Downward transport of ozone rich air and implications for atmospheric chemistry in the Amazon rainforest

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Abstract

From April 2014 to January 2015, ozone (O₃) dynamics were investigated as part of GoAmazon 2014/5 project in the central Amazon rainforest of Brazil. Just above the forest canopy, maximum hourly O₃ mixing ratios averaged 20 ppbv (parts per billion on a volume basis) during the June–September dry months and 15 ppbv during the wet months. Ozone levels occasionally exceeded 75 ppbv in response to influences from biomass burning and regional air pollution. Individual convective storms transported O₃-rich air parcels from the mid-troposphere to the surface and abruptly enhanced the regional atmospheric boundary layer by as much as 25 ppbv. In contrast to the individual storms, days with multiple convective systems produced successive, cumulative ground-level O₃ increases. The magnitude of O₃ enhancements depended on the vertical distribution of O₃ within storm downdrafts and origin of downdrafts in the troposphere. Ozone mixing ratios remained enhanced for

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>2 hours following the passage of storms, which enhanced chemical processing of rainforest-emitted isoprene and monoterpenes. Reactions of isoprene and monoterpenes with O_3 are modeled to generate maximum hydroxyl radical formation rates of 6×10^6 radicals $cm^{-3} s^{-1}$. Therefore, one key conclusion of the present study is that downdrafts of convective storms are estimated to transport enough O_3 to the surface to initiate a series of reactions that reduce the lifetimes of rainforest-emitted hydrocarbons.

Keywords: ***Isoprene, monoterpenes, air chemistry, convection, mesoscale convective storms***

1. Introduction

Ozone (O_3) mixing ratios in the atmospheric boundary layer of the remote Amazon region remain mostly below 40 parts per billion on a per volume basis (ppbv) during the wet period (e.g., Bela et al., 2015; Gregory et al., 1988). Low O_3 mixing ratios result from the reduced photochemistry associated with copious amounts of cloud cover and precipitation that limit actinic irradiance reaching near the surface (Gu et al., 2002). In the absence of biomass burning, nitrogen oxides (NO_X = nitric oxide (NO) plus nitrogen dioxide (NO_2)), which are the key O_3 precursors, only exist in trace mixing ratios in the atmospheric boundary layer (Torres and Buchan, 1988) because local soil emissions are small due to characteristically moist conditions. In the troposphere over the Amazon, O_3 mixing ratios monotonically increase with altitude (Kirchhoff et al., 1990). Ozone profile changes result from convection (e.g., Folkins et al., 2002; Folkins and Martin, 2005), enhanced formation in the upper troposphere due to the presence of NO_X from lightning (Goldenbaum and Dickerson, 1993; Thompson et al., 1997; Zhang et al., 2003), and surface deposition (Sigler et al., 2002).

Deep and moist convection is an important feature governing the distribution of trace gases and aerosols in the tropical troposphere (Garstang et al., 1988; Scala et al., 1990). Due to the internal dynamics of convective storms that have well defined updraft and downdraft regions, trace gases undergo frequent vertical redistribution in the troposphere. Within the storm updraft, boundary layer air is swiftly transported to the free troposphere where reactions of hydrocarbons, NO_X , and free radicals (such as hydroxyl radical, HO) can en-

hance oxidant and aerosol formation (Bertram et al., 2007). In contrast, within the storm downdraft, mid-tropospheric air parcels are transported towards the ground surface with reduced moisture content, lower equivalent potential temperature (θ_e) (Zipser, 1969, 1977), and higher (≥ 30 ppbv) O_3 content (Betts et al., 2002). While earlier studies (Garstang et al., 1988; Thompson et al., 1997; Pickering et al., 1996) examined the transport of trace gases from the surface into the free troposphere by mesoscale convective systems (MCS), more recent investigations (e.g., Betts et al., 2002; Grant et al., 2008; Hu et al., 2010; Sahu and Lal, 2006) indicated that convective-type storms also transport O_3 -rich air from the mid-troposphere to the Earth’s surface. In the areas impacted by the downdraft region of convective storms, driven by evaporative cooling from falling precipitation, ground-level O_3 can abruptly increase due to the rapidly moving air parcels from layers aloft where O_3 levels are much higher than at the surface. Ground-level O_3 can increase by up to 30 ppbv and the magnitude of these O_3 enhancements depends on the propagation velocity of MCS and origin of downdrafts within storms (Grant et al., 2008) and the tropospheric O_3 distribution, which can exhibit considerable day-to-day vertical variation in the Amazon (Kirchhoff et al., 1990).

In the Amazon region, maximum cloud cover and precipitation occur in the afternoon and early evening (Machado et al., 2004). Storms, with rainfall rates that can exceed 50 mm h^{-1} , vary in their organization from locally occurring systems to basin scale convection and squall lines (Greco et al., 1990). As a consequence, storm downdraft dynamics depend on the overall state and type of the storm systems. In turn, the ground-level O_3 enhancements associated with storms depend on the type of mesoscale convective systems. To date, these dynamics and their impact on atmospheric chemistry near the surface have rarely been explored.

