Response to reviews

Reviewer comments are in **bold**. Author responses are in plain text. Excerpts from the manuscript are in *italics*. Modifications to the manuscript are in *blue italics*. Page and line numbers in the responses correspond to those in the ACPD paper.

Review #1

The presented paper by de Sá et al, 'Urban influence on the concentration and composition of submicron particulate matter in central Amazonia' gives a very clear overview of the aerosol particle composition during the wet season in the Amazon region. The authors use two different methods to analyse AMS data. PMF, which gives an overview of the particle composition and fuzzy c-means algorithm to study the anthropogenic influence on the aerosol in Amazon. I have few minor comments which are addressed in the following:

We thank the reviewer for the input, and the revised manuscript takes into account the comments and questions, as detailed in the responses below.

1. in the Introduction line 30, information on isoprene emissions compared to other biogenic or even anthropogenic VOCs could be added. Eg., how much isoprene is estimated to be emitted globally, how much of it is emitted by the amazon rainforest?

We thank the reviewer for this suggestion. Information on the importance of isoprene emissions, especially in the Amazon, is added to the revised manuscript, as follows:

Line 36:
~~*For tropical forests, isoprene emissions are especially important in PM production (Martin et al., 2010a; Chen et al.,*~~ *2015Isoprene accounts for half of global BVOC mass emissions, and tropical forests are responsible for about 80% of terpenoid emissions (Guenther et al., 2012). In the Amazon, isoprene is the dominant BVOC emitted by vegetation and is estimated to contribute to about half of the organic PM concentrations under background conditions (Kuhn et al., 2010; Chen et al., 2015; Yáñez-Serrano et al., 2015) (Kuhn et al., 2010; Chen et al., 2015; Yáñez-Serrano et al., 2015).*

2.a Also in the Introduction,, in line with the measurement period that you are describing here, how many days of data did you collect during the IOP1.

The whole duration of IOP1 (Feb 1 to Mar 31, 2014) was the nominal operation time for all instruments including the AMS. The AMS data coverage is shown in Figure 1. The referred sentence in the introduction is clarified, as follows:

Line 60:
The analysis employs data sets collected in the wet season from February 1 to March 31, 2014, corresponding to the first Intensive Operating Period (IOP1) of the GoAmazon2014/5 experiment (Martin et al., 2016). ~~, corresponding to the wet season during the period of February 1 to March 31, 2014.~~

2.b How frequently was the site influenced by the Manaus pollution during the time period presented in the manuscript?

We appreciate the suggestion, and the revised text includes this information as follows.

Line 72:
The site was situated in a pasture of 2.5 km × 2 km surrounded by forest. Based on modeled flow trajectories of the pollution plume, the T3 site intercepted the plume about 40% of the time (Martin et al., 2017).

3. in Methodology you mention 'V' and 'W' mode data. Maybe this is common knowledge but in my opinion it is useful to add a short description of what that means at least in the supplementary material.

The text is adjusted to restrict the use of these technical terms to the Supplementary Material, and an explanation of what these modes mean is included there.

Line 95:
Organic, sulfate, ammonium, nitrate, and chloride PM mass concentrations were ~~obtained from "V-mode" data. The choice of ions to fit was aided by "W-mode" data, which were collected for one of every five days.~~ quantified.

Line 208:
Positive-matrix factorization was applied to the time series of the organic component of the high-resolution ~~"V-mode"~~ mass spectra (Ulbrich et al., 2009).

Supplementary material, line 3:
Quantification of mass concentrations by the AMS was obtained from "V-mode" data, which corresponds to the shorter ion time-of-flight path and is therefore the more sensitive mode. The choice of ions to fit was aided by "W-mode" data, which corresponds to the longer ion time-of-flight path and is therefore the mode with higher mass resolution. V-mode data were collected continuously, and W-mode data were collected for one of every five days. The time series of organic mass spectra measured by the AMS in V-mode was analyzed by positive-matrix factorization (PMF) using a standard analysis toolkit (Ulbrich et al., 2009). ~~High-resolution "V-mode" data were used.~~

4. in Auxiliary measurements and datasets, l. 124: it would be nice also for the supplementary measurements to add information for what time period that data was taken and how much of data was collected during each set of measurements.

Following this suggestion, the text is improved as follows.

Line 104:
In complement to the AMS data set, the analysis herein incorporated auxiliary gas and particle measurements ~~from~~ collected during IOP1 at T3 (Martin et al., 2016).

Line 124:
At T2, non-refractory particle composition and concentration were measured by an Aerosol Chemical Speciation Monitor (ACSM~~; Brito et al., in preparation).~~) during the wet season from March 9 to April 30, 2014 (Cirino et al., submitted). ACSM measurements were ~~also~~ made at T0a during the wet season of 2015 ~~(Carbone et al., in preparation).~~, from February 1 to March 31 (Andreae et al., 2015). Further AMS datasets collected ~~by AMS~~ at T0t during the wet season of 2008 (February 6 to March 22; AMAZE-08 campaign) were used in the analysis (Chen et al., 2009;Schneider et al., 2011). ~~AMS measurements made onboard the G-1 aircraft of the ARM Aerial Facility (AAF) during IOP1 also supported the analysis herein (Shilling et al., in preparation).~~

5. in Results and discussion, in line 180 it is important to mention here again that the measurements at T0 sites were taken in a different year. It helps the reader.

The reviewer raises a good point, and the text is adjusted as follows. (The reviewer mentioned line 180, but the information about T0 was at line 163, and we think this is what the reviewer meant.)

Line 163:
The NR-PM_1 mass concentrations at the T0 sites upwind of Manaus, although measured in different years, were consistently around ~~approximately~~ 1 μg m^{-3}.

6. Fig.3: This Figure contains too many data points, most of the points are hidden. I suggest to split the Figure into few sub-Figures, which enclose different time periods of the day. That allows to see any temporal trend of the particle evolution and to distinguish better what is happening at the different sites.

Based on this feedback, the figure is revised to provide a better visualization of the data points. The caption of Figure 3 is adjusted as follows:

Gray and blue circles correspond, respectively, to measurements at T3 and T2 during IOP1, in the wet season of 2014. For visualization purposes, the two datasets are plotted separately in panels a and b.

The intention of the authors for this figure is to provide a general comparison of the PM oxidation at both sites. For the reviewer's suggestion in relation to plume evolution, we think that a more elaborate analysis beyond the scope of the authors' intention would be necessary to take into account (i) the transport time between the sites for each individual data point, (ii) whether the plume passed over both sites, and (ii) meteorological factors. Cirino et al., submitted focused on this kind of complex plume analysis. The text is adjusted to reflect these important points.

Line 198:
The comparison depicted in Figure 3 ~~illustrates the effects of the plume over the 4 h of transport from T2 to T3 (Cirino et al., submitted).~~ indicates the effects of the plume over the 4 h of transport from T2 to T3, which were investigated in detail by Cirino et al. (submitted).

7. Fig.5: This Figure is easier to read and more informative, if the variables on the x-axis are grouped according to their source (biogenic, anthropogenic, background, biomass burning) other than the instrument they were measured with.

We appreciate this suggestion. Based on it, the authors prepared both possible figures for internal discussion. In the end, the authors believe that the original figure is better for presentation. The reason is that most of the tracers have contributions from several different and in some cases unknown sources so that a definitive classification would be uncertain, and the revised figure would be a scientific over-stretch. The exceptions, such as levoglucosan which is a specific tracer for biomass burning, are explicitly mentioned in the text.

8. Fig. 7: the airmass back-trajectories are more valuable if they are calculated as ensembles rather than single trajectories. Ensemble gives you a group of trajectories which are all equally likely.

We thank the reviewer for this thoughtful comment, which generated significant internal discussion among the authors. Although the idea is appreciated, the use of ensembles did not seem the most appropriate or necessary tool for the analysis of Figure 7.

The backtrajectories are employed in this study in a supportive rather than central role to the clustering analysis, i.e., trajectories are not used to generate clusters but rather to help in their interpretation. In each panel of Fig. 7, trajectories are representative of the case studies shown in Fig. 6. It is visually clear that trajectories within those time periods are already clustered. Calculating ensembles for all observation times (every 12 min) over the course of the two months of the study period would have added a very large computational time and human expense that could not be afforded. Hence,

the cost-benefit of a more complex trajectory analysis was not justified, while the single trajectories still added value to the data interpretation.

Review #2

1. [T]his manuscript provides an overview of particle mass and chemical composition, with a focus on organic species in the Amazon. The authors strive to understand the anthropogenic contribution(s) to mass and influence on speciation and approach this with 2 different statistical approaches applied to online measurements. The work is interesting but seems premature. The paper relies on and cites several manuscripts that are "in preparation" to justify some arguments and conclusions and this is problematic. For example, comparison among different data sets (and presented in Figure 1) includes data not previously published, nor fully explained here.: data from ATTO sampling location "T0a-2015" is from Carbone et al., in preparation and "T2-2014" is from IOP1 Brito in preparation.

We thank the reviewer for reading the manuscript and providing valuable feedback.

For the references "in preparation", the following revisions are made.

(i) Carbone et al. (in preparation) is replaced by Andreae et al. (2015), which already published the T0a-2015 data used in this study.

(ii) Brito et al. (in preparation) is replaced by Cirino et al. (submitted). This manuscript is in the final stages of peer review, and we expect that "submitted" can be replaced with a full citation for the ACP publication of the present manuscript. Both Brito and Cirino, responsible for ACSM data collection and analysis at T2, are co-authors in the present study.

For changes made to the text to address (i) and (ii) please see reply #4 to review #1. The references in the caption of Figure 1 are also accordingly updated.

We believe that these updates satisfy the reviewer's concern about "premature". Importantly, the comparison of the T3 composition to other sites only appears in one section of the manuscript (lines 155-205). The main conclusions, by contrast, largely come from the combined analysis of PMF and FCM on the data collected at T3, which is completely original and presented in detail in the following sections of the manuscript (lines 206-514).

2. Organic mass variability in relation to meteorology seems to be an important finding and necessary to the arguments in this manuscript but Cirino et al. 'in prep' is the provided proof and readers are not left with sufficient information to understand the reasonableness of the argument.

This reference was adjusted as follows:

Line 174:
This influence waxes and wanes with small northerly or southerly shifts of the trade winds as well as other changes in regional circulation tied to daily meteorology (~~*Cirino et al., in*~~ *preparationdos Santos et al., 2014; Martin et al., 2017).*

3. The authors also cite de Sá et al 'in prep' to explain why a certain analysis is beyond the scope of this paper and not presented here and explain that the analysis is currently underway (e.g., biomass burning influence (presumably screened here?)) will be discussed in the literature later and I think that is ok.

The current manuscript focuses on the wet season. As stated in the introduction (line 48), the influence of biomass burning is minimal during the wet season. The reference to de Sá et al. (in preparation) in the introduction (line 64) was intended to highlight that there is a separate manuscript under way for the dry season (to also be submitted to the GoAmazon2014/5 Special Issue of ACP). Although related, these studies are independent.

4. Many journals would not even accept 'in prep' References at all. To use such References for conclusions seems unreasonable to me. Prior to acceptance for publication I think the 'prior' work must first be published or properly backed up here.

We understand the reviewer's concerns. Please see replies 10 and 11.

5. specific comments: Line 19/20: The choice to cite Weber et al., 2007 and Goldstein et al., 2009 here is curious. Weber et al. state in that paper: "Although NOx may be another precursor that could be influencing this system, NOx-WSOC… was weakly correlated" The R2 is <0.2 I acknowledge time scales for complex chemistry matter and correlation for instantaneous values can be low even though there is a dependence, however the work by Weber does not provide support for NOx or SO2 dependence as suggested by the authors here. The work by Weber et al does demonstrate a link to CO. The Goldstein analysis for particles is limited to satellite-AOT. Seasonal and spatial patterns have found these AOT observations are not due to organic fine particle mass (Ford and Heald, ACP 2013; Nguyen et al. GRL, 2016) The authors cite Xu et al., 2015 later in the manuscript and that would be a good citation here. Because the authors are talking in the manuscript here about the Southeast US, citing recent findings from the Southeast field campaigns (e.g., SOAS as in the Xu paper) and making a link with the context of those field campaigns would improve the paper.

We greatly appreciate that the reviewer pointed out this mismatch in citations. The text is updated as follows:

Line 15:
In the northeastern USA, de Gouw et al. (2005) showed that ~~organic PM concentrations correlated well with anthropogenic tracers, yet the concentrations of anthropogenic precursors were insufficient to explain the observed PM. In the southeastern USA, observations suggested that organic PM was produced mainly from BVOCs, however modulated by anthropogenic emissions of NOx and SO2 (Weber et al., 2007; Goldstein et al., 2009).~~concentrations of organic particulate matter (PM) correlated well with anthropogenic tracers, yet the concentrations of the anthropogenic precursors were insufficient to explain the observed PM concentrations. In the southeastern USA, radioisotope analysis of organic PM determined that 70% to 80% of the carbon mass had a modern origin even as correlations were observed between SOM mass concentrations and anthropogenic VOC and CO concentrations (Weber et al., 2007). This finding and those of further field studies in the region together suggested that the organic PM was produced mainly from biogenic VOCs (BVOCs) yet modulated by anthropogenic emissions of NO_x and SO_2 (Hu et al., 2015; Xu et al., 2015a; Xu et al., 2015b; Zhang et al., 2018).

6. I have no idea what "V" and "W" mode mean. The authors should provide an explanation if the distinction is important as they suggest.

Please see reply #3 to review #1.

7. Line 165: When talking about Figure 1 the authors state 'concentrations at the T2 site were more than three times higher on average' All of the presented averages in Figure 1b overlap within the uncertainty. Can it be stated that there is statistically significance to the difference? Figure 2 suggests a factor of 2, not 3.

The reviewer raises an important point that needs clarification. Firstly, the bars in Figure 1b do not represent uncertainty but rather variability in the measurements. Secondly, the variability of concentrations among sites can only be fairly compared by considering different times of day as was done in Figure 2, since the variability is largely driven by the diel trends. To clarify this point to the reader, we removed the bars in Figure 1b and emphasized in the caption of Figure 1 as well as in the text that a comparison of the variability across sites is presented in Figure 2, as follows.

Figure 1 caption:
~~Bars represent means and whiskers represent the standard deviation of measurements.~~ The variability of measurements across sites is evaluated in Figure 2.

Line 170:

The diel trends of organic and sulfate mass concentrations as well as their variabilities across the four sites are shown in Figure 2.

8. Figure 2 caption: Please correct the text: "Error! Reference source not found." The panels of Figure 2 have different y-axes and this should be mentioned explicitly.

We thank the reviewer for catching these two points, and corrections are made in the figure caption as follows:

"… at four different sites (cf. Fig.1 and Fig. ~~Error! Reference source not found.~~ S1). The ordinate scale for the T2-2014 panel is twice that of the other panels. Mass concentrations were corrected to standard temperature and pressure (273.15 K and 105 Pa). Local time is (UTC - 4 h). Lines represent means, solid markers show medians, and boxes span interquartile ranges. ~~The ordinate scale for the T2 panel differs from the other three panels. Concentrations were adjusted to standard temperature (273.15 K) and pressure (105 Pa).~~

9. Figure 4 is nice, but it's hard to read and digest.

We understand that the information content of Figure 4 is high. This study heavily relies on the PMF results, and Figure 4 provides an important summary of the PMF factors. The authors discussed several alternative representations for this figure and believe that the present version is the best option. Importantly, the text is optimized to accompany the figure. Lines 228 - 349 of the text are paired to the reading of Figure 4. The text explains the characteristics of the factors one by one in each paragraph and systematically refers to each of the panels in that figure.

10. Figure 9 is excellent!

Thank you!

