We thank the reviewer for the constructive and thoughtful comments. Please find below detailed responses to each comment or question, including notations of improvements to the manuscript. Reviewer comments are in blue fonts. Changes to the text are highlighted in yellow.

General comments:

Study by Thalman et al. presents results of κ_{CCN} and mixing state derived from size resolved CCN observations collected during the GoAmazon2014/5 campaign. From κ_{CCN} and additional aerosol chemical composition measurements, the authors then estimate the hygroscopicity of the organic fraction κ_{org}. The results presented in the study, together with those presented by Pöhlker et al (2016) in another experimental site, represent the first long-term measurement of hygroscopic behaviour of aerosols in the Amazon. Overall, it is a well written manuscript on an important subject. Therefore, I recommend it for publication in ACP after minor corrections.

Specific comments:

Since chemical composition of aerosols in the study was largely dominated by the organic fraction, a discussion on the uncertainties related to limited solubility or surface active species could be relevant, even if no quantitative assessment of these uncertainties is provided.

Yes, limited solubility and reduced surface tension could impact the CCN activity and hygroscopicity of organics. As the κ value was derived from dry particle diameter and critical supersaturation assuming the surface tension of pure water, κ value reported in this manuscript represents the "apparent hygroscopicity", which includes the potential impact due to limited solubility and reduction of surface tension (Sullivan et al., 2009). We have clarified this by including the following sentence in the text:

As hygroscopicities reported in this study were derived from particle dry diameter and critical supersaturation, they represent "apparent hygroscopicity", which includes the potential impact due to the limited solubility of organics and the reduction of surface tension by surface active species (Sullivan et al., 2009).

P 21 L 431-440 Given that the importance of hygroscopicity to the aerosol CCN behavior is enhanced for κ values below 0.2, the choice of an adequate κ value to represent the Amazonian aerosol CCN behavior is important, for instance, to modeling studies. In this sense, it could be interesting to compare the presented results with κ_{HTDMA} results from campaigns previous to 2008 as well, since κ have already been calculated from the original data of some of these campaigns in other works (see, for example, Gunthe et al. (2009) and the Supplement of Sánchez Gácita et al. (2017)). In the authors opinion, differences between presented results and κ_{HTDMA} from earlier campaigns are solely due to the use of H-TDMA or CCN technique, or other factors could be important as well?

We thank the reviewer for this suggestion. We added particle hygroscopicity (κ_{HTDMA}) derived from HTDMA measurements during campaigns before 2008 in Figure 2 for comparison, including κ_{HTDMA} measured in July 2001, during a “recent biomass burning period” of the CLAIRE-2001 study (Rissler et al., 2004), and that measured from 11 September to 8 October 2002, during the dry period of the LBA-SMOCC (Rissler et al., 2006). During the above two periods, aerosols were strongly influenced by fresh local biomass burning emissions. The measurements during CLAIRE-2001 took place at Balbina, about 125 km northeast of Manaus, and the κ_{HTDMA} during the “recent biomass burning period” agrees well with κ_{CCN} derived at the T3 site for air masses with strong local biomass burning influences. In contrast, κ_{HTDMA} observed during the dry period of LBA-SMOCC is substantially lower than κ_{CCN} at T3 for local biomass burning air mass at all sizes. As LBA-SMOCC took place in the state of Rondônia in southwestern Amazonia with extensive biomass burning activities during the dry season, the difference in κ may be due to the differences in fire condition and the type of vegetation burned. Previous studies show particles sometime exhibit larger κ values for droplet activation (derived from CCN measurements under supersaturated conditions) than for particle growth (derived from particle GF under sub-saturated conditions), this could also contribute to the difference in κ values. We have updated Figure 2, and included following discussion in the text:

For the air masses with strong influence from local biomass burning, the value of κ_{CCN} and its size dependence are consistent with the κ value derived from particle growth factor measurements in July 2001, during a “recent biomass burning period” of the CLAIRE-2001 study (Rissler et al., 2004), which took place at Balbina, about 125 km northeast of Manaus. In contrast, κ values derived from particle growth factor measurements from 11 September to 8 October 2002, during the dry period of the LBA-SMOCC (Rissler et al., 2006) are substantially lower than κ_{CCN} observed at the T3 site for local biomass burning air masses at all sizes. As LBA-SMOCC took place in the state of Rondônia in southwestern Amazonia with extensive biomass burning activities during the dry season, the difference in κ could be due to the differences in fire condition and the type of vegetation burned. Previous studies show particles sometime exhibit larger κ values for droplet activation (derived from CCN measurements under supersaturated conditions) than for particle growth (derived from particle growth factor under sub-saturated conditions), this could also contribute to the differences in κ values.

Supp. P10 L172 Please provide a reference for equation S1 of supplement

The reference to the supplementary material in Mei et al. (2013) has been added, the formula as given in equation S1 converts the formula in the previous paper to the hygroscopicity dispersion instead of the critical supersaturation dispersion and hence is somewhat different.

Supp. P10 L174-175 The use of equation S2 of supplement was suggested by Petters and Kreidenweis (2007) for κ > 0:2. Considering that for most conditions in this study κ_{CCN} was below this threshold, perhaps an iterative approach on the original κ-Köhler equation (see, for example, Carrico 2008) would have been more adequate. A sensitivity test on a small fraction of the data would be desirable to show that uncertainties derived from the use of this simplified approach are indeed low or negligible.

We thank the reviewer for this suggestion. We carried out the sensitivity study using an iterative approach based on the original κ-Köhler equation as suggested by the reviewer. The relative and absolute uncertainties in κ_{CCN} derived using equation S2 are shown in Fig 1A and 1B below for each particle diameter. The lower κ_{CCN} limit of each curve represents 1st percentile of κ_{CCN} values derived at the corresponding particle diameter. The results show that the relatively uncertainty is less than 7% for 99% of the data at all particle diameters. Furthermore, the main conclusions of the manuscript are based on κ_{CCN} derived at 112, 142, and 171 nm (e.g., Figures 3-12), and the relative uncertainty is less than 4.5% for 99% of data at the three sizes. Therefore, the uncertainties derived from the use of the simplified approach are low and negligible.

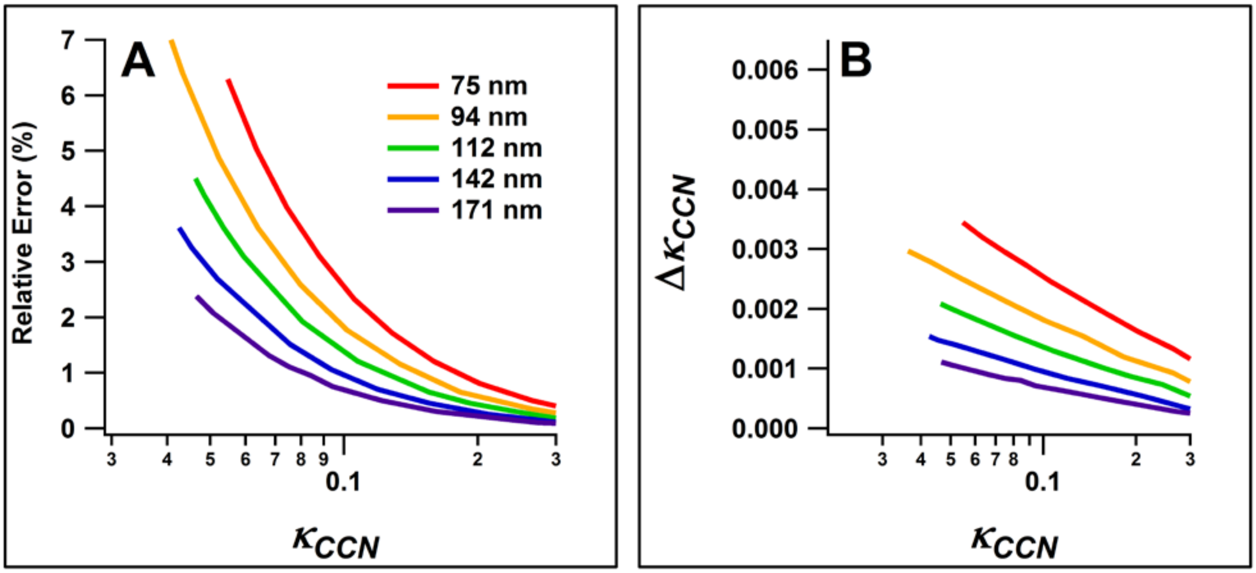

Figure 1: (a) Relative and (b) absolute uncertainties of κ_{CCN} derived using equation S2 at each of the particle diameters. The lower κ_{CCN} limit of the curves represents the 1st percentile of the κ_{CCN} value at corresponding particle diameter.

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We thank the reviewer for the constructive and thoughtful comments. Please find below detailed responses to each comment or question, including notations of improvements to the manuscript. Reviewer comments are in blue fonts. Changes to the text are highlighted in yellow.

Overall: The manuscript in overall is very well written, and in agreement with scope of ACP. The scientific issues were well addressed, and are relevant. Several important measurements were performed, which were well treated and discussed, being an important scientific contribution. Therefore, I recommend publish the manuscript in ACP. However, I have few specific questions and technical corrections.

Specific comments and questions:

Line 105: Include references to support the affirmation “The hygroscopicities of typical inorganic in ambient particles are relatively well known”

Reference to Petters and Kreidenweis (2007) is now included.

Line 106: Please comment this sentence and clarify: “atmospheric aerosols consist of a large number of organic compounds, which often dominate the total fine aerosol mass”. Which type of region, urban, rural, forest, etc?

The organics often dominate the total fine aerosol mass, especially in forested areas such as in Hyytiälä, Finland and the Amazon basin (Jimenez et al., 2009; de Sá et al. 2016). Organics also dominate total fine aerosol mass in some of the urban areas, such as the Mexico City, Edinburgh, and Zurich during summer time (Jimenez et al., 2009). We have updated the sentence and included additional references. The sentence is changed to:

…atmospheric aerosols consist of a large number of organic compounds, which often dominate the total fine aerosol mass, especially in forested areas (e.g., de Sá et al., 2016; Jimenez et al., 2009; Zhang et al., 2007).

Line 303-305: Why the authors use the same size distribution shape? What is the potential implications?

Given the low volume fraction of nitrate (see Figs 1 and 3-7), vast majority of the ammonium was associated with sulfate. Therefore, the assumption that ammonium had the same size distribution shape as sulfate should be appropriate.

Line 352: The authors said that it was correlated with concentrations of levoglucosan, vanillin and anthropogenic emission of aromatics. However, not mentioned in the section 2.4. this measurements. Please included.

These measurements and correlations are detailed in a manuscript that is in preparation (de Sá et al., 2017). The reference is included.

Line 393: Define CN

The definition (condensation nuclei) has been added to the text.

Line 428: The authors could explain or comment why no clear seasonal trend was observed for sulfate volume fraction?

This is a good question. The lack of a clear seasonal trend of sulfate volume fraction is consistent with observations at the ATTO site (Andreae et al., 2015). At this point, it is unclear what causes the relatively constant sulfate volume fraction despite the large variation in aerosol volume concentration. During dry season, there is a strong increase in aerosol volume concentration, and some of the sulfate is obviously from biomass burning. However the ratio of sulfate to organics is substantially higher than that of biomass burning aerosols, and additional sulfate from fossil fuel burning is likely needed to explain the ratio. This additional sulfate may come from a mix of emissions from the populated regions of northeastern Brazil, emissions along the river, and long range transport from Africa. A detailed analysis of the seasonal cycle of sulfate sources is outside of the scope of this manuscript. We have included the following sentence in the text:

The lack of clear seasonal trends of sulfate and organic fractions are consistent with observations at the T0a site (Andreae et al., 2015).

Lines: 431-432 and 442-443 its look contradictory as well in the conclusion, in lines 699-701 and 704-705. The authors said in lines 699-701: “The KCCN increased with particle size during all seasons, consistent with decreasing organic volume fraction: : :..”.However, when Korg increase the KCCN also increase according to text. Please clarify.

The statements are not contradictory. They address the impact on κ_{CCN} by organic volume fraction and κ_{org} value, respectively. Because of the relatively low κ_{org} value compared to those of inorganic species (e.g., sulfate), either a decreasing organic volume fraction or an increasing κ_{org} could lead to an increasing κ_{CCN}.

Technical corrections:

Line 105: “: : :typical inorganic in ambient particles: : :” better “: : :.typical inorganic particles in ambient: : :”

“typical inorganic in ambient particles” refers to inorganic species in ambient particles, which are often mixtures of both inorganic and organic species. Instead, “typical inorganic particles in ambient” implies ambient particles consisting of inorganic species only. Therefore, the first description is more accurate. We have changed “inorganics” to “inorganic species” for clarification.

Line 221: use PM2.5

The text already reads PM2.5 as suggested.

Line 228: missing comma or and

The platform described does have a lot of acronyms, but MAOS is a subset of AMF-1, as such, no and or comma is necessary.

Line 656: Use GoAmazon2014/5 as in others places (lines 687, 292, 249, etc)

Done.

Table 1: Put the meaning of K (Bkgd) in table footnotes

Done.

Figs. 9 and 10: increase the size of the word Korg as in fig. 11

Figures 9 and 10 have been updated.

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CCN activity and organic hygroscopicity of aerosols downwind of an urban region in central Amazonia: Seasonal and diel variations and impact of anthropogenic emissions

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Abstract

During the *Observations and Modeling of the Green Ocean Amazon* (GoAmazon2014/5) campaign, size-resolved cloud condensation nuclei (CCN) spectra were characterized at a research site (T3) 60 km downwind of the city of Manaus, Brazil, in central Amazonia for one year (12 March 2014 to 3 March 2015). Particle hygroscopicity (κ_{CCN}) and mixing state were derived from the size-resolved CCN spectra, and the hygroscopicity of the organic component of the aerosol (κ_{org}) was then calculated from κ_{CCN} and concurrent chemical composition measurements. The annual average κ_{CCN} increased from 0.13 at 75 nm to 0.17 at 171 nm, and the increase was largely due to an increase in sulfate volume fraction. During both wet and dry seasons, κ_{CCN}, κ_{org}, and particle composition under background conditions exhibited essentially no diel variations. The constant κ_{org} of ~ 0.15 is consistent with the largely uniform and high O:C value (~0.8), indicating that the aerosols under background conditions are dominated by the aged regional aerosol particles consisting of highly oxygenated organic compounds. For air masses strongly influenced by urban pollution and/or local biomass burning, lower values of κ_{org} and organic O:C atomic ratio were observed during night, due to accumulation of freshly emitted particles, dominated by primary organic aerosol (POA) with low hygroscopicity, within a shallow nocturnal boundary layer. The O:C, κ_{org}, and κ_{CCN} increased from the early morning hours and peaked around noon, driven by the formation and aging of secondary organic aerosol (SOA) and dilution of POA emissions into a deeper boundary layer, while the development of the boundary layer, which leads to mixing with aged particles from the residual layer aloft, likely also contributed to the increases. The hygroscopicities associated with individual organic factors, derived from PMF analysis of AMS spectra, were estimated through multi-variable linear regression. For the SOA factors, the variation of the κ value with O:C agrees well with the linear relationship reported

from earlier laboratory studies of SOA hygroscopicity. On the other hand, the variation in O:C of ambient aerosol organics is largely driven by the variation in the volume fractions of POA and SOA factors, which have very different O:C values. As POA factors have hygroscopicity values well below the linear relationship between SOA hygroscopicity and O:C, mixtures with different POA and SOA fractions exhibit a steeper slope for the increase of κ_{org} with O:C, as observed during this and earlier field studies. This finding helps better understand and reconcile the differences in the relationships between κ_{org} and O:C observed in laboratory and field studies, therefore providing a basis for improved parameterization in global models, especially in a tropical context.

1 Introduction

Atmospheric aerosols have a major impact on the radiative balance of the Earth's climate system by changing the microphysical structure, lifetime, and coverage of clouds. For the same liquid water content, high aerosol concentration leads to more, smaller cloud droplets, and therefore higher cloud albedo (Twomey, 1977). The smaller droplet size also delays or inhibits warm precipitation, leading to increases in both cloud lifetime and coverage (Albrecht, 1989), and ultimately invigoration of convective clouds (Rosenfeld et al., 2008). Currently, the effects of aerosol on clouds remain one of the largest uncertainties in simulated climate change during industrial era, and a large portion of this uncertainty is due to the natural aerosol properties and processes represented in models (Carslaw et al., 2013; Ghan et al., 2013). The Amazon represents more than half of the planet's rainforest and is a rapidly changing region where deforestation, human activity and natural resource needs are all at play in changing the ecosystem (Andreae et al., 2015; Batistella et al., 2013; Davidson et al., 2012). The Amazon basin also represents at times one of the cleanest continental regions on the planet where it is still possible to find extended periods of little or no impact of anthropogenic activity, although the long-distance transport of pollution is occasionally observed (Andreae et al., 2015; Hamilton et al., 2014; Martin et al., 2010b; Wang et al., 2016a; Wang et al., 2016b; Williams et al., 2002). This makes the Amazon Basin an ideal location to characterize aerosol under near natural conditions and assess the impact due to urban emissions and biomass burning (Kuhn et al., 2010). The biogenic activity of this region makes it a major source of organic carbon released into the atmosphere via isoprene and monoterpenes (Guenther et al., 2006; Guenther et al., 2012; Kesselmeier et al., 2002; Kuhn et al., 2007) which are mediated by biotic stress through heat, sunlight and changes in CO_2 (Heald et al., 2009).

To understand the impact of aerosol on clouds and climate requires knowledge of the concentration of cloud condensation nuclei, which are particles that are able to form cloud droplets under relevant atmospheric conditions. The minimum supersaturation required to activate a particle into a cloud droplet can be predicted using κ -Köhler theory based on particle size and the single hygroscopicity parameter κ, which combines a number of thermodynamic properties required for the description of water activity of the growing droplets (Petters and Kreidenweis, 2007). The value of κ is determined by the physicochemical properties of the solutes, including their molar volume, activity coefficient, and the effect on surface tension. For multi-component particles, κ is the volume average of participating species. Hygroscopicity also describes particle growth under sub-saturated conditions and can be derived from the particle growth factor (GF). However, particles sometime exhibit larger κ values for droplet activation (derived from CCN measurements under supersaturated conditions) than for particle growth (derived from particle GF under sub-saturated conditions) (e.g., Duplissy et al., 2008; Good et al., 2010; Mikhailov et al., 2013; Pajunoja et al., 2015; Wex et al., 2009). In this paper, "hygroscopicity" represents κ associated with droplet activation derived from CCN measurements unless noted otherwise.

The hygroscopicities of typical inorganic~~s~~ species in ambient particles are relatively well known (Petters and Kreidenweis, 2007) . However, atmospheric aerosols consist of a large number of organic compounds, which often dominate the total fine aerosol mass, especially in forested areas (e.g., de Sá et al., 2016; Jimenez et al., 2009; Zhang et al., 2007). The hygroscopicity of aerosol organics (κ_{org}) have been examined in both laboratory (e.g., Asa-Awuku et al., 2009; Duplissy et al., 2011; King et al., 2009; Lambe et al., 2011; Massoli et al., 2010; Prenni et al., 2007; Raymond and Pandis, 2003) and field studies (e.g., Cerully et al., 2015; Chang et al., 2010; Dusek et al., 2010; Gunthe et al., 2009; Jimenez et al., 2009; Lathem et al., 2013a; Mei et al., 2013a; Mei et al., 2013b; Moore et al., 2011; Moore et al., 2012; Pöhlker et al., 2016; Rose et al., 2010; Shantz et al., 2008; Wang et al., 2008). Overall, these studies show that aerosol organics exhibit a wide range of κ values from 0 to ~0.3, and κ_{org} often increases substantially during aerosol aging in the atmosphere (e.g., Duplissy et al., 2011; Jimenez et al., 2009; Lambe et al., 2011; Massoli et al., 2010; Mei et al., 2013a).