The regional enhancement of O_3 in the atmospheric boundary layer can influence several atmospheric chemical cycles. For example, during the daytime O_3 can undergo photodissociation to produce excited oxygen atoms ($O(^1D)$) that readily react with water vapor (H_2O) to form HO (see reactions 1 and 2). The HO initiates the oxidation of biogenic volatile organic compounds (BVOCs), methane (CH_4), and carbon monoxide (CO) (reactions 3 and

4). Combined with the enhanced sink due to surface deposition, chemical reactions involving the O_3 transported from the mid-troposphere reduce the greenhouse gas loading in the boundary layer (Hu et al., 2010). In addition, elevated O_3 mixing ratios can accelerate the oxidation rates of plant-emitted isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$), and sesquiterpenes ($C_{15}H_{24}$). Reactions of BVOCs with O_3 generate free radicals, acids, carbon dioxide, and HO (reactions 5–7). These photo-oxidation processes remain poorly understood but are of great importance in the Amazon basin because of the unusually strong source of BVOCs whose reaction products can lead to the formation of secondary organic aerosols (SOA) (Martin et al., 2010b) which can activate into cloud condensation nuclei (CCN) and thus influence cloud formation processes.

Thus, the present work determines the magnitude and the frequency of ground-level O_3 enhancements associated with convective systems in the central Amazon region of Brazil during April 2014 to January 2015. An additional objective is to investigate the storm attributes associated with downdraft events that enhanced ground-level O_3 . We also investigate the duration and the influences of ground-level O_3 enhancements on atmospheric chemistry above the rainforest. Yields of HO from reactions entailing BVOCs and O_3 are estimated to verify whether convective storms can measurably impact BVOC oxidation.

2. Methods

2.1. Study site characteristics

The data used in this work were gathered during a field campaign at the Cuieiras Biological Reserve (S 2°36.11', W 60°12.56'; managed by the Brazilian Institute of for Amazon Research – INPA) during April 2014 to January 2015 (Fuentes et al., in review). The study was part of the GoAmazon 2014/5 (Observations and Modeling of the Green Ocean Amazon) project, which designated the study site as T0k (also commonly referred to as ZF2). The reserve is located approximately 60 km north-north west of the City of Manaus, Amazonas, Brazil (Fig. 1). Due to prevailing easterly winds, air masses arriving at the site mostly come from areas with little human influence and show low aerosol concentrations (Martin et al., 2010a; Artaxo et al., 2013). However, the study site occasionally experiences the influences of Manaus' urban plume and biomass burning events that occur frequently during the dry season and are caused by both natural (e.g., lightning) and anthropogenic processes (e.g., deforestation). The vegetation surrounding the site is a closed primary forest with maximum tree heights of 30–40 m. Leaf area index is typically estimated between 6.1 and 7.3 m² m⁻² (Marques Filho et al., 2005; Tóta et al., 2012) depending on measurement technique and location. The forest covers valleys and plateaus with altitude differences of circa 60 m. Soils in the valleys are more sandy, and vegetation in the valleys tends to be less dense and tall. A 50-m tower (known as K34) was used as a platform to deploy measurement systems. The tower is located on the top of a plateau where canopy height was approximately 36 m.

2.2. Ozone and meteorological measurements

Nine sonic anemometers (model CSAT3, Campbell Scientific Inc, Logan, UT) were deployed on the tower to measure the three components of the wind speed (u, v, and w) and the sonic virtual temperature. The sonic anemometer located at the canopy top (35 m) was used to determine wind speed and direction. Measurement frequency was 20 Hz and data were processed to generate 30-minute averages. Relative humidity and temperature (model HMP-155, Vaisala, Vantaa, Finland) were measured at 32 m above ground. Rainfall mea-

Figure 1: Map of South America and the central Amazon indicating the location of the study site (ZF2) in relationship to the cities of Manaus and Manacapuru. The black lines mark roads.

surements (model RIMB500, McVan Instruments, Melbourne, Australia) from a site located 3.11 km away from the flux tower are used in this analysis.

Ambient O_3 levels were measured (model 49i, Thermo Fisher Scientific Inc., Waltham, MA) at a frequency of 1 Hz. A Proton Transfer Reaction Mass Spectrometer (PTR-MS, Ionicon Analytik, Innsbruck, Austria) was used to measure isoprene and monoterpene mixing ratios. The air sampling intake for both instruments was placed at 40 m above ground. The inlet was placed below a rain shield and had a filter holder with a $1\ \mu\text{m}$ pore size Teflon membrane to exclude dust and pollen. The membrane was changed weekly. The O_3 analyzer was housed in an environmentally controlled shed located at the ground level, approximately 5 m from the tower. A pump moved the air at 12 liters per minute from the inlet to the analyzer via a 3/8-inch (9.8 mm) outer diameter Teflon tube. The O_3 analyzer was calibrated before deployment and regularly zeroed to ensure high data quality.

Ozone data were averaged to produce 5- and 30-minute quantities. Air temperature (T), water vapor mixing ratio (r), and barometric pressure (p) were used to compute values of

113 equivalent potential temperature (θ_e)

$$\theta_e \approx \left(T + \frac{L_v}{c_{pd}} r \right) \left(\frac{p_0}{p} \right)^{\frac{R_d}{c_{pd}}}, \quad (8)$$

114 with the latent heat of vaporization (L_v), the dry heat capacity of air (c_{pd}), the gas constant
115 of dry air (R_d) and a reference pressure (p_0) of 1000 hPa, to identify the periods when storm
116 downdrafts occurred at the study site.