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

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Submitted: February 2018

Atmospheric Chemistry and Physics

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Abstract

Fundamental to quantifying the influence of human activities on climate and air quality is an understanding of how anthropogenic emissions affect the concentrations and composition of airborne particulate matter (PM). The central Amazon basin, especially around the city of Manaus, Brazil, has experienced rapid changes in the past decades due to ongoing urbanization. Herein, changes in the concentration and composition of submicron PM due to pollution downwind of the Manaus metropolitan region are reported as part of the GoAmazon2014/5 experiment. A high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) and a suite of other gas- and particle-phase instruments were deployed at the "T3" research site, 70 km downwind of Manaus, during the wet season. At this site, organic components represented on average 79 ± 7% of the non-refractory PM_1 mass concentration, which was in the same range as several upwind sites. The organic PM_1 was, however, considerably more oxidized at T3 compared to upwind measurements. Positive-matrix factorization (PMF) was applied to the time series of organic mass spectra collected at the T3 site, yielding three factors representing secondary processes (73 ± 15% of total organic mass concentration) and three factors representing primary anthropogenic emissions (27 ± 15%). Fuzzy c-means clustering (FCM) was applied to the afternoon time series of concentrations of NO_y, ozone, total particle number, black carbon, and sulfate. Four clusters were identified and characterized by distinct airmass origins and particle compositions. Two clusters, Bkgd-1 and Bkgd-2, were associated with background conditions. Bkgd-1 appeared to represent near-field atmospheric PM production and oxidation of a day or less. Bkgd-2 appeared to represent material transported and oxidized for two or more days, often with out-of-basin contributions. Two other clusters, Pol-1 and Pol-2, represented the Manaus influence, one apparently associated with the northern region of Manaus and the other

with the southern region of the city. A composite of the PMF and FCM analyses provided insights into the anthropogenic effects on PM concentration and composition. The increase in mass concentration of submicron PM ranged from 25% to 200% under polluted compared to background conditions, including contributions from both primary and secondary PM. Furthermore, a comparison of PMF factor loadings for different clusters suggested a shift in the pathways of PM production under polluted conditions. Nitrogen oxides may have played a critical role in these shifts. Increased concentrations of nitrogen oxides can shift pathways of PM production from HO_2-dominant to NO-dominant as well as increase the concentrations of oxidants in the atmosphere. Consequently, the oxidation of biogenic and anthropogenic precursor gases as well as the oxidative processing of pre-existing atmospheric PM can be accelerated. The combined set of results demonstrates the susceptibility of atmospheric chemistry, air quality, and associated climate forcing to anthropogenic perturbations over tropical forests.

1. Introduction

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

Several field observations, mainly in mid-latitudes of the Northern Hemisphere, and modeling efforts have suggested that the production of SOM from biogenic precursor compounds becomes more efficient in polluted air (Weber et al., 2007; Goldstein et al., 2009; Hoyle et al., 2011; Huang et al., 2014; Zhang et al., 2018~~).~~Weber et al., 2007; Goldstein et al., 2009; Hoyle et al., 2011; Huang et al., 2014; Zhang et al., 2018). In the northeastern USA, de Gouw et al. (2005) showed that ~~organic PM concentrations correlated well with anthropogenic tracers, yet the concentrations of anthropogenic precursors were insufficient to explain the observed PM. In the southeastern USA, observations suggested that organic PM was produced mainly from BVOCs, however modulated by anthropogenic emissions of NO_x and SO_2 (Weber et al., 2007; Goldstein et al., 2009).~~concentrations of organic particulate matter (PM) correlated well with anthropogenic tracers, yet the concentrations of the anthropogenic precursors were insufficient to explain the observed PM concentrations. In the southeastern USA, radioisotope

analysis of organic PM determined that 70% to 80% of the carbon mass had a modern origin even as correlations were observed between SOM mass concentrations and anthropogenic VOC and CO concentrations (Weber et al., 2007). This finding and those of further field studies in the region together suggested that the organic PM was produced mainly from biogenic VOCs (BVOCs) yet modulated by anthropogenic emissions of NO_x and SO_2 (Hu et al., 2015; Xu et al., 2015a; Xu et al., 2015b; Zhang et al., 2018). In the western USA, ground and aircraft measurements observed the highest organic PM increases when air masses having high BVOC concentrations ~~of biogenic VOCs (BVOCs)~~ intercepted anthropogenic emissions (Setyan et al., 2012; Shilling et al., 2013). A metastudy for several locations in the USA concluded that air downwind of urban ~~air~~areas had increased organic PM concentrations due to the photochemical production of SOM (De Gouw and Jimenez, 2009). Models have estimated that 50% to 70% of the biogenic SOM mass concentration in several locations is modulated by anthropogenic emissions (Carlton et al., 2010; Heald et al., 2011; Spracklen et al., 2011). In addition, global-scale modeling studies have estimated an increase of 20% to 60% in the global annual mean SOM concentration relative to the pre-industrial period (Tsigaridis et al., 2006; Hoyle et al., 2009).

Many possible mechanisms may contribute to the effects of anthropogenic emissions on increased SOM production, including changes in gas-particle partitioning, new particle production and growth, and particle acidity. Changes in the concentrations of nitrogen oxides, however, should be regarded as a critical factor (Hoyle et al., 2011 and references therein). Different NO_x regimes favor distinct gas-phase oxidation pathways, leading to different oxidation products and particle yields, as evidenced in isoprene photo-oxidation (Kroll et al., 2005, 2006; Hallquist et al., 2009; Worton et al., 2013; Liu et al., 2016b; Liu et al., 2016a). ~~For~~

~~tropical forests, isoprene emissions are especially important in PM production (Martin et al., 2010a; Chen et al., 2015~~Isoprene accounts for half of global BVOC mass emissions, and tropical forests are responsible for about 80% of terpenoid emissions (Guenther et al., 2012). In the Amazon, isoprene is the dominant BVOC emitted by vegetation and is estimated to contribute to about half of the organic PM concentrations under background conditions (Kuhn et al., 2010; Chen et al., 2015; Yáñez-Serrano et al., 2015). Under HO_2-dominant conditions (i.e., low NO_x), isoprene epoxydiols (IEPOX) are produced in the gas phase and, through heterogenous reactions involving sulfate, PM is produced (Paulot et al., 2009; Surratt et al., 2010). Depending on the relative importance of increased concentrations of sulfate and NO_x associated with pollution in a given region, an enhancement or suppression of IEPOX-derived PM production relative to background conditions may occur (Xu et al., 2015a; de Sá et al., 2017).

~~Amazonia, the largest tropical forest in the world and a large global source of SOM, is comparatively understudied relative to northern mid-latitude regions, especially with respect to the influence of pollution on the SOM lifecycle (Martin et al., 2010a). Manaus, a city of over two million people in the central Amazon, continuously releases an urban plume into an otherwise mostly unperturbed region (Kuhn et al., 2010; Martin et al., 2017). The region downwind of Manaus, especially in the wet season in the absence of regional fires (Artaxo et al., 2013), offers a natural laboratory for the investigation of biogenic-anthropogenic interactions and the resulting consequences for the amount and composition of PM in the region.~~ As part of GoAmazon2014/5, de Sá et al. (2017) demonstrated that PM derived from IEPOX generally decreased under polluted compared to background conditions downwind of Manaus. Nitrogen oxides in the pollution plume suppressed the production of isoprene hydroxyhydroperoxides (Liu et al., 2016b), leading to a decrease in the production of gas phase IEPOX and consequently of IEPOX-

derived PM (de Sá et al., 2017). ~~IEPOX-derived PM was the exclusive focus of de Sá et al. (2017).~~

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

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

2. Methodology

2.1 Site description

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

2.2 Aerosol Mass Spectrometry

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

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

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

2.3 Auxiliary measurements and datasets

In complement to the AMS data set, the analysis herein incorporated auxiliary gas and particle measurements ~~from~~ collected during IOP1 at T3 (Martin et al., 2016). Mass concentrations of molecular and tracer organic species in the gas and particle phases were measured by a Semi-Volatile Thermal Desorption Aerosol Gas Chromatograph (SV-TAG) at a time resolution of one hour (Isaacman-VanWertz et al., 2016). Concentrations of volatile organic compounds (VOCs) were measured by a Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS; Liu et al., 2016b). In the Mobile Aerosol Observing System (MAOS) of the ARM Climate Research Facility (ACRF; Martin et al., 2016), measurements of NO_y were made using a chemiluminescence-based instrument (Air Quality Design). The raw NO_y measurements (10-s resolution) were averaged across 30-min intervals to dampen the

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

Additional measurements from T0a, T0t, and T2 were also used in the analysis. At T2, non-refractory particle composition and concentration were measured by an Aerosol Chemical Speciation Monitor (ACSM~~; Brito et al., in preparation).~~) during the wet season from March 9 to April 30, 2014 (Cirino et al., submitted). ACSM measurements were ~~also~~ made at T0a during the wet season of 2015 ~~(Carbone et al., in preparation).~~, from February 1 to March 31 (Andreae et al., 2015). Further AMS datasets collected ~~by AMS~~ at T0t during the wet season of 2008 (February 6 to March 22; AMAZE-08 campaign) were used in the analysis (Chen et al., 2009;Schneider et al., 2011). ~~AMS measurements made onboard the G-1 aircraft of the ARM Aerial Facility (AAF) during IOP1 also supported the analysis herein (Shilling et al., in preparation).~~

2.4 Air mass backtrajectories and precipitation rates

Simulations of two-day backward air mass trajectories, starting at 100 m above T3, were made using HYSPLIT4 (Draxler and Hess, 1998). Input meteorological data were obtained

161 from the Global Data Assimilation System (GDAS), provided by the NOAA Air Resources
162 Laboratory (ARL), on a regular grid of 0.5° × 0.5°, 18 pressure levels, and 3-h intervals.
163 Trajectory steps were calculated for every 12 min.

164 Information on precipitation along the trajectories was obtained from the S-band radar of
165 the System for Amazon Protection (SIPAM) in Manaus (Machado et al., 2014). The radar had a
166 beam width of 1.8°, and it scanned 17 elevation angles every 12 min. Data were recorded to a
167 range of 240 km at 500-m gate spacing. The reflectivity fields were quality controlled to remove
168 non-meteorological echo and calibrated against the satellite precipitation radar of the Tropical
169 Rainfall Measuring Mission and Global Precipitation Measurement (TRMM-GPM; Kummerow
170 et al., 1998; Hou et al., 2014). Ground clutter was used to analyze the stability of the calibration.
171 The data were gridded at 2 km × 2 km in the horizontal and 0.5 km in the vertical using the
172 NCAR *Radx* software. The reflectivity at 2.5 km in altitude was converted to rain rates based on
173 the data sets of a Joss-Waldvogel disdrometer (Joss and Waldvogel, 1967), located at T3, 70 km
174 downwind of the radar.

175 **3. Results and discussion**

176 **3.1 Fine-mode PM composition**

177 The time series of mass concentrations of PM_1 species at T3 during the wet season of
178 2014 are plotted in Figure 1a. Organic material dominated the composition, contributing 79 ± 7%
179 (average ± one standard deviation), followed by sulfate (13 ± 5%). The standard deviation
180 quantifies the variability across the time series. Average non-refractory (NR) PM_1 mass
181 concentrations and compositions at T3 as well as at three other sites in the region are represented
182 in Figure 1b. The two T0 sites corresponded to predominantly background conditions. By
183 contrast, the T2 site represented conditions just downwind of Manaus, and depending on wind

direction experienced fresh Manaus pollution or background air. The comparison in Figure 1b demonstrates that the organic component consistently constituted 70% to 80% of NR-PM_1 across sites in this region in the wet season, for both background and polluted conditions, in line with previous observations (Chen et al., 2009; Martin et al., 2010a).

Even as the relative composition was similar across all sites, there were differences in the absolute mass concentrations (Figure 1b, top panel). The NR-PM_1 mass concentrations at the T0 sites upwind of Manaus, although measured in different years, were ~~approximately~~consistently around 1 μg m^{-3}. The concentrations at the T2 site just downwind of Manaus were more than three times higher on average (3.3 μg m^{-3}). Average concentrations at the T3 site (1.7 μg m^{-3}), several hours downwind of Manaus, were lower compared to those at T2. This relative progression from T0, to T2, and then to T3 can be understood as a first-order quantification of the overall effect of Manaus emissions in increasing the airborne PM burden in the downwind region.

The diel trends of organic and sulfate mass concentrations as well as their variabilities across the four sites are shown in Figure 2. Lines represent means, solid markers show medians, and boxes span interquartile ranges. Organic mass concentrations and associated variability were higher at the T3 site compared to the T0 sites, markedly so in the afternoon hours. The greater variability at T3 is in line with a time-varying influence of Manaus emissions. This influence waxes and wanes with small northerly or southerly shifts of the trade winds as well as other changes in regional circulation tied to daily meteorology ~~(~~Cirino et al., submitted~~).~~ (dos Santos et al., 2014; Martin et al., 2017). The higher afternoon mass concentrations at T3 can be attributed to a combination of (i) an oxidant-rich, sunlight-fed plume that increases the production rate of secondary PM and (ii) faster near-surface winds during the day that transport PM from Manaus

to T3 with less loss by deposition and dispersion compared to more-stagnant air at night. Among all sites, the T2 observations had both the highest average organic mass concentrations and the largest variability. These characteristics of the T2 dataset can be explained by a combination of (i) the proximity of the site to Manaus, (ii) the rapid and 180° changes in wind direction caused by the intersection of the trade winds with a local river breeze (dos Santos et al., 2014), and (iii) possible contributions of emissions from brick kilns, located mostly southwest of the site, especially during night time (Martin et al., 2016; Cirino et al., submitted).

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

Overall, the organic PM_1 at T3 was highly oxidized, as indicated by the position of gray markers in the plot of Figure 3. By contrast, the blue markers represent the dataset collected at T2 during the same period. The datasets encompass all times of days and all conditions at both sites. Datasets from background sites collected in different years are shown in Figure S2. Points to the upper left represent more oxidized material, and points to the lower right represent less oxidized material (Ng et al., 2011a). The comparison depicted in Figure 3 ~~illustrates the effects of the plume over the 4 h of transport from T2 to T3 (~~Cirino et al., submitted~~).~~ indicates the effects of the plume over the 4 h of transport from T2 to T3, which were investigated in detail by Cirino et al. (submitted). The plot suggests that the enhanced oxidative cycle associated with higher OH and O_3 concentrations in the pollution plume might cause (i) the production of highly

oxidized SOM, from both biogenic and anthropogenic precursors including aromatic compounds (Chhabra et al., 2011; Lambe et al., 2011), and (ii) the accelerated oxidative processing of pre-existing organic PM by OH and O_3 (Martin et al., 2017). The implication is that the emissions from Manaus can significantly affect the mechanisms that produce or modify fine-mode PM over the tropical forest.

3.2 Characterization of organic PM by positive-matrix factorization

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

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

The scientific interpretation of each factor was based on a combination of (i) the characteristics of the factor profile (i.e., "mass spectrum"), as referenced to a worldwide database of AMS spectra and PMF analyses (Ulbrich et al., 2009c; Ulbrich et al., 2009a, 2009b), and (ii) the temporal correlations between the factor loading and other co-located measurements. Three factors interpreted as primary emissions of organic PM were resolved: an anthropogenic-

dominated factor (hereafter, "ADOA"), a biomass burning factor ("BBOA"), and a fossil-fuel hydrocarbon-like factor ("HOA"). Three factors interpreted as secondary production and processing were resolved: a more-oxidized oxygenated factor ("MO-OOA"), a less-oxidized oxygenated factor ("LO-OOA"), and an isoprene epoxydiols-derived factor ("IEPOX-SOA").

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

The BBOA factor profile was characterized by distinct peaks of $C_2H_4O_2^+$ (*m*/*z* 60) and $C_3H_5O_2^+$ (*m*/*z* 73), as shown in Figure 4a. These peaks can be attributed to levoglucosan and other anhydrous sugars that result from biomass pyrolysis (Schneider et al., 2006; Cubison et al., 2011). Correlations of the factor loadings with the mass concentrations of levoglucosan and vanillin ($R > 0.8$) measured by SV-TAG corroborate the association with biomass burning (Figure 4c). The BBOA factor of this study had an O:C ratio of 0.61 ± 0.08 (Table 1), which is consistent with large contributions from levoglucosan (O:C of 0.83) and similar sugars. The factor loading on average accounted for 9% of the organic PM_1 mass concentration (Figure 4a, inset). This result is consistent with the low incidence of fires in the Amazon during the wet season (Martin et al., 2016). The BBOA factor loading typically decreased during the day (Figure 4b), which is suggestive of the dilution of local sources during the development of the PBL rather than long-range transport. Emissions from local fires around T3, including trash and tree burning, as well as from wood-fueled brick kilns along the road from Manaus to T3 might have contributed to this factor.

The ADOA factor profile, distinguished prominently by the $C_7H_7^+$ ion at *m*/*z* 91, also had characteristic ions of $C_4H_7^+$ at *m*/*z* 55 and $C_3H_5^+$ at *m*/*z* 41 (Figure 4a). A peak at *m*/*z* 91 can arise from many sources, including biogenic and anthropogenic emissions (Ng et al., 2011b). In itself, *m*/*z* 91 therefore does not serve as a tracer for a specific source or process without consideration of the atmospheric context. Factors having a characteristic *m*/*z* 91 peak (usually labeled "91fac") typically have been associated with biogenic emissions (Robinson et al., 2011; Budisulistiorini et al., 2015; Chen et al., 2015; Riva et al., 2016). The ADOA factor profile of this study, however, more strongly resembles the mass spectra previously reported for PM emissions from cooking activities (Lanz et al., 2007; Mohr et al., 2012) than those from "91fac" (Section S1; Figure S5).

