Response to reviews

Comments to the Author:
The authors have reasonably addressed the comments of the referees. However, a number of minor alterations are needed before the manuscript and its Supplement can be published in ACP.

We thank the editor for all the corrections. Changes are made accordingly.

For the main text:
Page 0, line 3: The affiliation is missing for Pauliquevis.
Line 36: Replace "BVOC" by "BVOCs".
Line 86: Replace "located 60 km NNW of Manaus and faced" by "is located 60 km NNW of Manaus and faces".
Line 112: Replace "because their" by "because of their".
Line 113: Replace "(PMF; (Paatero and Tapper, 1994))" by "(PMF) (Paatero and Tapper, 1994)".
Line 143: Replace "larger (up" by "larger levels (up".
Line 172: Replace "from Atlantic" by "from the Atlantic".
Line 178: Replace "Supplement. Other" by "Supplement). Other".
Line 182: Replace "on average," by ", on average,".
Line 269: Replace "on order" by "on the order".
Line 270: Replace "highly-oxidizedorganic" by "highly-oxidized organic".
Line 271: Replace "AMAZE-08(Chen" by "AMAZE-08 (Chen".
Line 280: Replace "correlation value" by "correlation values".
Changes are made to address the above comments.

Line 299: It is unclear what is meant by "statistical factories". Should it perhaps be "statistical factors" instead?
Yes, it should be "factors" instead of "factories". This change is made.

Page 18, lines 7-4 from bottom: "Andreae (2007)" should come before "Andreae et al. (1990)".
This change is made.

Pages 19-23: "Poschl" should be replaced by "Pöschl" (on 6 occasions).
We have replaced "Poschl" by "Pöschl" in the main text as well as in the Supplement.

For the Supplementary Material:
Page 1, line 7 from bottom: Replace "excluded from" by "and excluded from".
Page 2, line 11: Replace "readily undergo" by "readily undergoes".
Page 2, line 12: Replace "lead much" by "lead to much".
Page 2, line 2 from bottom: Replace "IC, and PIXE" by "ion chromatography (IC), and particle-induced X-ray emission (PIXE)".
Page 3, line 15: Replace "Roldin" by "Roldin et al.".
Page 4, line 4: Replace "from SFU" by "from the SFU".
Page 4, line 5: Replace "ion chromatography (IC) for" by "IC for".
Page 4, line 7: Replace "particle-induced X-ray emission (PIXE) for" by "PIXE for".
Page 5, last line: Replace "0.006 I" by "0.006 i".
Page 6, line 8: Replace "driven force" by "driving force".
Page 7, line 2: Replace "having signal-to-noise" by "having a signal-to-noise".
Page 8, line 2: Replace "strongly correlation" by "strong correlation".
Changes are made to address the above comments.

Pages 11-12: There is no reference made within the text to the following references that are in the Reference list: “Docherty et al. (2008)”, “Gomez-Gonzalez et al. (2008)”, “Iinuma et al. (2009)”, and “Surratt et al. (2008)”.
Those uncited references are removed.

Page 14, line 4: Replace “mass distributions” by “mass size distributions”.
Page 15, line 8 from bottom: Replace “chloride respectively and” by “chloride, respectively, and”.
Changes are made to address the above comments.

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

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Abstract

Real-time mass spectra of the non-refractory species in submicron aerosol particles were recorded in a tropical rainforest in the central Amazon basin during the wet season from February to March 2008, as a part of the Amazonian Aerosol Characterization Experiment (AMAZE-08). Organic material accounted on average for more than 80% of the non-refractory submicron particle mass concentrations during the period of measurements. There was insufficient ammonium to neutralize sulfate. In this acidic, isoprene-rich, HO_2-dominant environment positive-matrix factorization of the time series of particle mass spectra identified four statistical factors to account for the 99% variance of the signal intensities of the organic constituents. The first factor was identified as associated with regional and local pollution and labeled as "HOA" for its hydrocarbon-like characteristics. A second factor was associated with long-range transport and labeled as "OOA-1" for its oxygenated characteristics. A third factor, labeled "OOA-2," was implicated as associated with the reactive uptake of isoprene oxidation products, especially of epoxydiols to acidic haze, fog or cloud droplets. A fourth factor, labeled as "OOA-3," was consistent with an association to the fresh production of secondary organic material (SOM) by a mechanism of gas-phase oxidation of biogenic volatile organic precursors followed by gas-to-particle conversion of the oxidation products. The suffixes 1, 2, and 3 on the OOA labels signify ordinal ranking with respect to the extent of oxidation represented by the factor. The process of aqueous-phase oxidation of water-soluble products of gas-phase photochemistry might also have been associated to some extent with the OOA-2 factor. The campaign-average factor loadings were in a ratio of 1.4:1 for OOA-2:OOA-3, suggesting the comparable importance of particle-phase compared to gas-phase pathways for the production of SOM during the study period.

11. Introduction

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

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

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

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

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

2~~2~~. Site and Instrument Description

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

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

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

185 "robust mode"). Further aspects of the analysis and output evaluation are provided in Sect. C of
186 the Supplement. Because of the low mass concentrations, the signal-to-noise ratios were
187 insufficient for satisfactory PMF analysis of the high-resolution data. PMF results are reported
188 herein for unit mass resolution.

189 The AMS mass spectra of SOM produced in the Harvard Environmental Chamber (HEC)
190 by (i) the photooxidation of isoprene (C_5H_8), (ii) the dark ozonolysis of the monoterpene α-
191 pinene ($C_{10}H_{16}$) (adapted from Shilling et al. (2009)), and (iii) the dark ozonolysis of the
192 sesquiterpene β-caryophyllene ($C_{15}H_{24}$) are reported herein for the purpose of comparison to the
193 AMAZE-08 data. Experimental details are described elsewhere (Shilling et al., 2009; King et al.,
194 2010; Chen et al., 2011 and 2012). A library of spectra was collected at different SOM mass
195 concentrations.

196 **~~3~~3. Results and Discussion**

197 3.1 Mass concentrations

198 Figure 1 shows a time series of measurements by the AMS and other instruments during
199 AMAZE-08. The AMS detects the non-refractory chemical components of the submicron
200 fraction of the ambient particle population (NR-PM_1) (Fig. 1a-1c). As described in Chen et al.
201 (2009), organic material and sulfate were the two major components identified by the AMS,
202 with correspondingly low concentrations of ammonium and negligible concentrations of nitrate
203 and chloride. The campaign-average organic particle mass concentration was 0.76 ± 0.23 μg m^{-3},
204 corresponding to 0.45 ± 0.13 μg C m^{-3} of organic carbon and an OM:OC ratio of 1.7. The
205 campaign-average sulfate mass concentration of 0.19 ± 0.06 μg m^{-3} agreed well with the average
206 value of 0.21 ± 0.06 μg m^{-3} measured by ion chromatography (IC) and the value of 0.24 ± 0.05
207 μg m^{-3} measured by particle-induced X-ray emission (PIXE) for the fine-mode (PM_2) filters.

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

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

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

Figure 1f shows the time series of the particle light scattering coefficient measured by nephelometry at 550 nm for PM_7. The elevated scattering coefficients during 22 February to 3 March 2008 were driven by elevated mineral dust concentrations in the coarse mode, along with elevated submicron sulfate, BCe, and organic material arising from the advection of the Manaus pollution plume as well as long-range transport from Africa (Sect. B of the Supplement). Other temporal maxima corresponded to increases of submicron particle mass concentration. Figure 1g shows the elemental compositions of the submicron organic material measured by the AMS. The O:C and H:C ratios, corrected as described in Canagaratna et al. (2015), were 0.58 $\pm$0.16 (one standard deviation) and 1.60 $\pm$0.18, on average, respectively. The 10/90 quantiles were 0.40/0.74 and 1.42/1.80, respectively. The N:C ratios were 0.03 $\pm$0.01.

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

AMAZE-08 (Fig. S3). The molar ratio of $NH_4^+ : SO_4^{2-}$ was 0.80 (Fig. 2), meaning that there was insufficient ammonium to neutralize sulfate for the submicron particle population and suggesting a composition close to that of ammonium bisulfate. Similar molar ratios have been reported in several previous studies in the central and northeast Amazon basin (Talbot et al., 1988, 1990; Gerab et al., 1998; Graham et al., 2003b). The AMS is unable to quantify refractory components such as K^+, Na^+, Ca^{2+}, and Mg^{2+}. Mass-diameter distributions of these ions obtained by IC analysis of samples collected by a Multi-Orifice Uniform Deposit Impactor (MOUDI) on 22 March 2008 suggest that 40% of the mass of these ions was distributed to the submicron particle fraction. For comparison, Fuzzi et al. (2007) for the wet season reported 50-60% of K^+ and Ca^{2+} in the submicron fraction, compared to the predominance of Na^+ and Mg^{2+} in the supermicron fraction. The campaign-average fine-mode mass concentrations of K^+, Ca^{2+}, Na^+, and Mg^{2+} measured by IC were 0.03, 0.01, 0.02, and 0.01 $\mu g\ m^{-3}$, respectively. The implication of the relative concentrations (i.e., sulfate concentration of $0.19 \pm 0.06\ \mu g\ m^{-3}$) is that the submicron inorganic ion composition is reasonably approximated as ammonium bisulfate during AMAZE-08.

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

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

3.2. Mass spectra of laboratory biogenic SOM

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

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

Compared to the spectra of the other types of biogenic SOM, isoprene-derived SOM under HO_2-dominant conditions has a unique signature. "HO_2-dominant" refers to the fate of peroxy radicals with respect to reaction with HO_2 or NO. The relative intensities of CHO^+ at *m*/*z* 29, CH_2O^+ at *m*/*z* 30, CH_3O^+ at *m*/*z* 31, $C_3H_6O_2^+$ at *m*/*z* 74, and $C_3H_7O_2^+$ at *m*/*z* 75 in the spectra of isoprene-derived SOM are much greater, and the contributions of $C_xH_y^+$ ions are less, especially for *m*/*z* > 65. Moreover, *m*/*z* 82 that mainly consists of $C_3H_5O^+$ appears to be the most intense peak for $m/z \geq 75$. This fragment has been suggested as a characteristic fragment of isoprene-derived SOM (Robinson et al., 2011). Isoprene-derived SOM also does not follow the empirical linear relationship between O:C and I_{44}:I_{org} described by Aiken et al. (2008) (Fig. S5), indicating that deriving O:C from I_{44}:I_{org} requires careful judgments on the contribution of isoprene-derived SOM.

3.3 Multivariate factor analysis of the organic mass spectra

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

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

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

The factors OOA-1, OOA-2, and OOA-3 were ranked by the f_{44}:f_{43} ratios (high to low) and labeled based on Zhang et al. (2011), where $f_{m/z}$ represents the fractional contribution of the signal intensity at *m*/*z* to the statistical factor. The signal intensity was dominated at *m*/*z* 44 by the CO_2^+ fragment and at *m*/*z* 43 by the $C_2H_3O^+$ and $C_3H_7^+$ fragments. The f_{44}:f_{43} ratio has been used in some settings as a surrogate for the extent of oxidation (i.e., so-called 'atmospheric aging') of SOM (Ng et al., 2010 and 2011).