117 An automated algorithm detected O_3 enhancement events that had to satisfy the criteria
118 of an increase in 5-minute averaged O_3 mixing ratio of at least 2.5 ppbv and a simultaneous
119 decrease in θ_e of 2.5 K within a one-hour time window. Local minimum and maximum values
120 of O_3 within the time window were used to determine start and end times of the enhancement
121 events. After this automatic method, false detections were manually identified and removed.
122 The average duration of O_3 enhancement events was calculated to determine the periods
123 when the atmospheric boundary layer was regionally enhanced with O_3 .

124 The GOES-13 (Geostationary Operational Environmental Satellites) satellite data were
125 acquired through the Brazilian National Institute for Space Research (INPE) and used to
126 investigate large-scale convection dynamics and extent. In addition, the Sistema de Proteção
127 da Amazônia (SIPAM) operates a network of S-band (10-cm wavelength), Doppler radars
128 with 500 m gate spacing and a 1.8° beam width across the Amazon. One of SIPAM's radars is
129 located at the Manaus airport ($03^\circ 08.98'$ S, $59^\circ 59.48'$ W, elevation 102.4 m). The operational
130 scan strategy had 17 elevation angles every 12 minutes and data were recorded for scans
131 extending 250 km from the radar site. The radar data were analyzed to develop the three-
132 dimensional structure of storms impacting the ZF2 site.

133 3. Results and discussion

134 3.1. Seasonal ozone dynamics

135 Ozone mixing ratios at the rainforest study site differed between the wet and dry months
136 (Fig. 2). After the end of the wet months (precipitation $> 5 \text{ mm d}^{-1}$) in June, O_3 mixing
137 ratios started to increase as revealed by median and maximum mixing ratios. Maximum

138 O_3 mixing ratios occurred in August and coincided with the maximum period of biomass
 139 burning in the Amazon (e.g., Kuhn et al., 2010; Artaxo et al., 2013). From the start of the
 140 wet months in October, median O_3 mixing ratios declined while their maxima continued
 141 to rise until November. During December and January, O_3 mixing ratios approached the
 142 values observed at the beginning of the field experiment. While monthly maximum O_3 levels
 143 exceeded 35 ppbv during June to December, the overall frequency distribution indicated that
 144 these occurrences of elevated O_3 were infrequent and represented less than 2.5 % of the time
 145 and less than 5 % during dry months. During the wet months, the median O_3 mixing ratio
 146 remained close to 10 ppbv with the exception of the months of October and November.

Figure 2: Ozone mixing ratios during April 2014 to January 2015: (a) Monthly ozone mixing ratios in ppbv during April 2014 to January 2015. Gray circles indicate minimum and maximum ozone mixing ratios. Black diamonds denote the mean, the boxplot shows lower-quartile, median and upper-quartile ozone mixing ratios. The whiskers indicate 10th and 90th percentiles. Frequency distributions of 30-minute averaged ozone mixing ratios during (b) dry months (Jun–Sept) and (c) wet months. The red lines (right axis) indicate the cumulative frequency distribution.

147 Ozone levels showed a clear diurnal variation in response to source and sink processes
 148 (Fig. 3). Ozone mixing ratios decreased during the night as a result of surface deposition and

chemical reactions with plant-emitted hydrocarbons that were mostly confined in the shallow and stable nocturnal boundary layer (Jardine et al., 2011; Bouvier-Brown et al., 2009). After sunrise, O_3 mixing ratios increased due to photochemical formation and entrainment of O_3 -rich air into the boundary layer and to the forest. During the dry months, which included June to September, mean O_3 mixing ratios were higher than during the wet months (20 versus 15 ppbv). Air masses arriving at the study site most often originated from clean areas where NO_x remained in limited levels to contribute to O_3 formation. The influence of clean air masses was evident in both averaged wet and dry month values that were much lower than O_3 mixing ratios often recorded near populated areas. The lower O_3 mixing ratios during the wet months (i.e., 10–15 ppbv) resulted in response to increased cloud cover that attenuated the actinic irradiance to drive photochemical processes. Similarly, during the wet months maximum diurnal O_3 mixing ratios occurred earlier (plateauing 11:00–15:00 local time – LT) than during the dry months (peak at 16:00 LT). During the dry months forest fires and biomass burning increased NO_x concentrations and consequently contributed to enhanced O_3 formation. Despite its remote location, the study site also experienced some episodes of high O_3 levels during the wet months. Overall, such episodes were not uncommon and provided evidence of the increasingly important influences of human activities on the remote rainforest of the Amazon.

To investigate the potential influence of pollution plumes originating from Manaus and biomass burning associated with human settlements between Manaus and the study site on near-surface O_3 , daytime (06:00 – 18:00 LT) O_3 mixing ratios were segregated as a function of wind direction. During the dry months, elevated O_3 mixing ratios were mostly associated with air masses coming from south-easterly sectors. For such wind directions, the mean O_3 mixing ratio was 20 ppbv. Compared to the wet months, there were also more events during which O_3 levels exceeded one standard deviation from the mean. Similarly, these events occurred mostly during winds from southerly to easterly directions and reached O_3 levels exceeding 80 ppbv during one event (Fig. 3c + d). These high levels of O_3 indicate the influence of pollutants originating from the City of Manaus to the south-southeast.

