UNIVERSIDADE DE SÃO PAULO
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Transporte vertical, processos de crescimento e caracterização de aerossóis na Amazônia

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Vertical transport, growth processes, and aerosol characterization in Amazonia

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"There is perhaps no better demonstration of the folly of human conceits than this distant image of our tiny world. To me, it underscores our responsibility to deal more kindly with one another, and to preserve and cherish the pale blue dot, the only home we've ever known."

Carl Sagan, Pale Blue Dot

Abstract

The Amazon Tall Tower Observatory (ATTO) is a laboratory located in a primary forest region in the Central Amazon, ideal for studying the aerosol properties in the vertical profile, particularly at heights of 60 and 325 m from the ground. In this work, we identify and characterize the processes that control the aerosol population, their physicochemical properties, and the growth of particles in the vertical profile of the boundary layer. Measurements of particle number size distribution, scattering, and radiation absorption were used and the chemical composition of aerosols, together with remote sensing data. The analysis of the occurrence of aerosol particles growth was focused on particles from 10 to 50 nm, with measurements between February 2014 and September 2020. It was observed that in 14 % of the analyzed period (217 in 1596 days) we identified particle growth events, with 88 % of them occurring in the wet season. The diurnal cycle of growth frequency showed that 74 % of them occur during the day, indicating an association with photochemistry and boundary layer evolution. The median growth event rate was 5.2 nm h^{-1} , and the condensation sink during growth was 0.0011 s^{-1} . The relationship of growth events with meteorological variables showed that most event onsets coincide with the occurrence of descending convective currents (63 %). The aerosol chemical composition is mainly dominated by the organic fraction, with 80 % of the mass of PM_{10} . Organic aerosols are determinants of the aerosol scattering coefficient. The average absorption and scattering coefficients, $\sigma_{abs,637nm}$ and $\sigma_{scat,525nm}$, under atmospheric conditions without significant anthropogenic impacts were 0.14 Mm^{-1} and 4.4 Mm^{-1} , respectively. Apparent differences in aerosol physical properties between 60 and 325 m in height were observed for $\sigma_{scat,525nm}$, and aerosol volume. A strong spectral dependence of the mass scattering efficiencies with the incident radiation wavelength was observed, and, in particular, they were significantly larger at 60 m, showing that the aerosol population close to the canopy is more effective in scattering the radiation. In contrast the mass absorption efficiency is similar at the two heights. It was observed that the concentration of aerosols smaller than 50 nm increases with increasing convective activity and lightning occurrence. It was observed that 72 % of aerosol particle transport events occur first at 325 m, which is expected for processes dominated by convective downward currents. In contrast 28 % of the events started at 60 m, and only later were detected at 325 m. The results support the hypothesis of a source of aerosols smaller than 50 nm close to the canopy. We show that the physical characteristics of aerosols at heights of 60 and 325 m are different, with those closest to the canopy being dominated by biogenic emissions and those at 325 m being more processed and influenced by long-range transport.

Keywords: aerosol transport, meteorology, vertical profile, aerosol properties

Resumo

O Observatório da Torre Alta da Amazônia (ATTO) é um laboratório localizado em uma região de floresta primária na Amazonia Central, ideal para o estudo das propriedades de aerossóis ao longo do perfil vertical, em particular a alturas de 60 e 325 m do solo. Neste trabalho, identificamos e caracterizamos os processos que controlam a população de aerossóis, suas propriedades físico-químicas e o crescimento de partículas no perfil vertical da camada limite. Foram utilizadas medidas distribuição de tamanho, espalhamento e absorção de radiação, além da composição química dos aerossóis, conjuntamente a dados de sensoriamento remoto. A análise da ocorrência de crescimento de partículas de aerossol foi focada para partículas de 10 a 50 nm, com medidas entre fevereiro de 2014 a setembro de 2020. Observou-se que em 14 % do período analisado (217 em 1596 dias) identificamos eventos de crescimento de partículas, com 88 % deles ocorrendo na estação chuvosa. O ciclo diurno da frequência de crescimentos mostrou que 74 % deles ocorrem durante o dia, indicando uma associação com a fotoquímica e a evolução da camada limite. A mediana da taxa de eventos de crescimento foi de $5,2 \text{ nm h}^{-1}$ e o *condensation sink* durante o crescimento foi de $0,0011 \text{ s}^{-1}$. A relação dos eventos de crescimento com as variáveis meteorológicas mostrou que a maioria dos inícios dos eventos coincide com a ocorrência de correntes descendentes convectivas (63 %). A composição química do aerossol é principalmente dominada pela fração orgânica, com 80 % da massa do MP_1 . Os aerossóis orgânicos são determinantes no coeficiente de espalhamento dos aerossóis. Os coeficientes médios de absorção e espalhamento, $\sigma_{abs,637nm}$ e $\sigma_{scat,525nm}$, sob condições atmosféricas sem impactos antropogênicos significativos foram de $0,14 \text{ Mm}^{-1}$ e $4,4 \text{ Mm}^{-1}$, respectivamente. Diferenças claras nas propriedades físicas do aerossol entre 60 e 325 m de altura foram observadas para $\sigma_{scat,525nm}$ e o volume do aerossol. Foi observada uma forte dependência espectral das eficiências de espalhamento em massa com o comprimento de onda da radiação incidente e, em particular, eles foram significativamente maiores em 60 m, mostrando que a população de aerossóis próxima ao dossel é mais efetiva no espalhamento da radiação. Em contraste, a eficiência de absorção em massa é semelhante nas duas alturas. Foi observado que a concentração de aerossóis menores que 50 nm aumenta com o aumento da atividade convectiva e ocorrência de relâmpagos. Foi observado que 72 % dos transportes de partículas de aerossol ocorrem primeiro em 325 m, o que é esperado para processos dominados por correntes descendentes convectivas. Em contraste, 28 % dos eventos de transporte começaram primeiro em 60 m, e só mais tarde foram detectados a 325 m. Os resultados suportam a hipótese de uma fonte de aerossóis menores que 50 nm próxima do dossel. Mostramos que as características físicas dos aerossóis a alturas de 60 e 325 m são diferentes, sendo que os mais próximos ao dossel são dominados por emissões biogênicas e aqueles a 325 m são mais processados e influenciados pelo transporte de longo alcance.

Palavras-chave: transporte de aerossol, meteorologia, perfil vertical, propriedades do aerossol

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List of abbreviations and acronyms

AAOD	Absorption Aerosol Optical Depth
ABI	Advanced Baseline Imager
AERONET	Aerosol Robotic Network
AOD	Aerosol Optical Depth
ATN	Light Attenuation
ATTO	Amazon Tall Tower Observatory
BC	Black Carbon
BL	Boundary Layer
BrC	Brown Carbon
CCN	Cloud Condensation Nuclei
CI	Capping Inversion
CPC	Condensation Particle Counter
DMA	Differential Mobility Analyzer
DtoW	Dry-to-Wet season
eBC	Equivalent Black Carbon
EMBRAPA	Brazilian Agricultural Research Corporation
EZ	Entrainment Zone
FD	Frequency Distribution
GLM	Geostationary Lightning Mapper
GOES	Geostationary Operational Environmental Satellite
INPA	National Institute for Amazonian Research

INPE	National Institute for Space Research
IQR	Interquartile Range
ITCZ	Intertropical Convergence Zone
LBA	The Large Scale Biosphere-Atmosphere Experiment in Amazonia
LOD	Limit of Detection
LPM	Liters per Minute
LT	Local Time
MAAP	The Multi-angle Absorption Photometer
MAC	Mass Absorption Coefficient
MAE	Mass Absorption Efficiency
ML	Mixed Layer
MLR	Multiple Linear Regression
MPIC	Max Planck Institut for Chemistry
MSE	Mass Scattering Efficiency
NPF	New Particle Formation
PBL	Planetary Boundary Layer
PNSD	Particle Number Size Distribution
POA	Primary Organic Aerosol
Q-ACSM	Quadrupole Aerosol Chemical Speciation Monitor
RH	Relative Humidity
RL	Residual Layer
RMSE	Root Mean Square Error
SBL	Stable Boundary Layer
SE	Standard Error
SMPS	Scanning Mobility Particle Sizer
SOA	Secondary Organic Aerosol

SP2	Single Particle Soot Photometer
SW	Incoming Solar Shortwave Radiation
TIR	Infrared Brightness Temperature
UEA	Amazon State University
UFAM	Federal University of Amazonas
USP	University of São Paulo
UT	Upper Troposphere
VOC	Volatile Organic Compound
WDA	Wavelength Dependence of the Absorption Ångström Exponent
WtoD	Wet-to-Dry season
ZOTTO	Zotino Tall Tower Observatory

List of symbols

α_{scat}	Mass Scattering Efficiency [$\text{m}^2 \text{g}^{-1}$]
α_{abs}	Mass Absorption Efficiency [$\text{m}^2 \text{g}^{-1}$]
α_{BC}	Mass Absorption Efficiency exclusively due to Black Carbon [$\text{m}^2 \text{g}^{-1}$]
α_{ATN}	Spectral mass-specific attenuation cross-section for the AE33 [$\text{m}^2 \text{g}^{-1} \lambda^{-1}$]
α	Particle Transport Coefficient [$\text{cm}^{-3} \text{s}^{-1}$]
$\tilde{\alpha}_{scat}$	Scattering Ångström Exponent (unitless)
$\tilde{\alpha}_{abs}$	Absorption Ångström Exponent (unitless)
β_i	specific mass scattering efficiency of the <i>i-th</i> chemical species [$\text{m}^2 \text{g}^{-1}$]
Cl^-	Chloride
$\text{CN}_{<50}$	Aerosol particle fraction within the sub-50 nm mode
$\text{CN}_{<40}$	Aerosol particle fraction with diameter smaller than 40 nm
$\text{CN}_{<25}$	Aerosol particle fraction with diameter smaller than 40 nm
c_p	Specific heat at constant pressure
C_s	Mass concentration of the s-esm aerosol chemical component [$\mu\text{g m}^{-3}$]
C_{Org}	Mass concentration of the organic aerosol fraction [$\mu\text{g m}^{-3}$]
C_{Inorg}	Mass concentration of the inorganic aerosol fraction [$\mu\text{g m}^{-3}$]
CS	Condensation Sink [s^{-1}]
CS_{growth}	Average Condensation Sink of the particle growth event [s^{-1}]
D_p	Aerosol particle diameter [nm]
D_{pg}	Median geometric diameter [nm]
D_{dom}	Median geometric diameter inside a given size range [nm]

D_{AIT}	Aitken mode geometric diameter [nm]
D_{ACC}	Accumulation mode geometric diameter [nm]
$D_{CN<50}$	Sub-50 nm geometric diameter [nm]
D_{diff}	Diffusion coefficient of the precursor condensable vapor
e_{vp}	Vapor pressure
$f(D_p, D_i, N_i, \sigma_i)$	Multi-modal log-normal distribution function
g	Asymmetry factor
GR	Growth rate [nm h ⁻¹]
Γ	Lapse rate [6.5 K K m ⁻¹]
H ₂ SO ₄	Sulfuric acid
I_{scat}	Energy scattered by a particle cross-section [W m ²]
I_{abs}	Energy absorbed by a particle cross-section [W m ²]
κ	Size parameter
Kn	Knudsen number
λ	Wavelength [nm]
m	Normalized refractive index of the medium
m_{eBC}	Equivalent Black Carbon mass concentration [$\mu\text{g m}^{-3}$]
NH ₃	Ammonia
NH ₄ ⁺	Ammonium
NO ₃ ⁻	Nitrate
NR ₃	Amine radical
N_t	Total particle number concentration [cm ⁻³]
$N_{<50}$	Aerosol number concentration within the sub-50 nm size mode [cm ⁻³]
N_{AIT}	Aerosol number concentration within the Aitken mode [cm ⁻³]
N_{ACC}	Aerosol number concentration within the accumulation mode [cm ⁻³]
N_{CN}	Median total particle number concentration

$N_{10-400nm}$	Integrated particle number concentration of SMPS measurements
$N_{conc, \sum n-modes}$	Total number concentration obtained by the sum of each log-normal fitted size distributions
N_{ref}	Material's refractive index
p	Ambient pressure
P_{ATTO}	Rainfall/Precipitation
$P(\Theta)$	Phase function
PM_1	Particulate Matter with diameters up to 1μ m.
Q_{scat}	Scattering efficiency (unitless)
Q_{abs}	Absorption efficiency (unitless)
Q_{ext}	Extinction efficiency (unitless)
q_v	Water vapor specific humidity
r	Mixing ratio [g/Kg]
S_t	Total aerosol particle surface area [$\mu m^2 cm^{-3}$]
s_{scat}	Scattering cross-section [m^2]
s_{abs}	Absorption cross-section [m^2]
sg	Geometric cross-sectional area [m^2]
SO_2	Sulfur dioxide
SO_4^{2-}	Sulfate
σ_g	Geometric standard deviation
$\sigma_{CN_{<50}}$	Standard deviation of the $CN_{<50}$ modal fit
σ_{AIT}	Standard deviation of the Aitken modal fit
σ_{ACC}	Standard deviation of the accumulation modal fit
σ_{tot}	Total scattering coefficient [Mm^{-1}]
σ_{scat}	Scattering coefficient [Mm^{-1}]
σ_{bs}	Backscattering coefficient [Mm^{-1}]

σ_{abs}	Absorption coefficient [Mm^{-1}]
σ_{ext}	Extinction coefficient [Mm^{-1}]
σ_{BC}	Absorption coefficient exclusively due to the Black Carbon component [Mm^{-1}]
σ_{BrC}	Absorption coefficient exclusively due to the Brown Carbon component [Mm^{-1}]
t	Time flag
Δt	Temporal difference
T	Ambient temperature in degree Celsius
T_k	Ambient temperature in Kelvin
T_{dp}	Dew point temperature [K]
T_L	Lifting condensation level temperature [K]
θ	Potential temperature [K]
θ_e	Equivalent potential temperature [K]
θ'_e	Detrended equivalent potential temperature [K]
$\Delta\theta'_e$	Anomaly of the equivalent potential temperature (unitless)
V_t	Total aerosol particle volume [$\mu\text{m}^3 \text{ cm}^{-3}$]
ω_0	Single-scattering albedo (unitless)
Z_p	Electrical mobility [$\text{m}^2/(\text{V.s})$]

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Chapter 1

Introduction

The Amazon rain forest is considered an extensive and complex natural laboratory, comprising the most significant plant and animal biodiversity on the planet (HOORN et al., 2010; WITTMANN et al., 2013). The Central Amazonia is one of the few continental areas in which the atmosphere approaches conditions without significant anthropogenic influence during specific periods of the wet season (February to May) (ARTAXO et al., 2013; RIZZO et al., 2013; RIZZO et al., 2018; PÖHLKER et al., 2016; PÖHLKER et al., 2018). The Amazon basin exerts such influence on the atmosphere that it is considered a biogeochemical reactor, regulating local and regional climatic processes (ANDREAE; CRUTZEN, 1997).

Canopy emissions, such as organic gases and aerosols, combined with the high concentration of water vapor and intense solar radiation, resulting in an atmosphere particularly susceptible to different external forcings that may change its composition. Cloud formation induced by evaporation, strong convective systems, and the precipitation are directly connected to the aerosol number concentration in the atmosphere, which regulates the hydrological cycle of the basin (ANDREAE et al., 2001; ANDREAE, 2007). Previous studies have shown that clean atmospheric conditions are similar to those found in pre-industrial revolution periods, with low aerosol concentrations up to sizes of ~ 100 nm, with particle number concentration between 200 to 400 cm^{-3} (MARTIN et al., 2010b; PÖHLKER et al., 2016; RIZZO et al., 2018; PÖHLKER et al., 2018).

Those pristine conditions are obtained under the circumstances that air masses travel through clean oceanic and continental areas, i. e., places without emissions from biomass burning and other pollutants. Furthermore, the constant precipitation along the trajectory influences the wet deposition of aerosols (PÖHLKER et al., 2019). Clean atmosphere conditions are critical for studies of processes that control natural aerosol populations within the Amazon troposphere, i. e., the primary biogenic and secondary organic aerosols (SOA) populations in the Amazon ecosystem.

However, increases in aerosol emissions from biomass burning and urban pollutants have led to evident changes in the Amazon atmosphere (CIRINO et al., 2018; NASCIMENTO

et al., 2021). Even during the wet season and in preserved forest regions, aerosols from human activity can be detected. In particular, the primary sources are associated with heavy fires resulting from the expansion of agriculture through illegal deforestation. During the dry season (August to November), a period when vegetation is more susceptible to burning, the aerosol number concentration can easily reach concentrations higher than 10^3 cm^{-3} (PÖHLKER et al., 2016; RIZZO et al., 2018; HOLANDA et al., 2020).

Figure 1 – Comparative panel of a) aerosol optical depth (AOD) at 500 nm at five sites in Amazonia, b) deforested area, and c) Amazon fire outbreaks from 1999 to 2021. The AOD data were obtained from NASA/AERONET network website. Data on deforestation and fire outbreaks were obtained from INPE's website.

Figure 1 was obtained with remote sensing data from the National Aeronautics and Space Administration (NASA) network called Aerosol Robotic Network (AERONET) and the National Institute for Space Research (INPE). It shows the aerosol optical depth (AOD), the deforested area, and the number of fires in the Amazon between 1999 and 2021. The AOD, as will be discussed in detail in Chapter 4, is an optical property directly related to the vertically integrated radiation scattering in the atmosphere, which also depends on the aerosol number concentration. It is worth noting that the years with the highest deforestation rate and the highest number of fires have the highest AOD. Figure 1 draws attention to the dramatic reduction in deforestation that occurred between 2005 and 2012 due to changes in environmental policy related to law enforcement, interventions in the soy and beef supply

chains, restrictions on access to credit, and expansion of protected areas (NEPSTAD et al., 2009; NEPSTAD et al., 2014).

However, since 2011 the deforested area has started to grow again, which is directly related to an increase in the number of fires. The AOD in Figure 1 also follows the pattern. It is estimated that the total number of fire outbreaks in 2021 will be the highest one in more than 10 years, only comparable to what was observed in 2010. So far, the Brazilian Amazon rain forest has already lost around 20% of its original area (GATTI et al., 2021). New policies to encourage unsustainable exploitation have threatened to drastically increase this percentage, which has worried scientists and environmentalists about the future of the forest and the planet (SAMPAIO et al., 2007; GATTI et al., 2021). Recent studies show that the Amazonia no longer acts as a carbon reservoir. However, now it is a powerful source, which can seriously compromise the atmosphere's energy balance, influencing precipitation occurrence and climate change (GATTI et al., 2021).

Therefore, the study of the aerosol life cycle in Central Amazonia and their physico-chemical properties have a huge scientific relevance. It is directly related to the terrestrial energy balance, which impacts the radiative forcing and which, in turn, has high importance in climatic and cloud formation processes. The following sections explore the aerosol life cycle in Central Amazonia, starting from new particle formation, aiming to understand why this process is not typical in the region, together with these aerosols' physical and chemical characteristics. Finally, the knowledge gaps that are addressed in this study are presented.

1.1 New particle formation and aerosol life cycle in Central Amazonia

New particle formation (NPF) refers to the nucleation of nanometer-sized molecular clusters from gaseous precursors and their subsequent condensational growth (KULMALA et al., 2004; DAL MASO, 2005; KIRKBY et al., 2011; KULMALA et al., 2012; KERMINEN et al., 2018). Under favorable atmospheric conditions, the newly formed particles grow through condensation of semi- and low-volatile gases as well as self-coagulation into the cloud- and, thus, climate-relevant size range with diameters larger than ~ 80 nm (KERMINEN et al., 2018; PÖHLKER et al., 2018).

NPF is a unique process in the atmospheric aerosol life cycle. It has been observed worldwide in the course of ground-based observations in different environments, such as rural and remote continental areas, urban environments, the Arctic and Antarctica, marine areas, and mountain sites (KERMINEN et al., 2018). NPF is regarded as the most crucial contributor to atmospheric aerosol particle number concentrations, with significant relevance for the global cloud condensation nuclei (CCN) budget (MERIKANTO et al., 2009; SPRACKLEN et al., 2008; NIEMINEN et al., 2018; YLI-JUUTI; MOHR; RIIPINEN, 2020).

In the long list of locations worldwide where NPF within the planetary boundary

layer (PBL) has been found (KERMINEN et al., 2018), the Amazon rain forest is a remarkable exception. The characteristic ‘banana plots’ (a banana-shape in the aerosol number size distribution), starting at few nanometers and growing up to ~ 100 nm (KULMALA et al., 2012; KERMINEN et al., 2018) have rarely been observed (ANDREAE, 2013; RIZZO et al., 2018; WIMMER et al., 2018). This striking contrast to other environments has inspired researchers to investigate the underlying mechanisms that could explain the absence of NPF and alternative particle sources that sustain the Amazonian aerosol population. Reasons for the absence of NPF within the PBL could be:

1. A suppression by isoprene (KIENDLER-SCHARR et al., 2009; KANAWADE et al., 2011; MCFIGGANS et al., 2019; YLI-JUUTI; MOHR; RIIPINEN, 2020), which is the most abundant volatile organic compound (VOC) in the Amazonian atmosphere (ANDREAE et al., 2018; YÁÑEZ-SERRANO et al., 2020).
2. The very low concentrations of inorganic precursor gases such as sulfur dioxide (SO_2 , being converted into sulfuric acid H_2SO_4) as well as the bases ammonia (NH_3) and amines (NR_3) (ANDREAE et al., 1990; TREBS et al., 2004), which play critical roles in the binary $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$, and ternary $\text{NH}_3 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ nucleation mechanisms (KIRKBY et al., 2011).
3. The high levels of relative humidity (RH) and ambient temperature (T), which have been associated with a low occurrence of NPF (BONN; MOORTGAT, 2003; HYVÖNEN et al., 2005; HAMED et al., 2011; LEE et al., 2019).

In particular, the role of organic vapor precursors in nanoparticle growth is one of the most uncertain aspects of the process (YLI-JUUTI; MOHR; RIIPINEN, 2020), although recent studies have shown its significance (OLENIUS et al., 2018; MOHR et al., 2019). The occurrence of NPF is strongly dependent on the local conditions of individual sites, including meteorology, ecosystem, and anthropogenic pollution levels. (NIEMINEN et al., 2018) emphasized that the NPF occurrence and growth rates (GR) show a geographically inhomogeneous distribution, indicating that the underlying mechanisms are as manifold as complex. Typical atmospheric GR ranges from 1 to 12 nm h^{-1} (YLI-JUUTI; MOHR; RIIPINEN, 2020).

Measurements at the Zotino Tall Tower Observatory (ZOTTO) in Siberia, for example, showed a remarkably low occurrence of NPF with only 1.5 % of event days and relatively low GR of about 2.4 nm h^{-1} (WIEDENSOHLER et al., 2019). This is in strong contrast to the frequent NPF occurrence in boreal forests of northern Europe, and British Columbia (DAL MASO, 2005; D et al., 2007; KULMALA et al., 2004; KULMALA et al., 2013). Further, different meteorological conditions have been associated with the occurrence of NPF and particle growth. Specifically, photochemical reactions under daytime conditions have been regarded as a driving force for nucleation and condensational growth (NIEMINEN et al.,

Figure 2 – Conceptual scheme of sources, redistribution, and removal of aerosol particles and cloud condensation nuclei (CCN) over the Amazon rain forest. The scheme is inspired by previous conceptual illustrations by KREJCI et al.(2003), ANDREAE et al.(2018), and WILLIAMSON et al.(2019). It further integrates experimental data by WANG et al.(2016a), KREJCI et al.(2003), ANDREAE et al.(2018), BAARS et al.(2012) and WILLIAMSON et al.(2019). The three main categories of aerosol sources in the Amazon are shown in red. Emphasized are the aerosol cycling in the course of deep convective clouds with upward transport of volatile organic compounds (VOC), and aerosol particles, new particle formation within the free troposphere, downward transport with initial particle growth, and eventually downward transport of sub-50 nm particles within the cloud.

2018; KERMINEN et al., 2018; HAMED et al., 2011; MA; BIRMILI, 2015). This is in line with a significantly higher occurrence of NPF under clear sky conditions, as observed in Hyytiälä, Finland (DADA et al., 2017).

In addition, a remarkable association between the occurrence of NPF and convective clouds has been observed at different marine to continental sites (PERRY; HOBBS, 1994; CLARKE, 1992; WADDICOR et al., 2012; REUS et al., 2001; WEHNER et al., 2015; DADA et al., 2017). In particular, in boreal forests, the presence of clouds can be a suppressor factor for NPF, where most of the occurrences were detected under clear sky conditions with lower particle number concentration compared to nonevent days (DADA et al., 2017). Evidences for NPF and convective clouds were also observed in the Amazon, which was reported by ANDREAE et al.(2018). The mechanism is certainly different from that observed in boreal forests since convective downdrafts in tropical regions are associated with an increase in the concentration of fine mode aerosols, which eventually grow to sizes of CCN relevance. While different hypotheses have emerged to explain this phenomenon, the exact mechanisms, the existence of precursors, and the exact locations of the NPF in the context of clouds have remained open(KERMINEN et al., 2018).

NPF has likely been altered during the ongoing industrialization when anthropogenic

emissions started to dominate the atmospheric composition. Relative to remote sites, rural and urban locations tend to show higher NPF frequencies (typically 10 – 30 % event days) and higher particle GR ($4 - 12 \text{ nm h}^{-1}$) (KERMINEN et al., 2018; NIEMINEN et al., 2018). The process is related to the fundamental question of whether the atmospheric concentration of certain, mainly anthropogenically emitted species such as H_2SO_4 , have to exceed certain thresholds for NPF to occur. Recent evidence of pure biogenic ion-induced nucleation under controlled laboratory conditions offers mechanisms for pre-industrial pathways of NPF (KIRKBY et al., 2016; ROSE et al., 2018; ZHAO et al., 2020). Accordingly, environments with low anthropogenic influence are of particular interest to investigate processes under conditions that approximate a pre-industrial state of the atmosphere. Amazonia is an ideal outdoor laboratory for such investigations under pristine conditions (HAMILTON et al., 2014; PÖHLKER et al., 2018).

The contrasting atmospheric states in the seasonal back and forth between the natural and relatively clean wet season versus the anthropogenically polluted dry season makes the central Amazon an exciting region in terms of atmospheric chemistry, aerosol processes, and aerosol-cloud interactions. Of particular relevance is the wet season with its episodic occurrence of pristine periods, which allows studying atmospheric processes - such as the occurrence of sub-50 nm particles ($\text{CN}_{<50}$) - under conditions that approximate a pre-industrial state of the rain forest atmosphere (ANDREAE et al., 2015). At the Amazon Tall Tower Observatory (ATTO) – which is located in mostly untouched rain forest regions and has become a landmark site for atmospheric research (ANDREAE et al., 2015; PÖHLKER et al., 2019) – March to May represent the cleanest months of the year with about 10 % of the time being considered as pristine periods (PÖHLKER et al., 2018).

Figure 2 illustrates the main sources of aerosol particles and CCN in Amazonia, which can be broadly grouped into the following three categories:

1. A broad spectrum of biogenic emissions from the rain forest ecosystem exists, which includes the release of primary biological aerosol particles (e.g., pollen, spores, bacteria, fragments) (PÖHLKER et al., 2012; HUFFMAN et al., 2012; LÖBS et al., 2020; PRASS et al., 2021) as well as the emission of biogenic VOCs followed by their atmospheric oxidation – e.g., in the course of lightning (TOLEDO MACHADO et al., 2021) – and conversion into SOA (CHEN et al., 2015; LIU et al., 2016; SATURNO et al., 2018a; LEPLA et al., 2021).
2. Regional and long-range transport brings substantial amounts of advected African dust and pollution (PÖHLKER et al., 2018; NASCIMENTO et al., 2021; MORAN-ZULOAGA et al., 2018; HOLANDA et al., 2020), as well as biomass burning smoke from fires e.g., in the arc of deforestation into the central basin (ARTAXO et al., 2013).
3. Driven by deep convective clouds, biogenic VOCs are transported into the upper troposphere (UT) ($\sim 10 \text{ km}$), where VOC oxidation, nucleation of new aerosol particles,

and initial particle growth occurs, fostered by low temperatures and a low preexisting aerosol surface area (KREJCI et al., 2003; ANDREAE et al., 2018). Subsequently, the freshly formed particles are mixed downward into the rain forest BL, where they continue to grow to CCN-relevant sizes (KREJCI et al., 2003; WANG et al., 2016a).

Generally, organic aerosols – from primary and secondary sources (POA and SOA) – play key roles in the Amazonian aerosol cycling as they account for significant mass fractions (i.e., fine mode mass fractions of ~80 %) (MARTIN et al., 2010b; PÖSCHL et al., 2010). In terms of number concentration, a significant fraction of the organic aerosol particles likely originates from UT particle production (ANDREAE et al., 2018).

Several studies provide experimental and modeling support for the broad atmospheric relevance of UT particle production and the subsequent vertical mixing of the $CN_{<50}$ (KREJCI et al., 2003; WANG et al., 2016a; ANDREAE et al., 2018; WILLIAMSON et al., 2019; LEINO et al., 2019; ZHAO et al., 2020). Figure 2 visualizes the presence of a UT pool of sub-50 nm particles over the Amazon basin during the wet and dry seasons and an increase in particle diameter (D) with decreasing altitude due to condensational particle growth. Note here the remarkable consistency of the data from various studies, synthesized in Fig. 2. The downward motion of the $CN_{<50}$ can be driven by strong convective downdrafts or weaker downward motions in stratiform cloud regions (WANG et al., 2016a).

Major mechanistic questions on the vertical transport of the $CN_{<50}$ have remained open (TOLEDO MACHADO et al., 2021). ZHAO et al.(2020) recently suggested that pure organic NPF based on biogenic VOCs dominates above 13 km, whereas ternary NPF involving organics and H_2SO_4 dominate between 8 and 13 km. The mechanism corroborates that most of the observed sub-50 nm-Aitken mode particles inside the BL have relatively larger diameters (> 20 nm) due to the aging process while transported from the free troposphere into the BL. It means that the ion-induced biogenic nucleation in the uppermost troposphere potentially plays an important role and, therefore, substantially contributes to the particle population within the free troposphere and inside the PBL (WANG et al., 2016a; ANDREAE et al., 2018; GLICKER et al., 2019).

In addition, recent studies propose potential sources for sub-50 nm particles within the Amazonian PBL (RIZZO et al., 2018; TOLEDO MACHADO et al., 2021). In particular, the occurrence of sub-50 nm particle growth events ('Amazonian banana plots') was studied, which resemble the behavior of 'classical NPF' but starting at much larger initial growth diameters (> 20 nm) (RIZZO et al., 2018). During their long-term observations, these 'Amazonian banana plots' were observed in 3 % of the 749 days, and were associated mainly with convective downdraft. TOLEDO MACHADO et al.(2021) observed an increase of sub-50 nm particles, particularly in the early morning hours, suggesting a connection between those increased concentrations with vertical transport and deep convective clouds, as well as with lightning density. Both studies show the importance of considerable sources of sub-50 nm

particles within the PBL and stress out a potential relevance for subsequent processes like particle growth. That leads to the evidence for further, more detailed studies about the sources, occurrence, and growth of sub-50 nm particles in the Amazonian rain forest.

1.2 Aerosol physicochemical properties in Central Amazonia

Several studies have evaluated atmospheric aerosols' physical and chemical properties in Central Amazonia (RIZZO et al., 2011; ARTAXO et al., 2013; RIZZO et al., 2013; PÖHLKER et al., 2016; RIZZO et al., 2018; SATURNO et al., 2018b). In particular, at the ATTO site, the strong seasonality of the aerosol concentration was characterized, focusing on different aerosol sources (PÖHLKER et al., 2016). In the wet season, under very clean atmosphere conditions (defined as “empirically pristine conditions”, according to PÖHLKER et al. (2016)), the aerosol population is strongly dominated by particles of the Aitken ($D_{AIT} \sim 70$ nm), but also with a significant amount of aerosols of the accumulation mode ($D_{ACC} \sim 160$ nm). Moreover, the total aerosol concentration is of the order of 250 cm^{-3} . However, the aerosol optical properties have not yet been characterized under pristine conditions, which are fundamental in understanding the climatic influence of biogenic SOA.

During the wet season, the average scattering and absorption coefficients at 550 nm and 637 nm, respectively, are 7.5 and 0.68 Mm^{-1} , respectively, with a single scattering albedo, ω_0 , of 0.93 . In contrast, during the dry season, the scattering and absorption coefficients at 550 nm and 637 nm are, respectively, 33.0 and 4.0 Mm^{-1} , with ω_0 of 0.87 . This shows that the aerosols during the wet season have different radiative impacts from those of the dry season (SATURNO et al., 2018b). In addition, during the entire period, approximately 80% of the aerosol mass fraction up to $1 \mu \text{g m}^{-3}$ is dominated by the organic component, followed by sulfate ($\sim 8\%$), ammonia ($\sim 7\%$), and black carbon (BC, $\sim 5\%$) (PÖHLKER et al., 2016; PÖHLKER et al., 2018).

The wet season is also dominated by long-range aerosol plumes, as discussed in the previous section. These particles are also strongly dominated by aerosols of the Aitken and accumulation modes, with D_{AIT} and D_{ACC} of approximately 80 and 180 nm, respectively. Note the difference of up to 20 nm in the accumulation mode for local natural aerosols, indicating the aging effects on these particles. Aerosol concentrations during long-distance transport events can reach 430 cm^{-3} , whose chemical composition is strongly related to dust and sea salt. Coarse mode aerosols also vary significantly during these events (MORAN-ZULOAGA et al., 2018).

The dry season is characterized by an atmosphere strongly dominated by aerosols from biomass burning, although the contribution of long-range transport cannot be neglected (PÖHLKER et al., 2016; HOLANDA et al., 2020). The aerosol population is mainly within the accumulation mode, with $D_{ACC} \sim 170$ nm and an average concentration of $\sim 3500 \text{ cm}^{-3}$.

The results of the aerosol physical properties agree with similar studies conducted at the ZF2 site, located approximately 60 km upwind from Manaus.

Even during the dry season, aerosol populations are susceptible to long-range transport plumes, which have distinct physical characteristics from those emitted in local biomass burning (HOLANDA et al., 2020). In particular, long-range transport aerosol plumes, which are more aged, have higher BC mass concentrations, and curiously, with relatively lower ω_0 than the local biomass burning plumes (HOLANDA et al., 2020). It is worth mentioning the estimation of the mass absorption efficiency specifically due to BC, through measurements of the Single Particle Soot Photometer (SP2) and Aethalometer at the ATTO site. It was shown that, in contrast to the widely used value in the literature ($6.6 \text{ m}^2 \text{ g}^{-1}$), in Central Amazonia, the efficiency varies between 11.4 and $12.3 \text{ m}^2 \text{ g}^{-1}$ in the wet and dry seasons, respectively (SATURNO et al., 2018b). Furthermore, the contribution of the brown carbon (BrC) component, which is the aerosol fraction that absorbs radiation mainly in the near-ultraviolet frequency, to the total absorption was also estimated at 370 nm, which varies between 17 and 29% (first and second quartiles) (SATURNO et al., 2018b).

All studies that characterized long-term physicochemical aerosol properties and sources in Central Amazonia were carried out with *in situ* measurements in only one height profile. In particular, at the ATTO site, these measurements were taken at 60 m height, which is close to the canopy (that is located, on average, at ~ 40 m height). However, there is a lack of studies that assess the vertical aerosol variability along the lower troposphere in the region. It should also be noted that this variability is likely to depend on different sources of aerosols and meteorological factors. With the measurements developed on the 325 m tall ATTO tower, it is possible to characterize the aerosol populations at different height profiles: 60 and 325 m.

Therefore, the studies developed in this thesis address three important knowledge gaps: the identification and characterization of particle growth events within the size range of 10 to 50 nm, their potential sources and relationship with weather conditions; the characterization of aerosol physicochemical properties, focusing on the optical properties under pristine atmosphere conditions, and the variability of aerosol physical properties at 60 and 325 m height; and the relationship between aerosol particle transport, their variability in the vertical profile, and the occurrence of meteorological events such as lightning.

The thesis is organized as follows: Chapter 2 presents the objectives of this study; Chapter 3 discusses theoretical concepts of aerosols and boundary layer (BL) properties that are fundamental to this work; Chapter 4 introduces the experimental site, and data processing and analysis; Chapters 5, 6, and 7 present the results about aerosol particle growth events, physicochemical properties, and the relations between aerosol number concentration, particle transport and meteorology, respectively; and, finally, Chapter 8 concludes the study and presents future research perspectives on the aerosol life cycle in Central Amazonia.

Chapter 2

Objectives

This study aims to identify and characterize processes that control the aerosol population and its physicochemical properties in the vertical profile of the planetary boundary layer in Central Amazonia. In particular, the objective is to identify links between meteorology and aerosol particles transport from the free troposphere to the BL that grow to relevant sizes to act as CCN, which plays an essential role in radiative forcing. The main scientific questions addressed in this thesis can be summarized as:

1. How often and under which conditions do particles grow in the planetary boundary layer in Central Amazonia?
2. How does convective transport control the particle population within the lower Amazonian atmosphere, particularly during the wet season?
3. What are the optical and chemical properties of aerosols under pristine conditions in Central Amazonia?
4. Are there differences in the physicochemical properties and the aerosol concentration in the vertical profile of the lower Amazon troposphere during the wet season?

These questions are of fundamental relevance for studying the interaction between the biosphere and atmosphere in Central Amazonia. Their answers are important in understanding aerosol particles' transport, formation, and growth mechanisms in a tropical forest region with little anthropogenic influence. There are still uncertainties regarding the formation and growth of aerosols in atmospheres mostly dominated by volatile organic compounds. In Central Amazonia, for example, isoprene and terpene are the dominant VOCs.

Once processes that regulate the aerosol concentration within the lower Amazonian troposphere have been identified, it is also important to quantify their variability in the vertical profile of the atmosphere. Due to the dynamics of the PBL, aerosols are distributed unequally along with the atmospheric vertical profile. Particularly at night, there is a predominance

of the residual layer and a stable layer above the surface. Furthermore, meteorological and biological processes add particles to the boundary layer, making the aerosol dynamics even more complex.

The study of the gradient of aerosol physical properties in the vertical profile of the lower troposphere in a tropical forest region is an unprecedented component of this study. The measurements are only possible due to the unique character of the ATTO site. There are, in addition to two 80 m height towers, the 325 m height ATTO tower, and instrumentation to assess the vertical distribution of a diversity of aerosol properties. Therefore, to provide answers to those questions, the following specific objectives were fulfilled:

1. Identify and characterize the aerosol particle growth events of sub-50 nm size within the lower Amazon troposphere and under which meteorological conditions the aerosol particle growth events occur;
2. Characterize atmospheric mechanisms that lead to new particle formation and their transport into the planetary boundary layer;
3. Quantitatively characterize the aerosol optical and chemical properties under pristine atmospheric conditions;
4. Investigate the variability of the aerosol physical properties in the vertical profile of the lower Amazonian troposphere, with measurements in towers at the ATTO site;
5. Estimate possible differences in the transport of $\text{CN}_{<50}$ particles in the atmospheric vertical profile, characterizing their appearance at 60 and 325 m height. In addition, it is aimed to estimate the time difference in aerosol transport between these two levels.

Chapter 3

Atmospheric aerosols and planetary boundary layer characteristics

This chapter covers basic concepts regarding atmospheric aerosols and their general physical and optical properties, such as number concentration, size distributions, and aerosol extensive and intensive optical properties. In addition, a discussion is also presented regarding the planetary boundary layer and the potential temperature, which is a meteorological parameter that describes the thermodynamic properties of fluids, particularly of air parcels. All concepts discussed here are widely applied throughout this study.

3.1 Atmospheric aerosol

Atmospheric aerosols are solid or liquid particles suspended in the air, coming from both natural and anthropic sources, which have different characteristics, such as sizes, shapes, chemical composition (organic and inorganic), and physical properties (SEINFELD; PANDIS, 2012). The concentration of these particles in the atmosphere is highly variable since this is related to their high heterogeneity and their relatively short residence times, which can vary between hours and weeks (BOUCHER, 2015). Most aerosols are not visible to the naked eye because of their size, which ranges from a few nanometers to tens of micrometers. However, in high concentrations, their optical effects are easily visible, for example, during fires and dust events.

Aerosols are classified into two major groups according to the processes that generate them, and they can be primary or secondary. Primary aerosols are those introduced into the atmosphere directly from the source, already as particles. An example is regarded to aerosols originating from the friction of the wind with the surface of oceans and continents or even produced during incomplete combustion. Other examples of primary aerosols are fungi, bacteria, and fragments of plants and animals. Secondary aerosols are formed in the atmosphere through physical and chemical reactions that induce the gas-particle phase

transition, and whose sources can be both natural and anthropogenic (BOUCHER, 2015)c. The volatile compounds released by the sources are called precursor gases and undergo transformations in the atmosphere, giving rise to secondary aerosols (BOUCHER, 2015). The most important one in tropical forest regions are the SOA, which correspond to up to 80% of the aerosol mass fraction with sizes up to $2.5 \mu m$ (ANDREAE et al., 2018).

3.1.1 Atmospheric aerosol concentration and size distribution

The aerosol population is classified according to their size, measured in terms of the geometric diameter (D_p). Two groups emerge from this classification: the aerosol fine mode, which represents those aerosols with a few nanometers up to diameters in the order of $1 \mu m$. Moreover, the aerosol coarse mode includes particles with diameters larger than $1 \mu m$ (BOUCHER, 2015). Most atmospheric aerosols are in the fine mode, and they are the ones that most influence the ecosystem and human health (BOUCHER, 2015; SEINFELD; PANDIS, 2012).

The aerosol fine mode is commonly subdivided into three categories: nucleation mode (also known as ultrafine mode, or sometimes defined as sub-50 nm size mode), which ranges from few nanometers to ~ 30 -50 nm, Aitken mode, spanning from 30 - 50 nm to 100 nm, and accumulation mode, from 100 to 500 nm (BOUCHER, 2015). It is worth mentioning that this subdivision can vary a lot in the literature, mainly concerning the definition of limits of the nucleation-Aitken modes. Such cases generally occurs in exceptional cases, such as those observed in the lower Amazonian troposphere, where NPF processes are not commonly observed within the planetary boundary layer but in another troposphere region. This results in particles reaching the boundary layer with sizes that can be considered within the nucleation mode, but without having nucleation processes within the boundary layer. For those cases, it is used the terms ultrafine mode or sub-50 nm size mode (TOLEDO MACHADO et al., 2021; FAN et al., 2018).

The aerosol number size distribution is represented by a $n(D_p)$ function, such that $n_N(D_p)dD_p$ is the number of particles per cm^3 within the size range D_p to $D_p + dD_p$. The total aerosol number concentration N_t can be estimated from the sum of all contributions inside a given size range, for example, from D_1 to D_2 , which is, $N_t = \int_{D_1}^{D_2} n_N(D_p)dD_p$. It is necessary to define three more important distributions to estimate several aerosol properties: the surface area, volume, and mass distribution. The surface area distribution within the size range D_p to $D_p + dD_p$ can be defined as $n_s(D_p)dD_p$. In general, these calculations are performed by approximating the particle geometry by spheres. The surface area of spherical aerosols within the refereed size range is $n_s(D_p) = \pi D_p^2 n_N(D_p)$ [$\mu m cm^{-3}$]. Then, the total aerosol surface area S_t per cm^3 is:

$$S_t = \pi \int_0^\infty D_p^2 n_N(D_p) dD_p = \int_0^\infty n_s(D_p) dD_p [\mu m^2 cm^{-3}]. \quad (3.1)$$

Similarly, the infinitesimal volume of aerosol within the interval D_p to $D_p + dD_p$ is defined as $n_V(D_p) = (\pi/6)D_p^3 n_N(D_p) [\mu m^2 cm^{-3}]$. Therefore, the total aerosol volume per cubic centimeter (V_t) is:

$$V_t = \frac{\pi}{6} \int_0^\infty D_p^3 n_N(D_p) dD_p = \int_0^\infty n_V(D_p) dD_p [\mu m^3 cm^{-3}]. \quad (3.2)$$

In general, it is more convenient to express N_t , S_t and V_t in terms of $\ln D_p$ (SEINFELD; PANDIS, 2012), which facilitates many calculations since most instruments return the measures as a function of the logarithm of the number concentration:

$$N_t = \int_{-\infty}^\infty n_N(\ln D_p) d\ln D_p [cm^{-3}], \quad (3.3)$$

$$S_t = \pi \int_{-\infty}^\infty D_p^2 n_N(\ln D_p) d\ln D_p [\mu m^2 cm^{-3}], \quad (3.4)$$

$$V_t = \frac{\pi}{6} \int_{-\infty}^\infty D_p^3 n_N(\ln D_p) d\ln D_p [\mu m^3 cm^{-3}]. \quad (3.5)$$

3.1.1.1 The Log-normal distribution

The log-normal distribution is the function that has been more applied to obtain important parameters of atmospheric aerosol size distributions (BOUCHER, 2015). According to SEINFELD; PANDIS(2012), the function is very useful in atmospheric physics since it is relatively simple and describes very well the aerosol size distributions observed in nature with only a few parameters, such as standard deviation σ and the mean geometric diameter. The normal distribution for a certain quantity k is defined as:

$$n(k) = \frac{N_t}{\sqrt{2\pi}\sigma_k} \exp\left(-\frac{(k - \bar{k})^2}{2\sigma_k^2}\right), \quad (3.6)$$

where σ_k^2 is the variance, which quantifies the width of the distribution, $\bar{k}$ is the mean of the distribution, and N_t , the total aerosol particle number concentration, is defined as:

$$N_t = \int_{-\infty}^{+\infty} n(k) dk \quad (3.7)$$

It is considered that an aerosol population distribution with geometric diameter D_p is log-normally distributed if $k = \ln D_p$ satisfies 3.6. Then, equation 3.6 can be expressed in its final and more used form as:

$$n^*(D_p, \sigma_g) = \frac{dN}{d \ln D_p} = \frac{N_t}{\sqrt{2\pi} \ln \sigma_g} \exp\left(-\frac{(\ln D_p - \ln \bar{D}_{pg})^2}{2 \ln^2 \sigma_g}\right), \quad (3.8)$$

where $\bar{D}_{pg}$ and σ_g is the median geometric diameter and the geometric standard deviation of a specific aerosol population, respectively of a specific size mode. The mean diameter $\bar{D}_p$ can be obtained from the function 3.8 by performing:

$$\bar{D}_p = \frac{1}{N_t} \int_0^\infty D_p n^*(D_p) dD_p, \quad (3.9)$$

which results in:

$$\bar{D}_p = \bar{D}_{pg} \exp\left(\frac{\ln^2 \sigma_g}{2}\right). \quad (3.10)$$

Figure 3 – Example of an aerosol size distribution (black line), composed of three different aerosol populations, each represented by a colored log-normal distribution. A particular $\bar{D}_{pg}$ and σ_g characterize each distribution.

Therefore, the total size distribution can be reconstructed by knowing the parameters $\bar{D}_{pg}$ and σ_g , which are characteristic for each aerosol population size mode. In addition, important parameters such as mean surface area, mean volume, mean number concentration of a specific aerosol population can be obtained by those parameters. Figure 3 shows a simulated aerosol size distribution (black line), composed of 3 log-normal functions, each one with a specific $\bar{D}_{pg}$ and σ_g . The black curve can be reconstructed by knowing $\bar{D}_{pg}$ and σ_g of each log-normal, once that the area under the black curve is equal to the sum of the area under each one of the log-normal distributions. More details on applying the log-normal distribution to obtain the aerosol size modes for the size distributions discussed in this study are addressed in the methodology section 4.6.

3.2 Aerosol optical properties

Aerosols interact with the incident electromagnetic radiation so that the electrical charges on particles are excited and oscillate. A fraction of the radiation is converted into thermal energy and is absorbed. Another fraction is scattered in all directions. The degree of interaction of an aerosol particle with the incident radiation of wavelength λ depends on the scattering and absorption cross-sections, $s_{abs}(\lambda)$ and $s_{scat}(\lambda)$, respectively, which represent the surface that effectively interacts with the radiation (SEINFELD; PANDIS, 2012). In the case where the particles are very small compared to the wavelength of the incident radiation (e.g., particle diameter smaller than $\lambda/5$), and if $I_0(\lambda)$ is the intensity of the incident radiation on this particle, then the energy absorbed or scattered by it is proportional to its cross-section:

$$I_{scat}(\lambda) = s_{scat}(\lambda) I_0(\lambda), \quad (3.11)$$

$$I_{abs}(\lambda) = s_{abs}(\lambda) I_0(\lambda), \quad (3.12)$$

where $s_{abs}(\lambda)$ and $s_{scat}(\lambda)$ have units of m^2 . $I(\lambda)$ has unit of W m^{-2} . It is worth noting that the ratio I/I_0 is proportional to $1/\lambda^4$, which is called Rayleigh regime.

The parameters that govern the dynamics of radiation scattering and absorption in small particles such as aerosols depend on two main factors: (i) the wavelength (λ) of the incident radiation and (ii) the particle size diameter (SEINFELD; PANDIS, 2012). Depending on these quantities, different scattering/absorption regimes play a major role. The size parameter, κ , defines the regime of the interaction:

$$\kappa = \frac{\pi D_p}{\lambda}. \quad (3.13)$$

If $\kappa \ll 1$, it is the Rayleigh regime, where particles are smaller than the incident radiation. If $\kappa \sim 1$, then it is the Mie regime, where particles are of the same order of magnitude as

the incident radiation. Then, if $\kappa \gg 1$, it is the geometric regime, where particles are much larger than the incident radiation. In the study developed in this thesis, the optical properties obtained by the instrumentation are found in the Mie regime. Its mathematical description is complex, and the interested reader is referred to a specific literature (BOUCHER, 2015).

The scattering and absorption efficiency of a particle, Q_{scat} and Q_{abs} (unitless), respectively, are a dimensionless property defined as the ratio between the scattering or absorption cross-section and the geometric cross-sectional area s_g of the particle:

$$Q_{scat}(\lambda) = \frac{s_{scat}(\lambda)}{s_g}, \quad (3.14)$$

$$Q_{abs}(\lambda) = \frac{s_{abs}(\lambda)}{s_g}. \quad (3.15)$$

From the scattering and absorption efficiencies, the conservation of energy leads to the definition of extinction efficiency, which is the combination of $Q_{scat}(\lambda)$ and $Q_{abs}(\lambda)$:

$$Q_{ext}(\lambda) = Q_{scat}(\lambda) + Q_{abs}(\lambda). \quad (3.16)$$

The ratio between $Q_{scat}(\lambda)$ and $Q_{ext}(\lambda)$ is defined as the single-scattering albedo, $\omega_0(\lambda)$, which is one of the most critical spectral properties of the aerosol, since it influences aerosol direct radiative forcing (MOOS MÜLLER; SORENSEN, 2018):

$$\omega_0(\lambda) = \frac{Q_{scat}(\lambda)}{Q_{ext}(\lambda)} = \frac{Q_{scat}(\lambda)}{Q_{scat}(\lambda) + Q_{abs}(\lambda)} = 1 - \frac{Q_{abs}(\lambda)}{Q_{scat}(\lambda)}. \quad (3.17)$$

The $\omega(\lambda)$ values vary within the range of 0 to 1, where values close to 1 refer to strongly scattering aerosols, and values very close to 0 refer to strongly absorbing particles. The fraction of the radiation extinction that is scattered by the particle is, then, ω_0 , while the absorbed fraction is $1 - \omega_0$.

