statistical factors were identified and labeled as HOA, OOA-1, OOA-2, and OOA-3 (Fig. 5).
247 These four factors respectively accounted for 2%, 18%, 14%, and 66% of the variance in the data
248 matrix, with a residual variance of <1%. The time series of the loading of each statistical factor
249 are shown in Fig. 6. By definition, the mass spectrum of the organic chemical component itself
250 was at any time point a linear mix of the statistical factors, plus residual.

251 The HOA factor (Fig. 5a) was dominated by the ion series C_nH_{2n+1}⁺, C_nH_{2n-1}⁺, and C_nH_{2n-3}⁺
252 (*m/z* 27, 29, 39, 41, 43, 55, 57, 67, 69...), similar to that reported for other locations (e.g., Zhang
253 et al., 2005; Docherty et al., 2011; Robinson et al., 2011) and to that observed for engine exhaust

254 (Canagaratna et al., 2004; Chirico et al., 2010). This statistical factor is typically taken as an
255 organic component associated with fossil fuel combustion emissions that have not undergone
256 substantial atmospheric oxidation. This factor was especially prevalent in the early part of the
257 experiment. During this time period, other pollution tracers such as sulfate and NO_x were also at
258 elevated concentrations. Regional pollution from Manaus and local emissions (e.g., nearby roads,
259 highway, generator, and pump oil) were plausible contributors to the loading of the HOA factor
260 (Ahlm et al., 2009; Rizzo et al., 2013).

261 The factors OOA-1, OOA-2, and OOA-3 were ranked by the $f_{44}:f_{43}$ ratios (high to low)
262 and labeled based on Zhang et al. (2011), where $f_{m/z}$ represents the fractional contribution of the
263 signal intensity at m/z to the statistical factor. The signal intensity was dominated at m/z 44 by
264 the CO₂⁺ fragment and at m/z 43 by the C₂H₃O⁺ and C₃H₇⁺ fragments. The $f_{44}:f_{43}$ ratio has been
265 used in some settings as a surrogate for the extent of oxidation (i.e., so-called ‘atmospheric
266 aging’) of SOM (Ng et al., 2010 and 2011).

267 The OOA-1 factor had the feature of a singularly dominant peak at m/z 44 (Fig. 5b). This
268 marker has been linked to organic material that has undergone extensive oxidation during a
269 prolonged atmospheric residence time (on order of 10 days) (Ng et al., 2010; Lambe et al.,
270 2011). This factor is consistent with an association to finding of highly-oxidized organic material
271 delivered by long-range transport, as occurred during some periods of AMAZE-08 (Chen et al.,
272 2009). The source of this material was plausibly African biomass burning, as supported by
273 concurrent lidar measurements (Baars et al., 2011) and satellite observations (Ben-Ami et al.,
274 2010). Biomass burning in South America was much less significant during the wet season
275 (Martin et al., 2010b). The correlations of the statistical loadings of the OOA-1 factor with the
276 measured mass concentrations of biomass burning tracers, such as chloride ($R^2 = 0.52$),

277 potassium ($R^2 = 0.35$), and black carbon ($R^2 = 0.43$) in the submicron particle population, were
278 not high, possibly because of the mixing of sources to these tracers such as primary biological
279 particles (i.e., contributing chloride and potassium) and regional pollution from Manaus to (i.e.,
280 black carbon). These correlation value were, however, significantly greater than those of the
281 other three factors (HOA, OOA2, and OOA-3) with the tracers (i.e., $R^2 < 0.10$ for chloride, $R^2 <$
282 0.02 for potassium, and $R^2 < 0.20$ for black carbon) (Fig. 6b). Elevated sulfate mass
283 concentrations were also observed during periods having high OOA-1 loadings (Fig. 1b).

284 Features of the OOA-2 factor included (1) a $f_{44}:f_{43}$ ratio greater than unity and (2) a
285 characteristic peak at m/z 82 mainly consisting of $C_3H_5O^+$. This peak was the most abundant for
286 $m/z \geq 75$ (Fig. 5c). It is similar to that reported for PMF factors identified in the tropical
287 rainforest of Borneo (named as the “82Fac” factor) (Robinson et al., 2011), the rural area of
288 southwest Ontario, Canada (named as the “UNKN” factor) (Slowik et al., 2011), and isoprene-
289 rich downtown Atlanta, Georgia, USA (named as the “IEPOX-OA” factor) (Budisulistiorini et
290 al., 2013). Robinson et al. (2011) concluded that this factor derived from SOM produced by
291 isoprene photo-oxidation. In agreement, the time series of OOA-2 loading correlated with
292 isoprene concentration ($R^2 = 0.65$) as well as with the sum concentration of first-generation
293 isoprene oxidation products, specifically MVK + MACR ($R^2 = 0.74$) (Fig. 6c). The characteristic
294 m/z 82 also occurred in the spectra of our isoprene SOM produced in the presence of neutral
295 sulfate particles at 40% RH (Fig. 4a). Laboratory studies demonstrated that the reactive-uptake
296 of photo-oxidation products of isoprene, particularly IEPOX, in the presence of acidic particles
297 contribute to the m/z 82 signal detected by the AMS (Lin et al., 2012; Budisulistiorini et al.,
298 2013; Liu et al., 2014). Even so, the spectra of isoprene SOM or IEPOX SOM produced in the
299 laboratory have some important differences with the statistical factories (i.e., “OOA-2” of this