A number of recent studies examined the sensitivity of predicted CCN concentration and cloud droplet number concentration to aerosol properties (e.g., Ervens et al., 2010; Kammermann et al., 2010; McFiggans et al., 2006; Mei et al., 2013a; Reutter et al., 2009; Rissman et al., 2004; Roberts et al., 2002; Wang, 2007; Wang et al., 2008). These studies show that the predicted CCN concentration is often sensitive to κ_{org}, especially for aerosol under background conditions where organics tend to dominate submicron aerosol mass (Liu and Wang, 2010; Mei et al., 2013a). Using a constant κ_{org} may lead to large biases in predicted CCN concentrations and aerosol indirect forcing (Liu and Wang, 2010). Therefore, it is imperative to understand organic hygroscopicity under background conditions, such as in the Amazon forest, as well as the variation of organic hygroscopicity due to anthropogenic emissions.

There have been several studies of aerosol hygroscopicity in the Amazon Basin over the past 20 years (Gunthe et al., 2009; Mikhailov et al., 2013; Pöhlker et al., 2016; Rissler et al., 2006b; Roberts et al., 2001; Vestin et al., 2007; Whitehead et al., 2016; Zhou et al., 2002) . Gunthe et al. (2009) performed size resolved CCN measurements during the wet season in February and March 2008 as part of the AMAZE-08 campaign (Martin et al., 2010a). That study reported no diel cycle in the CCN concentration during periods with little or no influence of pollution. Pöhlker et al. (2016) measured size-resolved CCN spectra at a remote background site (Amazon Tall Tower Observatory ATTO) over a one-year period from March 2014 to February 2015 and observed no diel cycle and only weak seasonal trends in derived particle hygroscopicity, while CCN concentrations had a pronounced seasonal cycle as the background aerosol concentration was strongly influenced by regional biomass burning during the dry season. During the SMOCC-2002 campaign (Large scale Biosphere atmosphere experiment in Amazonia – SMOke, aerosols, Clouds, rainfall, and Climate) particle hygroscopicity was derived from HTDMA measurements in the state of Rondônia in the southwest of the Amazon region during the dry season from September to November of 2002 (Rissler et al., 2006b; Vestin et al., 2007). The study concluded that the diel variation in the aerosol hygroscopicity could be linked to the structure and dynamics of the boundary layer. Local sources dominated night-time aerosol properties with downward mixing from the residual layer aloft as the day progressed. All of these studies found that particle hygroscopicity increased with particle size (from the Aitken to accumulation modes), consistent with higher sulfate content at larger sizes (Gunthe et al., 2009). The same boundary layer evolution has been found to influence particle number and CCN evolution in a number of other related studies (Fisch et al., 2004; Martin et al., 2010a; Rissler et al., 2006b; Vestin et al., 2007; Whitehead et al., 2010; Zhou et al., 2002).

In this study we present measurements of size resolved CCN spectra at five particle diameters ranging from 75 to 171 nm downwind of Manaus, Brazil, in central Amazonia for a period of one year from March 12, 2014 to March 3, 2015. Particle hygroscopicity, mixing state, and organic hygroscopicity are derived from the size-resolved CCN activated fraction and concurrent aerosol composition measurements. The diel variations of these properties are examined for different seasons (i.e., wet season, dry season, and transition seasons) and for different types of representative air masses, including background conditions, as well as influences of urban pollution plumes and/or local biomass burning. During the wet season, the background air mass represents near natural conditions, with occasional impact from anthropogenic emissions, while in the dry season, the background is dominated by regional biomass burning aerosol particles. The relationship between organic hygroscopicity and particle oxidation level (i.e., O:C atomic ratio) is examined for both dry and wet seasons. Hygroscopicities associated with organic factors from Aerosol Mass Spectrometry (AMS) Positive Matrix Factorization (PMF) analysis are derived, and their relationship with the O:C ratio is compared with those from previous laboratory studies.

2 Experimental Setup

2.1 Measurement Sites

Observations and Modeling of the Green Ocean Amazon (GoAmazon2014/5), sponsored by the US Department of Energy (DOE) and several Brazilian and German agencies, took place at multiple surface sites surrounding Manaus, Brazil, from January 2014 through December 2015 (Martin et al., 2016b). This work focuses on the measurements carried out at a downwind site (T3, 3°12'47.82"S, 60°35'55.32"W, 60 km west of Manaus) from March 2014 to March 2015. Depending on the wind direction, the T3 site experienced conditions ranging from nearly natural to heavily polluted. More detailed characterizations of aerosol and gas phase chemical composition were carried out at the T3 site during Intensive Operating Periods (IOPs) from February 1, 2014 to March 31, 2014 and from August 15, 2014 to October 15, 2014. In addition, data from two sites normally upwind of Manaus are also used in this study. These background sites include the T0a site, (ATTO, 2° 8'47.88"S, 59° 0'18.00"W) (Andreae et al., 2015) and the T0t site, (2.6091°S, 60.2093°W) (Martin et al., 2010a).

2.2 Activated Fraction of size-selected Particles

The CCN activation fraction of size-selected particles was measured using a Differential Mobility Analyzer (DMA) coupled to a condensation particle counter (CPC, TSI Inc., 3010) and a cloud condensation nuclei counter (CCNC, Droplet Measurement Technologies, Boulder, CO) (Frank et al., 2006; Mei et al., 2013a; Moore et al., 2010; Petters et al., 2007). Aerosol particles were sampled with a total flow rate (Q_a) of 1.53 L min^{-1} from a height of 5 m above ground level and were dried to RH below 20% by a Nafion dryer immediately upon entering the instrument container. The dried aerosol particles then reached steady state charge distribution inside a Kr-85 aerosol charger (TSI, model 3077A), prior to being introduced into the DMA operated with a sheath flow rate (Q_{sh}) of 15.3 L min^{-1} to maintain a 10:1 sheath to aerosol flow ratio (Q_{sh} /Q_a). The aerosol particles were size-selected by the DMA and the size-selected particles were simultaneously characterized by a CPC (Q_{CPC} = 0.53 L min^{-1}) and a CCNC (see Fig. S1 in the Supplementary Information for further details). This system had been operated in previous field campaigns by scanning the particle size while CCNC supersaturation was held constant (Mei et al., 2013a; Mei et al., 2013b). During GoAmazon2014/5 the particle size classified by the DMA was stepped through seven particle diameters (51, 75, 94, 112, 142, 171, and 222 nm), while the CCNC supersaturation was also changed at each diameter by stepping the flow rates (Q_{CCN} ranging from 0.2 to 1.0 L min^{-1}) and temperature gradient (ΔT = 4.5, 5.5, 6.5, 8.0 and 10.0°C). At a given supersaturation, data were acquired for a minimum of 30 s and until 1500 particles were counted by the CPC or up to a maximum time of 120 s. Depending on the aerosol number size distribution, the measurement cycled through the seven particle sizes in 1 – 2 h (see Fig. S1 and S2 for further details of the measurement setup and sampling protocol). The sampling sequence was designed so that the change of CCNC supersaturation was mostly accomplished by stepping flow rates, as the CCNC reaches steady state faster following flow changes than temperature changes. Change of the temperature gradient was kept at a minimum frequency, but was necessary given the wide range of supersaturation explored. Given the low particle number concentration (e.g., ~200 cm^{-3} under background conditions during the wet season), these approaches were important to achieve adequate counting statistics with good time resolution to capture changes of air mass within 10 – 20 minutes (Liu et al., 2016). The supersaturation of the CCNC was calibrated using ammonium sulfate aerosol, as described previously in the literature (e.g., Mei et al., 2013a), at each operational set point (Q_{CCN} and ΔT), ranging from 0.075 – 1.1 %. Fluctuation of the temperature inside the instrument container, ranging from 20 to 30°C over the course of a day, led to substantial variation in the absolute temperature inside the CCNC growth chamber. Calibrations were therefore repeated under a range of container and associated growth chamber temperatures. The dependence of the supersaturation on the temperature at the top of CCNC column (instrument temperature T_1) was derived for each Q_{CCN} and ΔT pair and used to retrieve the supersaturation over the range of the instrument operating conditions (see Fig. S3 and further description in the Supplementary Information).

2.3 Aerosol Chemical Composition

Non-refractory sub-micron aerosol composition (organics, sulfate, nitrate, ammonium, and chloride) was measured by a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc. (DeCarlo et al., 2006) during the two IOPs, and by an Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research, Inc., Ng et al., 2011) from July 2014 to March 2015. The AMS sampled from an inlet equipped with a PM2.5 cyclone located at 5 m above ground level. The ambient sample was first dried outside the container by a poly-tube Nafion dryer (Perma Pure, model PD-100T). Once inside the container the sample was further dried by a mono-tube Nafion dryer (Perma Pure, model MD-110) to achieve RH < 40% and was split between the AMS and a Scanning Mobility Particle Sizer (SMPS, TSI, model 3081). Ambient measurements were obtained every 4 of 8 minutes. Further details of the AMS set up and operation are described in de Sá et al. (2016).

The ACSM was a part of the Aerosol Radiation Measurement (ARM) Mobile Facility-1 (AMF-1) Mobile Aerosol Observation System (MAOS). Aerosol was sampled through an inlet located 10 m above the ground. The aerosol sample was first dried through five large (40 x 1.75 cm I.D.) Nafion dryers before being distributed among various instruments including the ACSM. The ACSM sampling alternated between with and without an in-line filter using a 3-way valve, such that aerosol-free background could be subtracted from the ambient measurement. Twenty-eight ambient and background scans of the quadrupole mass spectrometer (unit mass resolution) were averaged to give one measurement every 30 min. The mass concentrations of organic species, sulfate, nitrate, ammonium, and chloride were derived from measurements using approaches described in Ng et al. (2011).

Refractory black carbon (rBC) was measured using both a Single Particle Soot Photometer (SP2, Droplet Measurement Technologies, Boulder, CO) and an aethalometer (Magee Scientific) co-located with the AMS and ACSM. The SP2 measures rBC using laser-induced incandescence, whereas the aethalometer measures equivalent black carbon (BC_e) (Andreae and Gelencsér, 2006) using light absorption from particles collected onto a filter. While these are fundamentally different aerosol properties, both species (rBC and BC_e) were treated as equivalent in this study, and BC_e concentration was adjusted to match that of rBC using the approach detailed in Section 2.2 of the Supplementary Information.

2.4 Additional Relevant Measurements

Additional measurements of aerosol microphysics, trace gas concentrations, and atmospheric conditions used in this study are briefly described here. These measurements were part of the deployment of the ARM AMF-1 facility during GoAmazon 2014/5 (Martin et al., 2016b). Relevant aerosol measurements include dry particle number-size distributions from 10 to 480 nm by a SMPS (TSI Inc. Model 3081) and the number concentration of particles with diameters greater than 10 nm by a CPC (TSI Inc. Model 3772). Mixing ratios of CO and O_3 were characterized by an Off-Axis Integrated Cavity Output Spectroscopy CO, N_2O and H_2O analyzer (model number 908-0014, Los Gatos) and UV Photometry O_3 analyzer (model 49i, Thermo Scientific Inc.), respectively. Oxides of nitrogen (NO, NO_x, NO_2, NO_y) were measured using a chemiluminescence technique (details given in Section S2.1 of the Supplementary Information). Meteorological data included relative humidity (RH), ambient temperature, wind speed and direction, and rain accumulation. The vertical profile of atmospheric backscatter (clouds and aerosol) and boundary layer heights were estimated from ceilometer (model CL31,Vaisala) measurements.

3 Methods

3.1 Derivation of Particle Hygroscopicity and Mixing State

The particle hygroscopicity parameter, κ (Petters and Kreidenweis, 2007), was derived from the activation spectrum (i.e., activated fraction as a function of supersaturation S) at the individual particle sizes using approaches detailed in the literature (Bougiatioti et al., 2011; Cerully et al., 2011; Lance et al., 2013; Mei et al., 2013a; Rose et al., 2008b). The activation spectrum of size-selected particles was first corrected for the influence of multiply charged particles, which is estimated using the size distribution measured by the SMPS in MAOS and the activation spectrum measured at the sizes of the doubly and triply charged particles (See Section S3.1). The corrected activation spectrum of size selected particles was then fit with a cumulative lognormal (Mei et al., 2013a; Rose et al., 2008a) functional form (See Fig. S6 for examples):

$$R_a(S) = \frac{E}{2}\left[1 + erf\left(\frac{\ln S - \ln S^*}{\sqrt{2\sigma_s^2}}\right)\right] \tag{1}$$

where R_a is the activated fraction as a function of supersaturation S, E is maximum activated fraction, and (1-E) represents the number fraction of particles consisting of only non-hygroscopic species (e.g., uncoated rBC) that cannot serve as CCN under typical atmospheric supersaturations. S^* is the supersaturation at which R_a reaches 50% of E, and represents the median critical supersaturation of size-selected particles that serve as CCN. The value of σ_s is related to the slope of the increasing R_a with S near S^* and reflects the heterogeneity of critical supersaturation, which to a large degree arises from the heterogeneity of the hygroscopicity among size-selected particles (Cerully et al., 2011; Mei et al., 2013a). The probability density function of hygroscopicity for size-selected particles is derived from the $R_a(S)$. The average hygroscopicity $\overline{\kappa_{\mathrm{CCN}}}$ and dispersion of the hygroscopicity $\sigma(\kappa)/\overline{\kappa_{\mathrm{CCN}}}$ for the size-selected CCN were then derived from the probability density function of hygroscopicity using the approach detailed in Section S3.4 in Supplementary Information. The dispersion of the hygroscopicity reflects the composition heterogeneity (i.e., mixing state) among size-selected particles (Mei et al., 2013a). For simplicity, we use κ_{CCN} to represent the average hygroscopicity of size-selected CCN in the following sections. As hygroscopicities reported in this study were derived from particle dry diameter and critical supersaturation, they represent “apparent hygroscopicity”, which includes the potential impact due to the limited solubility of organics and the reduction of surface tension by surface active species (Sullivan et al., 2009).

3.2 Derivation of Organic Aerosol Hygroscopicity

The average particle hygroscopicity was then combined with the chemical composition data to derive the hygroscopicity of the organic component of the size-selected particles, κ_{org} . Collectively, the AMS, ACSM, SP2, and aethalometer provided mass concentrations of organic species, sulfate, nitrate, ammonium, and rBC. The concentration of chloride was negligible (<<1% of aerosol mass) and was not included in the analysis. Given the low concentrations during GoAmazon 2014/5, size-resolved mass concentrations at the time resolution of the CCN measurement were not directly derived from AMS particle time of flight (PToF) mode data. For IOP 1, measurements were classified into three groups based on bulk organic mass fraction and the characteristic mass size distribution of each species was averaged from measurements in each group. For the dry season, the measurements were classified into three groups each for day and night periods based on the bulk aerosol organic mass fraction, and the mass size distribution of each species was averaged from measurements in each of the six groups. The size-resolved mass concentrations of sulfate, nitrate, and organics at the time resolution of the CCN measurement were then derived by scaling the total mass concentration using the average mass size distributions for the corresponding group (based on the bulk organic mass fraction) of either wet or dry season (de Sá, 2017). The shape of the NH_4^+ mass size distribution was assumed to be the same as that of sulfate, as ammonium cations were primarily associated with sulfate. rBC was assumed to have the same size distribution shape as the total aerosol mass (i.e., mass fraction of rBC was independent of particle size); though this assumption may not always be appropriate, the effect is expected to be very small as the monthly average volume fraction of rBC was always less than 4% (Fig. 1). A detailed description of the derivation of the size-resolved mass concentrations is given in Section S4.1.

In most cases, NH_4^+ was insufficient to completely neutralize SO_4^{2-}. The concentrations of both organonitrate and inorganic nitrate during the two IOPs were retrieved from AMS data based on the ratio of ions NO^+ and NO_2^+ (de Sá, 2017; Fry et al., 2009). When the inorganic nitrate mass concentration was negligible (i.e., less than 30 ng m^{-3}), as in most of the cases, the contributions of ammonium sulfate and ammonium bisulfate were calculated based on the mass concentrations of SO_4^{2-} and NH_4^+ (Nenes et al., 1998). In rare cases when the mass concentration of inorganic nitrate was greater than 30 ng m^{-3}, sulfate was assumed to be ammonium sulfate. During non-IOP periods, only the total nitrate mass concentration is available, all nitrate was assumed to be organonitrate (Cerully et al., 2015; Lathem et al., 2013b; Nenes et al., 1998; Zhang et al., 2005), and sulfate fully neutralized by ammonium (see Section S4.2 in the Supplement for a sensitivity study of these assumptions for non-IOP periods). The $-ONO_2$ portion of the organonitrate was added back to the organic mass. We note that the amount of $-ONO_2$ added back was typically small given the low mass fraction of nitrate in the aerosol. Cloud condensation nuclei were assumed to be internal mixtures of $(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3, organics, and rBC, and the volume fractions of the species were derived from the mass concentrations and densities. Densities of organics were estimated from the ratios of O:C and H:C measured by the AMS (Kuwata et al., 2012) and were on average 1450 ± 100 and 1470 ± 80 kg m^{-3} for IOP1 and IOP2, respectively. Densities of 1770, 1790, 1730, 1800 kg m^{-3} were used for $(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3, and rBC (Bond and Bergstrom, 2006; Park et al., 2004), respectively. In very rare cases, *E* was less than 100%, suggesting some of the size-selected particles were non-hygroscopic. The non-hygroscopic particles were assumed to consist entirely of rBC (Mei et al., 2013a). The volume concentration of the non-hygroscopic particles was derived as the product of (1-*E*) and the total volume concentration (i.e., the sum of volume concentrations of organics, $(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3 and rBCs) at the size classified by the DMA. The volume concentration of rBC internally mixed within the CCN-active particles was then calculated as the difference between the total rBC volume concentration and the volume concentration of the non-hygroscopic particles. (Mei et al., 2013a; Mei et al., 2013b). Assuming a κ value of zero for rBC, we can derive the hygroscopicity of the organic component of the CCN κ_{org} as:

$$\kappa_{\mathrm{org}} = \frac{1}{x_{\mathrm{org}}}\left(\kappa_{\mathrm{CCN}} - x_{(\mathrm{NH_4})_2\mathrm{SO_4}}\kappa_{(\mathrm{NH_4})_2\mathrm{SO_4}} - x_{\mathrm{NH_4HSO_4}}\kappa_{\mathrm{NH_4HSO_4}} - x_{\mathrm{NH_4NO_3}}\kappa_{\mathrm{NH_4NO_3}}\right) \quad (2)$$

where x_i is the volume fraction of the respective species. The κ values are 0.61, 0.7 and 0.67 for $(NH_4)_2SO_4$, NH_4HSO_4, and NH_4NO_3, respectively (Petters and Kreidenweis, 2007). The uncertainty in κ_{org} using these calculations has been derived using the approach detailed in earlier studies (Mei et al., 2013a; Mei et al., 2013b) and is on the order of 0.01 – 0.02 (which was generally between 10 and 20%) for this data set.