3.2.1 Absorption and scattering coefficients

When considering a population of aerosol particles, the discussed optical properties need to be integrated over the whole number size distribution $n(D_p)$ to obtain the parameters that are measured by the in-field instrumentation (BOUCHER, 2015; SEINFELD; PANDIS, 2012). The aerosol scattering ($\sigma_{scat,\lambda}$) and absorption ($\sigma_{abs,\lambda}$) coefficients (in units of m^{-1}), which are measured at a particular wavelength λ , are extensive properties that are directly related to the aerosol concentration at the atmosphere. It means that, for example, the higher the aerosol particle number concentration, the higher the coefficients. The $\sigma_{scat,\lambda}$ and $\sigma_{abs,\lambda}$ are defined as follows:

$$\sigma_{scat,\lambda} = \int_0^\infty \frac{\pi D_p^2}{4} Q_{scat}(D_p) n(D_p) d(D_p), \quad (3.18)$$

$$\sigma_{abs,\lambda} = \int_0^\infty \frac{\pi D_p^2}{4} Q_{abs}(D_p) n(D_p) d(D_p). \quad (3.19)$$

Thus, it is also possible to define the extinction coefficient, $\sigma_{ext,\lambda}$, and the single-scattering albedo $\omega_0(\lambda)$:

$$\sigma_{ext,\lambda} = \sigma_{scat,\lambda} + \sigma_{abs,\lambda}, \quad (3.20)$$

$$\omega_0(\lambda) = \frac{\sigma_{scat,\lambda}}{\sigma_{scat,\lambda} + \sigma_{abs,\lambda}} = 1 - \frac{\sigma_{abs,\lambda}}{\sigma_{scat,\lambda}}. \quad (3.21)$$

Equation 3.21 is very useful as it provides the $\omega_0(\lambda)$ as a function of the real measured coefficients. The $\omega_0(\lambda)$ is an intensive property of an aerosol population, which means that it does not depend on the particle number concentration but rather on the intrinsic characteristics of the population, such as the aerosol's chemistry and aging stage (BOUCHER, 2015; SEINFELD; PANDIS, 2012). It is interesting to note that $\omega_0(\lambda)$ is defined as the ratio of extensive properties.

From the extinction coefficient, the aerosol optical depth (AOD), which is the integral of $\sigma_{ext,\lambda}$ over the atmospheric vertical profile, is defined:

$$AOD = \int_{\text{surface}}^{\text{top of atmosphere}} \sigma_{ext}(z) d(z). \quad (3.22)$$

In particular, equation 3.22 is important for the AERONET photometer measurements, which are discussed in section 4.2.5. Those measurements evaluate the entire atmospheric layer of aerosols from the base where the photometer is located to the top of the atmosphere (TOA, ~ 100 km), providing the AOD component and many others aerosol optical properties. It is worth noting that the TOA is defined as the region of the atmosphere where the concentration of air molecules is so rarefied that it does not significantly interact with the radiation that leaves or enters the planet.

When dealing with aerosol populations, it is often useful to work with quantities that describe how effectively a given amount of particles absorb or scatter radiation. Therefore, the mass scattering efficiency, α_{scat} , and the mass absorption coefficient (MAC), α_{abs} are defined (in units of $\text{m}^2 \text{g}^{-1}$):

$$\alpha_{scat,\lambda} = \frac{\sigma_{scat,\lambda}}{m}, \quad (3.23)$$

$$\alpha_{abs,\lambda} = \frac{\sigma_{abs,\lambda}}{m}, \quad (3.24)$$

where m is the total mass of particles. Different optical instruments, such as those discussed in Chapter 4, have different α 's, as this depends on how they were calibrated to convert measured absorption to mass, for example, of absorbing aerosols. In general, the MAC at λ 637 nm is considered to be $6.6 \text{ m}^2 \text{ g}^{-1}$. However, this is highly dependent on the type of aerosol found in a particular location. For example, at the ATTO site, located in Central Amazonia, the MAC varies between the dry ($11.4 \text{ m}^2 \text{ g}^{-1}$) and wet ($12.3 \text{ m}^2 \text{ g}^{-1}$) seasons, with very different values from that usually observed on average in other sites (SATURNO et al., 2018a).

3.2.2 Phase function

Figure 4 – a) Schematic diagram of the geometry used to define the phase function, where Θ is the scattering angle. b) Scattered radiation intensity as a function of the scattering angle Θ for real measurements of aerosol optical properties in the city of São Paulo. The measurements on the curve were obtained on July 30, 2019, at 9:40 LT, with a set composed of a polarizer and a smartphone, as part of a teaching project.

When interacting with a particular aerosol, the radiation beam is scattered in a certain direction, Θ , which depends on the particle's geometry. The phase function describes the angular distribution of the scattered radiation relative to the scatter angle Θ , accordingly to the geometry shown in Figure 4a, and it is defined as the ratio of the scattered intensity ($I(\Theta)$) by the total incident radiation (YAMASOE; CORRÊA, 2016):

$$P(\Theta) = \frac{I(\Theta)}{\int_0^\pi I(\Theta) \sin(\Theta) d\Theta}. \quad (3.25)$$

The phase function is normalized when integrating it over the solid angle $d\Omega$ of a sphere centered at the particle:

$$\int_0^{2\pi} \int_0^\pi P(\Theta) \sin(\Theta) d\Theta d\phi = 4\pi. \quad (3.26)$$

Figure 4b shows a real example of how the scattered intensity $I(\Theta)$ varies with Θ . The curve was obtained by measuring radiation intensity variation through a polarizer in a specific region of the sky during the morning of July 30, 2019, in the city of São Paulo. One would notice that the intensity decreases as the angle tends to 180° . In theory, it is expected that the measured radiation intensity would be zero at 180° under ideal conditions. However, the measurements were obtained from a homemade polarizer and a smartphone sensor. Despite the simplicity of the apparatus, it demonstrates the principle of the phase function very well.

The proportion of radiation that is scattered in the forward or backward directions is defined by the asymmetry factor g , defined as:

$$g = \frac{1}{2} \frac{\int_0^\pi \cos(\Theta) I(\Theta) \sin \Theta d\Theta}{\int_0^\pi I(\Theta) \sin(\Theta) d\Theta} \quad (3.27)$$

$$= \frac{1}{2} \int_0^\pi \cos(\Theta) P(\Theta) \sin(\Theta) d\Theta. \quad (3.28)$$

if $g = 1$, then all the radiation is scattered at $\Theta = 0$ (the forward direction). If $g = -1$, then all the radiation is scattered at $\Theta = 180^\circ$ (the backward direction). And, if $g = 0$, then the radiation is scattered isotropically. The asymmetry factor is important in radiative transfer, climate, and atmospheric models such as the Weather Research and Forecasting model coupled with Chemistry (WRF-Chem) (NASCIMENTO et al., 2021).

3.2.3 Refractive index

The particle chemical composition, together with its physical properties, play a fundamental role in the aerosol-radiation interaction, which is mainly associated with the material's refractive index $N_{ref}(\lambda)$, defined as:

$$N_{ref}(\lambda) = n_{ref}(\lambda) + i k_{ref}(\lambda), \quad (3.29)$$

where n_{ref} is the real part, associated with the scattering properties of the aerosol and k_{ref} is the imaginary part, which is associated with the absorbing component of the particle. It is more common to express equation 3.29 normalized by the refractive index of the medium of interest ($m = N_{ref}/N_0$), which is the air in this case, with $N_{ref,0} = 1.00029 + 0i$ at $\lambda = 589 \text{ nm}$ (SEINFELD; PANDIS, 2012). For example, the black carbon (soot) has a refractive index of $1.95-0.79i$ ($\lambda = 550 \text{ nm}$), which shows its strong absorption component.

In contrast, mineral dust has a refractive index of $1.56-0.006$ at $\lambda = 550 \text{ nm}$, with a minimal absorption component. One of the biggest puzzles regarding the refractive indices of aerosols is its organic component. The SOA composition is strongly dependent on the precursors' VOC at a specific place. In particular, in tropical forest regions such as Amazonia,

the refractive index for the aerosol particle population, particularly for the SOA component is a component for future studies.

3.2.4 Ångström exponent

Scattering and absorption Ångström exponents, which are also intensive aerosol properties, represent the spectral dependence of the aerosol with the incident radiation. It is significantly influenced by the particles' chemical composition and physical parameters, such as shape and size (BOUCHER, 2015). The exponents can be described in terms of the measured scattering or absorption coefficients, and each one of them represents a different aspect of the atmospheric aerosol population. In general, the Ångström exponent is calculated for a pair of wavelengths λ_i and λ_j , with $\lambda_i < \lambda_j$:

$$\mathring{a}_{\lambda_i, j} = -\frac{\ln \frac{\sigma_{\lambda_i}}{\sigma_{\lambda_j}}}{\ln \frac{\lambda_i}{\lambda_j}}. \quad (3.30)$$

where σ_{λ_i} here can be the scattering or the absorption coefficient. If the scattering/absorption coefficients are measured at three wavelengths or more, it is also possible to obtain the Ångström exponents through the following linear fit:

$$\ln \sigma_{\lambda} = -a \ln \lambda + C, \quad (3.31)$$

where σ_{λ} is the scattering/absorption coefficient, the angular coefficient a is the mean Ångström exponent, and C is a constant resulted from the linear fit.

The scattering Ångström exponent, which varies from 0 to 4, is usually associated with the size of the scattering itself and may also be associated with the size of the particles. According to BOUCHER(2015), $\mathring{a}_{scat} \sim 4$ is associated with scattering by molecules, $\mathring{a}_{scat} \sim 2$ usually is related to scattering of accumulation mode particles, and $\mathring{a}_{scat} \sim 0$ may be related to coarse mode aerosols. However, it is necessary to point out that the refractive index plays an important role in this context, which means that particles of the same size but with different chemical compositions and shapes may have different scattering Ångström exponents.

The absorption Ångström exponent is directly associated with the aerosol population's chemical composition and age and only assumes positive values. Values of $\mathring{a}_{abs} \sim 1$ are usually associated with very absorbing aerosols, although it can vary for a coated black carbon (WANG et al., 2016b). In general, organic aerosols and dust particles have higher exponent values. Ångström exponents have been used to discriminate the different types of absorbing aerosols through clustering (CAZORLA et al., 2013). This technique, called Angstrom matrix, provides clues related to the type of aerosol mixture only based on the optical measurements, for

example, if the dominance is organic or inorganic carbon, or if the particles are dominated by dust.

3.3 Planetary boundary layer

The Earth's atmosphere is divided into six main layers, varying with altitude and different physical and thermodynamic characteristics. In particular, the Earth's troposphere is the extension of the atmosphere directly above the surface, that strongly interacts with the biosphere, and reaches altitudes of up to ~ 18 km (SEINFELD; PANDIS, 2012). Approximately 80 % of the entire mass of the atmosphere is concentrated in this region (SEINFELD; PANDIS, 2012). The troposphere is characterized by a decrease in temperature as a function of height, with a lapse rate of $\Gamma = 6.5 \text{ K K}^{-1}$, which allows the appearance and existence of clouds. The troposphere is also considered to be subdivided into two main sublayers: the planetary (or atmospheric) boundary layer and the free atmosphere (or free troposphere, FT), as shown in Figure 5a. The PBL is the troposphere region that is directly connected to the Earth's surface and reaches heights of up to 3 km. In PBL, practically all the processes of exchange of energy and matter between the atmosphere and the surface occur. These processes respond to surface forcing on time scales of one hour or less (STULL, 1988).

Figure 5 – Planetary boundary layer structure, where a) shows the tropospheric layers and their approximate heights, and b) shows the different PBL layers concerning the time when they appear. Source: adapted from WALLACE; HOBBS(2006).

In particular, the PLB is characterized by the concentration of most atmospheric aerosols. Furthermore, the region is strongly turbulent, which is a direct effect of the interaction with the ground. It is in PBL that the measures and analyzes developed in this thesis are concentrated. In contrast, the free atmosphere is mainly dominated by gases and meteorological processes that lead to cloud formation. In section 3.3.1, the difference between the two layers will become even more evident regarding potential temperature. The PBL has a characteristic diurnal cycle, arising from the availability of solar radiation, which heats the ground and, through heat exchange, causes turbulent processes in the layer. It results in

well-defined structures that vary throughout the day, which are shown in Figure 5b. The three main components of PBL are the mixed layer (ML), the residual layer (RL), and the stable (or nocturnal) boundary layer (SBL) (STULL, 1988).

With sunrise, heat is absorbed by the surface and re-emitted back into the atmosphere, warming the air next to it. In addition, there is also radiative cooling due to the cloud base (heat exchange), so these intense heat exchanges from the medium to the air result in strong turbulent processes. These processes effectively mix heat, moisture, and aerosols uniformly in the vertical profile of the PBL, giving rise to the ML structure (WALLACE; HOBBS, 2006). It reaches its maximum height when the intensity of solar radiation is maximum and decreases as it tends to disappear. In Amazonia, flux studies have shown that the mixed layer reaches 700 to 1100 m in the wet season, while in the dry season, it can reach up to 2000 m (FISCH et al., 2004; RANDOW et al., 2004). Above the mixed layer, there is a thin layer called the entrainment zone (EZ). Inside the EZ, there are exchanges of air mass parcels from the free troposphere, which, due to the turbulence of the mixed layer, are dragged down to the PBL. Thus, gases and particles from the free troposphere are incorporated into the mixed layer (WALLACE; HOBBS, 2006).

After sunset, turbulent processes tend to decrease in the formed ML due to the decrease of thermal processes (longwave radiative cooling) so that the RL appears (STULL, 1988). Despite having less turbulence, it still allows some level of mixtures of heat, matter, and energy. In the absence of advection, the turbulent processes of the RL present approximately the same intensity in all directions. Above RL, the EZ becomes the capping inversion (CI), characterized by high stability and little or no turbulence. It means that the weak but constant turbulence of the RL does not penetrate the CI, isolating the PBL from the free troposphere. As the night progresses, the air parcels closer to the surface are cooler, which strongly reduces turbulence. Thus, the SBL appears, which is characterized by weak or absence of air currents. In Amazonia, for example, the stable boundary layer can reach heights of the order of 240 m before sunrise (BETTS et al., 2009). Studies carried out in tall towers, such as those at the ATTO site, are essential since part of the turbulence that naturally occurs near the canopy due to the friction of air with the leaves can be avoided. Furthermore, it is possible to measure different atmospheric properties (gases, aerosols and fluxes.) under different PBL conditions (ANDREAE et al., 2015).

3.3.1 Potential temperature

The potential temperature θ is a conserved thermodynamic parameter that is defined as the temperature that an unsaturated air parcel would have if transported adiabatically from its original height in the atmosphere (with a given pressure p and temperature T) to a standard pressure p_0 . In general, it is considered $p_0 = 1000 \text{ hPa}$. The θ is written as:

$$\theta = T_K \left(\frac{p_0}{p} \right)^{R/c_p(1-q_v)}, \quad (3.32)$$

where T_K is given in Kelvin, $R \approx 287 \text{ J K}^{-1} \text{ kg}^{-1}$ is the gas constant, $c_p \approx 1004 \text{ J K}^{-1} \text{ kg}^{-1}$ is the specific heat at constant pressure, with $R/c_p \approx 0.286$, and q_v is the water vapor specific humidity. For a dry air, $q_v = 0$. The term $(1 - q_v)$ can be written as $(1 - 0.28 \times 10^{-3} r)$, where r is the mixing ratio (BOLTON, 1980). Therefore, θ is expressed in its general form as:

$$\theta = T_K \left(\frac{p_0}{p} \right)^{R/c_p(1-0.28 \times 10^{-3} r)} \quad (3.33)$$

Figure 6 – Variation of the potential temperature with the height. The dashed line represents a standard atmosphere, and the solid line is the modification of the standard atmosphere when turbulent mixing at the PBL is considered. Source: extracted from WALLACE; HOBBS(2006).

The potential temperature is used to compare the thermodynamic characteristics of different air parcels in different regions of the atmosphere. Figure 6 shows the variation of θ as a function of the height. It is observed that within the boundary layer, the potential temperature is practically constant along with the vertical profile, nearly adiabatic, which is

due to the mixing processes that take place there (WALLACE; HOBBS, 2006). A closer look at the PBL sublayers shows that θ is approximately constant in ML and RL, and there may be a slight decrease in RL overnight (STULL, 1988). Within the superficial layer, for example, θ also decreases with height, while within the SBL, CI, and EZ layers, θ increases with height (STULL, 1988). The potential temperature gradient is $3.3^\circ\text{C}/\text{Km}$ in the free troposphere (WALLACE; HOBBS, 2006).

3.3.2 Equivalent potential temperature

Instead of using the potential temperature to characterize air parcels at a given height, it is sometimes advantageous to look at what the temperature of an air parcel with potential temperature θ would be like if all the water vapor within the parcel was condensed. Therefore, the θ_e is defined as the temperature of an air parcel when it is lifted pseudo-adiabatically to a height where all the water vapor is condensed, releasing the latent heat, and brought adiabatically to a height where $p = p_0$. The θ_e is expressed according to BOLTON(1980) as:

$$\theta_e = T_K \left(\frac{1000}{p} \right)^{0.2854(1-2.8 \times 10^{-4}r)} \exp \left[\left(\frac{3.376}{T_L} - 0.00254 \right) r (1 + 8.1 \times 10^{-4}r) \right] [K], \quad (3.34)$$

$$T_{dp} = T - \frac{100 - RH}{5} [^\circ\text{C}], \quad (3.35)$$

$$T_L = \frac{1}{\frac{1}{T_k - 55} - \frac{\ln(\frac{RH}{100})}{2840}} [K], \quad (3.36)$$

$$e_{vp} = 6.11 \times 10^{\frac{7.5 \times T_{dp}}{273.3 + T_{dp}}}, \quad (3.37)$$

$$r = 621.97 \times \frac{e_{vp}}{p - e_{vp}} [g/kg], \quad (3.38)$$

where T_K is the ambient temperature in Kelvin, T is the ambient temperature in Celsius, p and r are the ambient pressure (mb) and the mixing ratio (g/Kg), which depends on the vapor pressure (e_{vp}) and the dew point temperature (T_{dp} [K]), respectively. T_L is the lifting condensation level temperature in Kelvin.

The equivalent potential temperature is mostly applied to estimate atmospheric stability (WALLACE; HOBBS, 2006). In general, a decrease in θ_e is associated with a decrease in the temperature and moisture of an air parcel. It causes a pronounced diurnal cycle in θ_e . However, equivalent potential temperature anomalies are often used as tracers of convective

events with downdraft activities (WANG et al., 2016a; RIZZO et al., 2018). These anomalies are obtained by removing the seasonal and diurnal trends in the equivalent potential temperature, and negative values are related to downdraft occurrences. The details of the detrending procedure are explored later in section 4.7.1.

Figure 7 – Time series of a) aerosol size distribution in size range of 10 to 400 nm, and b) equivalent potential temperature, θ_e , calculated with meteorological parameters measured at the ATTO site, Central Amazonia. The measurements were taken between January 12th and 13th, 2019, when a convective downdraft occurred.

Figure 7 shows the aerosol size distribution and θ_e , calculated with meteorological parameters for the same period at the ATTO site. At approximately 06 local time (LT), a convective event occurred at the site, which caused a decrease in aerosol concentration via wet deposition and a drop in θ_e . This decrease lasts until 12 LT, when convective downdraft stops, and both aerosol concentrations and θ_e increase again. An increase in θ_e represents an increase in temperature and moisture, which may be associated with unstable atmospheric systems (WALLACE; HOBBS, 2006). In this study, therefore, the concept of potential equivalent temperature decrease is used as a tracer for the occurrence of convective downdrafts, following other works that performed similar analyzes for the Amazonia (WANG et al., 2016a; RIZZO et al., 2018).

Chapter 4

Measurements, analysis procedures, and methods

This chapter introduces the Amazon Tall Tower Observatory, ATTO, a unique and remote site in Central Amazonia, whose atmosphere has pristine conditions during specific periods of the wet season. In addition, the aerosol measurements conducted there are presented, describing the main *in situ* instruments and satellite data used in the study. The methodology to process and analyze a large amount of data is also discussed in detail.

4.1 The Amazon Tall Tower Observatory (ATTO) site

The ATTO site is located ~150 km north-east of Manaus ($S\ 02^{\circ}\ 08.752'$, $W\ 59^{\circ}\ 00.335'$), Brazil, in the sustainable development reserve called Uatumã Scientific Reserve. This unique place in Central Amazonia's heart is considered one of the least disturbed continental areas by anthropogenic activities in the world (ANDREAE et al., 2015). The ATTO collaboration is a joint Brazilian-German scientific project held by the Max Planck Institute for Chemistry (MPIC) of Mainz, Germany, and several Brazilian scientific institutes and universities, such as INPA (National Institute for Amazonian Research), LBA (The Large Scale Biosphere-Atmosphere Experiment in Amazonia), UFAM (Federal University of Amazonas), UEA (State University of Amazonas), EMBRAPA (Brazilian Agricultural Research Corporation), USP (University of São Paulo), INPE, and many others. More specific details about the project, partnerships, and funding agencies can be found at <<https://www.attoproject.org/>>. Figure 8 shows the location of the ATTO site in comparison to some nearby cities and local communities.

The trip from Manaus to the ATTO site is an incredible journey in itself: via BR-174, approximately 101 km are traveled by car to a junction near the city of Presidente Figueiredo. From there, it is another 70 km on the AM-240 to a new junction, close to the Balbina dam. This dam is known to be the result of a devastating environmental disaster in an attempt to build a hydropower plant in the middle of the Amazon rain forest in the 1980s. A recent study

showed the tremendous socio-environmental impacts on the region and on the concentration of greenhouse gases (SCHÖNGART et al., 2021). It is necessary to travel another 38 km through a branch to Porto da Morena from the power plant. In this place, it is necessary to take a boat, which travels 61 km to Porto ATTO, located in the Uatumã Scientific Reserve. From there, and another 14 km are traveled through the native forest to the camp, where the towers and laboratories are located.

Figure 8 – Location of the ATTO site. The figure shows cities and communities relatively close to the site, in addition to relevant geographic markers. In particular, it shows the city of Manaus, with more than 2 million inhabitants, located downwind from the ATTO site.

The ATTO site houses two 80 m tall towers each, in full operation since 2014, and the ATTO tall tower, of 325 m, whose scientific activities started in 2017. The ATTO tower provides vertical measurements of aerosols and trace gases at different height levels. There are long inlet lines for aerosol sampling, meteorological sensors, and several other instruments for atmospheric and ground studies at the tower. Up to 30 researchers can be accommodated on-site simultaneously. The ATTO project has huge and impressive logistics of transporting researchers/staff, cleaning the camp, and cooking services twice a week.

An incredible variety of different scientific studies have been conducted on the site, such as biological fungus spores, ecological, soil, and wildlife characterizations. The site is supplied by diesel generators, located roughly 3 km away from the towers and the accommodation camps, in the downwind direction, which is necessary to avoid possible direct contamination. Figure 9 shows the scientific station with the ATTO tower, the surrounding vegetation, as seen from a height of 100 m, and the interior of one of the laboratories

connected to the tower used to measure aerosol physicochemical properties.

Figure 9 – The ATTO site in Central Amazonia. On the left, the 325 m ATTO tower; on the right (above): Amazonian vegetation, as seen from a height of 100 m; right (below): instrumentation allocated within one of the laboratories connected to the tower measuring aerosol physicochemical properties.

The site is surrounded by a dense drainage network, resulting in geographical patterns containing valleys and plateaus with a maximum gradient of 100 m in height. This is reflected in the local micrometeorology, causing significant upward and downward atmospheric movements within the planetary boundary layer. These turbulence effects from the lower troposphere affect more the smaller towers since they are closer to the canopy and, therefore, are more susceptible to vegetation photorespiration and the heterogeneity of the terrain (ANDREAE et al., 2015). The 325 m tower was proposed precisely to circumvent turbulence effects close to the canopy, allowing the detection of changes in the background composition of the atmosphere on a long-term basis. The local climate is predominantly humid tropical, with well-characterized wet and dry seasons.

Several air masses reach the ATTO site along the different seasons, which come from seasonal variations in the Intertropical Convergence Zone (ITCZ) in the Amazon region (PÖHLKER et al., 2019). Figure 10 shows the wind directions in the wet and dry seasons between the years 2012 and 2014, in which it is clear the preferred wind direction of northeast and southeast. Figure 11 shows the back trajectories of the air masses that reach the ATTO site, obtained for 14 days, in the dry and wet seasons, in which it is clear the long-range transport that reaches the site. In the wet season, air masses from the northeastern region of ATTO cross long covers of clean forest and bring marine aerosols, dust from the Sahara Desert in Africa,

and even episodic burning plumes from the western portion of the African continent. In particular, pristine conditions, characterized by very low black carbon concentration, in which the atmospheric composition looks similar to pre-industrial times, have been detected from March to May. The aerosol characteristics are different from those observed at the dry season, presenting a characteristic bi-modal size distribution shape, with a pronounced Aitken and accumulation mode and the presence of the Hoppel minimum.

Figure 10 – Wind roses for (a) dry and (b) wet seasons, based on semiannual averages of wind speed and direction from October 18, 2012, to July 23, 2014. Source: extracted from ANDREAE et al.(2015).

In contrast, most of the air masses originate from the Atlantic Ocean during the dry season, which carries fresh regional biomass burning plumes to the ATTO site, which increases the aerosol particle number concentration dramatically, changing its size distribution characteristic to a monomodal and strong accumulation mode. Although regional biomass burning plumes are the main source of the atmospheric aerosols at the site during the dry season, recent studies have shown the influx of African biomass burning aerosols through the transport of black carbon-rich smoke, also impacting the atmospheric aerosol characteristics of the site (HOLANDA et al., 2020).

Regarding distance from populated regions, the densest urban activity closest to the ATTO site in the northeast direction are Guyana and the State of Amapá, at approximately 1100 km. To the east, there are Santarém and Belem, whose distances are 500 and 900 km, respectively. Moreover, to the southeast, there are cities in the northeast of Brazil, located at least 1000 km away. Manaus polluted plumes do not reach the ATTO site because of the wind direction during wet and dry seasons. Recently, long-term studies comprehending several years of air masses back trajectories have been carried out to establish the characteristics of the various atmospheric components that get there and what are the possible long-term impacts (PÖHLKER et al., 2019).

Figure 11 – Back trajectories of air masses that reach the ATTO site during the a) wet (1 to 31 March 2014) and b) dry seasons (1 to 30 September 2014). The color code means the aging of the air masses, starting from 14 days before it reaches the site. Source: Figure extracted from PÖHLKER et al.(2019).

4.1.1 Aerosol vertical profile measurements

The study developed in this thesis used measurements of aerosol physicochemical properties in the vertical profile of the lower troposphere of the central Amazonia at two fixed height levels: 60 and 325 m. However, the simultaneous measurements were not performed at the same tower because of the following reasons:

- The instruments are not installed at the tower, but inside a laboratory in the ground level, located at the side of the tower.
- Aerosols are sampled at the tower, at a specific level, and transferred to the instruments by a long inlet line connected to a pump system. Every tower has only one inlet line system dedicated to aerosol measurements, which supplies with 16.7 liters per minute (LPM) the set of instruments.
- There is limited space inside of each laboratory and also in the surroundings of the towers. It is necessary to consider that there are other laboratories nearby but developed for different other studies.

Therefore, two main laboratories and towers were involved in the measurements: the A1 laboratory, connected to the 325 m inlet line at the ATTO tower, and the C4 laboratory, which is connected to the 60 m inlet line at the Triangular Mast tower of 80 m height ($S 02^{\circ} 08.602'$, $W 59^{\circ} 00.033'$). The two towers are separated by roughly 1.5 Km. Both laboratories were designed to house aerosol and trace gas instrumentation.

Figure 12 shows how the laboratories are as seen from inside, in which the different instruments are compartmentalized to optimize the spatial distribution of equipment, com-

puters, cables, and toolboxes. The instrumentation is allocated in metallic supports, which are grounded to avoid possible electrical outages. Each instrument generates a data packet daily, which is transferred by satellite internet for data servers in Brazil (at INPA and USP) and Germany (at MPIC). Weekly, the ATTO project generates reports containing all the main measures developed on the site to verify their quality and the operation of the instruments.

Figure 12 – Internal visualization of the laboratories a) A1 and b) C4 at the ATTO site. Figure c) shows an outline of the instrument configuration within laboratory A1.

4.1.1.1 Inlet transmission efficiency

The inlet system used at the towers to drag the sampled air to the instruments located at the surface is similar for both. It is composed of a total suspended matter head that samples air from all directions and a 25 mm stainless steel line (PM2.5). The ATTO tower has an inlet line of 325 m long, and the so-called Mast tower has a line of 60 m long, which is roughly 20 m higher than the canopy. The system is optimized to minimize particle losses due to turbulent flows. Before entering the instrumentation, the sampled air is dried to RH of about 40%.

Different dryer systems have been used at the site. In particular, for the Mast tower, from January 30, 2014, to 2 February 2, 2015, a silica gel diffusion dryer was used at the 60 m inlet line, which required frequent manual exchanges. From February 2, 2015, to March 2020, an electric and automated dryer has been used. From March 2020 on, a condensation dryer has been used. The instruments at the A1 container were always connected to an automatic

dryer, whose activities started officially in 2017. More specific details of the inlet and dryer systems can be found elsewhere (ANDREAE et al., 2015; PÖHLKER et al., 2016; MORAN-ZULOAGA et al., 2018). Figure 13 shows the schematic of the ATTO tower inlet system from the point where it leaves the tower and enters the laboratory. The quantities represented in the figure are the real ones. The values are necessary to estimate the inlet transmission curve from each tower system to compensate for the particle losses during the air transmissions inside the lines.

Figure 13 – Schematic of the inlet line geometry from where it leaves the ATTO tower and enters the laboratory (A1). The values for the sizes and angles (here represented as α in degrees) are the real ones and help determine the inlet line transmission efficiency curve for the sampled aerosol particles.

The calculation of the inlet line transmission efficiency curve is performed through software developed by WEIDEN et al. (2009). Several factors about the inlet line are considered, such as its geometry, sedimentation, diffusion losses, turbulent flow inertial deposition, and electrostatic deposition. Comparisons made with measurements obtained from aerosol size distribution in the 300 m ZOTTO tower, located in Siberia in a boreal forest region, showed good agreement for the transmission efficiency with the theoretical estimation within a relative uncertainty of 5% (BIRMILI et al., 2007). In particular, the referred work showed the viability of unusually long inlet tubes for atmospheric studies for the first time. Table 1

Table 1 – Inlet line geometric parameters for the 325 m and 60 m lines.

325 m					
Flow (L/min)	Tube length (m)	1st inner diameter (mm)	2nd inner diameter (mm)	Inclination angle (°)	Bend angle (°)
35	3.31	22.1	22.1	90	0
35	0.3	22.1	22.1	65	51
35	4.35	22.1	22.1	39	0
35	316.4	22.1	22.1	90	0
35	0.3	22.1	22.1	65	50
60 m					
Flow (L/min)	Tube length (m)	1st inner diameter (mm)	2nd inner diameter (mm)	Inclination angle (°)	Bend angle (°)
25	53	22.1	22.1	90	0
25	0.1	22.1	22.1	77	153.6
25	0.1	22.1	22.1	77	153.6
25	4.5	22.1	22.1	63.6	0
25	2.5	22.1	22.1	90	0
25	0.15	22.1	15.75	90	0
1.7	0.1	4	4	70	20
1.7	1.2	4	4	70	0
1	0.2	4	4	30	30
1	0.05	9	9	70	0
1	0.1	6	6	70	0

shows the inlet geometric parameters used to calculate the inlet efficiency transmission curve using the *Particle Loss Calculator* software (WEIDEN et al., 2009) for 60 and 325 m inlet lines. Transmission efficiency curves for both lines are shown in Figure 14. The transmission corrections for 60 m regarding specific details for the calculator are described in MORAN-ZULOAGA et al.(2018). Regarding 325 m, similar corrections were performed, with differences only in the inlet geometry.

As shown in Figure 7, the transmission efficiencies of the inlets increase with the increase in the geometric diameter of the sampled particle. Geometric diameters above 20 nm are transmitted with 83.5% efficiency in the 60 m height inlet line, while for the 325 m, the efficiency is 70%. Aerosol particles belonging to the Aitken and, in particular, the accumulation modes are practically not lost during the transmission, whose effects in studies of aerosol physicochemical properties are negligible. The efficiency only significantly decreases again for particles with geometric diameters larger than $3 \mu m$, that is, particles belonging to the coarse mode, which were not the object of study of this thesis. The core of this work is regarded only to the aerosol fine mode.

The aerosols smaller than 50 nm are the most affected by the particle losses due to

Brownian diffusion. Thus, to compensate for these losses, all particle number size distributions measured at both 60 and 325 m, within the entire measurement range of the instrument (10 to 400 nm) were corrected with the transmission efficiency curves. The aerosols that influence the optical properties measured by specific instruments belong to the Aitken and accumulation modes. Therefore, there was no need to correct such measures concerning the transmission of particles.

Figure 14 – Transmission efficiency curves obtained using the *Particle Loss Calculator* software with the geometric parameters of Table 1 for the 60 (black) and 325 m (blue) inlet lines.

4.2 Instrumentation at the ATTO site

The following instrumentation was used to obtain the aerosol physicochemical properties at the ATTO site. As discussed in Section 4.1.1, measurements were not performed at the same tower but within the laboratories connected to the ATTO tower and the Triangular Mast tower. Each of the laboratories has one (or sometimes more) of the following instruments.

4.2.1 Nephelometer

The nephelometer is an instrument developed to measure radiation scattered by aerosols through the scattering coefficient, σ_{scat} , and the backscattering coefficient, σ_{bsc} . Figure 15 a) shows the inside of the instrument and Figure 15 b) shows one of the instruments at the ATTO site. The sampled aerosol is pumped into the equipment, in which there is a set of LEDs that radiate the particles in such a way as to measure σ_{scat} and σ_{bsc} simultaneously

in three wavelengths: 450, 525, and 635 nm. The instrument's measures' theoretical principle is based on the assumption that the light inside the measuring chamber is attenuated both by scattering and by absorption due to particles and gases. It characterizes the extinction coefficient $\sigma_{ext,\lambda}$ for a specific wavelength λ :

$$\sigma_{ext,\lambda} = \sigma_{scat,\lambda} + \sigma_{abs,\lambda}, \quad (4.1)$$

where $\sigma_{scat,\lambda}$ and $\sigma_{abs,\lambda}$ are the scattering and absorption coefficients. According to GORDON; JOHNSON(1985), the absorption contribution can be neglected in equation 4.1 because the atmospheric air is mainly composed of N_2 and O_2 , which does not absorb significantly in the spectral range measured by the nephelometer. The most significant gas, in this case, would be O_3 , but it represents only 4×10^{-6} % of the atmospheric air composition. Therefore, the extinction coefficient can be approximated as:

$$\sigma_{ext,\lambda} \simeq \sigma_{scat,\lambda}. \quad (4.2)$$

The total scattering coefficient measured by the detector is defined as:

$$\sigma_{tot}^\lambda = 2\pi \int_0^\pi f^\lambda(\theta) \sin(\theta) d\theta, \quad (4.3)$$

where $f^\lambda(\theta)$ is the scattering function, dependent on the wavelength of the incident radiation, and represents the scattered energy in a solid angle increment $d\Omega$ in the direction θ . The total scattering component is composed of two parts: a forward scattering, σ_{fs}^λ ($0 \leq \theta \leq \pi/2$), and a backward scattering, σ_{bs}^λ ($\pi/2 \leq \theta \leq \pi$):

$$\sigma_{fs}^\lambda = 2\pi \int_0^{\pi/2} f^\lambda(\theta) \sin\theta d\theta \quad (4.4)$$

$$\sigma_{bs}^\lambda = 2\pi \int_{\pi/2}^\pi f^\lambda(\theta) \sin\theta d\theta. \quad (4.5)$$

Commercial nephelometers as the ones used at the ATTO site (Aurora 3000 Multi-Wavelength) measure the scattering coefficient not only between 0 and $\pi/2$, but within the semi-hemisphere of 0 to π due to the arrangement of the baffles. Backscatter is measured by blocking forward scattering through a shutter, allowing measurements within an angle of $\pi/2$ to π . More precisely, Aurora 3000 nephelometers measure light scattering from 9° to 170° , and light backscattering from 90° to 170° (ECOTECH TEAM, 2015). Note that there is naturally a loss in the efficiency of the measurements since edge angles are lost. During the data analysis, the measures are corrected for truncation errors according to the procedures of ANDERSON;

Figure 15 – Overview of a nephelometer. a) Internal components of an Aurora 3000 nephelometer, where 1) is the measurement chamber, 2) light source, 3) atmospheric measurement input connection, 4) filter connection for zero procedures, and 5) span gas connection. b) One of the Aurora 3000 nephelometers of the ATTO site. Source: Figure a) is adapted from ECOTECH TEAM(2015).

OGREN(1998) and RIZZO et al.(2013), which is based on Mie calculations to simulate the integral scattering coefficient from 0° to 180° to obtain parameters for the corrections.

The measured scattering (and also the backscattering) coefficient is the composition of the scattering coefficient from particulate matter, σ_{sp}^λ , from gas molecules (Rayleigh scattering), σ_{sg}^λ , and from the chamber walls, σ_{sc}^λ (which is assumed to be neglected by the manufacturer because of the paint used. Although the manual says this can be neglected, there are still some remaining diffuse scattering). In principle, the zero procedure of the instrument corrects the total scattering and subtracts the gas and chamber contributions.

The instruments at the ATTO site are calibrated frequently (every 3 or 4 months) with CO_2 as the span gas, to assure the quality of the measurements. The measured scattering coefficient has the unit of Mm^{-1} , which is 10^{-6} m^{-1} . According to the manual, the lower limit of detection (LOD) of the Aurora 3000 nephelometer is 0.3 Mm^{-1} over 60 seconds of integration. Both nephelometers are running with 5 liters per minute at the site, which is the optimal flow rate recommended by the manufacturer. The instrument has temperature and atmospheric pressure sensors, whose measures are helpful for the internal dryer system (not related to the inlet dryers) and for standard corrections, which will be described further.

4.2.2 Multi-angle Absorption Photometer and the Aethalometer AE33

The Multi-angle Absorption Photometer (MAAP) and the Aethalometer, model AE33, are instruments used to obtain the absorbing component of the atmospheric aerosol. Figure 16 shows both instruments at the ATTO site. In particular, both of them measure the equivalent Black Carbon (eBC) concentration using optical techniques at different wavelengths with real-time output (1 min of time stamp). Both instruments measure together at the site, and this redundancy is because, historically, the MAAP has been used as a reference for eBC measurements worldwide. At the same time, the AE33 obtains the aerosol absorbing coefficient in 7 different wavelengths. It is worth noticing that MAAP has been discontinued and that AE33 has been the main optical technique for obtaining the aerosol-absorbing component.

The MAAP measures the eBC performing the following: aerosol is sampled on a glass-fiber filter, which is irradiated by a 637 ± 1 nm light (instead of 670 nm, as reported by the instrument's manual (MÜLLER et al., 2011)). The transmitted light is detected by a set of photometers, which collect the light back scattering at the forward hemisphere at 130 and 165°. Another set of photodetectors also collects the reflected light and the equipment's software retrieves the eBC mass concentration by using a radiative transfer model (PETZOLD; SCHÖNLINER, 2004). The eBC concentration ($\mu\text{g m}^{-3}$), which is given as the output, is converted to the absorption coefficient by the following relation:

$$\sigma_{abs,637nm}^{MAAP} = m_{eBC} \cdot \alpha_{BC}, \quad (4.6)$$

where $\sigma_{abs,637nm}$ is the absorption coefficient in Mm^{-1} , m_{eBC} is the eBC mass concentration and $\alpha_{BC} = 6.6 \text{ m}^2 \text{ g}^{-1}$ is the MAC of the eBC used in the MAAP's firmware. The MAAP detection limit is about 20 nm m^{-3} , which corresponds to $\sim 0.10 \text{ Mm}^{-1}$, considering average measurements of 30 minutes. The total uncertainty of the measurements is about 10 % for this time stamp (RIZZO et al., 2013). In general, at the ATTO site, the MAAPs run at a flow rate of 10 L min^{-1} . However, the flow can be changed depending on unexpected conditions, such as the failure of other instruments connected to the same aerosol transmission line.

The AE33 measures the eBC concentration in 7 different wavelengths: 370, 470, 520, 590, 660, 880, and 950 nm. Its measurements principles are based on the Beer-Lambert-Bouguer law by measuring the light attenuation (ATN) on an aerosol quartz filter, where the sampled particulate material is deposited. The ATN is defined according to Beer-Lambert's law as:

$$ATN = -100 \cdot \ln\left(\frac{I}{I_0}\right), \quad (4.7)$$

where I_0 and I are the radiation intensities transmitted in the original and in the sampled

Figure 16 – Instrumentation for measuring optical properties of the aerosol-absorbing component, where a) is the AE33 and b) the MAAP, both photographed at the ATTO site.

filter, respectively. The instrument is set to measure the attenuation component of the aerosol by considering the changes in the aerosol load on the filter.

Then, it is defined the attenuation coefficient as:

$$\sigma_{ATN} = \frac{A_f}{Q} \frac{\Delta ATN}{\Delta t}, \quad (4.8)$$

where A_f is the light spot area, Q is the volumetric flow rate ($L \min^{-1}$) and ΔATN is the attenuation variation over a Δt time due to changes in the aerosol concentration on the filter. The eBC concentration at a specific wavelength λ is, therefore, defined as the ratio:

$$eBC = \frac{\sigma_{ATN}}{\alpha_{ATN}} [ng \ m^{-3}], \quad (4.9)$$

$$\alpha_{ATN} = \frac{6837.6}{\lambda[nm]} [m^2 \ g^{-1}], \quad (4.10)$$

where α_{ATN} is the spectral mass-specific attenuation cross-section for the AE33 (SATURNO et al., 2017; SATURNO et al., 2018b). For the AE31, for example, $\alpha_{ATN} = 14625 \ m^2 \ g^{-1} \ \lambda^{-1}$, meaning that this parameter depends on the instrument used at the site. According to the manual, the eBC measured at 880 nm is used as the standard value for Black Carbon concentration. The advantages of the AE33 are diverse: it is possible to obtain the spectral dependence of the aerosol absorption component as a function of the wavelength. This is essential for calculations of intrinsic optical properties, such as the absorption Ångström exponent and the Brown Carbon component (WANG et al., 2016b), whose methodology is described in section 4.5.

Despite the advantages, the AE33 measurements may present artifacts due to multiple scattering effects caused by the filter matrix and effects related to the filter loading. The corrections applied to the data used in this study were mainly based on SATURNO et al.(2017), RIZZO et al.(2011), and SATURNO et al.(2018a), in which further details can be found in the

articles mentioned above. The AE33 LOD is similar to the one from MAAP and, at the ATTO site, the AE33s are running at a flow rate of 4 L min^{-1} . Both instruments agree well, with differences of less than $\sim 5\%$. A comparison of the instruments performed with data from 325 m tower at the wet (March 2019) and dry (August 2019) seasons can be seen in Figure 17.

Figure 17 – Comparison of MAAP and AE33 in March and August 2019. The agreement between the instruments presents $R^2 = 0.99$ for both months in this example.

4.2.3 Condensation Particle Counter and Scanning Mobility Particle Sizer

The total aerosol number concentration is obtained using the condensation particle counters (CPC), which are based on radiation scattered by the condensed particles. These instruments can obtain the total number of particles with geometric diameters larger than 4 nm (TSI Team, 2017). The working principle of the CPC is through the induced growth of aerosol particles by saturation at the heterogeneous condensation condition. A laminar air flow drags the particles into the instrument, and they are transported to a saturation chamber, where there is a butanol atmosphere. The solution of particles and butanol is cooled by a thermoelectric device, which results in condensation nuclei that form larger droplets. They are then transported through a thin tube to another chamber, in which a diode laser, a lens system, and a photodiode detector collect the light scattered by the particles. At the ATTO

site, it is used CPCs from TSI, model 3722, and Grimm, model 5412, which are capable of measuring particle number concentrations as high as 5×10^4 particles cm^{-3} with an accuracy of $\sim 10\%$ (TSI Team, 2017). They are similar and measure similar number ranges of particles. According to the manual, the sample efficiency increases with the aerosol diameter, reaching about 95 % at 10 nm.

In addition to the CPCs, the particle number size distributions (PNSD) are measured by the Scanning Mobility Particle Sizer (SMPS). The SMPS is connected to a CPC, as shown in Figure 18, where the particle number concentration at a specific size range is determined. The theoretical principles of the SMPS are based on the mobility of particles in the presence of an electric field, which can be discriminated by their sizes, according to its electrical mobility, Z_p :

$$Z_p = \frac{neC}{3\pi\mu D_p}, \quad (4.11)$$

where n is the number of electrons at the particle, e is the electron charge (1.6×10^{-19} Coulomb), C is the Cunningham slip correction, which depends of the gas mean free path, μ is the gas viscosity ($\text{dyne} \cdot \text{s} \cdot \text{cm}^{-2}$) and D_p is the particle diameter (cm).

The sampled aerosol penetrates the instrument through a nozzle and reaches the impactor. In this location, particles above a specific size are removed when they impact the base of the chamber. In contrast, smaller particles are transported through the stream line to another chamber, in which the measurement process is initiated. The need for an impactor occurs because it is necessary to remove particles that can contribute to multi-charged aerosols. The remaining particles are then transported to a neutralizer, composed of a radioactive source of the Kr-85 isotope. There, the aerosol particles collide with ions due to their random thermal movement. The particles then reach an electrostatic equilibrium, in which they have a known bipolar charge distribution.

After the neutralizer, the particles are transported to the differential mobility analyzer (DMA). The DMA consists of a long metallic tube compartmentalized to allow the circulation of polydispersed particles and sheath air. In the DMA, a voltage is applied, which generates an electric field. It results in the movement of positively charged particles towards the negative pole. The final location of these particles will depend on Z_p . Those with very high or deficient mobility will be discarded, and only those within a well-defined range of Z_p will be transported to the CPC (approximately monodisperse particles). This well-defined range depends on the applied voltage and generates bins of size measured by the SMPS + CPC set. Thus, the SMPS does not precisely measure a specific size of the geometric diameter of the particles, but sizes within a range, for example, between 50 and 60 nm. The following equation describes the

particle diameter as a function of the applied voltage and geometric parameters of the DMA:

$$\frac{D_p}{C} = \frac{2ne\bar{V}L}{3\mu q_{sh} \ln\left(\frac{r_2}{r_1}\right)}, \quad (4.12)$$

where $\bar{V}$ is the average applied voltage, q_{sh} is the sheath air flow rate, L is approximately the length of the DMA, and r_1 and r_2 are the inner and outer radius of the DMA, respectively. The size range measured by an SMPS varies between 10 and approximately 800 nm. In general, the data measured at the ATTO site are focused on the range between 10 and 400 nm, which is a region of good instrument efficiency. A specific software imports SMPS data from the company TSI, which allows corrections for multiple loads and diffusion losses. It is worth noting that the corrections are always performed for the ATTO data. More details regarding SMPS data correction for the ATTO site can be found elsewhere (PÖHLKER et al., 2016; MORAN-ZULOAGA et al., 2018; TOLEDO MACHADO et al., 2021).

Figure 18 – Set of SMPS + CPC, in which it is possible to see the location of the radioactive neutralizer, DMA, and butanol, which feeds the CPC.

4.2.4 Quadrupole Aerosol Chemical Speciation Monitor (Q-ACSM)

This study used mass spectrometry measurements to obtain the organic and inorganic components of the atmospheric aerosol in Central Amazonia. At the ATTO site, two Aerodyne's Quadrupole Aerosol Chemical Speciation Monitor (Q-ACSM) was utilized, which measures the mass concentration of nitrate (NO_3^-), sulfate (SO_4^{2-}), ammonium (NH_4^+), chloride (Cl^-) and organics with a temporal resolution of about 10 - 30 minutes. The advantage of Q-ACSM

type mass spectrometers is that they can be operated remotely and continuously, measuring aerosols with sizes between 75-650 nm (NG et al., 2011). The aerosol particles enter the equipment from the inlet and are focused using aerodynamic lenses. They pass through two vacuum chambers until they reach a third chamber (detection chamber). The particle flow is controlled by the pressure differences between the turbo pumps in each chamber. The procedure is necessary for removing volatile gaseous compounds from the sample. In the detection chamber, the particles collide with a tungsten filament, whose temperature is around 600°C, where they are thermally vaporized.

The component of aerosols that vaporizes almost instantly is called the non-refractory fraction of the aerosol, and it is the fraction that will be measured. In this fraction, the contributions of mineral dust and BC components are not included. The vaporized gas is then ionized by an electron beam with energy in the order of 70 eV so that the fragments are transferred to a quadrupole type detector. An electromagnetic field is applied to select the fragments by their m/z ratio, where their intensities are measured. Simultaneously, naphthalene is used for routine monitoring of the instrument's performance by performing a simplified calibration regarding the ionization efficiency of the spectrometer. The equipment also analyzes the filtered atmosphere in the mass spectrometer, which is further used as a background and normalization of the ion signal. Thus the useful measurement is obtained from the subtraction between the ion signal and the atmospheric air signal (NG et al., 2011).

The instrument requires periodic calibrations to ensure ionization efficiency. They are made with an aerosol generator of ammonium nitrate or ammonium sulfate solution, connected to a DMA to select particle sizes in the order of 300 nm. Knowing the characteristics of the aerosol produced, it is then possible to obtain the mass concentration of the sample, which is used with the signal of the ions and a linear adjustment to obtain the response factor. The mass concentration C_s [$\mu\text{g m}^{-3}$] of the s-esm aerosol chemical component is obtained through the ion intensity $I_{s,i}$ by the following equation:

$$C_s = \frac{10^{12} \cdot MW_s}{IE_s \cdot Q \cdot Na} \times \sum_i I_{s,i}, \quad (4.13)$$

where Q [$\text{cm}^3 \text{s}^{-1}$] is the volumetric flux, Na is the Avogadro number, and IE_s is the ionization efficiency of the s-esm chemical species. Considering 30 min of average time, the detection limit for NO_3^- , SO_4^{2-} , NH_4^+ , Cl^- and organics are $0.012 \mu\text{g m}^{-3}$, $0.024 \mu\text{g m}^{-3}$, $0.284 \mu\text{g m}^{-3}$, $0.011 \mu\text{g m}^{-3}$ and $0.148 \mu\text{g m}^{-3}$, respectively (NG et al., 2011). For more information concerning the Q-ACSM that are running at the ATTO site, please see PÖHLKER et al.(2016).

4.2.5 AERONET sun and lunar Photometers

The AERONET network is a NASA measurement program that uses remote sensing to monitor optical and physical parameters of atmospheric aerosols. In particular, the AOD,

aerosol number size distribution, $\omega_{0,\lambda}$, absorption AOD (AAOD), scattering and absorption Ångström exponents, and water vapor in the atmosphere can be cited. AERONET uses automatic solar and lunar spectral radiometers, model CIMEL Electronic 318, which allow continuous measurements every 5 minutes. Figure 19 shows a CIMEL photometer at the top of the 80 m height tower at the ATTO site.

Figure 19 – CIMEL photometer from the AERONET network installed at the top of the 80 m tower at the ATTO site.