177 Increased human settlements along the highway from Manaus to the site, which is located to
 178 the east, could also contribute to the northward extension of forest fire plumes and additional
 179 pollution from human activities. In contrast, during the wet months mean O_3 mixing ratio
 180 only reached 10–15 ppbv for all sectors.

Figure 3: Average diel cycle of 30-minute mean ozone mixing ratios (red lines) as well as solar irradiance (black dashed lines) for (a) dry and (b) wet months. Standard deviation is indicated by bars (ozone) and thin dashed lines (solar irradiance). Subplots (c) and (d) display the mean daytime (06:00 LT – 18:00 LT) ozone mixing ratio based on wind direction. The standard deviation of daytime O_3 mixing ratios for each sector is indicated with the blue diamonds and red crosses show values exceeding one standard deviation.

181 3.2. Case studies of ozone enhancements

182 Due to its tropical location, the Amazon region experiences frequent occurrences of deep
 183 and moist convection. In addition to precipitation, storms are associated with downdrafts
 184 capable of generating substantial mass fluxes from the mid-troposphere to the surface. As
 185 air masses descend, O_3 in the atmospheric boundary layer can abruptly increase (e.g., Betts

et al., 2002; Grant et al., 2008) which can be detected by ground-level measurements. Two cases are provided to illustrate the unique signatures of O_3 enhancements associated with convective storms of varying degrees of organization.

3.2.1. *Single storm event*

On 19 June 2014, an isolated MCS with a leading convective line and trailing stratiform precipitation passed through the region around 9:30 LT (Fig. 4 a). The fast moving system produced a precipitation peak of approximately 6 mm within a 30-minute interval, during which the convective line moved over the measurement site with weaker stratiform rain persisting for a few hours thereafter (Fig. 5). During the passage of the convective line, the surface O_3 mixing ratio increased from 5 to more than 20 ppbv with a corresponding decrease in θ_e of approximately 9 K. Equivalent potential temperature is a conserved quantity in updrafts and downdrafts, indicating that the increase in O_3 was caused by the downward transport of air from higher levels in the troposphere. This convective system occurred in the late morning hours and regionally enhanced the atmospheric boundary layer with O_3 mixing ratios of 10 ppbv for the rest of the day.

3.2.2. *Multi-storm day*

On 9 May 2014, convective activity was widespread across the region, but much less organized than on the 19 June case (Fig. 4 b–d). The site was subject to a sequence of precipitation events of increasing strength that were separated by short periods of dry conditions (Fig. 6). Each successive rain event (8:00, 11:30, and 13:30 LT) corresponded to an increase in the O_3 mixing ratio and a decrease in θ_e . Downdrafts associated with the first rain event at 8:00 LT caused an increase of O_3 levels from 2 ppbv to more than 10 ppbv as well as a decrease in θ_e of approximately 4 K. However, the first event produced less than 5 mm of rain and radar reflectivity was weak (Fig. 4). After the event, O_3 mixing ratio decreased to 5 ppbv and θ_e rose in response to strong solar irradiance and photochemical activity. Also, the atmospheric boundary layer depth likely increased. The second precipitation event at 11:30 LT increased surface O_3 levels by 5 ppbv and a larger drop in θ_e than the first event. Rain rates were similar to the first rain event, but the duration of rainfall was longer and

Figure 4: SIPAM S-band (10-cm wavelength) radar images at 0.9° elevation angle for 19 June 2014 and 9 May 2014 at the time of the O_3 enhancement events. The black squares indicate the location of the measurement site and the location of Manaus is indicated by the black circles. The storms travel from north-east to south-west.

the convective system appeared stronger according the radar reflectivity. The third event at 13:30 LT produced the largest rain rates, increased O_3 levels further, and decreased θ_e approximately 10 K below the maximum. This convective system was also the strongest and most widespread of the three events. After 15:00 LT, stratiform rain set in and O_3 mixing ratio decreased towards characteristic nighttime levels.

While each of the individual convective events on 9 May 2014 produced O_3 increases in the order of 10 ppbv, in aggregate, their impacts on surface O_3 were close to the single large increase observed on 19 June 2014. With the passing of each convective storm, vertical gradients and absolute O_3 levels were reduced in the lower troposphere due to vertical redistribution. Therefore, the magnitude of ground-level O_3 enhancements depended on the altitude where air parcels originated in the troposphere. The third and final event on 9 May 2014 (Fig. 6) provided an example of a stronger downdraft emanating from a higher altitude to further increase ground-level O_3 .

Figure 5: Case study of a single storm ozone enhancement on 19 June 2014: (a) Ozone mixing ratio [ppbv], (b) equivalent potential temperature (θ_e , [K]), and (c) 30-minute accumulated precipitation [mm] and solar irradiance [W m⁻²] (red line). The dashed line indicates the times of the radar images in Figure 4.