3.2.1 Derivation of κ for AMS PMF Factors

PMF was applied to the AMS mass spectra (Lanz et al., 2008; Ulbrich et al., 2009), and six organic factors were identified for each of the two IOPs (de Sá, 2017). For IOP2 the PMF analysis included data from 24 August to 15 October 15, 2014, excluding a major regional biomass burning event from 16 to 23 August, which was treated separately in the PMF analysis. For IOP1 (wet season), the six factors were isoprene-epoxydiol-derived secondary organic aerosol (IE-

POX-SOA), more-oxidized oxygenated organic aerosol (MO-OOA, i.e., highly oxidized organics), less-oxidized oxygenated organic aerosol (LO-OOA), biomass burning organic aerosol (BBOA) with characteristic peaks at m/z = 60 and 73 and correlated with the concentrations of levoglucosan and vanillin, a factor with high contribution from m/z = 91 (Fac91) and correlated with anthropogenic emissions of aromatics, and hydrocarbon-like organic aerosol (HOA). The six factors for IOP2 included IEPOX-SOA, MO-OOA, LO-OOA, an aged biomass burning organic aerosol factor (aged-BBOA), a fresh biomass burning organic aerosol factor (fresh-BBOA), and HOA. Further details of PMF analysis and the characteristics of the factors can be found in de Sá (2017). The O:C ratio and calculated density for each factor are presented in Table 1. In this study, the O:C ratio was derived using Improved-Ambient Method (Canagaratna et al., 2015).

For each IOP, hygroscopicities associated with the six factors were attributed based on multilinear regression of κ_{org} with respect to the volume fractions of the factors (Levenberg-Marquardt algorithm, IGOR Pro, Wavemetrics):

$$\kappa_{\mathrm{org}} = \sum_{i}^{n} \kappa_i x_i \tag{3}$$

where κ_i and x_i are the hygroscopicity and volume fraction of the individual organic PMF factors. The volume fraction was derived from mass concentrations and the densities of the factors. κ_{org} represents the average organic hygroscopicity at particle diameters (D_{p}) of 142 and 171 nm. As the PMF analysis is based on the mass spectra of the bulk sub-micrometer aerosol (i.e., MS mode measurements), an implicit assumption of Eq. (3) is that the bulk volume fractions of the factors represented those over the sizes at which κ_{org} was derived (i.e., D_{p} = 142 and 171 nm). The validity of this assumption is discussed in the results section. The robustness of the factor hygroscopicity derived through linear regression depends on the variation of the factor volume fraction during the measurement period. The HOA hygroscopicity was assumed as zero based on the results from previous studies (Cappa et al., 2009; Cappa et al., 2011; Jimenez et al., 2009), and the hygroscopicity of the other five factors were derived by multilinear regression as described above.

3.3 Classification of Seasons and Air Masses

The one-year sampling period was divided into different seasons by grouping months according to the similarity of the aerosol properties and trace gas concentrations measured at the two background sites, T0a and T0t, as well as monthly accumulated rainfall. In this study, the seasons were defined as follows: the first wet season: March, April and May of 2014; the first transition season: June and July 2014; the dry season: August and September of 2014; the second transition season: October, November and the first half of December 2014; and the second wet season: the second half of December 2014 and January, February and the first few days of March 2015.

For each season, the air masses arriving at the T3 site were classified into three different types: background, urban pollution, and local biomass burning based on trace gas and aerosol measurements at all sites. During the wet season, the background air mass represented near natural conditions, with occasional impact from anthropogenic emissions, while in the dry season, the background was dominated by regional biomass burning aerosol particles. Polluted air masses represent those with strong influence from urban emissions, which were mostly from Manaus. The local-biomass-burning type describes those air masses strongly influenced by local (i.e., fresh) biomass burning activities, which dominated over the impact from urban pollution, if any. For each season, background conditions were identified when CO and CN concentrations were below the thresholds derived from measurements at the background T0a and T0t sites, and the NO_y mixing ratio was below 1.5 ppb. Non-background conditions were identified by condensation nuclei (CN) and CO concentrations above the respective threshold levels. As biomass burning aerosol typically has a higher fraction of accumulation mode particles, and the emissions from Manaus were more dominated by Aitken mode particles, the fraction of particles with diameter less than 70 nm was used to differentiate air masses strongly influenced by local biomass burning from those with more impact from urban pollution (see Table S2 in Supplementary Information for details). Contamination by the emissions from an on-site diesel generator, grass cutting activities, tractors, and other vehicles were evidenced by rBC concentrations above 1.0 μg m^{-3} or CN concentration above 10,000 cm^{-3}. Over the one-year measurement period, background, urban pollution, and local biomass burning represented 12.4%, 38.5%, and 28.4% of the CCN measurements, respectively (Table S3). We note that the air masses arriving at the T3 site often included contributions from different sources. The classification of the air masses using the above three types clearly represents a simplification, but is very helpful for understanding the properties of aerosols influenced by the various major sources.

4 Results

4.1 Seasonal Trend and Size Dependence of Hygroscopicity and Chemical Composition

The monthly average κ_{CCN} at the T3 site varied from 0.1 to 0.2 at five particle diameters ranging from 75 nm to 171 nm (Fig. 1a), and was substantially lower than the value of 0.3 ± 0.1 suggested for continental sites (Andreae and Rosenfeld, 2008). This was due to the large organic volume fraction, up to 95% observed at the T3 site. In this study, measurements at 51 and 222 nm were not included, because the range of supersaturation sampled inside the CCN counter only adequately captured the activation spectrum for 51/222 nm particles with relatively high/low κ_{CCN} values, leading to a positive/negative bias of the average κ_{CCN}. The value of κ_{CCN} exhibited similar seasonal variations at all five sizes. During the transition from wet to dry season, κ_{CCN} decreased by 20-30% with the absolute minimum of 0.116 occurring at 75 nm in September and October (Fig. 1a).

The seasonal trend of κ_{CCN} was mainly driven by the variation of κ_{org}, which shows the lowest value in September during the dry season (Fig. 1b). Despite a strong increase of aerosol mass concentration from wet to dry season due to biomass burning emissions, the organic volume fraction exhibited little season variation, and was ~90% or higher at the four sizes from 94 to 171 nm (Fig. 1c). A minor increase in organic volume fraction in October might have also contributed to the lower κ_{CCN} value observed. The species volume fractions at 75 nm are not shown due to the very low signal-to-noise ratio of the AMS PToF data in the small particle diameter range. No clear seasonal trend was observed for sulfate volume fraction, which ranged from 3% to 9% at the four sizes. The lack of clear seasonal trends of sulfate and organic fractions are consistent with observations at the T0a site (Andreae et al., 2015). Nitrate and rBC represented a small fraction of aerosol volume, and were less than 1% and ~4%, respectively.

The average κ_{CCN} increased with increasing particle size for all three air mass types and during all the seasons (Fig. 2), consistent with decreasing organic volume fraction with increasing particle size (Fig. 1c). The κ_{CCN} at 75, 94, 112, 142, and 171 nm averaged for the one-year measurement period were 0.130 ± 0.028, 0.144 ± 0.039, 0.148 ± 0.043, 0.164 ± 0.046, and 0.167 ± 0.042 respectively. The value of κ_{CCN} and its size dependence under background conditions were largely consistent among different seasons, and were in good agreement with those observed under near natural conditions during the AMAZE-08 campaign at T0t in the wet season (Gunthe et al., 2009) and during the one-year period from March 2014 to February 2015 at the background T0a site (Pöhlker et al., 2016). For the air masses with strong influence from local biomass burning, the value of κ_{CCN} and its size dependence are consistent with the κ value derived from particle growth factor measurements in July 2001, during a "recent biomass burning period" of the CLAIRE-2001 study (Rissler et al., 2004), which took place at Balbina, about 125 km northeast of Manaus. In contrast, κ values derived from particle growth factor measurements from 11 September to 8 October 2002, during the dry period of the LBA-SMOCC (Rissler et al., 2006) are substantially lower than κ_{CCN} observed at the T3 site for local biomass burning air masses at all sizes. As LBA-SMOCC took place in the state of Rondônia in southwestern Amazonia with extensive biomass burning activities during the dry season, the difference in κ could be due to the differences in fire condition and the type of vegetation burned. Previous studies show particles sometime exhibit larger κ values for droplet activation (derived from CCN measurements under supersaturated conditions) than for particle growth (derived from particle growth factor under sub-saturated conditions), this could also contribute to the differences in κ values. Compared to κ_{CCN}, κ_{org} was largely independent of particle size for all three air mass types, indicating that the size dependence of κ_{CCN} was mainly due to the size dependence of the organic volume fraction and particle composition (Fig. 1c – f). During the dry season, aerosols classified as urban pollution and local biomass burning exhibited lower κ_{org} values compared to background aerosols, contributing to the lower values of overall κ_{CCN}.

4.2 Diel Trends of Particle and Organic Hygroscopicities

The diel variations of aerosol properties are presented in Figs. 3-7 for different air masses during the two IOPs. Aerosol properties derived from the size-resolved CCN measurements, including $\kappa_{\text{CCN}}, \sigma_{\kappa_{\text{CCN}}} / \bar{\kappa}_{\text{CCN}}$, and κ_{org}, and the volume fractions of different species were averaged at the three largest sizes (D_p = 112, 142, and 171 nm). The fraction of organic mass at m/z = 44 (f_{44}) and O:C were derived from the AMS bulk measurements. Also shown are diel variations of planetary boundary layer height, CN, and aerosol volume concentrations based on 5-minute average data.

4.2.1 Wet Season Aerosol

Background conditions

Figures 3 and 4 show the diel variations of aerosol properties during the wet season of 2014 for background and urban pollution air masses, respectively. There were only 0.7% of data classified as local biomass burning (see Table S3), which is insufficient to evaluate the diel trends. During the wet season, the background air mass represents near-natural conditions, with minimum impact from anthropogenic emissions, although long-distance transport of African biomass burning may contribute to the aerosols observed (Chen et al., 2009; Wang et al., 2016b). Background aerosol constantly exhibited relatively high hygroscopicity of ~0.19 throughout the day. The lack of a diel trend in κ_{CCN} is also in agreement with the results from the T0a site (ATTO), which is upwind of Manaus and served as a background site (Fig. 8). The particle composition averaged for the three particles diameters was dominated by organics, representing ~ 90% of the aerosol volume. The lack of a diel trend in κ_{CCN} and κ_{org} suggest little variation in particle composition throughout the day. The nearly constant κ_{org} of ~0.16 is also consistent with the lack of a diel trend in f_{44} and O:C. The values of f_{44} and O:C are ~0.2 and ~0.8, respectively, indicating that the aerosol under background condition during the wet season was dominated by the aged regional aerosol particles consisting of highly oxygenated organic compounds.

Aerosol number and volume concentrations exhibited a minimum at ~310 cm^{-3} and ~0.3 μm^3 cm^{-3}, respectively, just before sunrise. The number and volume concentrations started increasing after sun rise, and peaking at 400 cm^{-3} and 0.8 μm^3 cm^{-3} in the afternoon. These diel variations are partially attributed to the wet scavenging of accumulation mode particles, which dominate the submicron particle concentrations under background conditions, and the mixing of the particles from the residual layer aloft down to the surface as the boundary layer develops in the morning. During the night, the radiative cooling at the surface leads to a shallow nocturnal boundary layer with low and variable winds. RH near surface was near 100%, and fog or mist was identified by the weather station (Present Weather Detector, Visalia) 62% of the time during the one-year measurement period. The gradual decrease of particle number and volume concentration during these fog events were due to the wet deposition of the accumulation mode particles activated into droplets. Similar decreases of particle number concentration were previously reported during night fog events in the tropical rainforest in Borneo (Whitehead et al., 2010). After sunrise, the boundary layer deepened on average from less than 200 up to 800 m as a result of solar heating (Fig. 3g). Consequently, particles in the residual layer aloft (Fisch et al., 2004; Rissler et al., 2006b), which were not impacted by the fog, were mixed down to the surface, leading in part to the observed increases in both number and volume concentrations. Such mixing of particles from the residual layer in the morning had been observed previously in the Amazon basin during the dry season (Rissler et al., 2006a). The formation of secondary organic aerosol (SOA) as a result of photochemical oxidation (in both gas and particle phases) likely contributed to the increase in volume concentration (Chen et al., 2015; Chen et al., 2009; Martin et al., 2010a; Pöschl et al., 2010).

Air masses impacted by urban pollution

Air masses arriving at the T3 site frequently had passed over urban and industrial areas upwind. When the air mass was influenced by the urban pollution, κ_{CCN} and its dispersion exhibited clear diel variations (Fig. 4). The value of κ_{CCN} was lower during the night at 0.15, and it increased from the early morning hours, peaking at a value of 0.19 around noon (local time, UTC – 4 h). The dispersion was anti-correlated with κ_{CCN}, exhibiting higher values (i.e., increased heterogeneity in particle chemical composition) during night and a minimum value around noon. To a large degree, the diel trend of κ_{CCN} was due to the variation of κ_{org}. The value of κ_{org} was lower during night at 0.10 and increased to 0.16 at noon. The increase of κ_{org} is consistent with the variation of O:C, which increased during the early morning and reached the highest value of 0.8 around noon time. The pollution strongly affected the particle number and volume concentrations, both exhibiting similar diel trends. Under polluted conditions, particle number concentration ranged on average from 1500 to 2300 cm^{-3}, an increase by a factor of ~5 from that under background conditions. In comparison, the increase of the volume concentration was only about a factor of 2 (i.e., from a range of 0.3 - 0.75 to 1.0 to 1.3 μm^3 cm^{-3}), as the urban pollution is dominated by Aitken mode particles that make a relatively small contribution to aerosol mass and volume concentration.

The diel variations of κ_{CCN}, its dispersion, κ_{org}, and O:C are explained as follows. During night, particles in freshly emitted pollution, which are dominated by primary organic aerosol (POA) and have low hygroscopicity, are mixed with more aged particles within a shallow nocturnal boundary layer (Bateman et al., 2016). In the absence of photochemical oxidation and aging, this external mixture leads to higher dispersion of particle hygroscopicity, as well as overall lower O:C and κ_{org}. As the pollution aerosols are mainly from isolated point sources, they are confined in the shallow nocturnal boundary layer during night, and the residual layer above the T3 site is expected to consist of aged background aerosols. Therefore, unlike under background conditions, the mixing of aerosol aloft in the residual layer down to the surface cannot by itself explain the increase in particle number and volume concentration during the day, both of which were substantially above the background values. These increases under polluted conditions might be due to the stronger urban influence at T3 during the day. The strong increase of CN concentration at 16:00 UTC (local time 12:00) could be caused by the arrival at the T3 site of the Manaus plume emitted during early morning traffic hours. To a large degree, the increases in O:C and κ_{org} are due to the formation and aging of SOA in the pollution, while the development of the daytime boundary layer, which leads to dilution of pollution and mixing with aged particles from the residual layer, can also contribute to the increases. The condensation of secondary species and photochemical aging also lead to more homogenous composition among particles (Mei et al., 2013a), and therefore lower dispersion of κ_{CCN}, as was observed. The O:C reached a maximum average value of 0.8, similar to that under the background conditions. This suggests that the formation and photochemical aging of SOA quickly led to highly oxygenated organic compounds (i.e. within several hours) (de Sá, 2017).

4.2.2 Dry Season Aerosol

Background conditions

Figures 5-7 show the diel variations of the aerosol properties observed during the dry season for background, urban pollution, and local biomass burning air masses, respectively. During the dry season, the background aerosol (Fig. 5) is strongly influenced by regional biomass burning, and air masses arriving at the T3 site often pass through urban and industrial areas along the Amazon River and in northeast Brazil (Andreae et al., 2015), indicating that the background aerosol is also impacted by more aged urban and industrial emissions (Martin et al., 2016a). Despite different aerosol sources and processes, the particle hygroscopicity, dispersion, and κ_{org} exhibited similar values as those of background aerosol during the wet seasons, and a lack of obvious diel variations. This is also consistent with the absence of a significant diel trend of κ_{CCN} observed at T0a (ATTO) during the dry season (Fig. 8). The O:C value increased slightly from 0.8 during night to 0.9 in the afternoon, possibly due to further oxidation and aging of background aerosols during the day time. The high value of O:C is consistent with the relatively high value of κ_{org} (0.15) and is close to that observed under background condition during the wet season, indicating highly oxygenated organic aerosol. The number and volume concentrations were lower just before dawn and increased during the early morning, again a result of wet scavenging of particles by fog followed by the mixing of aerosol aloft in the residual layer down to the surface as the boundary layer develops in the morning.

Air masses impacted by urban pollution and local biomass burning

For urban pollution (Fig. 6) and local biomass burning (Fig. 7) air masses during the dry season, κ_{CCN} (urban pollution: 0.12 – 0.20, local biomass burning: 0.10 – 0.17), its dispersion (urban pollution: 0.4 – 1.0, local biomass burning: 0.4 – 0.9), κ_{org} (urban pollution: 0.10 – 0.15; local biomass burning: 0.08 – 0.14), and O:C (polluted: 0.7 – 0.85; biomass burning: 0.7 – 0.86) showed similar values and diel variations as those under polluted conditions during the wet season. This is consistent with the picture that freshly emitted particles (in either the case of urban pollution or local biomass burning) lead to overall lower O:C, κ_{org}, and higher κ_{CCN} dispersion during night, followed by increases in O:C, κ_{org}, and a decrease in the dispersion during day time, which are mainly driven by the formation and photochemical aging of SOA, with contributions from the mixing of background aerosol aloft in the residual layer down to the surface and dilution of fresh emission as the boundary layer develops. Compared to urban pollution, local biomass burning air masses exhibited lower κ_{CCN} and κ_{org} values during night and stronger diel variations. In the afternoon, κ_{org} and O:C reached high values of 0.14 and 0.86, respectively, as observed for background aerosols.

For urban pollution air masses, aerosol number and volume concentrations showed similar trends for both seasons. The increases of number and volume concentration from early morning to noon were similar, about 1000 cm^{-3} and 0.5 $\mu\mathrm{m}^3/\mathrm{cm}^3$, respectively, for both wet and dry seasons. The percentage increases were less pronounced in the dry season due to the higher background values. In contrast to urban pollution, local biomass burning showed higher aerosol number and volume concentrations at night, and decreased during the morning. Local biomass burning activities typically peaked during evening hours, consistent with frequent classification of the night time aerosol as local biomass burning (Fig. 7i) (Vestin et al., 2007). Despite the wet removal of particles by fog, the strong emission from local biomass burning, largely confined within the shallow nocturnal boundary layer, led to higher surface aerosol concentrations than those in the residue layer aloft, which likely represented the regional background. As the boundary layer deepened in the morning, the mixing with aerosol from the residual layer led to decreases in both aerosol number and volume concentration observed at the surface (Fig. 7e,f).

4.3 Hygroscopicity of PMF Factors and the Variation of Organic Hygroscopicity with Oxidation Level

The hygroscopicities associated with the AMS PMF factors were estimated through multivariable linear regression using different subsets of the data, as well as the entire dataset for each of the two IOPs (IOP1 in Fig. 9 and IOP2 in Fig. 10). The different subsets included measurements during day, night, certain sampling periods, and ranges in particle hygroscopicity dispersion. Comparison of the hygroscopicities derived from the different subsets of data allowed us to examine the robustness of this approach. Uncertainty in the derived κ for individual factors was determined by the number of points available to fit in the time series, with greater data coverage and therefore lower uncertainty during the dry season. For the wet season (IOP1), the hygroscopicity associated with PMF factors derived using different subsets of the data are largely in agreement with those derived from the entire dataset. There are notable differences between the hygroscopicities of MO-OOA and Fac91 factors derived using data under background conditions only and those derived using the entire dataset. Such difference could be partially due to the limited data under the background conditions during IOP1 (Fig. 3). For the dry season (IOP2), the hygroscopicities of PMF factors derived using measurements under background conditions or data with hygroscopicity dispersion less than 0.4 are quite different from those derived using other data subsets and the entire dry season dataset. The agreement among the PMF factor hygroscopicities derived using different sub datasets during the wet season and the disagreements for the dry season are attributed to the applicability of the underlying assumption that the bulk volume fractions of PMF factors (i.e., derived from MS mode data) represented those at the sizes of CCN measurements. For the wet season, the average f_{44} was largely independent of particle size from 130 to 400 nm (Fig. S10), the size range that dominated bulk aerosol mass concentration measured by AMS. This is consistent with the assumption that the bulk volume fractions of the PMF factors represent those at the two CCN sizes (142 and 171 nm). For the dry season, the f_{44} averaged over local biomass burning air masses and the entire IOP2 exhibited an increase with particle diameter from 100 to 300 nm (Fig. S10). For periods with hygroscopicity dispersion less than 0.4 or under background conditions, the average size distribution of f_{44} was noisier due to fewer data points. Nevertheless, the size distribution shows f_{44} was largely independent of the particle size under these conditions, consistent with the assumption described above. In the following discussion, we focus on the PMF factor hygroscopicities derived using all data during the wet season, and under background conditions in the dry season.