The AERONET algorithm can automatically model the absorption and scattering of radiation through approximations in the geometry of the aerosol particles. In general, they are divided into two subcategories: spherical and non-spherical aerosols. For the spherical ones, the Mie scattering theory is considered, in which the particles are homogeneous spheres (i.e., with the same complex refractive index for all particles, regardless of size) of different diameters. In the case of non-spherical particles, a method is applied assuming that these aerosols have spheroidal shapes, are homogeneous, and are randomly oriented (DUBOVİK et al., 2006).

The algorithm also takes into account whether the measurements are direct or indirect (inversions). Direct measurements are obtained from direct radiance, made with the collimator of the radiometer pointed at the solar disk, and provide data on the aerosol optical depth and the scattering Ångström exponent. The optical depth of the aerosol (or extinction aerosol optical depth) is the sum of the scattering and absorption effects by the aerosol particle and is

obtained from the Lambert-Beer-Bouguer law. The Ångström exponent ($\mathring{a}$), which represents the spectral dependence of the optical depth, is obtained from the following equation:

$$\mathring{a} = \frac{\ln(AOD)}{\ln \beta \lambda}, \quad (4.14)$$

where λ is the radiation wavelength, and β is the Ångström turbidity coefficient.

Indirect measurements, obtained by inversions with a photometer from diffuse radiance data, allow us to know the size distribution of the aerosols, the effective radius of the distribution, the complex refractive index of the particle (obtained with the scattering and absorption components), and the $\omega_{0,\lambda}$. The size distribution of the aerosols, calculated through the particle volume by the atmosphere area, and $\omega_{0,\lambda}$ are obtained by:

$$\frac{dV}{d \ln r} = \frac{4}{3} \pi r^3 \frac{dN(r)}{d \ln r} \left[\frac{\mu m^3}{\mu m^2} \right], \quad (4.15)$$

$$\omega_{0,\lambda} = \frac{\tau^{scat}}{\tau^{ext}}. \quad (4.16)$$

In this study, we used data level 1.5 and 2.0 from the AERONET network, with preference for level 2. It is worth mentioning that the instruments of the AERONET network returned to NASA approximately every year for calibration and testing. All data collected by the various photometers around the planet, especially the one located on the ATTO website, can be freely downloaded on the website <<https://aeronet.gsfc.nasa.gov/>>.

4.3 Data processing and standardization

All data used in this study were processed following international protocols, which are adopted by the Atmospheric Physics group at the University of São Paulo (<<https://lfa.if.usp.br/>>). Specific details can be found at <http://ftp.lfa.if.usp.br/ftp/public/ATTO/LFA_Processed_Data/GoAmazon_USP_Data_processing.pdf> for each instrument. In general, the considered data is subdivided into three levels of processing:

- Level 1: Raw data is filtered for instrumental issues, contamination, high RH, and unrealistic values. Specific details are described in the document, as mentioned earlier. All the data produced has a temporal resolution of 5 and 30 minutes.
- Level 2: The data are corrected for specific aspects related to each instrument. All corrections are based on articles in the literature. It is worth mentioning the corrections for nephelometer truncation errors and multiple scattering effects of the AE33. All data are standardized for temperature and pressure (STP), considering a temperature of 0 ° and a pressure of 1013 hPa.

- Level 3: The data is validated against other instruments. For example, MAAP and AE33 data must be compatible within 30 %. SMPS and CPC must agree within 30 %. The SMPS data is also corrected for inlet transmission losses. For the ACSM, the data must agree within 30 % with SMPS integrated mass, considering an aerosol density of 1.4 g cm^{-3} .

Similar protocols are also followed by the Aerosol Analysis & Microscopy group, from MPIC, in Germany. In particular, all the aerosol data processed by the MPIC group is available at the ATTO data portal (<<https://www.attodata.org/>>).

4.4 Terminology

According to PÖHLKER et al.(2016), this thesis defines the Amazonian seasons as follows: the wet season spans from February to May, followed by the wet to dry transition period (WtoD), including June and July. The dry season is spanning from August to November, followed by the dry to wet transition period (DtoW), including December and January. For the Amazonian sub-micron particle population, which is characterized by a multi-modal size distribution, it is used the widely-established terms Aitken (50 – 100 nm) and accumulation (100 – 1000 nm) mode (PÖHLKER et al., 2016; TOLEDO MACHADO et al., 2021).

In addition, we introduced the term sub-50 nm mode, defined as particles between 10 and 50 nm. We avoided using the term nucleation mode for this particle population as this term is typically defined for particles $< 25 \text{ nm}$ and refers to aerosol population relatively soon after nucleation (KULMALA et al., 2012; NIEMINEN et al., 2018). The sub-50 nm particles analyzed here, however, have experienced initial aging and growth to diameters between 10 and 50 nm already. As a short version, we used $CN_{<50}$ to refer to the particle fraction in the sub-50 nm mode. In terms of particle number concentrations of the individual modes, we used the symbols $N_{<50}$, N_{Ait} , and N_{acc} . N_{CN} is defined as the median total particle number concentration.

4.5 Brown Carbon estimation

To obtain the BrC component within the radiation absorption measurements, the calculations here performed used a similar approach developed by WANG et al.(2016b), which considers the total absorption coefficient in a particular wavelength ($\sigma_{\text{abs},\lambda}$), with λ in nm, measured by the aethalometer as composed by the superposition of both BC ($BC\sigma_{\text{abs},\lambda}$) and BrC components ($BrC\sigma_{\text{abs},\lambda}$):

$$\sigma_{\text{abs},\lambda} = BC\sigma_{\text{abs},\lambda} + BrC\sigma_{\text{abs},\lambda}. \quad (4.17)$$

In particular, a slightly different approach based on Wang's was applied by SATURNO et al. (2018a) with aethalometer measurements from a site at the Central Amazonia, in which it was obtained a BrC contribution of 17 – 29% (25th and 75th percentiles) to total absorption coefficient at 370 nm. In particular, during biomass burning plume events, the BrC contribution reached 27 to 47%. An analogous approach is also used to subtract the contribution of BrC from the AOD measurements of the AERONET photometer.

The methodology first considers a theoretical BC absorption contribution to the total absorption coefficient and then retrieve the BrC contribution, according to equation 4.17. It considers that the BC component is wavelength-dependent with the particle size, which implies that the BC absorption Ångström exponent ($\mathring{a}_{abs}$) also admits values different of 1. This dependence is calculated considering three selected wavelengths which maximize the coverage of the radiation spectra from the near-ultraviolet (λ_1), with which the BrC component interacts more, the visible-red wavelength (λ_2) and the near-infrared (λ_3), where the BC plays a significant role. Then, it is defined the wavelength dependence of absorption Ångström exponent (WDA) as follows:

$$WDA = \mathring{a}_{abs,\lambda_{1,3}} - \mathring{a}_{abs,\lambda_{2,3}}, \quad (4.18)$$

Note that in the absence of the BrC, the $\mathring{a}_{abs,\lambda_{1,3}}$ and $\mathring{a}_{abs,\lambda_{2,3}}$ are the ones of the BC. Theoretical values for BC WDA ($BC\ WDA = BC\ \mathring{a}_{abs,\lambda_{1,3}} - BC\ \mathring{a}_{abs,\lambda_{2,3}}$), based on Mie Theory to retrieve $BC\ \mathring{a}_{abs,\lambda_{1,3}}$ and $BC\ \mathring{a}_{abs,\lambda_{2,3}}$, were obtained following the same approach as WANG et al. (2016b) and SATURNO et al. (2018a). It considers polydisperse coated BC particles with different size distributions composed of an internally mixed monodisperse BC core, of a refractive index of $1.95 - 0.76i$ (BOND; BERGSTROM, 2006), a coat with a refractive index of $1.55 - 0.001i$ and BC density of $1.8\ g\ cm^{-3}$ (SCHKOLNIK et al., 2007).

The BC WDA is compared to the WDA calculated with the measured data, and it was considered periods when BrC stands out. In this case, the BC WDA and WDA should differ more than 25 %. Therefore:

$$BC\ \mathring{a}_{abs,\lambda_{1,3}} = \mathring{a}_{abs,\lambda_{2,3}} + WDA, \quad (4.19)$$

$$BC\sigma_{abs,\lambda_1} = \sigma_{abs,\lambda_3} \times \left(\frac{\lambda_1}{\lambda_3}\right)^{BC\mathring{a}_{abs,\lambda_{1,3}}}. \quad (4.20)$$

Performing equation 4.20 in equation 4.17 the brown carbon contribution to the radiation absorption ($BrC\mathring{a}_{abs,\lambda_{1,3}}$) is derived:

$$\sigma_{BrC,\lambda_1} = \sigma_{abs,\lambda_1} - \sigma_{BC,\lambda_1}. \quad (4.21)$$

For the aethalometer data, we performed the calculations with $\lambda_1 = 470 \text{ nm}$, $\lambda_2 = 660 \text{ nm}$ and $\lambda_3 = 880 \text{ nm}$, and for the photometer data, we used $\lambda_1 = 440 \text{ nm}$, $\lambda_2 = 675 \text{ nm}$ and $\lambda_3 = 870 \text{ nm}$. The uncertainties of the methodology follow Wang's and Saturno's approach, in which it was considered the minimum and maximum values of WDA, which is based on Mie Theory.

4.6 Multi-modal log-normal fits of PNSD

Each measured PNSD was fitted by a multi-modal log-normal distribution function, based on HEINTZENBERG(1994), and described as follows:

$$f(D_p, D_i, N_i, \sigma_i) = \sum_{i=1}^n \frac{N_i}{\sqrt{2\pi} \ln(\sigma_i)} \exp \left\{ -\frac{[\ln(D_p) - \ln(D_i)]^2}{2 \ln^2(\sigma_i)} \right\}, \quad (4.22)$$

where D_p is the particle diameter, n is the number of aerosol size modes to be fitted (maximum is 3). Three main parameters characterize each size mode: the mode number concentration, N_i , the mode geometric median diameter D_i , and the mode geometric standard deviation σ_i . A script was developed similarly to HUSSEIN et al.(2005) to provide an automatic user-free decision algorithm to obtain the size modes. As a first step, the algorithm identifies the location of the dominant mode by searching for the peak with the highest particle number concentration (D_1).

Figure 20 – Examples of multi-modal log-normal fits obtained by the automatic algorithm. Sub-50 nm mode (green) is defined as $10 \leq D_p \leq 50$, Aitken mode (red) is defined as $50 \leq D_p \leq 100$, and accumulation mode (blue) is defined as $100 \leq D_p \leq 400$.

The geometric standard deviation of all modes was constrained within the range of 1.1 to 1.55, which was optimized for the measures at the site. The correct location of this

peak, defined within the range $D_{\text{dom}} \in (0.7D_1 \text{ to } 1.2D_1)$, is corrected by optimizing it, N_1 and, consequently, the σ_1 parameters by minimizing least squares. If the dominant mode is located at $D_1 \geq 100$ nm, which means that if the dominant mode is the accumulation mode, then the search for the second mode will be done within the interval of $D_i \in [9, 50)$ nm, referred to as the sub-50 nm size mode. If the dominant mode is the sub-50 nm (e.g., particle diameter smaller than 50 nm) or Aitken ($D_{\text{AIT}} \in [50, 100)$ nm), then the search for the second mode will be done by the accumulation mode ($D_{\text{ACC}} \in [100, 300]$ nm).

The second step is about finding the second and third modes. The algorithm sets the parameters obtained for the dominant mode and searches for the second mode, with initial diameter D_2 , whose second highest peak stands out. The whole process is about to proceed with a peak separation. As with the first mode, the entire process is optimized by least squares, and the correct location of the second peak is verified within the range between 0 and $1.2D_2$, which also returns the optimized σ_2 and N_2 . If there is a third mode, the process is analogous, fixing both found modes and looking for a third peak.

The third step concerns a final joint optimization of the previously obtained mode parameters. The procedure is developed by fixing two modes and leaving the third mode free so that its parameters are again optimized by minimization using the least-squares method. The optimization order in this process was to optimize the sub-50 nm size particle, then the accumulation mode, and, finally, the Aitken mode. In this case, all the free diameters of the fashions could vary between $0.5D_i$ and $1.5D_i$. The algorithm compares the integrated particle number concentrations calculated from the measured size distribution and the fitted curve as a measure of fitting quality. It obtains the R^2 value for each measure. Examples of fits can be seen in Figure 20.

Comparisons between the integrated particle number concentration of SMPS measurements ($N_{10-400 \text{ nm}}$) and the sum of each log-normal fitted size distribution ($N_{\text{conc}, \sum n\text{-modes}}$) were made to assure the quality of the fits. We considered only fits in which the agreement of $N_{10-400 \text{ nm}}$ and $N_{\text{conc}, \sum n\text{-modes}}$ returned $R^2 > 0.8$, which means that about 97% of the data are covered by the developed mode fitting. Within this data set, on average, fits with $R^2 = 0.97$ were obtained, which yielded a linear fit of $N_{10-400 \text{ nm}}$ and $N_{\text{conc}, \sum n\text{-modes}}$ with $R^2 = 0.997$ (Figure 21).

4.7 Meteorological measurements

The meteorological parameters T , incoming shortwave radiation (SW), rainfall (P_{ATTO}), air pressure (p), and RH were measured at the 80 m high tower, located approximately 100 m from the aerosol Mast tower. The measurements performed at the 80 m tower ranged from 2013 to 2018. Specifically, SW and P were measured at the top of the tower, whereas T , p , and RH were measured at 55 m, 55 m, and 81 m, respectively. From January 2019 to September

Figure 21 – a) Histogram of the R^2 resulted from the multi-modal log-normal fits, considering only the data with $R^2 > 0.8$. The average R^2 is 0.97. b) Linear fit of integrated $N_{10-400\text{ nm}}$ and estimated $N_{\text{conc}, \Sigma n\text{-modes}}$, with $R^2 = 0.997$.

2020, the meteorological parameters T , P_{ATTO} , p , RH were measured at the 325 m ATTO tower with a compact weather station (Lufft, WS600-LMB, G. Lufft Mess- und Regeltechnik GmbH, Fellbach, Germany). Overall, meteorological parameters span a time frame from May 2013 to September 2020. Furthermore, an optical fog sensor (OFS, Eigenbrodt GmbH, Königsmoor, Germany) measures the near-field visibility since October 2015 at the height of 50 m at the aerosol Mast tower. Here, fog occurrence is defined as visibility below 5000 m, implying a threshold for light fog. Detailed information on the meteorological instruments can be found in ANDREAE et al.(2015).

4.7.1 The anomaly of the equivalent potential temperature

Variations of the equivalent potential temperature, θ_e , as discussed in section 3.3, have been used as a proxy to indicate downdraft occurrences with studies developed with ozone and aerosol transportation from the free troposphere into the PBL (MACHADO; LAURENT; LIMA, 2002; BETTS et al., 2002; RIZZO et al., 2018; WANG et al., 2016a; GERKEN et al., 2016). To obtain the variations in θ_e , it was necessary to correct the temperature from natural trends related to seasonality and diurnal variations. The steps of this process are illustrated in Figure 22 and are described as follows: the θ_e was obtained by subtracting the mean seasonal trend value, in which it was considered both wet and dry seasons, for each year of the time series, resulting in a new time series named θ'_e .

Then, the calculated mean diurnal cycle of θ'_e was subtracted from θ'_e , at the same time of the day, resulting in a new time series: $\Delta\theta'_e$. The quantity $\Delta\theta'_e$ is the anomaly in the θ_e , and represents the deviation of θ_e from its expected value for that time of the day and

Figure 22 – Illustration of the procedure to obtain the anomaly of the equivalent potential temperature $\Delta\theta'_e$ at a particular season. For didactic purposes, it was selected the wet season of 2018 (Jan - Jun). a) The mean seasonal θ_e (blue line) is obtained from the time series of θ_e . b) Time series of θ_e detrended by its seasonal mean (θ'_e). c) The mean diurnal cycle of θ'_e . d) Time series of $\Delta\theta'_e$, which represents the variations of θ_e at a specific time of the day at a specific season.

season. Values of $\Delta\theta'_e < 0$ are mainly associated with downdrafts and indicate a decrease in θ_e due to air masses changes that come from the free troposphere and enter the boundary layer, typically related to the occurrence of rain, which was used in this work as a tracer for the process. Other processes may also be related to a decrease in θ_e , such as evaporation of rainfall, river breeze, and advection mechanisms.

4.8 GOES-16 brightness temperature and lightning activity

This study uses infrared brightness temperature (T_{ir}) data obtained by the Geostationary Operational Environmental Satellite (GOES), the GOES-16, from November 2017 to April 2020. This data set comprises 914 days with measurements every 10 min., as an indication of the troposphere's meteorological conditions. GOES-16 is a geostationary satellite launched in November 2016 and was operational at 95°W up to the middle of 2017. Then, from April 2019 up to now, it is located at 75°W . The Advanced Baseline Imager (ABI), a state-of-the-art 16-band radiometer onboard the GOES-16, was employed in this study, specifically,

the Band 13, the infrared window, that measurements at $10.3\mu m$. Those measurements are less sensitive than other infrared bands to absorption gases, which allows estimating the cloud-top brightness temperature. An area of 3x3 pixels centered at ATTO was selected for obtaining the time series of T_{ir} , representing around $6.0 \times 6.0 \text{ km}^2$.

Meteorological conditions related to shallow clouds/clear sky are described by a warm T_{ir} and deep convection conditions by a cold T_{ir} . Here, we considered $T_{ir} > 280\text{K}$ as a nearly clear sky condition, $245 \leq T_{ir} < 280\text{K}$ corresponding to shallow clouds and cumuliform clouds, and $T_{ir} < 245\text{K}$ to all convective clouds associated with deep (MACHADO; ROSSOW, 1993; MACHADO; LAURENT; LIMA, 2002). T_{ir} near clear sky conditions means roughly the temperature in the surrounding of the Amazonian PBL. The lightning activity was measured with the Geostationary Lightning Mapper (GLM) sensor of the GOES-16 satellite, which measures at $\lambda = 0.74 \mu m$. The sensor detects occurrences during the day and night (further details are found elsewhere (GOODMAN et al., 2013)). It was chosen to represent the lightning as a density of occurrences: number of events every 10 minutes in an area of 5x5 pixels. Each pixel corresponds to 5 km.

4.9 Identification of particle growth events

The investigation developed in Chapter 5 is focused on a phenomenological description and statistical analysis of growth particle events within the sub-50 nm size mode and Aitken mode size range (50 - 100 nm). The identification of the growth events within the sub-50 nm size range is based on 24 h subsets of the PNSDs and follows the guidelines outlined in KULMALA et al.(2012). Before this analysis, all data were cleaned from single exceptionally high or low values by applying a two-dimensional smoothing algorithm (moving average with moving windows of 25 minutes for time and 20 nm size for particle diameter). The procedure was adopted to avoid possible bias by short intense particle peaks.

The original methodology by KULMALA et al.(2012) is modified by taking a higher size threshold for the identification of growth particle events. Now it was considered D_p of 40 nm instead of 20 nm, to compensate the sub-50 nm size particles occurring at ATTO (ANDREAE et al., 2018; WANG et al., 2016a). Further following KULMALA et al.(2012), the total particle number concentration of particles larger than 40 nm in diameter is then subtracted from the smaller sizes, and positive values in the PNSDs are marked as regions of interest for the occurrence of sub-50 nm mode particles that could result in particle growth events. Days fulfilling these criteria are flagged as *particle growth event days*.

The concept of KULMALA et al.(2012) is strongly related to an ideal occurrence of NPF with a co-occurring decrease of the particle load and existing condensation sink. Consequently, this method is sensitive to the integral particle number concentration within the Aitken and accumulation modes and their seasonal variation, which might have implications

for its applicability in the Amazon rain forest. It corresponds to some limitations of the analysis. Nevertheless, the automated identification routine results were visually inspected, and potentially misinterpreted events were excluded from the filtering process and the analysis. The inspection followed the procedure described in DAL MASO(2005), in which a particle growth event is characterized by:

- i. The appearance of a distinct new mode of particles within the PNSD.
- ii. The particle size is inside the sub-50 nm size mode.
- iii. The mode prevails for more than one hour, and iv) it shows signs of growth in time.

Analysis of the algorithm's identification diameter (D_{id}) from 40 nm to other smaller sizes was performed to quantify its sensibility regarding the Amazonian PNSD. For example, if the identification diameter is set to 30 nm, the number of flagged events decreases significantly. The comparisons showed that this behavior might be related to the algorithm's sensibility in identifying events in the dry season and events in which the particle growth starts at larger diameter sizes. It was obtained that, proportionally, the percentage of dry season events decreases to roughly half when it is considered D_{id} from 40 to 30 nm. The result is related to the fact that smaller variations within the dominant accumulation mode in the dry season may overshadow the variations of the nucleation particle number concentration, reflecting the algorithm's sensibility to identify the growth events.

4.9.1 Growth-rate and Condensation Sink estimation

The GR and CS are two important physical parameters used to characterize the strength of an individual growth event. Both were calculated following the procedure of DAL MASO(2005) and KULMALA et al.(2012). The GR is defined as the rate at which the mean geometric diameter D_p of the aerosol population with diameters in the size range 10 – 50 nm changes linearly in time:

$$GR = \frac{dD_p}{dt} = \frac{\Delta D_p}{\Delta t} = \frac{D_{p2} - D_{p1}}{t_2 - t_1} [nm h^{-1}], \quad (4.23)$$

where D_{p1} is the geometric diameter obtained by the multi-modal fit at the beginning of the growth event at the time t_1 and D_{p2} is the geometric diameter at the end of the growth event at the time t_2 . The *beginning* of a growth event is defined as the instant in which the mean geometric diameter D_p starts to increase. The *end* of a growth event is reached when either (i) the mean particle diameter (10 – 50 nm) stops to grow, or (ii) the growth is not observed anymore because air masses cross the site, or (iii) the geometric diameter D_p reaches the Aitken mode – in this case, we selected D_2 as the last observed growth mean geometric diameter inside the $CN_{<50}$. There were a few events in which the growth stopped for a while,

and, afterward, it started growing again. In those cases, we considered the second growth as a new growth event. The growth events considered in this study have a duration of at least one hour.

Most of the geometric diameters D_{p1} and D_{p2} were visually selected and adjusted to ensure the best-fit conditions. This procedure was necessary once the flags were obtained to identify when the $CN_{<50}$ particles start to appear, not the growing event itself, which in Amazonia can occur even hours after the particle transport into the PBL. When the beginning and the end of the growth events coincide with the flags from the automatic algorithm, we decided to use them as the time and the mean geometric diameter intervals for the GR estimation. A moving average smooth filter was applied at the mean geometric diameter interval $D_{p1} \leq D_p \leq D_{p2}$, and the fit was obtained by applying a linear model fit at the referred diameter interval. The model returned the following parameters: R^2 , p-value, and GR. To assure the data quality during the analyses, we selected $R^2 > 0.6$ and p-value < 0.05 .

The CS is calculated from the particle number concentration as (DAL MASO, 2005):

$$CS = 2\pi D_{diff} \int_{D_{p,min}}^{D_{p,max}} D'_p \beta_m(D'_p) n(D'_p) dD'_p = 2\pi D_{diff} \sum_{D'_p} \beta_m(D'_{p,i}) D'_{p,i} N_i [s^{-1}], \quad (4.24)$$

where N_i is the particle number concentration in the diameter $D'_{p,i}$ of the i -th size bin; D_{diff} is the diffusion coefficient of the precursor condensable vapor, and β_m is the transition-regime correction (FUCHS; SUTUGIN, 1971), defined as:

$$\beta_m = \frac{1 + Kn}{1 + 1.677Kn + 1.333Kn^2} \quad (4.25)$$

which has a dependence on the dimensionless Knudsen number, $Kn = 2\lambda/D_p$. The Kn parameter represents the ratio of two length scales, where λ is the effective mean free path of the vapor molecules in the gas (DAL MASO et al., 2002).

Originally the integral in equation 4.24 should be performed from 0 to ∞ , but due to limitations in the instruments, this integral is then calculated directly from the lower and upper diameter limits. According to KERMINEN et al. (2018), the smaller particles that are not considered in equation 4.24 can be neglected due to their non-significant contribution to CS. Physically, CS is a parameter that quantifies the ability of the PNSD to remove condensable vapors from the atmosphere, incorporating them into the particle population and directly influencing the particle growth process. It is also proportional to the particle surface area, which provides an intuitive relation to the shape of the PNSD. The CS is also a measure of the average lifetime of a non-volatile (or low-volatile) compound (e.g., H_2SO_4) in the gas phase in the atmosphere. Large values of CS are regarded to a fast decrease in the compound concentration due to condensation.

In this study, CS was calculated considering $D_{diff} = 0.117 \text{ cm}^2 \text{ s}^{-1}$ of the H_2SO_4 (GONG et al., 2008), which is commonly used in the literature, allowing comparisons to other studies.

Recent findings have shown the importance of organic vapor to explain nanoparticle growth within the size range of 10 to 50 nm, which requires other compounds than only extremely low volatility organic compounds (MOHR et al., 2019). In particular, in a boreal forest environment, VOCs of low volatility are primarily responsible for the newly formed particle growth, which has also been observed under controlled conditions, with monomers having sufficient volatility to drive the particle growth (TRÖSTL et al., 2016; STOLZENBURG et al., 2018). As a matter of fact, of the most abundant VOCs in the Amazon, isoprene stands out.

However, its contribution is still uncertain to the process (YLI-JUUTI; MOHR; RIIPINEN, 2020). It is known that the compound can act as an NPF suppressor, but it also acts in the formation of SOA through its photooxidation (CLAEYS et al., 2004; LEE et al., 2016; KANAWADE et al., 2011; WANG et al., 2021). The contribution of organic vapors to the particle growth process represents one of the major open questions in the field, requiring further investigation, particularly for the Amazonian atmosphere. We use the term CS_{growth} as the average CS during the growth particle event.

Chapter 5

Aerosol particle growth events in the Amazon rain forest

The NPF, referring to the nucleation of molecular clusters and their subsequent growth into the CCN size range, is a globally significant and climate-relevant source of atmospheric aerosols. While ‘classical’ NPF within the PBL occurs worldwide, the Amazon rain forest represents a remarkable exception. Classical nucleation events are rarely observed in the PBL. Still, instead, NPF takes place in the UT, followed by downdraft transport of sub-50 nm ($\text{CN}_{<50}$) particles into the PBL, which grow subsequently (WANG et al., 2016a; ANDREAE et al., 2018). Central aspects of the mechanistic understanding of these processes in the Amazon have remained enigmatic, however.

This chapter analyzes the diurnal and seasonal patterns as well as meteorological conditions during Amazonian aerosol particle growth events, which show a sudden occurrence of particles between 10 and 50 nm within the PBL, followed by their growth to CCN sizes. This study is based on more than six years (Feb 2014 to Sep 2020) of aerosol and meteorological data from the ATTO site. The results of this chapter were presented at a series of international congresses (Section A.1) and is currently submitted for publication in the peer-reviewed periodic *Atmospheric Chemistry and Physics* (FRANCO et al., 2021).

5.1 Particle number size distributions for wet and dry season

Following previous studies, our long-term PNSDs measurements show the typical characteristics of the Amazonian wet and dry season aerosol particle population (ROBERTS et al., 2001; GUNTHER et al., 2009; ARTAXO et al., 2013; PÖHLKER et al., 2016; RIZZO et al., 2018). We chose a different representation of the typical PNSD shapes in Figure 23 by showing them as frequency distributions (FDs). Following the studies mentioned above, the PNSDs differ significantly for both seasons: during the wet season, a clear Aitken and accumulation modes stand out, separated by a distinct Hoppel minimum (HOPPEL; FRICK; LARSON, 1986).

Figure 23 – Frequency distribution (FDs) of particle number size distributions (PNSDs) for the Amazonian wet (a) and dry season (b). Data basis comprises 6.5 years of SMPS data from Feb 2014 to Sep 2020. Color code denotes the number of observations. Solid lines represent the median and dashed lines the mean PNSDs. Please note the different y-axes. The wet season PNSDs show pronounced Aitken and accumulation modes. An overwhelming accumulation mode dominates the dry season PNSDs. The wet and dry season FDs of PNSDs emphasize a comparatively sparse occurrence of $CN_{<50}$, which form a weak, though characteristic, mode below 50 nm.

The Aitken mode is centered at 71 nm, the Hoppel minimum is centered at 102 nm, and the accumulation mode is centered at 153 nm. In contrast, Figure 23b shows the typical dry season PNSDs characterized by a strong mono-modal shape with a dominating accumulation mode, reflecting the prevalence of biomass burning pollution (RISSLER et al., 2006; BRITO et al., 2014). The accumulation mode is centered at 146 nm. In addition, the overall distribution shape in Figure 23b reveals a contribution of the Aitken mode, visible as a small shoulder of the robust accumulation mode, centered at 68 nm.

In terms of the abundance of $CN_{<50}$, the FDs in Figure 23 reveals that aerosols in this size range are relatively sparse - though not absent - during both wet and dry seasons. The occurrence of $CN_{<50}$ particles in the central Amazonia along with the absence of 'classical' NPF, as detected, e.g., in the Scandinavian boreal forests and shown in, e.g., (KULMALA et al., 2004; HEINTZENBERG et al., 2017; KERMINEN et al., 2018; DALL'OSTO et al., 2018), is well documented in the literature (ROBERTS et al., 2001; PÖHLKER et al., 2016; RIZZO et al., 2018). Although occurring sparsely, the episodic presence of $CN_{<50}$ particles results in a distinct mode below about 50 nm, noticeable in the wet FDs in Figure 23a.

However, the $CN_{<50}$ does not show up in the corresponding mean and median PNSDs. It is further worth noting that the PNSDs under the *remote* rain forest conditions at ATTO as shown here differ significantly from PNSDs that were obtained in the rain forest atmosphere with an influence of the urban emission plume from Manaus (ARTAXO et al., 2013; FAN et al., 2018; WIMMER et al., 2018; GLICKER et al., 2019). These urban-influenced PNSDs are characterized by strongly enhanced particle number concentrations below about 20 nm. As the mean and median PNSDs do not sufficiently reflect the abundance and properties of $CN_{<50}$ in

Figure 24 – Characteristic examples of $CN_{<50}$ particle growth events, shown as the temporal evolution of the PNSD as a heat map. The figure presents the development of PNSDs on February 19, 2018, showing pronounced Aitken modes and particle growth events going from sub-50 nm particle mode to Aitken mode during daylight.

Figure 23, the following paragraphs summarize the in-depth analysis that allowed extracting their event characteristics, seasonal and diurnal variability well as estimated significance.

5.2 Particle growth events characterization

The abundance of $CN_{<50}$ that show up as a weak, though noticeable, mode during the wet season (see the overall outline in Figure 23) results from the episodic occurrence of $CN_{<50}$ particles events, including particle growth. Figure 24 shows a typical example of the Amazonian ‘banana plots’ representing two growth events observed at the ATTO site. The first example in Figure 24 starts in the morning hours around 08:30 LT, with an average initial growth diameter slightly larger than 30 nm. The particles grow for about four hours, reaching Aitken mode size ranges up to ~ 60 nm. On the same day, a secondary growth event starts around noon with an average initial growth diameter slightly larger than 20 nm, growing during the afternoon hours. The exemplary events in Figure 24 further illustrating that the initial growth diameters exceed the lower SMPS size detection limit (i.e., 10 nm), which implies that the growth event analysis is not distorted from the measurement range.

The growth events shown here resemble the events reported by WANG et al.(2016a). Note that for all previous studies in Amazonia, the growth events were observed during the wet season, indicating that this event type is a typical wet season phenomenon associated

Figure 25 – Comparative analysis of a) GR and b) CS at different site conditions. The error bars and the median data denote the 5th and 95th percentiles obtained from different studies compiled by KERMINEN et al.(2018) in its supplementary tables (available online at <<https://iopscience.iop.org/article/10.1088/1748-9326/aadf3c/data>>). For the Amazonian sites, it was chosen to present the medians of GR, because the GR percentiles obtained in the studies are regarding the different types of growth events analyzed, and not to different sites. Figure b only shows the sites that estimated CS.

with precipitation (ZHOU et al., 2002; WIMMER et al., 2018; RIZZO et al., 2018). The procedure described in section 4.9 returned 254 characteristic particle growth events on 217 days of the 1596 measured days, corresponding to a frequency of occurrence of $\sim 14\%$ of event days. It corresponds to about 30 event days per year. The events have a clear seasonality, with more cases in the wet season, corresponding to $\sim 88\%$ from January to June. In the dry season, only $\sim 12\%$ were reported, considering the range from July to December. Further aspects of seasonality are discussed in section 5.3.

Figure 26 shows the FD of GR and CS_{growth} values calculated solely for the 254 observed particle growth events. The GR frequency distribution in Figure 26a shows a clear peak centered around the median of 5.2 nm h^{-1} . The median GR of this study agrees well with the median GR of 5.5 nm h^{-1} obtained by RIZZO et al.(2018). Figure 25a contrasts median GR obtained at different sites in Amazonia and worldwide and shows that the median GR of this study is enclosed in GR ranges obtained at other remote boreal (0.5 to 5.3 nm h^{-1}) or polar sites (0.2 to 5.5 nm h^{-1}). The CS_{growth} frequency distribution in Figure 26b shows a clear peak

centered around the median of 0.0011 s^{-1} . In contrast, the median CS calculated for the entire observation days is 0.0032 s^{-1} , which corroborates that particle growth events in remote sites are expected when CS values are low (Figure 28). The Amazonian CS also agrees with what is observed in different remote regions (Figure 25 b). For example, boreal sites have average CS ranging from 0.00098 to 0.0039 s^{-1} , whose values varied according to the site's location.

Figure 26 – Frequency distribution of a) GR and b) CS_{growth} for the 254 particle growth events.

Figure 27a shows the FD of the PNSDs exclusively for growth event periods starting 3 hours before the beginning of the growth event and lasting until the calculated growth rate stops (according to section 4.9.1). Figure 27b shows the growth event-specific median PNSD for the separated $CN_{<50}$, Aitken, and accumulation modes. At those events, the characteristic multi-modal shape of the wet season PNSDs stands out. The FD for the growth events further underlines the sparse particle abundance $< 20 \text{ nm}$. Figure 27b shows that the Aitken mode is the dominant mode of the median PNSD. In particular, the $CN_{<50}$, although small and not perceptible from the median PNSD, has a significant contribution, and it is centered at $D_{CN_{<50}} = 37 \text{ nm}$ (mean), with $\sigma_{CN_{<50}} = 1.5$, characterizing the distribution. As a comparison, the diameters selected as the initials for the growth events $D_{p,i}$ have a median value of 26.1 nm , with 25th and 75th percentiles of 19.0 and 33 nm , respectively. The Aitken mode, which is the dominant mode, is centered at $D_{AIT} = 67 \text{ nm}$ (mean), with $\sigma_{AIT} = 1.4$. Moreover, the second strongest mode, the accumulation mode, is centered at $D_{ACC} = 170 \text{ nm}$ (mean), with $\sigma_{ACC} = 1.4$. As presented, the growth starts at larger particle sizes than different sites around the world (NIEMINEN et al., 2018).

5.3 Seasonality

The pronounced atmospheric seasonality in the central Amazonia has been characterized using meteorological, aerosol, and cloud microphysical data in previous studies (PÖHLKER et al., 2018; PÖHLKER et al., 2019; MORAN-ZULOAGA et al., 2018; SATURNI et al.,

Figure 27 – a) Frequency distribution of particle number size distributions exclusively for growth event periods. Color code denotes the number of observations, solid lines indicate the median, and dashed lines in the 75th and 90th percentile. The PNSDs for the growth events show a high frequency of $CN_{<50}$ and Aitken size modes, but a relatively low frequency of accumulation mode. The FDs do not show any evidence of *open* PNSDs towards the lower detection limit. b) Median PNSD (black line) of the 254 observed particle growth events, showing its 3 log-normal modes: in green, the sub-50 nm size particle mode; in red, the Aitken mode; and in blue, the Accumulation mode. The adjusted R^2 obtained for the calculated multi-modal log-normal fit is 0.99.

2018a). Here we focus on the seasonality of $CN_{<50}$ particle growth events and potential correlations with selected meteorological and aerosol parameters. Figure 28a emphasizes the typical seasonality of local rainfall, P_{ATTO} , at the ATTO site. The highest rain rate occurred during the wet season, with P_{ATTO} peaking in March and April. The minimum in P_{ATTO} occurred between July to September. A similarly pronounced seasonality can be found in various aerosol properties. N_{CN} in size range between 10 to 400 nm had their minimum in the wet season months March and April with $\sim 280 \text{ cm}^{-3}$ and its maximum in the dry season months August to November with the median value of $\sim 1400 \text{ cm}^{-3}$ (Figure 28c).

The same pattern can be found within the monthly median CS in Figure 28d. Note for comparison that PÖHLKER et al.(2018) reported the seasonality of the particle number concentrations within the Aitken and accumulation modes (N_{AIT} and N_{ACC}), which dominate the PNSD as shown in Figure 23. The strong seasonal differences in the physical aerosol properties - here manifested in a wide range of N_{CN} and different PNSD shapes - have a substantial influence on the concentration of available CCN and, thus, cloud micro-physical processes in the Amazon Basin (PÖHLKER et al., 2016; PÖHLKER et al., 2018). These results agree well with long-term measurements at another central Amazonian site presented by RIZZO et al.(2018) (ZF2 site) and further allow to put earlier campaign-wise measurements into a broader data context (ROBERTS et al., 2001; ROBERTS et al., 2003; ZHOU et al., 2002; RISSLER et al., 2004; RISSLER et al., 2006; MARTIN et al., 2010a).

Figure 28e shows a clear seasonal pattern in the $CN_{<50}$ growth event frequency. We found the highest frequencies during the wet season, peaking in April with about 26 % and

Figure 28 – The seasonal cycle of selected meteorological and aerosol parameters presented as monthly averages for the entire observation period from February 2014 to June 2020. From top to bottom: a) P_{ATTO} monthly rain measured at ATTO, error bars denote the standard deviation of the 5-min measurements. b) SMPS data coverage in the number of measurement days. c) Median total particle number concentration in size range of 10 nm < d < 400 nm, calculated from SMPS data, error bars denote the interquartile range (please note the logarithmic scale). d) Median condensation sink calculated from SMPS data, error bars refer to the interquartile range (please note the logarithmic scale). e) Annual cycle of the occurrence of $CN_{<50}$ particle growth events. It is worth noting that the growth events occur almost solely during the wet season months.

dropping down during WtoD (Jun and Jul) to the first minimum with almost zero events in August. The growth event occurrence stayed remarkably low during the dry season months, with frequencies below 3 % from July to November. Frequency levels increase again during DtoW. The seasonal trend of growth event occurrence matches the tendency of monthly rainfall (Figure 28a), but contrasts the trend of N_{CN} and CS .

The results agree with previous studies, suggesting a close link between atmospheres with low particle number concentrations and the appearance of $CN_{<50}$ and Aitken mode particles within the Amazonian PBL (KREJCI et al., 2003; WANG et al., 2016a). The low condensation sink might further favor the characteristic growth patterns of these events through the condensation of semi- and low-volatile gaseous compounds on the $CN_{<50}$ as available surfaces (see example in Figure 24a) (DAL MASO, 2005; D et al., 2007; DADA et al., 2017; KERMINEN et al., 2018; NIEMINEN et al., 2018; WIEDENSOHLER et al., 2019). Note that N_{CN} and CS as well as the characterization of $CN_{<50}$ particle growth events in Figure 28e, are all based on the same multi-year SMPS data set, which is the foundation of this study. The underlying data availability is documented in Figure 28b as the number of included measurement days.

Table 2 shows the GR and the median CS_{growth} of the growth event for all the months. In the wet season, with $\sim 88\%$ of the growth events, GR fluctuates around the median GR of 5.2 nm h^{-1} , which has the same behavior of CS_{growth} , which fluctuates around 0.0011 s^{-1} . The lowest median GR of the wet season is found in March, with 3.7 nm h^{-1} , while the lowest CS_{growth} of the wet season is found in April, with 0.0008 s^{-1} . As highlighted before, particle growth occurrences drop dramatically in the dry season, representing only $\sim 12\%$ of the total growth events. If we do not include December in the dry season, the percentage of growth events decreases to about 6% . The CS_{growth} in the dry season indicates that the events occur on days with a cleaner atmosphere than the monthly median CS , as they are similar to the CS of the events observed in the wet season. The only exceptions are the events from October, whose median CS_{growth} was 0.0044 s^{-1} .

The results have shown that particle growth events are likely related to the values of CS , in which the higher the median monthly CS the lower the occurrence of growth events. A higher amount of particles aging by coagulation returns higher values of CS , which means a decrease in the lifetime of the precursor vapor in the atmosphere. In the dry season, regional and long-range transport biomass burning plumes are the main source of aerosols in the lower troposphere, which suppresses the smaller ones from the sub-50 nm mode to grow. With the increase of the wet deposition processes related to the precipitation increase, the number of particles of the accumulation mode in the atmosphere decreases significantly. With fewer particles in the atmosphere, there is a decrease in CS . Thus, the occurrence of growth events increases again, as observed in December.

It is worth noting that other factors may also influence the lower amount of particle growth events when median CS values are high, such as temperature and relative humidity (DADA et al., 2017; KERMINEN et al., 2018). Note here that the identification method of growth-like events is sensitive to the accumulation mode concentration and might introduce a dry season bias due to the strong increase of accumulation mode concentrations that could, in principle, prevent the automatic detection of growth-like events. Nevertheless, the results

Table 2 – Monthly median, 25th and 75th percentiles (in brackets, respectively) of GR and CS_{growth} . The percentage of growth events in each month is also presented.

Month	GR [$nm\ h^{-1}$]	CS_{growth} [s^{-1}]	Fraction of events (%)	# of events
Jan	5.0 (2.5 - 6.9)	0.0012 (0.0008 - 0.0016)	8.7	22
Feb	5.2 (3.9 - 8.1)	0.0013 (0.0008 - 0.0021)	13.8	35
Mar	3.7 (2.6 - 6.3)	0.0010 (0.0005 - 0.0015)	18.1	46
Apr	5.3 (4.5 - 8.6)	0.0008 (0.0005 - 0.0012)	25.6	65
May	5.5 (4.0 - 8.2)	0.0011 (0.0006 - 0.0019)	16.1	41
Jun	6.1 (4.6 - 9.4)	0.0025 (0.0012 - 0.0030)	5.9	15
Jul	8.2 (6.2 - 8.6)	0.0034 (0.0026 - 0.0038)	1.2	3
Aug	5.2 (5.2 - 5.2)	0.0011 (0.0011 - 0.0011)	0.4	1
Sep	10.4 (3.7 - 18.8)	0.0017 (0.0012 - 0.0019)	1.6	4
Oct	8.8 (4.9 - 13.1)	0.0044 (0.0033 - 0.0052)	2.4	6
Nov	4.2 (4.2 - 4.2)	0.0037 (0.0037 - 0.0037)	0.4	1
Dec	6.2 (4.7 - 8.0)	0.0012 (0.0009 - 0.0015)	5.9	15

were carefully checked. The visual inspection confirmed the low event frequency of growth-like events during the dry season, which underlines that the seasonal trend in Figure 28e is reliable.

5.4 Diurnal trends

The diurnal patterns of growth event occurrence are characterized by meteorological parameters, such as air temperature, SW , P_{ATTO} , RH , and near-field visibility representing fog, which is shown in Figure 29. We contrasted the diurnal cycles for the entire observation period (i.e., Feb 2014 to Sep 2020, shown as solid lines) with wet season months Feb to May shown as dashed lines). In the diurnal cycles considering the whole period of observations, T and SW show the typical tropical rain forest conditions with about 12 h daylight and remarkably low amplitude in T spanning on average only 5°C . Rainfall is most intense in the afternoon hours, with the highest precipitation intensity at 15h LT, resulting in average annual rainfall of around 2000 mm, the data also shows a secondary maximum in the early morning, which has been associated with the mesoscale systems (TOLEDO MACHADO et al., 2021). The RH levels reach on average 100 % during the early morning and decrease to around 75 % during the day. Fog typically occurs in the second half of the night and most often in the early morning before sunrise (i.e., between 03:00 and 07:00 LT), when T is lowest. Sporadically, fog also occurs shortly after rain showers, which is not reflected by the average conditions.

Figure 29 – Diurnal cycle of selected meteorological parameters and the diurnal occurrence of growth particle events. From top to bottom: a) incoming shortwave radiation (SW, orange) and air temperature (T , red) at 26 m (at canopy level) height. b) average local rain rate (P_{ATTO} , blue). c) relative humidity (RH) at 26 m. d) visibility (blue) measured by a fog monitor and fog occurrence (black) with lines representing the first quartile, e) median diurnal cycle of $N_{<50}$ for all the data (black line) and only for the days in which particle growth events were observed (blue line). Black and blue shadows are the 25th and 75th percentiles for growth event days and all data, respectively. And f) the diurnal cycle of the particle growth events onset. All error bars denote the standard error. The shown data represent all observations (full lines) and wet season subsets (dashed lines), since the growth events are more prominent during the wet season.

Figure 29e) shows the diurnal cycle (blue line) of the median aerosol particle number concentration for sizes smaller than 50 nm exclusively during the particle growth event days. As a comparison, the median diurnal cycle of $N_{<50}$ comprehending all measured PNSD is also presented (black line). The particle number concentration on growth event days is significantly higher than considering all analyzed PNSDs, with median daily values and their respective 25th and 75th percentiles, of 64 (38 - 108) cm^{-3} , compared to 49 (29 - 81) cm^{-3} for

all days. The $N_{<50}$ diurnal cycle for growth event days shows a strong increase from midnight to 09:00 LT, reaching a peak in $N_{<50} = 88 \text{ cm}^{-3}$, compared to $N_{<50} = 56 \text{ cm}^{-3}$ at the same time for the total data. This indicates that aerosol particles are transported into the PBL during the late-afternoon-early night and last until mid-morning. The aerosol transport occurrence is simultaneous with the increase in precipitation rate in the morning, which can be seen in Figure 29b, and is described in detail in section 5.4, and stops when precipitation decreases.

The diurnal cycle of the onset's growth events has a broad maximum over the early morning hours, from 06:00 to 10:00 LT. It peaks at about 07:00 LT and then gradually decreases towards noon (see Figure 29e), which agrees with what is observed in Figure 29f). A second local and less pronounced maximum is visible from 13:00 to 15:00 LT. The growth events reported during daytime likely correspond to rainfall events as reported by TOLEDO MACHADO et al.(2021). The convective activity transports $CN_{<50}$ particles into the PBL as reported in WANG et al.(2016a) and ANDREAE et al.(2018). P_{ATTO} shows two maxima: a pronounced and rather defined maximum in the early morning at around 07:00 LT, which follows a gradual increase in precipitation during the second half of the night, and a broader maximum during the afternoon hours between 13:00 and 17:00 LT. Although about 74 % of events occur during the day, there are still ~26 % during night conditions, between 19:00 - 05:00 LT. In particular, the occurrence of growth events from 01:00 - 05:00, which represents about 16 % of the total observed events, evidences its complexity regarding causes and mechanisms.

Besides the P_{ATTO} levels, the evolution of the PBL certainly influences the diurnal pattern. At night, the nocturnal BL close to the forest canopy is decoupled from the residual layer above (FISCH et al., 2004). In the morning hours - as soon as convection is efficient - air masses transported into and within the residual layer are mixed into lower levels and measured at the canopy level. Consequently, $CN_{<50}$ and Aitken mode particles advected with the residual layer will be mixed downwards and appear at the 60 m inlet in the morning hours, typically around 8:00 LT. Section 5.5 further discusses the meteorological conditions regarding convective downdrafts and sky conditions observed in the growth events.

A contrast in GR and CS is observed when day and night events are compared, as showed in Figure 30. Daytime events, which corresponds to ~74 % of the events, have significantly higher GR and CS_{growth} , of 5.9 nm h^{-1} and 0.0012 s^{-1} , respectively. The nighttime events, which account for ~26 %, have GR and CS_{growth} of 4 nm h^{-1} and 0.0009 s^{-1} , respectively. The Wilcoxon rank-sum test was applied to verify the statistical significance of the difference between day and night values. The p-value obtained for GR is 3.61×10^{-6} , while the p-value obtained for CS_{growth} is 0.02, indicating that the data groups regarding day and night are statistically different, considering a significance level of 0.05. The observed differences are likely due to the different atmospheric mechanisms during daytime and nighttime. Daytime events are directly influenced by sunlight, which controls photochemistry and hence the oxidation of SOA precursors. Sunlight also drives the dynamics of the PBL. Other phenomena

also play an important role in daytime events, such as the peaks of precipitation that coincide with the peaks of growth events. In contrast, nocturnal events may have different causes and mechanisms, which can be related to meteorology, entrainment of air and particles from the free atmosphere into the BL, and perhaps the contribution of biogenic sources from the surface.

Figure 30 – Boxplot of a) GR and b) CS_{growth} related to growth events during the daytime nighttime. Nighttime events occurred between 19:00 and 05:00 LT, while daytime events occurred between 06:00 and 18:00 LT. The box represents the quartiles, whiskers represent 90th and 10th percentiles, and the horizontal lines represent the median.

5.5 Meteorological and cloud conditions during growth events

This section explores the weather and convective transport conditions linked to particle growth events. Figure 31a shows a histogram of the growth events frequency concerning the associated anomaly of the equivalent potential temperature, $\Delta\theta'_e$, at the events' onset (see section 3.3.1). A negative $\Delta\theta'_e$ is an indicator for air mass downdrafts from higher altitudes and was reported for the events characterized by WANG et al.(2016a). We found that ~63 % were associated with air mass downdrafts ($\Delta\theta'_e < 0$), whereas ~37 % were associated with $\Delta\theta'_e > 0$. Figure 31b shows a complementary histogram of all growth events concerning the associated brightness temperature (T_{ir}), which is an indicator for deep convective clouds ($T_{\text{ir}} < 245 \text{ K}$) vs. clear sky/shallow cloud conditions ($T_{\text{ir}} > 280 \text{ K}$). For all events after 2017 (when T_{ir} data is available), we found ~36 % being associated with deep convective clouds ($T_{\text{ir}} < 245 \text{ K}$, red), ~26 % with clear sky/shallow clouds ($T_{\text{ir}} > 280 \text{ K}$, blue), and ~38 % with mixed sky conditions ($245 \text{ K} < T_{\text{ir}} < 280 \text{ K}$, gray).

Figure 31 – Histogram of the a) values of $\Delta\theta'_e$ at the beginning of the particle growth events. Black bars represent events during downdraft conditions and the green bars during undefined conditions; and the b) values of T_{ir} at the beginning of the particle growth events. Red bars represent events during deep convection conditions, blue during clear sky/shallow clouds conditions, and gray during mixed sky conditions.

The most contrasting T_{ir} conditions were determined using T_{ir} values either within the lower quartile ($T_{ir} < 228 K$), representing deep convective cloud conditions, or within the upper quartile ($T_{ir} > 281 K$), representing clear sky conditions, with 36 events associated to each group. As an example, four of these 'extreme' events were selected (Figure 32). Further, for each case, one event represents daytime and the other one nighttime conditions. Figure 32 shows clear differences between the clear sky or deep convection condition events. The growth events under the clear sky conditions are characterized by a trimodal aerosol population with accumulation and Aitken modes as well as a third resolved mode below 50 nm.

