UNDERSTANDING THE OXIDATION OF BIOGENIC VOLATILE ORGANIC COMPOUNDS IN THE AMAZON RAINFOREST: FIELD OBSERVATIONS AND MODEL RESULTS

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Abstract

Biogenic volatile organic compounds (BVOCs) in the forested environments are receiving increased attention as more information emerges about their local, regional impacts on air quality and climate. The formation of tropospheric ozone (O$_3$) and the generation of secondary organic aerosols (SOA) are among the many processes influenced by oxidation of VOCs. Although large amounts of work have been done in this field, the chemical processes associated with biogenic VOCs still remain poorly understood in forested environments. An accurate understanding of the VOCs oxidation is necessary for quantitative predictions of the concentrations of particulate matter, oxidation capacity, and consequent environmental and climate impacts. In this work, we focus on: (i) the characterization of the meteorological and chemical background conditions in the Amazon rainforest using field data; (ii) the environmental and biological controls on the temporal variations in the most abundant BVOC species – isoprene; (iii) linking turbulence and chemistry to evaluate the in-canopy mixing and chemical processes using a one-dimensional canopy model.

As human encroachment increases in the Amazon rain forest, it is important to determine how anthropogenic emissions of reactive gases affect regional atmospheric chemistry. In the present study, we investigate the extent to which urban air plumes modify the levels of ozone (O$_3$) and nitrogen oxides (NO$_X$) in the downwind rain forest. The median mixing ratios of the background O$_3$, NO$_X$, and NO$_X$ oxidation products (NO$_Z$) were 20 (15 parts per billion on a volume basis, ppbv), 0.6 ppbv (0.6 ppbv), and 1.0 ppbv (0.5 ppbv) during the dry (wet) season at the study site. Compared to the background environment, air plumes from the city of Manaus had enhanced median mixing ratios for O$_3$ and NO$_Z$ by 30-50% and 40-90%, respectively. However, the enhancements of NO$_X$ in the air plumes were less than 20%, indicating that the majority of NO$_X$ was chemically converted to O$_3$ and NO$_Z$ during transport. Results from a photochemical model showed that an injection of 8 ppbv of NO$_X$ into the rain forest can cause up to 260% and 150% increases in O$_3$ and hydroxyl radical (OH) levels compared to the background conditions, indicating the likely extent that NO$_X$ can modify the air quality and oxidative capacity in the Amazon rain forest. Slopes of the O$_3$-temperature linear relationships increased with NO$_X$ levels from 3.7 to 6.5 ppbv per degree Kelvin during the dry season and 1.7 to 5.5 ppbv per degree Kelvin during the wet
season. Average rates of change of the slope with respect to $\text{NO}_Z$ were approximately 1.8 and 2.3 times higher than those with respect to $\text{NO}_X$ for the dry and wet seasons. One key conclusion of this study is that $\text{NO}_Z$ substantially contributed to the $\text{O}_3$ ozone formation response to temperature under enhanced $\text{NO}_X$ nitrogen oxide conditions in the forested environment.

The Amazon rain forest is a major global isoprene source, but little is known about its seasonal ambient concentration patterns. To investigate the environmental and phenological controls over isoprene seasonality, we measured isoprene mixing ratios, concurrent meteorological data, and leaf area indices from April 2014 to January 2015 above a rain forest in the central Amazon, Brazil. Daytime median isoprene mixing ratios varied throughout the year by a factor of two. The isoprene seasonal pattern was not solely driven by sunlight and temperature. Leaf age and quantity also contributed to the seasonal variations of isoprene concentrations, suggesting leaf phenology was a crucial variable needed to correctly estimate isoprene emissions. A zero-dimensional model incorporating the estimated emissions, atmospheric boundary layer dynamics, and air chemistry was used to assess the contributions of each process on the variability of isoprene. Surface deposition was an important sink mechanism and accounted for 78% of the nighttime loss of isoprene. Also, chemical reactions destroyed isoprene and during 6:00 to 18:00 hours local time 56, 77, 69, and 69% of the emitted isoprene was chemically consumed in June, September, December, and January, respectively. Entrainment fluxes from the residual layer contributed 34% to the early-morning above-canopy isoprene mixing ratios. Sensitivity analysis showed that hydroxyl radical (HO) recycling and segregation of isoprene-HO played relatively lesser roles (up to 16%) in regulating ambient isoprene levels. Nitric oxide (NO) levels dominated isoprene chemical reaction pathways associated with consumption and production of HO under low-NO and high volatile organic compound (VOC) conditions. While surface deposition and oxidative processes altered isoprene levels, the relative importance of these factors varied seasonally with leaf phenology playing a more important role.

Many scientific questions and uncertainties remain concerning in-canopy processes and forest-atmosphere exchange. Among those, chemical transformations and turbulent vertical mixing that occurs within and above the canopy play an important role in the formation pathways of SOA. We evaluate the eddy diffusivity parameterization in a one-dimensional coupled canopy-chemistry mode (CACHE). In-canopy mixing is weak in the original CACHE model, indicating the original K-theory parameterization may not be adequate to capture the turbulence within the canopy. The CACHE model with the observed eddy diffusivity enhanced turbulence within the canopy and effectively reduced in-canopy concentrations and weakened the vertical gradient for OH, isoprene, $\alpha$-pinene, limonene, and formaldehyde. The performances of the condensed chemical mechanism (RACM2) and nearly-explicit master chemical mechanism (MCM) in simulating the BVOC oxidation are evaluated. Both RACM2 and MCM show similar predictions of $\text{O}_3$, isoprene, monoterpenes, and formaldehyde. However, The MCM predicted higher OH and NO concentrations than RACM2,
indicating that the OH-NOX chemistry is sensitive to the choice of chemical mechanisms in the forested environment. We also access the dependence of OH on the ambient levels of NO. The classical dependence of OH on NO were reproduced by both RACM2 and MCM, with a threshold NO value of 1.0 ppbv above the canopy. Accompanying the increase of NO concentration from 0.2 ppbv to 1.0 ppbv, the OH concentrations above the canopy increased by 150% (from $0.8 \times 10^6$ to $2.0 \times 10^6$) predicted by CACHE with the MCM, highlighting the important role of NOX in sustaining OH concentrations in the remote Amazon rain forest.
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Thank you.
An expert is a person who has made all the mistakes that can be made in a very narrow field.

—Niels Bohr
Chapter 1

Introduction

Chemicals produced by the biosphere are emitted into the air where they can have a substantial impact on the chemistry of the atmosphere. These biogenic gases are dominated by volatile organic compounds (VOCs) both in total mass and number of compounds (Guenther et al., 2006). Biogenic VOCs (BVOCs) in the forested environments are receiving increased attention as more information emerges about their local, regional impacts on air quality and climate. The formation of tropospheric ozone and the generation of new aerosol particles are among the many processes influenced by oxidation of VOCs (Claeys, 2004). Although large amounts of work have been done in this field, the chemical processes associated with BVOCs still remain poorly understood. Hence, an accurate understanding of BVOCs is necessary for quantitative predictions of particulate matter, oxidation capacity, and consequent environmental and climate impacts. In an attempt to improve the current understanding of BVOCs, this study focuses on the characterization and modeling of the sources and sinks for BVOCs and key oxidant (i.e. ozone and hydroxyl radicals) in the Amazon rain forest.

The Amazon basin behaves as a giant biogeochemical reactor with biogenic emissions of VOCs and aerosol particles, in combination with high absolute humidity and strong solar radiation, maintaining chemical and physical cycles that sustain the aerosol particle population and the clouds (Fuentes et al., 2016). Low atmospheric concentrations of nitrogen oxides (NO+NO₂ = NOₓ ≤ 1 ppbv, parts per billion by volume) indicate little human influence in the interior of the rain forest (Kuhn et al., 2007; Gerken et al., 2016). Therefore, the Amazon rain forest is ideally located for studying the ecosystem’s interactions with the atmosphere in the absence of human influence. As increasing human encroachments in the forest, at times, there are intrusion of polluted air masses from the city of Manaus (Martin...
et al., 2017) or biomass burning (Artaxo et al., 2013). These human-induced changes to the atmosphere can have impacts on the chemical pathways of BVOCs (Liu et al., 2016) and cloud properties in the Amazon rain forest.