The ratio of *m*/*z* 55 to *m*/*z* 57 of the ADOA factor was 4.1. This ratio lies in the range of 2 to 10 reported for several factors representing primary cooking emissions and is well above the range of 0.8 to 1.4 reported for factors associated with traffic emissions, i.e., HOA (Mohr et al., 2012 and references therein; Hu et al., 2016). Even though the ADOA factor profile has a large contribution from non-oxygenated ions, similar to the HOA factor and consistent with a dominance by primary emissions, it also contains considerable signal from oxygenated ions, resulting in a relatively higher O:C of 0.40 ± 0.05 (Table 1). The factor loading on average accounted for 13% of the organic PM_1 mass concentration (Figure 4a, inset). The factor loading decreased as the PBL developed during the day, consistent with dominant non-photochemical, primary sources (Figure 4b). Furthermore, there were increases, albeit small, in factor loading at 12:00 and 18:00 (local time), suggestive of breakfast-time and lunch-time cooking activities in Manaus based on a transport time of 4 to 6 h between the city and the T3 site (Martin et al., 2016; Cirino et al., submitted). Manaus typically has four rush-hour periods each day from 6:30 to 8:00, 12:00 to 13:30, 16:30 to 18:30, and 21:00 to 22:00. Traffic peaking at these hours may therefore also have contributed to the ADOA factor. Correlations between factor loading and external measurements exceeded $R = 0.5$ for many anthropogenic markers, including concentrations of aromatics (e.g., benzene, toluene, and C_8 and C_9 species), carbon monoxide, particle count, and NO_y (Figure 4c, Figure 5). Contributions from secondary processes cannot be ruled out, and it is possible that PM production from anthropogenic VOCs might have also been captured in this factor. Overall, the ADOA factor was interpreted in the present study as an indicator of anthropogenic influence associated with several sources in Manaus, most importantly cooking and possibly traffic emissions.

The IEPOX-SOA factor profile had marker ions of $C_4H_5^+$ (*m*/*z* 53) and $C_5H_6O^+$ (*m*/*z* 82) (Figure 4a; Lin et al., 2012; Hu et al., 2015; de Sá et al., 2017). It had an O:C ratio of 0.9 ± 0.10 (Table 1). The factor loading on average accounted for 17% of the organic PM_1 mass concentration (Figure 4a, inset). There were high correlations ($R > 0.8$) between factor loadings and concentrations of C_5-alkenetriols and 2-methyltetrols, which are markers of IEPOX-derived PM, produced by the photo-oxidation of isoprene under HO_2-dominant conditions (Surratt et al., 2010; Lin et al., 2012; Figure 4c). The increase in factor loading during daytime was consistent with a photochemical source (Figure 4b). There were also correlations between factor loadings and concentrations of sulfate and some acids, such as tricarballylic acid (TCA; Figure 5), in agreement with the association of IEPOX-derived PM and sulfate/acidity observed in other studies (Budisulistiorini et al., 2013; Nguyen et al., 2014; Kuwata et al., 2015). Overall, this factor was therefore interpreted as representative of PM produced from isoprene photo-oxidation under HO_2-dominant conditions. The effects of urban pollution on the loadings of this factor were the focus of a previous publication (de Sá et al., 2017).

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

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

The LO-OOA factor loading on average accounted for 25% of the organic PM_1 mass concentration (Figure 4a, inset). The factor loading correlated better with the estimated concentrations of inorganic nitrate than with organic or total nitrate (Figure 5; Section S2 and Figure S6), which is consistent with the interpretation of the higher volatility associated with this factor (Jimenez et al., 2009; Zhang et al., 2011). The factor loading also correlated ($R > 0.7$) with the concentrations of 2-methylglyceric acid and methyl-butyl-tricarboxylic acid (MBTCA), which are products of isoprene and monoterpene oxidation, respectively, under NO-dominant conditions (Figure 4c; Figure 5). The factor loading increased starting at 9:00 (local time) and peaked in the afternoon hours (Figure 4b). This diel trend, tied to the sunlight cycle, tracked the typical daily emission patterns of isoprene and monoterpenes from the surrounding forest (Yáñez-Serrano et al., 2015). The absence of a sharp decline at sunset and the higher variability at nighttime may also indicate a contribution by terpene ozonolysis. For these several reasons, the LO-OOA factor was interpreted herein as secondary organic PM produced mostly within several hours of observations by many possible pathways, including (i) the photo-oxidation of isoprene along non-IEPOX pathways, (ii) the photo-oxidation of terpenes and other biogenic VOCs along both HO_2- and NO-dominant reaction pathways, (iii) the ozonolysis of terpenes, and (iv) the possible production of SOM from anthropogenic emissions from Manaus.

The MO-OOA factor loading on average accounted for 30% of the organic PM_1 mass concentration (Figure 4a, inset). The factor loading correlated ($R > 0.7$) with the mass concentrations of several particle-phase carboxylic acids as well as the concentrations of sulfate, ammonium, and ozone (Figure 5). The time series of malic acid and ozone concentrations are

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

3.3 Shifts in PM with anthropogenic influences

3.3.1 Cluster Analysis

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

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

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

Two clusters of data were interpreted as "background" and labeled "Bkgd-1" and "Bkgd-2". They were characterized by NO_y < 1 ppb, ozone < 20 ppb, and particle number < 1200 cm^{-3} (Table 2; Figure 6). The two clusters differed especially in that Bkgd-2 had significantly larger concentrations of sulfate and black carbon. A comparison of the datasets of Feb 13 (predominantly Bkgd-1) and Feb 16 (predominantly Bkgd-2) in Figure 6 highlights these differences. Concentrations of sulfate and black carbon were 0.15 and 0.10 μg m^{-3}, respectively, on Feb 13, compared to 0.40 and 0.15 μg m^{-3} on Feb 16. The backtrajectories associated with

412 Bkgd-1 had both northeasterly and southeasterly components. The wind fields, out of line with
413 the trade winds, may suggest passage through recent weather systems and may imply wet
414 deposition, which in turn might explain lower gas and particle concentrations (Table 2). These
415 recent weather systems might not have been excluded from the scoped dataset because of
416 inaccuracies in the intersections of the backtrajectories with precipitation data, as discussed
417 above, or because they were more distant than captured by the 10-h backtrajectories. Consistent
418 with this hypothesis, the centroid value calculated for the 4-h averaged solar irradiance at T3
419 (Section 3.3.2) was lower for Bkgd-1 (400 W m^{-2}) compared to the other clusters (600 W m^{-2}),
420 suggesting an association of Bkgd-1 with overcast conditions. By comparison, the
421 backtrajectories associated with Bkgd-2 were predominantly from the northeast, coming from the
422 direction of the T0t and T0a sites (Figure 7), in line with the dominant trade winds of the wet
423 season. The air masses of Bkgd-2 may have experienced less wet deposition and may represent
424 more extensive atmospheric oxidation than those of Bkgd-1. They may also have carried PM
425 contributions from out-of-basin sources, which would be consistent with the higher sulfate and
426 black carbon concentrations of Bkgd-2 compared to Bkgd-1 (Chen et al., 2009; Pöhlker et al.,
427 2017).

428 Two other clusters were interpreted as "polluted" and labeled "Pol-1" and "Pol-2". They
429 were characterized by concentrations of NO_y > 1 ppb, ozone > 20 ppb, and particle number >
430 1200 cm^{-3} (Table 2; Figure 6). The dataset of the afternoon of Mar 9 illustrates a shift in
431 dominance from Pol-2 to Pol-1 (Figure 6). Although Pol-1 and Pol-2 both have high
432 concentrations of sulfate and other pollutants, they differ in the extent of those high
433 concentrations. The explanation may be that these clusters represent different source regions.
434 Pol-1 may be associated with emissions from the northern region of Manaus, and Pol-2 may be

435 associated with emissions from the southern region of Manaus. Industry, power production, and
436 oil refineries are concentrated in the southeastern region of Manaus (Figure S9; Medeiros et al.,
437 2017). Population density and commercial activity is concentrated in the southwestern portion of
438 the city where downtown is located (Figure S10). Aircraft observations show that concentrations
439 of sulfate as well as other pollutants are higher in the urban outflow from the southern compared
440 to the northern region of Manaus (Figure S10). Directional plots of SO_2 and particle number
441 concentrations observed at the T2 site further demonstrate the heterogeneity in Manaus
442 emissions (Figure S10). This hypothesis of a geographical difference in source regions
443 qualitatively aligns with the differences in backtrajectories characteristic of times dominated by
444 Pol-1 and Pol-2 (Figure 7). This interpretation does imply, however, that the backtrajectories
445 may have a 20° inaccuracy. Such inaccuracy is reasonable for the application of HYSPLIT
446 modeling in this region given (i) the absence of surface weather stations and (ii) the relatively
447 large scale of input wind fields (i.e., 50 km) compared to the scale of modeling (i.e., 70 km from
448 T3 to Manaus and a city cross section of 20 km).

449 **3.3.2 Comparison of PM among clusters**

450 The characteristic PM composition associated with each cluster was determined by
451 calculating the centroid coordinates of the clusters for the AMS species and PMF factors
452 (Section S3). The centroid coordinate of a cluster for a given variable is defined as a weighted
453 mean of that variable across all points in time, where the weight is the degree of membership of
454 each data point to that cluster. A comparison of PM_1 concentrations and compositions for the
455 four clusters is shown in Figure 8. Values are listed in Table 2.

456 The NR-PM_1 mass concentrations increased by 25% to 200% in clusters Pol-1 and Pol-2
457 compared to clusters Bkgd-1 and Bkgd-2 (Figure 8a). Increases in sulfate and associated

458 ammonium concentrations had a smaller yet non-negligible role in the increased PM_1 mass
459 concentrations. Sources of sulfate other than Manaus sustain relatively high concentrations in the
460 Amazon basin, as represented by the Bkgd-2 cluster (Chen et al., 2009; de Sá et al., 2017).
461 Compared to these regional background concentrations (i.e., Bkgd-2 cluster), the increases in
462 sulfate concentrations were significant only for air masses associated with the heavily
463 industrialized and densely populated southern region of Manaus (i.e., Pol-2 cluster).
464 With respect to the composition of the organic PM, Figure 8b shows that the Bkgd-1
465 cluster had large contribution from the LO-OOA factor. By comparison, the Bkgd-2 cluster had
466 larger contributions from the MO-OOA and IEPOX-SOA factors. A comparison of 13 Feb and
467 16 Feb of 2014 (Figure 6d) illustrates these findings. The low mass concentrations and the
468 dominant contribution by the LO-OOA factor suggest that the Bkgd-1 cluster may represent
469 conditions under which secondary organic PM was produced within recent hours through photo-
470 oxidation of VOCs emitted by the forest and subsequent condensation of secondary organic
471 material. The low sulfate concentrations for Bkgd-1 may rationalize the absence of a significant
472 contribution by the IEPOX-SOA factor. Isoprene photo-oxidation may have contributed to PM
473 production by pathways other than IEPOX uptake (Krechmer et al., 2015; Riva et al., 2016). By
474 comparison, for Bkgd-2, the higher mass concentrations and the greater contributions by IEPOX-
475 SOA and MO-OOA factors suggest that this cluster may represent conditions under which
476 secondary organic PM was a combination of material produced both on that day as well as on
477 previous days. During transport, the organic PM may have undergone extensive atmospheric
478 oxidation by a combination of surface and condensed-phase chemistry, including cloud water
479 processes (Carlton et al., 2006; Ervens et al., 2011; Hoyle et al., 2011; Perraud et al., 2012).

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

The organic PM concentration and composition associated with the Pol-1 and Pol-2 clusters were distinct from those of the Bkgd-1 and Bkgd-2 clusters (Figure 8). The mass concentrations of organic PM were greater by 25% to 150% for Pol-1 and Pol-2. According to the PMF factors (Figure 8b), the larger part of this increase in organic PM between the background and polluted clusters was tied to the production of secondary organic PM, although primary emissions also contributed significantly. By comparison, for both Bkgd-1 and Bkgd-2 clusters, contributions by primary emissions were negligible, as indicated by the low summed contribution of factors of primary origin (i.e., ADOA, BBOA, and HOA) to the organic PM_1 (< 10%). For Pol-1 and Pol-2, the ADOA factor loading on average accounted for 10% of the organic mass concentration at T3, serving as a strong marker of Manaus pollution. A comparison of February 9 ~~Feb~~ and March 9 ~~Mar~~ with February 13 ~~Feb~~ and 16 ~~Feb~~ illustrates these findings (Figure 6d).

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

The shifts in the processes governing the production of secondary organic PM because of increased NO_x, OH, and O_3 concentrations characteristic of the pollution plume were complex and non-linear (Figure 9a). Overall, the oxidation pathways were driven faster. The relatively high $f_{CO_2^+}$ values and O:C ratios of all factors (Table 1), including those associated with primary emissions, compared to typical values at other locations worldwide (Canagaratna et al., 2015), corroborate this interpretation. Ozone concentrations in the plume increase by 200% to 300%, and hydroxyl radical concentrations increased by 250% or more (Liu et al., accepted). As HO_2-dominant pathways were inhibited, NO-dominant pathways became active. Increased oxidant concentrations may also have promoted additional multigenerational chemistry of semi- or intermediate-volatility species (Robinson et al., 2007). Oxidation of VOCs by aqueous-phase reactions, including in-cloud processing, and oxidation of biomass burning emissions may also have played roles to varying degrees on different days (Carlton et al., 2006; Ervens et al., 2011; Hoyle et al., 2011; Perraud et al., 2012). In addition, when primary and secondary PM mass concentrations increased, further uptake of oxidized semi-volatile molecules could have been thermodynamically favored according to partitioning theory, representing a positive feedback on the increase of mass concentrations (Pankow, 1994; Odum et al., 1996; Carlton et al., 2010).

The increase in the LO-OOA and MO-OOA factor loadings associated with Pol-1 and Pol-2 indicates that the net effect of this accelerated and modified chemistry was the quick production and further oxidation of secondary organic PM. Precursors may have included both the wide range of biogenic VOCs as well as contributions from anthropogenic precursors, such as gas-phase species from vehicle emissions or evaporated primary material (Nordin et al., 2013; Presto et al., 2014). The LO-OOA factor loading was important for the polluted conditions of Pol-1 and Pol-2 as well as for the clean conditions of Bkgd-1. This result is not necessarily

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

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

4. Summary and conclusions

Changes in the concentrations and the composition of fine-mode PM due to the influence of anthropogenic emissions were investigated for the Amazonian wet season. Organic material

548 dominated the submicron composition, consistently representing between 70% and 80% of the
549 PM_1 mean mass concentration across measurement sites upwind and downwind of Manaus and
550 across different levels of pollution. Absolute mass concentrations, however, varied significantly
551 among sites. Average concentrations downwind of Manaus were 100% to 200% higher than
552 those upwind. Furthest downwind at T3, the organic component was more oxidized compared to
553 that at the T2 site.

554 Positive-matrix factorization and Fuzzy c-means clustering were applied to the datasets to
555 obtain a composite analysis of the shifts in PM_1 concentrations and composition under polluted
556 conditions. Based on the FCM clustering, every point in time at T3 was interpreted as being
557 affected by a combination of four influences, as represented by four clusters. Two background
558 (Bkgd-1 and Bkgd-2) and two polluted (Pol-1 and Pol-2) clusters were identified. Particle mass
559 concentrations were double for polluted compared to background conditions. Contributions from
560 secondary processes dominated (> 80%) for both background and polluted conditions.

561 In terms of primary emissions, absolute contributions increased by a factor of five or
562 more under polluted conditions, corresponding to an increase from < 10% to 15% of total PM_1.
563 The ADOA factor loading increased over five-fold for the polluted compared to the background
564 clusters, and this factor thus served as a strong tracer of Manaus pollution. BBOA and HOA
565 factor loadings, associated with biomass burning and fossil fuels, respectively, increased by two-
566 fold with pollution. The ADOA factor loading represented 61% to 76% of the total primary
567 factor loadings for the Pol-1 and Pol-2 clusters.