For example, the event on 14 March 2019 was characterized by a significant amount of $CN_{<50}$ during the nighttime, starting after midnight. It showed a pronounced peak in the particle number concentration around 06:00 LT. The onset of the particle growth event

was also detected at 06:00 LT, lasting for about 12 h. These events could be associated with advection processes, e.g., by a downdraft in the gust front (clear sky nighttime) or by nighttime rainfall and subsequent growth in the early morning by PBL processes

The events under deep convective conditions resembles the events reported by WANG et al.(2016a). Here, downdrafted air masses in deep convection conditions transport $CN_{<50}$ from the upper troposphere into the PBL, followed by aerosol aging (particle growth) into the Aitken mode. The atmosphere has the characteristic of being very clean, meaning that the accumulation mode particles are sparse. In both examples, before the growth event, most of the particle population belonged to the Aitken mode, which was afterward removed by wet deposition during the precipitation event, when only the $CN_{<50}$ aerosol population remained. Note that only hours after the start of the growth event, the accumulation mode particles appeared.

Figure 32 – Selected particle growth events according to the T_{ir} value at the onset of the event. Events under clear sky/shallow cloud conditions during daytime (left) and nighttime (right) were selected considering $T_{ir} > 281$ K (third quartile), while deep convection events were chosen considering $T_{ir} < 228$ K (first quartile).

Figure 33 shows boxplots for GR in a) and CS_{growth} in b) for either clear sky or deep convection scenarios. The median GR for clear sky conditions is 7.0 nm h^{-1} , in contrast, the median GR for deep convection conditions is 3.8 nm h^{-1} . Regarding CS, under clear sky conditions, the median is 0.0016 s^{-1} , while under deep convection, the median CS is 0.0005 s^{-1} . The results show that different meteorological processes play an important role in the different particle growth events observed. Those events that occurred under deep convection conditions present lower CS_{growth} and GR. Two main factors may influence this

result: the precipitation during deep convection conditions cleans the atmosphere by wet deposition, resulting in lower CS_{growth} values, and the clouds, which reduce the availability of sunlight.

The daily frequency distribution of growth events (see Figure 29f) was divided into four groups (G1 to G4), where G1 and G4 represent the nighttime and G2 and G3 represent the daytime events. The daytime events were divided considering the occurrence of two frequency peaks: The first peak, representing 53 % of the growth events, is depicted within G2, covering 06:00 to 11:59 LT. The second peak, representing 21 % of the growth events, is depicted within G3, covering the time from 12:00 to 17:59 LT. The nocturnal events were divided according to the possible state of the PBL.

Figure 33 – Boxplot of a) GR and b) CS_{growth} for clear sky conditions ($T_{ir} > 281 \text{ K}$) vs. deep convection conditions ($T_{ir} < 228 \text{ K}$). The box represents the quartiles, whiskers represent 90th and 10th percentiles, and the horizontal line represents the median.

The G4 is then defined from 18:00 to 00:59 LT, which is the growth event population that may still have some influence from the ended day, since some convective events occur later in the day and early night and the convective BL is being broken, with 10 % of the events. Moreover, G1, representing 16 % of the total growth events, covers the time from 01:00 to 05:59 LT. At this time, the nocturnal BL is well established, and different mechanisms such as air masses entrainment into the BL, or nighttime rainfall events and biogenic process could play a role in the aerosol particle dynamics. Table 3 shows the median T_{ir} , $\Delta\theta'_e$, the initial diameter, D_i at the onset of the growth event, and its respective GR and CS_{growth} according to the 4 hourly groups.

Table 3 – Median, 25th and 75th percentiles (between parenthesis, respectively) for T_{ir} , $\Delta\theta'_e$, D_i , GR and CS_{growth} for each hourly group. T_{ir} , $\Delta\theta'_e$, D_i are referred to as the onset of the particle growth event.

Group	Hour (local time)	T_{ir} [K]	$\Delta\theta'_e$	GR [$nm\ h^{-1}$]	CS_{growth} [s^{-1}]	D_i [nm]	# of events (%)
G1	01:00 - 05:59	269 (238, 283)	-0.8 (-4.6, 1.5)	3.8 (2.3, 5.5)	0.0009 (0.0004, 0.0015)	27.7 (21.7, 35.3)	16
G2	06:00 - 11:59	268 (236, 282)	-1.9 (-5.3, 2.1)	6.3 (4.2, 8.6)	0.0012 (0.0007, 0.0020)	27.7 (20.6, 33.5)	53
G3	12:00 - 17:59	245 (219, 283)	-3.6 (-6.8, 0.5)	5.6 (4.0, 8.6)	0.0012 (0.0008, 0.0015)	24.6 (19.4, 29.9)	21
G4	18:00 - 24:00	274 (227, 276)	0 (-4.3, 2.1)	4.2 (2.1, 6.3)	0.0010 (0.0006, 0.0015)	27.8 (19.5, 32.7)	10

The results show a clear difference between the four groups (G1 to G4) regarding the T_{ir} and $\Delta\theta'_e$ conditions during the event's onset occurrence. The nocturnal groups G1 and G4 present median $\Delta\theta'_e$ of -0.8 and 0, respectively. The median T_{ir} present conditions closer to low clouds and clear skies, with median values equal to 269 K and 274 K for G1 and G4, respectively. The T_{ir} diurnal cycle (Figure 34) shows clear differences among the groups. Within the G1 period, T_{ir} shows a minimum at 04:00 LT, where the average brightness temperature reaches 256 K, indicating convective activity and early precipitation compared to all days. Afterward, T_{ir} increases again until close to clear sky conditions and shows another minimum again at 16:00 LT. The temperature reaches 259 K and is associated with the peak of precipitation in the afternoon.

This secondary peak has the same behavior as the one for all days showing that the G1 group accounts mostly for convective events during the night. The G4 group, which corresponds to the group with the smaller number of growing events, has no significant difference with the climatology. It follows what is expected for all the days, showing signs of convection at 16h LT, which coincides with the precipitation peak in the afternoon. This group indicates that this 10% of growing cases is not related to meteorological events. Afterward, the T_{ir} increases, going to clear sky conditions during the night. The median GR for G1 and G4 varies from 3.8 to 4.2 $nm\ h^{-1}$, respectively, and CS_{growth} is approximately constant around 0.0010 s^{-1} , while D_i remains stable. The lower GR in G1 can be explained by the typical growing event in the early morning when sunlight is available, and convective BL is developing.

The daytime groups G2 and G3 also have distinct characteristics among groups. Both have the lowest median $\Delta\theta'_e$ of the 4 groups at the onset of the events, with -1.9 and -3.6, respectively, indicating that convective downdraft activity plays an essential role during the growth events. The group G2 also presents in the early morning evident minimums coinciding with the precipitation peaks in the early morning and in the afternoon (Figure 29b). Although the valleys in the T_{ir} diurnal cycle agree with the precipitation peaks, it indicates that the convective activity was even more intense in these days compared to the whole set of days.

The G3 group is the one with more convective characteristics. T_{ir} values indicate a substantial occurrence of convective systems throughout the day, mainly in the afternoon. In particular, its pronounced valley at 15 LT reaches deep convection conditions, with $T_{ir} = 249$

Figure 34 – Average diurnal cycle of T_{ir} for the growth events of groups G1 to G4. The blue dashed line represents the average diurnal cycle of T_{ir} relating to the days when the particle growth events for a given group were observed. The black line represents the average diurnal cycle for all days on which PNSD measurements were made. The colored shadows represent the standard deviation.

K, approximately 1 hour earlier than expected considering the whole observation days. The median GR ranges from 6.3 to 5.6 $nm h^{-1}$ in G2 and G3, respectively, and the median CS_{growth} remains constant, at 0.0012 s^{-1} . The smaller value of GR in G3 compared to G2 (diurnal events) could be associated with the deep convection system, reducing the solar incidence and influencing the photochemical process. The presence of clouds has been associated with lowering GR and even lower occurrences of NPF and particle growth events (DADA et al., 2017; KERMINEN et al., 2018). The median D_i for G3 is the lowest of the 4 groups, of 24.3 nm, indicating that the strong convective downdrafts are more effective in transporting smaller particles from the free troposphere into the PBL, which agrees with what has been observed (WANG et al., 2016a). Therefore, the growth events of groups G2 and G3 are also induced by the strong convective systems during the daytime. In particular, the G3 group has the most significant characteristics of deep convection and intense occurrences of downdraft throughout the day.

Although the growth events have a strong association with the occurrence of convec-

Figure 35 – Ensemble analysis for a) $\Delta \theta'_e$ and b) T_{ir} considering 10h before and 10h after the event's onset. It is considered the cases where $\Delta \theta'_e$ at the event's onset is less than the 25th percentile (dashed lines) and more than 75th percentile (full lines).

tive downdrafts, when discriminating them by positive or negative $\Delta \theta'_e$ at the event's onset, the behavior of $\Delta \theta'_e$ and T_{ir} near the growth event is evident. Figure 35 shows the behavior of the mean ensembles of $\Delta \theta'_e$ and T_{ir} around $\Delta t = 0$ for $\Delta \theta'_e$ less than 25th percentile (-5.3) and higher than the 75th percentile (+1.5) at the event's onset. Considering the case where $\Delta \theta'_e < -5.3$ at the event's onset, both $\Delta \theta'_e$ and T_{ir} strongly decreases from 10h before the event on, and they reach a minimum at $\Delta t = 0$, where $\Delta \theta'_e = -7.6$ and $T_{ir} = 238$ K, which represents deep convection conditions with strong downdraft occurrence. Both parameters increase afterward to cleaner sky conditions and out-of-downdraft conditions.

In contrast, considering $\Delta \theta'_e > +1.5$ at the event's onset, the ensembles show an opposite behavior of the parameters. The $\Delta \theta'_e$ presents an increasing tendency from 10h before the event until $\Delta t = 0$, reaching a value of +4. Afterward, $\Delta \theta'_e$ decreases, but always assuming positive values, indicating a class of growth events that may not be driven by convective downdrafts. The T_{ir} values from 10h before the events up to $\Delta t = 0$ are equivalent to conditions close to clear skies ($T_{ir} \sim 208$ K), which agrees with the results obtained for $\Delta \theta'_e$, as an indication of sky conditions not dominated by convection systems around the event's onset. After $\Delta t = 0$, T_{ir} values decrease, but without presenting deep convection conditions. The results show that clear sky events can be associated either with advection or subsidence bringing particulates from another area (e.g., a nearby rain event) or from the upper troposphere.

Figure 36 – Dunn index as a function of the number of clusters obtained by k-means. Higher index values indicate better clustering.

5.6 Cluster analysis

K-means clustering analyzes were performed to identify and characterize the different atmospheric mechanisms' conditions through an algorithmic approach. It was considered a data set composed of Tir , $\Delta\theta'_e$ at the event's onset, GR and CS_{growth} . The whole data set comprised 139 growth events. The optimal number of clusters was obtained based on the Dunn index, as shown in Figure 36, where a higher index indicates the best clustering solution. Moreover, visual comparisons were performed to assure quality and physical interpretation. The best combination was obtained for four clusters. Figure 37 shows the centroid of each cluster regarding Tir , $\Delta\theta'_e$, GR, and CS_{growth} and Figure 38 shows the characteristics of each cluster regarding time, precipitation, and RH. We refer to the i -th cluster as C_i , with $i = 1, 2, 3, 4$.

We decided to introduce the results by presenting first the description of the clusters characterized by negative $\Delta\theta'_e$ and deep convection conditions: C_3 and C_4 . Their centroids, showed in Figure 37, have Tir and $\Delta\theta'_e$ values below the critical limit of 245 K (strong deep convection conditions) and the lowest values of $\Delta\theta'_e$. It also coincides with the lowest CS_{growth} , but they do not have the lowest GR. Figure 38 shows that C_3 mainly occurs during daytime, with the highest number of events between 06:00 and 15:00 LT. The events in C_4 are also frequently observed during the daytime, at 06:00-09:00 and 12:00-18:00, coinciding with the diurnal precipitation peaks. This explains why clusters C_3 and C_4 , despite being the most dominated by convective features, do not have the lowest GR values: photochemistry plays a key role in them. It was also observed that some events of C_4 occur during in the late

afternoon, which are still dominated by the turbulence of the PBL. The groups C_3 and C_4 are the characteristic $CN_{<50}$ particle events described by WANG et al.(2016a) and represents 41 % of the growth events.

Cluster C_2 is considered as an intermediate group of growth events, in which the centroid of Tir is located in a region close to mixed meteorological conditions. $\Delta\theta'_e$ is slightly negative, showing that downdraft conditions are still likely to occur. The centroid of CS_{growth} has a higher value than for the convective clusters C_3 and C_4 , but regarding GR, C_2 has the slowest growth events. The precipitation is still present, with RH relatively high compared to the other groups, but with lower values than the convective clusters. The events represented by C_2 are likely to occur both under daytime conditions, but they are more frequent from 00:00 to 03:00 LT. The events in cluster C_2 represent nearly 32 % of $CN_{<50}$ particle growth events.

Figure 37 – Cluster analysis was performed with 4 sets, showing the centroid of the meteorological and physical parameters identified for each cluster and the number of growth events in each cluster. The red and blue lines mean deep convection and clear sky conditions, respectively.

Cluster C_1 is the one that presents the most contrasting characteristics to the other groups. The centroid of Tir is located in clear sky conditions while and the centroid of $\Delta\theta'_e$ is positive. Cluster C_1 also presents the highest values of GR and CS. There is no sign of precipitation in it, and the higher frequency of occurrence of RH is about 80 %. The frequency of occurrence of the events in C_1 is concentrated under daytime, with the peak at 06:00-09:00 LT, but with an expressive number of events from 10:00 to 18:00 LT. Nocturnal events are also present, in particular from 00-06:00. The events in C_1 , represented by 27 % of the events, may not be directly driven by convective downdrafts as described by WANG et al.(2016a), and

Figure 38 – Qualitative analysis of the frequency of occurrence of the growth events regarding each set according to time, precipitation, and RH.

may have been caused by other mechanisms and sources, whose processes require further investigation.

5.7 Final remarks

This chapter reports the statistical characterization of aerosol particle growth events within the sub-50 nm size modes (10 - 50 nm), with continuous measurements (February 2014 to September 2020) of PNSDs at a remote site in Central Amazonia. In total, 254 particle growth events were detected, comprising about 14 % of the analyzed days, of which 88 % was found between January to June and 12 % from July to December. Growth event days have a significant increase in $N_{<50}$ during the night up to 09:00 LT, when it reaches a median value of 65 cm^{-3} , significantly higher expected at the same time of the day considering all measured PNSDs, of 49 cm^{-3} . After the peak in the morning, $N_{<50}$ strongly decreases up to 14h LT, from when it follows a smooth growth trend. The morning decrease is likely associated with the strong occurrence of growth events in the early morning.

The diurnal cycle of the growth events shows that most of them occur during the daytime, accounting for 74% with a significant number of events during the night, of 26%. In the daytime, 53 % of the growth events starts between 06:00 and 11:00 LT, with a pronounced peak at 07:00 LT. It shows that growth events have a direct relation to the photochemistry and evolution of the PBL. Those events also coincide with a precipitation peak in the morning as well as night and late afternoon. The nocturnal increase of $N_{<50}$ is likely related to convective systems resulting in the morning's precipitation peak. Its decrease is likely due to the coagulation process that ages $CN_{<50}$, resulting in growth. A second less pronounced but significant peak occurs at 15h LT, coinciding with the strongest precipitation peak, suggesting its relation to atmospheric convective systems.

Considering all the growth events, the median GR is 5.2 nm h^{-1} , which agrees with

what was reported by RIZZO et al.(2018). The median CS_{growth} is 0.0011 s^{-1} . Monthly variations in GR and CS show that the growth events occur under low CS values at the wet season, while the average value for the growth event itself does not change much from month to month, oscillating around 0.0011 s^{-1} .

A remarkable discrepancy is observed when contrasting day (median GR of 5.9 nm h^{-1} and median CS_{growth} of 0.0012 s^{-1}) and night growth events (median GR of 4.0 nm h^{-1} and median CS_{growth} of 0.0009 s^{-1}). Daytime events are directly influenced by sunlight, which controls photochemistry and hence the oxidation of SOA precursors. In contrast, nocturnal events may have different causes and mechanisms, which can be related to meteorology, entrainment of air and particles from the free atmosphere into the BL, and perhaps the contribution of biogenic sources from the surface.

Analysis performed with $\Delta\theta'_e$ and T_{ir} revealed that diverse atmospheric dynamics play different roles during particle growth event days. The event's onset coincides with downdraft occurrences when the smaller nanometric particles appear and grow afterward. It is also observed that particles processed in clouds belonging to the accumulation mode appear at a particular moment, causing a prominent Hoppel minimum. The growth events belonging to the group related to clear skies present GR and CS higher than those of deep convection: the median GR and CS for clear sky conditions are 7.0 nm h^{-1} and 0.0016 s^{-1} . In contrast, at deep convection conditions, the median GR and CS are 3.8 nm h^{-1} and 0.0005 s^{-1} .

The events were classified according to their frequency throughout the day cycle, showing that they are driven mainly by convective activities (63%). However, when discriminating the growth events by $\Delta\theta'_e$ at the event's onset, the occurrence of downdrafts does not explain all the cases. The contrast is evident in the ensembles of $\Delta\theta'_e$ and T_{ir} when selecting the growth event and its respective occurrence days by $\Delta\theta'_e > 75\text{th percentile}$ ($\Delta\theta'_e = +1.5$) at the event's onset. They showed that at the time $\Delta t = 0$, $\Delta\theta'_e$ is maximum and positive, and even ten hours before or after the growth event, it did not present negative values that could indicate the occurrence of convective downdrafts, representing about 37% of the growth events. Also, T_{ir} fluctuates at around 270 K over the observed period, what represents shallow clouds, instead of convective systems conditions. In contrast, events with $\Delta\theta'_e < 25\text{th percentile}$ ($\Delta\theta'_e = -5.3$) at the event's onset is associated to downdraft occurrences: $\Delta\theta'_e$ strongly decreases 10h after the growth event up to $\Delta t = 0$, which is also followed by a strong decrease in T_{ir} . Cluster analysis corroborated the ensemble analysis and showed that about 27 % of the growth events, considering a data set with cases from 2017 up to 2020, may not be directly driven by downdraft conditions and could be induced by other mechanisms.

Sources that could explain the observations could be related to primary biogenic aerosols emitted by the forest and smooth entrainment of air masses from the free troposphere to the PBL in the early morning. Moreover, different meteorological mechanisms such as gravity waves and lightning particle productions at the free troposphere, as described

by TOLEDO MACHADO et al.(2021), could contribute to the aerosol population. TOLEDO MACHADO et al.(2021), could contribute to the aerosol population. Another possible explanation is related to the advection mechanisms, such as the nighttime downdraft far upwind, which gets trapped above the nocturnal boundary layer, and travels in the jet above the nocturnal inversion for potentially quite a considerable distance, being mixed down into the PBL after sunrise. Therefore, upcoming studies are required to unveil the aerosol sources that could explain the diversity of particle growth events observed at the lower troposphere of the Central Amazônia.

Chapter 6

Vertical gradient of aerosol physicochemical properties

This chapter discusses the aerosol physical and chemical properties in the lower Amazonian troposphere, emphasizing the vertical gradient of the aerosol population between 60 and 325 m height. As discussed earlier, secondary Amazonian aerosols are not produced within the boundary layer but are transported to there by meteorological mechanisms. Also, primary aerosols play an essential role within the total aerosol population inside the PBL. These aerosols grow to sizes on the order of ~ 100 nm and act as CCN, influencing the atmospheric radiative balance.

Long-term measurements of aerosol physical and chemical properties are then presented, and a complementary approach is described to obtain aerosol properties under clean atmospheric conditions (empiric pristine). The results of this chapter were presented at a series of international conferences (shown in Appendix A.1), and some results are already partially published in scientific peer-reviewed articles in which I have co-authorship (HOLANDA et al., 2020; PRASS et al., 2021).

6.1 Long-term measurements of aerosol physical properties

Figure 39 presents the time series of about 8 years (from 2012 and to February 2021) of continuous measurements of aerosol optical properties (scattering, $\sigma_{scat,550nm}$, and absorption, $\sigma_{abs,637nm}$, coefficients), the AOD_{500nm}), and the aerosol particle number concentration ($N_{10-400nm}$) at the ATTO site in both 60 and 325 m height. The AOD time series in 500 nm was measured with the AERONET photometer at 80 m height, from 2016 to February 2021. AERONET data level 1.5 instead of data level 2.0 was chosen to represent the AOD in the analysis. The latter requires frequent instrument calibrations at NASA, particularly difficult in 2020-2021 due to the COVID-19 (coronavirus disease) pandemic. However, this does not influence the quality of the analysis and its results. Until approximately mid-2017, aerosol

physicochemical measurements were exclusively carried out at 60 m height. In the second half of 2017, measurements started to be performed also at the ATTO tower (325 m height). The inlet characteristics are presented in more detail in Section 4.1.1.1.

Figure 39 – Time series of aerosol optical properties (scattering and absorption coefficient at 550 and 637 nm, respectively) and particle number concentration within the size range from 10 to 400 nm from 2012 to February 2021 at the ATTO site, from top to bottom, respectively. In blue, the measurements at 60 m height level and, in green, the measurements at 325 m level. The AOD time series was obtained with photometer measurements at 80 m height.

In Figure 39, the seasonal characteristics of the aerosol properties are evident, following other studies in the literature for Amazonian aerosols (RIZZO et al., 2011; RIZZO et al., 2013; PÖHLKER et al., 2016; PÖHLKER et al., 2018; SATURNO et al., 2018b). Table 4 presents a comprehensive statistical compilation (median and interquartile ranges, IQR) of the annual and seasonal variability of $\sigma_{scat,550nm}$, $\sigma_{abs,637nm}$, AOD_{500nm} , and $N_{10-400nm}$ from 2014 to 2020 with measurements at 60 and 325 m height. In addition, the percentage of data coverage is also presented.

Table 4 – Annual and seasonal variability of aerosol physical properties in the vertical profile (60 and 325 m) of the lower troposphere of Central Amazonia based on 30 min averages. Statistics are presented in terms of median and interquartile ranges (IQR). The percentage of data coverage is also shown.

Period	$\sigma_{scat,550nm} [Mm^{-1}]^1$						$\sigma_{abs,637nm} [Mm^{-1}]^2$						$N_{10-40nm} [cm^{-3}]^3$						AOD _{500nm,lev.1.5}		
	60 m			325 m			60 m			325 m			60 m			325 m			Median	IQC	Coverage
	Median	IQR	Coverage	Median	IQR	Coverage	Median	IQR	Coverage	Median	IQR	Coverage	Median	IQR	Coverage	Median	IQR	Coverage			
Wet 2014	5.2	(2.9 - 11.3)	78%	-	-	-	0.44	(0.16 - 1.38)	72.5%	-	-	-	340	(250 - 460)	65.9%	-	-	-	-	-	-
Wet 2015	5.6	(2.6 - 9.6)	100%	-	-	-	0.37	(0.12 - 1.30)	89.2%	-	-	-	350	(290 - 430)	10.8%	-	-	-	-	-	-
Wet 2016	6.7	(4.7 - 9.7)	100%	-	-	-	0.32	(0.14 - 0.64)	100%	-	-	-	450	(290 - 650)	82.6%	-	-	-	0.08	(0.06 - 0.10)	25%
Wet 2017	4.4	(2.3 - 8.3)	97.5%	-	-	-	0.29	(0.12 - 0.63)	100%	-	-	-	370	(240 - 530)	56.7%	560	(450 - 700)	27.5%	0.06	(0.05 - 0.08)	31%
Wet 2018	8.8	(3.6 - 13.2)	54.2%	7.3	(4.8 - 8.7)	13.3%	0.29	(0.12 - 0.57)	97.5%	0.20	(0.09 - 0.41)	24.1%	400	(280 - 570)	99.17%	440	(300 - 640)	50%	0.06	(0.05 - 0.08)	28.3%
Wet 2019	5.7	(1.8 - 10.5)	49.2%	6.5	(3.1 - 11.7)	95.5%	0.26	(0.10 - 0.74)	79.2%	0.45	(0.16 - 1.12)	100%	350	(230 - 490)	93.3%	330	(230 - 500)	90%	0.10	(0.08 - 0.14)	20%
Wet 2020	6.3	(4.2 - 9.0)	54.6%	5.2	(2.2 - 11.3)	100%	0.18	(0.08 - 0.39)	63.6%	0.40	(0.13 - 1.40)	100%	330	(260 - 450)	60.3%	320	(230 - 440)	100%	0.12	(0.09 - 0.18)	40.5%
Dry 2014	24.4	(17.3 - 34.5)	95.8%	-	-	-	3.10	(2.20 - 4.30)	76.7%	-	-	-	1520	(1160 - 2000)	99.2%	-	-	-	-	-	-
Dry 2015	44.3	(34.4 - 65.8)	70%	-	-	-	4.70	(3.10 - 6.70)	95.8%	-	-	-	1390	(1220 - 1680)	12%	-	-	-	-	-	-
Dry 2016	23.0	(18.0 - 31.0)	47%	-	-	-	3.90	(2.80 - 5.60)	90.9%	-	-	-	1570	(1270 - 2230)	51%	-	-	-	0.19	(0.15 - 0.25)	81%
Dry 2017	35.7	(25.8 - 50.6)	94.2%	-	-	-	3.40	(2.30 - 4.90)	95.8%	-	-	-	1140	(690 - 2100)	75%	1410	(1120 - 1940)	39.2%	0.19	(0.14 - 0.26)	77%
Dry 2018	32.8	(22.7 - 42.6)	43.3%	23.1	(13.6 - 33.6)	65.8%	-	-	-	3.30	(2.00 - 5.10)	90%	1130	(730 - 1550)	82%	1200	(840 - 1580)	72.5%	0.20	(0.17 - 0.25)	46%
Dry 2019	28.4	(19.7 - 39.4)	88.3%	29.7	(20 - 39.1)	90%	3.90	(2.50 - 5.40)	65.8%	3.90	(2.30 - 5.80)	85%	1530	(1160 - 1980)	55%	1230	(820 - 1680)	50.8%	0.20	0.15 - 0.24	42.6%
Dry 2020	32.9	(21.6 - 46.7)	100%	30.6	(18.3 - 46.1)	100%	5.10	(2.30 - 7.60)	100%	4.00	(1.90 - 6.10)	100%	1300	(1000 - 1630)	46.3%	1750	(1170 - 2130)	65%	0.23	(0.17 - 0.30)	70.5%
WtoD 2014	8.2	(6.0 - 11.1)	85.2	-	-	-	0.84	(0.53 - 1.32)	100%	-	-	-	1080	(770 - 1380)	80.3%	-	-	-	-	-	-
WtoD 2015	10.4	(7.4 - 14.6)	98.4	-	-	-	0.99	(0.47 - 1.74)	100%	-	-	-	870	(640 - 1140)	86.9%	-	-	-	-	-	-
WtoD 2016	9.6	(7.1 - 13.2)	100	-	-	-	1.27	(0.57 - 2.07)	100%	-	-	-	1240	(720 - 1650)	88.5%	-	-	-	0.10	(0.08 - 0.12)	83.6%
WtoD 2017	13.9	(9.1 - 20.5)	91.8	-	-	-	1.08	(0.58 - 1.82)	100%	-	-	-	880	(690 - 1130)	80.3%	1240	(810 - 1400)	52.5%	0.10	(0.08 - 0.12)	29.5%
WtoD 2018	24.0	(17.1 - 41.8)	36.1	12.9	(8.2 - 16.3)	100%	-	-	-	1.30	(0.78 - 1.70)	100%	740	(490 - 1120)	39.3%	950	(700 - 1130)	73.8%	0.06	(0.05 - 0.10)	21.3%
WtoD 2019	13.3	(10.0 - 17.1)	82	11.4	(9.1 - 15.1)	100%	0.91	(0.52 - 1.59)	75.4%	1.08	(0.74 - 1.64)	100%	-	-	-	1090	(860 - 1360)	72.1%	0.09	(0.07 - 0.10)	49.1%
WtoD 2020	14.4	(10.6 - 18.1)	100	11.0	(7.2 - 15.1)	88.5%	1.79	(0.84 - 2.69)	100%	1.35	(0.67 - 1.96)	100%	930	(660 - 1200)	91.8%	1150	(640 - 1510)	93.4%	0.10	(0.09 - 0.12)	75.4%
DtoW 2014	28.9	(16.4 - 64.6)	24.2%	-	-	-	2.10	(0.94 - 5.60)	67.7%	-	-	-	1640	(960 - 2680)	22.6 %	-	-	-	-	-	-
DtoW 2015	32.8	(18.8 - 51.3)	51.6%	-	-	-	2.70	(1.70 - 4.30)	72.6%	-	-	-	1000	(590 - 1890)	58.1%	-	-	-	-	-	-
DtoW 2016	19.0	(9.4 - 32.5)	93.6%	-	-	-	2.10	(0.81 - 4.05)	100%	-	-	-	770	(490 - 1550)	91.9%	-	-	-	0.28	(0.19 - 0.32)	19.4%
DtoW 2017	11.6	(3.9 - 23.3)	77.4%	-	-	-	1.10	(0.45 - 3.9)	79%	-	-	-	600	(340 - 1460)	35.5%	1570	(1020 - 4320)	17.7%	0.14	(0.10 - 0.35)	37.1%
DtoW 2018	17.7	(4.9 - 35.8)	38.7%	5.2	(2.7 - 9.3)	50%	0.84	(0.49 - 2.37)	43.6%	1.09	(0.55 - 1.93)	50%	350	(260 - 450)	53.2%	350	(260 - 450)	43.6%	0.09	(0.07 - 0.13)	37.1%
DtoW 2019	12.5	(7.1 - 20.2)	32.3%	6.2	(3.6 - 8.8)	91.9%	0.97	(0.54 - 1.76)	32.3%	1.13	(0.66 - 1.98)	100%	340	(270 - 460)	61.3%	380	(280 - 530)	100%	0.11	(0.09 - 0.14)	29%
DtoW 2020	18.2	(12.1 - 23.5)	32.3%	11.4	(7.2 - 14.2)	87.1%	3.1	(1.68 - 4.22)	32.3%	2.36	(1.13 - 3.32)	87.1%	-	-	-	310	(240 - 370)	50%	0.13	(0.11 - 0.17)	46.8%

¹ Coefficient obtained by interpolation of scattering coefficients measured at $\lambda = 450, 525$, and 635 nm by the Aurora 3000 nephelometers. ² Data obtained with MAAPs. ³ Concentration obtained by integrating the SMPS size bins from 10.2 to 400.1 nm, measured by the SMPSSs.

The results showed that, during the wet season, the values of the aerosol physical properties are, as expected, significantly lower than those in the dry season. This behavior is likely due to a constant precipitation occurrence in the wet season. Moreover, the residual aerosol population comes from the interaction of the local biosphere with the atmosphere, despite episodic long-distance transport events with dust plumes from the Sahara Desert (PÖHLKER et al., 2019). In the wet season, the median scattering coefficient, $\sigma_{scat,550nm}$, varied between 5.2 (2.9 - 11.3) Mm^{-1} and 8.8 (3.6 - 13.2) Mm^{-1} at 60 m, while at 325 m, values were observed between 5.2 (2.2 - 11.3) Mm^{-1} and 7.3 (4.8 - 8.7) Mm^{-1} . On average, the scattering coefficient ($\pm$ standard deviation) was $8.0 \pm 7.6 Mm^{-1}$ and $8.5 \pm 8.1 Mm^{-1}$ at 60 and 325 m height, respectively, during the whole observation period.

The median absorption coefficient, $\sigma_{abs,637nm}$, varied between 0.18 (0.08 - 0.39) Mm^{-1} and 0.44 (0.16 - 1.38) Mm^{-1} at 60 m, while at 325 m, the values found were between 0.20 (0.09 - 0.41) Mm^{-1} and 0.45 (0.16 - 1.12) Mm^{-1} . On average, the absorption coefficient ($\pm$ standard deviation) was $0.67 \pm 1.20 Mm^{-1}$, and $1.10 \pm 1.80 Mm^{-1}$ at 60 and 325 m height, respectively, during the whole observation period. The median particle number concentration, $N_{10-400nm}$, at 60 m varied between 330 (260 - 450) cm^{-3} and 450 (290 - 650) cm^{-3} , while at 325 m, they varied between 320 (230 - 440) cm^{-3} and 440 (300 - 640) cm^{-3} .

Here, it was not considered the wet season of 2017 as the highest median value, once the data coverage was only about 28% of the total number of days, which returned an expressively high value for the particle number concentration (the measured days covered a Saharan dust event). On average, the aerosol number concentration ($\pm$ standard deviation) at the wet season was $420 \pm 240 cm^{-3}$ and $410 \pm 230 cm^{-3}$ at 60 and 325 m height, respectively, during the whole observation period. The AOD in the wet season varied between 0.08 (0.06 - 0.10) and 0.12 (0.09 - 0.18).

During the dry season, due to constant episodes of regional and long-range transport of biomass burning plumes transported towards the ATTO site (PÖHLKER et al., 2019; HOLANDA et al., 2020), and a considerable reduction in precipitation, the optical coefficients, and the aerosol concentration are significantly higher than during the wet season. The median $\sigma_{scat,550nm}$ at 60 m height varied between 23.0 (18.0 - 31.0) Mm^{-1} and 44.3 (34.4 - 65.8) Mm^{-1} , while at 325 m, they varied between 23.1 (13.6 - 33.6) Mm^{-1} and 30.6 (18.3 - 46.1) Mm^{-1} . On average, the $\sigma_{scat,550nm}$ at 60 and 325 m were, respectively, $37.2 \pm 26.9 Mm^{-1}$ and $33.3 \pm 24.9 Mm^{-1}$. Regarding the medians of $\sigma_{abs,637nm}$, at 60 m height, they varied between 3.1 (2.2 - 4.3) Mm^{-1} and 5.1 (2.3 - 7.6) Mm^{-1} , while at 325 m height, the variation was between 3.3 (2.0 - 5.1) Mm^{-1} and 4.0 (1.9 - 6.1) Mm^{-1} . On average, the absorption coefficients at 60 and 325 m were, respectively, $4.5 \pm 2.7 Mm^{-1}$ and $4.0 \pm 2.5 Mm^{-1}$.

The median particle number concentration, $N_{10-400nm}$, at 60 m height varied between 1130 (730 - 1550) cm^{-3} and 1570 (1270 - 2230) cm^{-3} , while at 325 m height, the concentrations varied between 1200 (840 - 1580) cm^{-3} and 1750 (1170 - 2130) cm^{-3} . On average, the concen-

tration at 60 and 325 m were, respectively, $1510 \pm 780 \text{ cm}^{-3}$ and $1490 \pm 850 \text{ cm}^{-3}$. The AOD in the dry season varied between 0.19 (0.14 - 0.26) and 0.23 (0.17 - 0.30). Note that the data coverage in the wet season for the AOD measurements is much lower than during the dry season. It is due to the permanent cloud cover at the ATTO site during the wet season months, where precipitation is significantly larger higher than at the dry season.

The transition seasons (WtoD and DtoW) showed intermediate values for the extensive properties compared to the wet and dry season results. In general, for all the optical coefficients and aerosol concentrations, the WtoD season presents values lower than the DtoW. It happens because the latter is often influenced by biomass burning plumes and the first long-distance transport occurrences of plumes from the African continent (HOLANDA et al., 2020). These events bring a significant amount of aged aerosols to the Central Amazonia. In contrast, precipitation decreases during the WtoD season, so wet deposition plays a less effective role. Dry deposition is not efficient enough to act as wet deposition (BOUCHER, 2015). As seen in Chapter 5, the condensation sink during the WtoD transition starts to get significantly higher than during the wet season. This is directly associated with the concentration of aerosols in the atmosphere.

The results obtained in Table 4 agree very well with previous works that also evaluated long-term measurements of optical properties and aerosol concentrations in Central Amazonia (RIZZO et al., 2011; RIZZO et al., 2013; PÖHLKER et al., 2016; PÖHLKER et al., 2018; SATURNO et al., 2018b). For further details, the reader is referred to the aforementioned studies. In particular, the measurements of optical properties and aerosol concentration obtained at 60 and 325 m, described in this section, are in good agreement with each other. However, some differences are notable, which will be studied, emphasizing the wet season in another section. In the next section, measurements of chemical concentrations of atmospheric aerosols at the ATTO site are presented, and their variability throughout the wet and dry seasons is discussed.

6.1.1 Aerosol chemical concentration in Central Amazonia

The measurements presented in this section, obtained with the Q-ACSM mass spectrometer, comprise data collected between February 2014 and December 2016 at the ATTO site at 60 m height. Figure 40 shows the time series of the chemical composition of PM_{10} , in which the contribution of organic aerosols stands out. It is observed, as in Figure 39, the strong seasonality of the different chemical components. In particular, the dry season presents large peaks of the organic component, which are associated with biomass burning, whose fresh plumes due to regional events reach the ATTO site (PÖHLKER et al., 2019; HOLANDA et al., 2020).

Figure 41 shows the mass fraction of the chemical composition of the Amazon aerosol

Figure 40 – Time series of the monthly average composition of PM₁ aerosol in Central Amazonia (ATTO tower), from February 2014 to December 2016.

for the wet and dry seasons, also with the average total aerosol loading for each season. During the wet season, the concentration of the organic component of PM₁ is, on average, $0.79 \pm 0.71 \mu\text{g m}^{-3}$, which corresponds to 77% of the entire mass fraction of PM₁. The SO_4^{2-} , with 8% of the mass fraction, has an average concentration of $0.11 \pm 0.13 \mu\text{g m}^{-3}$. The eBC has an average concentration of $0.10 \pm 0.14 \mu\text{g m}^{-3}$, with 7% of the mass fraction, NH_4^+ with an average concentration of $0.07 \pm 0.32 \mu\text{g m}^{-3}$ (4%), and nitrate, with an average concentration of $0.05 \pm 0.08 \mu\text{g m}^{-3}$ (3%). The Cl^- component is considered negligible since its values are close to the instrument's detection limit (which is 0.01 for Cl^-), so the measures are unreliable. The average aerosol total loading from January to July (extended wet season) is $1.4 \pm 0.04 \mu\text{g m}^{-3}$.

Figure 41 – Chemical composition of PM₁ aerosol in wet (left) and dry (right) seasons measured at the ATTO tower. Measurements of eBC were obtained with a MAAP instrument.

In contrast, during the dry season, the mean organic component is $4.44 \pm 4.2 \mu\text{g m}^{-3}$,

and represents 80% of the total mass fraction of PM_{10} . The SO_4^{2-} , with 8% of the mass fraction, has an average concentration of $0.62 \pm 0.39 \mu g m^{-3}$. The eBC is, in average, $0.62 \pm 0.36 \mu g m^{-3}$, with 6% of the mass fraction, NH_4^+ with an average concentration of $0.26 \pm 0.32 \mu g m^{-3}$ (3%), and nitrate, with an average concentration of $0.19 \pm 0.15 \mu g m^{-3}$, with 3% of the total mass fraction. The average aerosol total loading from August to December (extended dry season) is $5.3 \pm 1.3 \mu g m^{-3}$. PM_{10} mass density in the dry season is almost four times higher than during the wet season. This is mainly due to local and regional biomass burning events and the aerosol influx of very aged aerosol plumes from long-distance transport (HOLANDA et al., 2020).

In comparison with literature results, all chemical components obtained in this study agree, within the standard deviation, with what has already been published in PÖHLKER et al. (2018). Some differences are, however, noticeable regarding the nominal value of the mean. This may have occurred because a larger number of measurements were considered in this study than those in PÖHLKER et al. (2018). There, it was considered data between August 2014 and September 2016, while in this thesis, it was considered data between February 2014 and December 2016.

The results show that the aerosol physical properties, in particular the optical properties, are directly influenced by the organic components, eBC, and sulfate. However, the other contributions are still significant. To verify and obtain the dependence of the scattering coefficient, $\sigma_{scat,525nm}$, with chemical concentration, a multiple linear regression (MLR) model was applied. It was based on the hypothesis that $\sigma_{scat,525nm}$ is a linear combination of the scattering coefficients due to each of the chemical components measured by the ACSM (MALM; HAND, 2007):

$$\sigma_{scat,525nm} = \sum_{i=1}^5 \sigma_{scat PM_{10},525nm} + W = \sum_{i=1}^5 \beta_i \cdot C_i + W, \quad (6.1)$$

$$\sigma_{scat,525nm} = \beta_1 \cdot C_{Org} + \beta_2 \cdot C_{Sulf} + \beta_3 \cdot C_{Amm} + \beta_4 \cdot C_{Nit} + \beta_5 \cdot C_{Chl} + W \quad (6.2)$$

where C_i is the concentration of the i -th chemical species, β_i is the specific MSE of a given chemical species and W is an independent term that can account for attribution errors. In this study, we chose to develop two-component models related to the organic part (β_{Org}) and the inorganic part (β_{Inorg}) of PM_{10} . It aims to better understand the relationships between the aerosol composition in different cases. The inorganic part consists of the total mass of all inorganic species measured by the ACSM. Within the inorganic contribution, sulfate is the component that stands out the most, followed by nitrate and ammonia.

In order to circumvent possible events of dust from the Sahara and even some type of contamination by biomass burning or generator, the period between April 5 and April 23, 2016, was selected as representative for the wet season. In this period, it is considered that

Figure 42 – Comparison of measured and reconstructed scattering coefficients, $\sigma_{scat,525nm}$, with MLR results for the wet season case. a) Time series of the measured (blue) and reconstructed (black) coefficients, and b) linear regression with the scattering coefficients.

pristine conditions were reached. The Amazonian atmosphere is mainly dominated by the forest's biogenic activity and local atmospheric mechanisms. The MLR returned the following relation:

$$\sigma_{scat,525nm} = 2.2 \cdot C_{Org} + 1.0 \cdot C_{Inorg} + 1.6 \quad (6.3)$$

which showed that the organic component plays the most crucial role in the scattering coefficient, with a specific MSE of $2.2 \text{ m}^2 \text{ g}^{-1}$. However, the inorganic component cannot be neglected, which has specific MSE of $1.0 \text{ m}^2 \text{ g}^{-1}$. Figure 42 shows the measured $\sigma_{scat,525nm}$, and the reconstructed $\sigma_{scat,525nm}$ based on the model results. A simple linear model between the two components returned a significant $R^2 = 0.7$, and angular coefficient ($\pm \text{SE}$) of 0.923 ± 0.009 , showing good agreement.

It was also considered a case where biomass burning and Sahara dust events occurred in the same month (DtoW month). Thus, the period between January 13 and 31, 2016, was selected. The results contrast with those for the pristine period since the spectral aerosol properties changed due to the different aerosol populations in each period:

$$\sigma_{scat,525nm} = 5.2 \cdot C_{Org} + 2.7 \cdot C_{Inorg} + 6.3. \quad (6.4)$$

For this case, the organic component of the aerosols has specific MSE = $5.2 \text{ m}^2 \text{ g}^{-1}$ and the inorganic specific MSE = $2.7 \text{ m}^2 \text{ g}^{-1}$. Figure 43 shows the scattering coefficients measured

Figure 43 – Comparison of measured and reconstructed scattering coefficients, $\sigma_{scat,525nm}$, with MLR results for the DtoW season case. a) Time series of the measured (blue) and reconstructed (black) coefficients, and b) linear regression with the scattering coefficients.

and reconstructed from the MLR result for the case of the DtoW season. The model was able to reconstruct the measured scattering coefficient with better quality, which resulted in $R^2 = 0.83$ between the coefficients and slope ($\pm SE$) of 0.929 ± 0.009 .

The results are consistent with what is observed: during episodic events of biomass burning and Sahara dust, scattering coefficients increase considerably, which is associated with the capacity of dust aerosols (mainly composed of sulfate, but also aged), and biomass burning aerosols scatter radiation more efficiently. In contrast, during the period of empirical pristine, the aerosol population is strongly dominated by growth and aging processes due to coagulation of organic vapors and interaction with biogenic emissions from the forest, which reduces the aerosols' scattering efficiency. The specific MSE obtained for the organic and inorganic fraction of the PM_{10} also agrees with organic specific MSE measured at other locations (MALM; HAND, 2007), which, for the organic fraction, are within the range of $1.7 - 6.4 \text{ m}^2 \text{ g}^{-1}$, and for the inorganic fraction, within the range $1 - 18 \text{ m}^2 \text{ g}^{-1}$.

6.2 Aerosol optical properties under empirically pristine conditions

The investigation presented in this section characterizes the background physico-chemical properties of atmospheric aerosols under atmospheric conditions that most closely approximate those with minimal anthropogenic impact. We followed a slightly different but still complementary approach to that presented by PÖHLKER et al.(2018). In the aforementioned study, periods of empirically pristine atmospheric conditions (similar definition to PÖHLKER et al.(2018)) were considered those in which, among other characteristics, the eBC concentration (measured with MAAP) is below the instrument's detection limit. However,

other studies indicate that even remote sites present atmospheres with residual concentrations of pollution, despite being very low, which raises controversies about the real conditions for pristine atmospheres (ANDREAE, 2009; MARTIN et al., 2010b; PÖSCHL et al., 2010; CHI et al., 2013; HAMILTON et al., 2014). Furthermore, the Brown Carbon component associated with SOA and organic coatings resulting from aging processes by coagulation of natural organic vapors cannot be neglected either, as they are approximately 80% of PM_{10} in the wet season. It has a direct influence on the aerosol physicochemical properties, in particular on the optical properties. In the approach presented here, atmospheres close to pristine conditions (also denominated as empirically pristine conditions) are considered as those that fulfill the following requirements:

- The selected periods are exclusive during the wet season. It is necessary since previous studies indicate that during the dry season, the atmosphere in the Amazon basin is almost exclusively dominated by pollution from biomass burning (PÖHLKER et al., 2019).
- Precipitation occurred on most of the days considered in the analyses. The wet deposition process is the most efficient for cleaning the atmosphere, and even with the occurrence of downdraft that transport particles from the upper troposphere into the boundary layer, the atmosphere will be characterized by clean conditions and closer to what is expected to be natural, without anthropogenic influence (ANDREAE, 2007; ANDREAE et al., 2015; ANDREAE et al., 2018). Figure 44 presents the characteristics of aerosol size distribution, equivalent potential temperature, θ_e , and precipitation, P_{ATTO} , in a day in which the atmosphere was considered to have pristine conditions. Strong precipitation is observed at 12:00 LT, followed by a decrease in the potential temperature, which indicates a downdraft occurrence. The size distribution over time shows that, after precipitation, the aerosol population changes to much lower concentrations. The contribution of the aerosol accumulation size mode is scavenged, leaving the contribution of the Aitken mode and the sub-50 nm size mode. In Figure 44, considering the mean particle size distribution for both days, the Aitken mode is centered at 68.5 nm. The accumulation mode at 117.6 nm, with a mean particle number concentration of 280 cm^{-3} .
- There are no long-distance aerosol plume transport events on the days analyzed (i.e., West African aerosol plume). This condition is necessary because, although dust plumes from the Sahara are natural occurrences arising at ATTO from the ITCZ, in the plumes, there will always be the presence of Black Carbon from West African pollution (HOLANDA et al., 2020).
- The eBC concentration obtained by MAAP shows small fluctuations throughout the day, without clear signs of peaks.

This approach is not intended to be better or more precise than the previous one, but rather to complement the analyzes with other characteristics for, in particular, the aerosol optical properties, which were not described in PÖHLKER et al.(2018).

Figure 44 – Example of days (12 and 13 May 2016) in which the atmosphere was considered pristine. The Figure shows the a) PNSD, b) the equivalent potential temperature, c) the precipitation, and d) the average size distribution of the aerosols in each day, from top to bottom, respectively.

Figure 45 presents the mass fraction of the background chemical components measured by the ACSM, and Table 5 summarizes all the information collected for physicochemical properties of background atmospheric aerosols. Values obtained from the literature are added to the table for comparison purposes. The chemical component and particle number concentration results are compatible within the standard deviation with what is described in the literature, which confirms the validity of this approach to analyze the aerosol optical properties. Only the mass fractions show a certain discrepancy, as here, as mentioned earlier, the eBC concentration was also considered.

It was observed that the aerosol particle number concentration is much lower than during the wet season, with an average concentration of $270 \pm 110 \text{ cm}^{-3}$, and the organic fraction of the aerosol is even more present in periods of clean atmosphere, with a mass fraction

Table 5 – Background physicochemical properties of atmospheric aerosols at the ATTO site obtained with measurements in the wet season from 2014 to 2016, at 60m.

Component	Average $\pm \sigma$	Mass fraction (%)	Literature (PÖHLKER et al., 2018) ¹
eBC ($\mu\text{g cm}^{-3}$)	0.03 ± 0.04	4	– ²
Organics ($\mu\text{g cm}^{-3}$)	0.65 ± 0.55	80	0.64 ± 0.02 (90%)
Sulfate ($\mu\text{g cm}^{-3}$)	0.04 ± 0.05	5	0.04 ± 0.01 (6%)
Nitrate ($\mu\text{g cm}^{-3}$)	0.03 ± 0.04	4	0.03 ± 0.01 (4%)
Ammonium ($\mu\text{g cm}^{-3}$)	0.06 ± 0.25	7	0.17 ± 0.01 (–) ³
$\omega_{0,637\text{nm}}$	0.96 ± 0.04	–	–
$\sigma_{\text{scat},525\text{nm}}$	4.4 ± 2.7	–	–
$\sigma_{\text{abs},637\text{nm}}$	0.14 ± 0.16	–	–
N_{conc}	270 ± 110	–	260 ± 3
AOD_{bg}	0.075 ± 0.024	–	–
AAOD_{bg}	0.0180 ± 0.0003	–	–
$\omega_{0,\text{AERONET}}$	0.972 ± 0.004	–	–

¹ Uncertainty is the standard error (SE), defined as $\sigma/\sqrt{n}$, where n is the number of observations. ² The absence of data in the eBC line is because the authors did not consider the contribution of the eBC component. ³ Mass fraction not provided, as the authors question the quality of the data, as it is close to the instrument's detection limit.

of 80%, compared to 77% obtained for the whole wet season. The mean ($\pm \sigma$) concentration of the aerosol organic composition is $0.65 \pm 0.55 \mu\text{g m}^{-3}$. The sulfate, nitrate, and ammonia fractions show minor differences to the mass fraction for the whole wet season, emphasizing the sulfate mass fraction, which accounts for 5% compared to 8% for the entire wet season. In this regard, the most interesting component is eBC, which is not negligible despite having a low concentration and contributes with 4 % of the PM1 mass fraction, with an average concentration of $0.03 \pm 0.04 \mu\text{g m}^{-3}$, which is much lower than the wet season average. For background periods, on average, the total aerosol loading is $0.81 \pm 0.33 \mu\text{g m}^{-3}$.

The aerosol optical properties under clean atmosphere conditions returned consistent and important results. The average $\sigma_{\text{scat},525\text{nm}}$ is $4.4 \pm 2.7 \text{ Mm}^{-1}$ and the average $\sigma_{\text{abs},637\text{nm}}$ is $0.14 \pm 0.16 \text{ Mm}^{-1}$, whose coefficients are significantly lower than those for the entire wet season ($8.0 \pm 7.0 \text{ Mm}^{-1}$ and $0.67 \pm 1.20 \text{ Mm}^{-1}$ for $\sigma_{\text{scat},525\text{nm}}$ and $\sigma_{\text{abs},637\text{nm}}$ at 60 m height, respectively). In particular, the single-scattering albedo, ω_0 , during pristine conditions indicates that aerosols are strongly effective in scattering radiation with $\omega_{0,637\text{nm}} = 0.96 \pm 0.04$, which agrees very well with the one estimated with photometric measurements, $\omega_0 = 0.972 \pm 0.004$. In addition, characteristic values for AOD_{bg} and AAOD_{bg} were obtained, of 0.075 ± 0.024 and 0.0180 ± 0.0003 , respectively.