300 study and “82Fac”, “UNKN”, and “IEPOX-OA” of earlier studies) derived from atmospheric
301 data sets. In particular, there are significant differences at m/z 29 and m/z 39 through m/z 44. The
302 values of f_{44} of the laboratory results are approximately 25% of those of the cited PMF factors.
303 One possible explanation for these differences is that the laboratory experiments did not capture
304 the full range of atmospheric processes, such as possible synergistic chemistry among the range
305 of atmospheric precursors, aqueous-phase processing, and photochemistry under a range of
306 $\text{HO}_2\text{:NO}$ ratios (Ervens et al., 2011; Emanuelsson et al., 2013; Liu et al., 2013; Nguyen et al.,
307 2014). In particular, the laboratory experiments were typically carried out at low relative
308 humidity. The atmosphere during AMAZE-08 was humid (89 to 100% RH; 25 to 75%
309 quantiles). Pöhlker et al. (2012) showed evidence of multiphase processing in the larger
310 accumulation mode particles. The oxidized material produced by aqueous-phase oxidation (e.g.,
311 dicarboxylic acids (Lim et al., 2010)) may explain the higher f_{44} in the OOA-2 factor compared
312 to the laboratory spectra. In summary, the OOA-2 factor during AMAZE-08 was interpreted as
313 SOM produced by the reactive uptake of isoprene photo-oxidation products, including possible
314 aqueous-phase oxidation in haze, fog, and cloud droplets.

315 The OOA-3 factor had a prominent peak at m/z 43 (Fig. 5d). For $m/z > 80$, the most
316 intense peak occurred at m/z 91. The OOA-3 factor had similarities to the mass spectra recorded
317 for biogenic SOM produced under conditions relevant to the Amazon basin. Specifically, SOM
318 produced from isoprene under laboratory conditions had a prominent peak at m/z 43 (Fig. 4a).
319 Mass spectra of SOM derived from precursors of monoterpene α -pinene and sesquiterpene β -
320 caryophyllene had similar patterns as OOA-3 at m/z 55 and m/z 91. A linear combination of the
321 three chamber spectra largely reproduced the OOA-3 factor (Fig. 7; 50% isoprene-derived SOM,
322 30% α -pinene-derived SOM, and 20% β -caryophyllene-derived SOM). The intensity at m/z 29,

323 however, was overestimated by the linear combination. The remarkable result is that the ambient
324 factor could to large extent be explained by just three laboratory data sets given the wide range
325 of BVOC precursor compounds that can contribute to SOM production in the Amazon basin.
326 The explanation is three-fold, one that isoprene is the dominant BVOC for this rain forest, two
327 that the AMS breaks complex molecules into simpler building blocks by electron-impact
328 ionization, and three that the higher-order C₁₀, C₁₅, and possibly C₂₀ BVOCs are all assembled
329 biochemically from the isoprene (C₅) monomer. Moreover, the temporal variation of the OOA-3
330 loading tracked that of the BVOC concentrations (Fig. 6d). The OOA-3 statistical factor was
331 therefore interpreted as associated with freshly produced SOM similar to that produced in the
332 chamber experiments, meaning on a timescale of several hours by a mechanism of gas-to-particle
333 partitioning of the BVOC oxidation products.

334 Figure 8 shows the campaign-average diel profiles of the factor loadings. The HOA
335 loading had a daytime minimum, suggesting the buildup of local pollution during the night and
336 the removal by convective mixing during the day. In support of this interpretation, the nocturnal
337 boundary layer was approximately 100 m or less. At daybreak, the boundary layer rapidly
338 developed, reaching on order of 1000 m by local noon around the site (Martin et al., 2010b). The
339 OOA-1 loading peaked around noon without great variation throughout the day. This temporal
340 behavior is expected for homogeneous mixing in the atmospheric column without in situ sources,
341 such as for material arriving by long-range transport. The small daytime increase was consistent
342 with the daytime convective downward mixing of older, oxidized particles from aloft. By
343 comparison, the OOA-2 and OOA-3 loadings peaked in the early afternoon while the BVOC
344 concentrations were high (cf. Fig. 3c of Chen et al. (2009)). This temporal behavior was
345 consistent with the photochemically driven production of SOM.

346 Figure 9 shows the time series of fractional contribution by each of the four statistical
347 factors identified by PMF analysis. On average the relative loadings of HOA, OOA-1, OOA-2,
348 and OOA-3 were 14%, 14%, 34%, and 38%, respectively. For comparison, other studies reported
349 0 to 21% of HOA for remote locations (Jimenez et al., 2009) and 23% to 50% of OOA-2 (named
350 as “82Fac”, “UNKN”, and “IEPOX-OA” in earlier studies) (Robinson et al., 2011; Slowik et al.,
351 2011; Budisulistiorini et al., 2013). Figure 9 shows that the relative importance of each process
352 as a contributor differed with time and highlights two focus periods. Precipitation and
353 temperature were the major meteorological factors that differed between the two periods. The
354 first period was sunny, warmer with occasional clouds, and the second period had frequent heavy
355 rainfall events. Long-range back-trajectory analyses presented in Martin et al. (2010b) showed
356 that the air masses consistently arrived from the equatorial Atlantic Ocean passing as
357 northeasterlies through the Amazon basin. Local measurements showed that the daytime winds
358 mainly came from the north and northeast (Fig. 9, top). During the first period, the average
359 fractional contribution by the OOA-2 factor was five times greater than that of the OOA-3 factor.
360 During the second period, by comparison, the fractional contribution by the OOA-3 factor was
361 three times greater than that of the OOA-2 factor. The average organic mass concentrations of
362 the two periods were 1.84 and 0.59 $\mu\text{g m}^{-3}$, respectively.