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

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

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

this study and "82Fac", "UNKN", and "IEPOX-OA" of earlier studies) derived from atmospheric data sets. In particular, there are significant differences at *m*/*z* 29 and *m*/*z* 39 through *m*/*z* 44. The values of f_{44} of the laboratory results are approximately 25% of those of the cited PMF factors. One possible explanation for these differences is that the laboratory experiments did not capture the full range of atmospheric processes, such as possible synergistic chemistry among the range of atmospheric precursors, aqueous-phase processing, and photochemistry under a range of HO_2:NO ratios (Ervens et al., 2011; Emanuelsson et al., 2013; Liu et al., 2013; Nguyen et al., 2014). In particular, the laboratory experiments were typically carried out at low relative humidity. The atmosphere during AMAZE-08 was humid (89 to 100% RH; 25 to 75% quantiles). Pöhlker et al. (2012) showed evidence of multiphase processing in the larger accumulation mode particles. The oxidized material produced by aqueous-phase oxidation (e.g., dicarboxylic acids (Lim et al., 2010)) may explain the higher f_{44} in the OOA-2 factor compared to the laboratory spectra. In summary, the OOA-2 factor during AMAZE-08 was interpreted as SOM produced by the reactive uptake of isoprene photo-oxidation products, including possible aqueous-phase oxidation in haze, fog, and cloud droplets.

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

however, was overestimated by the linear combination. The remarkable result is that the ambient factor could to large extent be explained by just three laboratory data sets given the wide range of BVOC precursor compounds that can contribute to SOM production in the Amazon basin. The explanation is three-fold, one that isoprene is the dominant BVOC for this rain forest, two that the AMS breaks complex molecules into simpler building blocks by electron-impact ionization, and three that the higher-order C_{10}, C_{15}, and possibly C_{20} BVOCs are all assembled biochemically from the isoprene (C_5) monomer. Moreover, the temporal variation of the OOA-3 loading tracked that of the BVOC concentrations (Fig. 6d). The OOA-3 statistical factor was therefore interpreted as associated with freshly produced SOM similar to that produced in the chamber experiments, meaning on a timescale of several hours by a mechanism of gas-to-particle partitioning of the BVOC oxidation products.

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

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

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

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

44. Conclusions

Submicron particle mass concentration in the Amazonian rainforest during the wet season of 2008 was dominated by organic material. The environment was humid, HO_2-dominant, isoprene-rich, with the presence of acidic particles in the submicron fraction of the atmospheric particle population. Factors OOA-2 and OOA-3 were identified in the patterns of the collected mass spectra. These factors were interpreted as tied to the in-basin production of biogenic secondary organic material and together accounted for >70% of the factor loadings, with the balance from HOA and OOA-1. The OOA-2 factor was implicated as associated with the reactive uptake of isoprene oxidation products, especially of epoxydiols to acidic haze, fog or cloud droplets. The OOA-3 factor was consistent with an association to the fresh production of SOM by a mechanism of gas-phase oxidation of BVOCs followed by gas-to-particle conversion of the oxidation products. Although multivariate statistical factors do not correspond to segregated individual chemical components (e.g., unlike molecules or families of molecules), the factors nevertheless can be indicative of the relative importance of different atmospheric emissions and process pathways. With this caveat in mind, the PMF analysis herein finds that the factor loadings were, on average, in a ratio of 1.4:1 for OOA-2 compared to OOA-3 and were alternately dominated in different periods of AMAZE-08 by the OOA-2 and OOA-3. These findings suggest a comparable importance of gas-phase and particle-phase (including haze, fog,

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

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List of Figures

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~~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~~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~~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-caryophylene-derived SOM, and 50% isoprene-derived SOM at mass concentrations of 0.4 to 0.7 μg m^{-3}).

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

Figure 9~~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.

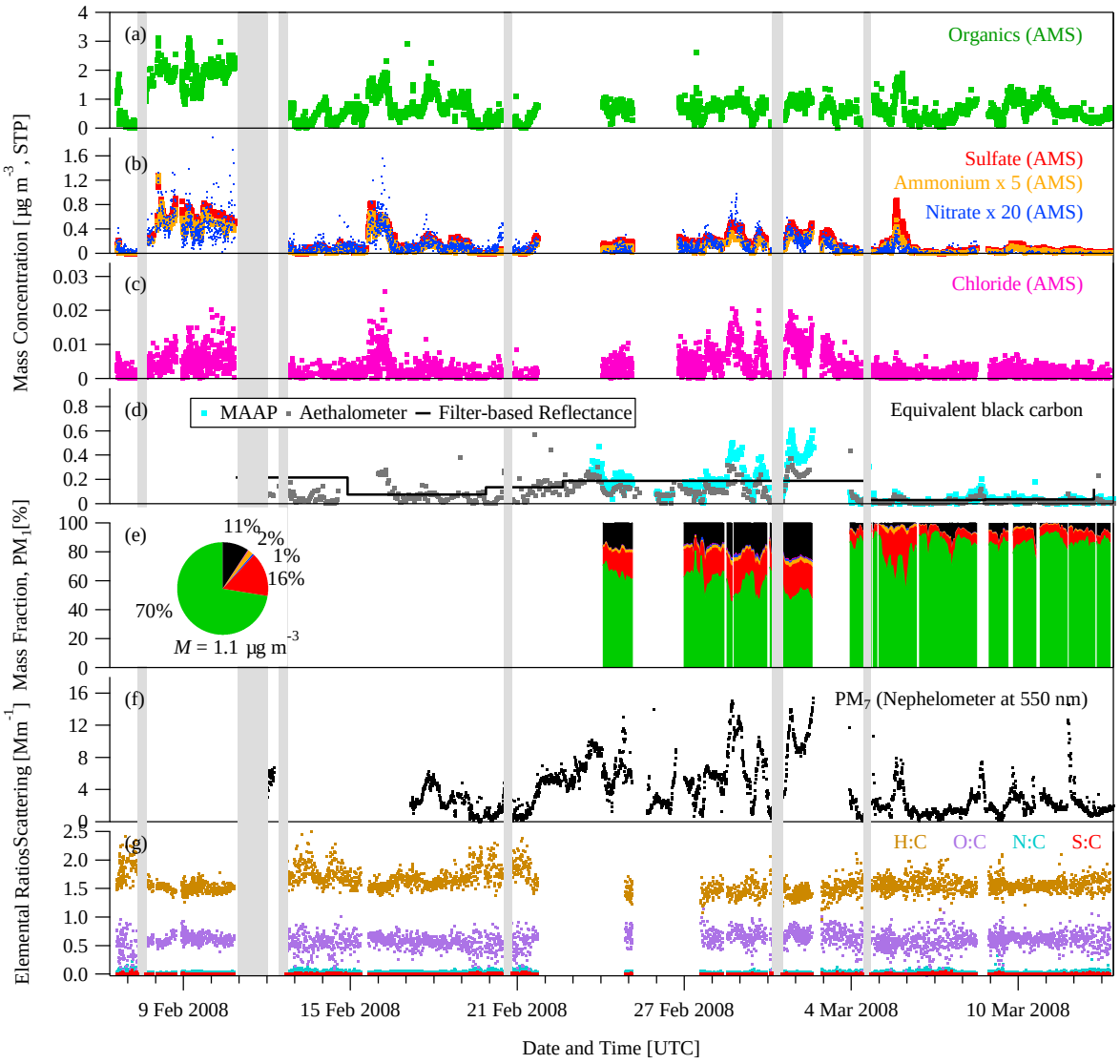
(a)
Organics (AMS)
(b)
Sulfate (AMS)
Ammonium x 5 (AMS)
Nitrate x 20 (AMS)
(c)
Chloride (AMS)
(d)
MAAP
Aethalometer
Filter-based Reflectance
Equivalent black carbon
(e)
11%
2%
1%
16%
70%
M = 1.1 µg m-3
(f)
PM7 (Nephelometer at 550 nm)
(g)
H:C
O:C
N:C
S:C
Mass Concentration [µg m-3, STP]
Mass Fraction, PM1 [%]
Scattering [Mm-1]
Elemental Ratios
9 Feb 2008
15 Feb 2008
21 Feb 2008
27 Feb 2008
4 Mar 2008
10 Mar 2008
Date and Time [UTC]

Figure 1

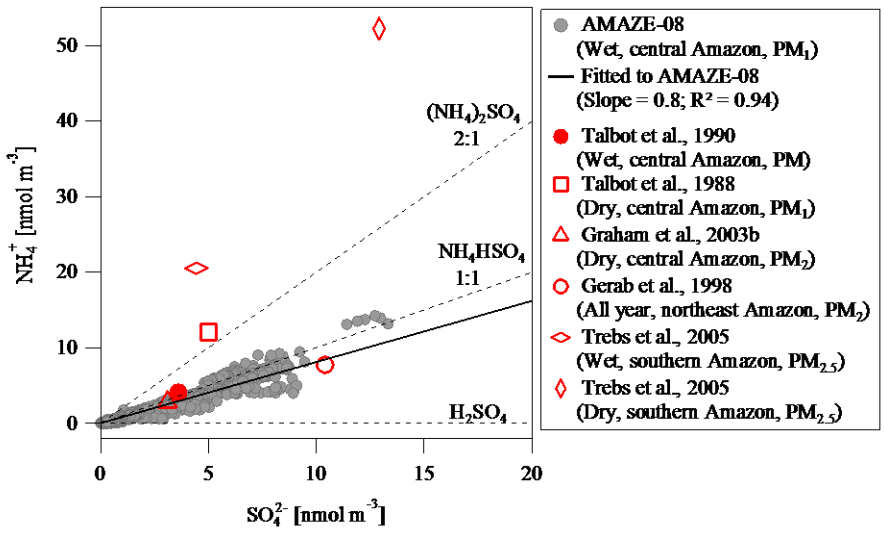
AMAZE-08
(Wet, central Amazon, PM1)
Fitted to AMAZE-08
(Slope = 0.8; R² = 0.94)
Talbot et al., 1990
(Wet, central Amazon, PM)
Talbot et al., 1988
(Dry, central Amazon, PM1)
Graham et al., 2003b
(Dry, central Amazon, PM2)
Gerab et al., 1998
(All year, northeast Amazon, PM2)
Trebs et al., 2005
(Wet, southern Amazon, PM2.5)
Trebs et al., 2005
(Dry, southern Amazon, PM2.5)
(NH4)2SO4
2:1
NH4HSO4
1:1
H2SO4
NH4+ [nmol m-3]
SO42- [nmol m-3]
0
10
20
30
40
50
0
5
10
15
20