568 As for the secondary processes, the analysis further finds that the pollution plume acted
569 both to shift pathways of secondary organic PM production and to accelerate the atmospheric
570 oxidation of pre-existing organic PM. The oxidation of biogenic PM precursors shifted from

571 HO_2- to NO-dominant pathways, and the oxidation of anthropogenic precursors possibly
572 contributed to increased PM concentrations. The IEPOX-SOA factor loadings were highest for
573 the Bkgd-2 cluster, associated with long-range transport under background conditions, and
574 decreased by almost 50% for the polluted clusters, in line with a shift of isoprene oxidation from
575 HO_2- to NO-dominant pathways. Concomitantly, the LO-OOA factor loading increased by more
576 than 50% for these clusters, suggesting rapid in-plume production of secondary organic PM
577 through several pathways. The LO-OOA factor was also important for the Bkgd-1 cluster,
578 associated with fresh background conditions, which is suggestive of recent biogenic organic PM
579 production. The MO-OOA factor had large relative contributions in the Bkgd-2, Pol-1, and Pol-2
580 clusters, suggestive of significant oxidative processing associated with these clusters. Increases
581 of up to 300% in the MO-OOA factor loadings for Pol-1 and Pol-2 relative to background
582 conditions of Bkgd-1 showed the effects of an accelerated oxidation cycle, leading to highly
583 oxidized PM downwind of Manaus. Based on this and related studies (Liu et al., 2016b; de Sá et
584 al., 2017; Martin et al., 2017), the critical lever seems to be increased concentrations of nitrogen
585 oxides in the pollution plume for both directly shifting and indirectly accelerating mechanisms of
586 secondary organic PM production in central Amazonia during the wet season.
587 The altered composition under anthropogenic influences also affects the physical
588 properties of the PM_1. Bateman et al. (2017), using the results of the PMF analysis presented
589 herein, reported a shift from predominantly liquid PM under background conditions to a
590 considerable presence of non-liquid PM above 50% RH under polluted conditions. Non-liquid
591 PM can have different reactive chemistry from liquid PM (Li et al., 2015; Liu et al., 2018). A
592 linear relationship between the increase in particle rebound fraction and the sum of ADOA,
593 BBOA, and HOA factor loadings had an R^2 of 0.7. The highest individual correlation was with

the ADOA factor loading (Bateman, personal communication). In addition, Thalman et al. (2017), also using the PMF results reported herein, concluded that the larger relative contribution of secondary organic material during the daytime compared to the nighttime was the primary driver of the diel trend of higher particle hygroscopicity during the day compared to the night, as tied to cloud condensation nuclei (CCN) properties.

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

Acknowledgments. Institutional support was provided by the Central Office of the Large Scale Biosphere Atmosphere Experiment in Amazonia (LBA), the National Institute of Amazonian Research (INPA), and Amazonas State University (UEA). We acknowledge support from the Atmospheric Radiation Measurement (ARM) Climate Research Facility, a user facility of the United States Department of Energy (DOE, DE-SC0006680), Office of Science, sponsored by the Office of Biological and Environmental Research, and support from the Atmospheric System Research (ASR, DE-SC0011115, DE-SC0011105) program of that office. Additional funding was provided by the Amazonas State Research Foundation (FAPEAM 062.00568/2014 and 134/2016), the São Paulo State Research Foundation (FAPESP 2013/05014-0), the USA National Science Foundation (1106400 and 1332998), and the Brazilian Scientific Mobility Program (CsF/CAPES). S. S. de Sá acknowledges support by the Faculty for the Future Fellowship of the Schlumberger Foundation. BBP is grateful for a US EPA STAR Graduate Fellowship (FP-91761701-0). The authors thank Paulo Castillo for his assistance in quality-checking the black carbon data from MAOS. Data access from the Sistema de Proteção da Amazônia (SIPAM) is gratefully acknowledged. The research was conducted under scientific license 001030/2012-4 of the Brazilian National Council for Scientific and Technological Development (CNPq).

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List of Figures

and pressure (273.15 K and 10^5 Pa). Local time is (UTC - 4 h). Lines represent means, solid markers show medians, and boxes span interquartile ranges. ~~The ordinate scale for the T2 panel differs from the other three panels. Concentrations were adjusted to standard temperature (273.15 K) and pressure (10^5 Pa).~~

Figure 3. Scatter plot of the AMS signal fraction at *m*/*z* 44 (f_{44}) against that at *m*/*z* 43 (f_{43}). Gray and blue circles correspond, respectively, to measurements at T3 and T2 during IOP1, in the wet season of 2014. For visualization purposes, the two datasets are plotted separately in panels a and b. Solid squares represent median values, and whiskers represent 10 and 90 percentiles. Dashed lines delineate the region where worldwide measurements of ambient organic PM_1 commonly lie (Ng et al., 2011a).

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

Figure 5. Column plot of Pearson *R* correlations between the loading of each PMF factor and values of selected measurements at T3. Abbreviations include tricarballylic acid (TCA), methyl-butyl-tricarboxylic acid (MBTCA), methyl vinyl ketone (MVK), methacrolein (MACR), and isoprene hydroxyhydroperoxides (ISOPOOH). SV-TAG measurements refer to particle-phase concentrations. Isomers could not be

distinguished by PTR-ToF-MS measurements; C_8 and C_9 aromatics include the xylene and trimethylbenzene isomers, respectively.

Figure 6. Results of the cluster analysis by Fuzzy c-means (FCM) for afternoon periods (12:00 to 16:00 h) are presented by several case studies. (a) Degree of membership in each of the four clusters. The sum of degrees of membership across all clusters is unity. Background conditions are abbreviated as "Bkgd", and polluted conditions are abbreviated as "Pol". (b) Pollution indicators: concentrations of NO_y, O_3, black carbon (BC), and particle number count are plotted. (c) PM_1 mass concentrations for organic, sulfate, nitrate, and ammonium species. (d) Fractional contribution of each factor to total organic PM_1.

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

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

Figure 9. Schematic representation of (a) atmospheric processes, illustrated in a simplified manner, associated with the production of organic PM_1 and (b) observables of these processes as captured by the datasets and analytical approach employed in this study. In panel (a), the left side depicts the emissions of biogenic volatile organic compounds (VOCs), their atmospheric oxidation, and the production of biogenic secondary

organic PM_1. The right side depicts anthropogenic emissions of gas species and particulate matter that can alter natural atmospheric concentrations and processes. There are primary organic PM_1 emissions from traffic, cooking, and industrial activities. Anthropogenic VOCs can be precursors for the production of secondary organic PM_1 and can affect the production of ozone and hydroxyl radical. NO_x emissions directly and indirectly alter the natural pathways of PM_1 production in the atmosphere. NO_x and SO_x can also directly contribute to the formation of secondary inorganic PM_1 (not shown), which can in turn play a role in changing pathways of secondary organic PM_1 production. In panel (b), different PMF factors represent distinct sources and/or processes. The IEPOX-SOA factor is at the intersection of the two, as it represents both a source (i.e., isoprene emissions from the forest) and a process (i.e., photo-oxidation under HO_2 dominant conditions, influenced by sulfate concentrations). The dashed black line represents the natural and anthropogenic oxidative processes that transform the chemical signature of the HOA, ADOA, BBOA, IEPOX-SOA, and LO-OOA factors after sufficient atmospheric residence time into the MO-OOA factor. The clusters represent different conditions at the receptor site (i.e., T3) and therefore incorporate the meteorological and geographical histories of the air masses that reach the site and affect the observed concentrations. The different PMF factors are associated to the different clusters (solid lines) to various extents (not detailed here for simplification purposes; cf. Figure 8).

Table 1. Characteristics of the PMF factors derived from the AMS datasets. Listed are signal fractions $f_{CO_2^+}$ at nominal m/z 44 and oxygen-to-carbon (O:C) and hydrogen-to-carbon (H:C) ratios. Values and associated uncertainties were calculated by running PMF in "bootstrap mode" (Ulbrich et al., 2009c). Elemental ratios were calibrated by the "improved-ambient" method, which has an estimated uncertainty of 12% for O:C and 4% for H:C (Canagaratna et al., 2015).

PMF factor	$f_{CO_2^+}$	O:C	H:C
MO-OOA	0.25 ± 0.01	1.09 ± 0.17	1.27 ± 0.12
LO-OOA	0.14 ± 0.02	0.72 ± 0.10	1.49 ± 0.07
IEPOX-SOA	0.17 ± 0.01	0.93 ± 0.10	1.39 ± 0.07
ADOA	0.11 ± 0.01	0.40 ± 0.05	1.63 ± 0.02
BBOA	0.123 ± 0.004	0.61 ± 0.08	1.57 ± 0.04
HOA	0.048 ± 0.006	0.18 ± 0.02	1.94 ± 0.02

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

Species	Cluster Centroid			
	Bkgd-1	Bkgd-2	Pol-1	Pol-2
Input variables				
Particle number (cm^{-3})	714	1117	2636	6697
NO_y (ppb)	0.64	0.95	1.2	2.2
O_3 (ppb)	14	17	26	36
Black carbon ($\mu g\ m^{-3}$)	0.05	0.16	0.21	0.18
Sulfate ($\mu g\ m^{-3}$)	0.15	0.36	0.44	0.57
AMS species concentrations ($\mu g\ m^{-3}$)				
Organic	0.96	2.0	2.5	2.6
Ammonium	0.05	0.12	0.15	0.21
Nitrate	0.03	0.07	0.10	0.12
Chloride	0.007	0.011	0.009	0.007
PMF factor loadings ($\mu g\ m^{-3}$)				
MO-OOA	0.29	0.83	1.13	1.13
LO-OOA	0.38	0.41	0.62	0.77
IEPOX-SOA	0.18	0.49	0.43	0.29
ADOA	0.044	0.086	0.19	0.32
BBOA	0.028	0.054	0.081	0.063
HOA	0.017	0.027	0.039	0.040

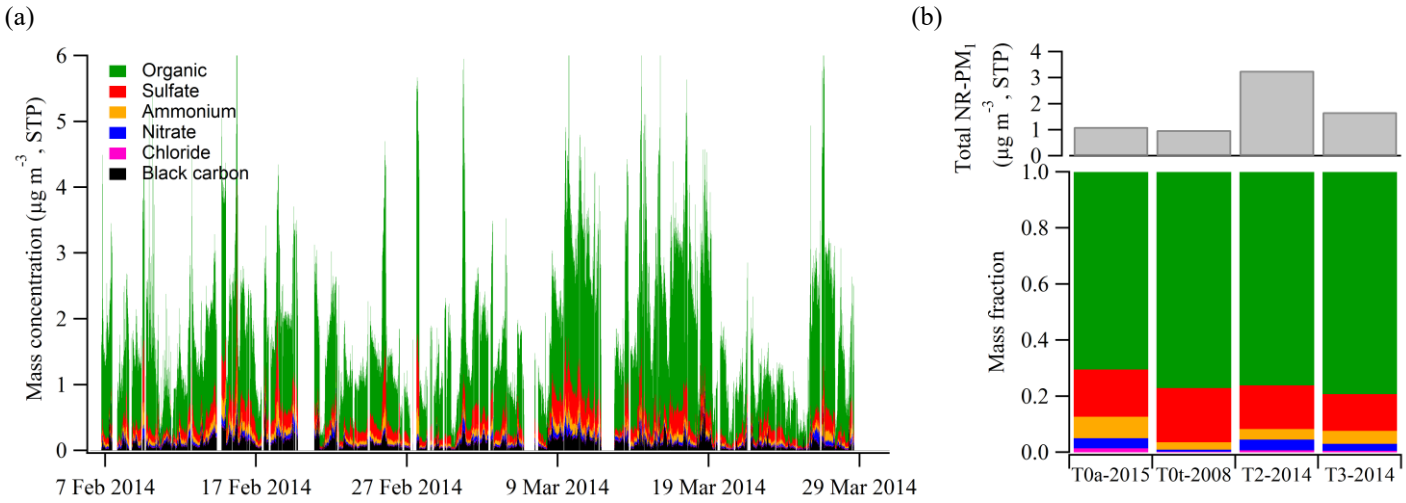
(a)
Organic
Sulfate
Ammonium
Nitrate
Chloride
Black carbon
Mass concentration (µg m-3, STP)
7 Feb 2014
17 Feb 2014
27 Feb 2014
9 Mar 2014
19 Mar 2014
29 Mar 2014
(b)
Total NR-PM1 (µg m-3, STP)
Mass fraction
T0a-2015
T0t-2008
T2-2014
T3-2014

Figure 1

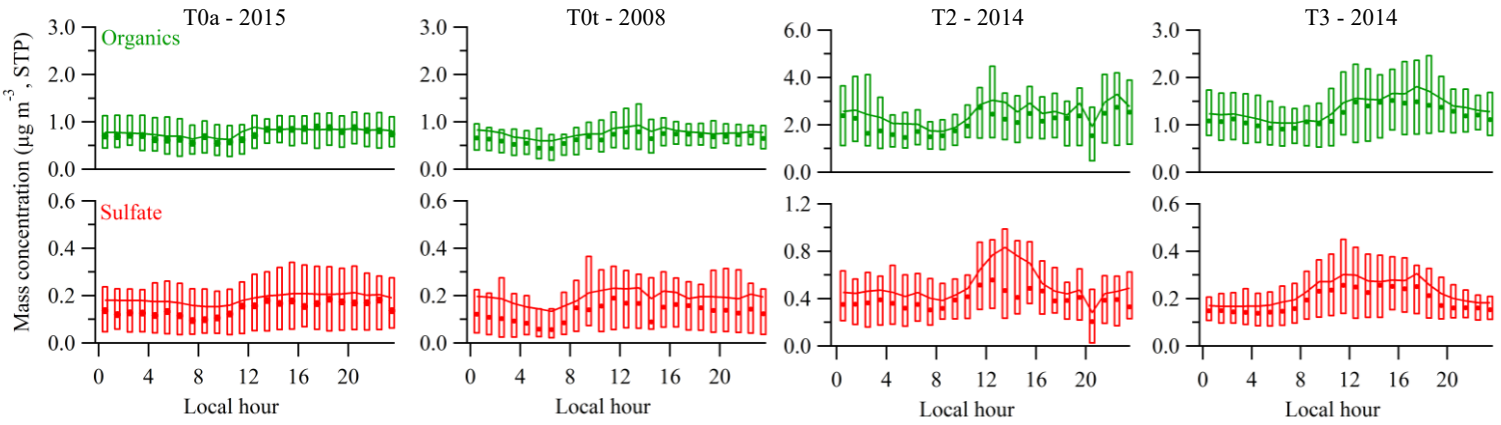
T0a - 2015
T0t - 2008
T2 - 2014
T3 - 2014
Organics
Sulfate
Mass concentration (µg m-3, STP)
Local hour
0
4
8
12
16
20

Figure 2

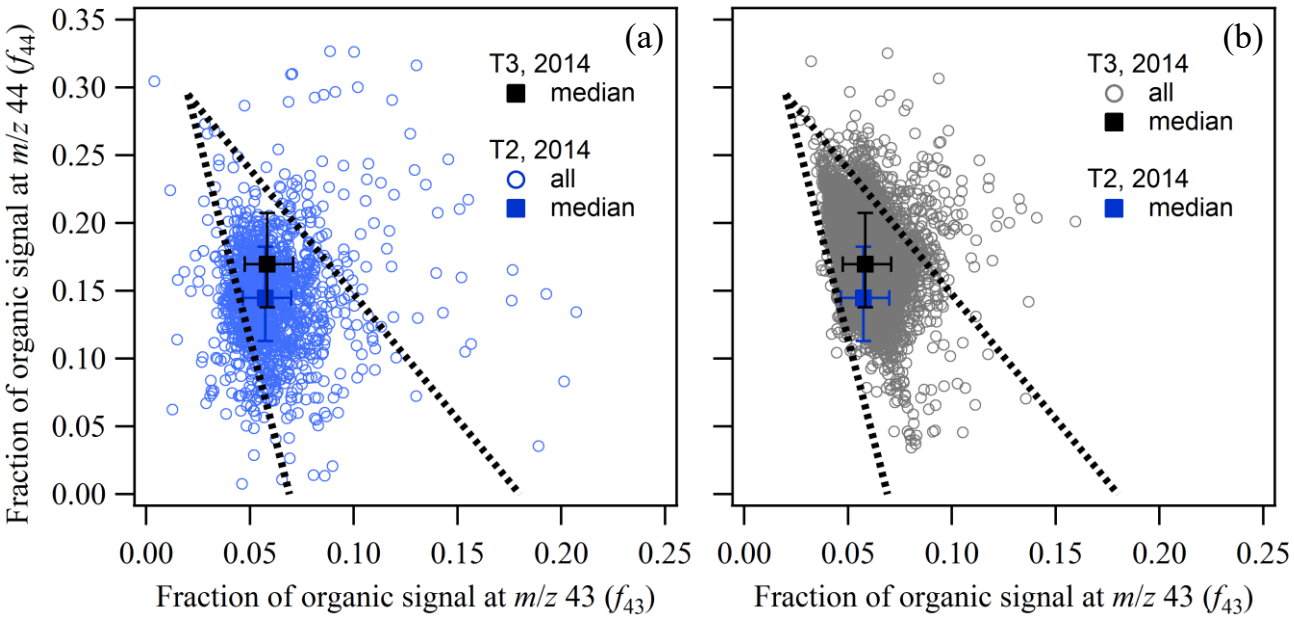
(a)
(b)
T3, 2014
median
T2, 2014
all
median
Fraction of organic signal at m/z 44 (f_{44})
Fraction of organic signal at m/z 43 (f_{43})
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35