363 Figure 9 shows that the loading fraction of the OOA-2 factor consistently dropped
364 following heavy rainfall events, suggesting more efficient in-cloud or below-cloud scavenging
365 for the types of material represented by OOA-2 than for those types represented by OOA-3. This
366 finding further supports the interpretation that the OOA-2 factor represents, at least in part,
367 aqueous-phase production pathways because SOM produced in this way has greater water
368 solubility and hence greater wet deposition rates than SOM produced freshly by gas-to-particle

369 condensation, as interpreted for the OOA-3 factor. Figure 9 also shows that the mode diameter of
370 organic material in period 1, which has a higher OOA-2 loading fraction, is significantly larger
371 than that in period 2, which has a higher OOA-3 loading fraction. Aqueous-phase processing is
372 anticipated to add additional organic material that results in larger mode diameters after
373 dehydration.

374 **4. Conclusions**

375 Submicron particle mass concentration in the Amazonian rainforest during the wet season
376 of 2008 was dominated by organic material. The environment was humid, HO₂-dominant,
377 isoprene-rich, with the presence of acidic particles in the submicron fraction of the atmospheric
378 particle population. Factors OOA-2 and OOA-3 were identified in the patterns of the collected
379 mass spectra. These factors were interpreted as tied to the in-basin production of biogenic
380 secondary organic material and together accounted for >70% of the factor loadings, with the
381 balance from HOA and OOA-1. The OOA-2 factor was implicated as associated with the
382 reactive uptake of isoprene oxidation products, especially of epoxydiols to acidic haze, fog or
383 cloud droplets. The OOA-3 factor was consistent with an association to the fresh production of
384 SOM by a mechanism of gas-phase oxidation of BVOCs followed by gas-to-particle conversion
385 of the oxidation products. Although multivariate statistical factors do not correspond to
386 segregated individual chemical components (e.g., unlike molecules or families of molecules), the
387 factors nevertheless can be indicative of the relative importance of different atmospheric
388 emissions and process pathways. With this caveat in mind, the PMF analysis herein finds that the
389 factor loadings were, on average, in a ratio of 1.4:1 for OOA-2 compared to OOA-3 and were
390 alternately dominated in different periods of AMAZE-08 by the OOA-2 and OOA-3. These
391 findings suggest a comparable importance of gas-phase and particle-phase (including haze, fog,

392 and cloud droplets) production of SOM during the study period.

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List of Figures

- Figure 1.** Time series of observations during AMAZE-08. **(a, b, c)** Organic, sulfate, ammonium, nitrate, and chloride mass concentrations measured by AMS. **(d)** Black-carbon-equivalent mass concentrations measured by filter-based reflectance (fine-mode) analysis as well as optically derived by MAAP (637 nm) and aethalometer (660 nm) measurements. **(e)** Component mass fractions of panels *a* to *d*. For panel *d*, MAAP data were used. The inset pie chart represents the campaign average. **(f)** Scattering coefficient measured by nephelometry at 550 nm. Only particles of 7 μm and smaller passed through the sampling inlet. **(g)** Elemental ratios O:C, H:C, N:C, and S:C for the submicron organic particles, as determined by high-resolution AMS data. Except for panel *f*, the data represent the submicron or fine-mode fraction of the ambient particle population. Concentrations are normalized to STP conditions (see main text). Periods in gray were influenced by local generator exhaust plume during times of local wind reversal and were excluded from the shown data sets and analysis.
- Figure 2.** Scatter plot of ammonium and sulfate mass concentrations (gray circles). The red symbols show campaign-average values reported in the literature for other measurements in the Amazon basin, both in the wet and dry seasons.
- Figure 3.** Diel profiles of (top) the temperature and relative humidity at the top of the measurement tower, (middle) normalized AMS-measured speciated mass concentrations (maximum concentrations in $\mu\text{g m}^{-3}$ (STP) are shown in parentheses), and (bottom) percent occurrence of rain. Data represent mean values.
- Figure 4.** High-resolution mass spectra of secondary organic material produced in the Harvard Environmental Chamber by the oxidation of isoprene, α -pinene, and β -caryophyllene.

The NO_x concentration was measured as < 1 ppbv during these experiments and was estimated later as < 70 ppt for typical operating of the HEC (Liu et al., 2013). The relative intensities of ions having $m/z \geq 65$ were multiplied by 10. The intensities at each m/z represent three experiments that were performed at different SOM particle mass concentrations. A single intensity bar is color-coded by the contribution of different ion families (i.e., fragments containing C, H, O, or N for subscripts of $x, y, z, i \geq 1$) as determined from analysis of the high-resolution spectra (Shilling et al., 2009). The relative intensities of the H_yO_1^+ family were derived from the intensity of CO_2^+ based on calibrations described in Chen et al. (2011).