The MO-OOA factors for the two IOPs exhibit very similar O:C and κ values. The O:C values were 1.19 and 1.24, and κ values were 0.20 and 0.21 for IOP1 and 2, respectively (Table 1). The O:C and κ values are consistent with those of some typical SOA compounds, such as malonic acid, which has an O:C value of 1.33 and a κ value of 0.23 (Kumar et al., 2003), and succinic acid, which has an O:C value of 1 and a κ value of 0.23 (Hori et al., 2003). For the LO-OOA and IEPOX-SOA factors, the hygroscopicities vary between the two IOPs. The κ of IEPOX-SOA were 0.18 and 0.08 during IOP1 and IOP2, respectively, and the κ of LO-OOA factor varied from 0.12 to 0.20 between IOP 1 and IOP 2. The difference in κ may be partially due to the change of O:C values of the factors derived for the two IOPs. Difference in SOA precursors and therefore composition in LO-OOA (Ng et al., 2010) may also contribute to the difference in its κ values between the two IOPs. The variation of IEPOX-SOA κ between the two IOPs could be a result of the different RH conditions, which may strongly influence the composition of IEPOX-SOA (Riva et al., 2016).

During the wet season, a factor with high contribution from *m/z* = 91 (Fac91) was identified. The Fac91 factor correlates with several tracers for anthropogenic emissions, including NO_x, benzene, toluene, trimethylbenzene (TMB) and xylenes, but not high NO_x isoprene products (e.g. methylglyceric acid) (de Sá, 2017). This factor likely represents SOA formed from aromatics emitted from urban areas, possibly combined with a mixture of freshly oxidized biogenic compounds within the urban-influenced air (de Sá, 2017). The Fac91 factor has a hygroscopicity value of 0.10, and a much lower O:C ratio of 0.328 compared to those of MO-OOA and LO-OOA.

Less oxidized organic factors identified by the PMF analysis were HOA of both IOPs, BBOA of IOP1 and fresh and aged BBOA of IOP2. These factors represent primary OA (POA), except that the aged BBOA of IOP2 likely included contributions from oxidized POA or SOA. The hygroscopicity of the HOA factors was fixed as zero in the multivariate regressions. All BBOA factors have a distinctive *m/z* = 60 peak and correlate with biomass burning traces including levoglucosan and vanillin (de Sá, 2017). The retrieved hygroscopicity values for the BBOA factors are substantially lower than those of SOA factors, especially for the fresh BBOA factor during IOP2. The extremely low hygroscopicity suggests that the fresh BBOA, likely produced by local fires, behaves very similar to HOA in term of CCN activation despite a substantially higher O:C.

Figures 11 and 12 show that for SOA factors, including IEPOX-SOA, LO-OOA, MO-OOA for both IOPs and Fac91 for IOP1, the κ value increases with increasing O:C, and the variation of κ with O:C agrees with the linear relationship derived from laboratory studies of SOA CCN activities (Lambe et al., 2011). The low hygroscopicity of the HOA and the BBOA factors, which are below the linear relationship for SOAs, are also consistent with laboratory results of POA and oxidized POA (Lambe et al., 2011). Cerully et al. (2015) derived κ of LO-OOA, MO-OOA, and IEPOX-SOA factors from data collected in the southeast US during Southern Oxidant and Aerosol Study (SOAS). A different name, Isoprene-OA, was used for the IEPOX-SOA factor in Cerully et al. (2015), as while this factor is mainly attributed to SOA formed from IEPOX uptake, it might not be entirely due to IEPOX (Schwantes et al., 2015; Xu et al., 2015a; Xu et al., 2015b). The O:C values calculated using the Improved-Ambient method (Canagaratna et al., 2015) are 0.59, 0.61, and 0.92 for the IEPOX-SOA, LO-OOA, and MO-OOA factors reported in Cerully et al. (2015), respectively (personal communication, L. Xu and N.L. Ng). For the LO-OOA, MO-OOA factors reported in Cerully et al. (2015), κ and O:C values are largely consistent with the linear relationship between κ and O:C derived from Lambe et al. (2011). Cerully et al. (2015) also reported IEPOX-SOA (i.e., called Isoprene-OA in their study) factor κ of 0.2, similar to 0.18 derived for IOP1. The O:C value of the IEPOX-SOA factor during the SOAS study was 0.59, somewhat lower than those derived from both IOPs of GoAmazon 2014/5. While the IEPOX-SOA factors identified using different datasets share many similar features, they are not identical and can consist of different groups of compounds. Such differences may be due to varying degrees of oxidation in different environment between the two field campaigns.

For comparison with earlier field studies, the values of κ_{org} and O:C were averaged according to the hours of the day over particle diameters of 142 and 171 nm for data under polluted conditions during IOP1 and all data during IOP2 (Figs. 11 and 12). For the one-hour diel averages, the slope of κ_{org} vs. O:C, derived through a bivariate least squares fit (i.e., Orthogonal distance regression), is steeper than that derived from laboratory studies of SOA hygroscopicity, especially during IOP2. This steep slope during IOP2 is consistent with the results from earlier field studies (Mei et al., 2013b), although there is a clear offset between the two relationships. The O:C ratios from Mei et al. (2013b) and Lambe et al. (2011) were scaled by a factor of 1.27 to account for changes in the method of calculating the O:C ratio (Improved-Ambient, Canagaratna et al., 2015) while all O:C values from this work were calculated using the Improved-Ambient method. This offset between the field studies may be partially due to the different precursors of the SOA for the campaigns, with higher anthropogenic VOC fraction expected for CalNex and CARES, which took place near Los Angeles and Sacramento, respectively. In addition, biomass burning represented a much smaller fraction of the organics during CalNex and CARES (Mei et al., 2013a; Mei et al., 2013b). The factors associated with secondary processes (e.g., MO-OOA, LO-OOA, and IEPOX-SOA), which have higher O:C values, exhibited higher volume fraction during the day, whereas the factors associated with primary emissions (e.g. HOA and BBOA), which have lower O:C, had higher volume fractions during the night (de Sá, 2017). As a result, the diel trend of overall O:C was to a large degree driven by the variations in volume fractions of the POA and SOA factors with very different O:C values. This is in contrast to laboratory studies, in which the increase of O:C was mainly driven by oxidation. As POA exhibits hygroscopicity values well below the linear fit between SOA hygroscopicity and O:C, mixtures with different POA and SOA fractions lead to a steeper slope for the increase of κ_{org} with O:C, as shown by the results from this and previous field studies (Mei et al., 2013b).

5 Conclusions

Size-resolved CCN spectra at five particle diameters ranging from 75 to 171 nm were characterized down-wind of Manaus, Brazil, in central Amazonia for a period of one year from March 12, 2014 to March 3, 2015 during GoAmazon2014/5. For each season, the air masses arriving at the site were classified into different types, including background, urban pollution, and local biomass burning. During the wet season, the background air mass represented near natural conditions, at times with impact from anthropogenic emissions, while in the dry season, the background was dominated by regional and long-distance biomass burning aerosol particles. Polluted air masses represented those with strong influence from urban emissions, which were mostly from Manaus. The local-biomass-burning type describes those strongly influenced by local (i.e., fresh) biomass mass burning activities that dominate over the impact from urban pollution, if any.

Particle hygroscopicity (κ_{CCN}), mixing state, and organic hygroscopicity (κ_{org}) were derived from size-resolved CCN activation fraction and concurrent aerosol composition measurements. The monthly mean κ_{CCN} exhibits the lowest values during the dry season, largely due to lower κ_{org} when aerosol was often strongly influenced by local biomass burning. The κ_{CCN} increased with particle size during all seasons, consistent with decreasing organic volume fraction with increasing particle size. Under background conditions, the value of κ_{CCN} and its size dependence were largely consistent among different seasons, despite the very different aerosol sources. During the dry season, aerosols classified as urban pollution and local biomass burning exhibited lower κ_{org} values compared to background aerosols, contributing to the lower values of overall κ_{CCN}.

Under background conditions during both wet and dry seasons, the largely constant diel trends of κ_{CCN} and κ_{org} suggest little variation in particle composition throughout the day. The constant κ_{org} of ~ 0.15 is consistent with the lack of a diel trend in f_{44} and O:C. The high values of f_{44} and O:C indicate that the aerosols under background conditions are dominated by the aged regional aerosol particles consisting of highly oxygenated organic compounds. When the air mass is influenced by urban pollution or local biomass burning, κ_{CCN}, κ_{org}, f_{44}, and O:C exhibit clear diel variations. The value of κ_{CCN} (0.1 - 0.2) is lower during the night, and increases from the early morning hours, peaking around noon (local time, UTC - 4 h). This diel trend of κ_{CCN} is largely driven by the variation in κ_{org} (0.08-0.15), consistent with the variation of O:C. The dispersion of κ_{CCN} is anti-correlated with κ_{CCN}, exhibiting higher values during night and a minimum value around noon, indicating an increased heterogeneity in particle chemical composition during night time. These diel variations for air masses strongly influenced by urban pollution and local biomass burning indicate that during night, freshly emitted particles, dominated by POA and with low hygroscopicity, are mixed with more aged particles within a shallow nocturnal boundary layer. In the absence of photochemical oxidation and aging, this external mixture leads to higher dispersion of particle hygroscopicity, as well as overall lower O:C and κ_{org}. The increases in O:C and κ_{org} during daytime are driven by the formation and aging of SOA and dilution of POA emissions into a deeper boundary layer, while the development of the boundary layer, which leads to mixing with aged particles from the residual layer, likley also contributes to the increases.

The hygroscopicities associated with individual PMF organic factors were derived through multi-variable linear regression. For the SOA factors, κ increases within increasing O:C, and the variation of κ with O:C agrees well with the linear relationship derived from laboratory studies of SOA hygroscopicity (Lambe et al., 2011). The low hygroscopicity of HOA and the BBOA factors, which are below the linear relationship, are also consistent with laboratory results of POA and oxidized POA (Lambe et al., 2011). In contrast, the slope of κ_{org} (i.e., overall organic hygroscopicity) vs O:C is much steeper when compared to that derived from laboratory studies of SOA hygroscopicity, especially for IOP2. Such difference is because the increase of O:C was driven primarily by oxidation in laboratory SOA studies, while the variation in O:C of ambient organics is to a large degree due to the variations in volume fractions of POA and SOA factors, which have very different O:C values. As POA factors show hygroscopicity values well below the linear fit between SOA hygroscopicity and O:C, mixtures with different POA and SOA fractions lead to a steeper slope for the increase of κ_{org} with O:C, as shown by the results from this and earlier field studies (Mei et al., 2013).

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Tables

Table 1: Density, O:C ratio and hygroscopicity associated with organic factors derived from Positive Matrix Factorization (PMF) analysis. For IOP1 and IOP2, hygroscopicities of PMF organic factors were derived from time series of particle hygroscopicity under all conditions and background conditions, respectively.

IOP1 (wet season)				IOP2 (dry season)			
PMF Factor	ρ (g cm^{-3})	O:C	κ	PMF Factor	ρ (g cm^{-3})	O:C	κ (Bkgd)*
IEPOX-SOA	1.47	0.798	0.18±0.02	IEPOX-SOA	1.42	0.711	0.08±0.03
MO-OOA	1.80	1.19	0.20±0.02	MO-OOA	1.81	1.24	0.21±0.03
LO-OOA	1.48	0.786	0.12±0.02	LO-OOA	1.52	0.883	0.20±0.03
BBOA	1.42	0.712	0.04±0.03	Aged BBOA	1.37	0.666	0.08±0.03
Fac91	1.14	0.328	0.10±0.03	Fresh BBOA	1.23	0.536	0.00±0.07
HOA	0.95	0.163	0	HOA	1.02	0.223	0

* κ (Bkgd) refers to κ values of PMF factors derived from the time series of particle hygroscopicity under background conditions (see Sections 4.2.2 and 4.3).

Figures

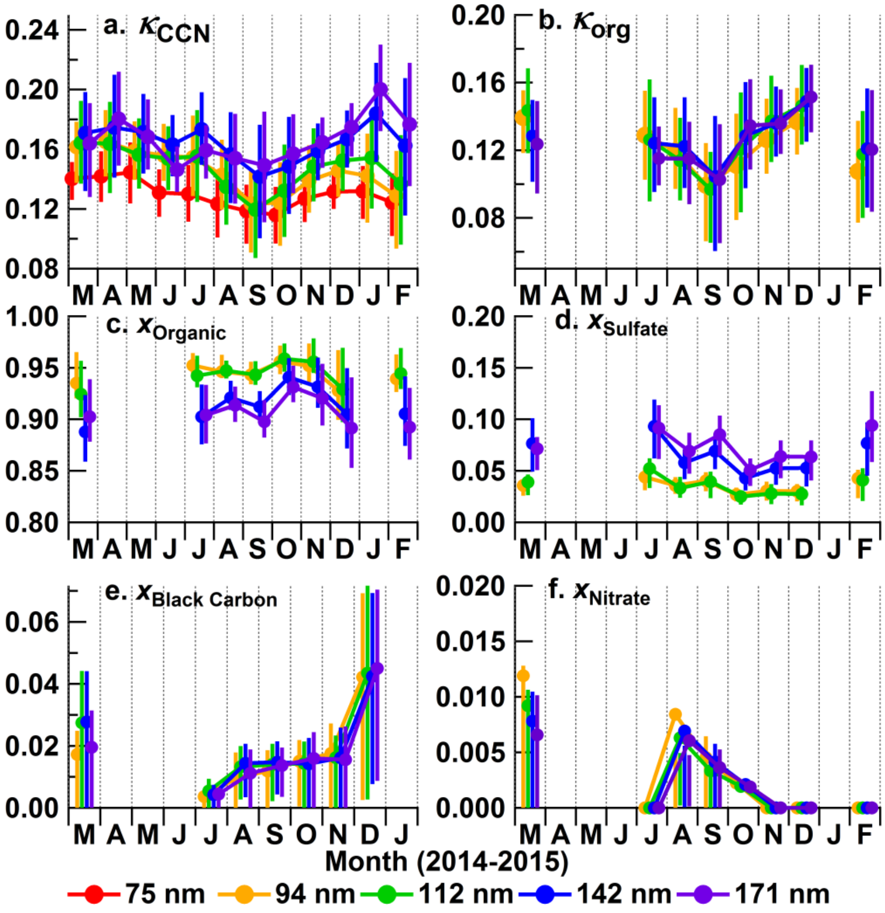
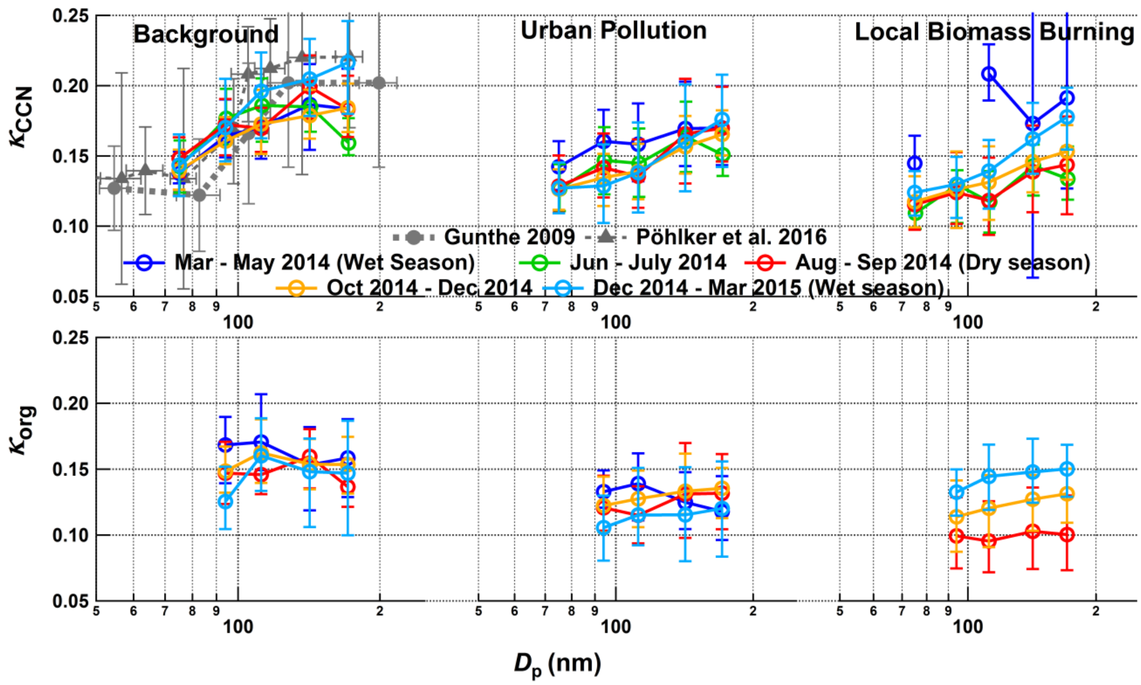


Figure 1: Seasonal variations of aerosol properties observed at the T3 site from March 2014 to March 2015, including (a) κ_{CCN}, (b) κ_{org}, and size resolved volume fraction of (c) organics, (d) sulfate, including $(NH_4)_2SO_4$ and NH_4HSO_4, (e) nitrate, and (f) refractory Black Carbon. Data points are the monthly mean; error bars represent the 25th and 75th percentiles.



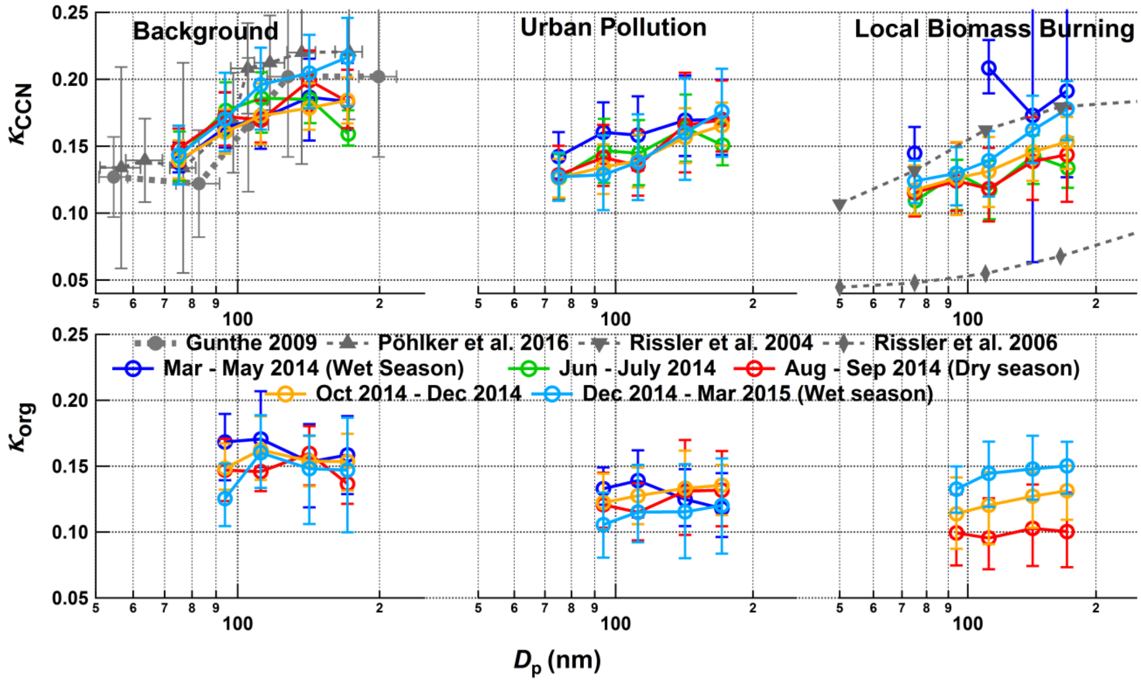


Figure 2: The variation of κ_{CCN} and κ_{org} with particle diameter during different seasons for each of three air mass types. Data points are the mean values; error bars are the 25 and 75 percentiles. The top left panel also includes κ_{CCN} observed under near natural conditions during the AMAZE-

08 campaign at T0t in the wet season (Gunthe et al., 2009) and during the one-year period from March 2014 to February 2015 at the background T0a site (Pöhlker et al., 2016). The top right panel includes *κ* derived from particle growth factor measurements in July 2001, during a “recent biomass burning period” of the CLAIRE-2001 study (Rissler et al., 2004) and from 11 September to 8 October 2002, during the dry period of the LBA-SMOCC (Rissler et al., 2006).