Figure 3

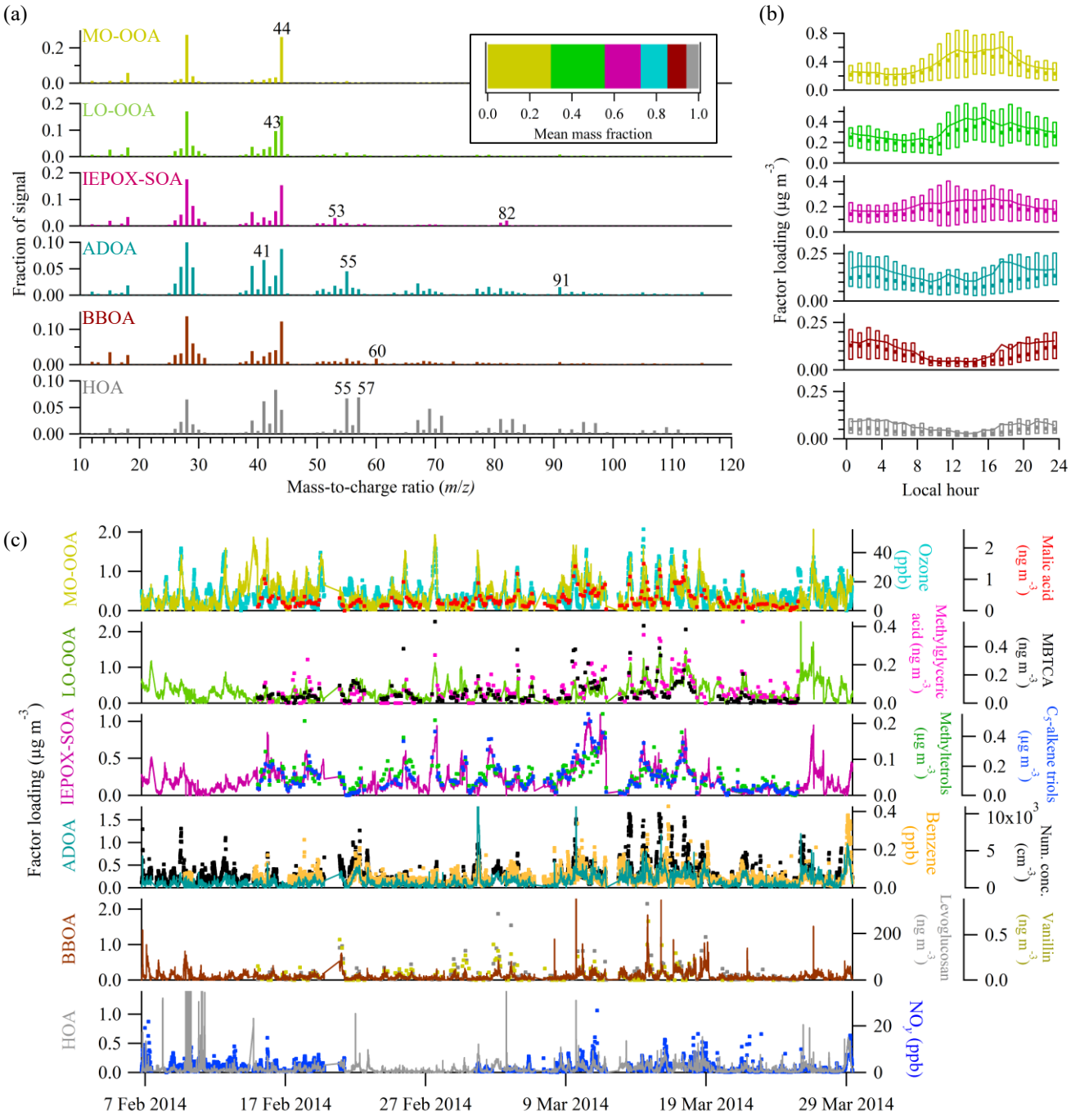
(a)
MO-OOA
LO-OOA
IEPOX-SOA
ADOA
BBOA
HOA
Fraction of signal
Mass-to-charge ratio (m/z)
Mean mass fraction
(b)
Factor loading (μg m-3)
Local hour
(c)
Factor loading (μg m-3)
Ozone (ppb)
Malic acid (ng m-3)
Methylglyceric acid (ng m-3)
MBTCA (ng m-3)
Methyltetrols (μg m-3)
C5-alkene triols (μg m-3)
Benzene (ppb)
Num. conc. (cm-3)
Levoglucosan (ng m-3)
Vanillin (ng m-3)
NOy (ppb)
7 Feb 2014
17 Feb 2014
27 Feb 2014
9 Mar 2014
19 Mar 2014
29 Mar 2014

Figure 4

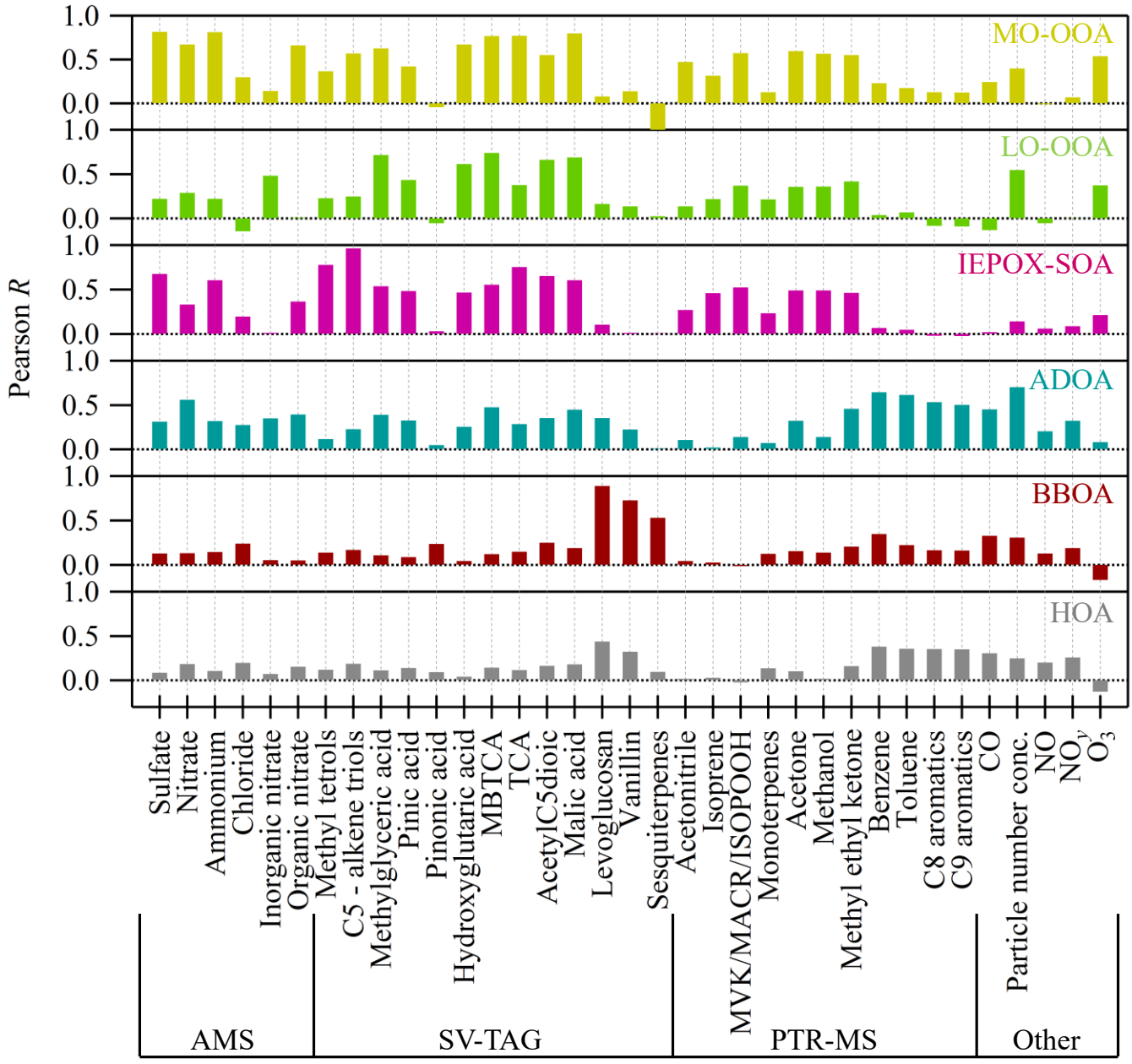
Pearson R
1.0
0.5
0.0
MO-OOA
LO-OOA
IEPOX-SOA
ADOA
BBOA
HOA
Sulfate
Nitrate
Ammonium
Chloride
Inorganic nitrate
Organic nitrate
Methyl tetrols
C5 - alkene triols
Methylglyceric acid
Pinic acid
Pinonic acid
Hydroxyglutaric acid
MBTCA
TCA
AcetylC5dioic
Malic acid
Levoglucosan
Vanillin
Sesquiterpenes
Acetonitrile
Isoprene
MVK/MACR/ISOPOOH
Monoterpenes
Acetone
Methanol
Methyl ethyl ketone
Benzene
Toluene
C8 aromatics
C9 aromatics
CO
Particle number conc.
NO
NOy
O3
AMS
SV-TAG
PTR-MS
Other

Figure 5

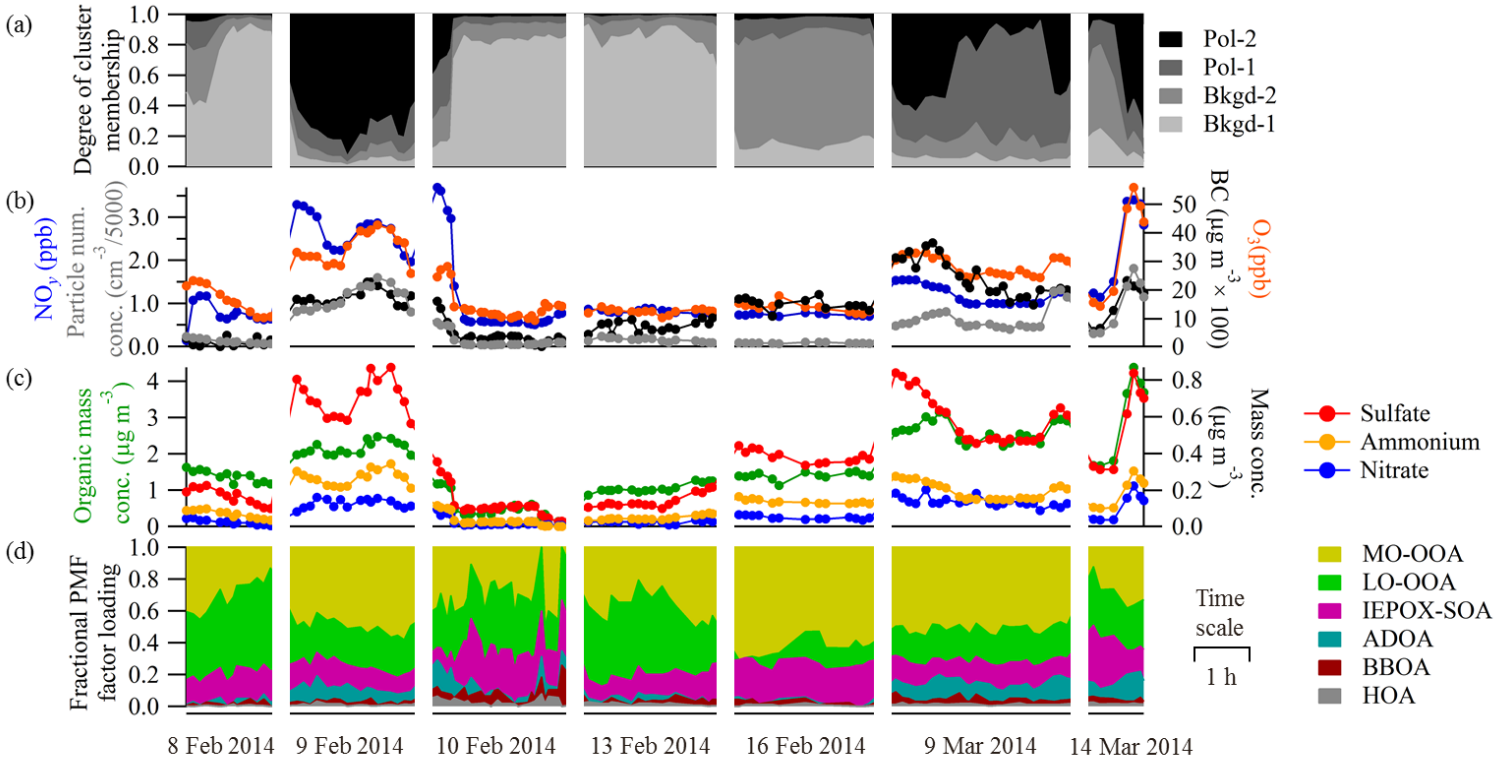
(a)
Degree of cluster membership
1.0
0.8
0.6
0.4
0.2
0.0
Pol-2
Pol-1
Bkgd-2
Bkgd-1
(b)
NOy (ppb)
Particle num. conc. (cm-3/5000)
3.0
2.0
1.0
0.0
BC (μg m-3 × 100)
50
40
30
20
10
0
O3(ppb)
(c)
Organic mass conc. (μg m-3)
4
3
2
1
0
0.8
0.6
0.4
0.2
0.0
Mass conc. (μg m-3)
Sulfate
Ammonium
Nitrate
(d)
Fractional PMF factor loading
1.0
0.8
0.6
0.4
0.2
0.0
Time scale
1 h
MO-OOA
LO-OOA
IEPOX-SOA
ADOA
BBOA
HOA
8 Feb 2014
9 Feb 2014
10 Feb 2014
13 Feb 2014
16 Feb 2014
9 Mar 2014
14 Mar 2014

Figure 6

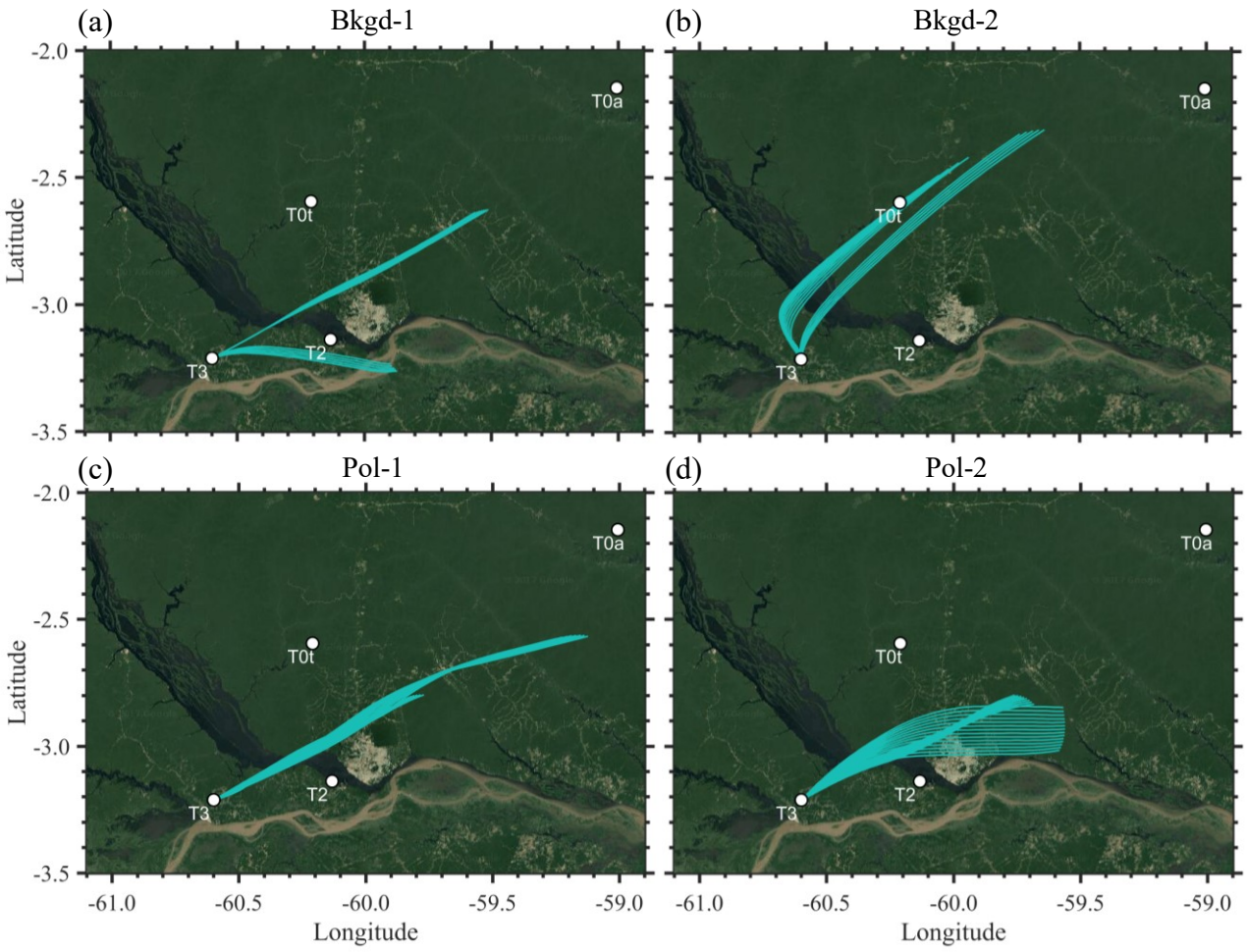
(a)
Bkgd-1
(b)
Bkgd-2
(c)
Pol-1
(d)
Pol-2
T0a
T0t
T2
T3
Latitude
Longitude
-2.0
-2.5
-3.0
-3.5
-61.0
-60.5
-60.0
-59.5
-59.0