The most abundant biogenic VOCs, accounting for more than half of their global emissions, are terpenoids. Terpenoids include compounds consisting of one to several isoprene units of \( \text{C}_5\text{H}_8 \), e.g., isoprene \( (\text{C}_5\text{H}_8) \), monoterpenes \( (\text{C}_{10}\text{H}_{16}) \), and sesquiterpenes \( (\text{C}_{15}\text{H}_{24}) \). The global emissions of isoprene are estimated to account for almost 50% of the total biogenic VOC flux (Guenther et al., 2006). Isoprene is widely known as a significant source of secondary organic aerosols (Claeys, 2004) and possibly help maintain the hydroxyl radical (OH) concentrations (Taraborrelli et al., 2012). The Amazon rain forest is a major global isoprene source. Thus, it is necessary to characterize physical and chemical processes controlling isoprene levels in the Amazon rain forest.

The OH is a key oxidant in the Earth’s atmosphere and responsible for the degradation of VOCs. Lelieveld et al. (2008) reported much higher measured OH measurements in the Amazon rainforest (Taraborrelli et al., 2012). However, the accuracy of the measurements is questionable due to interference issues (Feiner et al., 2016). There are many other aspects needed to be considered for better understanding of the OH concentrations. First, Hofzumahaus et al. (2009) proposed that additional possible OH source could derive from the recycling of peroxy radicals \( (\text{RO}_2) \) to hydroperoxy radicals \( (\text{HO}_2) \) and subsequently conversion of \( \text{HO}_2 \) radicals to OH via reaction with nitric oxide (NO). Second, the interaction of upward— and downward—moving eddies can produce incomplete mixing of isoprene and OH, slowing down the reaction rates (Krol et al., 2000; Kim et al., 2016). In short, possible new mechanisms for OH production under atmospheric conditions, possible artifacts in the measurements, and OH-isoprene segregation all remain to be reconciled.

One-dimensional models are a useful tool to investigate BVOC chemistry within and above forests (Forkel et al., 2006; Wolfe and Thornton, 2011a; Bryan et al., 2012; Pratt et al., 2012; Hu et al., 2013; Saylor, 2013; Ashworth et al., 2015). There are two main sources of uncertainties in these models. First, the first-order flux-gradient relationship (K-theory) has been found to break down completely within forest canopies, which is shown by frequent observations of counter-gradient fluxes in forests (Denmead, 1984; Denmead and Bradley, 1985, 1987; Thurtell, 1988; Gao et al., 1989). Second, most of the models use condensed chemical mechanisms, which lack key reactions of major oxygenated VOCs and could lead to missing significant sources and sinks for OH or other oxidation products.
As described thus far, the characterization and modeling of the BVOC chemistry in the Amazon rain forest still has room for improvements. Chapter 2 investigates the extent that the urban air plumes modify the atmospheric chemistry in the remote atmosphere of the downwind rain forest by comparing two data sets obtained from a clean site ZF2 and a frequently polluted site T3. Chapter 3 investigates the environmental and phenological controls over isoprene seasonality using a year-round isoprene dataset and a box model. Chapter 4 evaluates the turbulent mixing parameterization and chemical mechanisms in a one-dimensional model. The dependence of OH on NO levels are assessed by the model.
Chapter 2

Influences of nitrogen oxides and isoprene on ozone-temperature relationships in the Amazon rain forest

2.1 Introduction

In the Amazon rain forest, the year-round high temperature and insolation promote rapid chemical reactions with biogenic volatile organic compounds (BVOCs), making the within-canopy and overlying atmosphere behave like a photochemical reactor. Such reactions contribute to the formation of oxidants and aerosols, and therefore can influence regional weather and climate. Within the central Amazon forest lies the city of Manaus (Fig 2.1a) whose current population is 2.5 million inhabitants (Martin et al., 2017). Since the 1970s Manaus has grown explosively in terms of population and its land use currently encompasses residential, commercial, and industrial zones in an area over 400 km$^2$ in extent. As a result, emissions of pollutants form air plumes that are carried away from the city by trade winds to the nearby rain forest. Given that tropical forests everywhere are threatened by human encroachment (Soares-Filho et al., 2006; Malhi et al., 2008), it is necessary to assess how and to what extent urban air plumes laden with pollutants and aerosols influence the composition and aerosol loadings of the regional atmosphere.

Previous studies have investigated the air chemistry characteristics of urban plumes in
Manaus and their impacts on the oxidant and aerosol formation in the surrounding Amazon rain forest (Kuhn et al., 2010; Trebs et al., 2012; Thalman et al., 2017; de Sá et al., 2017; Palm et al., 2018; Liu et al., 2018). Due to the proliferation of industries in this equatorial environment and associated population growth, the electricity demand from both industry and households is high in Manaus. Petroleum-burning power plants supply electricity and, combined with heavy vehicular traffic, emit primary air pollutants such as nitrogen oxides (NO\(_X\) = nitric oxide (NO) + nitrogen dioxide (NO\(_2\))), sulfur dioxide (SO\(_2\)), ozone (O\(_3\)), particulate matter (PM\(_{2.5}\), PM\(_{10}\)), and VOCs (Kuhn et al., 2010; Rafee et al., 2017). Urban-emitted pollutants are often transported by easterly/northeasterly winds hundreds of kilometers to the west or southwest. The long-distance transported pollutants can perturb the air chemistry in the atmospheric boundary layer above the surrounding rain forest (Kuhn et al., 2010). Urban pollutant plumes, particularly those burdened with elevated NO\(_X\) concentrations, can substantially amplify hydroxyl radical (OH) formation (Liu et al., 2018), and alter chemical reaction pathways of biogenic VOC oxidation (Liu et al., 2016; de Sá et al., 2017). The ensuing chemical reactions consequently influence secondary organic aerosol and cloud condensation nuclei formation (Trebs et al., 2012; Cecchini et al., 2016; Palm et al., 2018; Thalman et al., 2017; Cirino et al., 2018).

One measure of the modified chemistry above forests in response to urban emissions is the O\(_3\) yield. Surface O\(_3\) is produced via photooxidation of VOCs in the presence of NO\(_X\). On one hand, in the remote rain forest, the NO\(_X\) levels remain near the crossover point from contributing to net O\(_3\) loss to net O\(_3\) production due to the weak sources (Torres and Buchan, 1988). Therefore, plant-emitted VOCs contribute little to O\(_3\) formation in the atmospheric boundary layer overlying the remote rain forest (Jacob and Wofsy, 1988; Wu et al., 2008). On the other hand, the photooxidation of VOCs in the presence of sufficient NO\(_X\) results in substantially elevated O\(_3\) levels. Isoprene is the most abundant BVOC species in the Amazon rain forest (Wei et al., 2018) and can play a key role in O\(_3\) production under sufficient NO\(_X\) (Fiore, 2005). Therefore, anthropogenic NO\(_X\) injection into the tropical forest is assumed to strongly impact O\(_3\) formation.

The perennial warm conditions above the rain forest can further amplify O\(_3\) formation. The formation of ground-level O\(_3\) increases linearly with rising temperature over hourly (Bloomer et al., 2009), daily (Sillman and Samson, 1995; Steiner et al., 2010; Day et al., 2008; Romer et al., 2018), monthly (Rasmussen et al., 2012), and interannual (Fu et al., 2015) time scales. The reported O\(_3\)-temperature slope ranges from 2 to 8 ppbv K\(^{-1}\), depending
on chemical and meteorological conditions (Pusede et al., 2015). Most studies regarding the 
O$_3$-temperature relationships have explored urban areas where NO$_X$ levels are ordinarily 
high. There is a dearth of information on the O$_3$-temperature relationship in environments 
such as the rain forest where low NO$_X$ levels (< 1 ppbv) ordinarily prevail in the presence 
of a major source of plant-emitted VOCs (Fuentes et al., 2016). It is necessary to discern the 
functional relationship of O$_3$ formation because the Amazon rain forest is warming at a pace 
of 0.25 °C per decade (Malhi and Wright, 2004), and climate predictions indicate that the 
ambient temperature in the Amazon rain forest will rise 3.3 °C by the end of this century 
(Solomon et al., 2007).