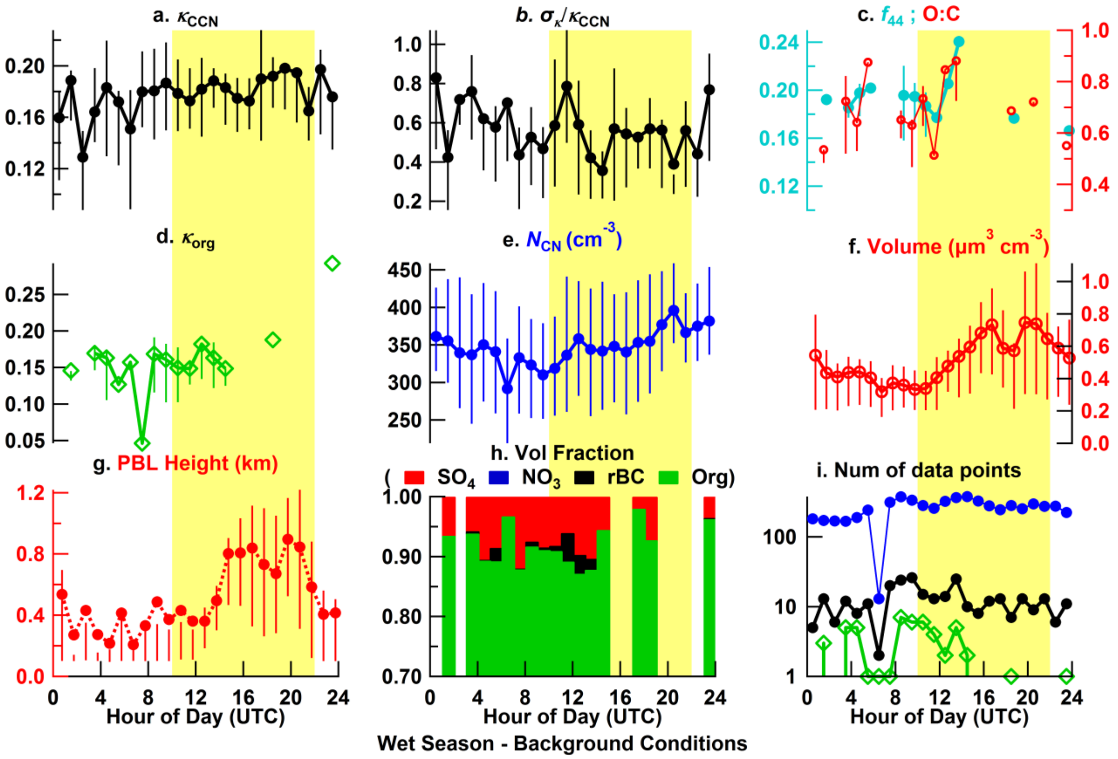


Figure 3: Diel variations of aerosol properties and meteorological parameter under background conditions during the wet season, including (a) κ_{CCN}, (b) $\sigma_{\kappa_{\mathrm{CCN}}} / \bar{\kappa}_{\mathrm{CCN}}$, (c) fraction of the organic mass at m/z = 44 (f_{44}) and the elemental ratio O:C, (d) κ_{org} derived using size resolved particle composition, (e) the total number of condensation nuclei (N_{CN}), (f) the total aerosol volume derived from size distribution measured by the SMPS in MAOS, (g) planetary boundary layer height as estimated using the ceilometer data, (h) the volume fractions of aerosol species, and (i) the number of samples in each hour bin corresponding to the data by the same colors and symbols in their respective panel. The values of κ_{CCN}, $\sigma_{\kappa_{\mathrm{CCN}}} / \bar{\kappa}_{\mathrm{CCN}}$, κ_{org}, and volume fraction of aerosol species were averaged over three particle diameters of 112, 142 and 171 nm. The values of f_{44} and O:C were derived from the AMS bulk measurements. Data include the last two weeks of March 2014 when valid data from both size-resolved CCN system and AMS were available. Data points are hourly averaged mean values; error bars represent the 25 and 75 percentiles of the data. Yellow shading represents the local daytime (10:00 – 22:00 UTC).

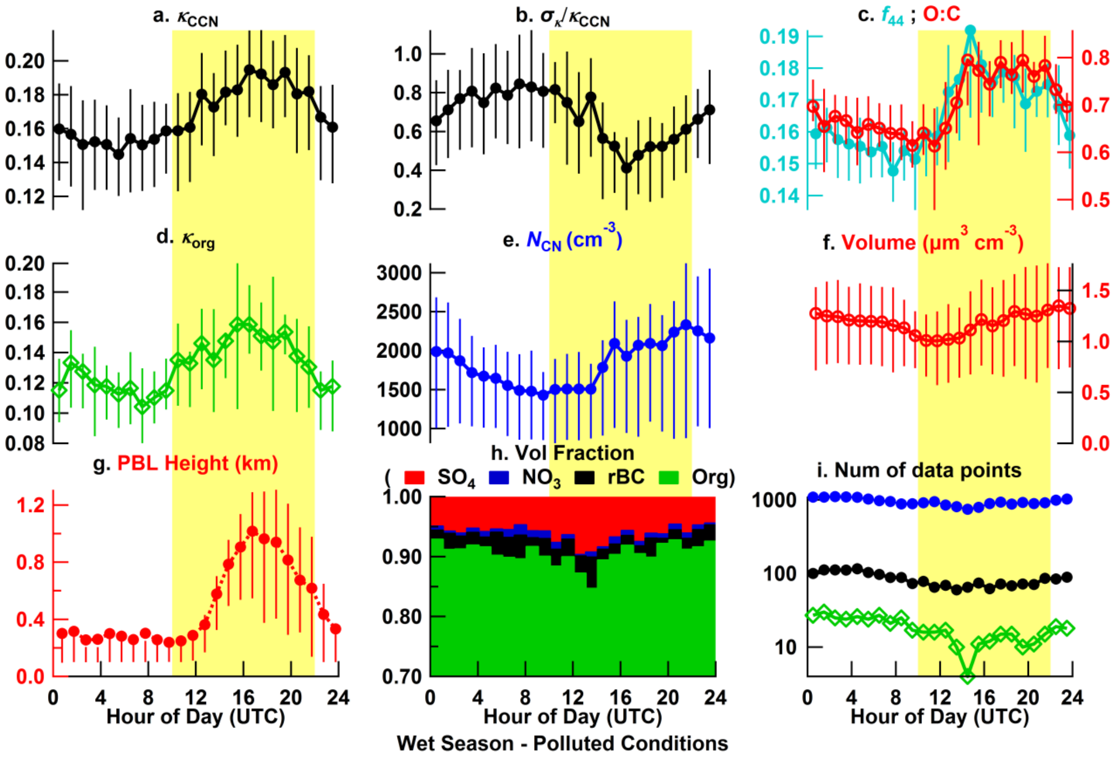


Figure 4: Diel variations of aerosol properties and meteorological parameters for urban pollution air masses during the wet season (analogous to Fig. 3).

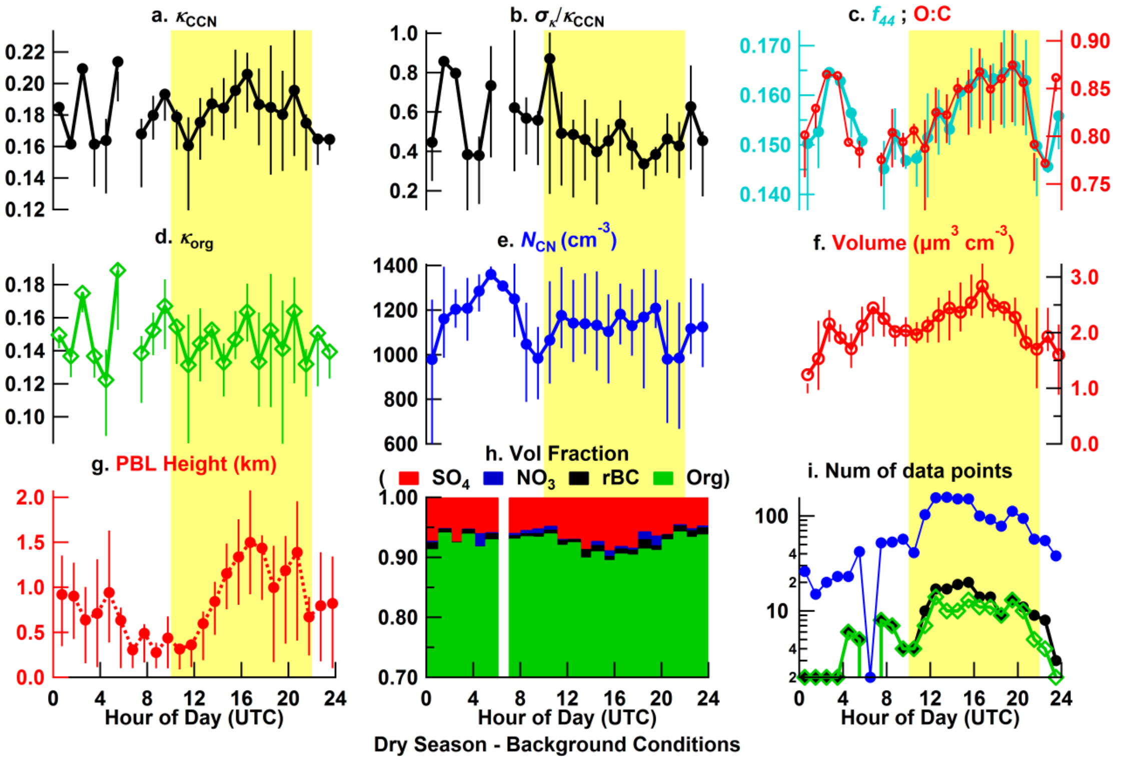


Figure 5: Diel variations of aerosol properties and meteorological parameters under background conditions during the dry season (analogous to Fig. 3).

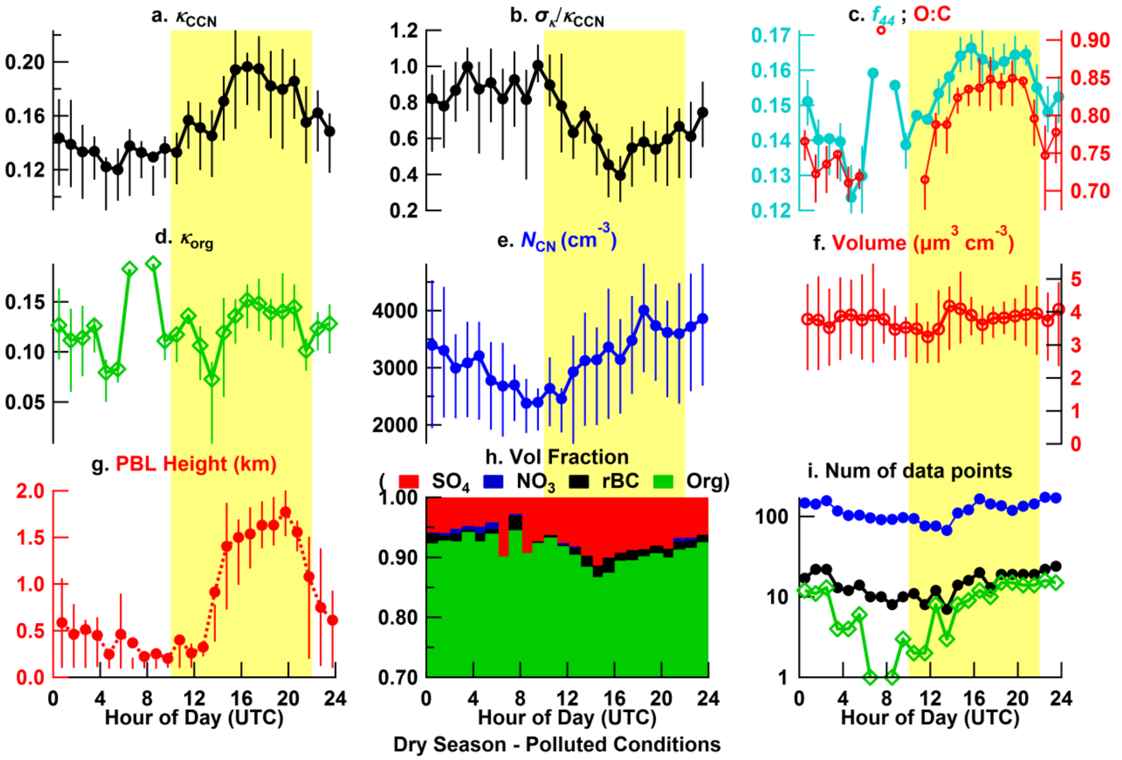


Figure 6: Diel variations of aerosol properties and meteorological parameters for urban pollution air masses during the dry season (analogous to Fig. 3).

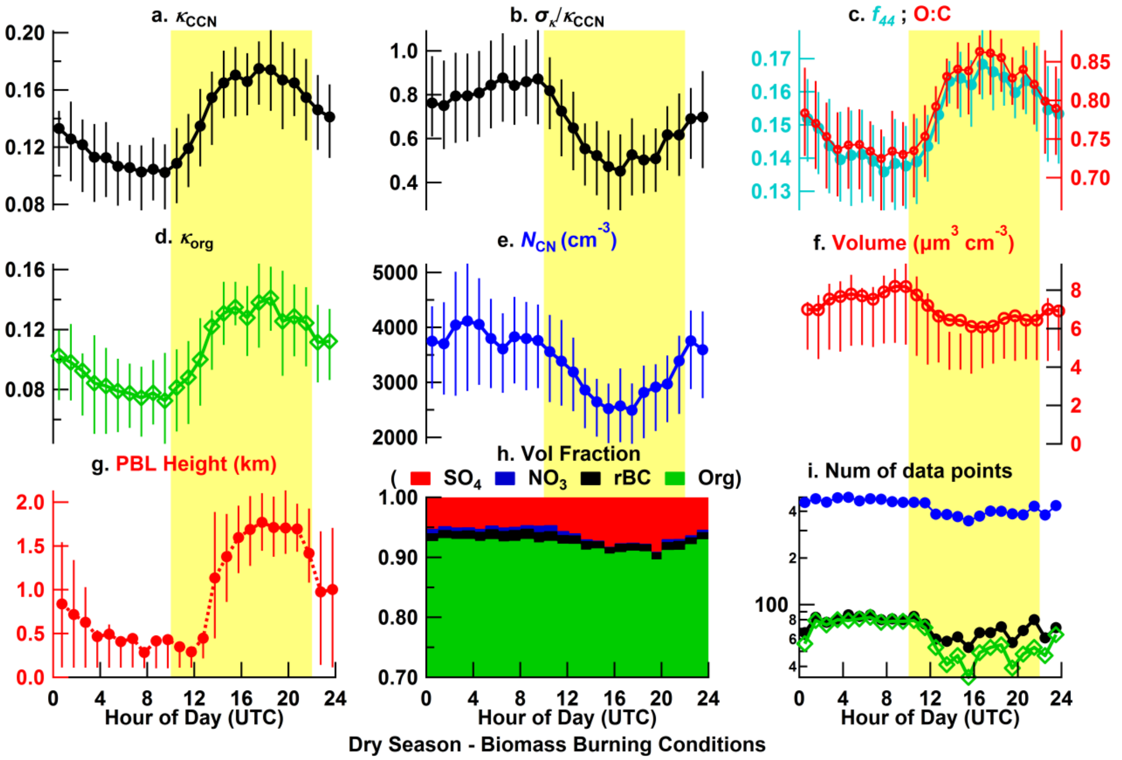


Figure 7: Diel variations of aerosol properties and meteorological parameters for local biomass burning air masses during the dry season (analogous to Fig. 3).

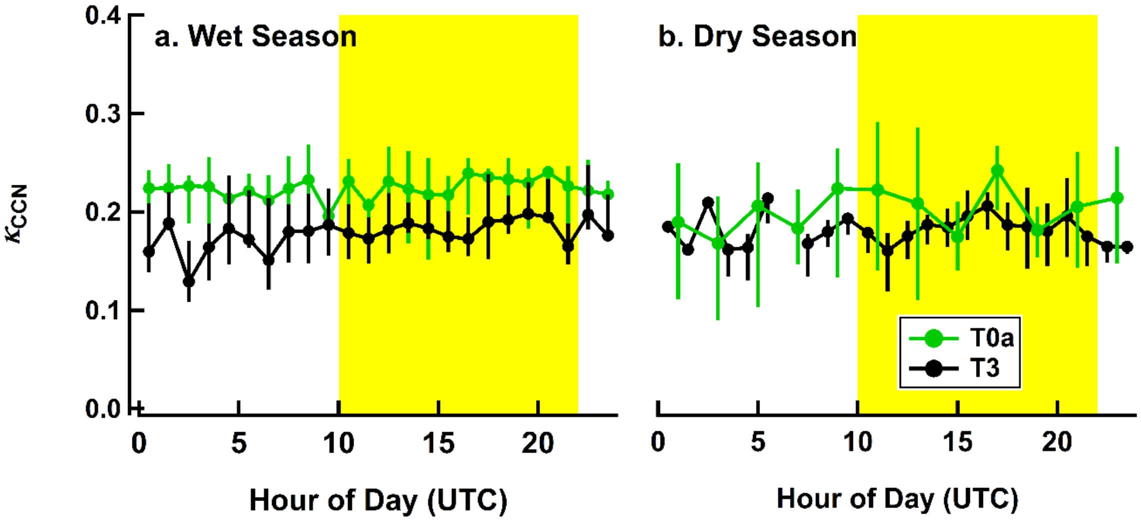
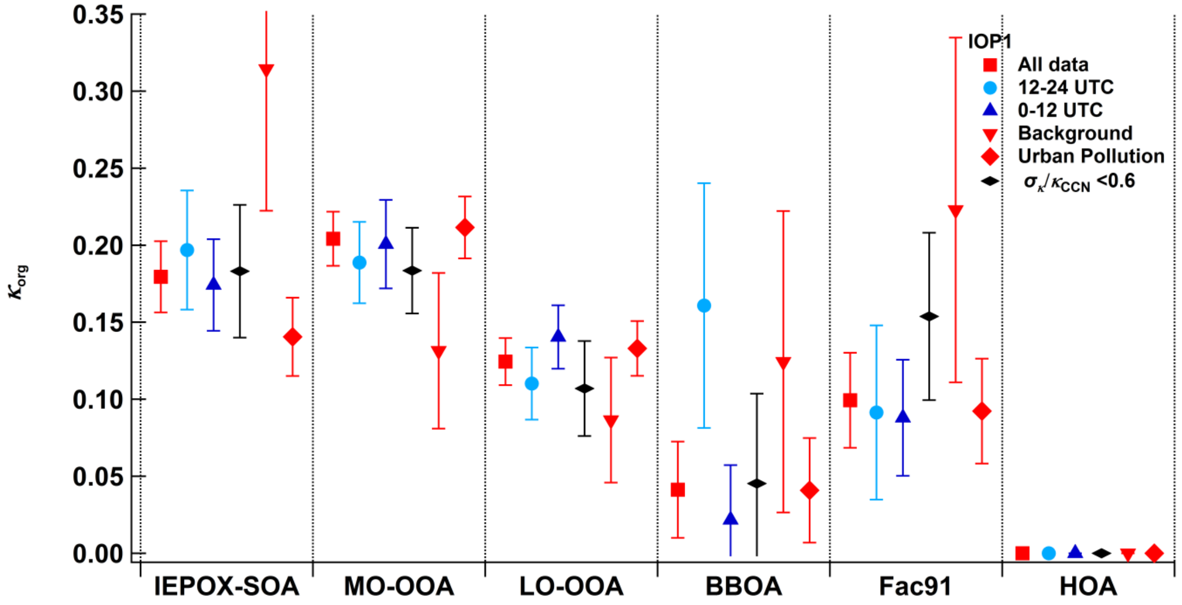


Figure 8: Comparison κ_{CCN} values derived from measurements at the T0a (ATTO) site (Pöhlker et al., 2016) and at the T3 site under background conditions (this study) during the (a) wet season (April and May 2014) and (b) dry season. The size resolved CCN data at T0a was collected by stepping the particle size at given CCNC supersaturations (Rose et al., 2008b). Data displayed for T0a is averaged over critical particle diameters ranging from 44 to 175 nm, while the T3 data is averaged from measurements at 112, 142, and 171 nm.