Figure 7

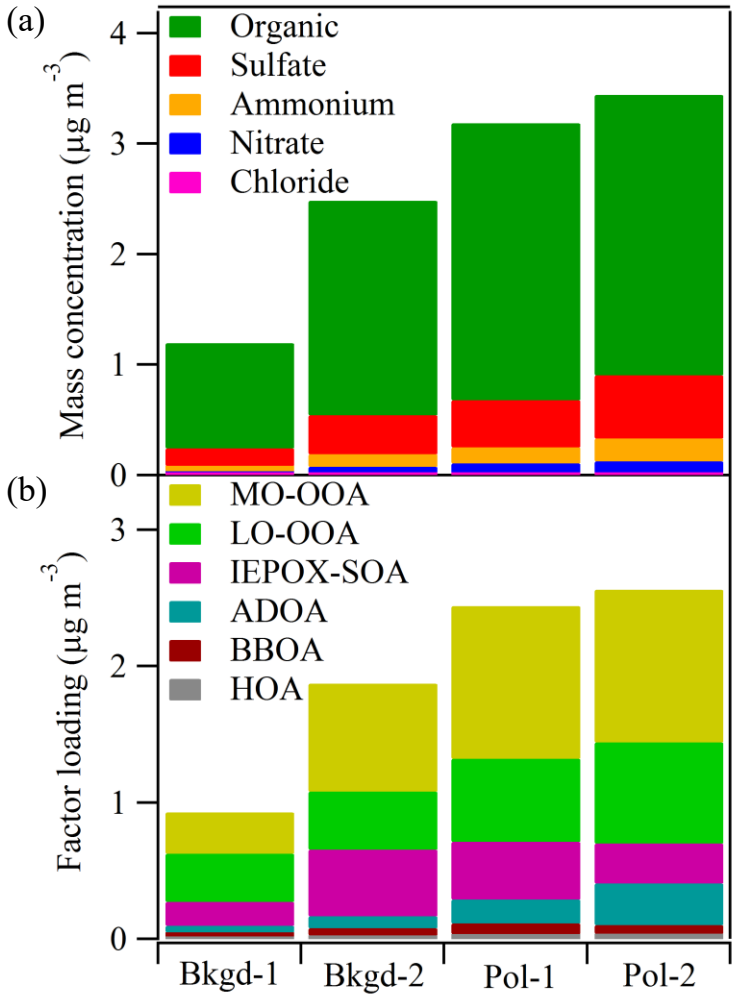
(a)
Organic
Sulfate
Ammonium
Nitrate
Chloride
Mass concentration (µg m-3)
0
1
2
3
4
(b)
MO-OOA
LO-OOA
IEPOX-SOA
ADOA
BBOA
HOA
Factor loading (µg m-3)
0
1
2
3
Bkgd-1
Bkgd-2
Pol-1
Pol-2

Figure 8

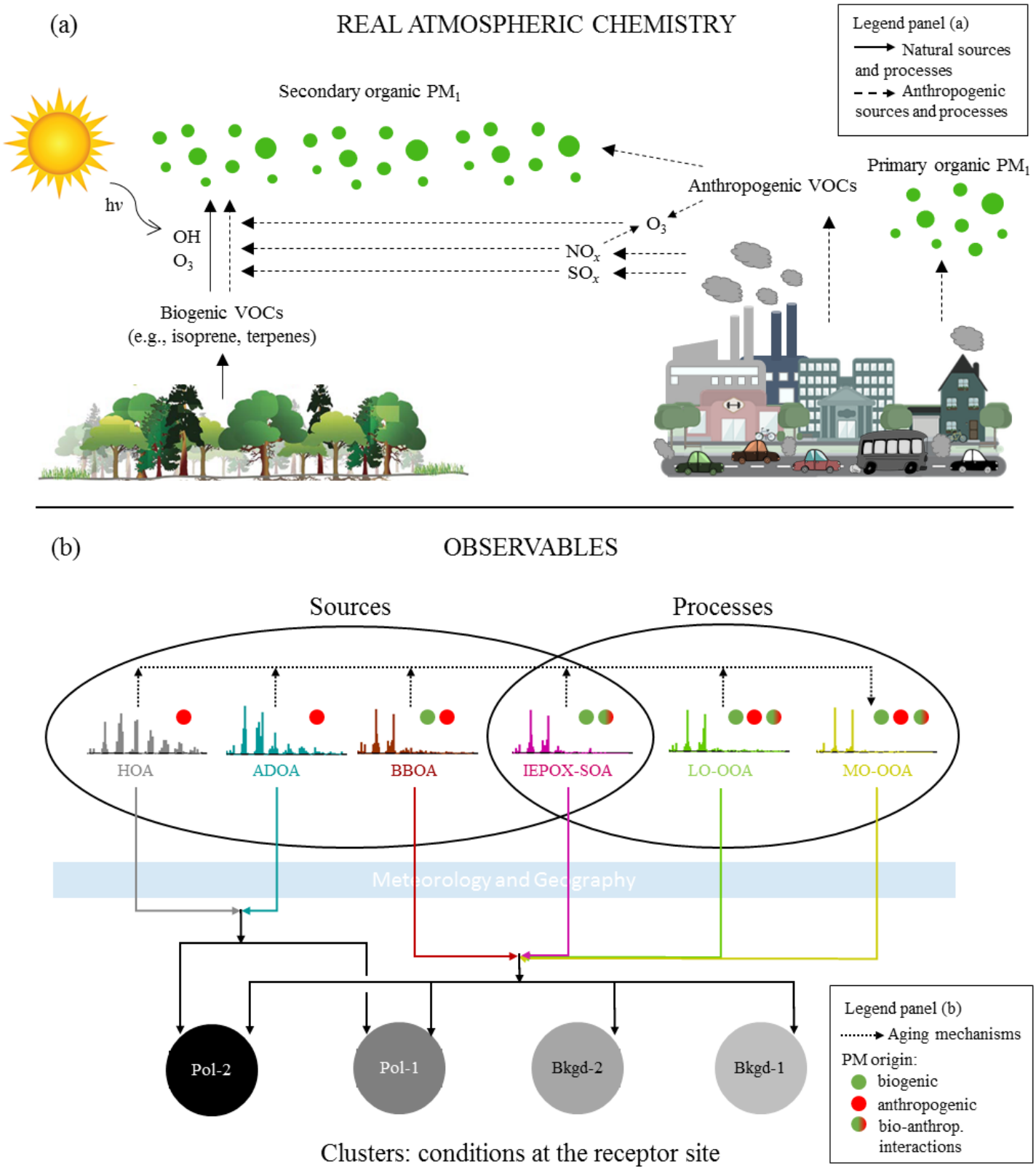
(a)
REAL ATMOSPHERIC CHEMISTRY
Legend panel (a)
Natural sources and processes
Anthropogenic sources and processes
Secondary organic PM1
Primary organic PM1
Anthropogenic VOCs
hν
OH
O3
O3
NOx
SOx
Biogenic VOCs
(e.g., isoprene, terpenes)
(b)
OBSERVABLES
Sources
Processes
HOA
ADOA
BBOA
IEPOX-SOA
LO-OOA
MO-OOA
Meteorology and Geography
Pol-2
Pol-1
Bkgd-2
Bkgd-1
Clusters: conditions at the receptor site
Legend panel (b)
Aging mechanisms
PM origin:
biogenic
anthropogenic
bio-anthrop. interactions

Figure 9

Supplementary Material for

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

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Submitted: February 2018

Atmospheric Chemistry and Physics

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S1. Positive-matrix factorization

S1.1 Diagnostics of the six-factor solution

Quantification of mass concentrations by the AMS was obtained from "V-mode" data, which corresponds to the shorter ion time-of-flight path and is therefore the more sensitive mode. The choice of ions to fit was aided by "W-mode" data, which correspond to the longer ion time-of-flight path and is therefore the mode with highest mass resolution. V-mode data were collected continuously, and W-mode data were collected for one of every five days. The time series of organic mass spectra measured by the AMS in V-mode was analyzed by positive-matrix factorization (PMF) using a standard analysis toolkit (Ulbrich et al., 2009). ~~High-resolution "V-mode" data were used.~~ The PMF solution was based on minimization of the "Q-value" (i.e., the sum of the weighed squared residuals for a chosen number of factors) and the physical meaningfulness of factors, as evaluated by profile characteristics and correlations with gas and particle phase measurements by other instruments.

Technical diagnostics of the six-factor solution are presented in Figure S3 in complement to the diagnostics presented in de Sá et al. (2017). The analysis was run for a number of factors from 1 to 10, and the rotational ambiguity parameter f_{peak} was varied from -1 to 1 in intervals of 0.2. Panel a shows the statistics of residuals for solutions with different number of factors. There was a large improvement in the solution when a sixth factor was introduced, as shown by a significant decrease in residuals, and only a marginal improvement when a seventh factor was added. Panel b shows, on the ordinate, the correlation between the time series of loadings for each pair of factors and, on the abscissa, the correlation between the profiles of each pair of factors. For the six-factor solution, the correlations among factor profiles are overall lower, also suggesting a better separation of factors and an improvement in the solution. Figure S4

corroborates this analysis by showing the factor profiles and loading time series of the 5- and 7-factor solutions. In the 5-factor solution, factors 4 and 5 seem to be a result of mixing of the three factors that are associated with secondary processing in the 6-factor solution (MO-OOA, LO-OOA, IEPOX-SOA). Conversely, in the 7-factor solution, some splitting seems to occur as factor 7 is physically meaningless, and a few pairs of factors have higher correlations between their loading time series (cf. Figure S3). An f_{peak} of zero was chosen for the final 6-factor solution, since it yielded the minimum quality of fit parameter $Q/Q_{expected}$ de Sá et al. (2017), and no significant improvements in the external validation of factors were observed by varying f_{peak}.

S1.2 Discussion of the ADOA PMF factor

ADOA is interpreted as a primary anthropogenic factor due to the correlation of its loadings with several tracers of anthropogenic activities (Figure 5), its spectral profile, and its diel behavior (Figure 4). Even though factors containing a characteristic *m*/*z* 91 have been reported in the literature as a biogenic factor (Robinson et al., 2011; Budisulistiorini et al., 2015; Chen et al., 2015; Riva et al., 2016), the ADOA of this study showed similarity with primary organic material from cooking activities. Figure S5 shows the high similarity of ADOA of this study to a factor representing cooking emissions at an urban background site in Barcelona, Spain (Mohr et al., 2012), and to a factor representing a cooking source tied to restaurants in an urban background site in Zurich, Switzerland (Lanz et al., 2007). By contrast, a lower similarity is found with the "91fac" factor found in the Borneo forest, a predominantly biogenic site. This result emphasizes that a characteristic marker ion $C_7H_7^+$ at *m*/*z* 91 does not directly imply either biogenic or anthropogenic origin, and the interpretation of a PMF factor with such marker should also strongly rely on the atmospheric context of the measurements, including the correlations of the factor loadings with external measurements and the diel behavior.

S2. Estimates of organic and inorganic nitrates based on AMS analysis

The typical AMS analysis reports total nitrate, meaning that nitrate fragments originating from both organic and inorganic nitrates are reported indistinctively as nitrate. In the absence of external measurements of inorganic nitrate, an estimation method using the ratio of NO_2^+ to NO^+ signal intensities measured by the AMS was employed (Figure S6; Fry et al., 2009; Farmer et al., 2010; Fry et al., 2013). Calculations were done on a 60-min time base to increase signal over noise. The obtained organic and inorganic nitrate time series were then interpolated into the original AMS timestamp for ambient measurements (i.e., one point every 8-min interval). The analysis excluded points that had total nitrate below the estimated detection limit, $DL_{Nitrate}$, which was estimated as three times the standard deviation for "closed AMS spectra", i.e., when chopper was in closed position and particles did not reach the vaporizer. Mathematically, $DL_{Nitrate} = 3\times\sqrt{E}$, where E is the "closed" error calculated by the standard *PIKA* software (Ulbrich et al., 2009). The dark blue dashed line in Figure S6c that defines NO_2^+/NO^+ for inorganic nitrate was determined by linear fit of ammonium nitrate calibrations performed regularly, as shown by the grey triangles. The small drift over time can be attributed to a gradual clean-up of the vaporizer. Worth noting, whether the linear fit or an average value was used for the calculations, the overall results did not change considerably, as all calibration ratios lied within ± 20% of the campaign-average ratio. The ratio NO_2^+/NO^+ for organic nitrates was assumed to be a factor of 2.25 lower than that of~~r~~ inorganic nitrate based on previous field studies (Farmer et al., 2010; Fry et al., 2013). The resulting IOP1-average for the fraction of organic nitrate in total nitrate (Figure S6b) was 87%.

S3. Fuzzy c-means clustering

Fuzzy c-means (FCM) clustering was applied to the dataset consisting of concentrations of particle number, NO_y, ozone, black carbon, and sulfate (Bezdek et al., 1984). The use of a fuzzy clustering method stems from the understanding that any point in time may be affected by a combination of different sources and processes and could therefore be anywhere on the scale between pristine background and extreme polluted conditions, as opposed to a simpler binary classification. Given the scope of the analysis as non-overcast afternoon times, data points were restricted to (i) local 12:00-16:00 h, (ii) local solar radiation over the past 4 h not less than 200 W m^{-2} (i.e., excluding the lower 20 percentile), and (iii) insignificant precipitation (< 0.1 mm) over the previous 10 h along backward trajectory (a threshold was used as most rain radar grid cells had non-zero yet negligible values). The data were normalized prior to the FCM analysis using the z-score method, which transforms all variables into a common scale with an average of zero and standard deviation of one.

The FCM algorithm minimizes the objective function represented in Eq. S1, which is a weighted sum of squared errors where the error is the Euclidean distance between each data point and a cluster centroid.

$$J(U,v)= \sum_{k=1}^{N} \sum_{i=1}^{c} u_{ik}^{m} \|y_k - v_i\|^2 \quad \text{(Eq. S1)}$$

The input data is given by the matrix $Y = [y_1, y_2, \ldots, y_N]$, where y_k is a vector of length X at the k-*th* time point. X is the number of variables (i.e., measurements) used as input in the analysis. The number of time points is represented by N, and the associated running index is k. N in this case was 313. The number of clusters is represented by c, and the corresponding running index is i. The coordinates of the centroid of each cluster i are represented by v_i, a vector of length X. The exponent of the Fuzzy partition matrix is represented by m. The algorithm returns (1) the Fuzzy partition matrix of Y, given by $U = [u_{ik}]$ where u_{ik} is the degree of membership of time point k to

cluster i, (2) the vectors of coordinates of cluster centers, given by $v = [v_i]$, as well as (3) the value J of the objective function.

The analysis was performed in MATLAB® using the "fcm" function in the Fuzzy logic toolbox™. The stop criterion of the algorithm is that either the maximum number of iterations is reached or the improvement of the objective function between two consecutive iterations is less than the minimum amount of improvement specified. The default value of 1×10^{-5} was used for the minimum amount of improvement, and the maximum number of iterations was set to 1000 so that convergence always happened before this maximum was reached. A default value of 2 was used for the exponent m of the partition matrix. Fuzzy clustering algorithms are not sensitive to small fluctuations in m (Chatzis, 2011), and a value in the range of 1.5 to 3 is recommended (Bezdek et al., 1984; Hathaway and Bezdek, 2001).