One important approach to quantify the O$_3$-temperature relationship is to investigate the 
sensitivity of O$_3$ yields to temperature changes. This sensitivity is largely dictated by NO$_X$ 
levels (Pusede et al., 2015) as demonstrated by the increased O$_3$-temperature slope from low 
to high NO$_X$ levels (Bloomer et al., 2009; Steiner et al., 2010; LaFranchi et al., 2011; Pusede 
et al., 2014; Romer et al., 2018). In addition, the sensitivity of O$_3$ to temperature is also 
influenced by NO$_X$ oxidation products (also referred to as NO$_Z$) because their reactions with 
OH or thermal decomposition can recycle NO$_X$ under warm conditions and thus influence O$_3$ 
production (Jacob et al., 1993; Fiore, 2005; Ito et al., 2009; Jacob and Winner, 2009; Steiner 
et al., 2010). The main NO$_Z$ species showing temperature-dependence and likely influencing 
O$_3$-temperature relationships in forested environments are organic nitrates (RONO$_2$) (Day 
et al., 2008; Browne et al., 2013) and peroxyacetyl nitrate (PAN) (Singh et al., 1990; Jacob 
and Wofsy, 1990). Hence, it is necessary to evaluate the extent that anthropogenic NO$_X$ and 
VOCs oxidation products (mainly RONO$_2$ and PAN) alter the O$_3$ sensitivity to temperature 
in the Amazon rain forest.

The Amazon rain forest provides a unique location to the atmospheric chemistry absent 
of anthropogenic influences in the low-NO$_X$ forested environments with modifications to at-
mospheric composition as a result of urban plumes due to human activities. In this study, 
we present trace gas and meteorological datasets obtained from two study sites during the 
2014/5 GoAmazon field campaign. The ZF2 site, largely absent of the influence from Man-
aus, serves as a continental reference of atmospheric properties under background conditions. 
The T3 site is downwind of Manaus and provides the opportunity to study the effects of 
the Manaus plume on the ‘pristine’ environment. By comparing O$_3$, NO$_X$, and isoprene 
data from the two sites, we can learn how and to what extent the urban plumes modify the 
background atmospheric conditions in the rain forest. We also examine the instantaneous
production rates and production efficiency of O\textsubscript{3} as a function of NO\textsubscript{X} to determine how the urban plumes influence O\textsubscript{3} production through chemistry. We then present the sensitivity of O\textsubscript{3} formation to temperature to estimate O\textsubscript{3} production rates as a function of the observed NO\textsubscript{X} levels.

2.2 Methodology

2.2.1 Description of study sites

The locations of Manaus and the two research sites (ZF2 and T3) are shown in Figure 2.1. Site T3 is in a 2.5 km $\times$ 2 km pasture (S 3°12.80', E 60°35.92'), situated 2 km to the north of a lightly-traveled two-lane road that connects the city of Manaus to Manacapuru (Martin et al., 2016). It is 70 km downwind of the city of Manaus, representing several hours of air parcel travel time depending on the daily wind speeds (Kuhn et al., 2010). Measurements were performed as part of the Atmospheric Radiation Measurement (ARM) Climate Research Facility of the United States Department of Energy (Mather and Voyles, 2013) from January 2014 to June 2015. The instruments were part of the ARM Mobile Facility One and the ARM Mobile Aerosol Observing System (MAOS) (Martin et al., 2016).

Site ZF2 is a forest located the Cueiras Biological Reserve (N 2°36.11', E 60°12.56') which covers approximately 230 km\textsuperscript{2} of largely undisturbed lowland evergreen trees with a canopy height of about 35 m (Luizao, 1995). The ZF2 site is approximately 60 km north-northwest of the city of Manaus (Figure 2.1). Due to prevailing easterly winds, the air masses arriving at the site mostly come from vast expanses of undisturbed rain forest. However, the site occasionally experiences the influences of biomass burning during the dry season when high NO (> 2 ppbv) and O\textsubscript{3} (> 50 ppbv) levels were recorded (Gerken et al., 2016). Measurements were carried out from March 2014 to January 2015 at the ZF2 site.

2.2.2 Measurements and data analysis

2.2.2.1 Meteorological and trace gas measurements

At the T3 study site, O\textsubscript{3} measurements were performed using a gas analyzer (model 49i, Thermo Fisher Scientific Inc., Waltham, MA) at a frequency of 1 Hz from January 2014 to June 2015. Instrumentation for measuring the mixing ratios of NO, NO\textsubscript{2}, and the total odd-
nitrogen compounds (NO\textsubscript{Y}) was part of the MAOS package. The NO, NO\textsubscript{2}, and NO\textsubscript{Y} data were collected every 10 seconds by a two-channel nitrogen oxide analyzer from February 2014 to June 2015. The main trace gas inlet (12.7-mm PFA; with a flow rate of 13 standard liters per minute (Lpm)) was placed 10 meters above ground. The operational detection limits of NO and NO\textsubscript{Y} were 70 pptv (parts per trillion by volume) and 100 pptv, respectively. The NO\textsubscript{Y} mixing ratios were smoothed by applying a 30-minute median filter to minimize the contribution of any local emissions. Additional information on the ARM Facility can be found in Miller and Slingo (2007).

At the ZF2 study site, a 50-m tower served as a platform to mount meteorological instruments and air samplers. A proton-transfer-reaction mass spectrometer (PTR-MS, Ionicon Analytik GmbH, Austria) (Jordan et al., 2009) was employed to measure the ambient levels of isoprene (C\textsubscript{5}H\textsubscript{8}). The PTR-MS was operated at a drift tube temperature of 80 °C and a drift tube pressure of 2.2 mbar. The drift tube voltage was set to 550 V. The inlet system of the PTR-MS subsampled air from the main trace gas sampling line. The inlet system inside the container was maintained above 27 °C to prevent condensation. Isoprene was detected as the C\textsubscript{5}H\textsubscript{9}\textsuperscript{+} ion. Details about the trace gas and meteorological measurements at ZF2 site can be found in Fuentes et al. (2016), Gerken et al. (2016), Freire et al. (2017), and Wei et al. (2018). The isoprene data at the T3 site were collected from 18 February to 31 March 2014 (IOP1), and from 17 August to 16 October 16 2014 (IOP2). Meteorological data at the T3 site were collected using the ARM Climate Research Facility. Temperature at 2 m and wind speed and direction at 10 m above the surface were measured on a 10-m tower throughout 2014. The meteorological data sets employed in this study were obtained through the ARM data archive.

2.2.2.2 Data analysis

All the data, including trace gas and meteorological data, were processed to generate 30-minute averages. Data collected during the stormy periods were removed because convective mesoscale systems transport O\textsubscript{3} rich air from aloft to the surface and increase surface O\textsubscript{3} concentrations (Gerken et al., 2016). The period from June to September 2014 is defined as the dry season, and the rest of the year is classified as the ‘wet season’ on the basis of substantially reduced rainfall during these months (Fuentes et al., 2016). The data were segregated into clean (background) and polluted conditions based on measured surface wind speed and directions for the T3 site. The main source of pollution, the city of Manaus, is
located to the east. Wind directions of 45 to 135 degrees with wind speeds greater than 2.5 m s$^{-1}$ were classified as potentially polluted conditions. The reason for choosing 2.5 m s$^{-1}$ as a criteria is that the distance between Manaus and the T3 site is 70 km, and the lifetime of NO$_X$ can be up to 8 hours. Therefore, the wind speed for NO$_X$ to travel from Manaus to the T3 study site before being completely consumed is at least 70 km per 8 hours, i.e. 2.5 m s$^{-1}$. Data obtained when air flow came from other directions with wind speed greater than 2.5 m s$^{-1}$ or when wind speeds were less than 1 m s$^{-1}$ were considered as clean (background) conditions.

2.2.3 Zero-dimensional photochemical model

2.2.3.1 Net ozone production rates

A zero-dimensional photochemical model based on the Regional Atmospheric Chemistry Mechanism, version 2 (Goliff et al., 2013) was executed to determine the net production rate of O$_3$ (PO$_3$). Inputs to the model were observed concentrations of O$_3$, NO$_X$, CO, and isoprene as well as observed temperature and pressure. Photolysis frequencies are calculated using tested algorithms (Madronich and Flocke, 1999; Seefeld and Stockwell, 1999), and required cross section and quantum yields as a function of wavelength ($\lambda$), $\sigma$ ($\lambda$) and $\phi$($\lambda$), respectively, are taken from previous studies (Sander et al., 2006). The model computes production and loss rates of all chemical species. The production (or loss) rates of each species are calculated as the sum of reaction rates of chemical reactions in which the individual species is produced (or consumed). The PO$_3$ and the production rates of NO$_Z$ (PNO$_Z$) are reported in this study. The NO$_Z$ are mainly comprised of nitric acid (HNO$_3$), PAN, RONO$_2$, nitrous acid (HONO), nitrate radical (NO$_3$), nitrogen pentoxide (N$_2$O$_5$), and particulate nitrates. Because we focus on daytime chemistry in this study, nighttime reactions of NO$_3$ and N$_2$O$_5$ are not considered. Also, the daytime loss of NO$_X$ via HONO production is also ignored because of its rapid photolysis. The particulate nitrates are not considered here. The PO$_3$ is calculated as the differences between the production ($P(O_3)$) and loss ($L(O_3)$) rates of O$_3$:

$$PO_3 = P(O_3) - L(O_3) \quad (2.1)$$

The PNO$_Z$ is the sum of the production rates of HNO$_3$, PAN, and RONO$_2$:

$$PNOZ = P(HNO_3) + P(PAN) + P(RONO_2) \quad (2.2)$$
2.2.3.2 Time evolution of chemical species