Figure 6: Case study of a multi-storm day on 9 May 2014.: (a) Ozone mixing ratio [ppbv], (b) equivalent potential temperature (θ_e , [K]), and (c) 30-minute accumulated precipitation [mm] and solar irradiance [W m⁻²] (red line). The dashed lines indicate the times of the radar images in Figure 4.

3.2.3. Dynamics of ozone enhancement events

The magnitude of O_3 enhancement depends on the strength of the downdraft and the origin of O_3 -enriched air parcels transported down to the surface. For the case of 19 June

Figure 7: Contoured frequency with altitude diagram (CFAD) of radar reflectivity observed by the SIPAM S-band radar located in Manaus for $22\text{ km} \times 22\text{ km}$ box centered above ZF2 during a 12-min period, on 19 June 2014. The contours represent the reflectivity occurrence at each height and a minimum count is applied so that the distribution at data sparse heights is not plotted.

2014, contoured-frequency-by-altitude diagrams (CFADs, see Yuter and Houze (1995)), show the storm's evolution between 9:24 and 10:00 LT, i.e., the period when the leading convective line passed over the site (Fig. 7). As the leading line passed over the site (09:24 LT), echo tops reached 12 km but radar reflectivity close to the surface was generally less than 30 dBZ. Twelve minutes later (09:36 LT), echo tops were greater than 14 km and an arm of strong reflectivity starting around 7 km descended to the surface with a large portion of reflectivity values greater than 40 dBZ. This feature persisted into the 09:48 LT volume scan and then disappeared by 10:00 LT as the leading line of the storm passed over the site and a more stratiform distribution of reflectivity (i.e., more tightly grouped contours at lower heights and reflectivity values) was subsequently observed. The descending arm of strong reflectivity was consistent with hydrometeors growing too large to be maintained by the convective updraft, creating a strong downdraft and heavy rain as they fall. The descending arm also coincided with the timing of the O_3 enhancement and θ_e drop (Fig. 5).

Figure 8: Contoured frequency with altitude diagram (CFAD) of radar reflectivity observed by the SIPAM S-band radar located in Manaus for $22\text{ km} \times 22\text{ km}$ box centered above ZF2 during a 12-min period, observing the storm system on 9 May 2014. The contours represent the reflectivity occurrence at each height and a minimum count is applied so that the distribution at data sparse heights is not plotted.

Figure 8 shows the evolution of the three convective systems that passed over the site on 9 May 2014. The first event during 7:36 LT shows echo tops reaching only 8 km and surface reflectivity never exceeding 40 dBz, consistent with the low reflectivity values in Fig. 4 and low rainfall rate in Fig. 6. Similarly, no descending arm was evident, although there appeared to be a broadening of the reflectivity values below 5 km, the nominal 0 °C level in the tropics, which may be indicative of re-evaporation of precipitation and thus downdrafts. While this event appeared to be much weaker than the 19 June 2014 case, it still produced a strong O₃ enhancement and θ_e reduction. Such an increase in O₃ still appears plausible, based on the O₃ mixing ratio profile from the AIRS-Instrument (Atmospheric InfraRed Sounder) on the Aqua satellite of 25 ppbv at approximately 2000 m above ground level. The second event during 11:00 LT had higher echo tops (note that upper level radar data is missing during the 11:48 LT scan) and stronger surface reflectivity than during 8:00 LT. Once again, a weak and more shallow descending arm occurred as the convective system passed over the site. The third and strongest event of 9 May 2014 had consistently high echo tops and the most robust descending arm of the case studies that appeared to be linked to processes above the 0 °C level.

3.2.4. *Contrasting local and basin-scale convection*

The local effects from the passage of convective systems are associated with the large-scale storm dynamics (Fig. 9). On 19 June 2014 (Fig. 9 a) a small, single MCS propagated quickly through the basin and over the site. Conversely, a large basin scale system was present on 9 May 2014 (Fig. 9 b), so that O₃ enhancements likely affected a much larger area of the Amazon basin. However, despite the small spatial extent of individual storms, once occurring simultaneously throughout the basin, these storm types can also substantially and regionally increase ambient O₃ levels in the atmospheric boundary layer.

In addition to the regional extent, large-scale dynamics also impact the photooxidation process discussed in section 3.4. Basin scale convection, produces persistent cloud cover, lowering the solar irradiance for extended periods of time, which can reduce actinic fluxes and the photooxidation of the BVOC. In contrast, local convection events are often followed

by clear conditions shortly after the enhancement of O_3 allowing for photooxidation to occur at high rates. Consequently, the type of convection as well as its spatial distribution within the Amazon basin, influence not only atmospheric chemistry within the atmospheric boundary layer, but can also constitute a mechanism of O_3 downward transport and subsequent destruction on the basin scale.

Figure 9: GOES-13 channel 4 images illustrating large-scale convection in the Amazon basin. (a) 19 June 2014 1400 UTC (10:00 LT), (b) 9 May 2014 1400 UTC (10:00 LT). Overlaid colors show cloud top brightness temperatures below -30°C . The cross indicates the location of the research site.