The analysis was run for a number of clusters varying from two to eight, and the value of the objective function for each run is shown in Figure S7. The choice of number of clusters hinges on a balance between increased complexity and additional information provided by each extra cluster. The improvement in the objective function was larger in the range of two to four clusters, with marginal improvements above four clusters (Figure S7). The location of cluster centroids was also examined for evaluation of cluster overlap (Figure S8). The addition of a fifth cluster made two pairs of clusters very similar, as can be seen by the locations of cluster centroids in Figure S8. The solution of four clusters was therefore a reasonable choice to represent the studied system. The subsequent characterization of the PM chemical composition associated with each cluster further confirmed the meaningfulness of the solution. Although the three-cluster solution could also provide a reasonable representation of the system, the four-

cluster solution provided further insight by differentiating two background and two polluted conditions.

Subsequently, the PM composition associated with each of the clusters was determined by calculating the corresponding coordinates of the centroids for AMS species concentrations and PMF factor loadings, which were not input to the FCM analysis. The calculation followed the mathematical definition of the centroid (Eq. S2). The resulting characterization of clusters is shown in Figure 8 and Table 2.

$$v_i = \frac{\sum_{k=1}^{N} (u_{ik})^m y_k}{\sum_{k=1}^{N} (u_{ik})^m} \quad \text{(Eq. S2)}$$

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List of Supplementary Figures

Figure S1. Location of the GoAmazon2014/5 sites relevant for this study. Image data: Google earth.

Figure S2. Scatter plot of the AMS signal fraction at m/z 44 (f_{44}) against that at m/z 43 (f_{43}). Green and yellow markers correspond to measurements made by two different AMS instruments at T0t in the wet season of 2008 during the AMAZE-08 campaign (Chen et al., 2009; Schneider et al., 2011). Red markers correspond to measurements made at the T0a (ATTO) by an ACSM during the wet season of 2015. A correction factor of 0.75 was applied to the f_{44} values of the ACSM based on calibrations with standards. Solid squares represent median values, and whiskers represent 10 and 90 percentiles. The plot shows a significant variability between the observations of 2008 and 2015 for the two background sites. An explanation of the differences is not attempted herein and warrants further investigation through longer-term continuous measurements.

Figure S3. Diagnostics of the PMF analysis. (a) Statistics of the sum of for solutions with different number of factors. Box plots show the interquartile ranges, including the medians as a horizontal line. Red markers show the means. Whiskers show the 5 and 95 percentiles. (b) Correlations expressed as between each pair of factors within each PMF solution, with number of factors varying from 2 to 7. The Pearson R value between factor loadings is shown on the coordinate and between factor profiles is shown on the abscissa. Numbers in red indicate the identity of the pair of factors.

Figure S4. Results of the PMF analysis for 5 factors (a and b) and 7 factors (c and d). Panels on the left (a and c) show the time series of factor loadings and panels on the right (b and

d) show the profiles of factors. The signals shown in panels b and d were summed to unit mass resolution.

Figure S5. Comparison of the ADOA factor profile from the present study to factors found in three other field studies. "COA" are factors representative of cooking activities, and the "91fac" from Robinson et al. (2011) was tied to biogenic sources.

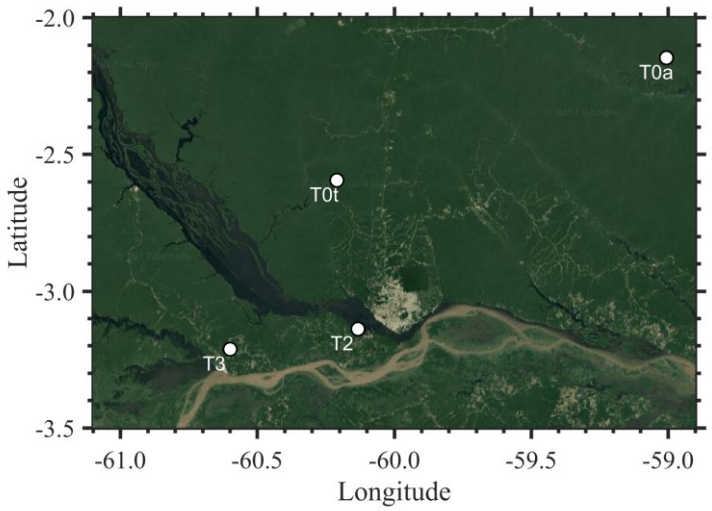
Figure S6. Summary of the analysis for estimating organic and inorganic nitrates from AMS bulk measurements. (a) Resulting time series of organic and inorganic nitrates are shown together with the original nitrate AMS times series. (b) Time series of the fraction of organic nitrate in total nitrate. (c~~b~~) Time series of the measured NO_2^+/NO^+ ratio is shown in red and values of NO_2^+/NO^+ from ammonium nitrate calibrations are shown in gray triangles. A linear fit to those calibration ratios is shown by the dashed dark blue line and constitutes the reference ratio for inorganic nitrate over time. The dashed light blue line is the reference ratio for organic nitrates over time. Calculations were done for data binned to one hour (as plotted), and the resulting time series were interpolated to the native time stamp for evaluation of correlations in the PMF analysis.

Figure S7. Value of the objective function of the FCM analysis (Eq. 1) in the last iteration plotted against the number of clusters.

Figure S8. Locations of cluster centroids from the FCM analysis as visualized by a 2-D projection on the plane defined by each pair of input variables. Results for two to five clusters are shown in panels a to d. Red circles are observational data and black squares are cluster centroids.

Figure S9. Map of Manaus city depicting population density as well as main avenues and representative locations of industry, restaurants, and other businesses. Population density data are from the 2010 census by the Brazilian Institute of Geography and Statistics (IBGE, 2010).

Figure S10. Measurements showing the geographical heterogeneity of emissions from Manaus. On the top row, concentrations of sulfate (red) and particle number (white) measured onboard the G-1 aircraft on (a) March 19 and (b) Mar 21. Image data: Google earth. On the bottom row, rose plots of mean (c) sulfate mass concentrations and (d) particle number concentrations observed at T2 during IOP1. The angles represent wind direction, the radial scale (0 to 5 m s^{-1}) represents wind speed, and the color scale represents the concentrations. The interactions of emissions from Manaus with the daily river breeze is complex, and the detailed interpretation of the data sets is not fully attempted herein. Of importance, the river breeze terminates well below 500 m based on the G-1 flights so that the complexities of the river breeze largely do not affect the measurements at T3 because most pollution is lofted above the river breeze before reaching T3 (Medeiros et al., in preparation). These surface-level plots, although complicated by the river breeze, demonstrate the heterogeneity of Manaus emissions.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-61.0
-60.5
-60.0
-59.5
-59.0
Longitude
T0a
T0t
T2
T3

Figure S1

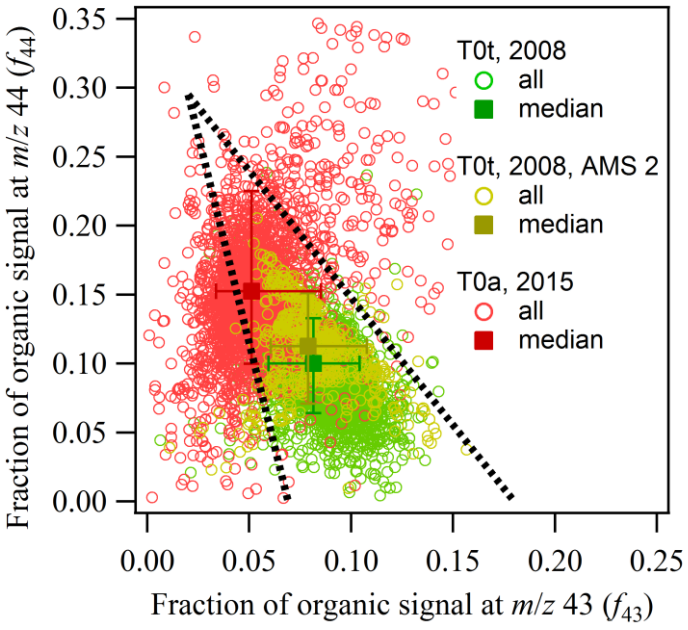
T0t, 2008
all
median
T0t, 2008, AMS 2
all
median
T0a, 2015
all
median
Fraction of organic signal at m/z 44 (f_{44})
Fraction of organic signal at m/z 43 (f_{43})
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35

Figure S2

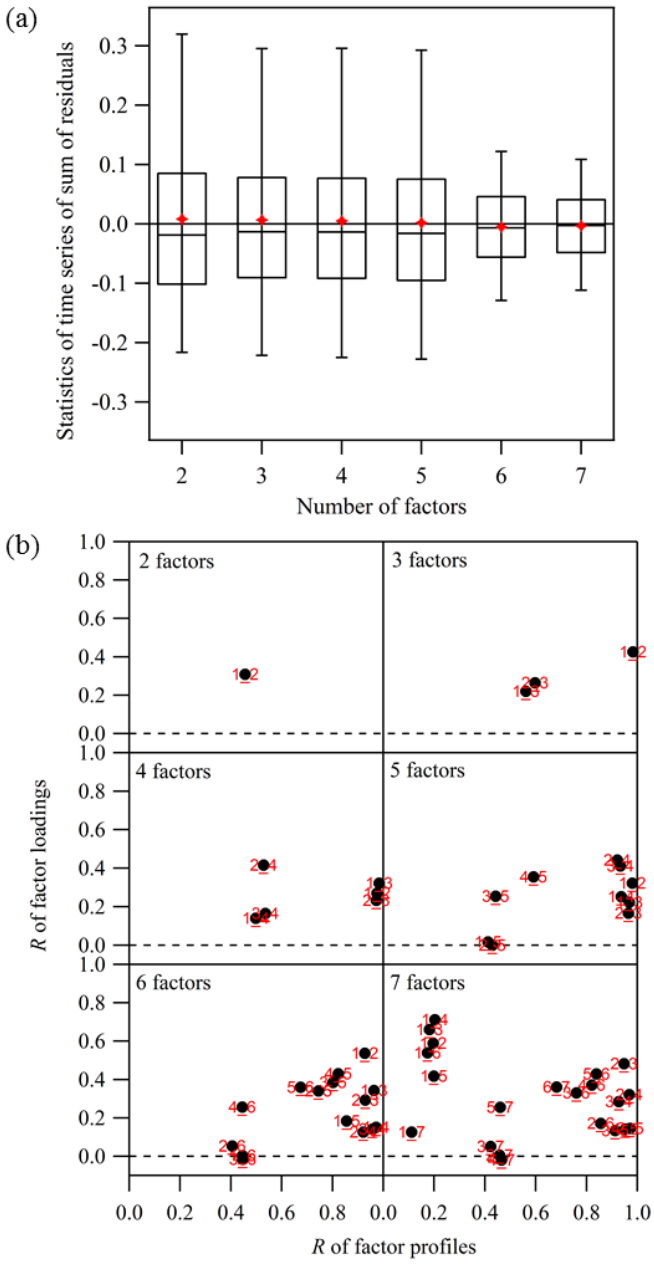
(a)
Statistics of time series of sum of residuals
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
2
3
4
5
6
7
Number of factors
(b)
2 factors
3 factors
4 factors
5 factors
6 factors
7 factors
R of factor loadings
R of factor profiles
0.0
0.2
0.4
0.6
0.8
1.0

Figure S3

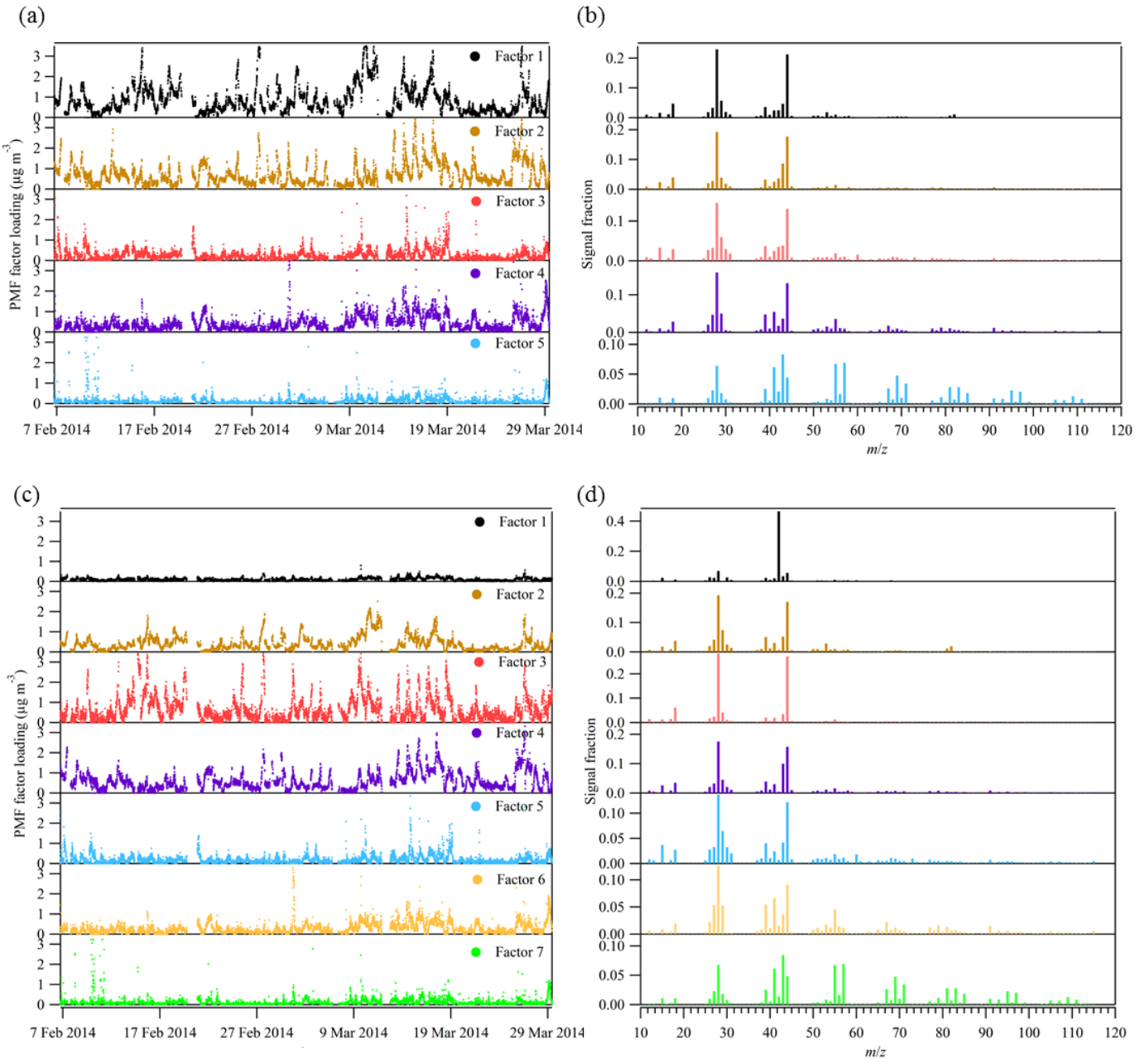
(a)
(b)
(c)
(d)
Factor 1
Factor 2
Factor 3
Factor 4
Factor 5
Factor 6
Factor 7
PMF factor loading (μg m-3)
Signal fraction
7 Feb 2014
17 Feb 2014
27 Feb 2014
9 Mar 2014
19 Mar 2014
29 Mar 2014
m/z