Figure 5. Statistical factors HOA, OOA-1, OOA-2, and OOA-3 identified by PMF analysis.

The relative intensities of ions having $m/z \geq 65$ were multiplied by 10.

Figure 6. Time series of the loadings for the factors HOA, OOA-1, OOA-2, and OOA-3 (left axes; dots) and time series of the concentrations of tracer species, including NO_x , CO, AMS chloride, AMS potassium, aethalometer black-carbon, MVK + MACR, isoprene, monoterpenes, and sesquiterpenes (right axes; lines). The BVOCs were measured by PTR-MS (Karl et al., 2009).

Figure 7. Comparison of the OOA-3 factor to a synthetic mass spectrum obtained from a linear combination of the mass spectra of laboratory-generated biogenic SOM (30% α -pinene-derived SOM, 20% β -caryophyllene-derived SOM, and 50% isoprene-derived SOM at mass concentrations of 0.4 to 0.7 $\mu\text{g m}^{-3}$).

Figure 8. Campaign-average diel profiles of the loadings of the factors HOA, OOA-1, OOA-2, and OOA-3.

Figure 9. (top) Mass-diameter distributions measured by the AMS and the daytime wind rose

for the two time periods shown in the bottom panel. (upper bottom) Time series of daily mean temperature measured at the top of the measurement tower TT34. (lower bottom) Time series of the fractional contribution by each of the four statistical factors identified by PMF analysis (left axes) and the rain counts (right axes). Two case periods that differ significantly in the fractional contribution of PMF factors are selected.