3.3. Ozone enhancement event characterization

In the tropical troposphere, O_3 mixing ratios increase with altitude while θ_e decreases. During the wet season near Manaus, Kirchhoff et al. (1990) found an average O_3 gradient of 6 ppbv km^{-1} within 3–5 km of the troposphere. Such O_3 vertical distribution resulted in a positive correlation between the strength of O_3 enhancements and the magnitude of change in θ_e (Fig. 10). Between 5 and 10 km, O_3 remained almost invariant with height (Kirchhoff et al., 1990). However, upper tropospheric O_3 mixing ratio for the same altitude exhibited large temporal variability (sometimes exceeding 25 ppbv) due to interactions between convection and vertical O_3 distribution (e.g., Folkins et al., 2002; Folkins and Martin, 2005) and increased O_3 formation from lightning-produced NO_x (Goldenbaum and Dickerson, 1993; Thompson et al., 1997; Zhang et al., 2003). Those variations in O_3 profiles and θ_e gradients

were likely the reasons for the observed scatter in the relationship of O_3 and θ_e changes. Furthermore, they may also help to explain the different magnitude of O_3 enhancements associated with single (e.g., 19 June) versus multiple storm events (e.g., 9 May).

The magnitude of O_3 enhancements depended on the time of day when storms occurred. During 2014, more daytime than nighttime storm events occurred (Fig. 10). This observation is in agreement with the preferential timing of convective precipitation during late morning and early afternoon hours. The nighttime response of O_3 to changes in θ_e appeared to be stronger than during the daytime, which could be in response to temporal O_3 variability in the atmospheric boundary layer. After sunset, O_3 in the stable boundary layer becomes mostly depleted due to dry deposition and chemical reactions while O_3 above the boundary layer does not exhibit much diurnal variability (Kirchhoff et al., 1990). As a result, large O_3 gradients likely developed between air in the stable boundary layer and the mid-troposphere, where the downdrafts originated. Conversely, during the daytime the net effect of O_3 -rich downdrafts was less pronounced as photochemical processes increased O_3 levels in the boundary layer, thereby likely yielding reduced O_3 gradients between the convective boundary layer and the mid-troposphere. The convective boundary layer, whose depths typically reach between 800 and 1200 m, remained well mixed with respect to O_3 . While there seemed to be little difference in the strength of O_3 enhancements between days with the passage of single or multiple convective systems, strong enhancements ($\Delta O_3 > 15$ ppb) for days with multiple events were rare. This finding seems to be counter-intuitive, as more organized and basin scale convection was associated with much stronger precipitation as well as downdraft strengths. However, the repeated passage of convective systems caused increased vertical mixing of mid-tropospheric air towards and into the boundary layer such that mixing ratio gradients between near surface O_3 and upper levels were reduced. It thus diminished the overall magnitude of individual events associated with the more organized and basin scale convection. Storm downdrafts increased O_3 between 5 and 25 ppbv (Fig. 10 b).

The length of time when the atmospheric boundary layer remains enriched with O_3 is needed to investigate whether O_3 enhancements significantly influence regional air chem-

Figure 10: Aggregated changes in ozone during enhancement events from April 2014 to January 2015: (a) Change in ozone with respect to change in equivalent potential temperature for daytime (yellow) and nighttime (blue) cases as well as single (circle) and multiple events (triangle); (b) Frequency distribution of ozone events.

istry. Prior to the event onset, daytime O_3 mixing ratios decreased while θ_e did not change significantly (as illustrated by an extreme case in Fig. 11 a + b) in response to atmospheric boundary layer air swiftly moving with storm updrafts. Stronger winds and updrafts transported warm, moist, and O_3 -depleted in-canopy air to sensor level above the canopy, thus increasing θ_e and decreasing O_3 for short periods of time. During the nighttime, there was no corresponding increases in θ_e due to reduced temperature. This can be explained by the difference of in-canopy gradients of O_3 mixing ratio and temperature as well as moisture, which dominate the observed changes in θ_e .

The median nighttime change in θ_e was smaller than the daytime change (approximately -3 and -5 K), as nighttime values of θ_e are generally smaller and have less temporal variation. Shortly before the start of the event, O_3 mixing ratios decreased during daytime conditions, while θ_e remained virtually unchanged. This was due to the dynamics of the passing storms. While chemical reactions and dry deposition cause noticeable O_3 -gradients within the canopy, the in-canopy air was much better mixed with respect to temperature and humidity. Subsequently, O_3 mixing ratios and θ_e started to change due to storm down-

330 drafts. As storms propagated, downdrafts dominated the transport process. On average,
 331 nighttime median changes of O_3 were greater than daytime changes with approximately 7.5
 332 and 4 ppbv, respectively. Maximum O_3 levels were reached after circa 1 h and 50 minutes
 333 for nighttime and daytime events followed by a gradual decline of O_3 mixing ratios during
 334 daytime conditions, which was likely due to chemical reactions with BVOCs. For nighttime
 335 events, increases in O_3 persisted for two hours.

336 The increase of the median O_3 levels for all events exceeded 5 ppbv, while 25% of all
 337 events exceeded 9 ppbv. Given the range of O_3 changes between 1 and 10 ppbv and typical
 338 ambient O_3 mixing ratios between 5 and 25 ppb, the impact of these events on air chemical
 339 processes cannot be neglected, especially as their influence on O_3 levels was still detectable
 340 for at least two hours after the onset of the event and thus had the potential to affect chemical
 341 reactions for extended periods of time. Similarly, Sigler et al. (2002) have shown that there
 342 is a difference in the diurnal cycle of O_3 mixing ratios for days with and without the passage
 343 of convective systems.