Figure 2

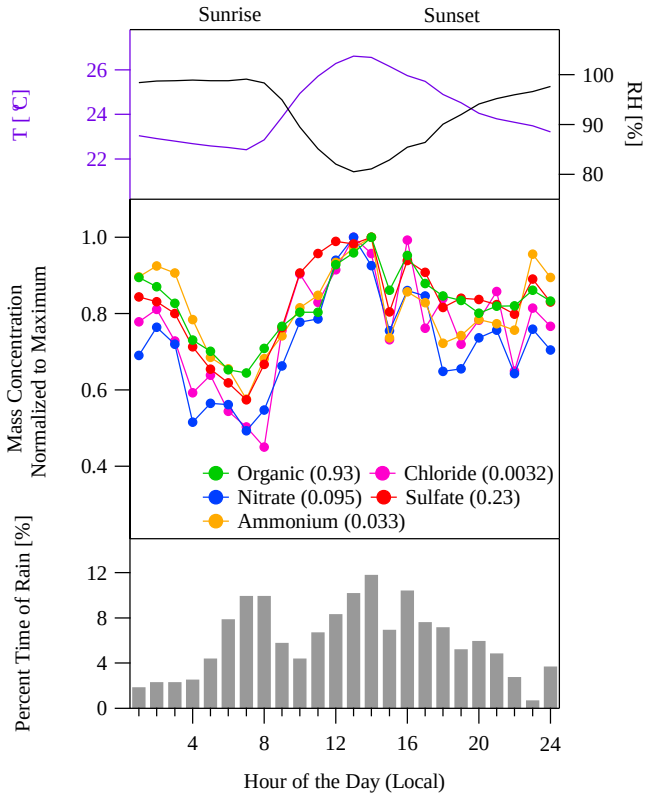
Sunrise
Sunset
T [°C]
26
24
22
RH [%]
100
90
80
Mass Concentration
Normalized to Maximum
1.0
0.8
0.6
0.4
Organic (0.93)
Chloride (0.0032)
Nitrate (0.095)
Sulfate (0.23)
Ammonium (0.033)
Percent Time of Rain [%]
12
8
4
0
4
8
12
16
20
24
Hour of the Day (Local)

Figure 3

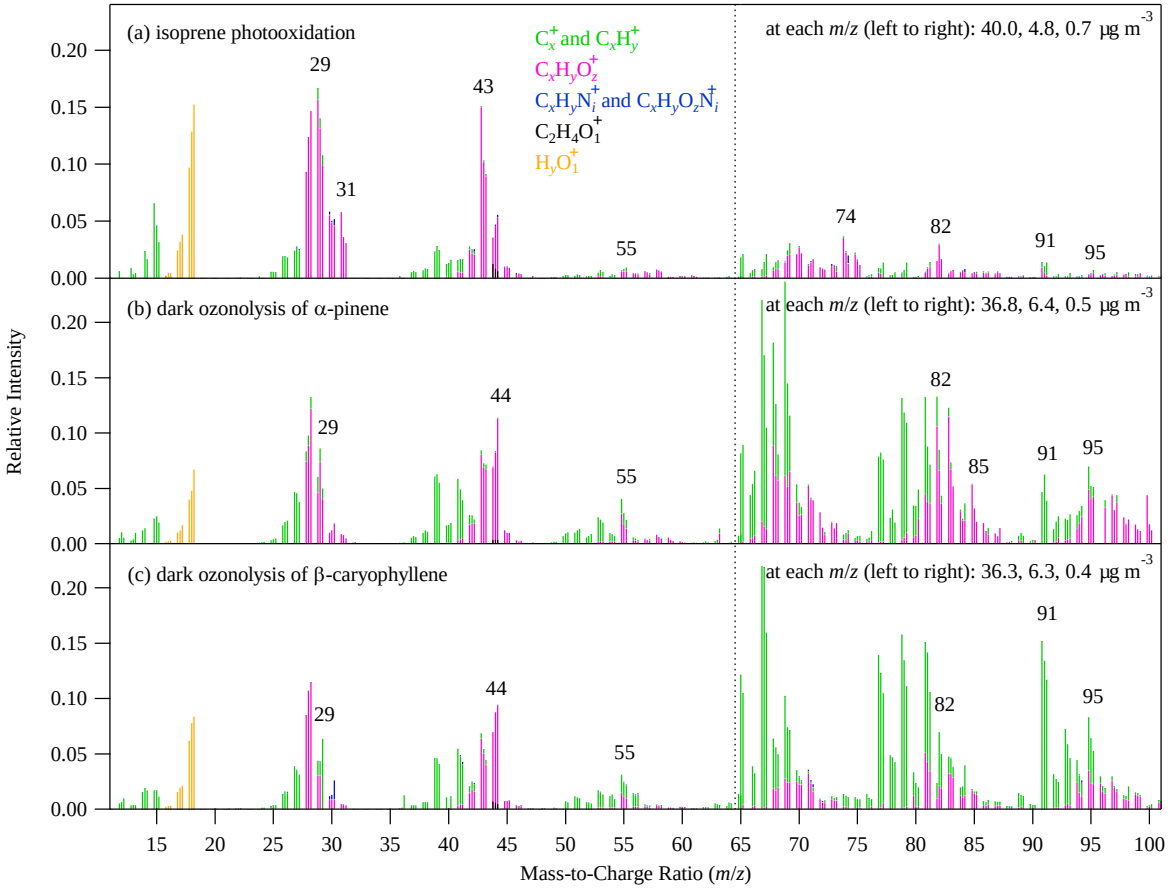
(a) isoprene photooxidation
C_x^+ and $C_xH_y^+$
$C_xH_yO_z^+$
$C_xH_yN_i^+$ and $C_xH_yO_zN_i^+$
$C_2H_4O_1^+$
$H_yO_1^+$
at each m/z (left to right): 40.0, 4.8, 0.7 μg m-3
(b) dark ozonolysis of α-pinene
at each m/z (left to right): 36.8, 6.4, 0.5 μg m-3
(c) dark ozonolysis of β-caryophyllene
at each m/z (left to right): 36.3, 6.3, 0.4 μg m-3
Relative Intensity
Mass-to-Charge Ratio (m/z)

Figure 4

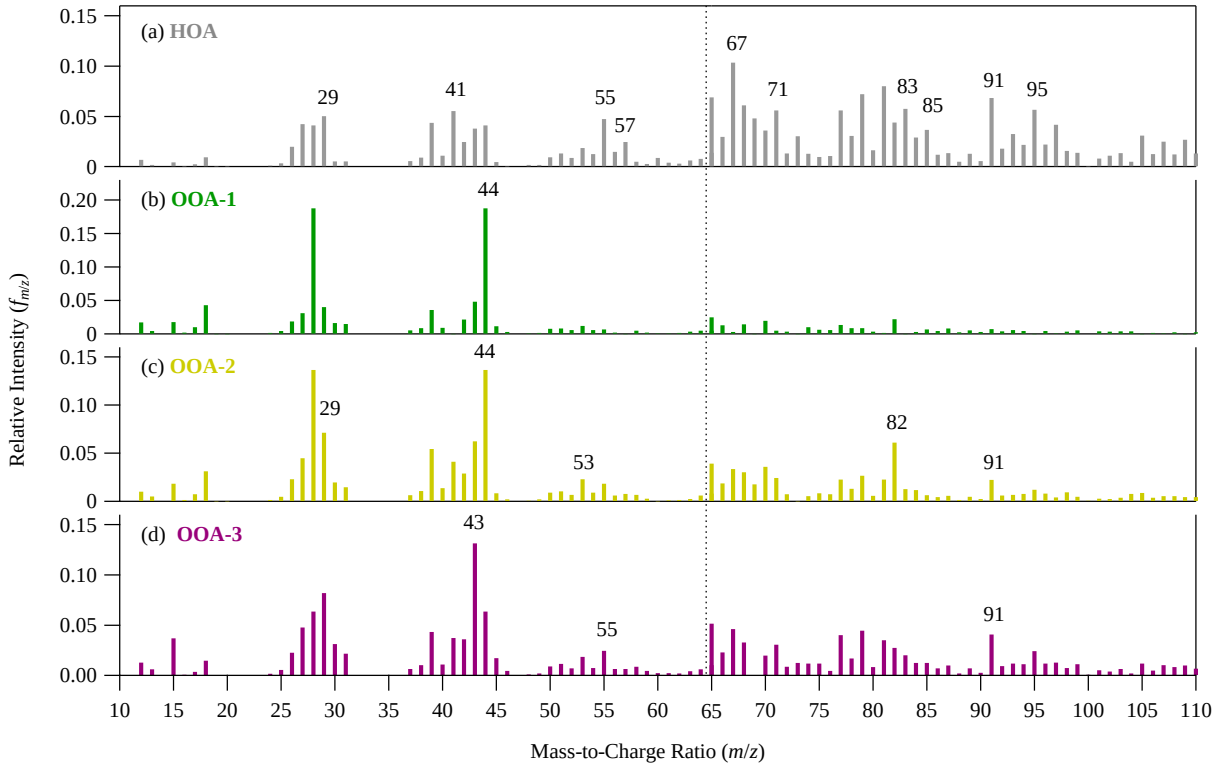
(a) HOA
(b) OOA-1
(c) OOA-2
(d) OOA-3
Relative Intensity ($f_{m/z}$)
Mass-to-Charge Ratio (m/z)

Figure 5

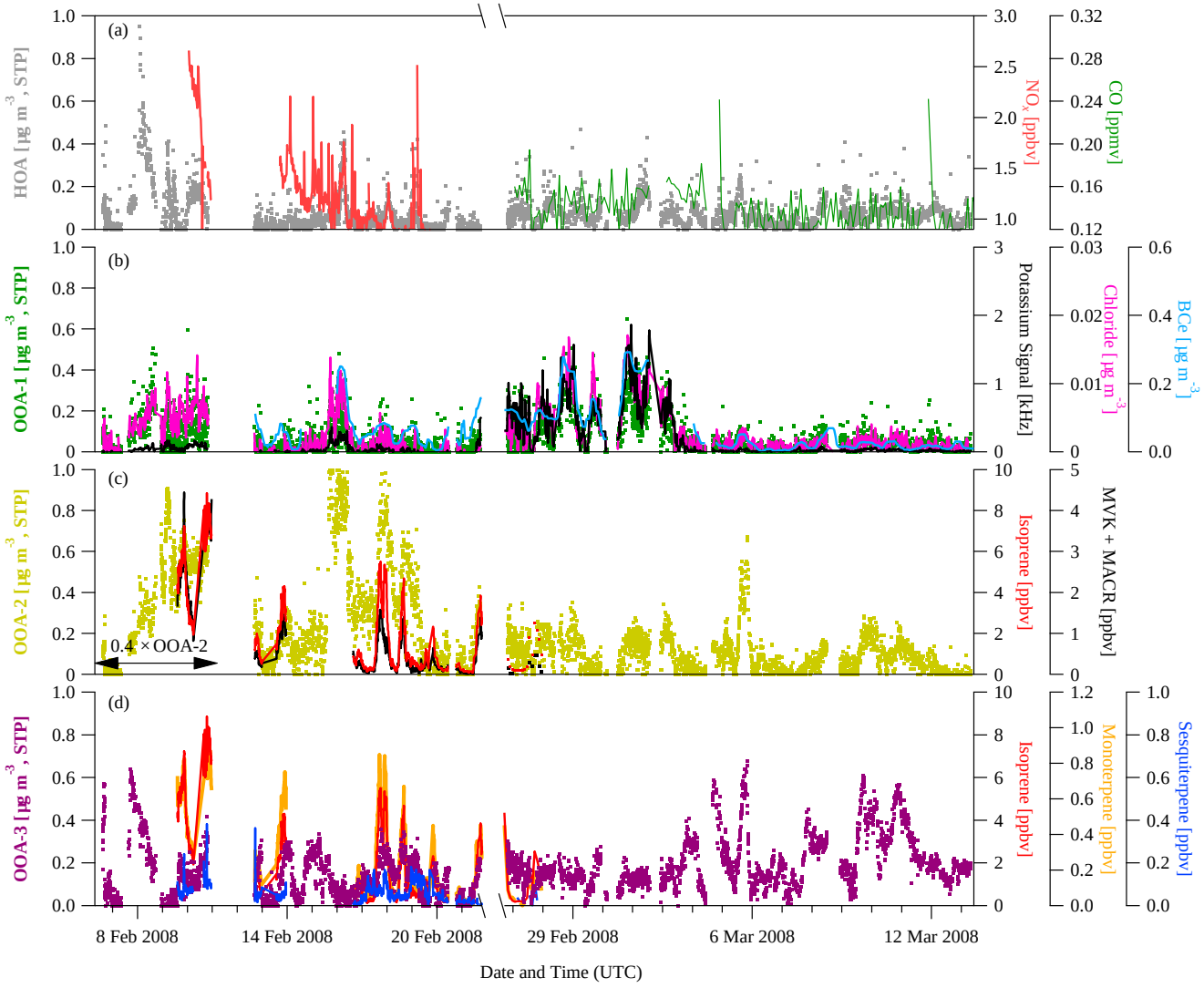
(a)
HOA [μg m-3, STP]
NOx [ppbv]
CO [ppmv]
(b)
OOA-1 [μg m-3, STP]
Potassium Signal [kHz]
Chloride [μg m-3]
BCe [μg m-3]
(c)
OOA-2 [μg m-3, STP]
0.4 × OOA-2
Isoprene [ppbv]
MVK + MACR [ppbv]
(d)
OOA-3 [μg m-3, STP]
Isoprene [ppbv]
Monoterpene [ppbv]
Sesquiterpene [ppbv]
8 Feb 2008
14 Feb 2008
20 Feb 2008
29 Feb 2008
6 Mar 2008
12 Mar 2008
Date and Time (UTC)