The zero-dimensional model was used to follow the time evolution of an air parcel after NO\textsubscript{X} is injected into the clean forest. The model was initialized with the gas concentrations listed in Table 2.1 (Supplement 2.5.1). The initial isoprene mixing ratio of 5 ppbv remained constant throughout the calculation to simulate the high-VOC environment in the ZF2 forest (Fuentes et al., 2016). An initial O\textsubscript{3} mixing ratio of 15 ppbv was used to simulate the background O\textsubscript{3} in the Amazon rain forest. Four simulations were executed with different initial NO\textsubscript{X} levels to determine the influences of NO\textsubscript{X} on O\textsubscript{3} formation. For the base simulations, the initial mixing ratio of NO\textsubscript{X} was set to 0.6 ppbv to represent the unpolluted conditions experienced at the study site. For the other three simulations, the initial NO\textsubscript{X} levels of 4, 6, and 8 ppbv were included to represent the conditions associated with air flows coming from the city of Manaus to the rain forest. Model simulations were performed for the time periods comparable to the temporal transport scales associated with air flows from Manaus to the study site. With an average wind speed of 3 m s\textsuperscript{-1}, computed from the data obtained at the T3 study site (Figure 2.1b), the transport times of approximately 6 hours were estimated. Therefore, model simulations were executed for 6 hours for the period from 10:00 to 16:00 hours local time. The start of the simulations represented the starting point of the air plume, and the end of the simulation likely captured the chemical conditions at the T3 site. An air dilution rate of 0.2 hour\textsuperscript{-1} was considered in the simulations to include the plume dilution effect (Kleinman et al., 2002). Because we focus on the chemical evolution of the air mass, no mixing or deposition was considered in the calculations.

2.2.3.3 Ozone production efficiency (OPE)

The OPE is used to specifically examine the number of O\textsubscript{3} molecules produced from the consumed NO\textsubscript{X}, and can be deduced from the atmospheric observations of O\textsubscript{3}, NO\textsubscript{X}, and NO\textsubscript{Y} (Trainer et al., 1993). In this study, OPE was estimated as the slope of a graph of O\textsubscript{3} concentration versus NO\textsubscript{Z}. The NO\textsubscript{Z} concentrations were determined as the difference between NO\textsubscript{Y} and NO\textsubscript{X} measurements (i.e., NO\textsubscript{Z} = NO\textsubscript{Y} - NO\textsubscript{X}). The box model allowed the calculation of OPE using the equation:

\[
\text{OPE} = \frac{P_{O_3}}{P_{NO_Z}}
\]  

(2.3)
To investigate how NO\textsubscript{X} levels influence PO\textsubscript{3} and OPE, several simulations were performed to consider initial NO\textsubscript{X} mixing ratios ranging from 0.05 to 70 ppbv.

### 2.3 Results and Discussion

In section 2.3.1, we first compare the O\textsubscript{3} and isoprene data obtained from the T3 and ZF2 sites to show how chemical conditions differ between the 'pristine' forested site ZF2 and the downwind pasture site T3. We then segregated the O\textsubscript{3} and NO\textsubscript{X} data obtained at the T3 site into clean and polluted conditions to investigate to what extent pollution from the city of Manaus alters the levels of O\textsubscript{3} and NO\textsubscript{X} at the T3 study site. In section 2.3.2, we used a box model constrained by observations to calculate the O\textsubscript{3} and OH levels as a function of NO\textsubscript{X}. In section 2.3.3, we investigated the O\textsubscript{3}-temperature relationship as a function of NO\textsubscript{X} and NO\textsubscript{Z}.

#### 2.3.1 Background conditions and air pollutants from Manaus

##### 2.3.1.1 Trace gas comparison between T3 and ZF2

The dominant wind directions at the two sites were from 45\textdegree{} to 135\textdegree{}, with frequencies of 44\% for the T3 site and 43\% for the ZF2 site (Figure 2.1b, c). The most frequent wind directions were 80\textdegree{} and 90\textdegree{} for T3 and ZF2, respectively, and wind speed mostly ranged from 0 to 2 m s\textsuperscript{-1} at the T3 site and from 2 to 4 m s\textsuperscript{-1} at the ZF2 site (Figure 2.1b, c). The wind speed was generally lower at the T3 site because measurements were made at 10 meters above the ground whereas at the ZF2 site wind was measured at approximately 40 meters above the ground (i.e., above the forest canopy).

On the seasonal scale, O\textsubscript{3} mixing ratios showed similar patterns for both sites with higher values during the dry season (Figure 2.2a, b), mainly due to greater photochemical production of O\textsubscript{3} associated with less frequent cloudiness and stronger solar radiation (Supplement 2.5.2). The maximum O\textsubscript{3} mixing ratios in September were 38.0 ± 11.6 ppbv for the T3 site and 23.0 ± 4.2 ppbv for the ZF2 site. Ozone mixing ratios at the T3 site were 34\% (November) - 100\% (May and December) higher than the ZF2 site on average. On a diurnal scale, O\textsubscript{3} mixing ratios at the T3 site showed substantial diel variations with the median values varying between 5 and 23 ppbv for the wet season and 5 to 32 ppbv for the dry season, while the diel variations of O\textsubscript{3} mixing ratios at ZF2 were smaller; 9 to 12 ppbv for the wet season.
and 10 to 20 ppbv for the dry season (Figure 2.2c, d). Frequency distributions (Figure 2.2e, f) showed that O$_3$ mixing ratios ranged from 5 to 60 ppbv at the T3 site and from 2 to 40 ppbv at the ZF2 site. Even though the most abundant mixing ratios at the two sites were similar to each other – (approximately 10 ppbv for the wet season and 20 ppbv for the dry season – the distribution of O$_3$ at the T3 site was flatter because of frequent occurrences of elevated O$_3$ levels. In summary, O$_3$ mixing ratios at the T3 site were substantially higher on seasonal and diel time scales and displayed greater variations. Given the similar meteorological conditions at both sites (Supplement 2.5.2), the higher O$_3$ mixing ratios at the T3 site likely resulted in response to transport from Manaus and local O$_3$ formation involving reactions of elevated NO$_X$ and isoprene. The region between Manaus and the T3 site was largely forested (Liu et al., 2018), so high levels of biogenic VOCs were expected. The NO$_X$ in the air plumes then could substantially elevate the O$_3$ levels in the presence of biogenic VOCs before arriving at the T3 site during the daytime (Kuhn et al., 2010). As for the nighttime, O$_3$ likely reacted to generate NO$_3$ through the reaction with NO$_2$. The results suggest that NO$_X$ contributed substantially to influencing the chemistry of O$_3$ and therefore

Figure 2.1: (a) The locations of the City of Manaus (marked as S3), the T3 site, and the ZF2 site (all study sites are denoted with red dots); the inset is a picture of the ARM instrumentation at the T3 site; (b) wind roses for the T3 site during 2014; (c) wind roses for the ZF2 site during 2014. The color bar scale is in the units of m per s.
led to different diel cycles and frequency distributions of \( \text{O}_3 \).

It is useful to examine at the characteristics of \( \text{NO}_X \) and VOCs for the T3 and ZF2 sites to better understand the \( \text{O}_3 \) differences between the two sites. During both measurement periods (February 18 to March 31 and August 18 to October 16, 2014), isoprene mixing ratios were higher at the ZF2 site than at the T3 site (Figure 2.3a, b), with maximum median values of 6 ppbv and 7 ppbv for the wet and dry seasons. The maximum median isoprene mixing ratios at T3 were 1.5 ppbv for the wet season and 4 ppbv for the dry season.
Figure 2.3: The diel variations in average isoprene mixing ratios at the T3 site (a) and the ZF2 site (b); the shaded areas indicate the standard deviations. Frequency distributions of daytime (10:00 - 16:00 local time) isoprene mixing ratios at the T3 site (c) and the ZF2 site (d).