Therefore, under pristine conditions, it was observed that most aerosols are organic, with a significant contribution from the absorbing component to the optical properties, which should not be neglected. This component can be either due to residual air pollution (smaller

Background chemical mass composition of PM₁, ATTO site, 60m, 2014 - 2016

Figure 45 – Background chemical composition of PM₁ aerosol in Central Amazonia. Measurements of eBC were obtained with a MAAP instrument.

scale), despite wet deposition processes, or (and most likely) due to SOA. Thus, Amazonian aerosols in background conditions are highly efficient in scattering radiation. Moreover, they are dominated by aging processes related to the coagulation of organic vapors, which also gives them an absorbing character.

6.3 Vertical profile of aerosol physical properties

This section discusses the vertical variability of aerosol optical properties, particle number concentration, and size distribution of atmospheric aerosols in the lower Amazonian troposphere. In particular, it seeks to understand whether there are significant differences in the aerosol physical properties between 60 and 325 m heights. Thus, only the periods in which instruments that measure the same characteristic operated simultaneously at both heights during a specific period of the wet season were considered: April and May of 2019 and 2020. The period is characterized by a low occurrence of biomass burning and long-range transport plumes. In addition, they had a high precipitation rate and a privileged wind direction from the northeast driven by the ITCZ (intertropical convergence zone), which transports clean air masses to the ATTO site (PÖHLKER et al., 2018; PÖHLKER et al., 2019).

In the considered period, the average T and RH, measured at 325 m height, were 24.6 °C and 85 %, respectively. In comparison, the average T and RH values for the entire wet season were 29.9 °C and 82.8 %, respectively. The average accumulated precipitation between April and May was 685 mm, representing ~63% of all accumulated precipitation for the whole wet season. Figure 46 shows the wind rose for the period studied (2019 and 2020). On average, the wind speed was ~4.4 m/s, which is lower than the wind speed during the entire wet season of 2019 and 2020, of 5.3 m/s. Note that the preferred wind directions coincide with the

wet season directions in Figure 10b, and what was obtained by previous studies (RIZZO et al., 2013; PÖHLKER et al., 2019).

Figure 46 – The wind rose for April and May a) 2019 and b) 2020. The colorbar expresses wind speed in m/s, and the percentages in the figure represent the data coverage.

The following data configuration was used in these analyses:

- Nephelometer data: April and May 2019. During this period, the two instruments were calibrated three times to ensure the quality of the comparisons. The scattering coefficient data for 2020 were not used for vertical comparison, as the COVID-19 pandemic did not make it possible to calibrate the instruments with regular frequency and thus guarantee the robustness of the comparisons.
- MAAp, AE33, SMPS, and CPC data: April and May 2019 and 2020. These instruments do not require frequent calibrations, and their data can be used for vertical comparisons. In particular, simultaneous AE33 data comprising the selected periods of the wet season was only available in May 2020.

Figure 47 shows the periods and data considered in the vertical comparative analysis. A reliable intercomparison between the instruments was achieved with simultaneous measurements at the same height to obtain the instrumental differences. In addition, intercomparisons between instruments that measure similar properties, such as MAAp and AE33, and CPCs and SMPSs were also performed. They were used for corrections of nephelometer/AE33 data and data quality validations, as discussed in Chapter 4. The comparisons were obtained according to technical availability, space/inlet lines available in the laboratory, and the possibility for instrument transportation, which was particularly unfeasible with the outbreak of the COVID-19 pandemic in 2020. Figure 17 shows an example of comparisons between instruments that measure similar properties, in which the differences between them are less than 5%.

Figure 47 – Time series of aerosol optical properties, particle number concentration, and aerosol volume obtained in the vertical profile in the wet season periods used in the analyzes (April and May). The blue and green colors represent the measurements at the levels 60 and 325 m height, respectively.

Figure 48 shows an example of intercomparison obtained with the two nephelometers of the site, both measuring air samples collected at the same height: 60 m. The comparison time series covered seven days of uninterrupted measurements, as shown in Figure 48 for the scattering coefficient, $\sigma_{\text{scat},525\text{nm}}$. The variability is similar for both instruments, which is even explicit in the boxplot in Figure 48b. The medians and the IQR are identical. The Wilcoxon rank-sum statistical significance test was applied, which returned a p-value of 0.45, indicating no significant statistical differences between both sets. In addition, Figure 48c shows the correlation between the measurements of the two nephelometers. The colors represent the 450 nm (blue), 525 nm (green), and 635 nm (red) wavelengths. On average, the slope of the curve was 0.993, with $R^2 = 0.975$, and the root mean square error (RMSE) of 0.65. The results, therefore, indicate that the instruments measure identically. Analogously to this example, all the other instruments used in this analysis had similar results. Any differences measured in the vertical profile could be attributed to the inlet transmission efficiency and natural atmospheric processes.

Figure 48 – Intercomparison between nephelometers obtained over 7 days with air sampled at 60 m height. In a) the time series of the scattering coefficient at 525 nm is presented. The blue color represents the nephelometer that usually measures at 60 m, and in green that measures at 325 m in height. In b), the comparative boxplot of measurements from a), and in c), the comparison between both measurements, where the colors represent the wavelengths 450 nm (blue), 525 nm (green), and 635 nm (red). The black curve is the 1:1 curve.

Instruments that measure aerosol optical properties detect the scattering and absorption coefficients of particles with geometric diameters larger than or equal to the Aitken mode up to $\text{PM}_{2.5}$. The transmission efficiencies for both inlets are higher than 85-90%, which allows comparisons with reasonable accuracy. However, for particle number concentration and size distribution measurements based on the CPC-SMPS set, the transmission efficiencies are

significantly lower for aerosol diameters below 50 nm, as shown in Figure 14, which may influence on the comparisons related to smaller sizes. It is important to emphasize that all measured size distributions, and consequently all the particle number concentrations, were corrected for transmission losses according to the curves in Figure 14 (section 4.1.1.1).

Figure 49 – Comparative boxplot of optical components of a) $\sigma_{scat,525nm}$ and b) $\sigma_{abs,637nm}$, c) particle number concentration, and d) aerosol volume at 60 and 325 m height. The box represents the quartiles, the whiskers represent 90th and 10th percentiles, and the horizontal line represents the median.

Figure 49 presents direct comparisons between optical properties, particle number concentration, and aerosol volume in the vertical profile, with simultaneous measurements for a given instrument. The scattering coefficient (Figure 49a), $\sigma_{scat,525nm}$, at 60 m height had a median and IQR of 5.4 (1.5 - 10.1) Mm^{-1} , while at 325 m height, the median and IQR were 6.6 (3.6 - 10.0) Mm^{-1} . The statistical significance of this difference was verified through the Wilcoxon rank-sum test, which returned a virtually null p-value, indicating that differences in scattering coefficients are, indeed, relevant. Figures 50a and b show the spectral dependence of the aerosol as a function of the wavelength at which the scattering coefficient is measured for 60 and 325 m height, respectively. It is observed that at all wavelengths, the scattering coefficients are higher at 325 m, whose medians are 8.6, 6.6, and 5.1 Mm^{-1} for $\lambda = 450, 525$, and 635 nm, respectively. At 60 m, the medians of the scattering coefficients are 6.8, 5.4 and 4.6 Mm^{-1} for $\lambda = 450, 525$, and 635 nm, respectively. These differences are directly reflected in the scattering Ångström exponent (Figure 50c), in which the median of this coefficient at 60 m is 1.29, while at 325 m, it is 1.61. Note that α_{scat} is an intensive property that does not depend on the concentration of particles and shows that aerosol populations at different heights have contrasting spectral dependencies on incident radiation, particularly with higher scattering coefficients at 325 m.

Figure 50b shows the comparisons of the absorption coefficients, $\sigma_{abs,637nm}$. At 60 m height, the coefficient had a median and IQR of 0.17 (0.07 - 0.35) Mm^{-1} , while at 325 m, the median $\sigma_{abs,637nm}$ its IQR were 0.20 (0.09 - 0.42) Mm^{-1} . The statistical significance obtained

Figure 50 – Comparative boxplot of aerosol scattering coefficients at wavelengths 450, 525, and 635 nm at a) 60 m and b) 325 m. In c) the comparative boxplot of the mean scattering Ångström exponent is presented. The box represents the quartiles, the whiskers represent the 90th and 10th percentiles, and the median horizontal line.

with the Wilcoxon rank-sum test for the absorption coefficient also presented a virtually null p-value, indicating that the differences are relevant. However, the relatively small difference could also be associated with the instrumental uncertainties, so that $\sigma_{abs,637nm}$ is approximately similar at both heights. Figures 51a and b show the spectral dependence of the absorption of the coefficients measured at 60 and 325 m, calculated with AE33 for May 2020, and corroborates the previous observations. Absorption coefficients are observed slightly higher at 325 than at 60 m. Specifically, at 325 m, the medians of the coefficient varied between 0.63 and 0.20 Mm^{-1} for $\lambda = 370$ and 950 nm, respectively. At 60 m, the medians varied between 0.60 and 0.18 Mm^{-1} for $\lambda = 370$ and 950 nm, respectively. Furthermore, the similarity between the absorbing component of aerosols is reflected in the Ångström absorption exponent, $\bar{a}_{Abs}$, whose medians at 60 and 325 m are, respectively, 1.27 and 1.24. Note that the medians of the absorption and scattering coefficients are very close to those estimated for pristine conditions in section 6.2.

The single-scattering albedo, $\omega_{0,637nm}$, also an intensive aerosol property, is identical for populations at both height levels. The median $\omega_{0,637nm}$ and its IQR at 60 m were 0.94 (0.90 - 0.96), while at 325 m, the median $\omega_{0,637nm}$ and its IQR were 0.94 (0.92 - 0.95). Figure 50c shows comparisons with the aerosol concentrations in the vertical profile within the 10-400 nm size range measured by the SMPS. The results presented medians at 60 m and 325 m with small differences between the two heights. At 60 m, the median and IQR of N_{10-400} were 340 (240-490) cm^{-3} , while at 325m, the median and IQR of N_{10-400} were 320 (220-460) cm^{-3} .

The differences in the median values were less than 10%, which also could be related to inlet losses for particles smaller than 50 nm. In contrast, the aerosol volume (Figure 50d) at each height showed significant differences. At 60 m, the median volume and its respective

Figure 51 – Comparative boxplot of aerosol absorption coefficients at $\lambda = 370, 470, 520, 590, 660, 880$ and 950 nm at a) 60 and b) 325 m height. In c) the comparative boxplot of the mean absorption Ångström exponent is presented. The box represents the quartiles, the whiskers represent the 90th and 10th percentiles, and the median horizontal line.

IQR were 0.50 ($0.32 - 0.88$) $\mu\text{m}^3 \text{cm}^{-3}$. At 325 m, the median and IQR of the volume were 0.68 ($0.43 - 1.07$) $\mu\text{m}^3 \text{cm}^{-3}$. The test of statistical significance presented a p-value virtually null, indicating that the differences are relevant. In particular, the difference of about 26% indicates that aerosol populations closest to the canopy are smaller than those at 325 m high.

Figure 52 – Median aerosol size distributions in the vertical profile. The blue line is the median aerosol size distribution at 60 m height, and the green line is the median aerosol size distribution at 325 m height. Colored shadows refer to interquartile ranges.

These results for the volume are in agreement with the medians of the aerosol size distributions at the two height levels, shown in Figure 52. The peak relative to the Aitken size mode for both measurements at 60 and 325 m, respectively, has the same geometric mean diameter, of $D_g = 68.5$ nm. In contrast, the accumulation mode at both heights showed differences that explain the described volumes. At 60 m the peak of the accumulation mode is centered at $D_g = 140.7$ nm, while at 325 m the peak is centered at $D_g = 165.5$ nm. This results in a difference of about 20 nm. The gradient observed in the volume may imply different scattering and absorption efficiencies in the vertical profile, likely to be related to different aging processes and meteorological transportation. The scattering and absorption efficiencies will be explored in more detail in section 6.3.2.

Figure 53 – Comparative boxplot of a) absorption coefficients measured by the AE33 at 470 nm, b) absorption coefficients exclusively due to the BC component, and c) absorption coefficients exclusively due to the BrC component at 60 and 325 m height. The box represents the quartiles, the whiskers represent the 90th and 10th percentiles, and the median horizontal line.

An interesting aspect of the aerosol absorbing properties was observed by calculating the BrC component using the AE33 data and the Wang-based methodology described in section 4.5. The method, as presented, obtains the BrC component at 470 nm, using for this $\hat{a}_{abs}$ calculations with two different pairs of wavelengths and the expected BC value obtained with Mie code simulations. Figure 53 presents the boxplots with comparative results for the total absorption coefficient, measured at 470 nm, and the exclusive absorption coefficients of BC and BrC at 470 nm for both height levels.

It was observed different contributions of BC and BrC in the vertical profile. At the 60 m level, the median and IQR of the BrC absorption coefficient were 0.10 (0.06 - 0.16) Mm^{-1} , while at the 325 m level, the median and IQR were 0.07 (0.05 - 0.10) Mm^{-1} . In contrast, the coefficients for BC were higher at 325 m, with a median and IQR of 0.46 (0.30 - 0.78) Mm^{-1} , while at 60 m, the median and IQR were 0.30 (0.17 - 0.56) Mm^{-1} . In percentage comparisons, the contribution of BrC in 60 m is approximately 27% (which agrees with previous stud-

ies (SATURNO et al., 2018b), while in 325 m, this contribution is 14%, which is a remarkable contrast. The BC at 60 m corresponds to approximately 73% of the total absorption, while at 325 m, the BC is about 86%.

The results show that in regions close to the canopy, the contribution of BrC to the total absorption coefficient at 470 nm is approximately twice that at 325 m, while at the highest level, the contribution of BC is more significant. There is, therefore, different dominance of sources at each height. At 60 m, fresh biogenic emissions of VOCs from the canopy play a significant role in the aging processes of SOA, in particular for the growth particle events. At 325 m, as the BC contribution seems to be higher, the aerosols are likely more influenced by long-range transport, which brings significant amounts of BC to the site, even during the cleanest atmosphere months, such as those studied in this work.

As particle volumes are larger at 325 m, they are likely more aged and homogenized at this level than particles at 60 m, which interact with fresh VOC emissions. In particular, future studies could investigate the differences in the coating of these aerosol populations, which may indicate different stages of processing. Thus, particles with larger volumes also result in larger scattering and absorption cross-sections, which explains the spectral differences obtained in the vertical profile, with more significant differences in the scattering coefficients and in the $\tilde{a}_{scat}$ for the aerosol populations at both height levels.

6.3.1 Diurnal cycle

The median diurnal cycles of the optical coefficients and the aerosol number concentration are shown in Figure 54, where the gray shadows refer to the nocturnal periods (from 18h LT to 06h LT). There is a clear diurnal profile, which accompanies sunrise and sunset. In particular, during the daytime, when the boundary layer reaches its highest vertical extension and when turbulent processes are maximized, the scattering and absorption coefficients are identical at 60 and 325 m. The median of the scattering coefficients in 525 nm for the vertical profile is about 8 Mm^{-1} . The absorption coefficients are about 0.25 Mm^{-1} at 14h LT when the quantities present the highest values. Although the coefficients are similar, aerosol number concentrations show some differences, with higher medians at 60 m, of about 380 cm^{-3} , while at 325 m, the median concentration is 320 cm^{-3} at 14h LT. The $\omega_{0,637nm}$ does not vary significantly throughout the day, with very similar values for both heights of approximately 0.94.

In contrast, during the nighttime, differences are more significant in optical properties. In particular, after establishing the stable nocturnal layer, whose height is around 200 - 300 m (FISCH et al., 2004), both absorption and scattering coefficients are slightly higher at 325 m. It is likely related to mixing processes that can still occur in 325m, within the residual layer, which ages the aerosol, increasing its absorption and scattering cross-sections. In addition,

Figure 54 – Median diurnal cycle of a) aerosol scattering coefficient, $\sigma_{scat,525nm}$, at 525 nm, b) particle number concentration ($N_{10-400nm}$), c) absorption coefficient, $\sigma_{abs,637nm}$, at 637 nm, and d) single-scattering albedo, ω_0 , calculated at 637 nm. Gray bars represent nighttime. Error bars are the standard error.

the processing of aerosols in clouds is more likely to occur at the highest level, unlike what occurs at 60 m, since the stable layer does not contribute efficiently to the aging of aerosol particles.

Figure 55 shows the median diurnal cycles of particle number concentrations in each of the three aerosol size modes: sub-50 nm, Aitken, and Accumulation mode. As in Figure 54, the diurnal behavior is quite evident. As discussed in Chapter 5, the sub-50 nm particle fraction has an inquisitive behavior: particle number concentrations tend to increase between 14h LT and 8h LT, with medians of 60 and 35 cm^{-3} , respectively for 60 and 325 m. From 8 to 14h LT, the concentrations decrease, with minimum values of 40 and 15 cm^{-3} , respectively to 60 and 325 m.

Differences in concentrations in the vertical profile, as shown in Figure 55a, are observed throughout the day. This result is likely related to the transmission efficiency of the inlets, as shown in Figure 14. Aerosol transmission efficiencies between 10 and 50 nm can vary between 50 and 91% at 325 m and between 65 and 95% at 60 m. It shows that losses cannot be neglected and can play an important role in sub-50 nm particles. Despite this, the possibility of an aerosol source close to the canopy cannot be neglected either, which inspires future studies to unveil this particular process.

The diurnal cycles of the Aitken and Accumulation modes (Figure 55b and c) have the same trend, in which concentrations decrease during the night until the beginning of the day, where they start growing again with the evolution of the PBL. . In particular, at night, there is a clear separation between the particle number concentrations at the two height levels. The

Figure 55 – Median diurnal cycle of particle number concentrations in modes a) sub-50 nm, b) Aitken, and c) Accumulation. Gray bars represent nighttime. The bars are the standard error.

values are higher at 325 m, which are likely related to the process of entrainment of Aitken mode particles into the PBL, or even meteorological processes such as gravity waves (TOLEDO MACHADO et al., 2021).

During the daytime, the particle number concentrations at both height levels within the Aitken mode are similar, showing the effectiveness of the mixed layer, in particular when the PBL reaches its highest height, at approximately 13-14h LT, with a median concentration of about 60 cm^{-3} . With the end of sunlight and eventual decoupling of the sublayers within PBL, the concentrations are different again. In contrast, accumulation mode particles, which represent most of the aerosol concentration, are higher at 60 m during the daytime. It could also be explained by a local aerosol source close to the canopy. Overnight, the accumulation mode concentrations at both height levels are similar, showing that these particles could likely be deposited by the reduction of the turbulence inside the nocturnal BL.

Therefore, the differences in the diurnal concentration profiles suggest that different processes can influence the aerosol population at each height level. In particular, aerosols closer to the canopy have higher concentrations of accumulation particles during the day, which is likely associated with sources close to vegetation. At 325 m, aerosol populations are higher within the Aitken mode during the night period, likely due to entrainment processes and meteorological mechanisms such as those mentioned above. More detailed investigations are suggested for future studies, seeking to identify and characterize in detail the sources of these particles and the importance of meteorology in the vertical profile of PBL in Central Amazonia.

Figure 56 – Scattering coefficient, $\sigma_{\text{scat},525\text{nm}}$, as a function of mass concentration for measurements at 60 and 325 m height. The colors in panels a) and b) are relative to $\omega_{0,637\text{nm}}$, and the colors in c) and d) are relative to $N_{10-400\text{nm}}$. The mass concentration is obtained by multiplying the aerosol volume (in size range 10 to 400 nm) by the average mass loading of the wet season ($1.4 \mu\text{g m}^{-3}$).

6.3.2 Vertical gradient of $\alpha_{\text{Scat}}(\lambda)$ and $\alpha_{\text{Abs}}(\lambda)$

This section explores the mass scattering and absorption efficiencies (or coefficients, as described in Chapter 4 - $\alpha_{\text{Scat}}(\lambda)$ and $\alpha_{\text{Abs}}(\lambda)$, respectively) of the aerosol populations in the vertical profile. The scattering and absorption efficiencies are calculated through the linear coefficient of the fitting curve between the scattering/absorption coefficient at a given wavelength and the mass concentration. The approximations for the mass concentrations used in the analyzes were retrieved with the aerosol volume at each height (within the size range of 10 to 400 nm) multiplied by the average total loading of the wet season, of $1.4 \mu\text{g m}^{-3}$, as shown in Figure 41. This procedure was necessary since, in the analyzed periods, there are no chemical concentration measurements obtained simultaneously in the vertical profile at the ATTO site with similar instruments.

Figure 56 shows the variability of scattering coefficients at 525 nm, $\sigma_{525\text{m}}$, as a function of the mass concentration, where the colors in panels a) and b) are relative to $\omega_{0,637\text{nm}}$, and in panels c) and d) are relative to total concentrations, $N_{10-400\text{nm}}$. As in the previous section, comparative analyses were obtained for periods when the instruments measured

simultaneously at 60 and 325 m high. In Figure 56, the scattering coefficient varies more with the mass concentration at 60 m than at 325 m. This implies more variability of the scattering efficiency at 60 m, as the slopes of the curves that could be fitted to adjust the data change more frequently according to different aerosol events. It is also observed that $\omega_{0,637nm}$ and $N_{10-400nm}$ also present more variability during specific aerosol events at 60 m, which seems more stable at 325 m.

Figure 57 – Spectral dependence of the scattering coefficient, σ_{scat} , as a function of mass concentration for measurements at 60 and 325 m height between 8th and 19th of May 2019. Panels a), b) and c) are relative to the scattering coefficient measurements at 60 m height, and panels d), e) and f) are relative to measurements at 325 m height, at wavelengths 635, 525, and 450 nm, respectively.

The period between 8th and 19th of May 2019 was chosen as representative clean days to assess the differences in scattering efficiencies in the vertical profile, now considering all wavelengths measured by the nephelometer (450, 525, and 635 nm). In addition, the referred period presents clear linearity in $\sigma_{scat} \times$ Mass concentration curves that were not interfered with by strong episodic events, as shown in Figure 57. The panels a) to c) are referred to measurements at 60 m height, the panels d) to f) are referred to measurements at 325 m height.

Figure 57 corroborates that there is more dispersion in the scattering coefficient and mass concentration at 60 m, while at 325 m, the linear relationship is less dispersed, therefore, more homogeneous. The result supports the hypothesis that the aerosol population in 325 m is more processed and aged than near the canopy. The spectral dependence is also clear in Figure 57. Shorter wavelengths have higher scattering efficiencies: at 60 m, it was

obtained $\alpha_{scat}(\lambda) \pm SE = 4.15 \pm 0.11$, 5.49 ± 0.11 and $7.74 \pm 0.12 \text{ m}^2 \text{ g}^{-1}$ for 635, 525, and 450 nm, respectively. At 325 m, the observed variability was $\alpha_{scat}(\lambda) \pm SE = 2.46 \pm 0.04$, 3.76 ± 0.05 and $5.26 \pm 0.06 \text{ m}^2 \text{ g}^{-1}$ for 635, 525, and 450 nm, respectively.

Figure 58 – Mass scattering efficiency, $\alpha_{scat}(\lambda)$, as a function of wavelength for measurements at 60 and 325 m height.

A direct comparison between the scattering efficiencies at 60 and 325 m as a function of the wavelength of the scattered radiation is presented in Figure 58. The dependence of scattering efficiency with height is evident. Aerosol populations near the canopy are more efficient at scattering radiation than at 325 m high for all wavelengths. The percentage differences vary with wavelength, but on average, they are approximately 35%. The results suggest that aerosols with larger volumes, as observed in Figure 52, are likely to be more processed are less efficient in scattering radiation. In contrast, smaller aerosols in direct contact with fresh VOC emissions from vegetation are more likely to scatter radiation more efficiently.

Figure 59 presents the absorption coefficient, $\sigma_{abs,637nm}$, as a function of the mass concentration in a representation similar to Figure 56. It was chosen here to use MAAP measures in the analyses since these comprise a period of simultaneous measures in the vertical profile significantly longer than the AE33. The figure shows a very peculiar behavior of the coefficient variability at 60 and 325 m height. In contrast to the case of scattering efficiencies, here the absorption efficiency varies significantly less at 60 m. As obtained from the comparisons in Figure 53, this is likely due to the influence of long-range aerosol transport

at 325 m, which increases the Black Carbon concentration more than at 60 m.

Figure 59 – Absorption coefficient, $\sigma_{abs,637nm}$, as a function of mass concentration for measurements at 60 and 325 m height. The colors in panels a) and b) are relative to $\omega_{0,637nm}$, and the colors in c) and d) are relative to $N_{10-400nm}$. The mass concentration is calculated by multiplying the aerosol volume (within the size range 10 to 400 nm) by the average mass loading of the wet season ($1.4 \mu\text{g m}^{-3}$).

It is worth noting the differences in $\omega_{0,637nm}$ at the particle events that change the slopes of the fitting curves (Figures 59a and b). The median at 60 m is 0.96, compared to the median at 325 m, of 0.92. The aerosol concentration has not a significant difference, as shown in Figures 59a and b. The results indicate the influence of different aerosol sources on their physical characteristics in the vertical profile: the aerosol population closer to the canopy is less susceptible to long-range transport events than the population at 325 m. The difference between this result and the one obtained in the comparisons in Figure 49 is that here are considered exclusively the periods in which the absorption and scattering coefficients and the aerosol size distribution were measured simultaneously, in the same time interval, at 60 and 325 m. In the case of Figure 49, as already mentioned, comparisons were performed for periods in which similar instruments that measure the same physical property operated simultaneously.

The comparison of the mass absorption efficiencies, $\alpha_{abs,637nm}$, in the vertical profile was made for the same period considered for the mass scattering efficiencies: May 8th to

Figure 60 – Total absorption coefficient, $\sigma_{abs,637nm}$, as a function of mass concentration for measurements at 60 and 325 m height. Panels a) and b) show the linear fits (black line) and the slopes ($\alpha_{abs,637nm}$) for 60 and 325 m, respectively.

19th, 2019. The absorption coefficients at 637 nm measured by MAAP were considered for the calculations of $\alpha_{abs,637nm}$. Figure 60 presents the absorption coefficient at 637 nm as a function of mass concentration, with linear fits for 60 and 325 m. The fits with $R^2 > 0.8$ showed strong contrast with the scattering efficiencies in the vertical profile, with very similar $\alpha_{abs,637nm}$ at 60 and 325 m height, of 0.210 ± 0.003 and $0.226 \pm 0.004 \text{ m}^2 \text{ g}^{-1}$, respectively. As with the spectral dependence on absorption coefficients shown in Figure 51, $\alpha_{abs,637nm}$ also does not vary significantly with height. It indicates that, although previous results show more influence of the BC component at 325 m and BrC at 60 m, the mass absorption efficiency of the total absorption coefficient is similar for the aerosol populations at both heights.

However, the results contrast when analyzing the BC and BrC components of the total absorption coefficient separately. Figure 61 shows comparative analyzes obtained with the BC and BrC components at 60 and 325 m height from 8 to 18 May 2020. This period was chosen because:

- AE33 measurements are available in the vertical profile.
- It represents clean atmosphere conditions, with no clear particle events that could change the linearity of $\sigma_{abs,470nm} \times \text{Mass concentration}$.

Panels a) and b) in Figure 61 show the absorption coefficients exclusively due to the

Figure 61 – Absorption coefficient, $\sigma_{abs,637nm}$, as a function of mass concentration for measurements at 60 and 325 m height. Panels a) and c) show the linear fits (black line) and the slopes ($\alpha_{abs,637nm}$) for BC and BrC absorption coefficients, respectively, at 60 m height, and panels b) and d) show the linear fits (black line) and the slopes ($\alpha_{abs,637nm}$) for BC and BrC absorption coefficients, respectively, at 325 m height.

BrC as a function of mass concentration for 60 and 325 m height, respectively. At 60 m (panel a), it is observed that there is no apparent linearity between the components, so it was not possible to estimate $\alpha_{BrC,470nm}$ in this case. At 325 m (panel b), despite some dispersion, it was possible to obtain a linear fit and estimate the mass absorption efficiency due exclusively to BrC, $\alpha_{BrC,470nm} = 0.049 \pm 0.007 \text{ m}^2 \text{ g}^{-1}$, despite the relatively low correlation, with R^2 of 0.4. It is worth noting that the BrC absorption coefficients are significantly smaller than the total absorption coefficients, which are very close to the detection limit of the technique. It increases the coefficient estimation uncertainty, which may explain the low correlation.

In contrast, the non-linearity at 60 m is likely to be related to the low homogeneity of the aerosol population, which is in direct contact with fresh VOC emissions. At 325 m, the aerosol is probably more processed, which would explain the linearity. Also, note that the absorption efficiency of BrC at 325 m is very low compared to the total mass absorption efficiency. This indicates that the BrC component contributes little to the total component and has a much less significant radiative effect than BC. Panels c) and d) in Figure 61 show the absorption coefficients exclusively due to the BC as a function of mass concentration for 60 and 325 m height, respectively. It was calculated linear fits for both cases, with satisfactory

correlation coefficients of $R^2 > 0.65$.

The results show clear differences in the mass absorption efficiencies of BC in the vertical profile. At 60 and 325 m, $\alpha_{BC,470nm} = 0.28 \pm 0.02$ and $0.55 \pm 0.04 \text{ m}^2 \text{ g}^{-1}$, respectively. The almost 50% difference in efficiencies highlights the strong absorption efficiency of BC in the aerosol population at 325 m height, even during the cleaner atmosphere months of the wet season. The result reinforces the hypothesis that this population is strongly influenced by long-range transport, bringing dust and biomass burning from West Africa and Northeast Brazil to Central Amazonia. The BC influence is less significant close to the canopy than at 325 m, most likely because the population of biogenic aerosols is more prevalent there.

6.4 Final remarks

This chapter, therefore, presented a summary of the variability of aerosol physical and chemical properties over the last eight years of continuous measurements in Central Amazonia. The strong seasonality of the optical components and the particle number concentration determines the aerosol population dynamics in Central Amazonia, which is corroborated by previous work carried out under similar conditions. The chemical component of aerosols was characterized in section 6.1.1, showing that the organic fraction is dominant in both the dry and wet seasons, varying between 80 and 77%, respectively. Sulfate and eBC together account for approximately 15% of all PM_{10} mass concentrations in Amazonia from the inorganic fraction.

It was also obtained that the fraction of organic aerosols is the most significant in the component of the aerosol scattering coefficient, with a mass scattering efficiency of $2.2 \text{ m}^2 \text{ g}^{-1}$ in the wet season, and whose efficiency is even higher in the DtoW transition, of $5.2 \text{ m}^2 \text{ g}^{-1}$, likely to be due to different sources of aerosols, mainly transported over long distances by atmospheric dynamics. Inorganic aerosols also play an important role in the scattering coefficient, emphasizing the sulfate component, as it is the chemical species with the highest concentration after the organics.

The approach to obtain atmospheric conditions defined by pristine conditions, complementary, and with the same terminology as used in PÖHLKER et al.(2016), showed that the organic fraction is even more relevant than for the entire wet season, 80%, followed by Ammonium (7%), Sulfate (5%), eBC (4%) and Nitrate (4%). Average values for the aerosol optical properties were also estimated, which is an unprecedented result. It was shown that, despite being low, the absorption coefficient, $\sigma_{abs,637nm}$, cannot be neglected, as discussed in PÖHLKER et al.(2016). In particular, it was also obtained the mean values of AOD and AAOD in background conditions, which may have future importance for computational atmospheric models.

Section 6.3 showed that differences in the extensive and intensive aerosol properties

are observed in the vertical profile. Overall, the differences in aerosol volumes and scattering coefficients were the extensive aerosol properties with more variability in the vertical profile. The analysis of diurnal cycles showed small differences in optical properties, with more significant ones in particle number concentrations of each size mode. The results showed a strong efficiency of the boundary layer in mixing aerosols during the day and the ability of the night layer to discriminate aerosol populations.

A strong spectral dependence in the vertical profile with the scattering coefficient was observed. However, no significant dependence was detected in the absorption coefficients measured at different wavelengths. This difference was observed in the Angstrom exponents, which were significantly different for the scattering component. The estimation of mass scattering and absorption efficiencies and their variability in the vertical profile of the troposphere in Central Amazonia is an unprecedented and relevant component of this study.

The results showed that the aerosol population close to the canopy has a higher scattering efficiency than at 325 m, with a clear spectral dependence. The result can be explained by the differences in aerosol volumes at each of the heights, which are smaller by 60 m, and possibly by the aging stage of the aerosol. In contrast, considering the total absorption coefficient, the mass absorption efficiency was identical at 60 and 325 m, approximately $0.21 \text{ m}^2 \text{ g}^{-1}$. To our knowledge, this is the only estimate of the mass absorption efficiency obtained for clean periods of the wet season in Central Amazonia.

By discriminating the contributions of BC and BrC components to the total absorption, it was observed that the mass absorption efficiency exclusively due to BC is higher at 325 m ($\alpha_{BC,470nm} = 0.55 \text{ m}^2 \text{ g}^{-1}$ in comparison to $0.28 \text{ m}^2 \text{ g}^{-1}$ at 60 m). This is likely due to the strong influence of long-distance transport and the processing stage of the aerosols. In addition, the processing and aging stage of aerosols at 325 m can also play an important role. It was possible to estimate the mass absorption efficiency for the BrC component at 325 m, most likely due to the homogenization of the aerosols at this point, which was not obtained at 60 m, with $\alpha_{BrC,470nm} = 0.05 \text{ m}^2 \text{ g}^{-1}$. Thus, despite being very low, the Brown Carbon component still plays a relevant role in the radiative component of aerosols at 325 m. Again, to our knowledge, this result is the only one obtained in Central Amazonia.

The results of this chapter have shown that there are many aspects of the aerosol life cycle in central Amazonia that need to be further investigated in more detail. In particular, physical and chemical characterizations of aerosols at 60 and 325 m are required to verify the hypotheses of sources and stages of aging of these particles presented here. Furthermore, the radiative forcing of different aerosol populations in the vertical profile of the lower Amazonian troposphere must be determined due to its climatic importance, its effects on vegetation, and, of course, the processes of cloud formation. Therefore, future scientific aircraft measurement campaigns and the continuation of *in situ* measurements at the ATTO site may help answering the many open questions in this study.

Chapter 7

Relationship between aerosol particle transport and weather events in the Amazon boundary layer

Chapter 5 showed that aerosol particle growth events are directly influenced by meteorology. In particular, it was observed that convective downdrafts are the main transport mechanism for these particles, formed in the free troposphere and transported into the PBL. Chapter 6 showed that it is very likely that different aerosol populations are dominant in the vertical profile of the lower troposphere since the aerosols' intensive characteristics and particle volume were contrasting at 60 and 325 m height. The likely differences in particle number concentrations of each size mode were significant, as shown in Figure 55.

This chapter assesses the effects of meteorology on aerosol number size distributions in Central Amazonia, focusing on the wet season. In addition, the occurrence of aerosol particle transports, characterized by the appearance of sub-50 nm particles, their temporal variability concerning the vertical profile (60 and 325 m), and their relationship with the occurrence of lightning, are investigated. The main results presented here are partially submitted to the scientific periodic *Atmospheric Chemistry and Physics*, in the article: "How weather events modify aerosol particle size distributions in the Amazon boundary layer" (TOLEDO MACHADO et al., 2021), a study in which I collaborated as the second author. For further details, the reader is referred to the aforementioned article.

This chapter, therefore, intends to show that the investigation of the aerosol life cycle in the Central Amazon is far from the end. Many studies resulting from this one are required to determine the different sources of aerosols, the particle transport mechanism, and the characteristics of NPF in the free troposphere of one of the regions least influenced by human activities in the world (ANDREAE et al., 2015).

7.1 Aerosol particle transport during downdraft conditions

Here, we define the term “aerosol particle transport event” as the cases where the abrupt appearance of $CN_{<50}$ within the PBL is measured by the SMPS. These particles can either grow to sizes on the order of ~ 100 nm, acting as CCN and becoming optically active, or remain in the atmosphere without showing signs of growth. In particular, the group of sub-50 nm aerosols that do not grow over time has been defined as aerosol particle bursts, which is a quite common event in Central Amazonia (RIZZO et al., 2018). Regardless of the aerosol characteristics after the particle transport event, there is a strong correlation between particle transport and its subsequent appearance into the PBL, and the occurrence of convective downdrafts. This mechanism is widely known and well described for the Amazonian atmosphere in several previous studies as discussed in section 1.1 and Chapter 5.

Figure 62 – Comparative box of the aerosol number size distributions at a) 325 and b) 60 m height, showing several occurrences of $CN_{<50}$. In c) there is the equivalent potential temperature, θ_e , and, in d), the precipitation, P_{ATTO} .

Measurements of aerosol particle concentration and number size distribution at 60 and 325 m allowed a more detailed and unprecedented investigation of aerosol particle transport and their characteristics along with the vertical profile. Figure 62 presents a panel composed of the size distributions at 60 and 325 m, the equivalent potential temperature,

Figure 63 – Diurnal cycle of PNSD at 60 m during a representative period of the dry season (Jun-Oct) in colors, and wet season (Dec-Apr) as black isolines. Monthly averages of cloud brightness temperature, *Tir*, and lightning activity are shown as solid and dashed gray lines for the dry and wet seasons, respectively. Source: Figure extracted from TOLEDO MACHADO et al.(2021).

θ_e , and the precipitation between January 13th and 15th, 2019. It is observed a simultaneity between the appearance of $CN_{<50}$, the occurrence of precipitation, and decreases in θ_e , indicating a direct relationship between convective activities and the transport of particles into the BL. There are also some differences in these transports through the vertical profile, wherein in most cases, the particle bursts occur first at 325 m and then at 60 m (which is likely due to convective downdrafts). However, particle bursts starting first at 60 m and then observed at 325 m were also detected. This last case could be characterized by local aerosol production close to the canopy.

Before directly investigating the temporal differences in the occurrence of particle transport in the vertical profile, it was verified whether there could be relationships between meteorological variables such as cloud cover, lightning frequency, and aerosol particle number concentration. Figure 63 shows in a mean diurnal cycle the relationship between particle number concentration at 60 m (heatmap and isolines for a representative period of the dry and wet season, respectively), the brightness temperature, *Tir*, and the lightning density, obtained by a satellite sensor (GLM CCD sensor from GOES-16). The time in Figure 63 is in UTC. Local time is UTC - 4.

Note that, despite the differences in particle number concentrations between the wet and dry season periods (up to 5 times), the diurnal concentration profile is similar between the seasons and has the same behavior as the one shown in Figure 55. Note that the maximum de *Tir* is very close to the maximum concentrations, indicating periods when there is no evident convective condition. In contrast, the periods of lowest *Tir* value are those under convection conditions, which occur close to 15-16h LT.

They coincide with the precipitation peak in the afternoon (Figure 29b), and they are also followed by a decrease in the concentration of N_{AIT} and N_{ACC} particles resulting from the wet deposition. It is worth noting that the peak in the lightning density coincides with the minimum in Tir , as expected for convective conditions. Thus, the association of convective events, lightning activity, and the variability in particle number concentrations in different size modes indicated a probable cause-and-effect relationship between meteorology and aerosol population in the boundary layer in Central Amazonia.

7.2 Relationship between aerosol particle number concentration and lightning activity

To verify the variability of particle number concentrations in the sub-50 nm, Aitken, and Accumulation size modes, composite analyzes similar to the ensemble analyzes performed in Chapter 5 were developed. According to BOSCHAT et al.(2016), composite analyzes are important when accessing associations between environmental and meteorological parameters. In Figure 64, the composite analysis shows the variability in the concentrations of $CN_{<50}$, N_{AIT} , and N_{ACC} 400 minutes before and after the maximum of lightning activity comprising all data set (not only wet season). In particular, black lines in Figure 64b show the GLM density variability for different percentiles, all with the same pattern regarding the maximum intensity.

A curious behavior was observed regarding the concentrations of each of the size modes. The $CN_{<50}$ concentration (Figure 64a) increases exponentially from approximately 100 minutes before the peak of lightning activity, reaching a peak concentration approximately 200 minutes later. Note that it nearly doubles between before the lightning activity and after. This behavior is consistent with different percentile choices for lightning density. Previous studies have shown that the ozone and nitrogen dioxide concentrations increase during storms, which are fundamental in the oxidation processes of VOCs in the production of new SOA particles (MARTIN et al., 2010b).

In contrast, N_{AIT} and N_{ACC} have a similar pattern, with a strong decrease from 100 minutes before the maximum lightning activity. This behavior is likely related to the approaching convective meteorological condition, together with precipitation that scavenges those particles from the atmosphere via wet deposition. Thus, as discussed in more detail in TOLEDO MACHADO et al.(2021), there is a possibility that secondary aerosols may form due to thunderstorms, which are transported into the boundary layer. However, our study does not have an experimental design to prove the hypothesis, so further studies will be needed in this regard.

A composite analysis with the particle flux before and after the maximum lightning activity was obtained for the particle number concentrations of the three size modes at 60

Figure 64 – Composites obtained with different aerosol populations (a) $\text{CN}_{<50}$, b) Ait and c) Acc) as a function of different percentiles of the maximum lightning activity. Panel b) also presents a composite of the frequency of lightning occurrence as black lines under different percentile conditions. The shaded areas are confidence intervals of 95%. Source: Figure adapted from TOLEDO MACHADO et al.(2021).

Figure 65 – Rates of change (dN_i/dt) in aerosol particle number concentration from a) sub-50 nm, b) Aitken, and c) accumulation size modes. The blue and red lines represent measurements at 60 and 325 m, respectively. Source: Figure adapted from TOLEDO MACHADO et al.(2021).

and 325 m height. This analysis aims to evaluate how the particle flux at each height (60 and 325 m) changes as a function of time as the lightning activity also changes ($t = 0$ is the maximum lightning activity). The flux is obtained by the derivative of the numerical concentration as a function of time: dN_i/dt [$cm^{-3} h^{-1}$], where $i = 1, 2, 3$ is the i -th aerosol size mode. Figure 65 shows the particle flux in each of the size modes (a) sub-50 nm, b) Aitken, and c) accumulation) between 400 minutes before and after the maximum lightning activity during the wet season.

The results showed that the rates of change in particle number concentration depend on height. Note that the rate of change of $CN_{<50}$ tends to increase between $t = -200$ minutes and $t = 0$, where it has its maximum value. After the maximum lightning activity, the rate decreases again over time. An inquisitive behavior was obtained for the flux of $CN_{<50}$ at 60 m height, which presents a much higher variability than at 325 m. In addition, the rates at 60 m are also higher, in particular, at time $t = 0$. The result indicates that an aerosol source of very small particles close to the canopy is likely, explaining, for example, the significant difference in concentration of these particles in the diurnal cycle in Figure 55a.

N_{AIT} and N_{ACC} present the same behavior, in which the rate of change in particle number concentration decreases rapidly from $t = -100$ minutes, reaching a minimum at $t = 0$ for both measurements at 60 and 325 m. This shows the fast loss of particles by scavenging near the maximum lightning activity. After the convective event, the rate is approximately similar to what was observed before the event. Substantial variability in the accumulation mode at 325 m after the maximum lightning event is worth noting, which may be associated with diurnal cloud variability.

7.3 A novel approach to identifying aerosol particle transport events

The results of section 7.2 showed a direct relationship between the increase of $CN_{<50}$ particles and the lightning activity. Moreover, it showed that the rate of change of aerosol particle number concentration also varies with the height at which they are measured, with a possibility of a $CN_{<50}$ source close to the canopy. To identify the initial instant at which sub-50 nm aerosols are detected, we developed a new approach, different from the one used in Chapter 5.

It is worth noticing that the approach for identifying aerosol particle growth events used in Chapter 5 is based on KULMALA et al.(2012), which detects regions of interest in the PNSD where there are likely growth events. The method, however, is supposed to discard all those particle events that are configured as aerosol bursts, that is, the aerosol population where the particle geometric diameter did not grow over time. The method developed here does not consider what happens to the sub-50 nm particles after their detection by the SMPS, but only obtains the time instant they were first observed.

The method, therefore, consists of identifying the appearance of sub-50 nm particles, considering the variability in the particle number concentration of this specific fraction over time. The following steps are considered in the approach:

- a) The aerosol number concentration up to 40 nm ($CN_{<40}$) is considered the most sensitive marker to particle variability. This definition is based on several visual inspections and sensibility tests performed with different number concentrations.
- b) A filter based on moving average is applied with 3 data points in the window (each data point is regarding a 5-minute average concentration) to smooth the whole time series of $CN_{<40}$.
- c) A new moving window containing 10 data points, which corresponds to 50 min average, is considered. We define this concentration as $CN_{50min,<40}$.
- d) Each moving window calculates the angular coefficient (α) based on a linear fit of $CN_{50min,<40}$. We defined α as the *particle transport coefficient*, with units of $cm^{-3} 5min^{-1}$. Positive or negative values of α represent an increase or decrease in the $CN_{<40}$ within the moving window, respectively.
- e) The mean concentration of $CN_{50min,<40}$ is obtained. We also consider a window with 1h of data, which corresponds to 12 data points, $CN_{60min,<40}$, and calculate its average.
- f) The following conditions need to be fulfilled to consider the time t_i as a flag for the aerosol particle transport event: $CN_{50min,<40} > CN_{60min,<40}$, $\alpha > k$, where k must be positive, and $R^2 > 0.80$ (regarding the linear fit inside each moving window). We defined k as $30 cm^{-3} 5min^{-1}$ based on several visual optimizations for our data set.
- g) If within 1 hour there is more than one flag (t_i and t_{i+1} , for example), the first flag (t_i) is considered the particle transport event onset.

Figure 66a presents a time series of characteristic particle transport events (coincidentally classified as growth events). The dashed black line represents the 40 nm limit. Figure 66b shows the time series of $CN_{<40}$ and $CN_{<25}$ over the period, which shows the strong variability of concentrations during each particle transport event. Time series similar to this one was used to obtain the most sensitive concentration to particle transport events during the tests. Figures 66c and d present the flags and the particle transport coefficients, α , respectively, obtained automatically by the novel method, highlighting the event identification quality.

The method is robust in identifying the most pronounced particle transport events and can be used in the most obvious identifications. However, the need for parameter adjustments for different environmental conditions (i.e., the method applied to another experimental site) should be emphasized, which can be considered even somewhat subjective, as so far, they

Figure 66 – Box of a) PNSD time series containing particle transport events between February 19 and 24, 2018. The dashed black line represents the diameter at 40 nm. b) Time series of $CN_{<40}$ (black line) and $CN_{<25}$ (blue line) concentrations. c) Event flags obtained by the novel approach. d) Particle transport coefficient α during the events.

depend on visual inspection. In the future, there is the intention to optimize this methodology to avoid human dependence as much as possible.

7.4 Vertical occurrence of aerosol particle transport events

In this section, a case study was developed considering only PNSD measurements during the 2019 wet season. Figure 67 shows the diurnal frequency of particle transport events detected at 60 and 325 m height, obtained with the methodology described above (section 7.3). It is observed that there are discrepancies between the maximum and minimum occurrences of the events at 60 and 325 m height. The peak at 325 m occurs at 5:00 LT, while at 60 m, it occurs at 7:00 LT. This difference of 2 h may be related to the transport of particles from the free troposphere into the boundary layer, which arrives first in the highest level and, with the evolution of the boundary layer during the day, then detected in 60 m. Here, the transport time of particles within the inlet line between the top of the ATTO tower and the ground was not considered. However, it is estimated to be of the order of a few minutes, which does not interfere in the results.

As discussed in Chapter 5, the transport event peak observed in the morning is likely

Figure 67 – Histograms of the frequency of particle transport events throughout the day at a) 325 (green) and b) 60 m (blue) height.

due to the occurrence of precipitation (concomitant to convective downdrafts), shown in Figure 29b. Note that around 15:00 LT, there is also an increase in particle transport events at both 60 and 325 m, which is likely associated with convective events. There is a frequent occurrence of particle transport events at night, detected at 60 and 325 m. The result is in good agreement with what is shown in Figure 29e and Figure 63, which presents an increase in $CN_{<50}$ concentration in the evening until early morning. However, at 60 m, the occurrence of not clear peaks at 325 m is observed, particularly at 21:00 LT, 23:00 LT, and 3:00 LT.

Figure 68 is an example of a particle burst that first occurs at 60 m, and after approximately 1h it is detected at 325 m height. This case is likely related to primary biogenic emissions resulting from the increase in the relative humidity of the air due to the approach of a convective event. Further studies are required to investigate this kind of phenomenon to characterize the particle source properly. Note that the case of Figure 68 is the same as Figure 62 (left side corner), where there is a strong peak of precipitation around 7h LT. Also, note that there is a strong increase in $CN_{<50}$ after precipitation due to convective downdrafts.

In particular, the time difference in the particle transport events at 60 and 325 m was estimated. The temporal difference between the events at the different levels is defined as $\Delta t = t_{325m} - t_{60m}$, where t_{325m} and t_{60m} are the onsets of particle transport events at 325 and 60 m height, respectively. $\Delta t = 0$ is when particle transport is observed at approximately the same time in 60 and 325 m (between 0 and 59 minutes of time difference). Positive Δt values

Figure 68 – Example of an aerosol particle burst event first detected in 60 m and, ~ 1 h later, at 325 m. The event is followed by precipitation, which removes Aitken, and Accumulation mode particles, and transports sub-50 nm aerosols from the free troposphere into the PBL through convective downdraft.

are related to cases where events start first at 60 m, and negative Δt values to cases where events start first at 325 m. Figure 69 shows the frequency of occurrence of Δt with a maximum difference of 4h between events.

The results show that $\sim 35\%$ of events occur with differences of up to 59 minutes between 60 and 325 m (which is considered to be roughly simultaneous), followed by $\sim 37\%$ of events that start first at 325 m and then are detected at 60 m. These cases are expected, as they are related to aerosol transports from the FT into the PBL mainly by a convective downdraft and particle entrainment. In contrast, $\sim 28\%$ of events occurred first at 60 m and only later at 325 m. This case is remarkable, as a primary biogenic natural source close to the canopy is needed to first explain the transport of sub-50 nm particles from the canopy into the atmosphere. It is also remarkable the similarity of this result with the one obtained in Chapter 5, for the cases of particle growth that are not directly related to the occurrence of convective downdrafts.

It is worth noting the cases of long temporal differences in detecting transport events in the vertical profile. These are cases likely related to nocturnal events, in which there is a distinction of PBL sublayers. Furthermore, advection events can also be crucial in the processes that were observed. For example, in cases where aerosols were transported at 325 m, but due to the low turbulence of the PBL (night events), they were not transported to 60 m,

Figure 69 – Histogram of the frequency of Δt occurrences, defined as $\Delta t = t_{325m} - t_{60m}$. Values between 0 and 59 minutes are considered as $\Delta t = 0$ and represent events in which the transport occurrence was detected almost at the same time at 60 and 325 m. Positive Δt values represent events that occurred first at 60 and then at 325 m. Negative values of Δt represent events that occurred first in 325 and later in 60 m.

and detection at this height will only occur after sunrise. This hypothesis can be supported by observing that the transport event detection peaks occur in the early morning (Figure 67).

7.5 Final remarks

This section presented the relationship between meteorology and aerosol number concentration in the Central Amazonian troposphere. Convective downdrafts are one of the most powerful mechanisms in transporting aerosols produced within the free troposphere into the boundary layer. The results showed a direct relationship between particle number concentration variability and meteorological variables such as T_{ir} and lightning activity. Composite analyzes showed a remarkable relationship between increased sub-50nm particles and lightning activity. The results showed an exponential increase in $CN_{<50}$ concentration, which starts from ~ 100 minutes before the maximum lightning activity and lasts ~ 200 minutes later. Lightning is very likely to induce the formation of new particles within the free troposphere since they are sources of ozone and NO_x , key products in the oxidation of VOCs to become SOA.