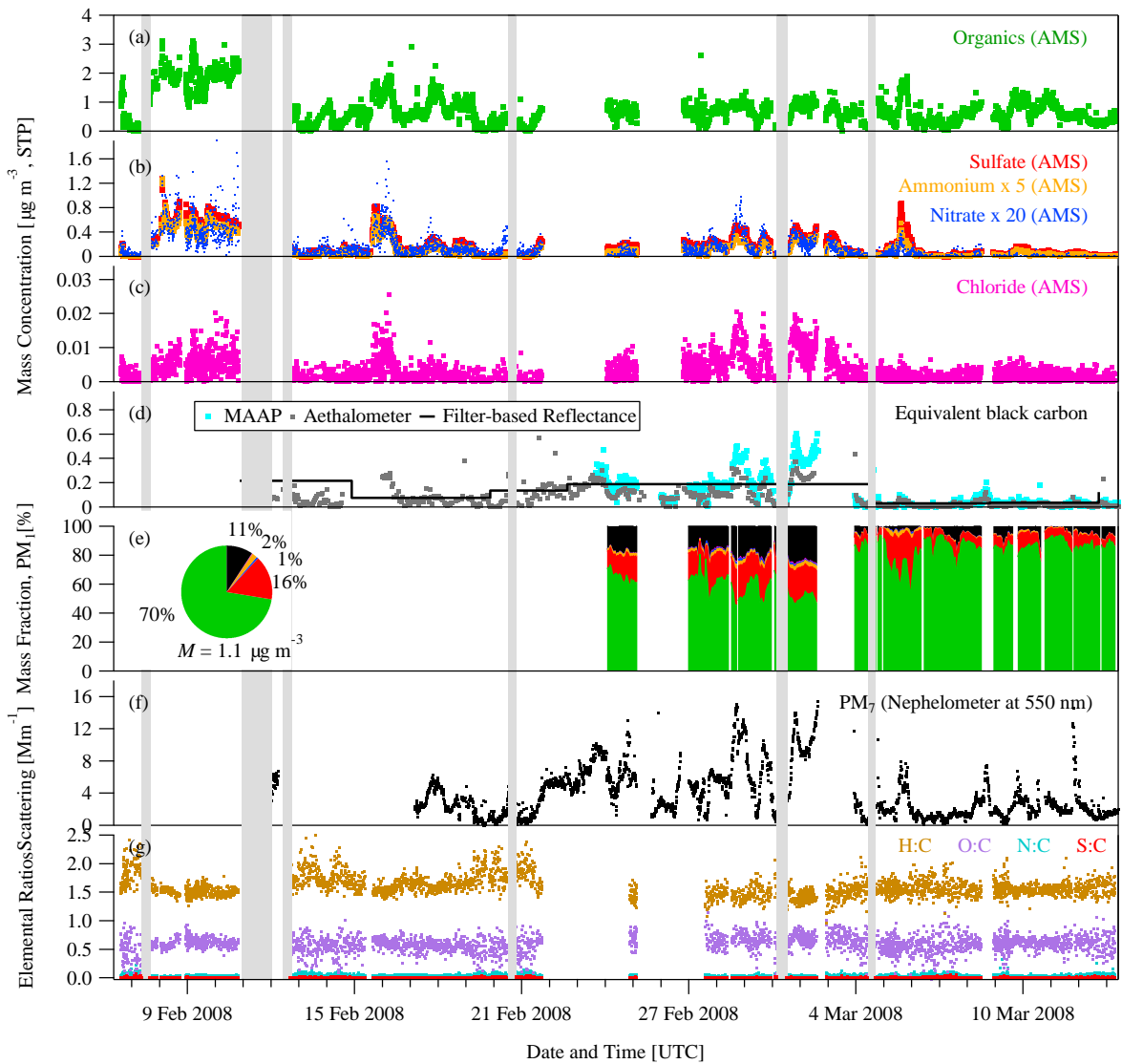


Figure 1

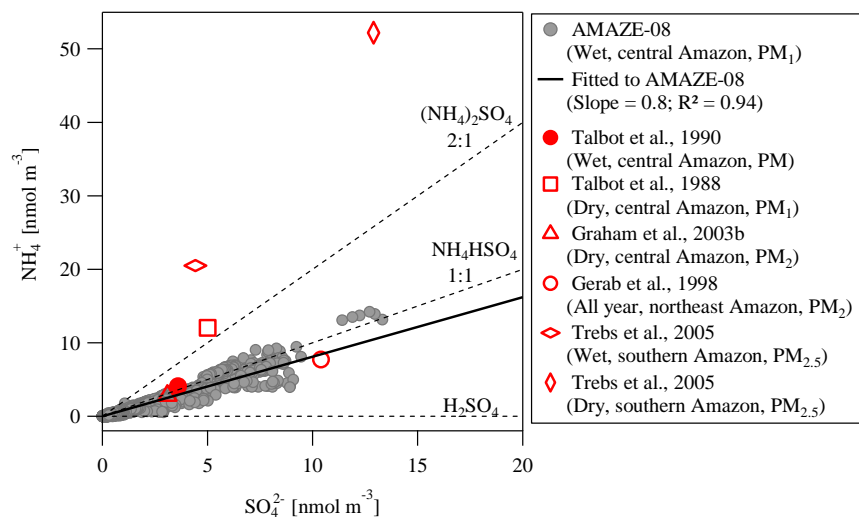


Figure 2