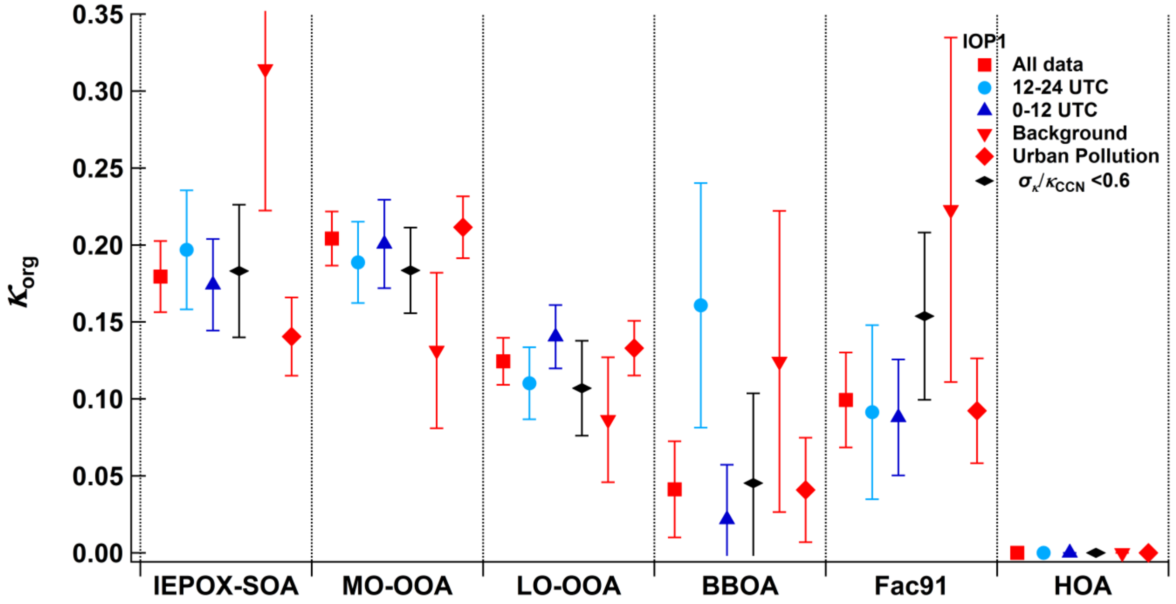


Figure 9: Hygroscopicity of AMS PMF factors for IOP1 (i.e., wet season) retrieved by multi-linear regressions using all data (red square), data from UTC 12:00-24:00 (cyan circle), data from UTC 0:00-12:00 (blue triangle), data under background conditions (red triangle), data un-

der polluted conditions (red diamond), and data with hygroscopicity dispersion $\sigma_{\kappa_{CCN}} / \overline{\kappa}_{CCN}$ less than 0.6 (black diamond).

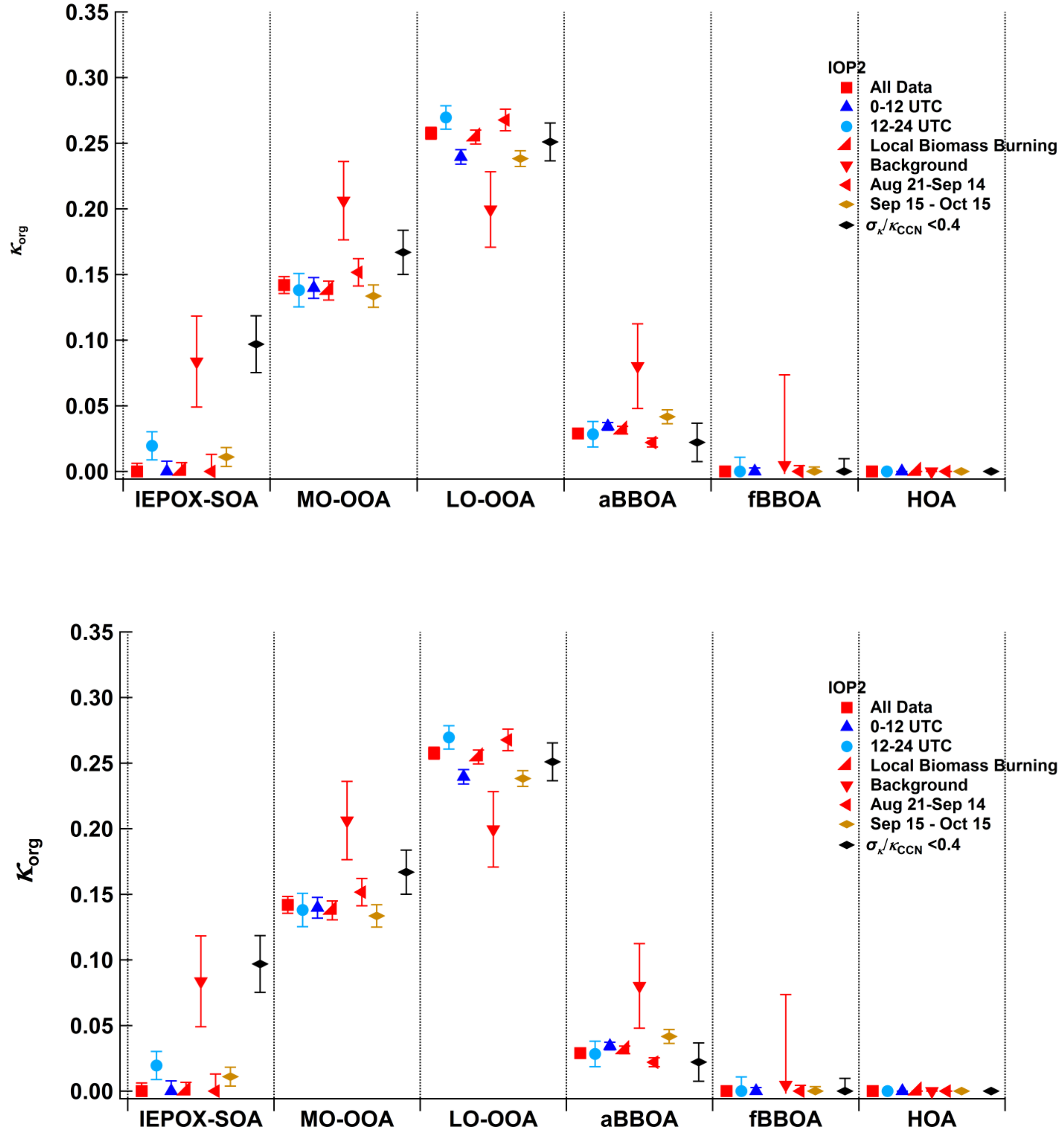


Figure 10: Hygroscopicity of PMF factors for IOP2 (i.e., dry season) retrieved by multi-linear regressions using all data (red square), data from UTC 12:00-24:00 (cyan circle), data from UTC 0:00-12:00 (blue triangle), data with strong influence from local biomass burning (red right triangle), data under background conditions (red upside-down triangle), data from Aug 21 to Sep

14, 2014 only (red left pointing triangle), data from Sep 15 to Oct 15 only (brown diamond), and data with a dispersion ($\sigma_{\kappa_{CCN}} / \bar{\kappa}_{CCN}$) < 0.4 (black diamond).

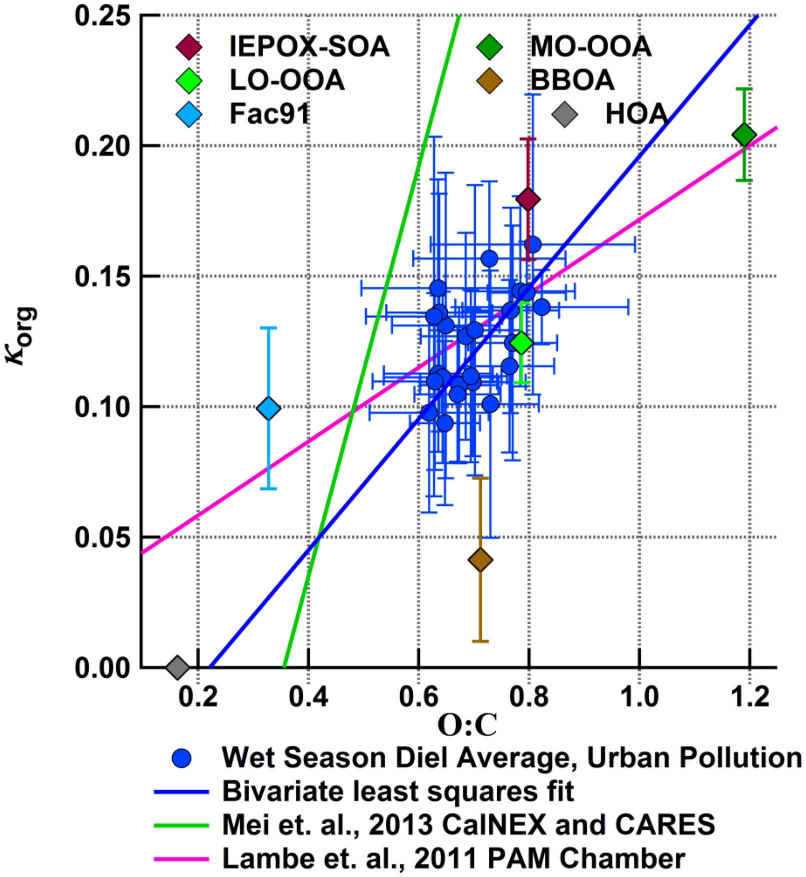


Figure 11: The variation of PMF factor hygroscopicity, 1-hour diel average of organic hygroscopicity and O:C ratio at 142 and 171 nm for urban pollution air masses. Also shown are the relationships between κ_{org} and O:C reported by earlier field and laboratory studies.

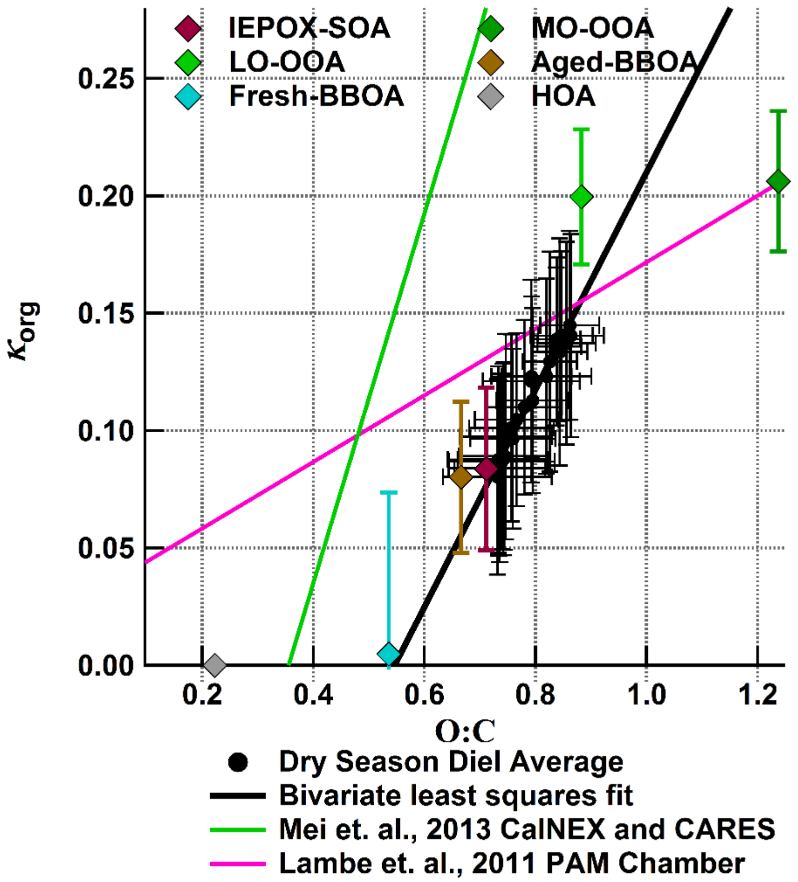


Figure 12: The variation of PMF factor hygroscopicity, 1-hour diel average of organic hygroscopicity, and O:C ratio at 142 and 171 nm for local biomass burning air masses. Also shown are the relationships between κ_{org} and O:C reported by earlier field and laboratory studies.

Supplement to:

CCN activity and organic hygroscopicity of aerosols downwind of an urban region in central Amazonia: Seasonal and diel variations and impact of anthropogenic emissions

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1 Calibration and Operation of the CCN counter

The system used to measure size-resolved CCN spectra during GoAmazon 2014/5 is shown in Fig. S1, and the operation sequences of DMA classified particle diameter, Q_{CCN} and ΔT are present in Fig. S2. The CCN counter was calibrated at each flow and temperature setting using ammonium sulfate as an inorganic aerosol standard (Lance et al., 2006; Mei et al., 2013; Roberts and Nenes, 2005; Shilling et al., 2007). As the temperatures at the top of the CCN counter column (T_1) varies with room temperature, the calibration was repeated for each pair of Q_{CCN} and ΔT over a range of T_1 typically encountered during GoAmazon 2014/5. The calibration results are shown as a function of Q_{CCN} and ΔT conditions at T_1 = 25°C in Fig. S3, and the variation of instrument supersaturation (SS) with respect to T_1 is present in Fig. S4. Instrument supersaturation during the measurements was calculated using the Q_{CCN}, ΔT, and T_1 based on the calibrations.

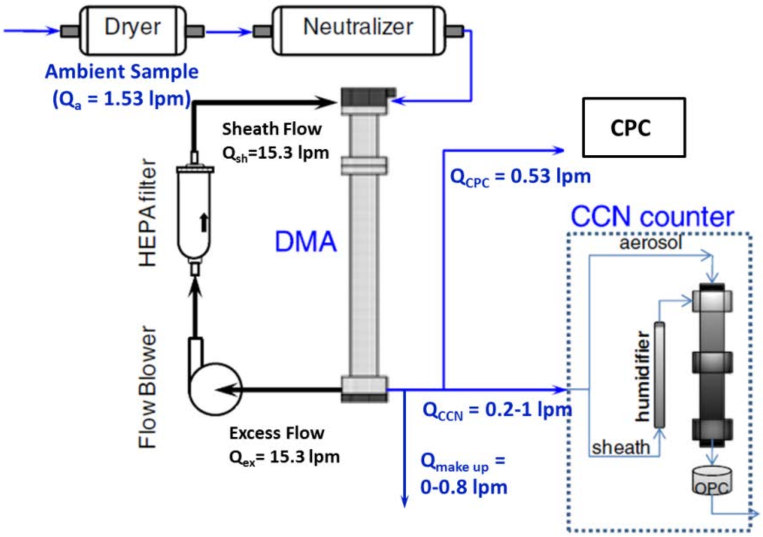

Figure S1: Schematic of the system for measuring size-resolved CCN spectra during GoAmazon 2014/5.

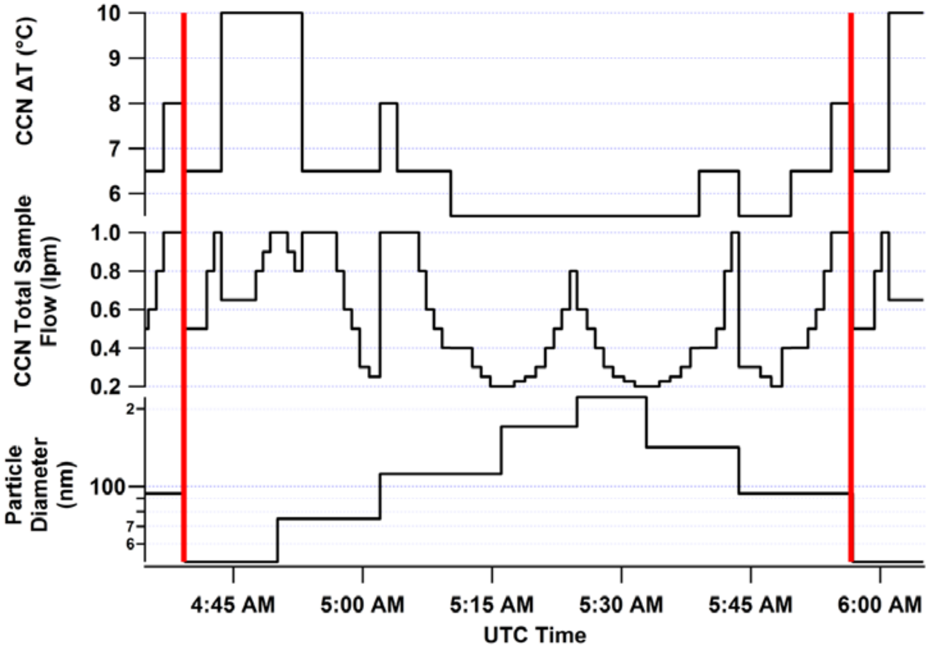

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Figure S2: Instrument operation sequence showing set points of DMA classified particle diameter, Q_{CCN} and ΔT for one full measurement cycle. Red vertical lines mark the start and finish of one cycle.