Figure S4

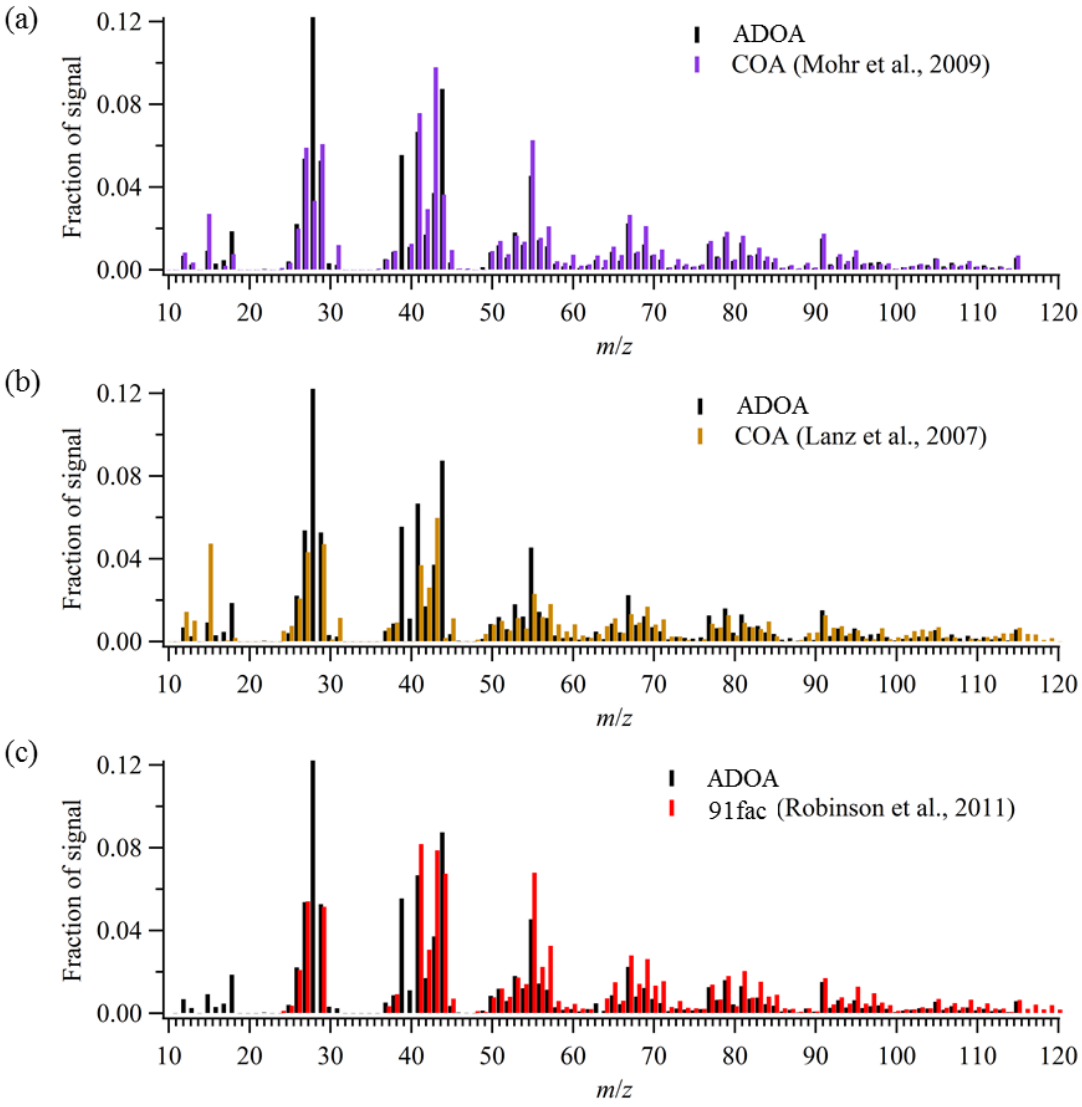
(a)
Fraction of signal
0.12
0.08
0.04
0.00
ADOA
COA (Mohr et al., 2009)
10 20 30 40 50 60 70 80 90 100 110 120
m/z
(b)
Fraction of signal
0.12
0.08
0.04
0.00
ADOA
COA (Lanz et al., 2007)
10 20 30 40 50 60 70 80 90 100 110 120
m/z
(c)
Fraction of signal
0.12
0.08
0.04
0.00
ADOA
91fac (Robinson et al., 2011)
10 20 30 40 50 60 70 80 90 100 110 120
m/z

Figure S5

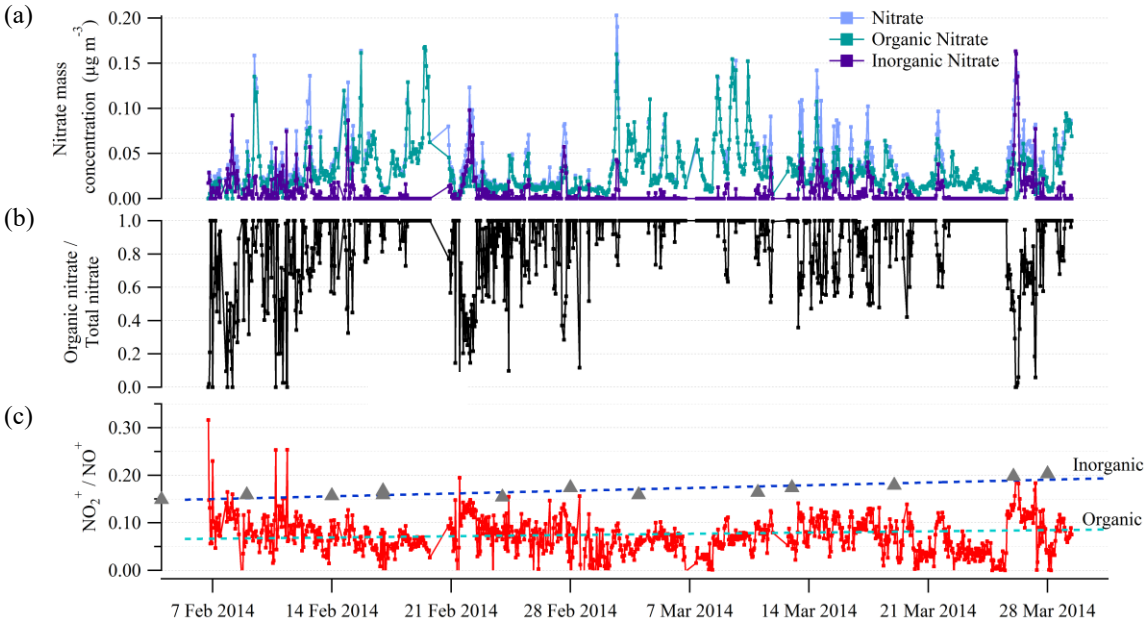
(a)
Nitrate mass concentration (μg m-3)
0.20
0.15
0.10
0.05
0.00
Nitrate
Organic Nitrate
Inorganic Nitrate
(b)
Organic nitrate / Total nitrate
1.0
0.8
0.6
0.4
0.2
0.0
(c)
NO2+ / NO+
0.30
0.20
0.10
0.00
Inorganic
Organic
7 Feb 2014
14 Feb 2014
21 Feb 2014
28 Feb 2014
7 Mar 2014
14 Mar 2014
21 Mar 2014
28 Mar 2014

Figure S6

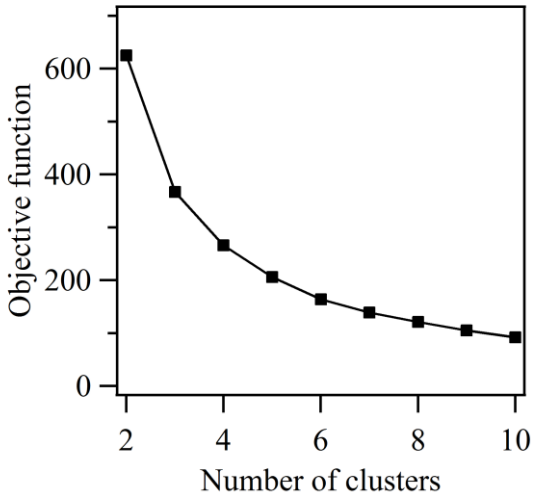

Figure S7

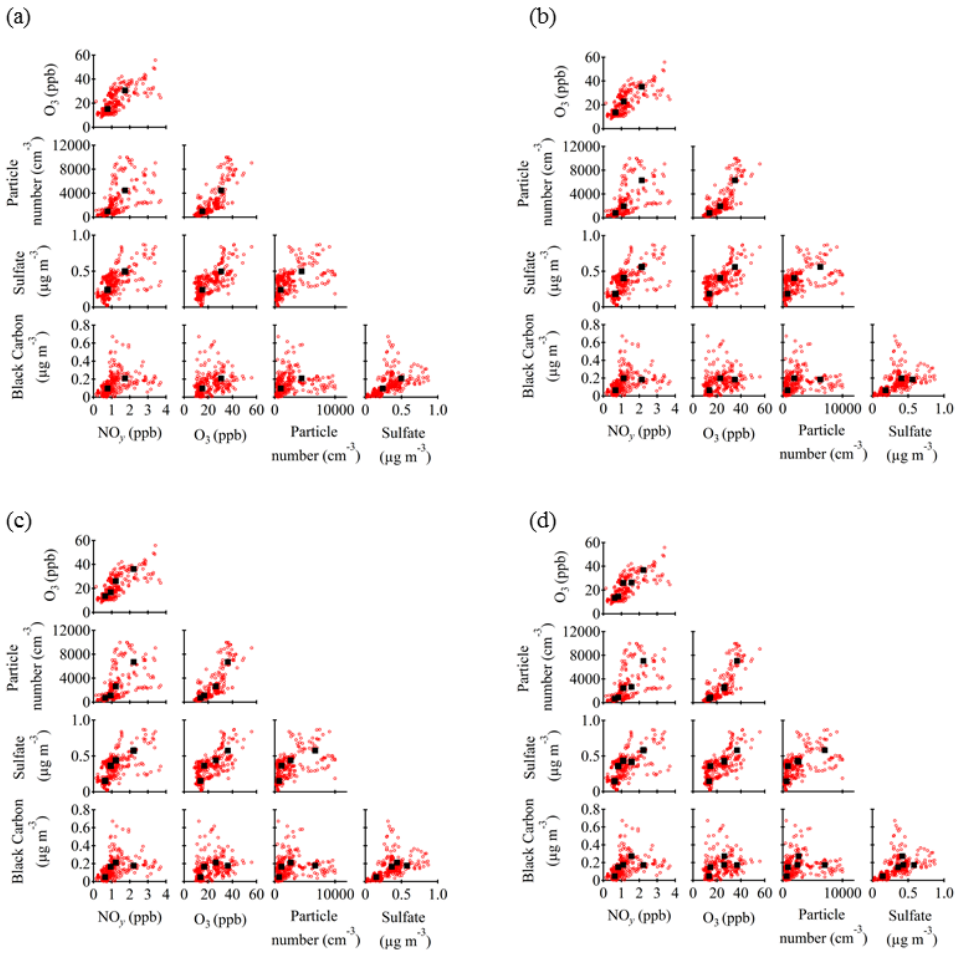
(a)
(b)
(c)
(d)
O3 (ppb)
Particle number (cm-3)
Sulfate (μg m-3)
Black Carbon (μg m-3)
NOy (ppb)
O3 (ppb)
Particle number (cm-3)
Sulfate (μg m-3)

Figure S8

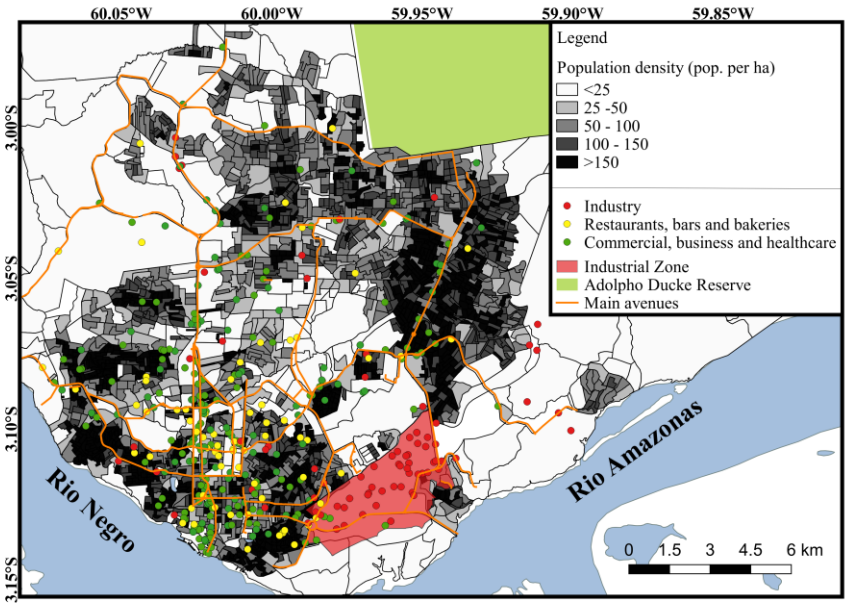
60.05°W
60.00°W
59.95°W
59.90°W
59.85°W
3.00°S
3.05°S
3.10°S
3.15°S
Legend
Population density (pop. per ha)
<25
25 -50
50 - 100
100 - 150
>150
Industry
Restaurants, bars and bakeries
Commercial, business and healthcare
Industrial Zone
Adolpho Ducke Reserve
Main avenues
Rio Negro
Rio Amazonas
0 1.5 3 4.5 6 km

Figure S9

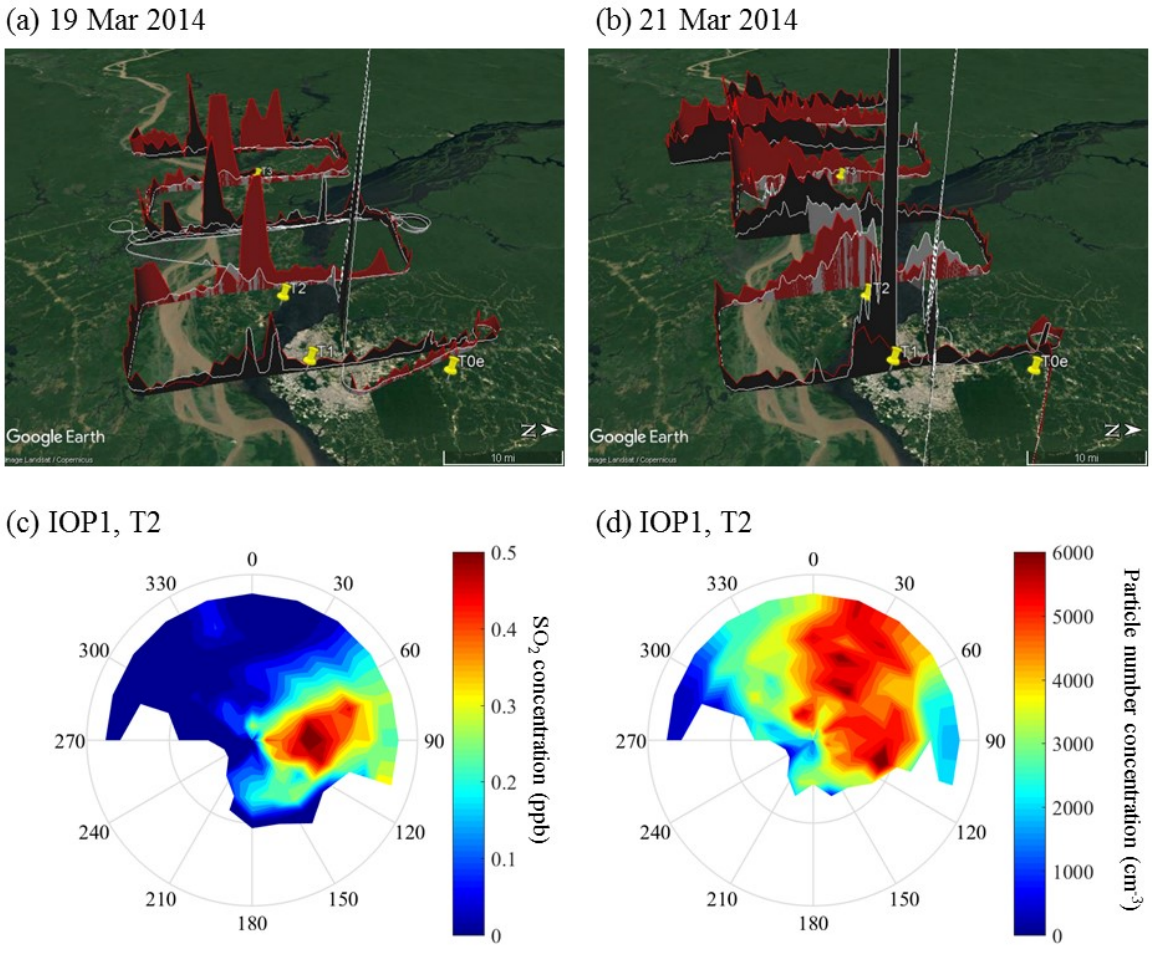
(a) 19 Mar 2014
(b) 21 Mar 2014
T3
T2
T1
T0e
Google Earth
10 mi
(c) IOP1, T2
(d) IOP1, T2
0
30
60
90
120
150
180
210
240
270
300
330
0.5
0.4
0.3
0.2
0.1
0
SO2 concentration (ppb)
6000
5000
4000
3000
2000
1000
0
Particle number concentration (cm-3)

Figure S10