Figure 6

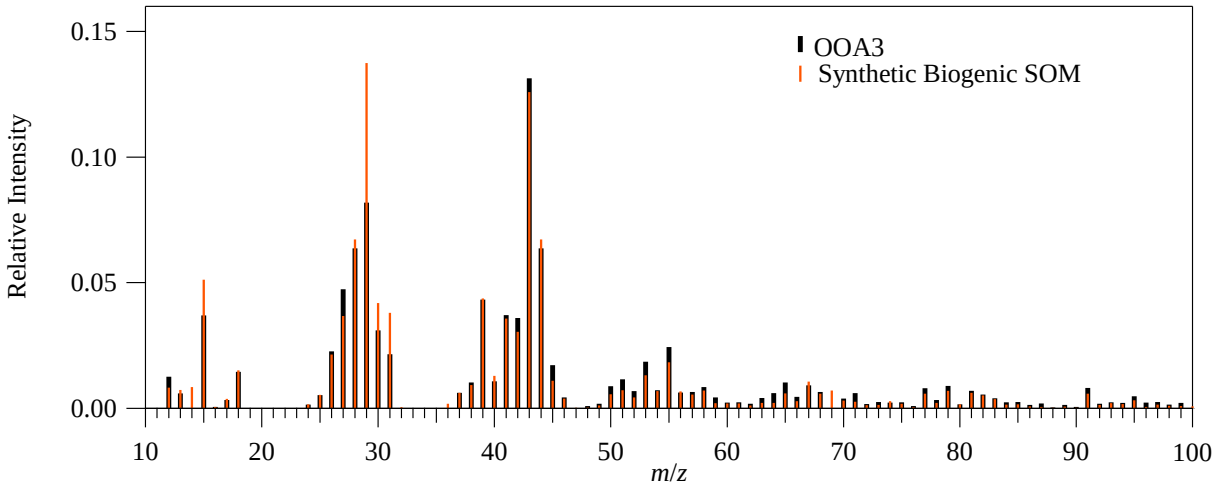
OOA3
Synthetic Biogenic SOM
Relative Intensity
0.15
0.10
0.05
0.00
10
20
30
40
50
60
70
80
90
100
m/z

Figure 7

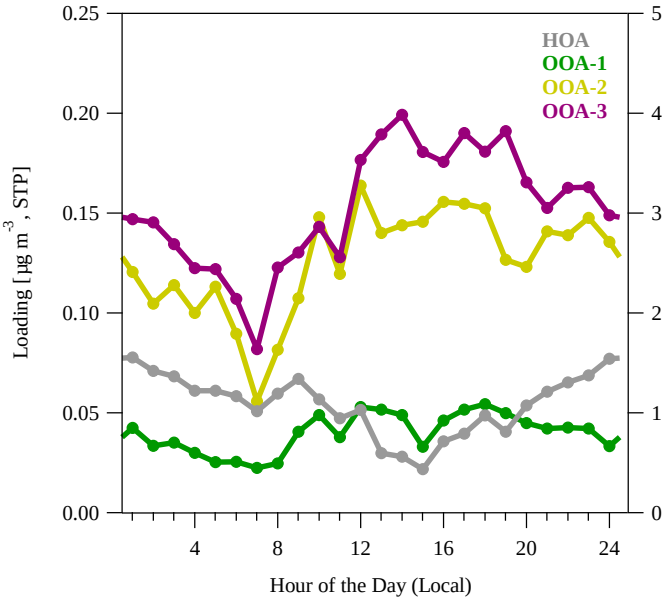
HOA
OOA-1
OOA-2
OOA-3
Loading [µg m-3 , STP]
Hour of the Day (Local)
0.25
0.20
0.15
0.10
0.05
0.00
5
4
3
2
1
0
4
8
12
16
20
24

Figure 8

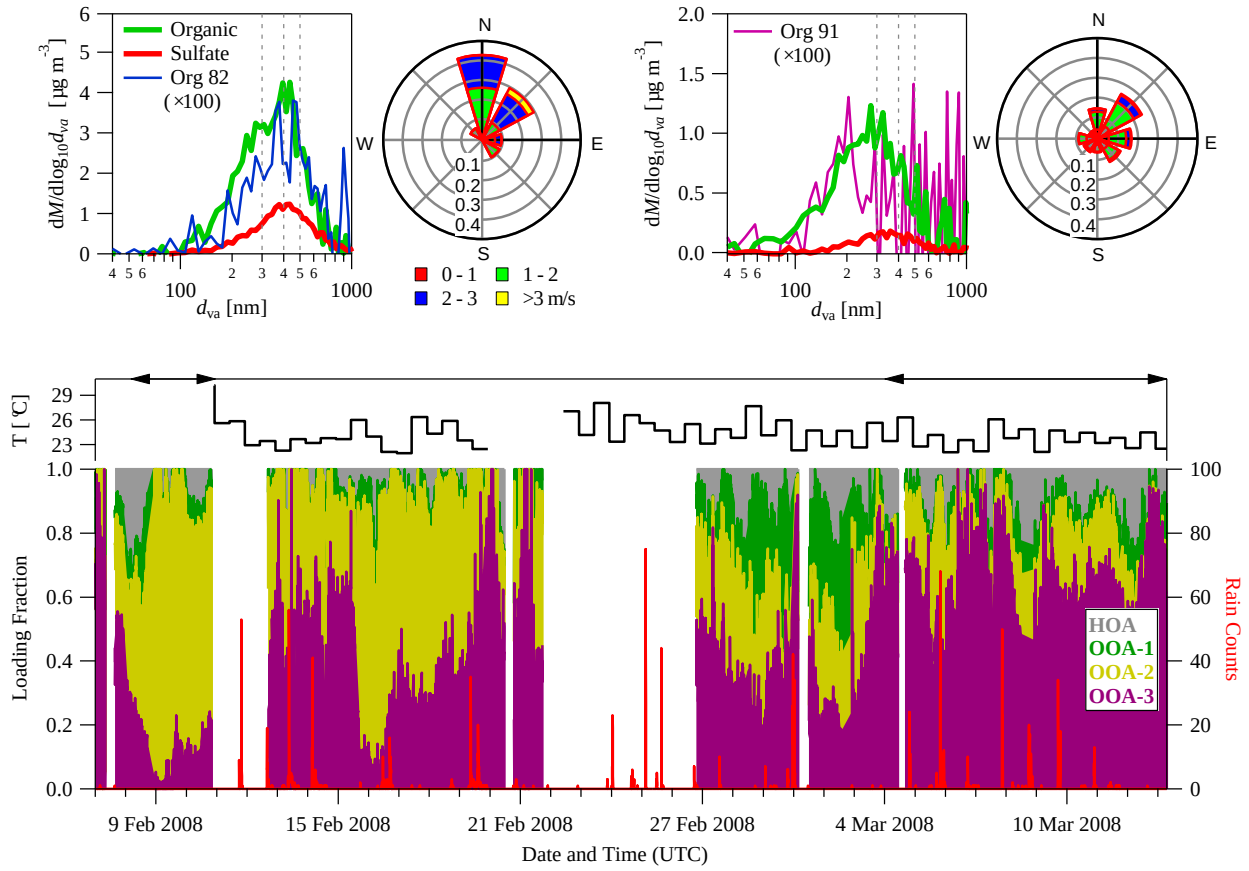
Organic
Sulfate
Org 82
(×100)
dM/dlog10dva [μg m-3]
dva [nm]
N
W
E
S
0.1
0.2
0.3
0.4
0 - 1
1 - 2
2 - 3
>3 m/s
Org 91
(×100)
T [℃]
Loading Fraction
Rain Counts
HOA
OOA-1
OOA-2
OOA-3
9 Feb 2008
15 Feb 2008
21 Feb 2008
27 Feb 2008
4 Mar 2008
10 Mar 2008
Date and Time (UTC)

Figure 9

Supplementary Material For

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

A. AMS sampling and data processing

Chen et al. (2009) described the AMS sampling and data processing. Additional details are provided herein. Standard relative ionization efficiencies (RIE) were used in the analysis, including 1.1 for nitrate, 1.2 for sulfate, 1.4 for organic molecules, 4.0 for ammonium, 1.3 for chloride, and 2.0 for water (DeCarlo et al., 2006; Mensah et al., 2011). Unlike the analysis in Chen et al. (2009), the organic signals of C_3H^+ at *m*/*z* 37, $C_3H_2^+$ at *m*/*z* 38, $C_3H_3^+$ at *m*/*z* 39, and $C_3H_4^+$ at *m*/*z* 40, which made up 5-8% of the total organic signal, were calculated time-dependently based on the ratio of them to $C_2H_2^+$ at *m*/*z* 26. In the present study particle-phase water was not included in the calculations of species mass concentrations. Occasionally the sampling site was influenced by the exhaust plumes from the site power source, which was a diesel generator located 0.72 km from TT34 and typically downwind. Abrupt increases in AMS-measured sulfate mass concentrations, even greater than the organic concentrations, were indicators of influence by the local pollution source. These pollution events were defined herein and excluded from the data sets analyzed (Fig. 1). Chen et al. (2009) excluded more data by using a broader pollution filter defined by Martin et al. (2010).