(Figure 2.3a, b). The lower isoprene mixing ratios at the T3 site also demonstrated (Figure 2.3c) that the most abundant values of isoprene were 1 ppbv and 2 ppbv for wet and dry season, respectively. The frequency distributions at the ZF2 site were flatter (Figure 2.3d), indicating frequent occurrences of high isoprene levels. This is primarily because: (1) the isoprene measurements at the ZF2 site were made just above the canopy which is the source of isoprene; (2) pasture or agricultural fields have low isoprene emissions compared to tropical rain forests (Guenther et al., 2012). In terms of seasonality, isoprene temporal variations at the ZF2 site were small due to the suppressed isoprene emission in the beginning of the dry season (June) and strong emission in the wet season (December), which was associated with the phenological cycle of leaves in the Amazon rain forest (Wei et al., 2018). The seasonality of isoprene at the T3 site varied by a factor of 2 (Figure 2.3a, b).

The frequency distributions of NO, NO$_2$ and NO$_X$ were similar between wet and dry
seasons, with the most abundant values of 0.04 ppbv, 0.3 ppbv, and 0.5 ppbv, respectively (Figure 2.4a-c), indicating the NO\textsubscript{X} levels were not highly meteorology-dependent. The main NO\textsubscript{X} sources at the T3 site are local emissions, biomass burning, and urban plumes from the city of Manaus (Liu et al., 2018). Studies show that pasture in the Amazon rain forest has low nitric oxide fluxes (Garcia-Montiel et al., 2001). Hence, the local NO\textsubscript{X} emission was expected to contribute little to NO\textsubscript{X} mixing ratios at the T3 site. The maxima of NO, NO\textsubscript{2}, and NO\textsubscript{X} were up to 1 ppbv, 2 ppbv, and 6 ppbv (Figure 2.4a-c). Because the local emissions were small, those high values were assumed to be resulted in response to biomass burning or urban plumes. The NO\textsubscript{Y}, on the other hand, showed different patterns for wet and dry seasons, with most abundant values comparable to NO\textsubscript{X} (0.5 ppbv) during the wet season and twice than NO\textsubscript{X} (1 ppbv) during the dry season (Figure 2.4d). Given the similar NO\textsubscript{X} in the wet and dry seasons, the higher NO\textsubscript{Y} values during the dry season was mainly due to the enhanced NO\textsubscript{Z} in response to higher temperature and solar radiation.

Even though forest soils had higher nitric oxide fluxes than pasture in the Amazon rain forest (Garcia-Montiel et al., 2001), only a small fraction of NO can escape the canopy (Bakwin et al., 1990; Jacob and Wofsy, 1990; Davidson et al., 2001). In summary, the two study sites showed similar temperature and radiation conditions, with considerate differences between wet and dry seasons. The ZF2 site showed doubled isoprene and halved O\textsubscript{3} levels compared to those at the T3 site on average, indicating that isoprene had a limited contribution to O\textsubscript{3} production due to insufficient NO\textsubscript{X} mixing ratios at the ZF2 site. Therefore, the differences in O\textsubscript{3} levels between the two sites most likely resulted in response to the NO\textsubscript{X} availability and long-range transport of O\textsubscript{3} from the city of Manaus.

### 2.3.1.2 Background conditions and polluted conditions at T3

To learn how and to what extent the urban plumes from the city of Manaus modify the atmosphere composition at the T3 site, we grouped the O\textsubscript{3} and NO\textsubscript{X} data into the categories of clean (background) and polluted conditions for the T3 site, and then investigated the enhancements of O\textsubscript{3} and NO\textsubscript{X}. Figures 2.5a, c show the O\textsubscript{3} distributions with wind directions when the wind speeds were greater than 2.5 m s\textsuperscript{-1} during the dry and wet seasons at the T3 site. Elevated O\textsubscript{3} mixing ratios were observed in the wind directions of 90-180° compared to those in other wind directions (Figure 2.5a, c) at the T3 site, indicating the influences of the urban plumes from the city of Manaus. The elevated O\textsubscript{3} mixing ratios were higher during the dry season with the median ambient O\textsubscript{3} of 32 ppbv and 28 ppbv in the wind
Figure 2.4: Frequency distributions of nitric oxide (NO) (a), nitrogen dioxide (NO$_2$) (b), nitrogen oxides (NO$_X$) (c), and the sum of the odd nitrogen oxides (NO$_Y$) (d) at the T3 site.

directions of 45-90° and 90-135°, respectively. During the wet season, the enhancements were less significant with median ambient O$_3$ of 20 ppbv and 24 ppbv in the wind directions of 45-90° and 90-135°, respectively. In addition, the variations of O$_3$ from the wind direction of 45-135° were also larger as demonstrated by the 90th percentiles of approximately 60 ppbv for both seasons. The main reason for this large variability in the wind direction of 45-135° is that there are occurrences of significantly elevated O$_3$ levels (up to 80 ppbv) due to urban plumes. Ozone data from wind directions of 45-90° and 90-135° were grouped as the polluted conditions. Combining the two groups of O$_3$ data, O$_3$ under polluted conditions showed a median of 32 ppb (20 ppb) and a 90th percentile of 60 ppb (55 ppb) during the dry (wet) season (Figure 2.6a).

Figure 2.5a, c shows the O$_3$ mixing ratio data when wind speed is smaller than 1 m s$^{-1}$,
Figure 2.5: The O$_3$ distribution with wind directions under high wind speed conditions and under calm conditions during the dry (a) and wet (c) season at the T3 site. The O$_3$ distribution with wind directions during dry (b) and wet (d) seasons at the ZF2 site. The boxplot shows lower-quartile, median and upper-quartile. The whiskers indicate 10$^{th}$ and 90$^{th}$ percentiles.

which indicates calm conditions and presumably locally-produced O$_3$. We assume these data are absent of influences from Manaus and thus serve as the background O$_3$ levels. Because there were very few occurrences of northwest winds ($315-360^\circ$) (Figure 2.1a), we ignored the O$_3$ data from this sector due to the lack of statistical significance. We then observed consistency in O$_3$ distribution in each wind direction category under calm conditions (Figure 2.5a, c), which further confirms the consistent local O$_3$ levels. We can then be confident to combine the O$_3$ data under calm conditions which represent local background conditions, and the O$_3$ data from 0-45 $^\circ$ and 135-360 $^\circ$ which represent the regional background conditions into one group, referred to as the clean conditions. Accordingly, the O$_3$ mixing ratios under clean conditions showed a median of 20 ppbv (15 ppbv) and a 90$^{th}$ percentile of 50 ppbv (40 ppbv) during the dry (wet) season (Figure 2.6a). Median O$_3$ mixing ratios were enhanced
Figure 2.6: The distribution of O$_3$ (a), NO$_X$ (b), and NO$_Z$ (c) under polluted and clean conditions at the T3 site. The boxplot shows lower-quartile, median and upper-quartile. The whiskers indicate 10$^{th}$ and 90$^{th}$ percentiles. The enhancements indicate the relative increases of median O$_3$, NO$_X$, and NO$_Z$ mixing ratios under polluted conditions (d).

by 50% and 30% under polluted conditions during the dry and wet season, respectively (Figure 2.6d). In summary, the median background O$_3$ were 5 ppbv higher during the dry season than that during the wet season due to stronger photochemical production of O$_3$. The pollution can enhance the median O$_3$ by 50% and 30% during the dry and wet season, respectively. However, large uncertainties (variations) in the background O$_3$ levels were present during the dry season.

As a comparison, we plotted the O$_3$ distribution with wind directions for the ZF2 site (Figure 2.5b, d). No significant enhancements of O$_3$ were observed in any particular wind direction, indicating the homogeneous chemical conditions all around the ZF2 site. The median O$_3$ mixing ratios of 18 ppbv for the dry season and 13 ppbv for the wet season were close to the median background O$_3$ at the T3 site during the wet season (15 ppbv).
Therefore, wet seasons at the forested site can be considered as the reference of background conditions in the central Amazon basin. The 90th percentile of O3 at the ZF2 site (up to 40 ppbv) was less than that at the T3 site during the dry season (55 ppbv).