Figure 11: Changes in ozone and equivalent potential temperature (θ_e) during ozone enhancement events: 1-minute averages for (a) ozone and (b) θ_e on 22 Aug 2014, 20:55 LT; (c + d) median change for nighttime events; and (e + f) daytime events from 5-minute averaged data. The colored patches give the interquartile range of events.

3.4. Influences on atmospheric chemistry

The rainforest emits numerous hydrocarbon species including isoprene, monoterpenes (e.g., α -pinene), sesquiterpenes (e.g., caryophyllene), and oxygenated compounds (e.g., methanol). At the study site, the most abundant and important hydrocarbons measured above the rainforest included isoprene and monoterpenes whose daily maximum mixing ratios reached 15 and 2 ppbv, respectively (Fuentes et al., in review). Isoprene and monoterpenes react with O_3 and the reactions provide an important source of HO (Paulson and Orlando, 1996), which can subsequently enhance the oxidation of rainforest-emitted hydrocarbons. To determine the magnitude of HO formation from reactions of O_3 with BVOCs, the HO formation rates were computed following equation 9.

$$\frac{\partial[OH]}{\partial t} = \sum_i^N [BVOC]_i K_i [O_3] \text{Yield}_i \quad (9)$$

N denotes the total number of identified hydrocarbons above the rainforest, $[BVOC]_i$ represents the concentration (molecules cm^{-3}) of speciated hydrocarbon, i (i.e., isoprene, α -pinene, etc.), K_i is the reaction rate coefficient ($\text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$) of $[BVOC]_i$ with O_3 , $[O_3]$ is the O_3 concentration (molecules cm^{-3}), and Yield_i is the HO yield (unitless) from the reaction of $[BVOC]_i$ with O_3 . The speciated monoterpenes measured above the forest (Jardine et al., 2015), associated O_3 reactivities, and HO yields are included in Table 1. Following storms, isoprene and monoterpene mixing ratios exhibited an interquartile ranges of 1.5 to 3.0 and 0.3 to 0.7 ppbv.

Ozone enhancements due to storms resulted in substantial HO production rates. For example, an O_3 enhancement from 5 to 30 ppbv would increase HO production rates from $0.15\text{--}0.29 \times 10^5$ free radicals $\text{cm}^{-3} \text{s}^{-1}$ to $0.88\text{--}1.75 \times 10^5$ free radicals $\text{cm}^{-3} \text{s}^{-1}$ for the range of 1.5 to 3.0 ppbv of isoprene (Fig. 12 a). Likewise, HO formation rates increase from $0.18\text{--}0.42 \times 10^6$ free radicals $\text{cm}^{-3} \text{s}^{-1}$ to $1.08\text{--}2.53 \times 10^5$ free radicals $\text{cm}^{-3} \text{s}^{-1}$, for a monoterpene range of 0.3 to 0.7 ppbv (Fig. 12 b).

These HO formation rates closely compare with estimates obtained for regions supporting intense summertime photochemical activity dominated by enhanced NO_x and BVOC

370 levels (Fuentes et al., 2007). Ozone enhancements also substantially reduced the lifetimes of
 371 isoprene and monoterpenes, defined as $\tau_{Isop} = (K_{Isop} [O_3])^{-1}$ and $\tau_{Mono} = \sum_i^N (K_i [O_3])^{-1}$.
 372 For instance, an O_3 enhancements from 10 to 40 ppbv caused τ_{Isop} to decline from 90 to 20
 373 hours whereas τ_{Mono} decreased from 40 to 8 hours (Fig. 12 c). The reductions in isoprene
 374 and monoterpene lifetimes (Fig. 12) do not include the sinks resulting from reactions with
 375 HO. Nonetheless, in environments such as the rainforest, where BVOCs exist in elevated
 376 concentrations (e.g., Jardine et al., 2015), O_3 initiates a chain of chemical reactions involv-
 377 ing BVOCs that in the process generate not only abundant amounts of HO but also reaction
 378 products which serve as precursors of secondary organic aerosols.

Figure 12: Hydroxyl radical formation rates from the oxidization of (a) isoprene with ozone, (b) monoterpenes with ozone and (c) isoprene and monoterpene lifetimes as a function of ambient ozone mixing ratios.

Figure 13: Hydroxyl radical formation rates [radicals $\text{cm}^{-3} \text{s}^{-1}$] during the single storm day (19 June 2014) in response to (a) ozone, (b) isoprene (red) and monoterpene (yellow) mixing ratios for oxidation of (c) isoprene and (d) monoterpenes. Monoterpene mixing ratios were multiplied by a factor of 3 for scale reasons.

The passage of the storm on 19 June 2014 provides one example of the impact of O₃ enhancement events on HO formation rates (Fig. 13). The increase in O₃ of this event compensated for the decrease in isoprene and monoterpene levels, leading to increased HO formation rates during and after the storm. The increase HO formation rates coincided with a period of low actinic irradiance (as deduced from incoming solar irradiance).