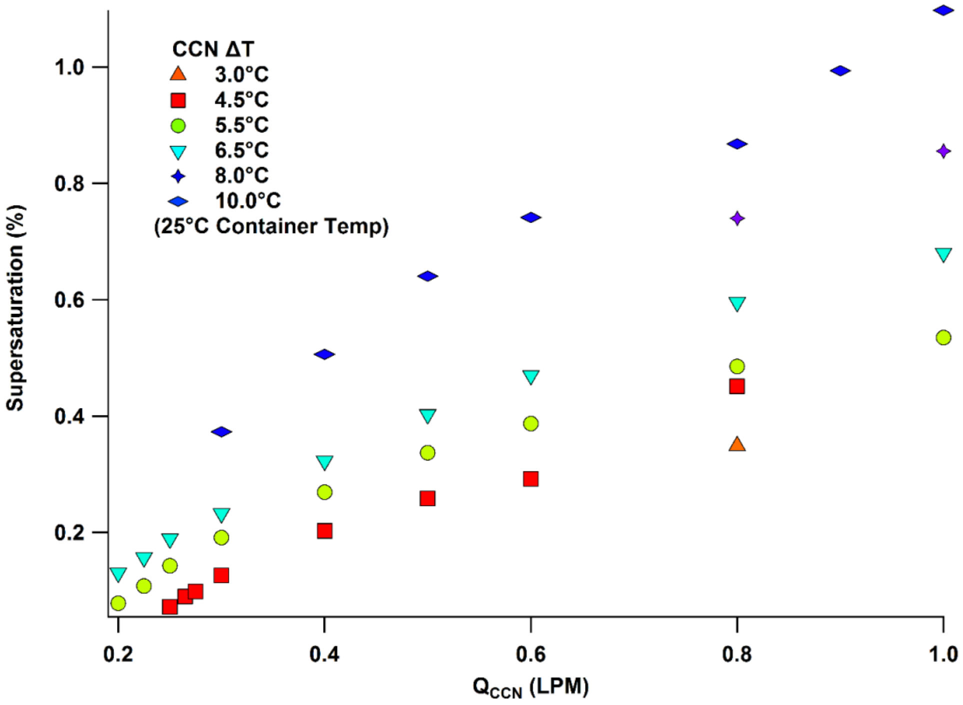

Figure S3: Calibrated CCN counter supersaturation as a function of ΔT at T_1 of 25°C for Q_{CCN} ranging from 0.2 to 1.0 LPM.

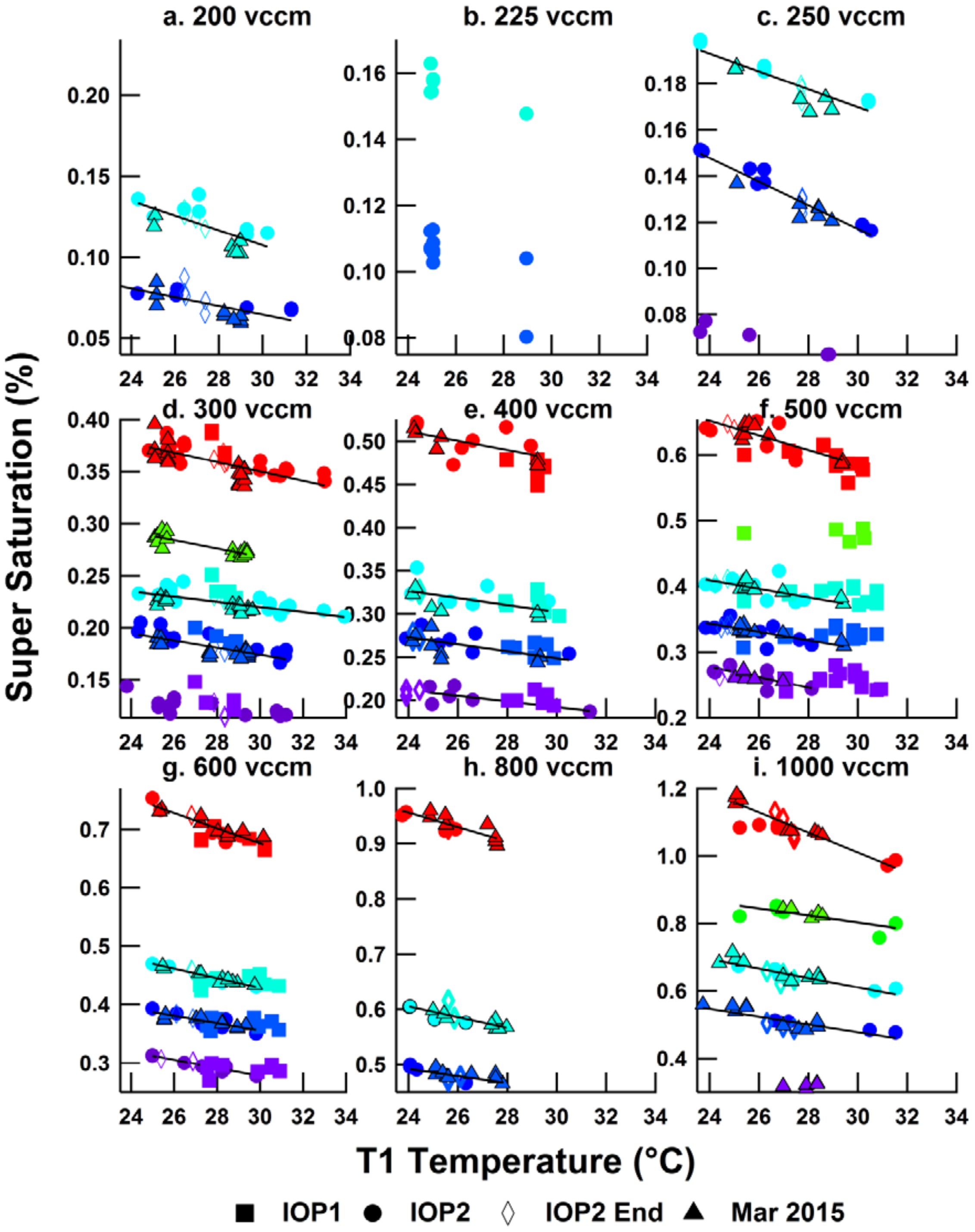

Figure S4: Calibrated instrument supersaturation as a function of T_1 for different ΔT and Q_{CCN} values. The symbol colors of purple, dark blue, light blue, green and red correspond to ΔT values of 4.5, 5.5, 6.5, 8.0, and 10.0°C, respectively. Calibrations were carried out throughout the entire campaign (February/March 2014 - ■; August 2014 - ●; October 2014 - ◊; March 2015 - ▲). The lines represent least square fits of the calibration results.

2 ARM Facility Instruments

2.1 Measurements of Oxides of Nitrogen

Oxides of nitrogen were measured by catalytic conversion to NO and chemiluminescence at one minute time resolution. The NO/NO_2/NO_y system is based on two Thermo Scientific 43i instruments and customized by Air Quality Design, Inc. (Wheatridge, CO) for detection of NO. The inlet/converter box is external and located at 10 meters above ground level and is environmentally controlled. A dedicated channel converts total NOy (NO + NO_2 + HNO_3 + peroxy acyl nitrates + aerosol nitrates, but not NH_4) to NO via a Mo catalyst heated to 325°C. A second channel converts NO_2 to NO by a light emitting diode (LED) photolysis cell with 50% conversion efficiency (C.E.). The LED is toggled on and off on a two minute cycle to measure ambient NO and NO + C.E.× NO_2, and the NO_2 mixing ratio is derived from the difference of the measurements. The inlet box contains mass flow controllers (MFCs) so that the residence time to the chemiluminescence cells is minimal and occurs at reduced pressure. The unit is calibrated daily with standard additions of NO and NO_2 to measure the conversion efficiency of both the Mo converter (1.00±0.02) and the photolysis cell.

2.2 Refractory Black Carbon Measurements

The incandescence signal measured by SP2 is proportional to the mass of rBC in the particles irrespective of whether the rBC is coated or not (Moteki et al., 2007; Schwarz et al., 2010; Stephens et al., 2003). The SP2 was calibrated using size-selected fullerene soot with no corrections for non-rBC content. The detectable size range of the SP2 is 75 – 600 nm (volume equivalent diameter), which typically provides a direct measurement of > 90% of rBC mass concentrations. If necessary, the complete mass size distribution is extrapolated to include rBC outside of this size range assuming a log-normal distribution (Mei et al., 2013). During

GoAmazon 2014/5, rBC mass was mostly within the detectable range. In contrast to the SP2, the seven-wavelength Aethalometer (Arnott et al., 2005; Hansen et al., 1984) reports an equivalent black carbon mass loading by converting a light absorption measurement from aerosols accumulated on a filter relative to a manufacturer-supplied conversion. However, there is substantial and growing evidence relating to measurement artifacts attributed to aerosol loading effects and enhanced light absorption through multiple-scattering of photons (Collaud Coen et al., 2010; Rizzo et al., 2011; Schmid et al., 2006; Virkkula et al., 2015; Virkkula et al., 2007; Weingartner et al., 2003). Given the more complete dataset of the Aethalometer, our analysis utilized the Aethalometer data only when SP2 data was unavailable. The available concurrent SP2 and Aethalometer datasets were used to derive a linear relationship to correct for Aethalometer measurement artifacts cited above. The mass concentrations of refractory black carbon (rBC) derived from SP2 and Aethalometer data were averaged to a common time base and the least square linear fit between both rBC mass concentrations is shown in Fig. S5 for both the wet and dry seasons. The linear relationship exhibited a seasonal dependence, which might be driven by variations in RH, the ratio of mass concentrations of organics to BC, or a combination of both. The rBC mass concentration derived from the Aethalometer measurement was used to fill the gaps in the SP2 data after scaled using the linear relationship corresponding to the respective season.

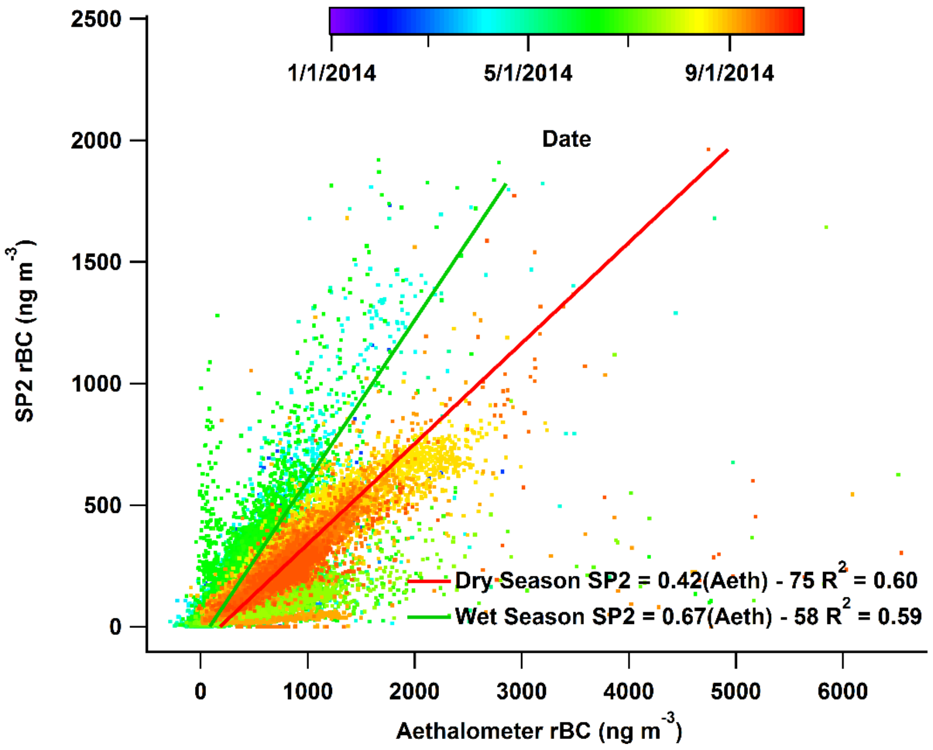

Figure S5: Correlation between rBC mass concentrations derived from the Aethalometer and SP2 measurements. Data points are colored by the time of the measurements. The red and green lines represent least square fit of data collected during the dry and wet seasons, respectively.

3 Reduction of the size resolved CCN activation spectrum

3.1 Correction for multiple charging

Size-resolved CCN activation fraction was characterized at particle diameters of 51, 75, 94, 112, 142, 171 and 222 nm. These sampling sizes were selected to form a progression of particle diameters corresponding to doubly and triply charged particles (e.g. 112 nm corresponds to the diameter of doubly charged particles, when the DMA is set to select particles with a diameter of 75 nm. See Table S1 for more details). The contribution of doubly and triply charged particles to the activation fraction was corrected using the size distribution measured by the SMPS (Model 3080 TSI, Inc) in MAOS and particle charging probabilities (Wiedensohler, 1988). In cases when the size distribution data were not available, we used the concentrations of classified particles measured by the CPC in the size-resolved CCN system when sampling at corresponding multiple-charged sizes. The impact of multiple-charged particles on activation fraction was then accounted for using the concentration of multiple-charged particles and the measured activation fractions at the corresponding sizes. This is similar to the methods established in the literature (Rose et al., 2008). When direct measurements of the activation fraction of multiple charged particles were not available, the multiple charged particles were assumed to have the same distribution of κ as the singly charge particles, and the activation fraction was corrected using the following iterative approach. First, the activation fractions of multiple charged particles were derived from the measured activation factions, taken into consideration the same κ distribution but larger particle diameters. These derived activation fractions at multiple charged sizes were then used to correct measured activation fraction using the approach described above. This process was continued until the corrected activation fraction of singly charged particles converged.

3.2 Data quality control criteria

Several quality-control criteria were applied to the data and results from the fitting of activation spectrum. The measurement of the entire activation spectrum at a single particle diameter took about 5-20 minutes. Individual points (i.e., activation fraction at a single S) of an activation spectrum were excluded from the fitting if the standard deviation of 1-sec measurements of the classified particle concentration is greater than 30% of the mean value for the current size, or single data points are more than 1.5 times the mean. This is to remove large fluctuation or spikes in CPC concentration due to contamination by emission of site generator or traffic. The removal of measurement at single supersaturation typically does not prevent fitting of the activation spectrum using data at remaining supersaturation points. Parameters derived from the fitting of activation spectrum were flagged and excluded from further analysis in this study for the following scenarios:

1. The fitted S^* is outside the supersaturation range of the measured activation spectrum.
2. The fitted maximum activated fraction (E) is not within 15% of any activated fraction measured at the three highest supersaturations. This indicates that the activation fraction did not reach a plateau even at the highest supersaturations sampled, and therefore E is not well constrained by the activation spectrum.
3. The residue of the fit is greater than 0.1. This indicates relatively poor fit, which represented less 1% of the activation spectra.
4. The fitted E is less than 0.5, indicating external mixtures with substantial fraction of fresh black carbon and primary organic aerosols emitted by the generator, vehicles, and grass cutting activities at or near the site.

For the one-year measurement period, 6.5 % of the total activation curves were removed by the above data quality filters.

3.4 Deriving average particle hygroscopicity and hygroscopicity dispersion from activation spectrum

For particles with the same size and composition (i.e., hygroscopicity), a step increase of R_a from 0% to 100% with increasing supersaturation is expected because all particles would have the identical critical supersaturation (S_c). The measurements of ambient aerosols show more gradual increase in R_a (i.e., instead of a step change), suggesting heterogeneity in particle S_c. The heterogeneity in particle S_c, as described by σ_s is due to a combination of width of DMA transfer function (particles classified by a DMA do not have exactly the same size), instrument non-idealities, and the heterogeneity in particle hygroscopicity. The value of σ_s due to the heterogeneity in particle hygroscopicity alone can be estimated by:

$$\sigma_s = \sqrt{\sigma_{s,\mathrm{m}}^2 - \sigma_{s,\mathrm{AS}}^2} \tag{S1}$$

Where $\sigma_{s,\mathrm{m}}$ and $\sigma_{s,\mathrm{AS}}$ are the values corresponding to the ambient measurement and the calibration using ammonium sulfate, respectively (Supplementary Information, Mei et al., 2013). Particle critical supersaturation S_c is related to hygroscopicity κ by (Petters and Kreidenweis, 2007):

$$S_\mathrm{c}(\kappa) = \left(\frac{4A^3}{27D_\mathrm{p}^3\kappa}\right)^{1/2}, \quad A = \frac{4\sigma_\mathrm{w}M_\mathrm{w}}{RT\rho_\mathrm{w}} \tag{S2}$$

Where D_p is the particle diameter, M_w, ρ_w and σ_w are the molecular weight, density and surface tension of water, respectively. The probability distribution function of particle hygroscopicity $p(\kappa)$ can be derived as the following:

$$p(\kappa) = -\frac{dR_\mathrm{a}\left(S_\mathrm{c}(\kappa)\right)}{d\kappa} \tag{S3}$$

Where R_a is the fitted active spectrum with σ_s adjusted using Eq. (S1). We note that Eq. (S2) represents an approximation (Petters and Kreidenweis, 2007). For this study, the uncertainty of derived κ values due to this approximation is negligible. The dispersion of κ, which describes the heterogeneity of hygroscopicity for activated particles, is given by (Mei et al., 2013):

$$\sigma(\kappa)/\overline{\kappa_\mathrm{CCN}} = \left[\exp\left(4\sigma_s^2\right) - 1\right]^{1/2} \tag{S4}$$

where $\sigma(\kappa)$ and $\overline{\kappa_{\mathrm{CCN}}}$ are the standard deviation and average value of the hygroscopicity for activated particles.

It is worth noting that because of the skewness of the lognormal distribution, the average particle hygroscopicity $\overline{\kappa_{\mathrm{CCN}}}$ is higher than κ*, which corresponds to the fitted S*, and represents the median hygroscopicity of activated particles (Fig. S6). The difference between $\overline{\kappa_{\mathrm{CCN}}}$ and κ* becomes significant at high σ_s values (Fig. S7). In this study, $\overline{\kappa_{\mathrm{CCN}}}$ is derived from the probability density function using the following equation:

$$\overline{\kappa_{\mathrm{CCN}}} = \frac{\int_0^{0.65} \kappa \cdot p(\kappa)\, d\kappa}{\int_0^{0.65} p(\kappa)\, d\kappa} \qquad \text{(S5)}$$

The upper limit of the integration is limited to 0.65, which reflects the maximum particle hygroscopicity expected at the T3 site. The organic hygroscopicity is derived from the average particle hygroscopicity $\overline{\kappa_{\mathrm{CCN}}}$ and average chemical composition.

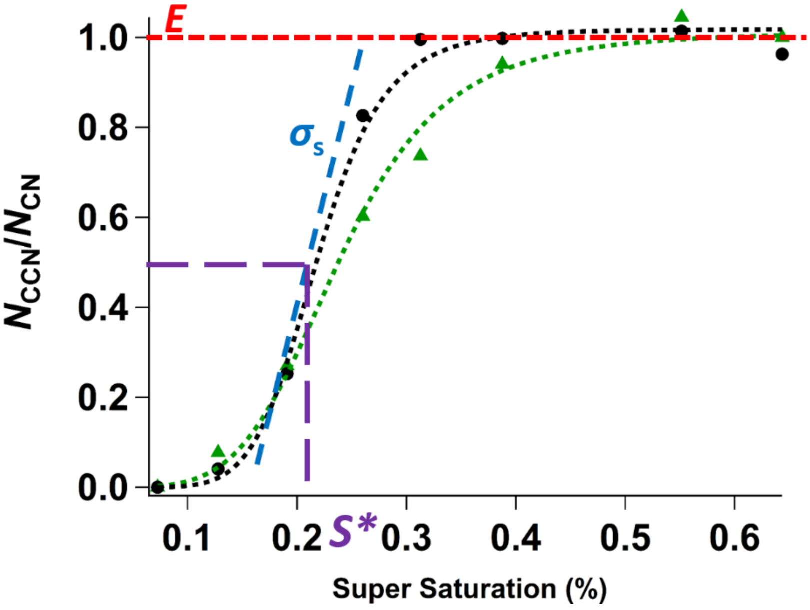

Figure S6: Sample activation spectra for particles with diameter of 142 nm. The black dots and green triangles represent spectra with a low dispersion (σ_s = 0.2; $\sigma\left(\kappa\right)/\overline{\kappa_{\mathrm{CCN}}}=0.4$) and a much higher dispersion (σ_s = 0.4; $\sigma\left(\kappa\right)/\overline{\kappa_{\mathrm{CCN}}}=0.9$), respectively.