To find out how the urban plumes modify the NOX levels at the T3 site, we did similar analyses for NOX data and grouped the NOX into clean and polluted conditions. The NOX mixing ratios under polluted conditions showed comparable median values (0.6-0.7 ppbv) but higher variability (a 90th percentile of up to 2.0 ppbv) (Figure 2.6c). The enhancement in median NOX mixing ratios under polluted conditions was less than 20% (Figure 2.6d). This small enhancement, compared with up to 50% enhancement in median O3 mixing ratios during the dry season, which was probably due to the fact that NOX were chemically converted to O3 and other NOX oxidation products in the plumes during the transport from Manaus to the T3 site in the presence of large amounts of biogenic VOCs. To evaluate the enhancement in the NOX oxidation products due to the urban plumes, similar analyses were done for NOZ data (Figure 2.6b). The enhancements in median NOZ due to urban plumes were 40% and 90% during the dry and wet season, respectively (Figure 2.6d). In summary, the urban plumes increased the median O3 levels at the T3 site by 30% to 50%, depending on the season. The O3 enhancements coincided with enhanced NOZ of 40% to 90%. There was no significant NOX enhancements (less than 20%) observed at the T3 site. We conclude that the majority of the NOX injected into the forest was chemically converted to O3 or to other reservoir species during the transport in the presence of biogenic VOCs.

2.3.2 Influences of chemistry on O3 production

To investigate how the injected NOX influences the atmospheric chemistry in the Amazon rain forest, we used a box model constrained by observations to calculate the O3 production rate (PO3) as a function of NOX under two different isoprene levels. The two different levels of isoprene, 5 ppbv and 2 ppbv, representing the typical isoprene values observed at the ZF2 and T3 sites, respectively, were used in the calculations.

Depending on atmospheric conditions, PO3 can either be NOX-limited, where additional NOX causes PO3 to increase, or NOX-saturated, where additional NOX suppresses O3 formation (Figure 2.7a). Based on the NOX distributions at the T3 site (Figure 2.4c), the PO3 was NOX-limited in the Amazon rain forest, suggesting that changes to chemistry that affects the NOX loss rate can affect PO3 by changing the amount of NOX available for pho-
tochemistry. The OPE can be used to examine the number of O_3 molecules produced from a molecule of NO_X consumed. The observed OPE at T3 site ranged from 10 to 20 ppbv ppbv\(^{-1}\), with higher values at low NO_X levels. The observed OPE values at the T3 site (Figure 2.7b) were nearly twice than the typical OPE for rural (10 ppbv ppbv\(^{-1}\)) and urban (5 ppbv ppbv\(^{-1}\)) sites (Kleinman et al., 2002). The calculated OPE was in good agreement with the observed OPE values. The OPE decreases as NO_X increases, with a value of less than 5 ppbv ppbv\(^{-1}\) when NO_X was greater than 10 ppbv. Magnitudes and variations of the calculated OPE with NO_X were in good agreement with previous studies (Kleinman et al., 2002). When NO_X was less than 0.4 ppbv, the OPE calculated for 5 ppbv of isoprene was greater than the OPE estimated for 2 ppbv of isoprene (Figure 2.7b). The reason for this result may be that under high-VOC conditions, peroxyl radicals (RO_2), formed by OH oxidation of VOCs, were more abundantly available to form NO_2 from NO than those in the low-VOC environments.

Based on the OPE results (Figure 2.7b), the total amount of O_3 formed in a plume can be estimated given the amount of NO_X added to the rain forest. We considered an idealized case in which there was no mixing, dilution, or downwind emissions. A certain amount of NO_X, NO_X(t_0), was injected into rain forest at an initial time t_0 in the form of NO. The background O_3, O_3(t_0), existed just before NO_X(t_0) was added to the air mass. At a later time t, some NO_X was oxidized and some O_3(t) was formed. The increase in O_3, \(\Delta O_3 = O_3(t) - O_3(t_0)\) was estimated as:

\[
\Delta O_3 = \int_{NO_X(t_0)}^{NO_X(t)} OPE \cdot dNO_X - [NO_X(t_0) - NO(t)]
\]

(2.4)

where O_3(t_0) is the background O_3, and O_3(t) is the O_3 at time t; NO_X(t_0) is the NO_X at initial time (all in the form of NO), and NO_X(t) is the NO_X at time t. The \(\Delta O_3\) includes a contribution due to titration equal to the initial NO (Kleinman et al., 2002). Assuming the background O_3(t_0) = 20 ppbv (Figure 2.5), O_3(t) = 80 ppbv, NO_X(t) = 0.6 ppbv (Figure 2.6), and NO(t) was negligible, we estimated 8 ppbv for the initial NO_X(t_0) based on the observed OPE at the T3 site. Because mixing and dilution were not considered, this 8 ppbv of NO_X was a lower bound of the NO_X needed to produce 80 ppbv of O_3 in the rain forest. This value was in good agreement with the observations in the vicinity of Manaus having NO levels of up to 10 ppbv (Kuhn et al., 2010).

It was hypothesized that NO_X were converted to NO_Z during the transport downwind
Figure 2.7: (a) The production rates of O$_3$ (PO$_3$) as a function of NO$_X$ under two different isoprene (ISOP) levels. (b) The observed (cross symbols) and modeled (lines) O$_3$ production efficiency (OPE) and the production rates of NO$_Z$ (PNO$_Z$) as a function of NO$_X$ under two different isoprene levels. (c) The production rates of nitric acid (PHNO$_3$), peroxyacetyl nitrate (PPAN), organic nitrates (PONIT), and the sum of PHNO$_3$, PPAN, and PONIT (referred to as the production rate of NO$_Z$ PNO$_Z$) as a function of NO$_X$ under two different isoprene levels. (d) Time evolutions of O$_3$ (solid lines) and hydroxyl radical (dashed lines) mixing ratios under different NO$_X$ levels. (e) Time evolutions of NO$_X$ (solid lines) and the sum of nitric acid (HNO$_3$), peroxyacetyl nitrate (PAN), and organic nitrates (ONIT) mixing ratios (dashed lines) under different NO$_X$ levels. In the base run, the initial NO$_X$ mixing ratio is 0.5 ppbv.

to the T3 site. Therefore, the production rates of NO$_Z$, HNO$_3$, PAN, organic nitrates under high-isoprene levels which represent characteristic ZF2 values were evaluated (Figure 2.7c). When NO$_X$ were greater than 8 ppbv, the formation of HNO$_3$ dominated the NO$_X$ loss, when NO$_X$ were less than 8 ppbv, the generation of PAN took over. In addition, production rates of organic nitrates were also relatively high under high-NO$_X$ conditions. In summary, when the plumes loaded with NO$_X$ entered into the high-VOC forest, the chemistry had
lower OPE but higher PO3 as well as higher PNOZ. This provided evidence to the stated hypothesis that the NOX added to the forest were mostly chemically converted to O3 and NOZ before arriving at the T3 site, leading to least significant NOX enhancement (less than 20%) compared to O3 and NOZ enhancements.

When considering the modification of the atmospheric chemistry due to polluted air, total amounts of O3 and NOZ produced over the course of the plume transport are more representative metrics than the instantaneous PO3 values. Four simulations were considered to determine the time evolution of the atmospheric chemistry after NOX is injected into the clean air. The initial conditions, except the initial NOX levels, for the four calculations were the same (See details in Section 2.2.3.2). At the end of each simulation, which represents the chemical conditions at the T3 site, the median background O3 of 15-20 ppbv was reasonably reproduced by the base calculation (Figure 2.7d). This is accompanied by an estimated OH concentration of $0.65 \times 10^6$ radicals cm$^{-3}$ which is in general good agreement with the estimates by Liu et al. (2018). The NOX injections of 4, 6, and 8 ppbv at the pollution source region caused the O3 mixing ratios to increase to 34, 45, and 54 ppbv after 6 hours of simulations (Figure 2.7d). These O3 mixing ratios are in good agreement with the observed median (32 ppbv) and the 90th percentile (approximately 60 ppbv) O3 mixing ratios at the T3 site (Figure 2.5c). Meanwhile, the OH concentrations increased to $1.2 \times 10^6$, $1.4 \times 10^6$, and $1.6 \times 10^6$ radicals cm$^{-3}$ in response of NOX injection of 4, 6, 8 ppbv, respectively. To summarize, an injection of 8 ppbv NOX into the rain forest can cause up to 260% and 150% increases in O3 and OH levels compared to the background conditions, suggesting NOX can substantially modify the chemistry of the atmosphere overlying the Amazon rain forest. Additional oxidation of the urban plume, after 6 hours of simulations, led to NOX levels that were well below the observed background NOX level of 0.6 ppbv (Figure 2.7e), further explaining why no significant (< 20%) enhancement of NOX was observed near the surface at the T3 site (Figure 2.6). However, the sum of HNO3, PAN, and RONO2 of up to 1.4 ppbv were produced after 6 hours of evolution of the air mass (Figure 2.7e), which was in good agreement with the observed enhancements in NOZ (1.2-1.5 ppbv) shown in Figure 2.6b. Model results indicated that most of the NOX were converted to O3 and NOX reservoir species such as PAN or RONO2 before the air mass arrived at the T3 site.
2.3.3 Influences of temperature on O$_3$ mixing ratios