Table 1: Ozone reactivities and HO yields for the speciated hydrocarbons found over the rainforest at the Cuieiras Biological Reserve during the wet months of 2014.

Chemical species	Ozone reactivities [cm ³ molecules ⁻¹ s ⁻¹] ^ψ	HO yield [Unitless]	Reference
Isoprene	1.30 x 10 ⁻¹⁷	0.25	(Paulson et al., 1998)
α-pinene	2.35 x 10 ⁻¹⁷	0.83	(Rickard et al., 1999)
β-pinene	3.79 x 10 ⁻¹⁷	0.35	(Atkinson et al., 1992)
3-Carene	2.35 x 10 ⁻¹⁷	0.86	(Aschmann et al., 2002)
Camphene	9.00 x 10 ⁻¹⁹	0.18	(Atkinson et al., 1992)
Limonene	2.50 x 10 ⁻¹⁶	0.67	(Aschmann et al., 2002)
Sabinene	2.50 x 10 ⁻¹⁶	0.33	(Aschmann et al., 2002)
β-Myrcene	4.70 x 10 ⁻¹⁶	0.63	(Aschmann et al., 2002)
α-Ocimene	5.40 x 10 ⁻¹⁶	0.55	(Aschmann et al., 2002)
Terpinolene	1.90 x 10 ⁻¹⁵	0.74	(Aschmann et al., 2002)
γ-Terpinene	1.40 x 10 ⁻¹⁶	0.81	(Aschmann et al., 2002)

^ψ: Kinetics data are from (Atkinson et al., 2006).

4. Summary and conclusions

Convective storms are ubiquitous features that redistribute O₃ in the tropical troposphere. In the Amazon region, convective downdrafts frequently transport air parcels to the surface that provide distinct signatures of O₃ enhancements. Isolated storms generate

single and abrupt O₃ enhancements whereas convectively active days produce multiple and successive O₃ increases. Depending on the strength of storm downdrafts and height from which air parcels emanate, O₃ enhancements can reach as much as 30 ppbv. Such O₃ enhancements are associated with rapid declines in θ_e , ranging from 3 to 20 K. Radar and θ_e data indicate that air parcels, which transport O₃-rich air to the surface originate 2–7 km above the ground. While there are comparatively few O₃ enhancement events during the nighttime, these events typically lead to greater O₃ enhancements due to the O₃ difference in the atmospheric surface layer and the free troposphere. Following convective storms, the atmospheric boundary layer can be enriched with O₃ for periods lasting >2 hours, the first hour experiencing the greatest O₃ enhancements. Due to their long lifetime and large size, basin scale systems increase cloud cover which reduces photochemical processes for extended times, whereas local systems are often followed by clear conditions and thus enhance photochemistry.

Convective storms sufficiently enhance the atmospheric boundary layer with O₃ to initiate a chain of chemical reactions involving rainforest-emitted hydrocarbons. Reactions of O₃ with hydrocarbons generate substantial amounts of HO which additionally contribute to the oxidation of hydrocarbons. In response to reactions of O₃ with prevailing monoterpenes and isoprene, maximum HO formation rates can reach 6×10^6 radicals cm⁻³ s⁻¹. Moreover, O₃ enhancements can substantially reduce the lifetimes of isoprene and monoterpenes. Therefore, one key conclusion derived from this investigation is that, in the Amazon rainforest, convective systems can transport sufficient O₃ to the canopy to drive oxidation of rainforest-emitted hydrocarbons. It is hypothesized that O₃ enhancement events can thus accelerate the production of SOAs which can activate into cloud condensation nuclei, and thereby might influence cloud formation.

5. Acknowledgments

The U.S. Department of Energy Office of Biological and Environmental Research's Climate and Environmental Sciences Division supported the field studies as part of the GoAmazon 2014/5 project (grant SC0011075). Fundação de Amparo à Pesquisa do Estado de

São Paulo (FAPESP) and Fundação de Amparo à Pesquisa do Estado do Amazonas (FAPEAM) funded the Brazilian component of the field studies. We acknowledge the support from the Central Office of the Large Scale Biosphere Atmosphere Experiment in Amazonia (LBA), the Instituto Nacional de Pesquisas da Amazonia (INPA), and the Universidade do Estado do Amazonia (UEA). The work was conducted under 001030/2012-4 of the Brazilian National Council for Scientific and Technological Development (CNPq). We acknowledge logistical support from the ARM Climate Research Facility. Juliane Mercer and Brazilian students Raoni Aquino Silva de Santana, Debora Tanya, and Francisco assisted with the field studies. Satellite images are courtesy of Instituto Nacional de Pesquisas Espaciais (INPA) Divisão de Satélites e Sistemas Ambientais. Radar data are courtesy of SIPAM and Hannah Upton and Aaron Funk of Texas A&M University. The SIPAM radar analysis and imagery were completed with support from DOE ASR grant DE-SC0008561 and the Texas A&M University-CAPES Collaborative Research Grant Program. LATM acknowledges the support of FAPESP (Grant 2009/15235-8). PCS acknowledges the support from the Alexander von Humboldt Foundation.

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