In contrast, N_{AIT} and N_{ACC} decreased with increased lightning activity, which may be associated with the presence of convective events and precipitation, which remove these aerosol populations mainly by wet deposition. It was observed that the proximity of the occurrence of lightning affects the particle flow, with clear differences in the populations of

60 and 325 m in height. For the case of sub-50 nm particles, the particle flux increases with the approach of the lightning maximum and decreases with its distance. In particular, it was observed that the variability is much higher at 60 than at 325 m. The results pointed to the existence of a sub-50 nm particle source close to the canopy, corroborating other findings from chapters 5 and 6. Regarding aerosols from Aitken and accumulation modes, there is a strong decrease in the particle flow as it approaches the maximum of lightning. It evidences the aerosol losses due to wet deposition.

The results pointed to the need to investigate the variability of particle transport events in the vertical profile, between 60 and 325 m. It was necessary to develop a new approach for the automatic identification of particle transport events, regardless of what would happen to the particles after their appearance in BL. The evaluation of particle transport events in the vertical profile showed a diversity of occurrences at 60 and 325 m. In particular, ~72% of the transport events occur either first or simultaneously at 325 m and at 60 m, which is expected for processes dominated by convective downdrafts. In contrast, ~28% of the transports started first at 60 m, and only later were detected at 325 m, indicating the hypothesis of an aerosol source close to the canopy.

The results presented so far point to several possibilities for continuity to characterize in detail aerosol sources and their influence on the Amazon ecosystem. First, the meteorological influence on both the transport and the production of aerosols must be considered. Second, the strong biogenic contribution with primary emissions of VOCs that oxidize and eventually become SOA. This study, therefore, leaves many open questions for future studies that will investigate the life cycle of aerosols in Central Amazonia.

Chapter 8

Conclusions

This study investigated the life cycle characteristics of aerosol particles, emphasizing the wet season and their physicochemical properties in the vertical profile of the lower troposphere in Central Amazonia. This was only possible due to the infrastructure and experimental instrumentation at the ATTO site, particularly with measurements in towers at 60 and 325 m heights. It is worth mentioning that many methods were developed for processing and analyzing the various measurements obtained *in situ* throughout the work to improve the quality and robustness of the results. The investigation of the occurrence of particle growth in the size range from 10 to 50 nm at 60 m height (Chapter 5), addressing the first and second scientific question of Chapter 2, showed that at ~14% of the analyzed period (217 in 1596 days - Feb 2014 to Sep 2020) those events have occurred. The months between January and June had the highest event occurrence rate, 88%, compared to 12% between July and December. The diurnal cycle of growth frequency showed that 74% occurred during the day and 26% during the night. A high fraction of 53% of growth events was detected between 06:00 and 11:00 LT, with a pronounced peak at 07:00 LT, indicating a direct relationship with photochemical process and PBL evolution.

The particle growth events are closely related to meteorology. The peaks of particle growth events coincide with the peaks of precipitation in the morning and afternoon, indicating that the most significant fraction of the aerosol particles that grew were transported from the high or middle troposphere into the boundary layer by convective downdrafts. The median GR of the Amazonian growth events was 5.2 nm h^{-1} , and the CS during the growth process was 0.0011 s^{-1} . In particular, daytime events have higher GR and CS than nighttime events, indicating the strong influence of photochemistry on the aging of these particles. The results showed that particle growth events are more likely to occur in periods with smaller CS, directly related to the concentration of aerosols in the atmosphere. This reflects, for example, that there are significantly fewer growth events during the dry season when CS is higher than in the wet season, and the number concentration of particles is so high that it can mitigate the occurrence of particle growths. It is worth remembering that the primary source of aerosols

in the dry season is regional (Amazonian) biomass burning with a small contribution of long-distance transport of pollutants from West Africa. The particles are mainly within the accumulation size mode since these are aged aerosols.

The relationship of growth events with meteorological variables such as cloud cover through brightness temperature, T_{ir} and anomalies in the equivalent potential temperature, $\Delta\theta'_e$, showed that the vast majority of event onsets coincides with the occurrence of convective downdrafts (>63%). In contrast, approximately 37% of events do not appear to be directly related to the occurrence of downdrafts, which was an observation that deserves further investigation. The particles that originate these events were likely transported into the boundary layer by other still unknown processes (advection mechanisms are likely) or could be transported from the canopy and vegetation into the BL. Chapter 7 showed that a very likely source of aerosols arises from the products of lightning, which are formed within the free troposphere. It has been shown that the concentration of sub-50 nm aerosols, precisely those that eventually grow within the boundary layer, increases with an increase in lightning activity. In particular, the concentration of those particles starts to grow exponentially from about 100 minutes before the maximum lightning activity and lasts until about 200 minutes later. This sub-50 nm particle transport is directly related to convective downdrafts, which are crucial during in thunderstorms.

In contrast, the aerosol concentrations of the Aitken and accumulation modes decrease with the arrival of convective events, which is likely mainly associated with the high efficiency of wet deposition in scavenging those particle populations. Particle number concentration analyzes at 60 and 325 m height showed, as expected, that $CN_{<50}$ increases with the lightning activity, although at 60 m, the rate of change in particle number concentrations is significantly higher than at 325 m. This is indicative of a sub-50 nm aerosol source close to the canopy. Motivated by the gradient of particle number concentrations in the vertical profile, the aerosol particle transport events were investigated with a new approach. Based on moving windows and the variability of particle number concentration over time, the method can derive the timing of appearance of sub-50 nm particles. Although there are still parameters that must be visually optimized, the method proved to be quite robust.

About ~72% of particle transports occur either first or almost simultaneously at 325 m and 60 m, i.e., sub-50 nm aerosols detected within a time difference of up to 59 minutes or first at 325 m height. This is the expected case for processes dominated by convective downdrafts. In contrast, while ~28% of events started first at 60 m, and only later were detected at 325 m. This result supports the hypothesis of a sub-50 nm aerosol source close to the canopy and may even be directly related to the particle growth events discussed in Chapter 5. However, advective mechanisms cannot be neglected since they are likely to play an important role in the aerosol particle population. This case is a knowledge gap that future studies will be able to address.

After being transported into the boundary layer and growing, aerosols reach sizes within the Aitken and accumulation modes, becoming optically active. The strong seasonality of optical components and particle number concentration affects the aerosol population dynamics in Central Amazonia, which is corroborated by previous studies under similar conditions. Here, the third and fourth scientific questions of Chapter 2 were addressed in detail. The aerosol chemical composition shows that the organic fraction is dominant in the dry and wet seasons, varying between 80 and 77% in terms of PM_{10} mass, respectively, which agrees with previous studies. Sulfate and eBC together account for approximately 15% of PM_{10} mass concentrations in Central Amazonia.

The aerosol organic fraction is the most significant in the aerosol scattering coefficient, with a mass scattering efficiency of $2.2 \text{ m}^2 \text{ g}^{-1}$ in the wet season, and whose efficiency is even higher in the DtoW transition, of $5.2 \text{ m}^2 \text{ g}^{-1}$. Inorganic aerosols also play an important role, that cannot be neglected, with mass scattering efficiency that varied from $1.0 \text{ m}^2 \text{ g}^{-1}$ in the wet season to $2.7 \text{ m}^2 \text{ g}^{-1}$ in the DtoW season. It shows that the mass scattering efficiency is strongly dependent on the season, which drives the different sources of aerosols.

The approach applied to obtain the empirically pristine atmospheric conditions, complementary and with the same terminology as used in PÖHLKER et al. (2016), showed the absorption coefficient is very low but not negligible, with an average of $\sigma_{abs,637nm} = 0.14 \text{ Mm}^{-1}$. This represents a different point of view from what was considered in PÖHLKER et al. (2016). It should be noted that the value we obtained is higher than the LOD of the instruments that measured eBC at the site, meaning that the eBC component is present in clean atmosphere periods in Central Amazonia. The nature of this eBC component is an issue still unclear in natural biogenic aerosols since it can not consist of pure black carbon because of the lack of combustion in the clean wet season. This absorption component could be associated with brown carbon from humic-like substances and natural biogenic primary particles.

The approach we developed also obtained other aerosol optical properties, such as the average scattering coefficient under pristine conditions of 4.4 Mm^{-1} . In addition, the mean values of AOD and AAOD in background conditions were estimated as 0.075 and 0.0180 at 550 nm. These estimates are new components of this work and are relevant for appropriate aerosol radiative forcing calculations in regional and global models.

Differences in the extensive and intensive aerosol properties were observed in the vertical profile, where the highest differences were obtained for the scattering coefficient and the particle volume. The more significant ones were observed at night, possibly due to the clear discrimination between the stable and residual layers. Differences in aerosol volumes and scattering coefficients at each height resulted in higher mass scattering efficiency at 60 m, which varied between 7.74, 5.49, and $4.14 \text{ m}^2 \text{ g}^{-1}$ for 450, 525, and 635 nm, respectively. At 325 m, $\alpha_{scat}(\lambda)$ varied between 5.26, 3.76 and $2.46 \text{ m}^2 \text{ g}^{-1}$ for 450, 525, and 635 nm,

respectively. The differences are likely due to different aerosol populations at each height, with particle production at the canopy level. In contrast, considering the total absorption coefficient, the mass absorption efficiency was identical at 60 and 325 m.

Interesting results were obtained by calculating the eBC and BrC fractions of the total absorption coefficient at 470 nm. The mass absorption efficiency exclusively due to eBC is higher at 325 m ($\alpha_{BC,470nm} = 0.55 \text{ m}^2 \text{ g}^{-1}$ compared to $0.28 \text{ m}^2 \text{ g}^{-1}$ at 60 m), which is likely due to the strong influence of long-distance transport and the processing stage of the aerosols. The mass absorption efficiency for the BrC was only possible to be estimated at 325 m, since at 60 m, the data did not show linearity between the absorption coefficient and mass. It was obtained $\alpha_{BrC,470nm} = 0.05 \text{ m}^2 \text{ g}^{-1}$, which is a very low value compared to all the other mass absorption efficiencies estimated.

Therefore, the results of this study properly addressed the four main scientific questions presented in Chapter 2. Specifically, this work calculated the conditions and frequency at which aerosol particle growth events occur in the lower troposphere of Central Amazonia. Moreover, the importance of convective transport in providing the boundary layer with aerosol particles was discussed. Meteorological convective activity and precipitation events are sources of $\text{CN}_{<50}$ aerosols in the lower Amazonian atmosphere. Furthermore, the analyzes considering optical properties in the vertical profile showed significant differences in the intensive properties of these aerosols, which is directly related to different properties of aerosol populations predominant at each height. We also showed the production of secondary organic aerosols within the forest canopy and its optical properties. Previous studies have shown the primary biological aerosol particles emissions at the canopy level, but this work also emphasizes SOA's relevance at the canopy level.

8.1 Future perspectives

Several possibilities for future studies can be addressed, which are directly derived from this work. Two of them are fundamental: the detailed investigation of the variability of the aerosol optical, chemical, and size distribution properties with meteorology and sub-50 nm particle sources characterization. There are many open questions, in particular, regarding the process of new particle formation within the free troposphere that has never been studied before. Aircraft campaigns, such as CAFE-Brazil, scheduled for mid-2022, are fundamental in this aspect to clarify the mechanisms of particle production within the upper troposphere and the role of convection in transport these particles to the lower troposphere.

Although the hypotheses about the SOA formation within the free troposphere due to VOCs oxidation and its subsequent phase shift from gas to particle, very little is known about the physical parameters of these particles. For example, their size distributions, growth and formation rate (number of particles per unit of time), and spatial distribution at the

upper troposphere must be characterized. Concerning the characterization of sub-50 nm particle sources, results from this study and others (RIZZO et al., 2018; TOLEDO MACHADO et al., 2021) suggest the existence of a possible source close to the canopy. So far, there is no direct evidence of these particles, although the contribution from biological activities and atmospheric chemistry are likely. The relevance of the continuous analysis of variability of aerosol properties in the vertical profile is worth mentioning, focusing on aerosol chemical composition obtained by mass spectroscopy. In particular, these analyzes should provide more clues to the different particle sources, for example, from the Positive Matrix Factorization (PMF) analyses. This statistical model could discriminate through the mass spectrum the different contributions of organic species to different aerosol sources. Thus, by correlating the chemical information with the scattering and absorption coefficients and particle number concentrations, the characterizations of the diverse aerosol populations will be complete.

The results of this work were focused on the wet season, as there is less influence of pollutants from human activities, such as biomass burning by deforestation. Nevertheless, studying the vertical variability of these biomass burning aerosols is also a very fruitful component for future studies. Again, the use of mass spectrometers can provide more details about the chemical characteristics of these aerosols, looking at the aging stages of the particles and their relationship with the aerosol coating. Once the dry season aerosol loading also influences biomass burning aerosols transported from West Africa to the Central Amazonia, a detailed chemical characterization of these different aerosol populations contributes to understanding the life cycle of these particles in the Amazon ecosystem.

Note that the study developed in this work did not address advective and turbulent components of the atmosphere. Currently, sonic anemometers are being installed at the ATTO tower in at least 16 levels of its vertical profile, which will provide high-resolution measurements of the vertical turbulent transport. The detailed measurements of the vertical profile transport will characterize the PBL dynamics in unprecedented detail. Future studies that will use ceilometer and Lidar data should also be considered, as they will extend the aerosol analyzes well above 325 m height. This is necessary, as there are few *in situ* studies regarding the coupling of processes within the lower troposphere with the free troposphere. It would then be possible to study the impact of this processing on the size distribution of aerosols and their optical properties in more detail. Remote sensing of aerosols could provide a larger scale of processes that influence the advection component around Central Amazonia.

Finally, no coupled aerosol-meteorology modeling component has yet been developed specifically for the ATTO site conditions. In particular, the study of the relationship between the component of VOCs emitted by the canopy and the interaction with meteorological components to produce processed aerosols is fundamental to understanding these particles' life cycle in the Amazon basin. Models such as WRF-Chem are very useful in evaluating the physicochemical properties of atmospheric aerosols and are powerful tools for predict the

vertical profile of particle production. This investigation may provide significant advances in identifying different sources of sub-50 nm particles in the Amazon, particularly to characterize the relationship between aerosol populations in PBL and meteorological events.

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APPENDIX A

Published or submitted scientific peer-reviewed articles

Please find below the scientific articles the student collaborated on, which have already been published or submitted to international peer-reviewed journals and presented at national (Brazil) and international conferences and schools. The last two chapters of the appendix fully present the two main articles arising from this doctoral thesis up to the defense.

1. **Franco, M. A.**, Ditas, F., Machado, L. A. T., Kremper, L. A., Rizzo, L. V., , et al.: Occurrence and growth of ultrafine aerosol particles in the boundary layer after particle production in the upper troposphere over the Amazon Basin. *Atmospheric Chemistry and Physics Discussions*, v. 2021, p.1-36. DOI:<<https://doi.org/10.5194/acp-2021-765>>.
2. Machado, L. A. T.; **Franco, M. A.**; Kremper, L. A.; Ditas, F.; Andreae, M. O.; Artaxo, P.; Cecchini, M. A.; Holanda, B. A.; Pöhlker, M. L.; Saraiva, I.; Wolff, S.; Pöschl, U.; Pöhlker, C. How weather events modify aerosol particle size distributions in the Amazon boundary layer. *Atmospheric Chemistry and Physics Discussions*, v. 2021, p. 1–31, 2021. DOI:<<https://acp.copernicus.org/preprints/acp-2021-314>>.
3. Artaxo, P., Hansson, H.-C., Andreae, M. O., Bäck, J., Alves, E. G., Barbosa, H. M. J., **Franco, M.A.**, et al.: Tropical and Boreal Forest – Atmosphere Interactions: a Review, submitted to *Tellus*, 2021. Ms. No. ZELB-2020-0011.
4. Milena Ponczek, **Marco A. Franco**, Samara Carbone, Luciana V. Rizzo, Djacinto Santos Junior, Fernando G. Morais, Alejandro Duarte, Henrique M. J. Barbosa, Paulo Artaxo. Linking chemical composition and optical properties of biomass burning aerosols in Amazonia. Submitted to *Environmental Science Atmospheres*. 2021. Ms. No. EA-ART-07-2021-000055.
5. da Silva Palácios, R., Romera, K. S., Curado, L. F. A., Banga, N. M., Rothmund, L. D., da Silva Sallo, F., Morais, F., **Franco, M.A.M.**,..., Rodrigues, T. R. (2020). Long term analysis

- of optical and radiative properties of aerosols in the Amazon Basin. *Aerosol and Air Quality Research*, 20(1), 139-154. DOI: <<https://doi.org/10.4209/aaqr.2019.04.0189>>
6. Da Silva, Jonatan ; Morais, F ; **Franco, M. A.** ; Lopes, F J. S. ; Arruda, G. A. ; Yoshida, A. C. ; Correia, A. ; Landulfo, E. . Exploring the Twilight Zone: A Multi-Sensor Approach. *EPJ WEB OF CONFERENCES*, v. 237, p. 07015, 2020. DOI: <<https://doi.org/10.1051/epjconf/202023707015>>
 7. Holanda, B. A., Pöhlker, M. L., Walter, D., Saturno, J., Sörgel, M., Ditas, J., **Franco, M.A.**, et al. Influx of African biomass burning aerosol during the Amazonian dry season through layered transatlantic transport of black carbon-rich smoke. *Atmospheric Chemistry and Physics*, 20(8), (2020), 4757-4785. DOI: <<https://doi.org/10.5194/acp-20-4757-2020>>
 8. Nascimento, J. ; BELA, M. M. ; Meller, B. ; Banducci, A. L. ; Rizzo, L. V. ; Vara-Vela, A. L. ; Barbosa, H. ; Gomes, H. ; Rafee, S. A. A. ; **Franco, M. A. M.** ; Carbone, S. ; Cirino, G. G. ; Souza, R. A. F. ; Mckeen, S. A. ; Artaxo, P . Aerosols from anthropogenic and biogenic sources and their interactions - modeling aerosol formation, optical properties, and impacts over the central Amazon basin. *Atmospheric Chemistry and Physics (Online)*, v. 21, p. 6755-6779, 2021. DOI: <[dx.doi.org/10.5194/acp-21-6755-2021](https://doi.org/10.5194/acp-21-6755-2021)>
 9. Prass, M.; Andreae, M. O.; Araujo, A. C. de; Artaxo, P.; Ditas, F.; Elbert, W.; **Franco, M. A.**; Angelis, I. Hrabe de; Kesselmeier, J.; Klimach, T. et al. Bioaerosols in the amazon rain forest: Temporal variations and vertical profiles of eukarya, bacteria and archaea. *Biogeosciences*, Copernicus GmbH, p. 1–23, 2021. DOI: <<https://doi.org/10.5194/bg-2020-469>>.

A.0.1 Covid-19 related

At the end of 2019, the COVID-19 pandemic had become a serious problem worldwide. In particular, Brazil has suffered heavily from the pandemic, where so far, almost 600,000 people have died. One of the most effective ways to avoid the coronavirus is through the use of good face masks. Thus, I was honored to collaborate with the analysis and writing of a scientific article that evaluated the filtration efficiency of 227 Brazilian homemade face masks used to mitigate the spread of COVID-19. It was a way for me to apply what I have learned about atmospheric aerosols to help the Brazilian population face the pandemic immediately.

10. Morais, F ; Sakano, V. K. ; LIMA, L. N. ; **Franco, M. A.** ; Reis, D. C. ; Zanchetta, L. M. ; Jorge, F ; Landulfo, E. ; Catalani, L. H. ; Barbosa, H. ; John, V. M. ; Artaxo, P . Filtration efficiency of a large set of COVID-19 face masks commonly used in Brazil. *Aerosol Science and Technology*, 2021. DOI: <<https://doi.org/10.1080/02786826.2021.1915466>>.

A.1 Papers presented at scientific conferences

The following studies were presented at national and international congresses and schools:

1. **FRANCO, M. A. M.**; Morais, F ; GUIMARAES FILHO, Z. ; LANDULFO, E. ; ARTAXO, P. . Statistical approach to assess the impact of polluted regions on the Aerosol Optical Depth measured by AERONET photometers. In: X Workshop Lidar Measurements in Latin America (WLMLA), 2018, Medellín. X Workshop Lidar Measurements in Latin America (WLMLA). Medellín, 2018. v. 1. p. 36-36.
2. MORAIS, F ; LANDULFO, E. ; ARTAXO, P. ; BARBOSA, H. ; **FRANCO, M. A. M.**; PALACIOS, R. . Long Term Scattering and Absorption Properties of Aerosols in Amazonia Using AERONET Measurements. In: X Workshop on Lidar Measurements in Latin America, 2018, Colombia. X Workshop on Lidar Measurements in Latin America. Colombia, 2018.
3. **FRANCO, M. A. M.**; RIZZO, L. V. ; ARTAXO, P. . Evaluation and Comparison of Aerosol Properties at Two Background Sites in the Central Amazon Rainforest. In: 10th International Aerosol Conference, 2018, St. Louis, MO, EUA. 10th International Aerosol Conference - Final Program. Reston, VA: American Association for Aerosol Research, 2018. v. 1. p. 79-79.
- Morais, F ; LANDULFO, E. ; ARTAXO, P. ; **DE MENEZES FRANCO, MARCO AURÉLIO**; SCHAFER, J. ; HOLBEN, B. . Long Term Characterization of Brown Carbon in Amazonia using AERONET and in situ Measurements. In: American Geophysical Union - Fall Meeting 2019, 2019, São Francisco, CA. Abstract book of AGU Fall Meeting 2019. São Francisco, CA, 2019.
4. **FRANCO, MARCO AURÉLIO**; ARTAXO, P. ; RIZZO, L. V. ; BARBOSA, H. ; Morais, F ; Carbone, S. ; POHLKER, C. ; HOLANDA, B. ; DITAS, F. ; ANDREAE, M. O. . Vertical Variability of Aerosol Physical Properties at the Central Amazonia ATTO Tower in the Wet Season. In: American Geophysical Union - Fall Meeting 2019, 2019, São Francisco, CA. Abstract book of AGU Fall Meeting 2019. São Francisco, CA, 2019.
5. **FRANCO, M. A. M.**; ARTAXO, P. ; Carbone, S. ; RIZZO, L. V. ; BARBOSA, H. ; Morais, F ; POHLKER, C. ; HOLANDA, B. ; DITAS, F. ; ANDREAE, M. O. . Aerosol physical properties at the vertical profile of the ATTO tower in the central Amazon rainforest. In: Sao Paulo School of Advanced Science on Atmospheric Aerosols: Properties, Measurements, Modeling, and Effects on Climate and Health, 2019, São Paulo. SP School of Advanced Science on Atmospheric Aerosols: Properties, Measurements, Modeling, and Effects on Climate and Health, 2019.

6. BRITO, J. ; **FRANCO, M. A. M.**; BURGUER, A. ; Carbone, S. ; JORGE, F. ; Morais, F. ; RIZZO, L. V. ; STERN, R. ; BARBOSA, H. ; ARTAXO, P. . Western Amazonia aerosol and VOC measurements: Overview of 2018 intensive campaign and associated measurements. In: General Assembly 2019 of the European Geosciences Union (EGU), 2019, Vienna. Geophysical Research Abstracts, 2019. v. 21.
7. HOLANDA, B. ; SATURNO, J. ; DITAS, F. ; BARBOSA, H. ; BRITO, J. ; Carbone, S. ; CHENG, Y. ; DITAS, J. ; **FRANCO, M. A. M.**; KLIMACH, T. ; KRUGER, O. ; Morais, F. ; POHLKER, M. ; PRASS, M. ; ARTAXO, P. ; ANDREAE, M. O. ; POHLKER, C. . Aerosol physical properties over the Amazon basin. In: General Assembly 2019 of the European Geosciences Union (EGU), 2019, Vienna. Geophysical Research Abstracts. Vienna, 2019. v. 21.
8. ARTAXO, P. ; RIZZO, L. V. ; Carbone, S. ; BARBOSA, H. ; **FRANCO, M. A. M.**; POHLKER, C. ; POHLKER, M. ; HOLANDA, B. ; DITAS, F. ; PRASS, M. ; POSCHL, U. ; ANDREAE, M. O. . Long term measurements of physical and chemical properties of biogenic atmospheric aerosols at the ATTO tower, Central Amazonia. In: General Assembly 2019 of the European Geosciences Union (EGU), 2019, Vienna, Austria. Geophysical Research Abstracts. Vienna: EGU General Assembly 2019, 2019. v. 21
9. **FRANCO, M. A. M.**; ARTAXO, P. ; Carbone, S. ; RIZZO, L. V. ; BARBOSA, H. ; Morais, F. ; POHLKER, C. ; HOLANDA, B. ; DITAS, F. ; ANDREAE, M. O. . Aerosol physical properties at different heights of the ATTO tower in the central Amazon rainforest. In: General Assembly 2019 of the European Geosciences Union (EGU), 2019, Vienna, Austria. Geophysical Research Abstracts. Austria: EGU General Assembly 2019, 2019. v. 21.
10. PONCZECK, M. ; **FRANCO, M. A. M.**; Carbone, S. ; SANTOS JR, D. M. ; Morais, F. ; RIZZO, L. V. ; BARBOSA, H. ; ARTAXO, PAULO . Composition, sources, and chemical processes of submicrometric aerosol over Southern Amazonian city highly impacted by biomass burning emissions. In: American Geophysical Union - Fall Meeting 2020, 2020, San Francisco (online event). Abstract book of AGU Fall Meeting - 2020. San Francisco, 2020.
11. Morais, F. ; **FRANCO, M. A. M.**; SAKANO, V. K. ; LIMA, L. N. ; REIS, D. C. ; ZANCHETTA, L. M. ; JORGE, F. ; LANDULFO, E. ; CATALANI, L. H. ; JOHN, V. M. ; ARTAXO, P. . The performance of a large number of COVID-19 facial masks used in Brazil for breathability and aerosol collection efficiency. In: American Geophysical Union - Fall Meeting 2020, 2020, San Francisco (online event). Abstract book of AGU Fall Meeting - 2020. San Francisco, 2020.
12. **FRANCO, M. A. M.**; Morais, F. ; HOLANDA, B. ; DITAS, F. ; KREMPER, L. ; Carbone, S. ; RIZZO, L. V. ; MACHADO, LUIZ A. T. ; NASCIMENTO, J. ; PONCZECK, M. ; BARBOSA, H. ; ANDREAE, M. O. ; PÖSCHL, ULRICH ; POHLKER, C. ; ARTAXO, P. . The Vertical Gradient of Aerosols in the Amazonian ATTO Tower: Optical Properties and Size Distributions. In:

American Geophysical Union - Fall Meeting 2020, 2020, San Francisco (online event).
Abstract book of AGU Fall Meeting - 2020. San Francisco, 2020.

13. MACHADO, LUIZ A. T. ; POHLKER, M. ; ARTAXO, PAULO ; CECCHINI, M. ; DITAS, F. ; **FRANCO, M. A. M.**; KREMPER, L. ; ANDREAE, M. O. ; SARAIVA, I. ; PÖSCHL, ULRICH ; POHLKER, C. . How Weather Events Modify Amazonian Surface Aerosol Particle Size Distributions. In: <https://doi.org/10.5194/egusphere-egu21-11283>, 2021, Vienna (online event). European Geophysical Union. Vienna: EGU, 2021.
14. **FRANCO, M. A.**, Ditas, F., Machado, L. A. T., Krempfer, L. A., Rizzo, L. V., , et al.: Occurrence and growth of ultrafine aerosol particles in the boundary layer after particle production in the upper troposphere over the Amazon Basin. ATTO Workshop (online event), 2021.

APPENDIX B

Article - Occurrence and growth of ultrafine aerosol particles in the boundary layer after particle production in the upper troposphere over the Amazon Basin

Occurrence and growth of sub-50 nm aerosol particles in the Amazonian boundary layer

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Abstract. New particle formation (NPF), referring to the nucleation of molecular clusters and their subsequent growth into the cloud condensation nuclei (CCN) size range, is a globally significant and climate-relevant source of atmospheric aerosols. Classical NPF exhibiting continuous growth from a few nanometers to the Aitken mode around 60-70 nm is widely observed in the planetary boundary layer (PBL) around the world, but not in central Amazonia. Here, classical NPF events are rarely observed in the PBL, but instead, NPF begins in the upper troposphere (UT), followed by downdraft injection of sub-50 nm (CN_{<50}) particles into the PBL and their subsequent growth. Central aspects of our understanding of these processes in the Amazon have remained enigmatic, however. Based on more than six years of aerosol and meteorological data from the Amazon Tall Tower Observatory (ATTO, Feb 2014 to Sep 2020), we analyzed the diurnal and seasonal patterns as well as meteorological conditions during 254 of such Amazonian growth events on 217 event days, which show a sudden occurrence of particles between 10 and 50 nm in the PBL, followed by their growth to CCN sizes. The occurrence of events was significantly higher during the wet season, with 88 % of all events from January to June, than during the dry season, with 12 % from July to December, probably due to differences in the condensation sink (CS), atmospheric aerosol load, and meteorological conditions. Across all events, a median growth rate (GR) of 5.2 nm h⁻¹ and a median CS of 0.0011 s⁻¹ were observed. The growth events were more frequent during the daytime (74 %) and showed higher GR (5.9 nm h⁻¹) compared to nighttime events (4.0 nm h⁻¹), emphasizing the role of photochemistry and PBL evolution in particle growth. About 70 % of the events showed a negative

anomaly of the equivalent potential temperature ($\Delta\theta'_e$) – as a marker for downdrafts – and a low satellite brightness temperature (T_{ir}) – as a marker for deep convective clouds – in good agreement with particle injection from the UT in the course of strong convective activity. About 30 % of the events, however, occurred in the absence of deep convection, partly under clear sky conditions, and with a positive $\Delta\theta'_e$ anomaly. Therefore, these events do not appear to be related to downdraft injection and suggest the existence of other currently unknown sources of the sub-50 nm particles.

1 Introduction

New particle formation (NPF) refers to the nucleation of nanometer-sized molecular clusters from gaseous precursors and their subsequent condensational growth (e.g., Kulmala et al., 2004; Dal Maso, 2005; Kirkby et al., 2011; Kulmala et al., 2012; Kerminen et al., 2018). Under favorable atmospheric conditions, the newly formed particles grow through condensation of semi- and low-volatile gases as well as coagulation into the cloud- and, thus, climate-relevant size range with diameters, D , larger than ~ 80 nm (Kerminen et al., 2018; Pöhlker et al., 2018). NPF has been observed worldwide in the course of ground-based observations in different environments, such as rural and remote continental areas, urban environments, the Arctic and Antarctica, marine areas, and mountain sites (Kerminen et al., 2018, and references therein). Its wide and frequent occurrence makes NPF a major source of aerosol particle number concentrations and cloud condensation nuclei (CCN) worldwide (e.g., Merikanto et al., 2009; Spracklen et al., 2008; Nieminen et al., 2018; Yli-Juuti et al., 2020).

In the long list of locations where NPF has been detected in the planetary boundary layer (PBL) (Kerminen et al., 2018), the Amazon rain forest is a remarkable exception since the characteristic ‘banana plots’ – starting at few nanometers and growing up to the Aitken-accumulation mode (see definitions in Kulmala et al., 2012; Kerminen et al., 2018) – have rarely been observed (e.g., Andreae, 2013; Rizzo et al., 2018; Wimmer et al., 2018). In particular, Rizzo et al. (2018) discussed the occurrence of sub-50 nm particle growth events (‘Amazonian banana plots’), which resemble the behavior of ‘classical NPF’, but starting at much larger initial diameters (> 20 nm). These ‘Amazonian banana plots’ were observed in 3 % of the 749 days and were associated mainly with convective downdrafts. It is worth noting that the detection of growth events depends on the methodology used. However, it is clear that in Amazonia these characteristic events are less frequent.

This striking contrast to other environments has inspired researchers to investigate the underlying mechanisms that could explain the absence of NPF as well as alternative particle sources that sustain the Amazonian aerosol population. Reasons for the absence of NPF in the PBL could be:

1. A suppression by isoprene (e.g., Kiendler-Scharr et al., 2009; Kanawade et al., 2011; McFiggans et al., 2019; Yli-Juuti et al., 2020), which is the most abundant volatile organic compound (VOC) in the Amazonian atmosphere (e.g., Andreae et al., 2018; Yáñez-Serrano et al., 2020).
2. The very low concentrations of inorganic precursor gases such as sulfur dioxide (SO_2 , being converted into sulfuric acid H_2SO_4) as well as the bases ammonia (NH_3) and amines (NR_3) (Andreae et al., 1990; Trebs et al., 2004), which play key roles in the binary H_2SO_4 – H_2O and ternary NH_3 – H_2SO_4 – H_2O nucleation mechanisms (Kirkby et al., 2011).

3. The high levels of relative humidity (RH), which have been associated with a low occurrence of NPF (e.g., Bonn and Moortgat, 2003; Hamed et al., 2011; Hyvönen et al., 2005).

Figure 1. Conceptual scheme of sources, redistribution, and removal of aerosol particles and cloud condensation nuclei (CCN) over the Amazon. The scheme is inspired by previous conceptual illustrations by Krejci et al. (2003), Andreae et al. (2018), and Williamson et al. (2019). It further integrates experimental data by Wang et al. (2016), Krejci et al. (2003), Andreae et al. (2018), Baars et al. (2012); Williamson et al. (2019); Lauer et al. (2021). The study by Williamson et al. (2019) investigated the particle formation in the marine atmosphere but has been included here due to the mechanistic analogy. The three main categories of aerosol sources in the Amazon are shown in red. Emphasized are the aerosol cycling in the course of deep convective clouds with upward transport of volatile organic compounds (VOC) and aerosol particles, new particle formation in the free troposphere, downward transport with initial particle growth, and eventually downward injection of sub-50 nm particles in the clouds.

The occurrence of NPF is strongly dependent on the local conditions of individual sites, including meteorology, biogenic emissions, and air pollution levels. Nieminen et al. (2018) emphasized that the NPF occurrence and growth rates (GR) show a geographically inhomogeneous distribution, indicating that the underlying mechanisms are as manifold as complex. Typical atmospheric GR ranges from 1 to 12 nm h⁻¹ (Yli-Juuti et al., 2020). Further, different meteorological conditions have been associated with the occurrence of NPF and particle growth. Specifically, photochemical reactions under daytime conditions have been regarded as a driving force for both, nucleation and condensational growth (e.g., Nieminen et al., 2018; Kerminen et al., 2018; Hamed et al., 2011; Ma and Birmili, 2015). This is in line with a significantly higher occurrence of NPF under

clear sky conditions, as observed for instance in Hyytiälä, Finland (Dada et al., 2017). In addition, an association between the occurrence of NPF and convective clouds has been observed at different marine to continental sites (e.g., Perry and Hobbs, 1994; Clarke, 1992; Waddicor et al., 2012; De Reus et al., 2001; Wehner et al., 2015). Evidence of this phenomenon in the Amazon has also been reported by Andreae et al. (2018). While different potential explanations have emerged, the exact mechanisms, precursors, and the spatial distribution in the context of clouds have remained unknown (Kerminen et al., 2018).

NPF has likely been altered as a result of industrialization, when anthropogenic emissions started to influence the atmospheric composition of trace species. Relative to remote sites, rural and urban locations tend to show higher NPF frequencies (typically 10 – 30 % event days) and higher particle GR ($4 - 12 \text{ nm h}^{-1}$) (Kerminen et al., 2018; Nieminen et al., 2018). This relates to the fundamental question whether atmospheric concentration of certain, mainly anthropogenically derived, species such as H_2SO_4 , have to exceed certain thresholds for NPF to occur. Recent evidence of pure biogenic ion-induced nucleation under controlled laboratory conditions offers mechanisms for pre-industrial pathways of NPF (Kirkby et al., 2016; Rose et al., 2018; Zhao et al., 2020). Accordingly, environments with low anthropogenic influence are of particular interest to investigate processes under conditions that approximate a pre-industrial state of the atmosphere. Amazonia is an ideal outdoor laboratory for such investigations under pristine conditions (Hamilton et al., 2014; Pöhlker et al., 2018). Of particular relevance is the wet season with its episodic occurrence of pristine periods, which allows studying atmospheric processes - such as the occurrence of sub-50 nm particles ($\text{CN}_{<50}$) - under conditions that approximate a pre-industrial state of the rain forest atmosphere (Andreae et al., 2015). At the Amazon Tall Tower Observatory (ATTO) – which is located in mostly untouched rain forest regions and has become a landmark site for atmospheric research (Andreae et al., 2015; Pöhlker et al., 2019) – March to May represent the cleanest months of the year with about 10 % of the time being considered as pristine periods (Pöhlker et al., 2018).

Figure 1 illustrates the main sources of aerosol particles and CCN in Amazonia, which can be broadly grouped into the following three categories:

1. A spectrum of biogenic emissions from the rain forest ecosystem, including the release of primary biological aerosol particles (i.e., pollen, spores, bacteria, fragments) (e.g., Pöhlker et al., 2012; Huffman et al., 2012; Löbs et al., 2020; Prass et al., 2021) as well as the emission of biogenic VOCs followed by their atmospheric oxidation and conversion into secondary organic aerosols (SOA) (e.g., Chen et al., 2015; Liu et al., 2016; Saturno et al., 2018a; Leppla et al., 2021).
2. Long-range transport of transatlantically advected African dust and pollution (e.g., Pöhlker et al., 2018; Nascimento et al., 2021; Moran-Zuloaga et al., 2018; Holanda et al., 2020) as well as regional biomass burning smoke (Artaxo et al., 2013).
3. Driven by deep convective clouds, biogenic VOCs are transported into the upper troposphere ($\sim 10 \text{ km}$) where VOC oxidation, nucleation of new aerosol particles, and initial particle growth occurs, which is fostered by low temperatures and a low preexisting aerosol surface area (Krejci et al., 2003; Andreae et al., 2018). Subsequently, the freshly formed particles are mixed downward into the PBL, where they continue to grow to CCN-relevant sizes (e.g., Krejci et al., 2003; Wang et al., 2016).

Several studies provide experimental and modeling support for the broad atmospheric relevance of UT particle production and the subsequent vertical mixing of the $CN_{<50}$ (e.g., Krejci, 2003; Krejci et al., 2005; Wang et al., 2016; Andreae et al., 2018; Williamson et al., 2019; Leino et al., 2019; Zhao et al., 2020; Rizzo et al., 2018; Toledo Machado et al., 2021). Figure 1 shows the presence of a $CN_{<50}$ pool in the Amazonian UT during the wet and dry seasons as well as an increase in D with decreasing altitude due to condensational particle growth. The downward motion of the $CN_{<50}$ can be driven by strong convective downdrafts or weaker downward motions in stratiform cloud regions (Wang et al., 2016). Zhao et al. (2020) recently suggested that pure organic NPF based on biogenic VOCs dominates above 13 km, whereas ternary NPF involving organics and H_2SO_4 dominate between 8 and 13 km. In addition, an increase of sub-50 nm particles was observed, in particular in the early morning hours, suggesting a connection between these increased concentrations with vertical transport and deep convective clouds, as well as with lightning density. Major mechanistic questions regarding the vertical transport of the $CN_{<50}$ remain open (e.g., Toledo Machado et al., 2021), however.

This study aims to identify and characterize the occurrence of particle growth events in the size range from 10 to 50 nm in the PBL of Central Amazonia. Based on long-term observations, including complementary in-situ aerosol and meteorological measurements and satellite data, this work provides a robust 6-year data set to characterize Amazonian particle growth events ('Amazonian banana plots') and to give new insight into the occurrence and potential sources of sub-50 nm particles and related weather conditions. The knowledge obtained here about the sub-50 nm particle growth events addresses an important gap in our understanding of the Amazonian aerosol life cycle and will help to constrain the CCN sources and properties in this globally important ecosystem.

2 Measurements and data analysis

2.1 The Amazon Tall Tower Observatory (ATTO) site

The Amazon Tall Tower Observatory (ATTO) is located 150 km northeast of Manaus, Brazil, in a forest reserve. Detailed descriptions of the site, its location, instrumentation, and scientific missions can be found elsewhere (Andreae et al., 2015; Pöhlker et al., 2019). At the ATTO site, the first aerosol measurements were initiated in 2011 (e.g., Pöhlker et al., 2012; Saturno et al., 2018b). Since 2014, multiple continuous measurements of physical and chemical particle properties have been established and gradually extended (e.g., Pöhlker et al., 2016, 2018; Holanda et al., 2020; Saturno et al., 2018a; Schrod et al., 2020).

2.2 Terminology

According to Pöhlker et al. (2016) we define the Amazonian seasons as follows: the wet season is spanning from February to May, followed by the wet to dry transition period (WtoD) including June and July. The dry season is spanning from August to November, followed by the dry to wet transition period (DtoW) including December and January. For the Amazonian sub-micron particle population, which is characterized by a multi-modal size distribution, we use the widely established terms

Aitken mode (50 – 100 nm) and accumulation mode (100 – 1000 nm) (Pöhlker et al., 2016; Toledo Machado et al., 2021). In addition, we introduce the term sub-50 nm mode, defined as particles between 10 and 50 nm. We avoid using the term nucleation mode for this particle population as this term is typically defined as particles < 25 nm and refers to aerosol population relatively soon after nucleation (Kulmala et al., 2012; Nieminen et al., 2018). The sub-50 nm particles analyzed here, however, have experienced initial aging and growth to diameters between 10 and 50 nm already. As a short version, we use $CN_{<50}$ to refer to the particle fraction in the sub-50 nm mode. For the particle number concentrations of the individual modes, we use the symbols $N_{<50}$, N_{Ait} , and N_{acc} . N_{CN} is defined as the median total particle number concentration.

2.3 Aerosol measurements

This study focuses on particle number size distributions (PNSDs) obtained from a Scanning Mobility Particle Sizer (TSI Inc., Shoreview, USA; classifiers: first model 3080, later 3082; DMA: 3081; condensation particle counter: CPC 3772) sampling from the 60 m inlet at the 80 m high so-called triangular mast (02° 08.602'S, 59° 00.033'W; 130 m a.s.l.) at the ATTO site. The inlet height was chosen to be approximately 30 m above the average canopy height, which enables measurements close to the canopy without direct contact with the largest trees. The SMPS is located in an air-conditioned laboratory container at the foot of the mast. Sample air is transported through a 25 mm stainless steel tube (finetron tubes, Dockweiler AG, Neustadt-Glewe, Germany) and dried to relative humidity (RH) below 40 %. An automatic regenerating silica gel adsorption aerosol dryer, as described in Tuch et al. (2009) was installed upstream of the instruments in 2014 and was replaced by a custom-built and automated condensation aerosol dryer in March 2020. For more detailed information on the aerosol measurements setup, see Andreae et al. (2015).

The SMPS measurements cover a particle size range from 10 to 400 nm and yield a temporal resolution of 5 min. The PNSD data covers almost six years, from February 2014 to September 2020, covering 1 596 measurement days, and comprise 426 272 sample runs in total. The data coverage of ~67 % over the entire time frame (i.e., Feb 2014 to Sep 2020) can be considered as a robust data foundation and statistical basis for the observations and conclusion presented here.

The sizing accuracy of the SMPS was frequently checked with monodisperse polystyrene latex particles. Additionally, the data quality was continuously verified by complementary measurements with a Condensation Particle Counter (CPC, model 5412, Grimm Aerosol Technik, Ainring, Germany) measuring the total particle number concentration (N_{CN}) > 4 nm. All particle data were visually inspected for malfunction and contamination and further corrected for standard temperature and pressure (STP, 273.15 K, 1013.25 hPa) as well as inlet transmission efficiency according to Moran-Zuloaga et al. (2018). PNSD data was used for the analysis if N_{CN} from SMPS and CPC agreed within 15 %.

$CN_{<50}$ are particularly prone to diffusion losses at surfaces (e.g., the tube surfaces of the inlet lines) (von der Weiden et al., 2009). Accordingly, the generally sparse occurrence of $CN_{<50}$ in the Amazon frequently raises questions about whether these results are (systematically) biased by unaccounted diffusion losses (e.g., in the 60 m long inlets). The observations outlined below suggest the absence of large and unaccounted-for particle losses in the size range that is particularly relevant here (i.e., 10 to 100 nm) and further indicate that the observed PNSDs correctly reflect the actual atmospheric aerosol distribution:

- The inlet and particle transport is optimized for high particle transmission efficiency and short residence time of the sample air. According to the particle loss calculator provided by [von der Weiden et al. \(2009\)](#) and corresponding sensitivity tests, the 50 % transmission efficiency of the inlet at the lower end of the PNSD is reached at $D_{50\%} \approx 8$ nm. All PNSDs in this study have been corrected for diffusional, sedimentation, and inertial losses according to [von der Weiden et al. \(2009\)](#).
- Experiments with the SMPS running at the 60 m inlet line and a separate and mobile CPC running without inlet lines at the height of 60 m directly on the tower agreed well, which underlines that no significant fractions of $CN_{<50}$ were lost in the inlet lines.
- Finally, the PNSDs with the sparse particle occurrence < 20 nm reported here agree well with results in previous studies (e.g., [Gunthe et al., 2009](#); [Rizzo et al., 2018](#)).

2.4 Multi-modal log-normal fitting of PNSDs

Each measured PNSD was fitted by a multi-modal log-normal distribution function, according to [Heintzenberg \(1994\)](#):

$$f(D_p, D_i, N_i, \sigma_i) = \sum_{i=1}^n \frac{N_i}{\sqrt{2\pi} \ln(\sigma_i)} \exp \left\{ -\frac{[\ln(D_p) - \ln(D_i)]^2}{2 \ln^2(\sigma_i)} \right\}, \quad (1)$$

where D_p is the particle diameter, n is the number of aerosol size modes to be fitted (with $n \leq 3$, see Sec. 2.2). Each mode is characterized by 3 main parameters: the mode number concentration, N_i , the mode geometric median diameter D_i , and the mode geometric standard deviation σ_i . A script was developed – similarly to the procedure in [Hussein et al. \(2005\)](#) – to provide an automatic user-free decision algorithm to obtain the size modes according to the following steps:

1. The diameter with the highest particle number concentration was used as the start parameter for the mean diameter of the dominant mode, D_{dom} . The least-squares fit of D_{dom} was constrained within the range of -30% and $+20\%$ of the start parameter.
2. For $D_{\text{dom}} \geq 100$ nm – corresponding to the accumulation mode being dominant – the mode with the second highest concentration was searched in the size ranges of the sub-50 nm mode, $D_{<50} \in [9, 50)$, and Aitken mode, $D_{\text{Ait}} \in [50, 100)$. For $D_{\text{dom}} < 100$ nm – corresponding to either the sub-50 nm or Aitken mode being dominant – the mode with the second highest concentration was searched in the size range of the accumulation mode ($D_{\text{Acc}} \in [100, 300]$). For the second and (if present) the third mode, the same fitting routine as for the first (dominant) mode was applied.
3. The geometric standard (σ_i) deviation of all modes was constrained within the range of 1.1 to 1.55, which was optimized for the ATTO conditions.
4. Subsequently, a joint optimization of the previously obtained fit parameters (D_i , σ_i , and N_i) for the modes was conducted. The procedure is developed by fixing two of the modes and leaving the third free so that its parameters are again optimized by minimization using the least-squares method. The optimization order in this process was to optimize the

sub-50 nm mode, then the accumulation mode, and, finally, the Aitken mode. In this case, all the free diameters of the modes could vary between $0.5D_i$ and $1.5D_i$. As a measure of fitting quality, the algorithm compares the integrated particle number concentrations calculated from the measured size distribution and from the fitted curve and obtains the R^2 value for each measure. Examples of fits can be seen in Figure S1.

- 5 5. Comparisons between the integrated particle number concentration of SMPS measurements ($N_{\text{conc, SMPS}}$) and log-normal fitted size distributions ($N_{\text{conc, } \sum \text{n-modes}}$) were made to assure the quality of the fits. We considered only fits in which the agreement of $N_{\text{conc, SMPS}}$ and $N_{\text{conc, } \sum \text{n-modes}}$ returned $R^2 > 0.8$, which means that about 97% of the data are covered by the developed mode fitting. Within this data set, on average, fits with $R^2 = 0.97$ were obtained, which yielded a linear fit of $N_{\text{conc, SMPS}}$ and $N_{\text{conc, } \sum \text{n-modes}}$ with $R^2 = 0.997$ (Figure S2).

10 2.5 Identification of particle growth events

We analyzed the occurrence and properties of *particle growth events* ('Amazonian bananas plots') in the sub-50 nm, and Aitken mode size range. Characteristic examples of such growth events are shown and discussed in Sect. 3. The growth event identification is based on the following main steps:

- 15 1. All data were smoothed to eliminate single exceptionally high or low values to avoid possible bias due to short intense particle peaks or dips. Accordingly, a two-dimensional smoothing algorithm (moving average with moving windows of 25 minutes for time and 20 nm size for particle diameter) was applied.
2. All PNSD data were divided into 24 h subsets.
3. Particle growth event days were then automatically flagged based on the guidelines in Kulmala et al. (2012). These guidelines were slightly modified by increasing the size threshold for the initial growth event identification from 20 nm
 20 to 40 nm to account for the characteristics of the Amazonian banana plots and PNSDs.
4. Further following Kulmala et al. (2012), the total particle number concentration of particle diameters > 40 nm was then subtracted from the total particle number concentration of particle diameters $10 \leq D_p \leq 40$ nm. Positive values in the PNSDs are marked as regions of interest for the occurrence of $\text{CN}_{<50}$ that could result in particle growth events. Days fulfilling these criteria are flagged as *particle growth event days*.
- 25 5. This method is sensitive to the integral particle number concentration in the Aitken and accumulation modes, and their seasonal variation, which might result in false positive or false negative event flagging. To account for that, the results from the automated identification routine were visually inspected and potentially misinterpreted events were excluded from the analysis. The inspection followed the procedure described in Dal Maso (2005), in which a particle growth event is characterized by i) the appearance of a distinct new mode of particles in the PNSD, ii) the particle size is inside the
 30 sub-50 nm mode, iii) the mode prevails for more than one hour, and iv) it shows signs of growth in time.

2.6 Growth rate and condensation sink

The growth rate (GR) and condensation sink (CS) – both important physical parameters in the characterization of growth events – were calculated following the procedures of Dal Maso (2005) and Kulmala et al. (2012). The GR is defined as the rate at which the mean geometric diameter D_p of the $CN_{<50}$ population changes linearly with time:

$$GR = \frac{dD_p}{dt} = \frac{\Delta D_p}{\Delta t} = \frac{D_{p2} - D_{p1}}{t_2 - t_1} [nm \ h^{-1}], \quad (2)$$

where D_{p1} is the geometric diameter of the sub-50 nm mode obtained by the multi-modal fit at the beginning of the growth event at time t_1 and D_{p2} is the geometric diameter at the end of the growth event at time t_2 . Thereby, the *beginning* of a growth event is defined as the moment at which D_p starts to increase. The *end* of a growth event is reached when either (i) D_p (10 – 50 nm) stops to grow, or (ii) the growth is interrupted due to sudden changes in air masses, or (iii) D_p reaches the Aitken mode – in this case, we selected D_2 as the last observed growth D_p inside the sub-50 nm mode. There were a few events in which the growth stopped for a while and, afterward, restarted again. In these cases, we considered the second growth as a new growth event. The growth events considered in this study have a duration of at least one hour.