The AMS detection limits, calculated as three times the standard deviation of mass concentrations for filtered air obtained at 150-s intervals, were 0.06, 0.02, 0.001, 0.006, 0.002 $\mu g\ m^{-3}$ for organic material, sulfate, ammonium, chloride, and nitrate, respectively. The AMS is capable of focusing particles with 30-1000 nm with size-dependent particle transmission efficiency (Liu et al., 2007). As described in Gunthe et al. (2009), we operated the AMS at

sampling pressures of 867–907 hPa. Under these conditions, the transmission efficiency is close to 100% for particles with vacuum aerodynamic diameter d_{va} of 100–400 nm and is greater than 20% for particles with d_{va} of 50-1000 nm. For organic measurements, the estimated uncertainty is 30% at concentrations of 1 μg m^{-3} to 40% at concentrations of 0.5 μg m^{-3}. It can increase to 100% for low organic concentrations (0.1 μg m^{-3}). For sulfate measurements, the uncertainty is <10% for high concentrations (0.5 μg m^{-3}) and about 40% for low concentrations (0.05 μg m^{-3}).

Atomic ratios of oxygen-to-carbon (O:C), hydrogen-to-carbon (H:C), and nitrogen-to-carbon (N:C), as well as the mass ratios of organic material to organic carbon (OM:OC), were calculated from the W-mode data following previously described methods (Aiken et al., 2008). A recent study shows that organic aerosol with mixed keto-, hydroxyl-, and acid-functionalities readily undergoes thermally-induced dehydration and decarboxylation on the AMS vaporizer (Canagaratna et al., 2015). Such dehydration and decarboxylation can lead to much greater $(CO^+)_{org}$:$(CO_2^+)_{org}$ and $(H_2O^+)_{org}$:$(CO_2^+)_{org}$ ratios than the ones that have been empirically used in the "general" elemental analysis described by Aiken et al. (2008). A correction of 34% increase in O:C and 17% increase in H:C was applied based on the correction formula reported by Canagaratna et al. (2015).

In the AMS, the organosulfate species can fragment to organic ions ($C_xH_yO_z^+$), organosulfur ions ($C_xH_yO_zS^+$), and ions with a pattern indistinguishable from inorganic sulfate (e.g., SO_2^+) (Farmer et al., 2010). Similarly, the organonitrate species also fragment to the NO_x^+ ions and are detected as inorganic nitrate by the AMS. For the AMAZE-08 data set, signal intensities for $C_xH_yO_zS^+$ ions were not above noise in the collected high-resolution mass spectra. The agreement among AMS, ion chromatography (IC), and particle-induced X-ray emission (PIXE) sulfate mass concentrations, as well as the absence of organosulfur ions in the

high-resolution mass spectra, suggest minimal mass concentration of organosulfate species, at least at concentrations above uncertainty levels. Nitrate had a campaign-average concentration of 7 ± 2 ng m^{-3}. This value was greater than the average fine-mode concentration of 4 ± 1 ng m^{-3} measured by IC. As a test against possible significance of organonitrate species to the results of the present study, a limiting assumption that assigns all AMS-measured nitrate to organonitrate increases the average O:C ratio by <0.01 for the elemental analysis and corresponds to a maximum of 5% contribution of organonitrates to the total organic particle mass concentration for an assumed molecular weight of 360 g mol^{-1} (Chen et al., 2011). The low mass concentration of particle-phase organonitrates is expected because of the low prevailing NO_x concentrations and humid environment (Day et al., 2010; Liu et al., 2012).

B. Other concurrent measurements and comparisons among measurements

Instruments making measurements during AMAZE-08 at the TT34 site are listed in Martin et al. (2010). The size distribution of particles between 0.010 and 0.48 μm (mobility diameter) was measured every 5 min by a Scanning Mobility Particle Sizer (Lund SMPS) (Roldin et al., 2008). Particle volume concentrations were calculated from the SMPS size distributions for an assumption of spherical particles. The total number concentration for particles greater than 0.010 μm was measured every 3 s by a Condensation Particle Counter (CPC, TSI 3010). Particle scattering coefficients at multiple wavelengths were measured every 1 min by a nephelometer (TSI 3563) and averaged to 10 min. The light absorption at 637 nm of deposited particles was measured every 1 min by the Multiangle Absorption Photometer (MAAP, Thermo 5012). These several instruments sampled through a laminar-flow line (i.e., separate sampling from the AMS line) that was characterized by lower and upper limits of transmission for particle diameters of 0.004 and 7 μm, respectively (Martin et al., 2010). Several particle filter

samples were collected (Artaxo et al., 2013). Total-particle filters (TPF; PM_3) were collected in-line with the turbulent inlet used by the AMS. Stacked filter units (SFU) were installed separately at 10 m to sample fine- (PM_2) and coarse-mode particles ($PM_{2\text{-}10}$). The two types of filters show reasonable agreement on the particle mass concentration (Table S2). The fine-mode data from the SFU are reported herein. Filter samples were analyzed by ~~ion chromatography (IC)~~IC for water-soluble ionic components, including sulfate, nitrate, and ammonium, among other components. The filters were also analyzed by PIXE~~particle-induced X-ray emission (PIXE)~~ for elemental composition. Concentrations were adjusted to STP conditions.

The AMS data can be compared to other concurrent measurements of AMAZE-08. The mass ratio of NR-PM_1 measured by the AMS to PM_2 by filter assays was 0.65 as a campaign average (Table S2). The ratio was less than unity because PM_2 included contributions by black carbon and mineral dust (Sect. 3.1) as well as organic material in the diameter range of 1 to 2 μm (Pöschl et al., 2010). Particle mass-diameter distributions obtained from gravimetric analysis of stages of a Multi-Orifice Uniform Deposit Impactor (MOUDI) showed that an average of 30% of the particle mass concentration was associated with diameter range from 1 to 2 μm (cf. Fig. 16 in Martin et al. (2010)).

Figure S6a shows a line of slope m of 1.24 and correlation R^2 of 0.81 in a scatter plot between the AMS-calculated and the SMPS-derived particle volume concentrations. Figure S6b shows the scatter plot of the number concentrations obtained by integrating the SMPS measurements and those directly measured by the CPC. The slope of 0.6 (R^2 = 0.90) indicates that the CPC measured more particles than the corresponding SMPS-derived quantity. The SMPS bias to particle undercounting can explain $m > 1$ in the scatter plot of Fig. S6a. The scatter plot between sulfate particle mass concentrations measured by the AMS and those measured by

IC analysis of the filters is fit by a line of m = 0.90 and R^2 = 0.50 (Fig. S6c).

The combined AMS and SMPS data sets were used to estimate the particle effective density ρ_{eff} (kg m^{-3}) based on an in-common mode diameter (Katrib et al., 2005). For nonporous spherical particles, material density ρ has the same values as ρ_{eff}, and this condition was assumed to hold in the performed data analysis. The organic material density ρ_{org} was then derived by assuming volume additivity and by using ρ_{inorg} of 1780 kg m^{-3} as ammonium bisulfate for the inorganic components. The estimated campaign-average value of ρ_{eff} for submicron Amazonian particles is 1390 $\pm$ 150 kg m^{-3}. Figure S7 shows one example of the mass-diameter distribution measured by the AMS compared to that derived from the SMPS measurements. Assuming that the chemical components either do not mix or alternatively have a numerically small excess volume of mixing, we can derive ρ_{org} of 1270 $\pm$ 110 kg m^{-3} based on the campaign-average chemical composition and a density of 1770 kg m^{-3} for all inorganic components (Cross et al., 2007). The value of ρ_{org} is consistent with the density of 1200-1500 kg m^{-3} observed for laboratory-generated biogenic secondary organic material (Bahreini et al., 2005; Shilling et al., 2009; Chen et al., 2012).

Figure S6d shows the linear regression of the light scattering derived from the AMS (PM_1) and the nephelometer measurements (PM_7), all for 550-nm wavelength. In total, 74 time periods having nearly identical mass concentrations of sulfate were selected to obtain the averaged particle mass-diameter distributions measured by the AMS. For comparison, nephelometer data at 550 nm were averaged for the same time periods. The mass-diameter distributions were multiplied by diameter-dependent mass extinction efficiencies (m^2 g^{-1}) to estimate light scattering coefficients. The mass extinction efficiencies were calculated at 550 nm using Mie theory for a refractive index of 1.42 - 0.006~~*i*~~*i* (Guyon et al., 2003). An agreement was found

between calculated and measured aerosol scattering coefficients, particularly for periods free of influence of long-range advection of mineral dust. During the period of 22 February to 3 March 2008, the ratio of the AMS volume concentration to the nephelometer scattering is high (Fig. S8b). Elevated mass concentrations of mineral dust are observed by the lidar measurements (Baars et al., 2011) and the filter-based PIXE analysis (Prenni et al., 2009). Local wind and Hysplit back trajectories showed a Manaus plume on March 1, 2008. The elevated scattering is, therefore, plausibly a combination of African advection and Manaus plume influence although the coarse-mode contribution from mineral dust is the major drivingen force of the a weak correlation (R^2 = 0.21) between the nephelometer and AMS dataset. In contrast, a strong correlation (m = 0.62; R^2 = 0.82) of the two data sets is shown for other periods, suggesting a dominant contribution of the non-refractory submicron volume to the total particle scattering. This non-refractory submicron volume is mainly organic material. The scattering coefficients related to the submicron organic material can go up to 6 Mm^{-1} at 550 nm.

C. Positive-Matrix Factorization

Positive-matrix factorization (PMF) is a receptor-based model using a weighted least squares method to identify patterns in data. With caveats, it can be a useful tool to derive the source profiles of organic components from AMS data sets (Ulbrich et al., 2009). In this study, the PMF analysis was conducted on the V-mode organic UMR spectra (m/z 12 to 220). The spectra were analyzed using the SQUIRREL tookit. Prior to PMF analysis, the data set was pre-filtered to remove inorganic contributions, and the analysis was carried out only on the residual data set of the organic component. Fifteen m/z values were omitted because of the absence of organic ions. The time periods associated with random spikes, abrupt increase in sulfate mass concentrations, and little temporal variation caused by the instrument adjustments (Fig. 1) were

removed. The error values were calculated using the method described by Ulbrich et al. (2009). Fragments having a signal-to-noise ratio less than 2 and fragments set proportionally to *m*/*z* 44 were downweighted by increasing their error estimates (Ulbrich et al., 2009). C_xF_y ions contributed significantly to the signals at *m*/*z* 69, 119, 131, 169, 181, and 219, indicating the contamination of Fomblin lubricating oil, possibly from instrument pumps at the site (Cross et al., 2009). These signals appeared always as one statistical factor, with a spiky time series for the loading of that factor. These fragments were downgraded by increasing their error by 100 times. The PMF analysis was conducted with (1) different model error and (2) different seed number. The former was introduced to add modeling uncertainty to the instrumental uncertainty, reflecting the errors that may occur when the true factors do not have constant mass spectra. The latter represents the pseudo-random starting values. Unless otherwise noted, results are presented for both the model error and the seed number of zero. PMF produces a fit to the data, which is called a solution. The solution contains a set of factors and concentrations. For AMAZE-08, four statistical factors were identified and labeled as HOA, OOA-1, OOA-2, and OOA-3 (Fig. 4). The four factors HOA, OOA-1, OOA-2, and OOA-3 respectively accounted for 2%, 18%, 14%, and 66% of the variance in the data matrix, implying a residual variance of <1%.