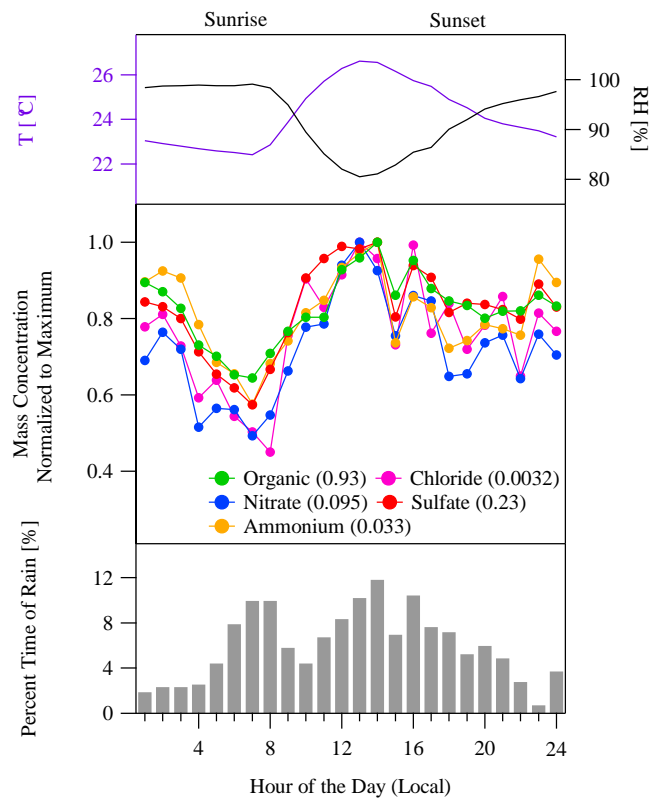


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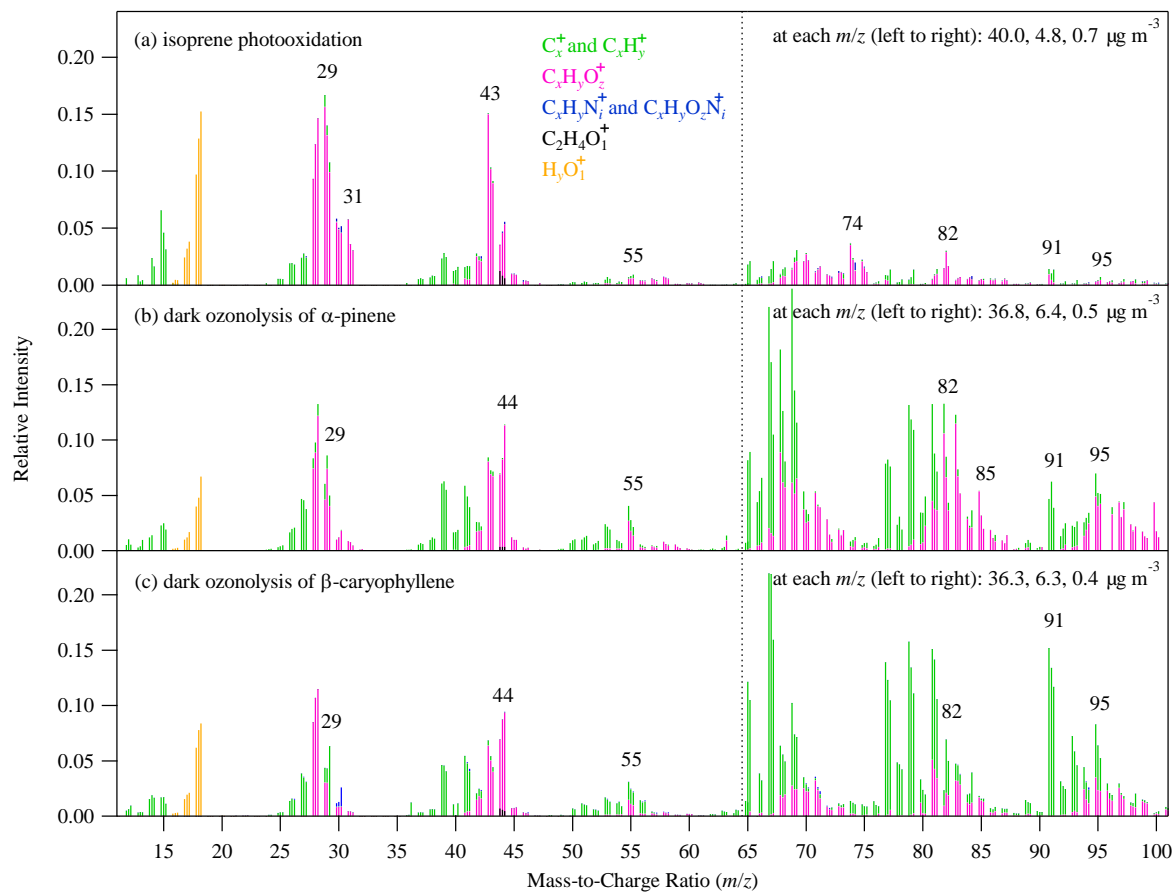