A moving average smoothing filter was applied at the mean geometric diameter interval $D_{p1} \leq D_p \leq D_{p2}$ and the fit was obtained by applying a linear model fit at the referred diameter interval. The model returned the following parameters: R^2 , p-value, and GR. To assure the data quality during the analyses, we selected $R^2 > 0.6$ and p-value < 0.05 .

The CS was calculated from the particle number concentration as (Dal Maso et al., 2002):

$$CS = 2\pi D \int_{D_{p,min}}^{D_{p,max}} D'_p \beta_m(D'_p) n(D'_p) dD'_p = 2\pi D \sum_{D'_p} \beta_m(D'_{p,i}) D'_{p,i} N_i [s^{-1}] \quad (3)$$

where N_i is the particle concentration at the diameter $D'_{p,i}$ of the i -esm size bin; D is the diffusion coefficient of the precursor condensable vapor, and β_m is the transition-regime correction (Fuchs and Sutugin (1971)), defined as:

$$\beta_m = \frac{1 + K_n}{1 + 1.677K_n + 1.333K_n^2} \quad (4)$$

which depends on the dimensionless Knudsen number, $Kn = 2\lambda/D_p$. The Kn parameter represents the ratio of two length scales, where λ is the effective mean free path of the vapor molecules in the gas (Dal Maso et al., 2002).

Physically, CS is a parameter that quantifies the ability of particles to remove condensable vapors from the atmosphere, incorporating them into the particle population and directly influencing the particle growth process. In this study, CS was calculated assuming $D = 0.117 \text{ cm}^2 \text{ s}^{-1}$, i.e., the value for sulfuric acid (H_2SO_4) (Gong et al., 2008), which is commonly used in the literature, allowing comparisons to other studies. We used the term CS_{growth} as the average CS during the growth particle event.

2.7 Meteorological parameters measurements

The meteorological parameters air temperature (T), incoming shortwave radiation (SW), rainfall (P_{ATTO}), air pressure (p), and relative humidity (RH) were measured at an 80 m high tower (02° 08.647'S, 59° 59.992'W; 130 m a.s.l.) located approximately

100 m from the ATTO aerosol mast. The measurements performed at the 80 m tower ranged from 2013 to 2018. Specifically, SW and P_{ATTO} were measured at the top of the tower, whereas T , p , and RH were measured at 55 m, 55 m, and 81 m, respectively. From January 2019 to September 2020, the meteorological parameters air temperature (T), rainfall (P_{ATTO}), air pressure (p), and relative humidity (RH) were measured at the 321 m ATTO Tall Tower with a compact weather station (Lufft, WS600-LMB, G. Lufft Mess- und Regeltechnik GmbH, Fellbach, Germany). Overall, meteorological parameters span the time frame from May 2013 to September 2020. Furthermore, an optical fog sensor (OFS, Eigenbrodt GmbH, Königsmoor, Germany) measured the near-field visibility since October 2015 at the height of 50 m. Fog occurrence is defined as visibility below 5000 m, which represents a threshold for light fog. Detailed information on the meteorological instruments can be found in [Andreae et al. \(2015\)](#).

2.8 Equivalent potential temperature

Variations of the equivalent potential temperature, θ_e , have been used as a proxy to indicate downdraft occurrences ([Machado et al., 2002](#); [Betts et al., 2002](#); [Rizzo et al., 2018](#); [Wang et al., 2016](#); [Gerken et al., 2016](#)). θ_e quantifies the temperature of an air parcel, when lifted to a certain height where it condenses (characterized by its lift temperature, T_L), releasing the latent heat, and lowered adiabatically to 1000 hPa. In this study, θ_e was calculated with meteorological parameters measured in-situ and was analyzed similarly to [Wang et al. \(2016\)](#) and [Rizzo et al. \(2018\)](#), using the definition described in [Bolton \(1980\)](#) as:

$$\theta_e = T_k \left(\frac{1000}{p} \right)^{0.2854(1-2.8 \times 10^{-4}r)} \exp \left[\left(\frac{3.376}{T_L} - 0.00254 \right) r (1 + 8.1 \times 10^{-4}r) \right] [K], \quad (5)$$

$$T_L = \frac{1}{\frac{1}{T_k - 55} - \frac{\ln\left(\frac{RH}{100}\right)}{2840}} [K], \quad (6)$$

where T_k is the ambient temperature in Kelvin, p and r are the ambient pressure (hPa), and the water mixing ratio (g/kg), respectively, and T_L is the lifting condensation level temperature in Kelvin. To obtain the variations in θ_e , it was necessary to subtract seasonality and diurnal variations.

The steps of this process are illustrated in Figure S3 and are described as follows: θ'_e was obtained by subtracting the mean seasonal trend values, in which we considered both wet and dry seasons, for each year of the time series. Then, the calculated mean diurnal cycle of θ'_e was subtracted from θ'_e , at the same time of the day, resulting in a new time series: $\Delta\theta'_e$. The quantity $\Delta\theta'_e$ is the anomaly in θ_e , and represents the deviation of θ_e from its expected value for that time of the day and season. Values of $\Delta\theta'_e < 0$ are a proxy to the occurrence of downdrafts and indicate a decrease in θ_e due to air masses from the free troposphere that enter the PBL, typically related to the occurrence of rain [Wang et al. \(2016\)](#); [Rizzo et al. \(2018\)](#). Other processes may also be related to a decrease in θ_e , such as evaporation of rainfall, river breeze, and advection mechanisms.

2.9 GOES-16 cloud brightness temperature

This study uses infra-red brightness temperature (T_{ir}) data obtained by the Geostationary Operational Environmental Satellite (GOES), GOES-16, from November 2017 to April 2020. This data set comprises a total of 914 days with measurements every 10 min, as an indication of the troposphere's meteorological conditions. The Advance Baseline Imager (ABI) – a state-of-the-art 16-band radiometer on board GOES-16 – was employed in this study, specifically, Band 13, the infrared window at $10.3\mu m$. These measurements are less sensitive than other infrared bands to gas absorption, which allows estimating the cloud-top brightness temperature. An area of 3×3 pixels centered at ATTO was selected for obtaining the time series of T_{ir} , representing around $6.0\times 6.0\text{ km}^2$. Meteorological conditions related to shallow clouds/clear sky are described by a warm T_{ir} and deep convection conditions by a cold T_{ir} . Here, we considered $T_{ir} > 280\text{K}$ as a nearly clear sky condition, $245 \leq T_{ir} < 280\text{K}$ corresponding to shallow clouds and cumuliform clouds, and $T_{ir} < 245\text{K}$ to all convective clouds associated with deep convection (Machado and Rossow, 1993; Machado et al., 2002). T_{ir} in nearly clear sky conditions corresponds roughly to the temperature in the PBL.

3 Results and discussion

3.1 Particle number size distributions for wet and dry season

In agreement with previous studies, our long-term PNSD measurements showed the distinct characteristics of the Amazonian wet and dry season aerosol populations (e.g., Roberts et al., 2001; Gunthe et al., 2009; Artaxo et al., 2013; Pöhlker et al., 2016; Rizzo et al., 2018). We chose a different representation of the typical PNSD shapes in Figure 2 by showing them as frequency distributions (FDs). The PNSDs differ significantly between both seasons: during the wet season, clear Aitken and accumulation modes stand out, separated by a distinct Hoppel minimum (Hoppel et al., 1986). The Aitken mode is centered at 71 nm, the Hoppel minimum is centered at 102 nm and the accumulation mode is centered at 153 nm. In contrast, Figure 2b shows the typical dry season PNSDs characterized by a strong mono-modal shape with a dominating accumulation mode, reflecting the prevalence of biomass burning pollution (e.g., Rissler et al., 2006; Brito et al., 2014). The accumulation mode is centered at 146 nm. In addition, the overall distribution shape in Figure 2b reveals a contribution of the Aitken mode, centered at 68 nm and visible as a small shoulder on the dominant accumulation mode.

In terms of the abundance of $\text{CN}_{<50}$, the FDs in Figure 2 reveal that aerosols in this size range are rather sparse - though not absent - during both seasons. The occurrence of $\text{CN}_{<50}$ in central Amazonia along with the absence of 'classical' NPF, as it is detected, e.g., in the Scandinavian boreal forests and shown in e.g., Kulmala et al. (2004); Heintzenberg et al. (2017); Kerminen et al. (2018); Dall'Osto et al. (2018), is well documented in the literature (e.g., Roberts et al., 2001; Pöhlker et al., 2016; Rizzo et al., 2018). Although occurring sparsely, the episodic presence of $\text{CN}_{<50}$ causes a distinct mode below about 50 nm, noticeable in the wet season FDs in Figure 2a. However, the $\text{CN}_{<50}$ do not clearly show up in the corresponding mean and median PNSDs. It is further worth noting that the PNSDs under the *remote* rain forest conditions at ATTO as shown here differ significantly from PNSDs that were obtained in the rain forest atmosphere with an influence of the urban emission plume

Figure 2. Frequency distribution (FDs) of particle number size distributions (PNSDs) for the Amazonian wet (a) and dry season (b). Data basis comprises 6.5 years of SMPS data from Feb 2014 to Sep 2020. Color code denotes the number of observations. Solid lines represent the median and dashed lines the mean PNSDs. Please note the different y-axes. The wet season PNSDs show pronounced Aitken and accumulation modes. An overwhelming accumulation mode dominates the dry season PNSDs. The wet and dry season FDs of PNSDs emphasize a comparatively sparse occurrence of $CN_{<50}$, which form a weak, though characteristic, mode below 50 nm.

from Manaus (e.g., Cirino et al., 2018; Fan et al., 2018; Wimmer et al., 2018; Glicker et al., 2019). These urban-influenced PNSDs are characterized by strongly enhanced particle concentrations below about 20 nm. As the mean and median PNSDs do not sufficiently reflect the abundance and properties of $CN_{<50}$ in Figure 2, the following paragraphs summarize the in-depth analysis that allowed us to extract their event characteristics, seasonal and diurnal variability, and their estimated significance.

5 3.2 Particle growth events characterization

The abundance of $CN_{<50}$, which show up as a weak, though noticeable, mode during the wet season (see the overall outline in Figure 2a), results from the episodic occurrence of $CN_{<50}$ events and their subsequent growth. Figure 3 shows a typical example of an 'Amazonian banana plot' representing two growth events, as often observed at ATTO. The first example in Figure 3 starts in the morning hours around 08:30 local time (LT) with an average initial diameter slightly larger than 30 nm. The particles grow for about four hours reaching the Aitken mode size range up to ~ 60 nm. On the same day, a secondary growth event starts around noon with an average initial growth diameter slightly larger than 20 nm, growing during the afternoon hours. The initial diameters at the onset of the growth events in Figure 3 are well above the lower size limit of the SMPS (i.e., 10 nm), which implies that the event characterization is not distorted or limited by the effectively measured size range.

The growth events shown here resemble the events reported by Wang et al. (2016). Note that for all previous studies in Amazonia, the growth events were observed during the wet season, indicating that this event type is a typical wet season phenomenon associated with precipitation (Zhou, 2002; Wimmer et al., 2018; Rizzo et al., 2018). The procedure described in

Figure 3. A characteristic example of a $CN_{<50}$ growth event at ATTO on 19 February 2018. The temporal evolution of the particle number size distribution (PNSD) is shown as a heat map, emphasizing the pronounced Aitken mode as well as a particle growth events from the sub-50 nm particle to the Aitken mode during daylight.

Sec. 2.5 returned 254 characteristic particle growth events on 217 days of the 1596 measured days, corresponding to a frequency of occurrence of $\sim 14\%$ of event days. For the entire measurement period (Apr 2014 – Sep 2020) this further corresponds to about 30 event days per year. The events have a clear seasonality, with more cases in the wet season, corresponding to $\sim 88\%$ of events from January to June, while in the dry season from July to December, only $\sim 12\%$ were observed. Additional aspects of seasonality are discussed in Sec. 3.3.

The GR frequency distribution in Figure 4a shows a clear peak centered around the median of 5.2 nm h^{-1} . The median GR of this study agrees well with the median GR of 5.5 nm h^{-1} obtained by Rizzo et al. (2018). Figure S4a contrasts median GR obtained at different sites in Amazonia and worldwide and shows that the median GR of this study is within the GR ranges obtained at remote boreal (0.5 to 5.3 nm h^{-1}) or polar sites (0.2 to 5.5 nm h^{-1}). The CS_{growth} frequency distribution in Figure 4b shows a clear peak centered around the median of 0.0011 s^{-1} . In contrast, the median CS calculated for the entire observation days is 0.0032 s^{-1} , which corroborates that particle growth events at remote sites are expected when CS values are low (Figure 6d). The Amazonian CS also agrees with what is observed in other remote regions (Figure S4 b). For example, boreal sites have average CS ranging from 0.00098 to 0.0039 s^{-1} (Kerminen et al., 2018).

Figure 5a shows the FD of PNSDs exclusively for the periods of growth events, starting 3 hours before the event's onset and lasting until the time when growth stopped being observed (according to Sec. 2.6). Figure 5b shows the separated $CN_{<50}$, Aitken and accumulation modes for the median SD of Figure 5a. The characteristic multi-modal shape of the wet season PNSDs stands out. The FD for the growth events further underlines the sparse particle abundance below 20 nm. Figure 5b shows that

Figure 4. Histograms showing the frequency distribution of the growth rate, GR, (a) and condensation sink during the growth events, CS_{growth} , (b) for all observed 254 particle growth events.

the Aitken and accumulation modes are the dominant modes of the median PNSD. The $CN_{<50}$ mode, although small and not readily perceptible from the median PNSD, has a significant contribution, however, and is centered at $D_{CN_{<50}} = 37 \text{ nm}$ (mean), with $\sigma_{CN_{<50}} = 1.5$. For comparison, the diameters selected as the initial values for the growth events, $D_{p,i}$, have a median value of 26.1 nm, with 25th and 75th percentiles of 19.0 and 33 nm, respectively. The Aitken mode is centered at $D_{AIT} = 67 \text{ nm}$ (mean), with $\sigma_{AIT} = 1.4$, and the accumulation mode is centered at $D_{ACC} = 170 \text{ nm}$ (mean), with $\sigma_{ACC} = 1.4$. This clearly shows that the initial diameter of growth events in the Amazon is typically larger than reported in other regions (Nieminen et al. (2018)).

3.3 Seasonality

The pronounced atmospheric seasonality in central Amazonia has been characterized by means of meteorological, aerosol, and cloud microphysical data in previous studies (e.g., Pöhlker et al., 2018, 2019; Moran-Zuloaga et al., 2018; Saturno et al., 2018a). Figure 6a shows the typical seasonality of P_{ATTO} . The highest rain rate occurs during the wet season, with P_{ATTO} peaking in March and April, while the minimum in P_{ATTO} occurs between July to September. A similarly pronounced seasonality can be found in various aerosol properties. The N_{CN} in the size range between 10 to 400 nm had its minimum in the wet season months March and April with a median of $\sim 280 \text{ cm}^{-3}$ and its maximum in the dry season months August to November with a median of $\sim 1400 \text{ cm}^{-3}$ (Fig. 6c).

The same pattern can be found in the monthly median CS in Figure 6d. The strong seasonal differences in the physical aerosol properties - here manifested in a wide range of N_{CN} and different PNSD shapes - have a substantial influence on the

Figure 5. a) Frequency distribution of particle number size distributions exclusively for growth event periods. Color code denotes the number of observations, solid lines indicate the median and dashed lines the 75th and 90th percentiles. The PNSDs for the growth events show a high frequency of $CN_{<50}$ and Aitken size modes. The FDs do not show any evidence of *open* PNSDs towards the lower detection limit. b) Median PNSD (black line) of the 254 observed particle growth events, showing its 3 log-normal modes: in green, the sub-50 nm size particle mode; in red, the Aitken mode; in blue, the accumulation mode; and in black, the total distribution. The adjusted R^2 obtained for the calculated multi-modal log-normal fit is 0.99.

concentration of available cloud condensation nuclei (CCN) and, thus, cloud micro-physical processes in the Amazon Basin (Pöhlker et al., 2016, 2018; Lauer et al., 2021). These results agree well with long-term measurements at another central Amazonian site (i.e., ZF2 site) presented by Rizzo et al. (2018) and allow to put earlier campaign-wise measurements into a broader data context (e.g., Roberts et al., 2001; Roberts, 2003; Zhou, 2002; Rissler et al., 2004, 2006; Martin et al., 2010).

- 5 Figure 6e shows the seasonal pattern in the $CN_{<50}$ growth event frequency. We found the highest frequencies during the wet season, peaking in April with about 26 %, and dropping down during the transition period (WtoD, Jun and Jul) to a minimum with almost zero events in August. The growth event occurrence stayed remarkably low during the dry season months with frequencies mostly below 3 % from July to November. Frequency levels increase again during the transition period (DtoW, Dec and Jan). The seasonality in growth event occurrence corresponds well with the seasonality in monthly rainfall and appears
- 10 inversely related to the seasonality in N_{CN} and CS . This agrees with previous studies in the Amazon, suggesting a close link between generally low particle concentrations and the appearance of $CN_{<50}$ and Aitken mode particles in the PBL (e.g., Krejci, 2003; Wang et al., 2016). The low CS might further favor the characteristic growth patterns of these events through the condensation of semi- and low-volatile gaseous compounds on the $CN_{<50}$ particle fraction as available surfaces (see example in Fig. 3a) (Dal Maso, 2005; Dal Maso et al., 2007; Dada et al., 2017; Kerminen et al., 2018; Nieminen et al., 2018; Wiedensohler
- 15 et al., 2019).

The N_{CN} , CS , and growth event occurrence in Figure 6 are all based on the same multi-year SMPS data set. The underlying data availability is documented in Figure 6b as the number of valid measurement days. Table 1 shows the GR and the median

Figure 6. The seasonal cycles of selected meteorological and aerosol parameters presented as monthly averages for the entire observation period from February 2014 to June 2020. From top to bottom: a) P_{ATTO} monthly rain measured at ATTO, where error bars denote the standard deviation. b) SMPS data coverage in the number of measurement days. c) Median total particle number concentration in size range of $10 \text{ nm} < d < 400 \text{ nm}$, calculated from SMPS data, error bars denote the interquartile range (please note the logarithmic scale). d) Median condensation sink for the month calculated from SMPS data, error bars refer to the interquartile range (please note the logarithmic scale). e) Annual cycle of the occurrence of $CN_{<50}$ particle growth events.

CS_{growth} of the growth event for all the months. In the wet season, when $\sim 88\%$ of all growth events occurred, the values of GR fluctuate around the median GR of 5.2 nm h^{-1} . The CS_{growth} shows a similar behavior, fluctuating around 0.0011 s^{-1} . The lowest median GR of the wet season is found in March, with 3.7 nm h^{-1} , while the lowest CS_{growth} of the wet season is found in April, with 0.0008 s^{-1} . The number of particle growth occurrences drops in the dry season, comprising only $\sim 12\%$ of the total

growth events. If December is not included in the dry season, the percentage of dry season growth events decreases to $\sim 6\%$. The CS_{growth} in the dry season indicates that the events occur on days with a cleaner atmosphere compared to the monthly median CS, as they are similar to the CS of the events observed in the wet season. The only exceptions are the events from October, whose median CS_{growth} was 0.0044 s^{-1} .

Table 1. Monthly median, 25th, and 75th percentiles (in brackets, respectively) of GR and CS_{growth} . The percentage of growth events in each month is also presented.

Month	GR [nm h^{-1}]	CS_{growth} [s^{-1}]	Fraction of events (%)	# of events
Jan	5.0 (2.5 - 6.9)	0.0012 (0.0008 - 0.0016)	8.7	22
Feb	5.2 (3.9 - 8.1)	0.0013 (0.0008 - 0.0021)	13.8	35
Mar	3.7 (2.6 - 6.3)	0.0010 (0.0005 - 0.0015)	18.1	46
Apr	5.3 (4.5 - 8.6)	0.0008 (0.0005 - 0.0012)	25.6	65
May	5.5 (4.0 - 8.2)	0.0011 (0.0006 - 0.0019)	16.1	41
Jun	6.1 (4.6 - 9.4)	0.0025 (0.0012 - 0.0030)	5.9	15
Jul	8.2 (6.2 - 8.6)	0.0034 (0.0026 - 0.0038)	1.2	3
Aug	5.2 (5.2 - 5.2)	0.0011 (0.0011 - 0.0011)	0.4	1
Sep	10.4 (3.7 - 18.8)	0.0017 (0.0012 - 0.0019)	1.6	4
Oct	8.8 (4.9 - 13.1)	0.0044 (0.0033 - 0.0052)	2.4	6
Nov	4.2 (4.2 - 4.2)	0.0037 (0.0037 - 0.0037)	0.4	1
Dec	6.2 (4.7 - 8.0)	0.0012 (0.0009 - 0.0015)	5.9	15

- 5 The results show that particle growth events are likely related to CS, in which the higher the median monthly CS the lower the occurrence of growth events. Higher amount of particles aging by coagulation returns higher values of CS, which means a decrease in the lifetime of the precursor vapor in the atmosphere. In the dry season, regional and long-range transport biomass burning plumes are the main source of aerosols in the lower troposphere, which suppresses the smaller ones from the sub-50 nm mode to grow. With the increase in precipitation (thus, in the wet deposition), the number of particles of the
- 10 accumulation mode in the atmosphere decreases significantly. This influences on the decrease of CS, so that the occurrence of growth events increases again, as observed in December (DtoW transition).

3.4 Diurnal trends

- The diurnal patterns of the growth event occurrence are shown in Fig. 7 in relation to meteorological parameters, such as air temperature, SW , P_{ATTO} , RH , and near-field visibility representing fog. Note that we contrasted the diurnal cycles for the
- 15 entire observation period (i.e., Feb 2014 to Sep 2020, shown as solid lines) with the wet season months (i.e., Feb to May, shown as dashed lines). In the diurnal cycles considering the whole period of observations, T and SW show the typical tropical rain forest conditions with about 12 h daylight and a remarkably low amplitude in T spanning on average only 5°C . Rainfall is most intense in the afternoon hours, with the highest precipitation intensity at 15:00 LT, resulting in average annual rainfall of

around 2000 mm. The data also shows a secondary maximum in the early morning, which has been associated with nocturnal long-lived mesoscale systems (Toledo Machado et al., 2021). The RH levels reach on average 100 % during the early morning and decrease during the day to around 75 %. Fog typically occurs in the second half of the night and often in the early morning before sunrise (i.e., between 03:00 and 07:00 LT), when T is lowest. Sporadically, fog also occurs shortly after rain showers, which is not reflected in the average conditions.

Figure 7e shows the diurnal cycle (blue line) of the median $CN_{<50}$ number concentration, $N_{<50}$, exclusively during the particle growth event days. For comparison, the median diurnal cycle of $N_{<50}$ comprising all measured PNSD is also presented (black line). The particle concentration on growth event days is significantly higher than that including all analyzed PNSDs, with median daily values of $64 (38 - 108) \text{ cm}^{-3}$, compared to $49 (29 - 81) \text{ cm}^{-3}$ for all days. The $N_{<50}$ diurnal cycle for growth event days shows a strong increase from midnight to 09:00 LT, peaking at $N_{<50} = 88 \text{ cm}^{-3}$, compared to $N_{<50} = 56 \text{ cm}^{-3}$ at the same time for the total data. This suggests that $CN_{<50}$ are injected into the PBL by rainfall events during the late afternoon and early night and last until mid-morning. Similar behavior for $CN_{<50}$ has been reported by Toledo Machado et al. (2021).

The diurnal cycle of the growth event onsets has a rather broad maximum spanning over the early morning hours, from 06:00 to 10:00 LT. It peaks at about 07:00 LT and then gradually decreases towards noon (see Fig. 7e), which is in agreement with what is observed in Figure 7f. A second local and less pronounced maximum is visible from 13:00 to 15:00 LT. The growth events reported during daytime likely correspond to rainfall events as reported by Toledo Machado et al. (2021) and probably the vertical transport of $CN_{<50}$ and Aitken size particles due to strong downdrafts in the course of convective rainfall, and the injection of these particle populations into the PBL as reported in Wang et al. (2016) and Andreae et al. (2018).

P_{ATTO} shows two maxima: A pronounced and rather defined maximum in the early morning at around 07:00 LT, which follows a gradual increase in precipitation during the second half of the night, and a broader maximum during the afternoon hours between 13:00 and 17:00 LT. Although about 74 % of events occur during the day, there are still ~26 % that take place during night conditions, between 19:00 - 05:00 LT. In particular, the occurrence of growth events from 01:00 - 05:00, which represents about 16 % of the total observed events, is evidence for complexity in the causes and mechanisms of particle injection and growth.

The evolution of the PBL also has a strong influence on the diurnal pattern. At night, the nocturnal BL close to the forest canopy is decoupled from the residual layer above (Fisch et al., 2004). In the morning hours - as soon as convection becomes effective - air masses transported into and within the residual layer are mixed into lower levels and measured at the canopy level. Consequently, $CN_{<50}$ and Aitken mode particles advected with the residual layer will be mixed downwards and appear at the 60 m inlet in the morning hours, typically around 8:00 LT. Section 3.5 further discusses the meteorological conditions regarding convective downdrafts and the atmospheric conditions under which the growth events are observed. Toledo Machado et al. (2021) discuss this daily mechanism of particle growth in more detail.

A contrast in GR and CS is observed when day and night events are compared, as shown in Figure 8. Daytime events, which correspond to ~74 % of the events, have significantly higher GR and CS_{growth} , at 5.9 nm h^{-1} and 0.0012 s^{-1} , respectively. The nighttime events, which account for ~26 %, have GR and CS_{growth} of 4.0 nm h^{-1} and 0.0009 s^{-1} , respectively. To verify the statistical significance of the difference between day and nighttime values, the Wilcoxon rank-sum test was applied. The

Figure 7. Diurnal cycle of selected meteorological parameters and the diurnal occurrence of particle growth events. From top to bottom: a) incoming shortwave radiation (SW , orange) and air temperature (T , red) at 26 m (canopy level) height. b) average local rain rate (P_{ATTO} , blue). c) relative humidity (RH) at 26 m. d) visibility (blue) measured by a fog monitor and fog occurrence (black) with lines representing the first quartile, e) median diurnal cycle of $N_{<50}$ for all the data (black) and only for the days in which particle growth events were observed (blue). And f) the diurnal cycle of the particle growth event onsets. All error bars denote the standard error. The data shown represent all observations (full lines) and wet season subsets (dashed lines).

p-value obtained for GR is 3.6×10^{-6} , while the p-value obtained for CS_{growth} is 0.02, indicating that the data groups regarding day and night are statistically different considering a significance level of 0.05. The observed differences are likely due to the different atmospheric mechanisms during daytime and nighttime. Daytime events are directly influenced by sunlight, which

controls photochemistry and hence the oxidation of SOA precursors. Sunlight also drives the dynamics of the PBL. Other phenomena also play an important role in daytime events, such as the peaks of precipitation that coincide with the peaks of growth events. In contrast, nocturnal events may have different causes and mechanisms, which may be related to meteorology, entrainment of air and particles from the free atmosphere into the PBL, and perhaps the contribution of biogenic sources from the surface.

Figure 8. Boxplot of a) GR and b) CS_{growth} related to growth events that occurred during the day or night. Nighttime events occurred between 19:00 and 05:00 LT, while daytime events occurred between 06:00 and 18:00 LT. The box represents the quartiles, whiskers represent 90th and 10th percentiles, and the horizontal lines represent the median.

3.5 Meteorological and cloud conditions during growth events

This section explores the weather and convective transport conditions linked to particle growth events. Figure 9a shows a histogram of the growth event frequency as a function of the associated anomaly of the equivalent potential temperature ($\Delta\theta'_e$) at the onset of the growth events (see sec. 2.8). A negative $\Delta\theta'_e$ is an indicator for air mass downdrafts from higher altitudes, as has been shown for the events analyzed by Wang et al. (2016). We found that $\sim 63\%$ of events were likely associated with air mass downdrafts ($\Delta\theta'_e < 0$), whereas $\sim 37\%$ were likely associated with $\Delta\theta'_e > 0$. We do not consider $\Delta\theta'_e = 0$ as it is a boundary region between meteorological conditions. Figure 9b shows a histogram of all growth events as a function of the associated cloud brightness temperature, which is an indicator for deep convective clouds ($T_{\text{ir}} < 245\text{ K}$) vs clear sky/shallow cloud conditions ($T_{\text{ir}} > 280\text{ K}$). For all events after 2017 (when T_{ir} data is available), we found that $\sim 36\%$ were likely

associated with deep convective clouds ($T_{ir} < 245\text{ K}$, red), $\sim 26\%$ with clear sky/shallow clouds ($T_{ir} > 280\text{ K}$, blue), and $\sim 38\%$ with mixed sky conditions ($245\text{ K} < T_{ir} < 280\text{ K}$, gray).

Figure 9. Histogram of the a) values of $\Delta\theta'_e$ at the beginning of the particle growth events. Black bars represent events during downdraft conditions and the green bars during undefined conditions, and the b) values of T_{ir} at the beginning of the particle growth events. Red bars represent events during deep convection conditions, blue during clear sky/shallow clouds conditions and gray during mixed sky conditions.

The most contrasting T_{ir} conditions were observed between the lower quartile ($T_{ir} < 228\text{ K}$), representing deep convective cloud conditions, and the upper quartile ($T_{ir} > 281\text{ K}$), representing clear sky conditions, with 36 events contained in each group. As an example, four of these 'extreme' events were selected (Figure 10) in daytime and nighttime conditions. The growth events under clear sky conditions are characterized by a trimodal aerosol population, with accumulation and Aitken modes as well as a third mode below 50 nm. As an example, the daytime event on 14 March 2019 was characterized by the occurrence of a significant amount of $CN_{<50}$ during nighttime (starting after 00:00 LT), with a pronounced peak in concentration around 06:00 LT and with an onset of particle growth also at 06:00 LT, which lasted for about 12 h. These events could be associated with advection processes, e.g., by a downdraft in the gust front (clear sky nighttime) or by nighttime rainfall and subsequent growth in the early morning by PBL processes.

The events under deep convective conditions – both, during daytime and nighttime – resemble the events reported by Wang et al. (2016). Here, downdrafted air masses in the course of deep convection inject $CN_{<50}$ particles from the upper troposphere into the PBL, followed by particle growth into the Aitken mode. In both these cases, the atmosphere is very clean, with low concentrations in the accumulation mode. Before the growth event, most of the particle population is in the Aitken size mode, which is removed by the injection of upper or mid-tropospheric air during the downdraft event, so that only the $CN_{<50}$ aerosol population remained. Note that about 4 hours after the start of the growth event, the accumulation mode particles (re)appeared, probably by mixing with surrounding airmasses.

Figure 10. Selected particle growth events according to the T_{ir} value at the onset of the event. Events under clear sky/shallow cloud conditions during daytime (left) and nighttime (right) were selected based on $T_{ir} > 281$ K (third quartile), while deep convection events were chosen based on $T_{ir} < 228$ K (first quartile).

Figure 11 shows boxplots for GR in (a) and CS_{growth} in (b) for clear sky and deep convection conditions. The median GR for clear sky conditions is 7.0 nm h^{-1} , whereas the median GR for deep convection conditions is 3.8 nm h^{-1} . Regarding CS, under clear sky conditions the median is 0.0016 s^{-1} , while under deep convection, the median CS is 0.0005 s^{-1} . The results show that different meteorological processes play an important role for the different particle growth events observed. The events that occurred under deep convection conditions present lower CS_{growth} and GR. Two main factors may influence this

Figure 11. Boxplot of a) GR and b) $\text{CS}_{\text{growth}}$ for clear sky conditions ($T_{\text{ir}} > 281 \text{ K}$) vs deep convection conditions ($T_{\text{ir}} < 228 \text{ K}$). Boxes represent the quartiles, whiskers represent 90th and 10th percentiles, and the horizontal line represents the median.

result: the precipitation during deep convection conditions cleans the atmosphere by wet scavenging, resulting in lower $\text{CS}_{\text{growth}}$ values, and the presence of clouds, reduces the availability of sunlight and thereby suppresses photochemical production of condensable species.

The daily frequency distribution of growth events (see Figure 7f) was divided into four groups (G1 to G4), where G1 and G4 represent the nighttime and G2 and G3 represent the daytime events. The daytime events were divided considering the occurrence of two frequency peaks: the first peak, representing 53 % of the growth events, is included in G2, covering the time from 06:00 to 11:59 LT. The second peak, representing 21 % of the growth events, is included in G3, covering the time from 12:00 to 17:59 LT. The nocturnal events were divided according to the possible state of the PBL. Group G4, with 10 % of the events, is defined from 18:00 to 00:59 LT, when the growth event population may still have some influence from late in the day, since some convective events occur later in the day and early night, and the convective BL is collapsing at this time. Group G1, representing 16 % of the total growth events, covers the time from 01:00 to 05:59 LT, when the nocturnal BL is well established and different mechanisms such as air mass entrainment into the BL, nighttime rainfall events, or biogenic processes could play a role in the aerosol particle dynamics. Table 2 shows the median T_{ir} , $\Delta\theta'_e$, the initial diameter at the onset of the growth event, D_i , and the GR and $\text{CS}_{\text{growth}}$ for the four hourly groups.

The results show a clear difference between the four groups (G1 to G4) regarding the T_{ir} and $\Delta\theta'_e$ conditions during the event onset. The nocturnal groups G1 and G4 have median $\Delta\theta'_e$ of -0.8 and 0, respectively. Their median T_{ir} indicates conditions closer to low clouds and clear skies, with median values equal to 269 K and 274 K for G1 and G4, respectively.

Table 2. Median, 25th and 75th percentiles (in parenthesis) for T_{ir} , $\Delta\theta'_e$, D_i , GR and CS_{growth} for each hourly group. T_{ir} , $\Delta\theta'_e$, D_i correspond to the onset of the particle growth event.

Group	Hour (local time)	T_{ir} [K]	$\Delta\theta'_e$	GR [nm h ⁻¹]	CS_{growth} [s ⁻¹]	D_i [nm]	Fraction of events (%)
G1	01:00 - 05:59	269 (238, 283)	-0.8 (-4.6, 1.5)	3.8 (2.3, 5.5)	0.0009 (0.0004, 0.0015)	27.7 (21.7, 35.3)	16
G2	06:00 - 11:59	268 (236, 282)	-1.9 (-5.3, 2.1)	6.3 (4.2, 8.6)	0.0012 (0.0007, 0.0020)	27.7 (20.6, 33.5)	53
G3	12:00 - 17:59	245 (219, 283)	-3.6 (-6.8, 0.5)	5.6 (4.0, 8.6)	0.0012 (0.0008, 0.0015)	24.6 (19.4, 29.9)	21
G4	18:00 - 24:00	274 (227, 276)	0 (-4.3, 2.1)	4.2 (2.1, 6.3)	0.0010 (0.0006, 0.0015)	27.8 (19.5, 32.7)	10

The T_{ir} diurnal cycle (Figure 12) shows clear differences between the groups. Within the G1 period, T_{ir} shows a minimum at 04:00 LT, when the average brightness temperature reaches 256 K, indicating convective activity and early precipitation compared to all days.

The G4 group, with the smallest number of growth events, is not significantly different from the median diurnal cycle for all days, suggesting that this 10 % of growth cases appears not be related to specific meteorological events. There are signs of convection at 16 LT, which coincides with the precipitation peak in the afternoon. Afterward, T_{ir} increases, going to clear sky conditions during the night. The median GR for G1 and G4 varies from 3.8 to 4.2 nm h⁻¹, respectively, and CS_{growth} approximately constant around 0.0010 s⁻¹, while D_i remains stable. The daytime groups G2 and G3 have the lowest median $\Delta\theta'_e$ at the onset of the events, with -1.9 and -3.6, respectively, indicating that convective downdraft activity plays an essential role during these growth events. The diurnal cycle of T_{ir} presents lower values during the whole day compared to the overall average, and the group G2 also shows minima in the early morning coinciding with the precipitation peaks, and also in the afternoon (Figure 7b).

The G3 group is the one with the most convective characteristics. The T_{ir} values indicate a strong occurrence of convective systems throughout the day, mainly in the afternoon. In particular, the pronounced decrease at 15 LT reaches deep convection conditions, with $T_{ir} = 249$ K, approximately 1 hour earlier than expected considering the whole observation days. The median GR ranges from 6.3 to 5.6 nm h⁻¹ in G2 and G3, respectively, and the median CS_{growth} remains constant, at 0.0012 s⁻¹. The smaller value of GR in G3 compared to G2 (diurnal events) could be associated with deep convection systems, which reduce the solar irradiance and thereby influence the photochemical processes. The presence of clouds has been associated with lowering GR and even lower occurrences of NPF and particle growth events (Dada et al., 2017; Kerminen et al., 2018). The median D_i for G3 is the lowest of the four groups, at 24.3 nm, indicating that the strong convective downdrafts are more effective in transporting smaller particles from the free troposphere into the PBL, which agrees with what has been observed previously (Wang et al., 2016). Therefore, the growth events of groups G2 and G3 are probably influenced by the strong convective systems during daytime. In particular, the G3 group has the most significant characteristics of deep convection and intense occurrences of downdraft throughout the day.

When discriminating the growth events by positive or negative $\Delta\theta'_e$ at the event's onset (here defined as $\Delta t = 0$) and looking 10 hours before and after this time, the different behavior of $\Delta\theta'_e$ and T_{ir} near the growth event is evident. Figure 13 shows the behavior of the mean ensembles of $\Delta\theta'_e$ and T_{ir} around $\Delta t = 0$ for $\Delta\theta'_e$ less than the 25th percentile (-5.3) and higher than

Figure 12. Average diurnal cycle of T_{ir} for the event days in the groups G1 to G4. The blue dashed line represents the average diurnal cycle of T_{ir} relating to the days when the particle growth events for a given group were observed. The black line represents the average diurnal cycle for all days on which PNSD measurements were made. The colored shadows represent the standard deviation.

the 75th percentile (+1.5) at the event's onset. Considering the case where $\Delta\theta'_e < -5.3$ at the event's onset, both $\Delta\theta'_e$ and T_{ir} strongly decrease from 10 h before the event and reach a minimum at $\Delta t = 0$, where $\Delta\theta'_e = -7.6$ and $T_{ir} = 238$ K, which represents deep convection conditions with strong downdraft occurrence. Both parameters increase afterward to cleaner sky conditions and out-of-downdraft conditions.

- 5 In contrast, for $\Delta\theta'_e > +1.5$ at the event's onset, the ensembles show an opposite behavior of the parameters. The $\Delta\theta'_e$ presents an increasing tendency from 10 h before the event until $\Delta t = 0$, reaching a value of +4. Afterward, $\Delta\theta'_e$ decreases, but always retains positive values, indicating that there is a class of growth events that may not be driven by convective downdrafts. The T_{ir} values from 10 h before the events up to $\Delta t = 0$ are equivalent to conditions close to clear skies ($T_{ir} \sim 280$ K), which agrees with the results obtained for $\Delta\theta'_e$, as an indication of sky conditions not dominated by convection systems around the
- 10 event's onset. After $\Delta t = 0$, T_{ir} values decrease, but without presenting deep convection conditions. This shows that clear sky

Figure 13. Ensemble analysis for a) $\Delta\theta'_e$ and b) T_{ir} considering 10 h before and 10 h after the event's onset. The cases where $\Delta\theta'_e$ at the event's onset is less than the 25th percentile (dashed lines) and more than the 75th percentile (full lines) are shown. In total, 72 cases were considered in the analysis (36 cases for each condition).

events can be associated either with advection or subsidence bringing particulates from another area (e.g., a nearby rain event) or from the upper troposphere.

4 Summary and conclusions

This study reports the statistical characterization of aerosol particle growth events in the sub-50 nm size modes (10 - 50 nm), with continuous measurements (February 2014 to September 2020) of PNSDs at a remote site in Central Amazonia. In total, 254 particle growth events were detected, comprising about 14 % of the analyzed days, of which 88 % was found between January to June and 12 % from July to December. The diurnal cycle of the growth events shows that most of them occur during the daytime, accounting for 74%, but with a significant amount of events during the night (26%). In the daytime, 53 % of the growth events start in the early afternoon, between 06:00 and 11:00 00 LT, with a pronounced peak at 07:00 LT, showing a direct relation to the photochemistry and evolution of the PBL. These events also coincide with a precipitation peak in the morning. The nocturnal increase of $N_{<50}$ is likely related to convective systems that result in the precipitation peak in the morning. The subsequent decrease of $N_{<50}$ is likely due to the coagulation process that ages $CN_{<50}$ particles, resulting in growth. A second,

less pronounced but significant peak occurs around 15h LT, coinciding with the strongest precipitation peak, also suggesting a relation to atmospheric convective systems.

The median GR, considering all the growth events, is 5.2 nm h^{-1} , which agrees with what was reported by [Rizzo et al. \(2018\)](#). The median $\text{CS}_{\text{growth}}$ is 0.0011 s^{-1} . Monthly variations in GR and CS shows that during the wet season the growth events occur under low CS values, although the average $\text{CS}_{\text{growth}}$ does not change much from month to month, oscillating around 0.0011 s^{-1} . A remarkable contrast is observed when comparing day (median GR of 5.9 nm h^{-1} and median $\text{CS}_{\text{growth}}$ of 0.0012 s^{-1}) and night growth events (median GR of 4.0 nm h^{-1} and median $\text{CS}_{\text{growth}}$ of 0.0009 s^{-1}). Daytime events are directly influenced by sunlight, which controls photochemistry and hence the oxidation of SOA precursors. In contrast, nocturnal events may have different causes and mechanisms, which may be related to meteorology, entrainment of air and particles from the free troposphere into the BL, and perhaps the contribution of biogenic sources.

Analysis performed using $\Delta\theta'_e$ and T_{ir} revealed that diverse atmospheric dynamics play different roles during particle growth event days. Many event onsets coincide with downdraft occurrences, when $N_{<50}$ appear and grow afterward. We also observed that accumulation mode particles processed in clouds appear sporadically, causing a prominent Hoppel minimum. The growth events occurring under clear skies present GR and CS higher than those related to deep convection: the median GR and CS for clear sky conditions are 7.0 nm h^{-1} and 0.0016 s^{-1} , whereas under deep convection conditions, the median GR and CS are 3.8 nm h^{-1} and 0.0005 s^{-1} .

The events were classified according to their frequency of occurrence throughout the day, showing that they are mostly driven by local convective activities (73%). However, when analyzing the growth events by $\Delta\theta'_e$ at the event's onset, the occurrence of downdrafts does not explain all the cases. The contrast is more evident in the ensembles of $\Delta\theta'_e$ and T_{ir} when growth events and their respective occurrence days are selected by $\Delta\theta'_e > 75\text{th percentile } (\Delta\theta'_e = +1.5)$ at the event's onset. For these events, representing about 27% of the growth events, $\Delta\theta'_e$ is maximum and positive at time $\Delta t = 0$, and even ten hours before or after the growth event, it did not present negative values that could indicate the occurrence of convective downdrafts. Also, T_{ir} fluctuates at around 270 K over the observed period, which represents shallow clouds, instead of convective systems conditions. In contrast, events with $\Delta\theta'_e < 25\text{th percentile } (\Delta\theta'_e = -5.3)$ at the event's onset are associated with downdraft occurrences: $\Delta\theta'_e$ strongly decreases 10 hours after the growth event up to $\Delta t = 0$, which is also followed by a strong decrease in T_{ir} .

Sources that could explain growth events in the absence of deep convection are likely related to primary biogenic aerosols emitted by the forest, smooth entrainment of air masses from the free troposphere to the PBL in the early morning, and even different meteorological mechanisms such as gravity waves and particle production by lightning in the free troposphere, as reported by [Toledo Machado et al. \(2021\)](#). Another possible explanation is related to nighttime downdrafts far upwind, which get trapped above the nocturnal boundary layer, and travel in the jet above the nocturnal inversion for potentially quite a large distance, being mixed down into the PBL after sunrise, as suggested by [Krejci et al. \(2005\)](#). Therefore future studies are required to unveil the aerosol sources that could explain the diversity of particle growth events observed in the lower troposphere over Central Amazônia.

Data availability. The data of the key results presented here have been deposited in supplementary data files for use in follow-up studies. Particle number size distributions for the entire observation period are available via the ATTO data portal through <https://www.attoproject.org/>. For data requests beyond the available data, please refer to the corresponding authors.

Author contributions. MAF and FD contributed equally to this work. MAF, FD, and CP designed the study. MAF and FD analyzed the data. MAF, FD, LAK, BAH, FGM, JS, SC, JB, and SW collected and processed the ATTO aerosol data. LATM processed the satellite data. AA and MS collected the micrometeorological data at the INSTANT tower at ATTO. SW, FGM, PA, MOA and UP provided essential scientific support for the ATTO measurements. DW supported the data management. MAF, CP, and FD wrote the paper. LATM, MOA, LVR, HMJB, JPN, FGM, MP, SC, JB, and SC contributed with valuable ideas and comments to the analysis and the manuscript. All authors contributed to the discussion of the results as well as the finalization of the manuscript. PA and CP supervised the study.

10 *Competing interests.* The authors declare that they have no known competing interests that could have influenced the work reported in this paper.

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Supplement of

Occurrence and growth of sub-50 nm aerosol particles in the Amazonian boundary layer

Franco et al.

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Figure S1. Examples of multi-modal log-normal fits obtained by the automatic algorithm. Sub-50 nm size particle mode (green) is defined as $10 \leq D_p \leq 50$, Aitken mode (red) is defined as $50 \leq D_p \leq 100$ and accumulation mode (blue) is defined as $100 \leq D_p \leq 400$.

Figure S2. a) Histogram of the R^2 resulted from the multi-modal log-normal fits, considering only the data with $R^2 > 0.8$. The average R^2 is 0.97. b) Linear fit of integrated $N_{conc, SMPS}$ and estimated $N_{conc, \Sigma n-modes}$, with $R^2 = 0.997$.

Figure S3. Illustration of the procedure to obtain the anomaly of the equivalent potential temperature $\Delta\theta'_e$ at a particular season. For didactic purposes, it was selected the wet season of 2018. a) The mean seasonal θ_e (blue line) is obtained from the time series of θ_e . b) Time series of θ_e detrended by its seasonal mean (θ'_e). c) The mean diurnal cycle of θ'_e . d) Time series of $\Delta\theta'_e$, which represents the variations of θ_e at a specific time of the day at a particular season.

Figure S4. Comparative analysis of a) GR and b) CS at different site conditions. The error bars and the median data regarding the sites different from the Amazon sites denotes the 5th and 95th percentiles of the median GR values obtained from different studies compiled by Kerminen et al. (2018) in its supplementary tables (available online at <https://iopscience.iop.org/article/10.1088/1748-9326/aadf3c/data>). For the amazonian sites, it was chosen to present only the medians of GR, since the GR percentiles obtained in the studies are regarding to the different types of growth events analyzed, and not to different sites. In figure b, the missing sites did not present CS results in their respective papers.

APPENDIX C

**Article - How weather events modify
aerosol particle size distributions in the
Amazon boundary layer**

How weather events modify aerosol particle size distributions in the Amazon boundary layer

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Abstract. This study evaluates the effect of weather events on the aerosol particle size distribution (PSD) at the Amazon Tall Tower Observatory (ATTO). This research combines in-situ measurements of PSD and remote sensing data of lightning density, brightness temperature, cloud top height, cloud liquid water, and rain rate and vertical velocity. Measurements were obtained by a scanning mobility particle sizers (SMPS), the new generation of GOES satellites (GOES-16), the SIPAM S-band radar, and the LAP 3000 radar wind profiler recently installed at the ATTO-Campina site. The combined data allow exploring changes in PSD due to different meteorological processes. The average diurnal cycle shows a higher abundance of ultrafine particles (N_{UFP}) in the early morning, which is coupled with lower concentrations in Aitken (N_{AIT}) and accumulation (N_{ACC}) mode particles. From the early morning to the middle of the afternoon, an inverse behavior is observed, where N_{UFP} decreases and N_{AIT} and N_{ACC} increase, reflecting a typical particle growth process. Composite figures show an increase of N_{UFP} before, during, and after lightning was detected by the satellite above ATTO. These findings strongly indicate a close relationship between vertical transport and deep convective clouds. Lightning density is connected to a large increase in N_{UFP} , beginning approximately 100 minutes before the maximum lightning density and reaching peak values around 200 minutes later. In addition, the removal of N_{ACC} by convective transport was found. Both the increase in N_{UFP} and the decrease in N_{ACC} appear in parallel with the increasing intensity of lightning activity. The N_{UFP} increases exponentially with the thunderstorm intensity.

In contrast, N_{AIT} and N_{ACC} show a different behavior, decreasing from approximately 100 minutes before the maximum lightning activity and reaching a minimum at the time of maximum lightning activity. The effect of cloud top height, cloud liquid water, and rain rate shows the same behavior, but with different patterns between seasons. The convective processes do not occur continually but are modulated by gravity waves in the range of 1 to 5 hours, creating a complex mechanism of interaction with a succession of updrafts and downdrafts, clouds and clear sky situations.

The radar wind profiler measured the vertical distribution of the vertical velocity. These profiles show that downdrafts are mainly located below 10 km, while aircraft observations during the ACRIDICON-CHUVA campaign had shown maximum

concentrations of ultrafine particles mainly above 10 km. Our study opens new scientific questions to be evaluated in order to understand the intricate physical and chemical mechanisms involved in the production of new particles in Amazonia.

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25 1 Introduction

The Fifth Assessment Report of the Intergovernmental Panel on Climate Change (AR5 of IPCC, 2013) shows that clouds and aerosols contribute the largest uncertainty in our understanding of the Earth's changing energy budget. Aerosols impact climate, clouds, and precipitation by the direct and indirect effects. Studies based on observations and modeling have improved knowledge and reduced uncertainties regarding the aerosol direct effect (e.g., Ramanathan et al., 2001; Hansen et al., 1997);
30 see also Haywood and Boucher (2000) for a review of the estimated direct global annual mean radiative forcing. The effects of natural and anthropogenic sources, such as forest fires and urban pollution, on aerosol-cloud-precipitation interactions, including cloud invigoration as well as precipitation reduction by increased aerosol loading and the associated effects on cloud microphysics have been intensely studied (e.g., Albrecht, 1989; Andreae et al., 2004; Rosenfeld, 2018; Twomey and Warner, 1967; Rosenfeld, 1999; Koren et al., 2005; Rosenfeld et al., 2008; Cecchini et al., 2017a; Heikenfeld et al., 2019). In addition,
35 the knowledge about aerosol characteristics, cloud condensation nuclei (CCN), secondary organic aerosol (SOA), and volatile organic compounds (VOCs) has been greatly improved, specifically in the Amazon region (e.g., Pöschl et al., 2010; Pöhlker et al., 2016, 2018; Palm et al., 2018; Yáñez-Serrano et al., 2020; Holanda et al., 2020; Saturno et al., 2018; Leppla et al., 2021; Schrod et al., 2020). Recently, Artaxo et al. (2021) presented a comprehensive review and discussion of the aerosol effects on climate with a particular focus on tropical and boreal forests. Although these studies have advanced our knowledge
40 of aerosol-cloud interactions, only very few attempts have been made to describe how clouds modify the aerosol properties.