Number p of factors

Several mathematical metrics were used to set the number *p* of factors. The ratio Q:Q_{exp} of the sum of the squares of the uncertainty-weighted residuals to the expected values decreased by 16%, 8%, 3%, and 3% for *p* increasing from 2 to 5. Three or more factors therefore significantly account for the variance of data. The residual was 1% for $p = 2$ or 3 and < 0.3% for $p = 4$. Structure in the residual was significantly reduced by increasing from *p* of 3 to 4 (Fig. S9). For these reasons, a choice of $p = 4$ was made for the PMF analysis.

The choice of $p = 4$ was also evaluated with respect to factor similarity and correlations of the time series of the factors. Increasing the p from 4 to 5 resulted in strongly correlation ($R^2 = 0.96$) among the factors (Fig. S10). No sufficient information from the correlations with other tracers exists to anticipate this correlation; correlation among factors for p of 5 is believed to arise from a splitting of real factors.

Rotational ambiguity of solutions (*FPEAK*).

FPEAK is the rotational parameter. For simplicity, *FPEAK* = 0 was used as the best representation of the PMF solution for this study. The PMF solution was evaluated for uniqueness under linear transformations ("rotations") by varying the *FPEAK* parameter (Ulbrich et al., 2009). Solutions with *FPEAK* between -0.6 and 0.6 increase Q:Q_{exp} by 1%. Figure S11 shows the time series of factor concentrations over this *FPEAK* range. Changes in time series are relatively small compared to the changes in the features of the factors. The largest change is for the HOA factor. This factor accounts for a low fraction of the total signal and hence its features can change without causing a great increase in the residual. The rotational uncertainty causes no conflicts in the interpretation of the PMF factors.

Uncertainty of the solutions.

The results of running the PMF analysis for different pseudo-random starting values (i.e., seeds of 0 to 10) show negligible changes in the factors ($R^2 > 0.999$; $m > 0.995$) and the time series of the concentrations ($R^2 > 0.999$; $m > 0.95$). Testing a "model error" of 5% in the PMF analysis leads to changes in the factor profiles ($R^2 > 0.80$; $m > 0.90$) and in the time series of concentrations ($R^2 > 0.95$; $m > 0.75$) that are close to tolerance.

Quantitative assessment of the uncertainty of the factors is also made by 100 bootstrapping runs (Ulbrich et al., 2009). The results show that the uncertainties in the time

series of the concentrations are 15% for the OOA-2 and OOA-3 factors and 30% for the OOA-1 and HOA factors. The uncertainties in the factor spectra are <4% for OOA-2 and OOA-3 and <9% for OOA-1 and HOA. The mass spectrum of the HOA factor has the largest uncertainty (Fig. S12).

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Table S1. Summary of the regression coefficients *m* of instrument comparisons. Expected *m* values are shown in parentheses. These values are estimated on the basis of the diameter domain of the various instruments and an assumed AMS collection efficiency of 1.0, in conjunction with typical mass size distributions obtained by MOUDI measurements during the wet season in the Amazon basin (Martin et al., 2010; Pöschl et al., 2010).

	Volume concentration	Number concentration	Sulfate mass concentration	Particle mass concentration	Light scattering at 550 nm
	SMPS	CPC	Filter-based	Filter-based	Nephelometer
AMS	1.24 (1.0)	-	0.90 (1.0)	0.65 (0.7)	0.62 (< 1.0)
SMPS	-	0.59 (< 1.0)	-	-	

Table S2. Summary of the particle mass concentration (μg m^{-3}, STP) measured by the stacked filter units on the 10-m inlet (SFU), by the total-particle filter on the 38-m turbulent inlet (TPF), and by the AMS during AMAZE-08.

Sampling Periods (MM/DD/YY)	SFU: PM_2	TPF: PM_3	AMS: NR-PM_1	AMS/SFU	AMS/TPF
02/10/08 – 02/14/08	2.51	n.a.	1.75	0.70	n.a.
02/14/08 – 02/16/08	1.41	1.30	1.37	0.97	0.87
02/16/08 – 02/19/08	0.87		0.89	1.02	
02/19/08 – 02/22/08	1.14	1.48	0.85	0.75	0.57
02/22/08 – 02/26/08	2.44		0.85	0.35	
02/26/08 – 02/29/08	3.20	2.86	0.96	0.30	0.33
02/29/08 – 03/04/08	3.38		0.99	0.29	
03/04/08 – 03/08/08	1.02	1.02	0.73	0.72	0.72
03/08/08 – 03/12/08	1.01	1.09	0.74	0.73	0.68
Average	**1.89**	**1.55**	**1.02**	**0.65**	**0.63**

List of Figures

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periods as the AMS mass-diameter distributions. Valued in all panels are normalized to STP.

Figure S~~7~~7. Example of the mass-diameter distribution measured by the AMS compared to that derived from the SMPS measurements. The effective particle density ρ_{eff} is determined by the mode diameters. The SMPS mass-diameter distributions were derived by multiplying the SMPS volume-diameter distributions by $\rho_{eff.}$ Data were sampled on March 11, 2008.

Figure S~~8~~8. (**a**) Time series of the particle volume concentrations obtained by the AMS and the SMPS measurements. (**b**) The ratio of the particle volume concentrations derived from the AMS measurements to the PM_7 light scattering coefficients measured by the nephelometer at 550 nm. The AMS data were averaged to the nephelometer timebase. Gray areas represent the periods that were influenced by the generator exhaust plumes.

Figure S~~9~~9. Time series of the model residuals e_{ij} for the PMF analysis with *FPEAK* of zero. Terms include factor *j*, time *i*, and error σ.

Figure S10~~10~~. Pearson's R (black dots) for the correlations between the time series and the mass spectra of any two factors (tagged as x_y) for the PMF solutions for a preset of different number of factors (*p*).

Figure S11~~11~~. (**a**) The mass spectra of the statistical factors identified by the PMF analysis for four-factor solutions and selected *FPEAK* (f_{peak}) values. (**b**) Time series of mass concentrations for the statistical factors.

Figure S12~~12~~. The mass spectrum of HOA from the bootstrapping analysis of four-factor PMF solutions. Average (black) with 1-σ error bars (red) are shown.

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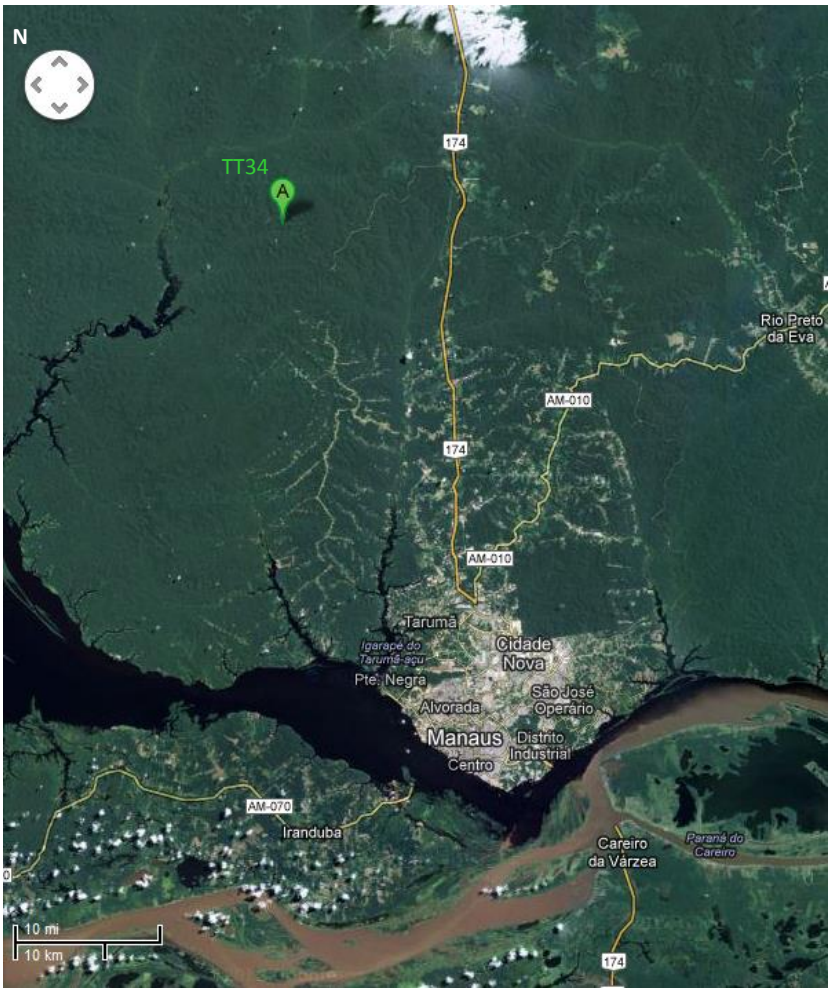
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São José
Operário
Alvorada
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Figure S1

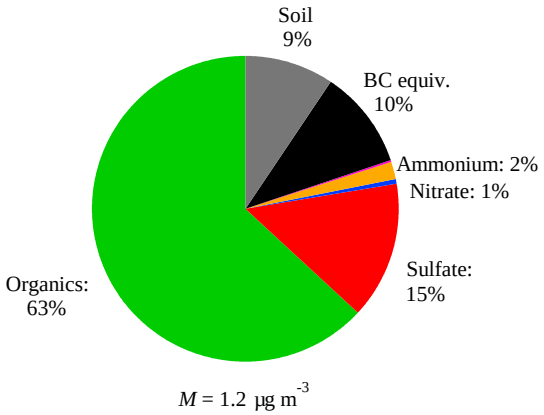

Soil
9%
BC equiv.
10%
Ammonium: 2%
Nitrate: 1%
Sulfate:
15%
Organics:
63%
M = 1.2 µg m-3