Figure 4

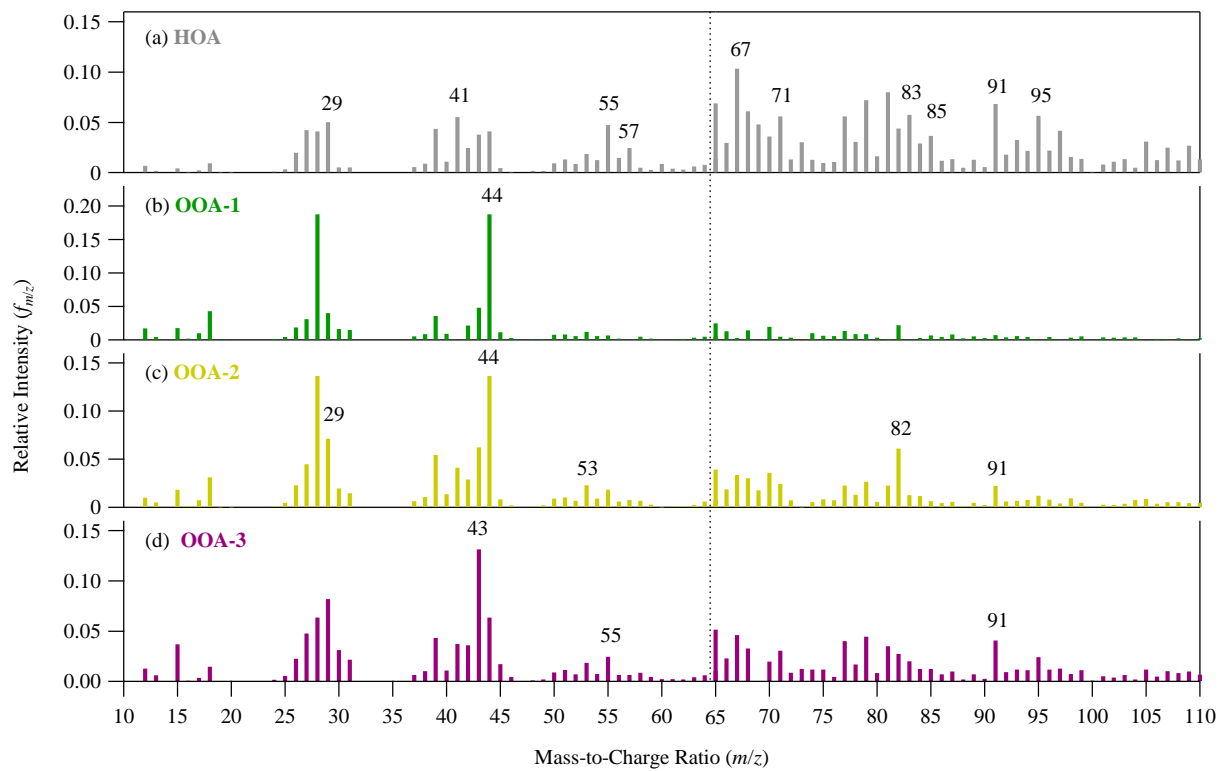


Figure 5

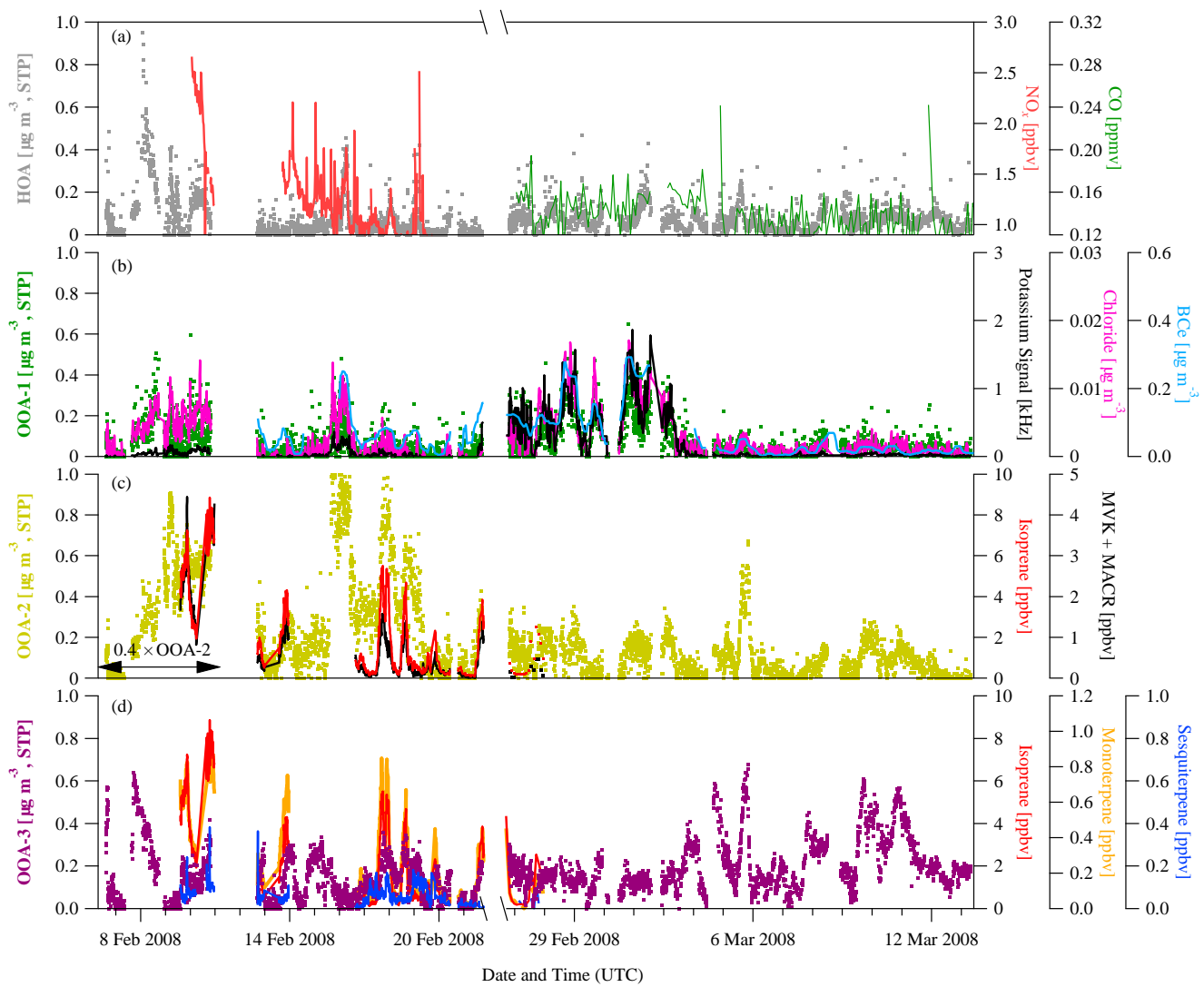


Figure 6