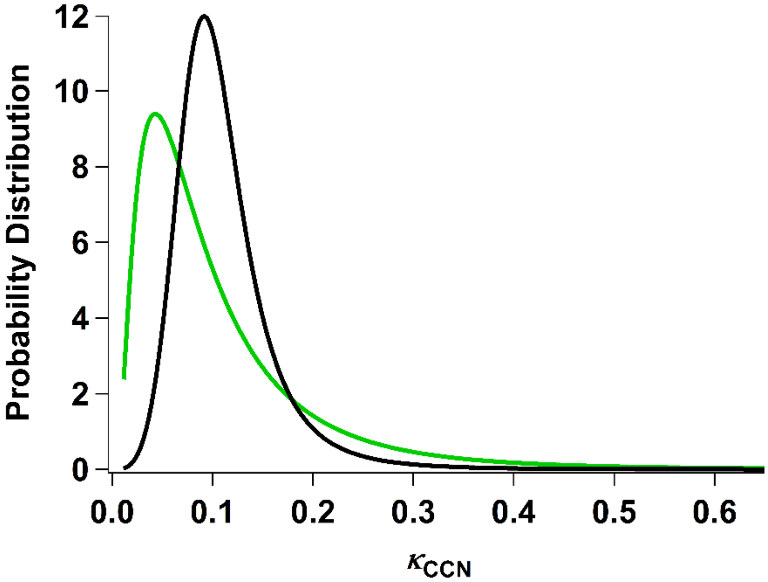

Figure S7: Probability density distributions of particle hygroscopicity derived from the fitted activation spectra shown in Figure S6. As dispersion increases, the distribution becomes increasingly asymmetric, and the difference between $\overline{\kappa_{\mathrm{CCN}}}$ and κ* increases.

4 Aerosol composition derived from AMS and rBC measurements

4.1 Bulk and size-resolved mass concentration of aerosol species

Given the very low aerosol mass concentration in the Amazon basin, the signal to noise ratio of particle time-of-flight (P-ToF) mode measurement was not sufficient to directly provide size resolved species mass concentrations for individual CCN activation spectrum. Instead, the size resolved species mass concentrations were constructed by combing the bulk mass concentrations measured in MS mode, which have higher signal to noise ratio, and P-ToF mode size resolved species mass distributions averaged over extended time periods. For both IOPs, the bulk organics mass fraction was derived from MS mode portion of individual AMS measurement. Based on the bulk organic mass fraction, measurements during IOP1 were then classified into three groups with equal number of measurements, and the characteristic mass size distribution of each species (i.e., organics, SO_4, NO_3, and NH_4) was averaged from P-ToF measurements within each group. For IOP2, the measurements were classified into three groups each for day and night periods based on the bulk aerosol organic mass fraction, and the mass size distribution of each species was averaged from P-ToF measurements in each of the six groups. The average mass size distributions of the four species for the three groups during the daytime of IOP2 are shown in Fig. S8 as examples. The underlying assumption is that observed aerosols exhibiting similar bulk composition (i.e., organic mass fraction) during the IOPs also had species mass size distributions with the same shapes. The vacuum aerodynamic diameter (D_{va}) measured by the AMS was converted to particle mobility diameter (D_{m}) and volume equivalent diameter (D_{v}) using the particle density with the assumption of spherical particles, which is reasonable given most of the aerosol observed at T3 site were quite aged. The average densities were calculated using the approach described in Kuwata et al. (2012), and were 1.45 µg m^3 and 1.47 during IOP 1 and 2, respectively. In this study, unless otherwise indicated, particle diameter D_{p} represents the mobility diameter (D_m), which is equivalent to the volume average diameter given the assumption of spherical particles.

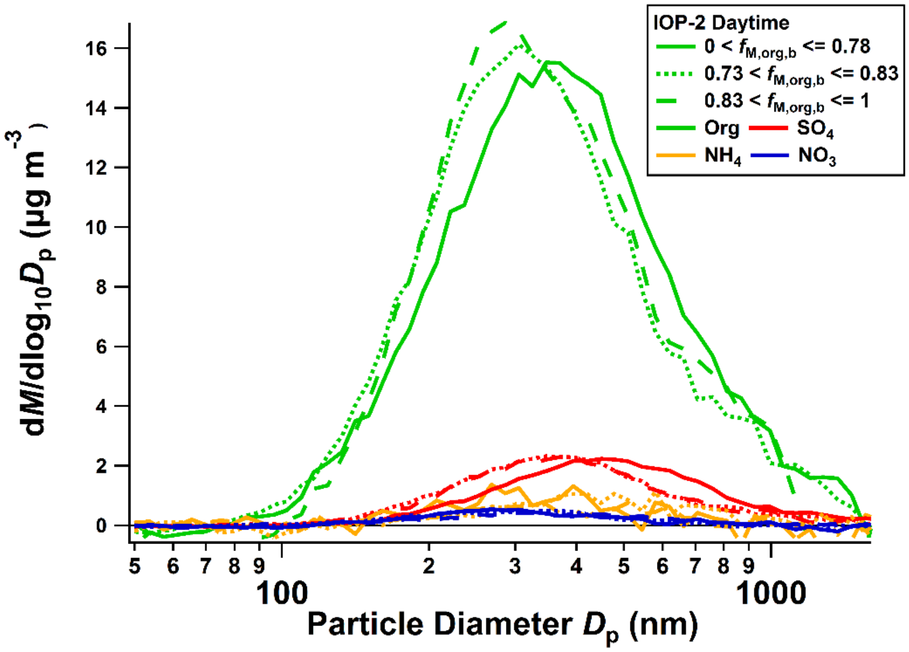

Figure S8: Size resolved mass concentrations of organics, SO$_4$, NO$_3$, and NH$_4$ averaged from P-ToF measurements for each of three groups during the day time of IOP2 (dry season). The three groups were classified based on bulk organics mass fraction ($f_{M,org}$).

For individual AMS measurements, the size resolve chemical composition was then derived as follows: the organic mass concentration at the particle diameter of CCN measurements, $m_{org}\left(D_p\right)$, was calculated as:

$$m_{org}\left(D_p\right)=M_{org,b}\times\frac{\overline{m}_{org}\left(D_p\right)}{\int_{D_{p,\max}}^{D_{p,\max}}\overline{m}_{org}\left(D_p^{'}\right)d\log D_p^{'}}\qquad\text{(S6)}$$

where $M_{org,b}$ is the bulk organic mass concentration from MS mode measurement, $\overline{m}_{org}(D_p)$ is the average organic mass size distribution with respect to $\log D_p$, $D_{p,\max}$ and $D_{p,\min}$ are the maximum and minimum diameters of the average mass size distribution. Using the same approach, the mass concentration of $\mathrm{SO_4^{2-}}$, $\mathrm{NO_3^-}$, and $\mathrm{NH_4^+}$ at specific D_p are calculated using the corresponding average mass size distributions. Mass concentration for black carbon $m_{rBC}(D_\mathrm{p})$ is derived with the assumption that the mass size distribution of rBC has the same shape of the total mass size distribution:

$$f_{M,rBC} = \frac{M_{rBC,b}}{M_{total,b}} = \frac{m_{rBC}(D_p)}{m_{\mathrm{SO_4^{2-}}}\left(D_p\right) + m_{\mathrm{NO_3^-}}\left(D_p\right) + m_{\mathrm{NH_4^+}}\left(D_p\right) + m_{org}(D_p) + m_{rBC}(D_p)} \qquad \text{(S7)}$$

where $f_{M,rBC}$ is the bulk mass fraction of refractory black carbon, $M_{rBC,b}$ and $M_{total,b}$ are the bulk rBC and total aerosol mass concentrations, respectively. From Eq. (S7), $m_{rBC}(D_p)$ can be derived as:

$$m_{rBC}\left(D_p\right) = \frac{f_{M,rBC}\left[m_{\mathrm{SO_4^{2-}}}\left(D_p\right) + m_{\mathrm{NO_3^-}}\left(D_p\right) + m_{\mathrm{NH_4^+}}\left(D_p\right) + m_{org}\left(D_p\right)\right]}{\left(1 - f_{M,rBC}\right)} \qquad \text{(S8)}$$

The fractional chemical composition at the size of CCN measurement D_p was then derived from the species mass concentrations calculated above. While not perfect, this approach allowed us to take both the temporal variation and size dependence of species mass concentrations into consideration when deriving particle composition at the sizes of CCN measurements. This is important because the organic volume fraction, required to derive the organic hygroscopicity was often much higher at the sizes of CCN measurements than that based on the bulk measurements.

4.2 Sulfate and nitrate

Outside of the IOP periods, particle composition was derived from ACSM data, and the retrieval of organonitrate mass concentration is not available. In addition, the detection limit of NH_4^+ for the ACSM is very high, such that the measurement of NH_4^+ mass concentration was too noisy for determining aerosol ionic balance. The sensitivity of derived κ_{org} to the assumption on nitrate was examined using the AMS data from the two IOPs to inform the appropriate assumptions for the analysis outside the IOP periods. Organic hygroscopicity was calculated using three different approaches: (1) the approach based on the retrievals of both inorganic and organic nitrate mass concentrations from AMS, as described in section 3.2 of the main text, (2) all NO_3^- was assumed from NH_4NO_3 and all sulfate from ammonium sulfate, and (3) all NO_3^- was from organonitrate with all sulfate from ammonium sulfate. κ_{org} derived using the three different assumptions are shown in Figure S9 for both IOPs. When all NO_3^- is assumed from organonitrate (i.e., approach 3), the derived κ_{org} values are very close to those based on retrieved organonitrate and inorganic nitrate concentrations from AMS data (i.e., approach 1). As a result, for measurements outside of the two IOPs when only ACSM measurements are available, all measured NO_3^- was assumed from organonitrate and sulfate was assumed from ammonium sulfate.

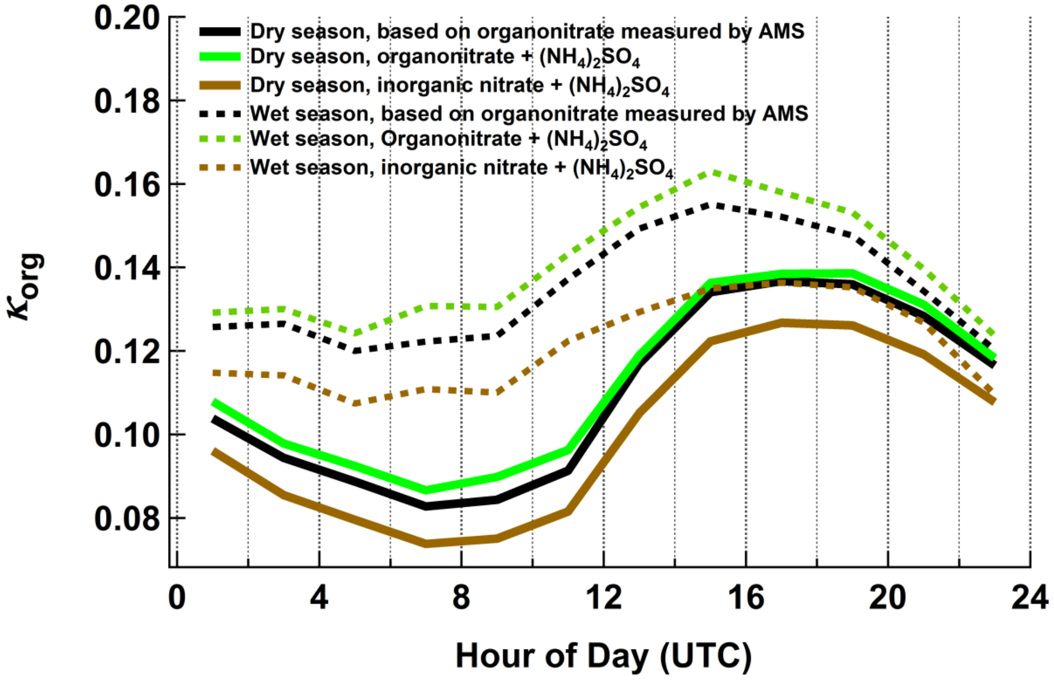

Figure S9: Diel variations of organic hygroscopicity derived using the three different assumptions on nitrate described in the text (i.e., mixed inorganic/organic nitrates, all organic nitrate, and all inorganic nitrate).

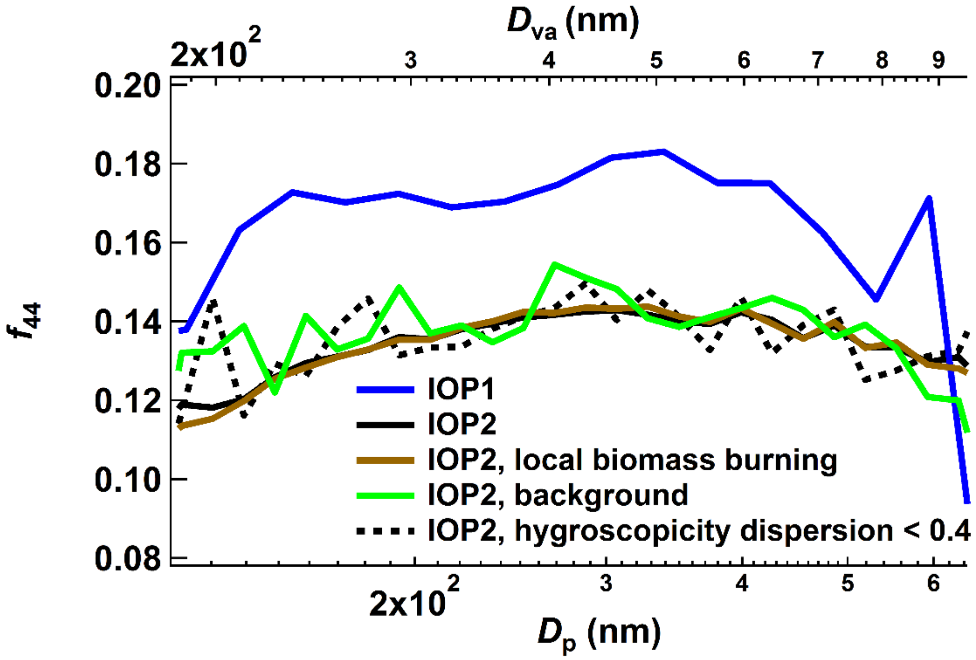

Figure S10: Size dependence of the fraction of the organic mass at m/z = 44 (f_{44}), which is indicative of the extent of oxidation. The f_{44} averaged during IOP1 was essentially independent of particle diameter D_p from 140 to 400 nm, a size range that dominated bulk organic mass concentration and encompasses the diameters of CCN measurements (i.e., 142 and 171 nm). During the IOP2, f_{44} averaged for all data and local biomass burning air mass type showed a clear dependence on D_p. In comparison, f_{44} averaged for the background condition and the periods with low hygroscopicity dispersion ($\sigma_{\bar{\kappa}}/\bar{\kappa} < 0.4$) during IOP2 had lower signal to noise ratio due to the low mass loading, but were largely independent of particle size.

Tables

Table S1: Particle diameter classified by the DMA and the corresponding diameters for doubly and triply charged particles. Diameters in the parenthesis represent the measurements (if available) used to correct the contribution of doubly and triply charged particles to the measured activation fractions.

DMA classified singly charged particles, D_p (nm)	Doubly charged particles D_p (nm)	Triply charged particles D_p (nm)
51	75 (75)	94 (94)
75	112 (112)	142 (142)
94	142 (142)	182(171)
112	171 (171)	222 (222)
142	221 (222)	293 (N/A)
171	272 (N/A)	365 (N/A)
222	364 (N/A)	498 (N/A)

Table S2: Criteria used to classify air mass type for different seasons. The threshold values of CN and CO concentrations used to identify background conditions are the mean plus one standard deviation of respective measurements at the background sites T0a and T0t.

Air mass type	Season			
	Wet/Wet 2	Transition 1	Dry	Transition 2
Background	CN<500 cm^{-3} CO<0.14 ppm NO_y<1.5ppbv	CN<900 cm^{-3} CO<0.14 ppm NO_y<1.5ppbv	CN<1500 cm^{-3} NO_y<1.5ppbv	CN<1500 cm^{-3} NO_y<1.5ppbv
Urban Pollution	CN>500 cm^{-3} *$f_{<70} > 0.45$	CN>900 cm^{-3} $f_{<70} > 0.45$	CN>1500 cm^{-3} $f_{<70} > 0.45$	CN>1500 cm^{-3} $f_{<70} > 0.45$
Local biomass burning	CN>500 cm^{-3} $f_{<70} < 0.45$ CO>0.14 ppm	CN>900 cm^{-3} $f_{<70} < 0.45$ CO>0.14 ppm	CN>1500 cm^{-3} $f_{<70} < 0.45$	CN>1500 cm^{-3} $f_{<70} < 0.45$
Site Contamination	BC>1 μg m^{-3} CN>10^4 cm^{-3}	BC>1 μg m^{-3} CN>10^4 cm^{-3}	BC>1 μg m^{-3} CN>10^4 cm^{-3}	BC>1 μg m^{-3} CN>10^4 cm^{-3}

* $f_{<70}$: number fraction of particles with diameters less than 70 nm, derived from SMPS measurement.

Table S3: Classification of air masses for size resolved CCN measurements at 112, 142, and 171 nm, and relevant measurements (CN, CO, SMPS, rBC) averaged to 5-min intervals.

Season	Classification	Percentage of air mass types	
		Size resolved CCN	Relevant measurements
Wet Season 2014	Background	10.2%	17.5%
	Urban Pollution	65.1%	63.7%
	Local Biomass Burning	0.7%	0.6%
	Site Contamination	1.1%	1.3%
	Invalid CCN spectra Fit[#]	12.5%	N/A
	Unclassified[$]	10.5%	17.0%
Transition Season 1	Background	8.9%	11.8%
	Urban Pollution	59.2%	59.1%
	Local Biomass Burning	3.4%	3.6%
	Site Contamination	1.0%	1.2%
	Invalid CCN spectra Fit[#]	4.0%	N/A
	Unclassified[$]	23.6%	24.2%
Dry Season	Background	7.9%	9.7%
	Urban Pollution	14.4%	16.4%
	Local Biomass Burning	68.1%	58.6%
	Site Contamination	1.3%	1.1%
	Invalid CCN spectra Fit[#]	2.9%	N/A
	Unclassified[$]	5.5%	14.3%
Transition Season 2	Background	26.5%	26.9%
	Urban Pollution	11.0%	10.1%
	Local Biomass Burning	50.4%	53.8%
	Site Contamination	1.7%	2.0%
	Invalid CCN spectra Fit[#]	3.3%	N/A
	Unclassified[$]	7.0%	7.3%
Wet Season 2015	Background	8.1%	12.6%
	Urban Pollution	39.6%	41.2%
	Local Biomass Burning	25.6%	24.5%
	Site Contamination	0.8%	0.9%
	Invalid CCN spectra Fit[#]	8.3%	N/A
	Unclassified[$]	17.6%	20.8%
Mar 2014 - Mar 2015	Background	12.4%	16.5%
	Urban Pollution	38.5%	41.2%
	Local Biomass Burning	28.4%	24.7%
	Site Contamination	1.2%	1.3%
	Invalid CCN spectra Fit[#]	6.5%	N/A
	Unclassified[$]	13.0%	16.3%

[#] An invalid fit of the CCN actiation spectrum (Sec. S3.2)

[$] One or more of the measurements (CN, SMPS, CO, rBC) neede to classify air mass is missing or air mass is not classifed as one of the four types using the the criteria described in Table S2.

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