Increased VOC emissions and decreased sequestration of NO$_X$ in short-term reservoirs (i.e., NO$_Z$) can explain the increased O$_3$ concentrations with temperature in urban areas (Jacob and Winner, 2009). At the T3 site, the O$_3$-temperature relationships, segregated based on different ranges of NO$_X$ (with bins of widths of 0.5 ppbv) and NO$_Z$ levels and dry and wet seasons (Figure 2.8), revealed strong linear responses. The median background value of NO$_X$ was approximately 0.5 ppbv, so the NO$_X$ bin of 0-0.5 ppbv is considered as clean conditions for both dry and wet seasons. During the dry season, the O$_3$-temperature relationship exhibited strong linear responses with R$^2$ values of > 0.7 (Figure 2.8a). In addition, during the dry season, the O$_3$-temperature slopes increased with NO$_X$ levels from 3.7 to 6.5 ppbv °C$^{-1}$, with 3.7 ppbv °C$^{-1}$ being the typical value observed in rural sites (Romer et al., 2018) and other higher slopes values calculated for polluted environments (Pusede et al., 2015). During the wet season, the O$_3$-temperature relationship was weak under low-NO$_X$ conditions with a R$^2$ value of 0.38. However, the slopes increased in response to enhanced NO$_X$ levels during the wet season (Figure 2.8b). The more significant O$_3$-temperature relationships during the dry season, as demonstrated by greater slopes and R$^2$ values, were most likely caused by the stronger photochemistry associated with higher solar irradiance. The O$_3$ versus temperature relationship as a function of NO$_Z$ levels (Figure 2.8c, d) showed that the slope values increased with NO$_Z$ levels during the dry and wet seasons, particularly for the high NO$_Z$ (NO$_Z$ > 0.5 ppbv) conditions. Based on the results (Figure 2.8), we calculated the rate of change of the slope with respect to NO$_X$ and NO$_Z$ (Figure 2.9). The average rates of change of the slope with respect to NO$_Z$ were approximately 1.8 and 2.3 times higher than those with respect to NO$_X$ for dry and wet seasons. This result could be due to the weak dependence of NO emission on temperature or the reservoir species behaving as a NO$_X$ source under hot conditions. Therefore, the reservoir species, which substantially contributed to the O$_3$ sensitivity to temperature, are important parts of the atmospheric chemistry in the Amazon rain forest, particularly under enhanced NO$_X$ conditions.

To examine if the O$_3$-temperature relationship at a daily time scale and also at ZF2 site, we plotted the daily average O$_3$ versus daily temperature for both T3 and ZF2 sites (Figure 2.10). The O$_3$-temperature relationships were significant when NO$_X$ levels were greater than 0.5 ppbv, with R$^2$ values ranging from 0.59 to 0.71 (Figure 2.10a, c). However, compared with high-NO$_X$ conditions, the O$_3$-temperature relationship was less significant with smaller
Figure 2.8: The O₃-temperature relationship as a function of NOₓ on a half hourly time scale during the dry (a) and wet (b) season at T3 site. The O₃-temperature relationship as a function of NOₓ on a half hourly time scale during dry (c) and wet (d) seasons at T3 site.

slopes when NOₓ levels were less than 0.5 ppbv, which represented clean conditions (Figure 2.10a, c). As the NOₓ levels above the canopy at the ZF2 site were low (data not shown), we expected the O₃-temperature relationship was similar to that at the T3 site when NOₓ levels were less than 0.5 ppbv. This result (Figure 2.10b, d) showed weak O₃ sensitivity to temperature with slopes of similar magnitudes as those at the T3 site under clean conditions. In summary, O₃ mixing ratios were linearly correlated with temperature on half hourly and daily time scales when NOₓ levels were greater than 0.5 ppbv, and the values of the slopes increased with NOₓ levels. Given the same ambient NOₓ levels, the sensitivity of O₃ to temperature was higher during the dry season than the wet season. Under clean conditions (NOₓ < 0.5 ppbv) during the wet season, the O₃-temperature relationship was weak with a
2.4 Conclusions

Ozone production in the Amazon rain forest is NO\textsubscript{X}-limited, showing a high sensitivity to the available NO\textsubscript{X} levels. The O\textsubscript{3} mixing ratios at the T3 site were significantly higher (34-100\%) on seasonal and diel time scales compared to the remote forest site. Given the similar meteorological conditions at both sites, the higher O\textsubscript{3} mixing ratios at the T3 site resulted from the anthropogenic plumes from the city of Manaus loaded with high levels of NO\textsubscript{X} and O\textsubscript{3} produced from oxidation of biogenic VOCs. In contrast, biogenic VOCs contributed little to O\textsubscript{3} production due to insufficient NO\textsubscript{X} levels at the remote forested site.

The polluted conditions associated with wind directions of 45-135\(^\circ\) enhanced the median O\textsubscript{3} and NO\textsubscript{Z} mixing ratios by 30-50\% and 40-90\%, respectively, depending on the season. However, the NO\textsubscript{X} levels were increased by the polluted conditions by less than 20\%, in-
Figure 2.10: The O₃-temperature relationship as a function of NOₓ on a daily time scale during the dry (a) and wet (c) season at T3 site. The O₃-temperature relationship on a daily time scale during the dry (b) and wet (d) season at the ZF2 site.

indicating the majority of NOₓ were chemically converted to O₃ and NOₓ under high-VOC conditions during transport. During the dry season, the O₃ and NOₓ levels under polluted conditions showed large variations, most likely due to the high intensity of photochemistry associated with strong solar irradiance. In addition, during the wet season, the atmospheric conditions at the remote forested site, as well as at the T3 site when NOₓ levels were less than 0.5 ppbv, can be considered as the regional background conditions in the central Amazon rain forest.

The observed O₃ production efficiency (OPE) was 10-20 ppbv ppbv⁻¹, which is approxi-
mately twice the value observed in rural and urban areas. The estimated OPE indicated a lower bound of NO\textsubscript{X} of 8 ppbv to produce 80 ppbv O\textsubscript{3} with an isoprene level of 5 ppbv in the Amazon rain forest. Photochemical model results showed that an injection of 8 ppbv NO\textsubscript{X} into the rain forest can cause up to 260% and 150% increases in O\textsubscript{3} and OH levels compared to the background conditions, suggesting NO\textsubscript{X} can significantly modify the air quality and oxidative capacity in the Amazon rain forest.

Ozone mixing ratios showed significant linear correlations with air temperature on half hourly and daily time scales. The O\textsubscript{3}-temperature slopes increased rapidly with NO\textsubscript{X} and NO\textsubscript{Z}. The rate of change of the slope with respect to NO\textsubscript{Z} was approximately twice higher than that with respect to NO\textsubscript{X}, suggesting the NO\textsubscript{Z} produced during transport contributed significantly to the O\textsubscript{3} production at the T3 site under warm weather conditions. In summary, pollution plumes from the city of Manaus constituted the main source of NO\textsubscript{X} in the downwind rain forest and pasture sites, and largely influenced the air quality and the lower atmosphere oxidation capacity, enhanced by the abundant amounts and different species of biogenic VOCs and the prevailing warm weather conditions.
2.5 supplement

2.5.1 Initial mixing ratios of chemical species included in the photochemical simulations
Table 2.1: Initial mixing ratios (in ppbv) of chemical species included in the photochemical simulations.