For the Amazon, this topic was recently addressed by two field experiments: Observations and Modeling of the Green Ocean Amazon (GoAmazon2014/5) (Martin et al., 2016, 2017) and ACRIDICON-CHUVA¹ (Wendisch et al., 2016; Cecchini et al., 2017b; Machado et al., 2018). Gerken et al. (2016) discussed the downward transport of ozone by convective clouds and used the surface equivalent potential temperature (θ_e) as a proxy of convective events that produced an increase in ozone
45 concentration at the surface during rainfall events. Wang et al. (2016) analyzed the origin of small aerosol particles in the boundary layer (BL). They found high concentrations of these particles in the free troposphere up to 6 km and concluded that they were transported down by convective downdrafts during intense precipitation events. Andreae et al. (2018) showed enhanced concentrations of ultrafine particles in the upper troposphere, which were much higher than in the planetary BL. They suggested that these particles were produced in the outflow from deep convective events and were returned to the surface
50 by convective downdrafts. Williamson et al. (2019), using aircraft measurements over the Pacific and Atlantic Oceans also

¹ Aerosol, Cloud, Precipitation, and Radiation Interactions and Dynamics of Convective Cloud Systems—Cloud Processes of the Main Precipitation Systems in Brazil: A Contribution to Cloud Resolving Modeling and to the GPM

observed new particle formation in the tropical upper troposphere and suggested that these particles descend towards the lower troposphere, where they can act as CCN, modifying cloud properties.

This study evaluates the effect of weather events on particle number size distribution (PSD) changes, combining satellite and radar data with measurements from two scanning mobility particle sizers (SMPS) at 60 and 325 m height at the Amazon Tall Tower Observatory (ATTO) (Andreae et al., 2015). The PSD data is analyzed for the main cycles and cloud characteristics in the Central Amazonian region, highlighting the relationship between lightning storms and changes in PSD. This study explores changes in PSD by the atmosphere's seasonal and diurnal cycles and intradiurnal variability, and evaluates the relationships between PSD and lightning, rainfall, cloud top height, cloud liquid water, and brightness temperature during the dry and wet seasons. These analyses will help to understand the new particle formation observed during convective events.

2 Data and Methods

This study combines different types of datasets, all colocated at the ATTO site, which has been described in detail by Andreae et al. (2015). The data were obtained from the new generation of GOES satellites (GOES-16), the SIPAM S-band radar, two SMPS instruments sampling from 60 and 325 m height above ground, and the LAP 3000 radar wind profiler installed at the ATTO-Campina site. ATTO-Campina is a new site to complement ATTO measurements with cloud physics instruments, specifically designed for the study of aerosol-cloud-precipitation interactions. The Campina site is located about 4 km from the main tower in a small isolated clearing, characterized by relatively dry and sandy soils as well as the typical low Campina vegetation type (Junk et al., 2011). The small size of the trees allowed the installation of remote sensing instruments to measure cloud physics. All datasets used in this study were organized and compiled to produce two years of data with 10-minute time resolution, from October 2017 to September 2020. Detailed descriptions of the individual datasets are presented below.

2.1 Scanning Mobility Particle Sizers

This study focuses on particle number size distribution measurements obtained from two Scanning Mobility Particle Sizers (SMPS, TSI Inc., Shoreview, USA), each comprising a differential mobility analyzer (DMA) and condensation particle counter (CPC). Both SMPS systems were measuring in parallel at two different sampling heights at the ATTO site. One SMPS was sampling from the 60 m inlet of the triangular mast and the second from the 325 m inlet of the Tall Tower. Due to several instrument failures in the course of the long-term measurements, the DMA and CPC instruments were replaced as necessary. These replacements involved different DMA and CPC models: the measurements at the 60 m inlet involved the classifier models 3080 and 3082, the DMA model 3081, and the CPC model 3722). The measurements at the 325 m inlet involved the classifier model 3082, the DMA model 3081, and the CPC models 3722 and 3750 (for details, see Andreae et al., 2015; Pöhlker et al., 2016). Both instruments are located in air-conditioned laboratory containers at the foot of the towers. Sample air was transported through stainless steel tubes (finetron tubes, Dockweiler AG, Neustadt-Glewe, Germany) and dried to a relative humidity (RH) below 40 %. At the 60 m inlet, an automatic regenerating silica gel adsorption aerosol dryer, as described in Tuch et al. (2009), was installed upstream of the instruments since 2014 and was replaced by a custom-built and

automated condensation aerosol dryer in March 2020. At the 325-m inlet, an automated condensation drier was used since the beginning of measurements. Both SMPS instruments cover a particle size range from 10 to 400 nm, and the sizing accuracy was frequently checked using monodisperse polystyrene latex particles. Data were acquired and exported with the Aerosol Instrument Manager Software (AIM, Version 9 & 10, TSI Inc., Shoreview, USA). The original temporal resolution was 5 minutes and was integrated to 10 minutes to maintain the same time resolution as the other data. The data were adjusted for standard temperature (273.15 K) and pressure (1013.25 hPa). The theoretical losses due to the long inlets at 60 m and 325 m were corrected based on a methodology using size-dependent correction factors, as described by von der Weiden et al. (2009).

For the purpose of our analysis, we divided the PSD, obtained by the SMPS over the range from 10 to 400 nm, into the following three individual size classes: (a) ultrafine aerosol particles (UFP) from 10 to 50 nm, (b) Aitken mode particles from 50 to 100 nm and (c) accumulation mode particles from 100 to 400 nm (see also multimodal fitting in Pöhlker et al., 2016). In order to evaluate the particle characteristics along the classes, we computed the cross-correlation between the different particles sizes for the Central Amazonian dry (Jun to Oct) and wet (Dec to Apr) seasons. Figure 1 shows how well the multimodal PSDs are described by the aforementioned modes by means of a cross-correlation plot for the dry season. The accumulation mode particles and Aitken mode particles have a clearly defined separation at 100 nm, mainly during the wet season, which is the location of the Hoppel minimum (Hoppel et al., 1996) as observed in Central Amazonia by Pöhlker et al. (2016). However, the separation between Aitken mode particles and UFP is not clearly evident. The Aitken mode particles have a smaller cross-correlation between the particles, which can likely be explained by the fact that this range of particles is in the transition between the other two modes. Specifically, the Aitken mode particles appear to have sometimes nucleation mode particle properties and sometimes accumulation mode particles properties. Clearly, the UFP and accumulation mode particles are well cross-correlated between the different particle sizes; however, for the wet season this separation is not well defined. In the wet season there is an increase in cross-correlation from Aitken particles to UFP, but the cross correlation inside the population of the UFP is smaller than during the dry season. The UFP are in a size range where Aitken and nucleation particles modes overlap, therefore we adopted the ultrafine particle denomination for this size range, which showed to be very sensitive and with a different behavior from the other particle classes, as will be shown in this study. Fan et al. (2018) used the same size range to show the effect of UFP in the strengthening of convective updrafts. Given the overlap between the nucleation and Aitken modes and the growth of particles from one mode into the other, the cut at 50 nm is somewhat arbitrary, but as will be shown below, provides a practical basis for discussing the behavior of these particle classes in response to meteorological events and across diurnal and seasonal time scales. Table 1 summarizes the definitions, abbreviations and size ranges of aerosol particle classes used in this study.

Table 1. Definitions, name abbreviations, and symbols of the three aerosol particle size ranges used in this study.

Name of aerosol particle class	Concentration	Diameter (D) range [nm]
Ultrafine particles (UFP)	N_{UFP}	$10 < D \leq 50$
Aitken mode particles	N_{AIT}	$50 < D \leq 100$
Accumulation mode particles	N_{ACC}	$100 < D \leq 400$

Figure 1. Particle number size distribution cross-correlation sampled at 60 m height at ATTO. a) Dry season (Jun to Oct) and b) wet season (Dec to Apr). The cross-correlation underlines the distinction into ultrafine, Aitken, and accumulation modes.

2.2 Geostationary Operational Environmental Satellite

The Geostationary Operational Environmental Satellite (GOES) is the operational NOAA (National Oceanic and Atmospheric Administration) satellite covering South America. In 2016, NOAA launched the new generation of geostationary satellites, GOES-16, located at 75.2 W degrees. GOES-16 has a new set of instruments, in particular, used in this study, are the Advanced Baseline Imager (ABI) and the Geostationary Lightning Mapper (GLM). The GOES-16 ABI sensor data employed are the ABI channel 13 (10.35 μm). The ABI channel 13 has 2 km and the GLM has 8 km spatial resolution, both of them in their original satellite projection. Channel 13 is usually used to estimate the convective cloud depth, where lower brightness temperature (T_{IR}) relates to higher cloud tops simply because the temperature decreases with height in the troposphere (Adler and Mack, 1986). From ABI channel 13, three variables were selected, namely, the ATTO colocated T_{IR} as well as the frequency of occurrence of $T_{IR} < 284 \text{ K}$ and $T_{IR} < 245 \text{ K}$, in a grid of 5 by 5 pixels centered on ATTO. Clear sky radiance in Amazonia is associated with the mixed layer brightness temperature due to the high amount of water vapor near the surface. Machado et al. (2002) used the 284 K threshold to estimate the total cloud cover. The threshold of 245 K is usually employed to describe clouds associated with convective events in tropical regions.

The lightning data were obtained from the GLM, which detects lightning from a 0.74 μm CCD array with a very high temporal resolution, so it can compare the energy peak at different times to define whether it is a lightning event or not (detailed

description in Goodman et al., 2013). To obtain a better representation of lightning around ATTO, the GLM information was computed as the lightning density: the number of events every ten minutes in an area of 5 by 5 GLM pixels, which corresponds to a description of lightning activity in a 25 km radius.

130 2.3 S-Band Radar

The SIPAM S-band radar is a weather radar, located in Manaus and operated by SIPAM – (Sistema de Proteção da Amazônia). This S-band radar (10 cm wavelength – 3.0 GHz) has a beam width of 1.8° and a 240 km radius coverage. The radar run occurs every 12 minutes, a volume scan strategy covering 17 elevations. The volume scan produces a 3-D description of the atmosphere. The following parameters were obtained from the 3-D field: The constant altitude plan position indicator (CAPPI) is the reflectivity (dBZ) field at a specific height, in this case we have used the CAPPI at 3 km. There is a direct relationship between reflectivity and rainfall; the Marshall-Palmer relationship assumes an exponential drop-size distribution and defines rain rate (R) as: $Z = 200R^{1.6}$, where Z is the reflectivity in ($\text{mm}^6 \text{m}^{-3}$) and R is in mmh^{-1} . The CAPPI 3 km is usually associated with the rain rate if rainfall evaporation below 3 km is neglected. The 3 km height is employed to be free of clutter and the Earth curvature effects in the 240 km radius. The echo top corresponds to the maximum height of cloud threshold of 20 dBZ and can be considered as the height of the top of the rain rate associated with the reflectivities describe above. The 20 dBZ echo top is approximately the height of the cloud top with rain drops corresponding approximately to the rain rate of 1 mmh^{-1} . The VIL is the vertically integrated liquid (kg m^{-2}). VIL is obtained by the vertical integration of the reflectivity as described by Greene and Clark (1972).

2.4 LAP3000

The LAP3000 radar wind profiler (RWP) is a vertically pointing radar capable of measuring Doppler velocity spectra profiles under both clear sky and precipitation conditions. It operates in the 1290 MHz frequency range, with a 7.1° beam width, and obtains the Doppler spectra based on oscillations of the refractive index of air in the case of clear sky or based on droplet relative motion in the case of precipitation. The instrument is set up to operate in three different modes, one optimized for clear sky and the other two for precipitation. The precipitation modes are obtained in a similar fashion as in Tridon et al. (2013), which aims to convert the RWP to an S-band-like profiler. A similar approach has already been used in the Amazon during the two-year deployment of the Atmospheric Radiation Measurement (ARM) Mobile Facility (AMF) during the GoAmazon2014/5 experiment (Martin et al., 2017, 2016; Giangrande et al., 2017). The present study only used data from one of the precipitation modes, which is able to sample between 1 and 15 km altitude with spatial and temporal resolutions of 210 m and 9.5 s, respectively. The pulse repetition frequency (PRF) is set to 8300 Hz, and the velocity range is between -20 ms^{-1} and $+20 \text{ ms}^{-1}$ with 0.1 ms^{-1} resolution. The spectra moments are integrated into 5-min intervals for the analysis of the up- and downdrafts.

This instrument was employed to compute the statistical profile of the vertical velocity inside convective clouds. The analysis of resultant vertical velocity obtained by the RWP at the ATTO-Campina site was done by computing the contoured frequency-by-altitude diagram, a tool normally used in radar data analysis (detailed description in Yuter and Houze, 1995). As this is a

160 new instrument installed at ATTO site, the calculation was performed for only 54 days of measurements between 16 October and 8 December 2020. The vertical resolution of the contoured frequency-b- altitude diagram is set to 840 m, while the vertical velocity resolution is 0.1 m s^{-1} .

3 Results

This section explores how particle size distribution changes as a function of the main atmospheric cycles and cloud cover characteristics. The main atmospheric cycles in Amazonian are the seasonal and diurnal cycles. But, the atmosphere also varies in the intradiurnal and interdiurnal frequencies. This section will also evaluate how the intradiurnal variability is associated with the PSD. Intradiurnal cloud variability is mainly forced by gravity waves, and this topic will be discussed in subsection 3.7. The PSD associated with the cloud characteristics will be evaluated mainly by looking at the lightning density as a proxy of deep convection. This study also evaluates PSD as a function of cloud top height, rainfall, cloud-integrated liquid water, and brightness temperature. These evaluations allow building a holistic view of how weather modifies the particle size distribution. One of the main topics covered in this study is the association between BL dynamics and new particle formation. One remarkable feature already observed in case studies is the increased concentration of UFP during deep convective events. Section 4 will discuss and evaluate the different possibilities and the associated processes.

3.1 Seasonal Cycle

175 The seasonal cycle in the Amazonian region is very important to be studied because this region presents a very well-defined annual variation, with a dry season in the austral winter and a wet one in the austral summer. Moreover, the transition phases between wet to dry and dry to wet seasons present distinct behaviors of chemical and atmospheric properties. The dry season has higher particle concentration and the most intense thunderstorms. In contrast, the wet season has higher precipitation accumulation but with lower rain rates and particle concentration. Machado et al. (2004) and Pöhlker et al. (2018) present a completely description of the seasonal variability. The total particle number concentration varies by about one order of magnitude between wet and dry seasons (Andreae et al., 2015; Andreae, 2009). Pöhlker et al. (2016) discuss the seasonal variation of cloud condensation nuclei (CCN) in Central Amazonia and conclude that the variability in the CCN concentrations is mostly driven by the aerosol particle number concentration and size distribution. Moran-Zuloaga et al. (2018) present multi-year accumulation and coarse mode measurements at ATTO and discuss the large diversity of the aerosol sources. Varanda Rizzo et al. (2018) present a multi-year analysis of submicrometer particle size spectra at ATTO for the wet and dry season. Figure 2 clearly shows this high variability for all sizes, with a maximum number concentration at the end of the dry season, mainly in the range between 100 and 200 nm.

In addition, Fig. 2 shows the seasonal evolution of the brightness temperature (T_{IR}) and the lightning density. The brightness temperature starts to increase from May to July, characterizing the decrease in cloud cover and the frequency of occurrence of convective clouds, followed by the increase in particle number concentration. High T_{IR} values ($T_{IR} > 284 \text{ K}$) are associated with low cloud cover or shallow convection and cold T_{IR} ($T_{IR} < 235 \text{ K}$) are associated with deep convection. April is the

Figure 2. Seasonality of particle size distributions at ATTO (60 m sampling height), brightness temperature (T_{IR}), and lightning density (number of lightnings per 5 minute time bins in area of $50 \times 50 \text{ km}^2$ around ATTO). All values are shown as monthly means. Average time frame for all parameters ranges from Oct 2018 to Sep 2020.

month with the coldest T_{IR} and the rainiest month, but the maximum lightning activity is in September when deep convective rainfall events become more frequent. The brightness temperature and PSD relationship is straightforward, where higher T_{IR} is associated with reduced rain and higher particle concentration during the dry season and lower particle concentration during the wet season when T_{IR} is colder, representing higher (colder) cloud tops. However, the lightning activity shows the sharpest increase at the time when the aerosols have the maximum concentration (August). The transition between dry to wet season is the time when clouds are deeper and more intense, consequently having more electrification activity.

The seasonal cycle of the particle number concentration at different altitudes shows interesting features. From the wet to the dry season, the N_{UFP} is nearly constant at 60 m, but increases at 325 m (Figure 3a). The absolute value of the difference between the concentration at 60 m and 325 m is small and could depend on the correction employed for losses in the long inlet tubing at 325 m. The N_{ACC} (Figure 3b) has the same phase and nearly the same average concentration at 60 m and 325 m (511 and 556 cm^{-3} , respectively).

3.2 Diurnal Cycle

Clouds in Amazonia have a typical diurnal cycle during both the wet and dry seasons (Machado et al., 2004). The cloud diurnal cycle as well as BL processes modify the PSD (Betts et al., 2002; Saturno et al., 2018). Figure 4 shows the diurnal cycle of the PSD for the dry (color image) and wet seasons (isolines). Although the dry season has a much larger aerosol concentration

Figure 3. Seasonal and Diurnal variation of the number concentration of ultrafine and accumulation mode particles: a) Monthly average of the ultrafine particles at 60 m and 325 m, b) Monthly average of the accumulation mode at 60 m and 325 m, c) Hourly average of ultrafine particles at 60 m and 325 m, d) Hourly average of accumulation mode at 60 m and 325 m. The shaded area corresponds to a confidence interval of 95 %. Time in UTC, LST is UTC-4hours

than the wet season – on average about factor 5 higher (Moran-Zuloaga et al., 2018) – the diurnal cycle for the wet and dry seasons commonly shows a minimum in N_{ACC} and N_{AIT} at the end of the night and during early morning (i.e., 04:00 to 08:00 local time (LST), which is UTC -4h). It affects mainly the smaller sizes in the accumulation mode. This minimum during late night and early morning is followed by an increase in N_{ACC} up to the time when T_{IR} starts to decrease and lightning density increases in the afternoon. This is the time when the maximum in N_{ACC} is observed. Moran-Zuloaga et al. (2018) show, for the wet season, that episodic intrusions of African long-range transport of aerosols strongly increase the coarse mode in the early afternoon, when air is mixed down into the PBL from the dust-laden layer aloft.

The increase in the number concentration between morning and noon is coincident with the time when surface sensible heat flux becomes positive, the nocturnal BL is eroded, and the convective BL is rapidly built (Stull, 1988; Angevine et al., 2020; Fisch et al., 2004). At this time, the BL evolves from the stable stage (nocturnal BL) to the convective BL (mixed layer). Following Stull (1988) classification of the stages of BL evolution, Henkes et al. (2021) show in detail the BL height evolution and surface fluxes for these stages of the development of the convective BL in Central Amazonia during the dry season. The growing stage begins at sunrise and is determined by the time when the surface heat flux passes above zero and the turbulent

Figure 4. Diurnal cycle of the particle size distribution at ATTO (60 m sampling height) during the dry season (Jun-Oct) in color and wet season (Dec-Apr) as black isolines. The monthly mean brightness temperature and lightning density (number of lightning events in 5 minutes in $50 \times 50 \text{ km}^2$) are plotted as white and gray lines with solid lines for the dry season and dashed lines for the wet season. Time is UTC, LST is UTC -4 hours

kinetic energy promotes rapid growth of the convective BL. At this time, the BL exports particles to the free troposphere (the Earth's atmosphere above the planetary BL), and later in the afternoon, they are removed by precipitation scavenging. The differences between wet and dry season convective processes are very clear; from the meteorological point of view, the dry season has higher lightning activity and warmer T_{IR} , and vice versa in the wet season.

To observe the diurnal modulation of PSD in more detail, the daily evolution and relative variation (variation around the mean value) were computed for N_{UFP} , N_{AIT} , and N_{ACC} (Figure 5). N_{ACC} and N_{AIT} decrease during the night; the nocturnal BL height is normally above 60 m (Carneiro and Fisch, 2020), so this decrease is likely related to the interaction between the surface and the BL. Henkes et al. (2021) discuss the shallow and deep convective events. For both types of events, the nocturnal boundary layer has nearly zero and sometimes negative latent and sensible surface flux, as well as nearly zero turbulence kinetic energy, consequently no effective mechanism to support exchange between BL and free atmosphere. Therefore, this behavior can be attributed to dry deposition to the vegetation and ground surfaces, as there are no other sinks because the exchange across the top of the BL is very small due to the large stability in this layer. Fog, usual in the early morning (Anber et al., 2015), could also contribute to this behavior, though the night-time decrease is a systematic behavior during the dry and wet season. Whereas N_{ACC} and N_{AIT} decrease during the night, the UFP number concentration remains nearly constant (dry season) or even increases in the wet season. This topic will be specifically discussed in the next section.

Figure 5. a) Diurnal cycle of the ultrafine (black), Aitken (red), and accumulation mode particles (blue) at 60 m sampling height. The shaded area corresponds to a confidence interval of 95 %. b) Mean deviation of the diurnal cycle of ultrafine, Aitken, and accumulation mode particles during dry (dashed line) and wet (solid line) seasons. Time is UTC, LST is UTC-4 hours.

235 This behavior changes completely at sunrise, when accumulation and Aitken particles start to increase and N_{UFP} decreases, with the typical behavior of a particle size growth process, from ultrafine to Aitken and eventually to accumulation mode sizes (note that N_{AIT} starts to decrease at approximately 13:00 UTC (9:00 LST). This process is observed up to the middle or end of the afternoon, when the concentration of accumulation particles begins to decrease and ultrafine particles increase in phase with the increase in the afternoon convective processes. Figure 5b shows the proportional diurnal variation, relative to the overall mean value, for the dry and wet seasons. It is interesting to note that despite their lower concentration relative to the accumulation mode particles, the UFP have the largest relative diurnal variation in both seasons. N_{UFP} diurnally changes up to 40 % of the average number concentration. N_{ACC} , as already shown, varies in absolute number much more, but as the number concentration is very high, mainly in the dry season, the relative variation is very small. An exception occurs during the wet season, when N_{ACC} is reduced by up to 30 % during the night. Thus, despite the much larger concentration in the dry season, 245 the relative daily variability is larger during the wet season. This result indicates that the diurnal cycle not only mainly controls N_{UFP} , but also provides a modest decrease in the concentration of the larger modes during the night and shows a growth process from morning to the time that rainfall starts.

The diurnal cycle of N_{UFP} (see Figure 3c) has an oscillation in phase among the two heights, with minimal values in the early afternoon. However, the diurnal cycle of N_{ACC} (see Figure 3d) shows the number concentration at 60 m having its minimal 250 value earlier than at 325 m, and a similar concentration in the early morning when the convective BL is developing. This feature shows the importance of the BL evolution in shaping the particle size distribution.

3.3 Lightning Density and Particle Size Distributions

This section explores the relationship between lightning events and PSD. To understand how the PSD changes as function of the weather events, we evaluate the relationship between thunderstorms (i.e., storms producing lightning) and the evolution of 255 N_{UFP} , N_{AIT} and N_{ACC} from 400 minutes before to 400 minutes after the maximum lightning activity.

To describe the evolution of ultrafine, Aitken, and accumulation mode particles, composite analyses were produced based on the maximum lightning density activity. Composite analyses are useful tools to form physical hypotheses on the associations between environmental variables that occur over time (Boschat et al., 2016). Composite analysis is a useful technique to determine basic characteristics of a particular phenomenon. This type of analysis involves collecting large numbers of standardized 260 cases of a given phenomenon and compositing them together as a collection. It involves computing the composite mean and statistical significance of the selected pattern, in this case the lightning occurrence and other cloud characteristics.

The composite depends on the specified threshold to create a collection of cases. For lightning, the threshold was computed as percentiles of the lightning density distribution. This procedure allows comparing different thunderstorm intensities and their effect on PSD, as well as the effect of the other parameters describing cloud activity, such as cloud top height, rainfall, 265 and cloud liquid water. In order to have a comparable selection of lightning intensity and cloud properties, the lightning density selected was defined as a function of the percentile values of 25%, 45%, 65%, 85% and 95%; these percentiles correspond to lightning density events of 2, 30, 137, 494 and 1192 (number of lightning events in 10 minutes in an area of 5 by 5 pixels centered at ATTO), respectively. The composites were produced by selecting the particle number concentration 400 minutes

before and after the maximum lightning density for the different values of the selected percentiles. Figure 6 shows the typical evolution of N_{UFP} , N_{AIT} , and N_{ACC} as a function of the maximum lightning density for different percentiles. Figure 6b also shows the composite of the lightning density for the different percentiles. The number of cases in each composite depends on the percentile and ranges from 2520 for 25% to 159 cases for 95%. Statistical significance was evaluated using t-student test and there is a significant difference ($>99\%$) between the different modes and percentiles.

At approximately 100 minutes before the maximum lightning density, for any lightning intensity, N_{UFP} particles increase in concentration, reaching maximum values of nearly double the initial concentration 200 minutes later. The difference in N_{UFP} increases exponentially with the lightning density percentiles, i.e., the thunderstorm intensity controls the rate of change of the ultrafine number concentration. Deierling and Petersen (2008) found a high correlation between volume updraft and total lightning. Jadhav et al. (1996) showed an increase in ozone (O_3) and nitrogen dioxide (NO_2) column densities during thunderstorm events. Oxidation products of volatile organic compounds form Secondary Organic Aerosol (SOA) to create new particles. Martin et al. (2010) discuss the mechanisms in the production of SOA in Amazonian forests and highlight the importance of nitrogen oxides and ozone in the oxidation processes and new particle formation. The increase in volume updraft also increases air mass flux exchange in mesoscale and consequently more frequent updrafts and downdrafts. Subsection 3.7 discusses these successive pulses of vertical movements forced by gravity waves. This cloud variability increases the frequency of downward transport, and consequently, the advection of ultrafine particles as suggested by Wang et al. (2016) and Andreae et al. (2018). In contrast, N_{AIT} and N_{ACC} decrease, reaching their minimum at nearly the same time as the maximum lightning activity. The main reason for this change could be an exchange of PBL air with air from the free troposphere, which is higher in N_{UFP} and depleted in N_{ACC} , or it could be due to the scavenging by the intense rainfall (more efficient for larger particles). These processes will be discussed in section 4.

The reason for this increase in concentration of the UFP cannot be answered with the experimental design of this study. Still we can hypothesize that the reason is related to the UFP being brought down by the convective cloud downdrafts. The layer of UFP in the upper troposphere is about 10 km above the surface. The time interval between the onset of the lightning activity and the maximum UFP at the surface (60 m) is around 100 minutes. This implies a mean downdraft velocity of about 1.6 ms^{-1} . Schiro and Neelin (2018) show mean vertical velocity profiles for organized and isolated convective cells in the Central Amazonian region, with the downdraft velocities from the surface up to 10 km being between 1 and 2 ms^{-1} . This estimation agrees with the results from Wang et al. (2016) and Andreae et al. (2018), suggesting that the source of these UFP particles observed at the surface is in the upper troposphere. We will discuss in section 4, that the downdraft core is below this upper tropospheric (10-14 km) source of ultrafine particles. A further possibility that needs to be considered is the production of UFP by the lightning discharges themselves, as has been demonstrated for a site in China by (Wang et al., 2021)

Figure 6. a) Composite N_{UFP} as a function of the maximum lightning density events for different lightning density percentiles. b) Composite N_{AIT} as function of the maximum lightning density events for different lightning density percentiles. The composite lightning frequency is shown for each percentile from continuous to dashed lines c) Composite N_{ACC} as function of the maximum lightning density events for different lightning density percentiles (60 m sampling height). The shaded area corresponds to confidence intervals of 95%.

3.4 Relationship Between Lightning Activity and Aerosol Background

300 As already mentioned, the changes in N_{AIT} and N_{ACC} happen in an opposite direction to N_{UFP} ; these particles are removed, and specifically, N_{ACC} also starts to decrease 100 minutes before the maximum of lightning density (the same time when N_{UFP} starts to increase). This observation indicates that the rainfall begins at approximately this time and intensifies up to the time of maximum lightning density, 100 minutes later. Interestingly, Figure 6 shows that even before the onset of scavenging (i.e., more than 100 minutes prior to the lightning density peak), a higher density of lightning is associated with a higher accumulation
305 number concentration. Higher lightning activity appears to be associated with a higher aerosol background condition. The aerosol concentration earlier than 100 minutes before the maximum lightning event is 30% higher at the 95th percentile value than that at the 25th percentile. Nonetheless, when approaching the time of maximum lightning activity and even later, the differences in N_{ACC} at the different lightning intensities become equal.

To understand this relationship of higher lightning activity at the time of higher aerosol background, a box-whisker diagram
310 was computed relating lightning density and N_{ACC} , 150 minutes before the maximum lightning event (Fig. 7). This time interval of 150 minutes before the intense weather event is an average time to detect the aerosol concentration before it is modified by the rain event. This figure highlights the positive correlation between the concentration of accumulation mode particles several hours before the maximum lightning activity and the increase in the frequency of the lightning events. During these periods of high activity convective events, with intense turbulence and well developed convective BL, the planetary BL is thoroughly
315 mixed. The time interval considered could be related to the time needed to clean up all the atmosphere by rainfall. This is behavior could also explain the time interval between the beginning of the increase of ultrafine particles and the maximum lightning activity.

The relationship between high aerosol background and lightning activity is not clearly observed for all months of the year, although a trend of higher intensity lightning events related to high N_{ACC} is easily observed. Applying a t-student statistical test
320 we can reject the null hypothesis for specific classes, indicating that there is a significant difference (>95 %) between the means of the classes with lightning density smaller and larger than 400 lightning events. During the period from April to August, this relationship is not clearly observed. However, when we look at the less polluted months from December to February (Fig. 7b), this trend is clearer but less significant because the number of lightning is smaller during this season. The reason cannot be answered with the present dataset, but the effect is better represented in this period than in a highly polluted situation. The
325 sensitivity for invigoration should be higher at low aerosol loadings and become saturated at higher loadings (Rosenfeld et al., 2008). During May and April, the cleanest months (Pöhlker et al., 2018), this relationship is also observed but less pronounced than for the period from December to February. One possible explanation is the very low aerosol particle concentration that reduces the total number of CCN.

Lightning acting to help increase the concentration of UFP, which hours later grow to accumulation particles and in turn
330 favor more lightning activity is likely related to the convective invigoration processes (Rosenfeld et al. (2008)). This is an interesting behavior, but as we will show, convection is mainly controlled by convective activity, which is strongly related to gravity waves and not to aerosol loading.

(a)

(b)

Figure 7. a) Whisker diagram between lightning density classes and accumulation particle mode number concentration (60 m sampling height), 150 minutes before the maximum lightning density for the two analyzed years. b) The same as (a) but for December to February.

3.5 Cloud Characteristics and Particle Size Distributions

The same kind of composite figures were prepared to analyze the effect of the rain rate (reflectivity at 3 km), cloud top height, cloud liquid water content, and brightness temperature on the PSD. In an effort to combine the different composites in the same figure, the deviations of the means were computed because the absolute magnitudes are different between these weather parameters. The composites are presented only for the maximum event defined by the threshold percentile value of 65 %. Different from the other variables, brightness temperature is a continuous value from clear sky to deep convective clouds. Therefore, a selection of the percentile value of 65 % would be associated with many thousands of values, in contrast to rainfall/lightning events, where the data are only reported for rainfall or thunderstorm (lightning case) events. Therefore the percentiles for T_{IR}

were defined only for values smaller than 245 K, normally classified as the clouds associated with convective events (Machado and Rossow, 1993).

Figure 8 presents the evolution of N_{UFP} , N_{AIT} , and N_{ACC} from 400 minutes before to 400 minutes after the maximum of T_{IR} , vertically integrated liquid water (VIL), the 20 dBZ cloud top height (echo top), reflectivity at 3 km (rainfall), and lightning density, respectively, for wet and dry seasons. The results were split into dry and wet seasons to highlight the different behaviors. The effect on the evolution of particles is similar to the scenario shown for lightning, with a similar phase but with different amplitudes. The larger the amplitude, the more important is the effect of a specific meteorological variable in the modification of aerosol concentration. During the wet season, one can note changes around the mean value on the order of 25 cm^{-3} for the number concentrations from all variables, with the exception of lightning density, which produces larger variations of approximately 40 cm^{-3} in N_{UFP} , N_{AIT} and N_{ACC} . Thunderstorms that produce lightning are more intense than ordinary storms, and the stronger convective updrafts and downdrafts could explain this behavior.

The same feature is not observed for the dry season; lightning events are tied to similar or even smaller particle number concentration changes than the other variables. There are some possible reasons for this behavior, such as the large area of 5 by 5 pixels where lightning density is observed and the more localized convective cells during the dry season (Machado et al., 2018). This effect could likely minimize the variation of the number concentration at ATTO for smaller systems in the searched region that are farther from ATTO. One interesting point is the similar effect exhibited by the cloud liquid water, cloud top, and rainfall on the evolution of the particle number concentration. These variables are well correlated, but the general effect on particles appears to be mainly related to the rainfall processes and associated updrafts and downdrafts. Recall that GLM captures only lightning that is more intense and closer to the cloud top; therefore, the population of rainfall clouds could also be associated with less intense and shallower lightning events. A second aspect observed in this figure are the different amplitudes of the rainfall effect on the particle number concentration between the wet and dry seasons. For N_{ACC} , for instance, echo top changes imply values of approximately 47 cm^{-3} in the wet season versus 156 cm^{-3} in the dry season.

We concluded that convective events have a typical behavior, increasing N_{UFP} , and reducing N_{AIT} , and N_{ACC} . However, this PSD modulation by weather events depends on the intensity of the convective event and has different sensitivities during the dry and wet seasons.

3.6 The Rate of Change of PSD at 60 and 325 m

The preceding sections discussed how the concentrations of different particle modes evolve during convective events and how convective events are modulated by particle size concentrations. One way to evaluate in more detail how weather events modify the PSD is looking at the rate of change of the number concentrations of a specific mode as a function of lightning, at two different heights of 60 and 325m. The rate of change in the particle number concentrations (N_a) at two different heights gives an idea of how the flux of particles is being modified at a given instant during the occurrence of a lightning event. For the purpose of evaluating this rate of change of a specific mode in response to weather events, we select the composite of the lightning density and compute the rates of change of the number concentrations. This rate is computed as $\frac{dN_a}{dt}$ in units of $\text{cm}^{-3} \text{ hour}^{-1}$. Figure 9 presents the rate of change of particles in the wet and dry seasons for the lightning density composite.

Figure 8. Composite reflectivity, vertically integrated liquid water (VIL), 20 dBZ echo top, brightness temperature, and lightning density for the percentile value of 65 % for a) N_{UFP} during the wet season, b) N_{UFP} during the dry season, c) N_{AIT} for the wet season, d) N_{AIT} for the dry season, e) N_{ACC} for the wet season, and f) N_{ACC} for the dry season (60 m sampling height). The shaded area corresponds to the 95 % confidence interval.

375 Some noteworthy features can be observed in Figure 9. First, UFP concentration changes have nearly the same phase in the wet and dry seasons; they are mainly negative between -400 and -200 minutes and between +200 and +400 minutes, and positive between -200 and +200 minutes. The rate of change in the wet season is larger and more than twice that of the dry season value at the time of maximum lightning density (minute zero). The rate of change at 60 m is higher than that at 325 m.

Figure 9. Rate of change in number concentrations from 400 minutes before to 400 minutes after the maximum lightning density (0.65 quartile) for a) N_{UFP} at 60 and 325 m during the wet season, b) N_{AIT} at 60 and 325 m during the wet season, c) N_{ACC} at 60 and 325 m during the wet season, d) N_{UFP} at 60 and 325 m during the dry season, e) N_{AIT} at 60 and 325 m during the dry season, and f) N_{ACC} at 60 and 325 m during the dry season

The ultrafine number concentration increases/decreases in one hour nearly 4 times more at 60 m than at 325 m. This observation indicates that the surface could also contribute as a source of UFP, increasing the UFP divergence flux in the BL. Even if the correction for the long inlet at 325 m is not sufficiently accurate to correct fully the losses of the concentration of small particles, this derivative does not depend on the absolute value. It, therefore, confirms the different behavior between 60 and 325 m. For N_{AIT} and N_{ACC} , in general, between -100 and +100 minutes there is a decrease in concentration and nearly no change during this period, except for N_{ACC} later than +100 minutes, which shows a trend of increased concentration. For the accumulation mode particles, the rates of change of the number concentrations at 325 and 60 m have nearly the same magnitude. However, this effect is slightly larger during the dry season at 325 m and during the wet season at 60 m.

The rate of change also decreases with height. It is possible that when the convective BL is being built, UFP are advected to higher levels, or the dilution due to the growth of the well-mixed BL be the reason for such a decrease with height. When the sun rises, N_{UFP} decreases, likely by growth into the Aitken mode particle range, reducing N_{UFP} in the BL where the concentrations of the Aitken and accumulation mode particles are higher than that in the free troposphere (Schulz et al., 2018).

Another interesting feature is the high variability of the rate of change of particle concentrations. It is clear that the variability is in the frequency of hours, indicating pulses of increase/decrease in the rate of change in the number concentration. This

intradiurnal oscillation observed in the rate of change of particle concentrations could be associated with the intradiurnal oscillation of the cloud cover. One of the main forcings of intradiurnal oscillation are the gravity waves. In the next section, we will explore the cloud modulation as well as the downdrafts and updrafts in this range of hundreds of minutes.

3.7 Cloud Intradiurnal Variability

The increase in UFP during convective events could result from new particle formation due to the increase of nitrogen oxides, ozone, and ions produced by the lightning discharges or by the vertical advection of UFP from upper levels. Both processes depend on the cloud dynamics, such as the downdraft/updraft intensity and frequency. Therefore, evaluating the cloud variability and what drives these oscillations is an important aspect of understanding how weather events modify PSD. Another aspect is the rate of change of the particle number concentration, in all modes, in response to weather events. It shows a well-marked oscillation of order of hundreds of minutes with positive and negative rates at both heights. These successive pulses observed in Figure 9, here nominated as intradiurnal oscillation, could be the result of a series of updrafts and downdrafts or clear/cloud sky in a time interval of the order of hundreds of minutes. A specific analysis was performed to investigate this behavior. The main goal of this analysis is to verify if the cloud cover time-evolution has variability in this time range. In a region with smooth topography and homogeneous surface conditions, the forcing and trigger mechanisms of gravity waves produced by convective towers could be the reason for this intradiurnal variability observed in the rate of change of the particle number concentrations.

Gravity waves modulate the deep convection, and at the same time, deep convection produces gravity waves that will modulate convection far away from the source. Lane and Zhang (2011) show that gravity waves control the variability of convective clouds. Vertical propagation of gravity waves produced by convective towers has an important effect on cloud variability (Alexander et al., 1995). In addition, strong updrafts induce tropopause fluctuations that are spread throughout the troposphere, and latent heat release due to convection and interactions with the mean flow produce gravity waves (Grimsdell et al., 2010). Wang (2007) observed plume formation above thunderstorm anvils, and in simulating this case, they observed high instability and breaking of the gravity waves excited by the strong convection inside the storm. Using the day/night band from the Suomi National Polar-orbiting Partnership (NPP) satellite, Miller et al. (2015) shows several examples of thunderstorms triggering a broad spectrum of gravity waves.

Wavelet transforms were employed to evaluate if cloud cover variability has the same pattern as the rate of change of the particle number concentrations. The wavelet transform provides information about the time and the frequency, making it possible to evaluate the amplitude of a specific frequency range in time, and in this case, every 10 minutes. This methodology will create a time series of the amplitude of the frequencies in intervals with a range of 1-5 hours. The Morlet wavelet was applied to a frequency of $T_{IR} < 284\text{ K}$, to account for the variability of the total cloud cover. The variability in 1-5 hours was integrated and produced a 10-minute time series; the higher values of this time series were used as a proxy of high cloud oscillation in the interval of 1-5 hours. Like the composite studies employed in this study, we compute the maximum interdiurnal activity and perform composite studies.

Figure 10a shows the intradiurnal composite for the echo top and lightning density. We can see the high variability of the convection with a succession of moments of more intense convection, with a peak of lightning followed by a higher cloud top.

Figure 10. Composite at 400 minutes before and after the maximum of variability in the frequency interval from 1 to 5 hours of the total cloud cover ($T_{IR} < 284K$). a) Echo top and lightning density. b) T_{IR} , frequency of occurrence of $T_{IR} < 245 K$ and $T_{IR} < 284K$ in the area of $12 \text{ by } 12 \text{ km}^2$. The shaded area corresponds to a confidence interval of 95%.

Figure 10b shows the composite for the parameters describing the cloud variability, T_{IR} , and the frequencies of occurrence $T_{IR} < 245 K$, a proxy for convective cloud cover, and $T_{IR} < 284 K$, a proxy for total cloud cover. This figure describes a typical variability in this frequency range. Convection in Amazonia, forced by this time scale, control the intracloud or intercloud variability and consequently the addition or loss of particles. During thunderstorms, the updrafts advect particles upward, followed by downdrafts advecting cloud content to the surface. This implies particle modulation by in-cloud scavenging of BL particles and by the downdraft bringing air rich in oxidants and/or UFP to the BL. This intermittent series of updrafts/downdrafts modifies the particles in the BL through a rich spectrum of processes, dominated by UFP enhancement and reduction of N_{AIT} and N_{ACC} that occur hundreds of minutes before and after the maximum convective events, not continuously but in a high variability environment.

4 Discussion

In the introduction, we referred to a large set of studies discussing aerosol-cloud-precipitation interactions. The present research brings new features to complement conceptual models of the effects of weather events on particle size distributions and vice-versa in the Amazonian region. However, several important questions are still open, and further studies are needed to develop a coherent conceptual model. This section will present some of the well-known processes, adding the new findings from the current investigation and putting in evidence other questions that are fully open.

One of the open questions is related to the source of UFP in the BL that nearly double in concentration during convective events. On one side, recent results show high concentrations of ultrafine particles in the upper troposphere (UT), although the formation processes are still unknown. Wang et al. (2016) described, for case studies, the phenomenon of sharply increasing N_{UFP} and the simultaneous decrease in the N_{AIT} and N_{ACC} during rainfall events, in agreement with the composite studies presented in this study. They showed high concentrations of UFP in the FT, increasing with height, and proposed that convec-

tive downdrafts bring down UFP from the free troposphere into the BL. On the other hand, they suggest that these particles arise from new particle formation in the outflow regions of deep convective systems, followed by condensation and coagulation growth. Andreae et al. (2018) described the high concentrations of UFP in the UT based on the ACRIDICON-CHUVA campaign. They suggested that downdrafts transport these particles to grow into new CCN in the planetary BL by VOC oxidation and growth processes. However, downdrafts from deep convection are expected to occur preferentially below the 10-14 km layer of the source of high concentration of UFP. To evaluate this hypothesis, we analyzed the vertical velocity profile inside the clouds at the ATTO-Campina site. With the new radar wind profile, we have computed a statistical analysis of the vertical velocity. Figure 11 shows the contoured frequency by altitude diagram of the resultant vertical velocity for the thunderstorms season (October-November); therefore, it describes the period of maximum extension of the updraft vertical distribution. The instrument measures the vertical movement of the rain drops, which is a combination of the droplet terminal velocity and air vertical motion. To provide a reference of the expected droplet terminal velocity, Martins et al. (2010) discuss rain droplets in the Amazonian region and mention peaks of 0.5, 1.0, and 2.0 mm size distributions for rainfall events, which approximately corresponds to a terminal velocity between 4 and 7 m s⁻¹. However, the main feature to be explored in this Figure is not the absolute value of the air vertical velocity, but the layer on which the vertical velocity acts. This Figure shows that downdrafts are mostly located below 10 km, but the layer of maximum concentration of UFP is mainly above 10 km. Wang et al. (2018) compute the vertical velocity distribution for convective and stratiform clouds for the GoAmazon and confirm weaker composite vertical air velocity above 10 km. Therefore, the UFP are more prone to be advected through the Hadley and Walker cells to middle latitudes than to return to the surface tropics as discussed in Kida (1983) using a Lagrangian general circulation model of air parcels. However, the concentration of UFP in the upper troposphere is very high, order of magnitudes more elevated than the surface UFP. Therefore, even if the maximum downdraft is below the layer of maximum concentration, the small fraction advected downward could be enough to be the source of UFP particles at the surface during rainfall events.

On the other side, the biogenic volatile organic compounds produced by forests undergo oxidation reactions to form secondary organic aerosol (SOA) further, and SOA accounts for a substantial fraction of tropospheric aerosol in the Amazon. Pfannerstill et al. (2021) show an increase in OH reactivity during rain events. The OH reactivity spikes have similar behavior to the spikes of UFP during lightning events, and OH is an efficient mechanism to oxidize the biogenic volatile organic compounds and further form new particles in the BL. The mechanisms effectively describing the processes between rainfall events, the UFP in the upper troposphere, and the SOA formation close to the surface should be investigated to clarify these aspects.

If the new particle formation from thunderstorm events presents these Pleiades of processes from the UFP in the upper troposphere to the VOC production by the forest, the daily cycle of new particle formation appears to be very clear. There is a typical diurnal cycle behavior, N_{UFP} exhibits a maximum concentration during the night; and as soon as the sun rises and the convective BL is built, conversion processes to Aitken and accumulation begin, and particle growth occurs up to the time that convection is initiated. Franco et al. (2021) studied ultrafine particle growth and found the most frequent starting cases approximately at twilight time before the convective BL is developed. Consequently, there is likely a combination of effects, such as the photochemical effect that begins the processes of UFP growing into the Aitken particle size range and the development of the convective BL that contributes to the dynamics of the aerosol (upward advection). In the late afternoon,

larger particles start to decrease by rain out, scavenging, and updraft removal. This process of increasing UFP and decreasing Aitken and accumulation particles occurs over a large range of variability with successive rain cells, updrafts, and downdrafts, controlled by the gravity waves. The rainfall scavenges the larger particles and the associated downdraft contributes to the increase in N_{UFP} .

Related to the seasonal variation, one can note that in the wet season the weather-PSD interaction is stronger than in the dry season. For instance, for the diurnal cycle, the percentage of relative variability of N_{UFP} is similar, but the consequent effect on N_{ACC} is only observed during the wet season. It could be associated with the reduction of concentration during the night followed by a growth process from UFP to accumulation mode particles, in the early morning, that is around 30 % in the wet season and nearly imperceptible in the dry season due to the very high absolute concentration of accumulation mode particles in the dry season. Also, related to the effect of lightning on PSD, the effect during the dry season is small and shows a small difference among the different types of rainfall events (storm, thunderstorm, cloud top height, total liquid water). The dry season is the maximum lightning activity season, but it is in the wet season that a relationship between lightning and N_{ACC} (150 minutes before the maximum lightning event) is observed. Hernández Pardo et al. (2021) using observation and modeling for Amazonian clouds, concluded that the width of the cloud droplet size distribution for clean clouds (aerosol concentration $< 900 \text{ cm}^{-3}$), varies as function of the adiabaticity of the cloud. However, for polluted clouds (aerosol concentration $> 2000 \text{ cm}^{-3}$), the distribution width is not a function of the adiabaticity, and varies very little. There are clear differences between the seasons as shown in the present study, the high concentration of particles during the dry season is relatively less sensitive to weather conditions than during the wet season, with lower aerosol concentrations, when the different types of weather events dominate the weather-PSD interactions.

Figure 11. Contoured frequency by altitude diagram of the vertical velocity W obtained by the RWP collected during 54 days of measurements between October 16 and December 8, 2020. The vertical resolution is 840 m, while the W resolution is 0.1 m s^{-1} . The contours show the number of data points (magenta curves).

5 Conclusions

Particle size distribution data from two SMPS instruments at ATTO at 60 and 325 m was combined with satellite and radar data to provide the basis for exploring the relationship between weather events and changes in particle size distributions in the BL of the Central Amazon forest. A colocated time series for ATTO at 10-minute resolution was produced, combining the different types of measurements. Several features describing the evolution of the particle size distribution could be observed for different weather cycles, forcings, and characteristics.

The seasonality is pronounced, with particle concentrations in the dry season being an order of magnitude greater than that during the wet season, and the brightness temperature followed this behavior, with colder brightness temperatures during the wet season (cold cloud tops) than during the dry season. However, lightning has a completely different behavior, and the transition season is the period where the maximum lightning activity is observed.

The diurnal cycle shows a typical behavior with nearly the same phase in both seasons. The maximum concentration of UFP is observed at sunrise, and at this time, N_{AIT} and N_{ACC} present a minimum. As the sun rises and the convective BL develops, the UFP begin to show a decrease in the number concentration followed by an increase in N_{AIT} and N_{ACC} , with a typical behavior of growth in the particle size. At the end of the afternoon, an inverse situation occurs, and N_{AIT} and N_{ACC} decrease

515 while N_{UFP} increases due to the more intense rainfall. Despite the higher concentration of accumulation particles, it is N_{UFP} that has the larger relative amplitude, except during the wet season in which the concentration of accumulation particles mode also has a significant relative variation.

The composite with the lightning activity describes the typical characteristics of the evolution of particle size changes due to convective rainfall. At approximately 100 minutes before and 200 minutes after the maximum lightning activity, N_{UFP} increases
520 and Aitken and accumulation particles decrease. Another interesting property is the larger number of lightning events when the aerosol background is higher, which appears to be an indication of convective cloud invigoration.

The same behavior as for lightning is observed in the composites of the echo top, rain rate (reflectivity at 3 km), integrated cloud liquid water (VIL), and brightness temperature (T_{IR}). Notably, a different behavior is observed between wet and dry seasons. During the wet season, lightning correlates with a greater change in the particle size distribution in comparison with the
525 dry season for the other weather parameters. This feature should be investigated in future campaigns to explain the reasons for this large sensitivity during the wet season. It seems that for small aerosol concentrations, weather-PSD interaction is dominated by the weather events, however, during the dry season this interaction is dominated by the total aerosol concentration.

The interdiurnal variability modulates the convective activity and produces a high variability at hourly time scales, making the particle size distribution evolution much more complex and controlling the succession of rain cells, updrafts, and
530 downdrafts. The increase of UFP and reduction of Aitken and accumulation mode particles is modulated by a succession of updrafts/downdrafts and cloud types.

Finally, using the radar wind profiler at the Campina site, the vertical distribution of the vertical velocity was computed. The data were collected in the season of the most intense convective activity (October – December) and show that downdrafts are mainly located below 10 km, while the layer of maximum concentration of UFP is mainly above 10 km. However, if even a
535 small fraction of UFP from the UT is advected downward, it could support the concentration of UFP in the surface observed during convective events because N_{UFP} in the upper troposphere is several orders of magnitude higher than at the surface. However, the source of the UFP at the surface during convective events is still an open question because there is also the mechanism of particle formation related to the increase of OH during convective events.

This study clarifies the processes related to modulation of PSD and new particle formation associated with the seasonal
540 and diurnal cycle, intradiurnal variability, and different types and characteristics of convective events. But, it opens further questions that need to be pursued in detail in new field campaigns, such as CAFE-Brazil scheduled for 2022 and the new ATTO-Campina site that provides measurements of atmospheric and cloud physical properties.

Data availability. ATTO data can be found in the ATTO data portal under <https://www.attodata.org/> (ATTO, 2020). For data requests beyond the available data, please refer to the corresponding authors.

545 *Author contributions.* LATM conceptualized this study, conducted the data analysis and wrote the paper. MAF, LAK, FD, and BAH conducted the SMPS measurements at ATTO and took care for data quality checks and processing. MLP, PA, and SW supported the ATTO measurements and data analysis. MAC contributed with the LAP3000 data treatment and analysis MOA, UP and CP contributed to the interpretation of the data and finalization of the paper in various discussions. All the authors contributed to the interpretation of the results and writing of the paper.

550 *Competing interests.* The authors declare that they have no conflict of interest.

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