Figure S2

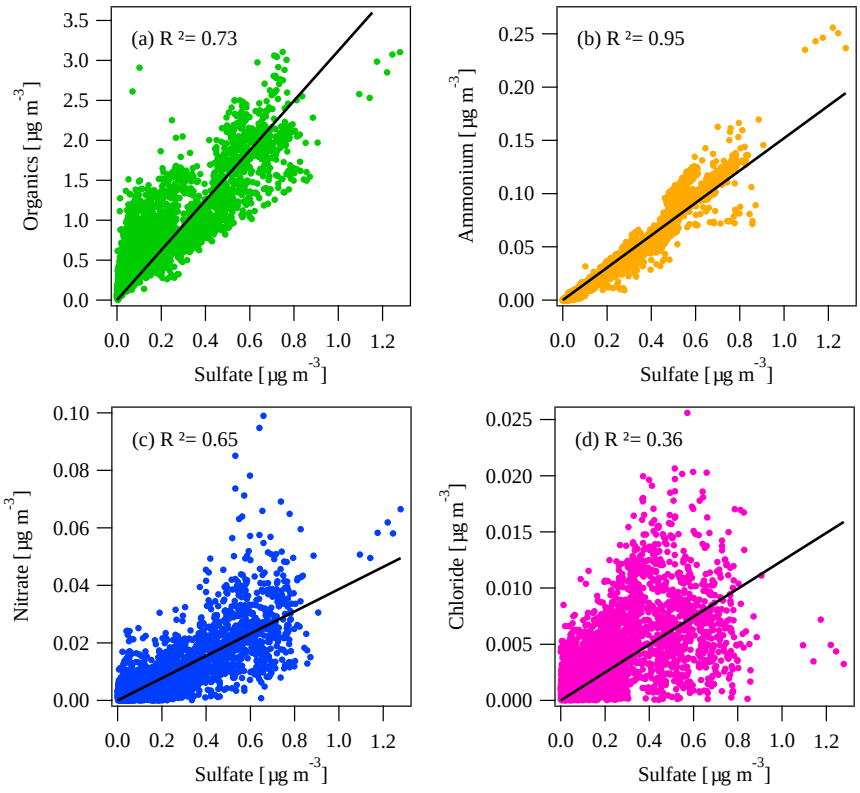
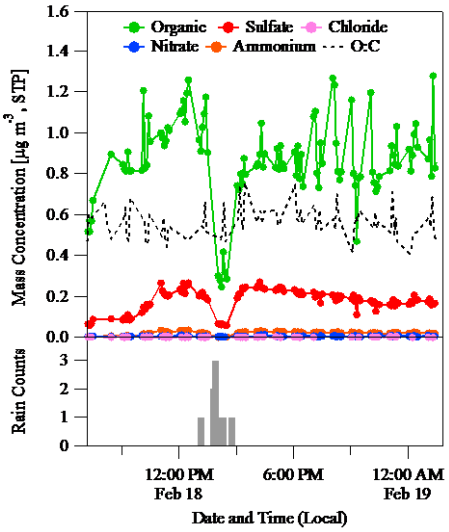

(a) R ²= 0.73
Organics [µg m -3]
Sulfate [µg m -3]
(b) R ²= 0.95
Ammonium [µg m -3]
Sulfate [µg m -3]
(c) R ²= 0.65
Nitrate [µg m -3]
Sulfate [µg m -3]
(d) R ²= 0.36
Chloride [µg m -3]
Sulfate [µg m -3]

Figure S3


Organic
Sulfate
Chloride
Nitrate
Ammonium
O:C
Mass Concentration [µg m-3, STP]
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Rain Counts
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2
1
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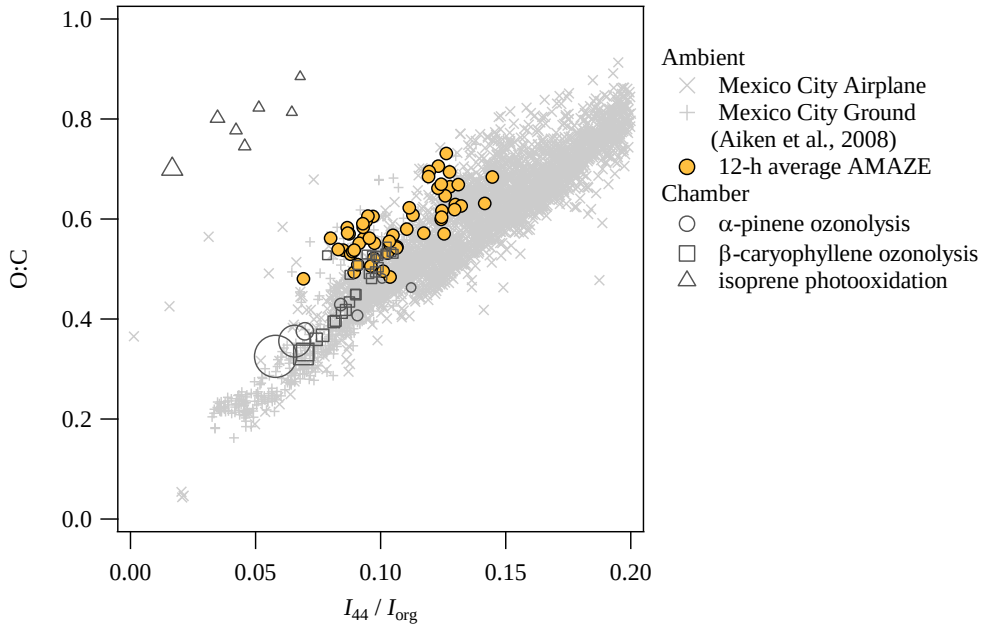
12:00 AM
Feb 19
Date and Time (Local)

Figure S4


1.0
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0.00
0.05
0.10
0.15
0.20
I_{44} / I_{org}
Ambient
Mexico City Airplane
Mexico City Ground
(Aiken et al., 2008)
12-h average AMAZE
Chamber
α-pinene ozonolysis
β-caryophyllene ozonolysis
isoprene photooxidation

Figure S5

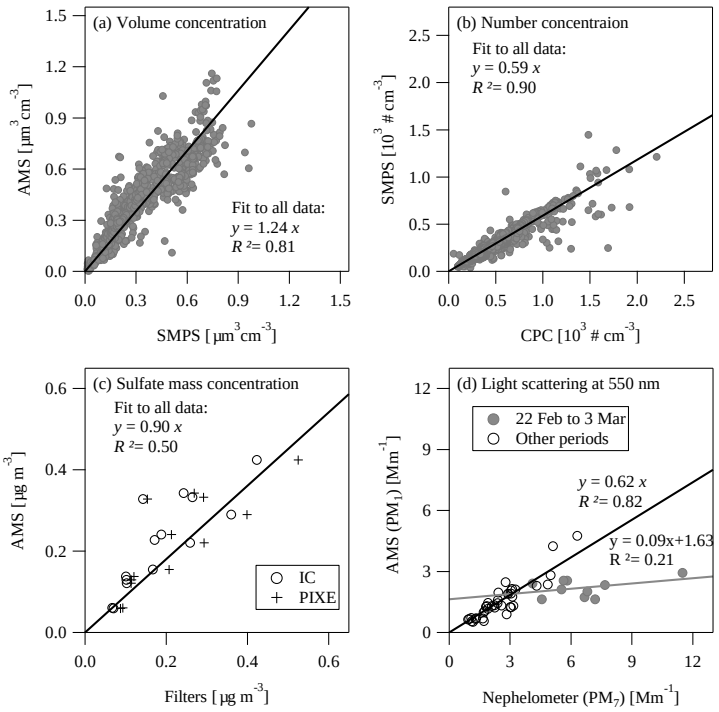
(a) Volume concentration
Fit to all data:
y = 1.24 x
R ²= 0.81
AMS [μm³ cm⁻³]
SMPS [μm³ cm⁻³]
(b) Number concentraion
Fit to all data:
y = 0.59 x
R ²= 0.90
SMPS [10³ # cm⁻³]
CPC [10³ # cm⁻³]
(c) Sulfate mass concentration
Fit to all data:
y = 0.90 x
R ²= 0.50
IC
PIXE
AMS [μg m⁻³]
Filters [μg m⁻³]
(d) Light scattering at 550 nm
22 Feb to 3 Mar
Other periods
y = 0.62 x
R ²= 0.82
y = 0.09x+1.63
R ²= 0.21
AMS (PM1) [Mm⁻¹]
Nephelometer (PM7) [Mm⁻¹]

Figure S6

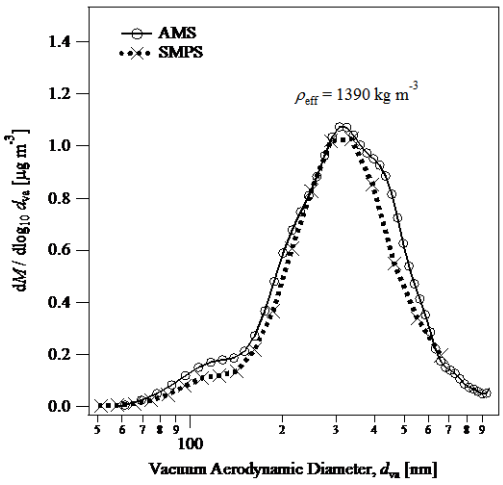
AMS
SMPS
ρ_{eff} = 1390 kg m^{-3}
dM / $d\log_{10} d_{va}$ [μg m^{-3}]
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
5 6 7 8 9
100
2 3 4 5 6 7 8 9
Vacuum Aerodynamic Diameter, d_{va} [nm]

Figure S7

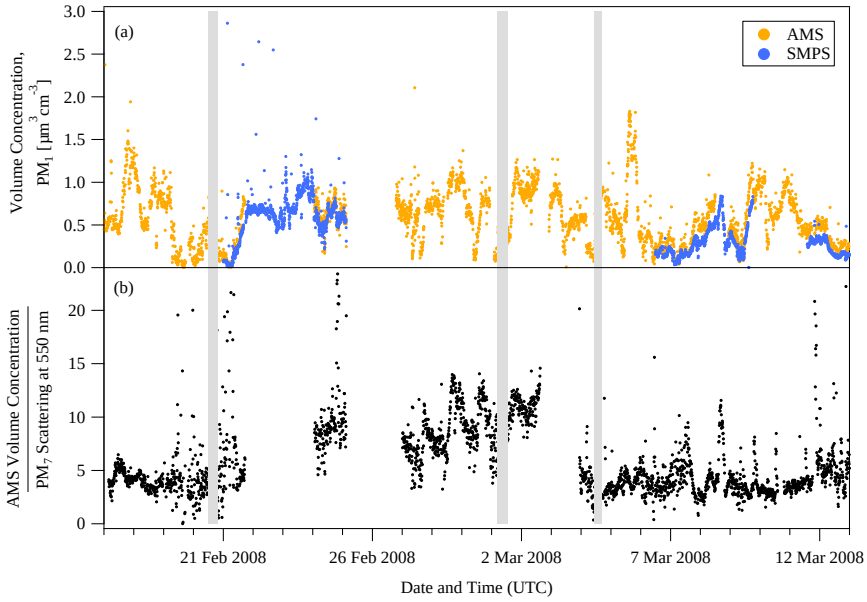
(a)
AMS
SMPS
Volume Concentration, PM1 [μm3 cm-3]
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(b)
AMS Volume Concentration / PM7 Scattering at 550 nm
20
15
10
5
0
21 Feb 2008
26 Feb 2008
2 Mar 2008
7 Mar 2008
12 Mar 2008
Date and Time (UTC)