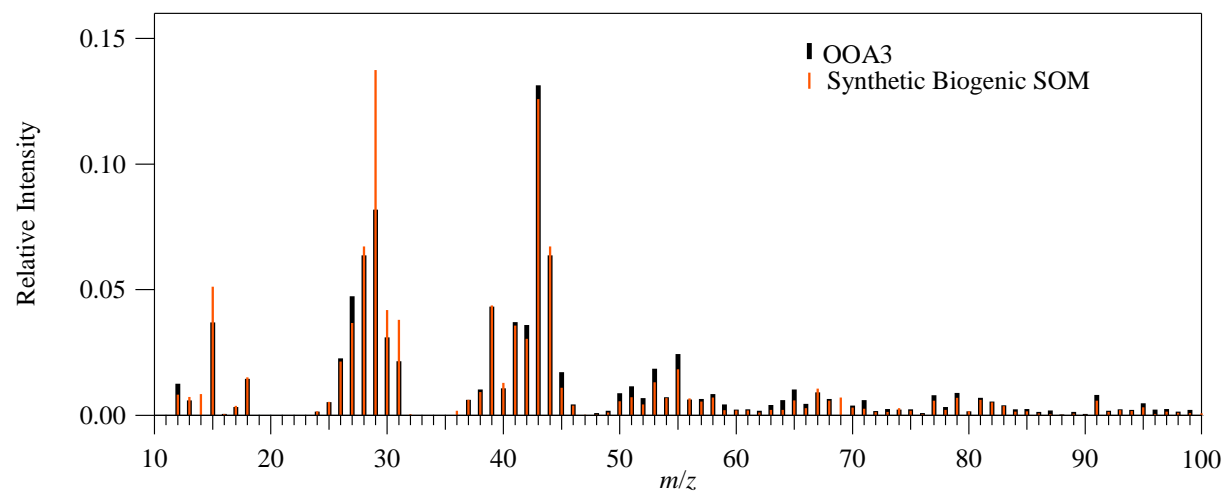


Figure 7

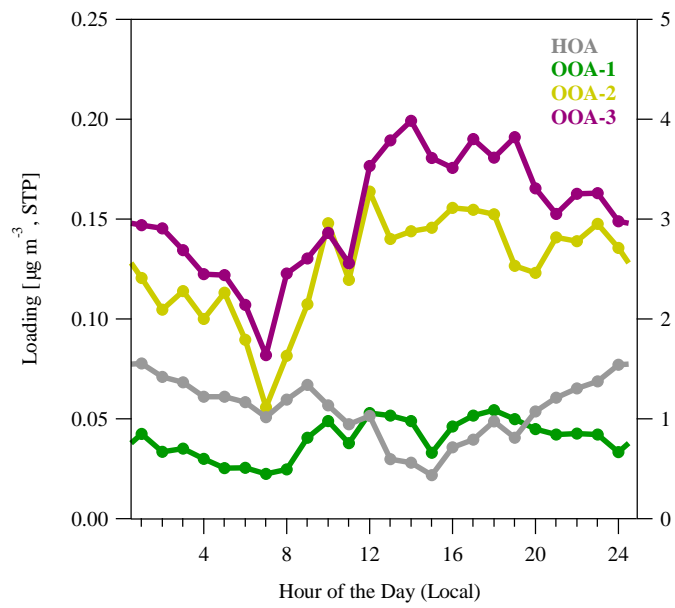


Figure 8

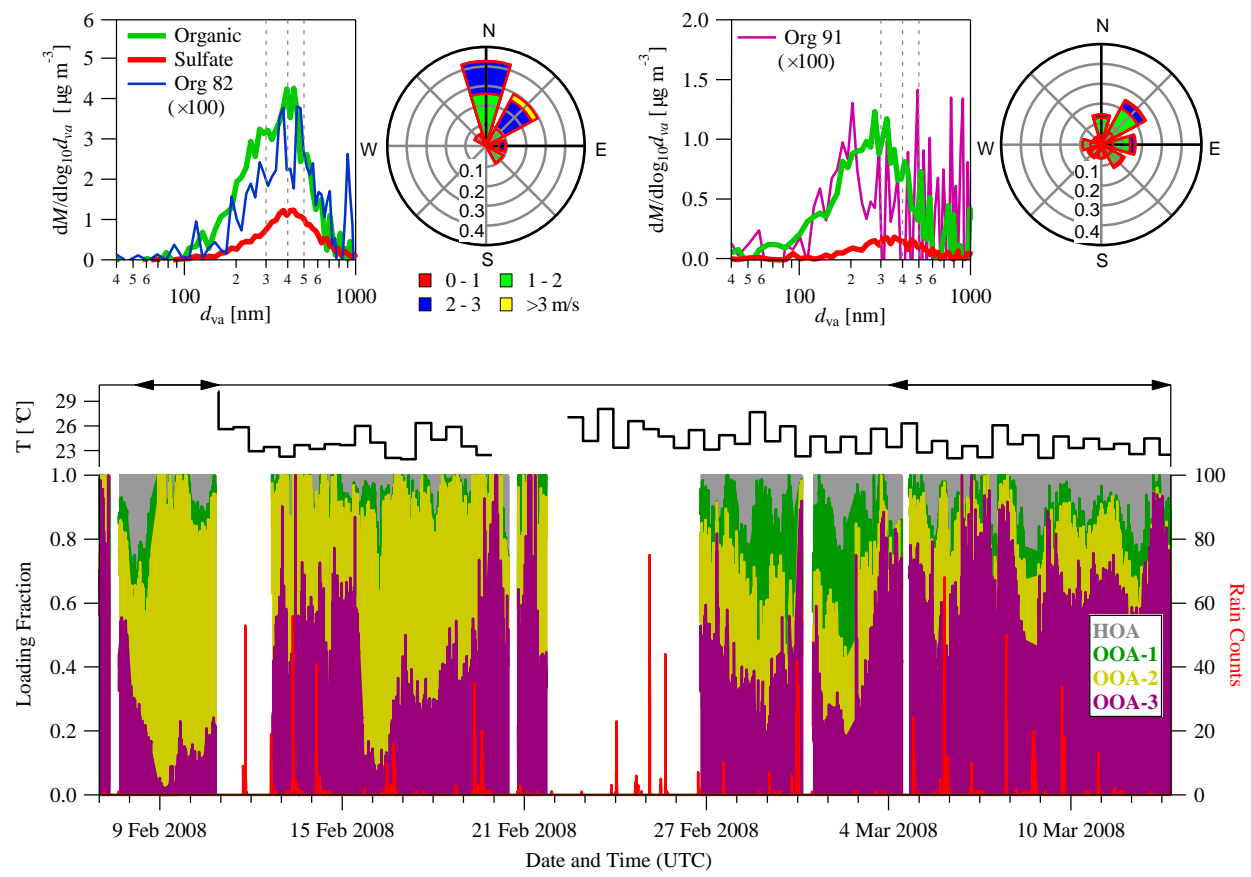


Figure 9