Figure S8

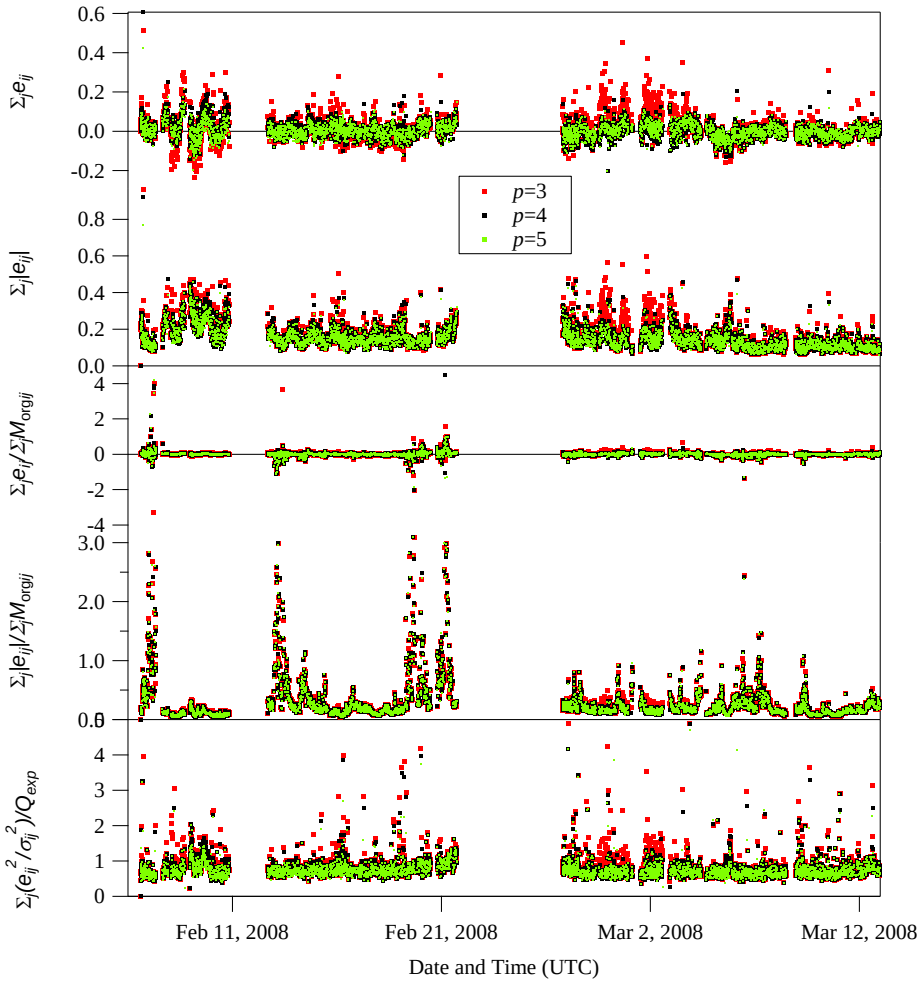
p=3
p=4
p=5
Feb 11, 2008
Feb 21, 2008
Mar 2, 2008
Mar 12, 2008
Date and Time (UTC)

Figure S9

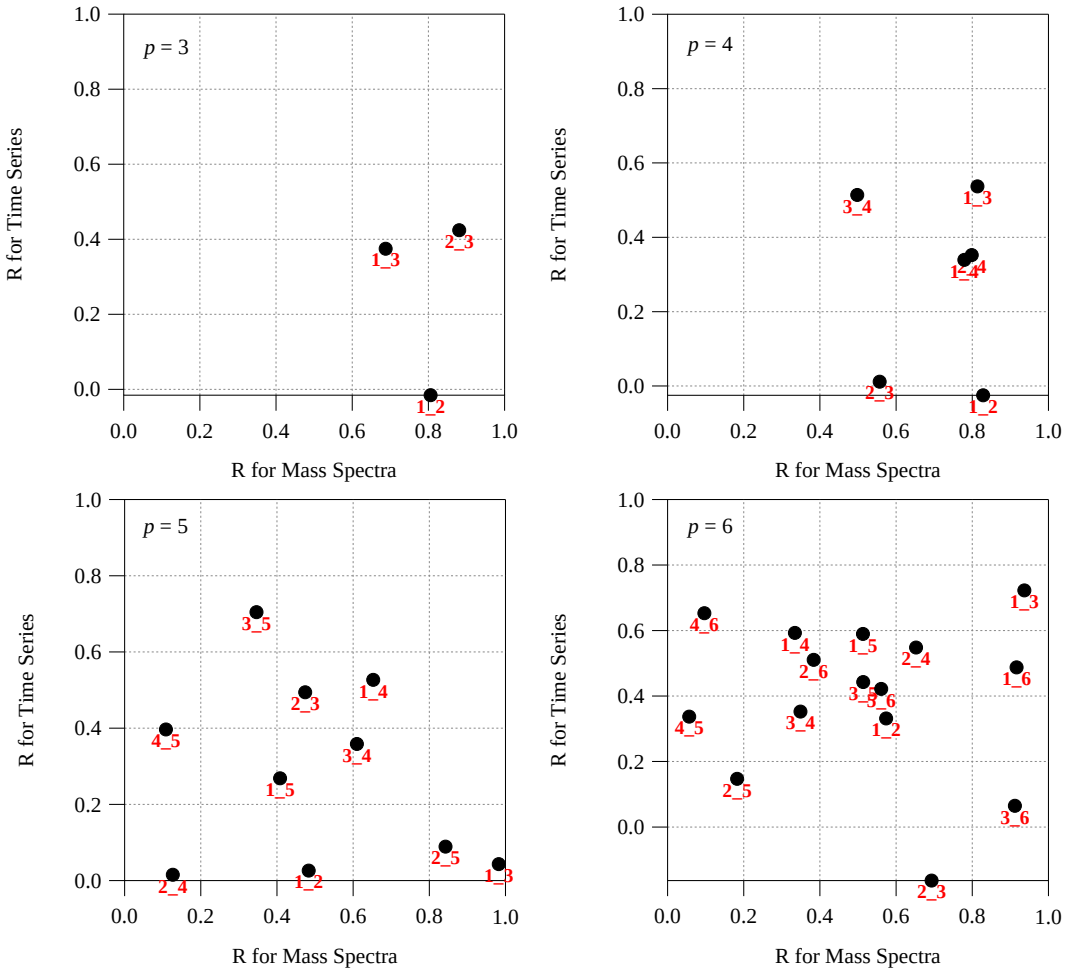
p = 3
p = 4
p = 5
p = 6
R for Time Series
R for Mass Spectra
0.0
0.2
0.4
0.6
0.8
1.0
1_2
1_3
2_3
1_3
1_4
2_3
3_4
1_3
1_2
2_3
1_2
3_5
2_3
1_4
4_5
3_4
1_5
2_4
2_5
1_3
1_2
4_6
1_4
1_5
2_4
2_6
1_3
1_6
3_4
1_2
4_5
2_5
3_6
2_3

Figure S10

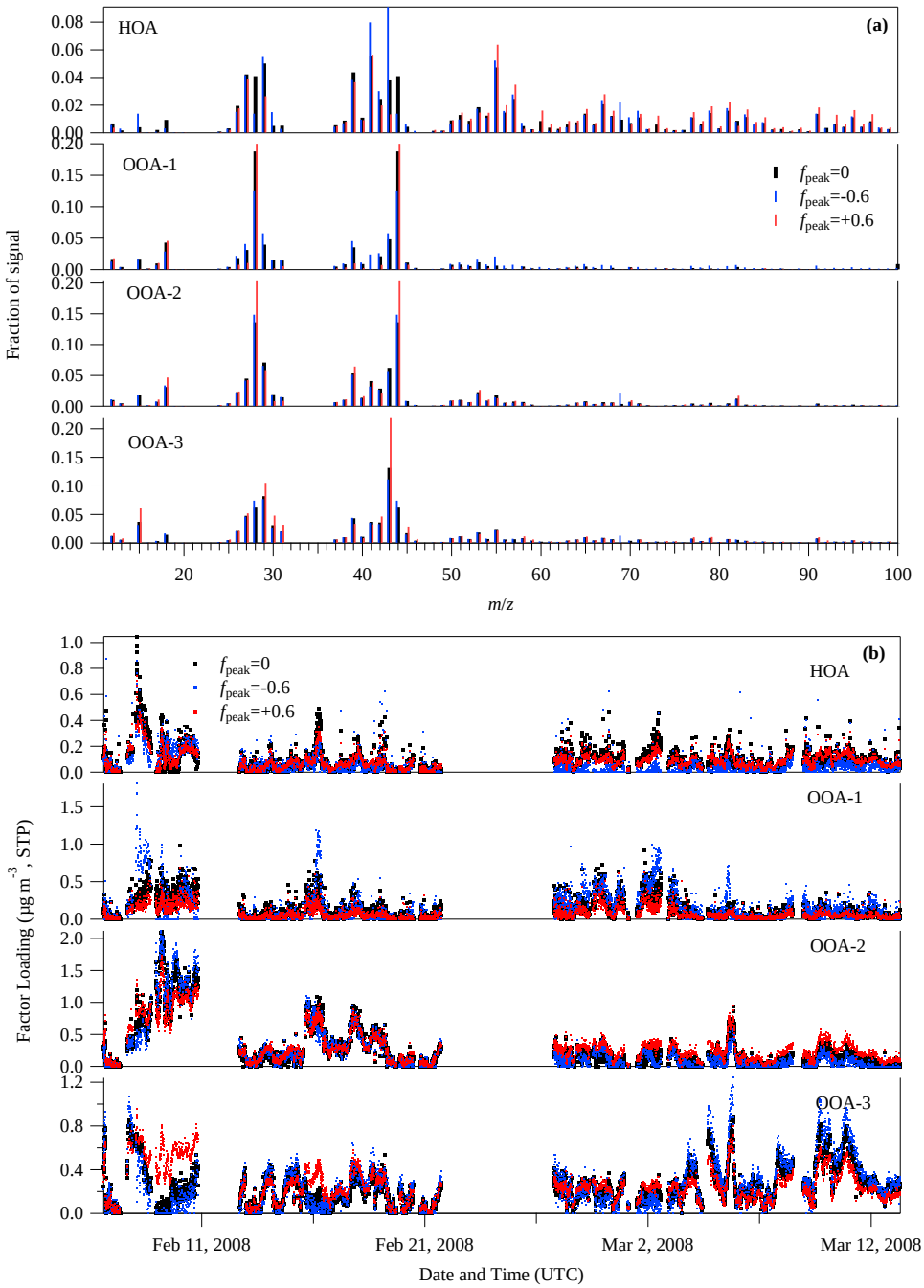
HOA
(a)
OOA-1
OOA-2
OOA-3
f_{peak}=0
f_{peak}=-0.6
f_{peak}=+0.6
Fraction of signal
m/z
(b)
Factor Loading (μg m^{-3}, STP)
Feb 11, 2008
Feb 21, 2008
Mar 2, 2008
Mar 12, 2008
Date and Time (UTC)

Figure S11

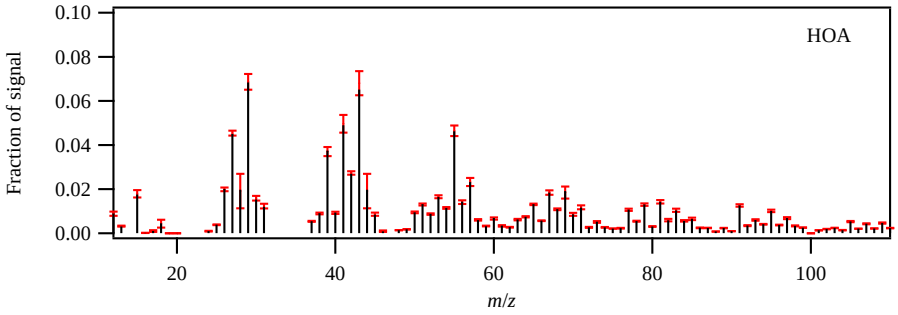
HOA
Fraction of signal
0.10
0.08
0.06
0.04
0.02
0.00
20
40
60
80
100
m/z

Figure S12