<table>
<thead>
<tr>
<th>Model species</th>
<th>Definition</th>
<th>Initial values</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISOP</td>
<td>Isoprene</td>
<td>5</td>
</tr>
<tr>
<td>O3</td>
<td>Ozone</td>
<td>15</td>
</tr>
<tr>
<td>NO\textsubscript{X}</td>
<td>Nitrogen oxides</td>
<td>0.5, 4, 6, 8</td>
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<tr>
<td>CO</td>
<td>Carbon monoxide</td>
<td>300</td>
</tr>
<tr>
<td>CH4</td>
<td>Methane</td>
<td>1800</td>
</tr>
<tr>
<td>HCHO</td>
<td>Formaldehyde</td>
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</tr>
<tr>
<td>H\textsubscript{2}O\textsubscript{2}</td>
<td>Hydrogen peroxide</td>
<td>2</td>
</tr>
<tr>
<td>ETH</td>
<td>Ethane</td>
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<tr>
<td>ETE</td>
<td>Ethene</td>
<td>0.58</td>
</tr>
<tr>
<td>OLT</td>
<td>Terminal alkenes</td>
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</tr>
<tr>
<td>OLI</td>
<td>Internal alkenes</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>0.063</td>
</tr>
<tr>
<td>DIEN</td>
<td>Butadiene and other anthropogenic dienes</td>
<td>0.0066</td>
</tr>
<tr>
<td>TOL</td>
<td>Toluene and less reactive aromatics</td>
<td>0.056</td>
</tr>
<tr>
<td>API</td>
<td>Alpha-pinenes and other cyclic terpenes with one double bond</td>
<td>0.0089</td>
</tr>
<tr>
<td>LIM</td>
<td>d-limonene and other cyclic diene-terpenes</td>
<td>0.0046</td>
</tr>
<tr>
<td>MACR</td>
<td>Methacrolein</td>
<td>0.47</td>
</tr>
<tr>
<td>MVK</td>
<td>Methyl vinyl ketone</td>
<td>1.0</td>
</tr>
<tr>
<td>BEN</td>
<td>Benzene</td>
<td>0.031</td>
</tr>
<tr>
<td>PAN</td>
<td>Peroxyacetyl nitrate and higher saturated PANs</td>
<td>0.005</td>
</tr>
</tbody>
</table>

2.5.2 Meteorological conditions at the two study sites

The T3 and ZF2 sites experienced similar seasonal patterns in air temperature and incoming solar radiation, with maxima observed in September and lower values measured during the wet season (Figure 2.11). Diel variations in air temperature exhibited similar patterns at the two sites (Figure 2.12a, b). Maximum average temperature at the T3 site was only 1.0 °C and 0.6 °C higher than those at the ZF2 site during the wet and dry season, respectively. On average, air temperature varied by 6-8 °C within a day (Figure 2.12a, b). The maximum mean temperature was 1.5 °C higher during the dry season for the T3 site, and 1.9 °C for the ZF2 site (Figure 2.12a-d). These differences in temperature are due to the different measurement heights and vegetation types. There were no significant differences observed in diurnal variations of incoming solar radiation between the two sites likely in response to
Figure 2.11: The seasonal variations in mean temperature and standard deviation at the T3 site (a) and the ZF2 site (b). The seasonal variations in average and standard deviation incoming solar radiation at the T3 site (c) and the ZF2 site (d). The shaded areas indicate the dry season.

similar cloud cover (Figure 2.12c, d).

2.5.3 A case study of a polluted episode

A case study of a polluted episode from November 29 to December 3 is shown in Figure 2.13. The weather conditions were sunny except for the afternoon on December 2, as demonstrated by the solar radiation in Figure 2.13a. The daytime wind mostly came from the east (45-135 degrees) and increased O₃ levels except on December 2. Thus the days of November 29, November 30, December 1, and December 3 are considered as polluted days, and the morning of December 2 was a clean day before a storm passed by in the afternoon. The O₃ mixing ratios increased rapidly in the early afternoons of the polluted days (Figure 2.13b), accompanied by rapid increases in NOₓ and carbon monoxide (Figure 2.13d-e). Carbon monoxide (CO) is a tracer of anthropogenic emissions with well-known sources from com-
bustion, industry, and oxidation of hydrocarbons. The primary fire season is during most of August and September with about 300,000 fires seasonally being typical in the Amazon rain forest (Setzer and Pereira, 1991). Therefore, the elevated CO levels during this episode are not expected to be from biomass burning. Because of its long chemical lifetime and relatively small biogenic exchange rates (Kuhn et al., 2010), it can be assumed that the elevated CO levels were due to the urban plumes from the city of Manaus. The polluted days showed considerably higher NO\textsubscript{Y} mixing ratios, generally greater than 2 ppbv but slightly higher NO\textsubscript{X} levels of approximately 1 ppbv than the clean day (Figure 2.13d). In contrast, the NO\textsubscript{X} did not increase as drastically as the NO\textsubscript{Y}. Figure 2.13 shows that the polluted episodes can be detected by the wind information and thus justified our categorization method for the clean and polluted conditions at the T3 site (See details about the method in 2.2.2.2).
Figure 2.13: A pollution episode due to the urban plumes from November 29 to December 3, 2014 at the T3 site. The time evolution of incoming solar radiation (a), wind speed and direction (b), O₃ mixing ratios (c), NO, NO₂, and NOₓ mixing ratios (d), and CO mixing ratios (e).
Chapter 3

Environmental and biological controls on seasonal patterns of isoprene above a rain forest in central Amazonia

3.1 Introduction

Among the biogenic volatile organic compounds, isoprene (C₅H₈, 2-methyl-1,3-butadiene) is the most abundantly emitted from the foliage of woody plant species. Its ecological function is still unclear, but current and prevailing consensus indicates that isoprene may act to increase the thermal protection of photosynthesis at high temperature (> 313 K) by either stabilizing the thylakoid membranes (Sharkey and Yeh, 2001) or quenching reactive oxygen species (Loreto and Velikova, 2001). The biosynthesis of isoprene is associated with the carboxylation process in the leaf chloroplast (Sharkey et al., 2008), and foliage temperature and intercepted photosynthetically active radiation (PAR) regulate emissions via stomata (Fall and Monson, 1992). Foliage temperature activates the enzyme responsible for isoprene biosynthesis (Monson and Fall, 1989) whereas PAR provides the energy to acquire the necessary carbon substrate to produce isoprene (Sharkey et al., 1991). Isoprene emissions occur only during the daytime and vary greatly with foliage phenology. Laboratory (Grinspoon et al., 1991) and field (Monson et al., 1994; Fuentes and Wang, 1999) studies demonstrate that leaves older than 2-4 week emit isoprene but younger leaves do not, even though they are competent to assimilate carbon dioxide (CO₂) (Fuentes et al., 1999; Wilkinson et al., 2009).
In this study we aim to (i) investigate the degree of seasonality in isoprene concentration using field experiments and (ii) identify the main processes explaining such seasonality via a zero-dimensional model that includes sources and sinks of isoprene as well as atmospheric boundary layer dynamics. Additional verifications on modeled links between ambient isoprene and its sources/sinks were conducted using diurnal concentration variations across different seasons. Once released from foliage, isoprene molecules can undergo surface deposition onto the plant canopy, can be oxidized, and can be transported into and out of the atmospheric boundary layer (ABL) (Figure 1). Isoprene oxidation occurs via reactions with hydroxyl radical (HO), ozone (O$_3$), and nitrate radical (NO$_3$). Because of chemical reactions, isoprene molecules tend to reside in the atmosphere for just a few hours (Table 3.1).

Table 3.1: Isoprene chemical lifetimes with respect to assumed mixing ratios (in parts per billion on a volume basis, ppbv) of hydroxyl radical (HO), ozone, and nitrate radical.

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Rate coefficient $^\dagger$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>Mixing ratio (ppbv)</th>
<th>Chemical lifetime (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO</td>
<td>$1.0 \times 10^{-10}$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>1</td>
</tr>
<tr>
<td>Ozone</td>
<td>$1.28 \times 10^{-17}$</td>
<td>20.0</td>
<td>44</td>
</tr>
<tr>
<td>Nitrate</td>
<td>$6.86 \times 10^{-13}$</td>
<td>$5.0 \times 10^{-3}$</td>
<td>3</td>
</tr>
</tbody>
</table>

$^\dagger$: Reaction rate coefficients are from Atkinson (1997) at temperature of 298 K

Isoprene has a substantial impact on the chemistry of the atmosphere in the boundary layer overlying forested environments. The Amazon rain forest mostly experiences low levels of nitrogen oxides (NO$_X$ = NO + NO$_2$). Occasionally, high NO$_X$ levels are observed due to biomass burning (Gerken et al., 2016). Under higher NO$_X$ conditions, isoprene oxidation processes contribute to the formation of O$_3$ (Kuhn et al., 2007). In addition, products of isoprene photooxidation are important precursors to secondary organic aerosols (SOA), particularly in the rain forest where isoprene is abundantly produced year round (Claeys, 2004; Paulot et al., 2009b; Surratt et al., 2009). Because SOAs can grow sufficiently large to activate and become cloud condensation nuclei (CCN) and scatter and absorb solar irradiance, they play critical roles in weather and climate (Pöschl et al., 2010). Also, theoretical and experimental studies (Taraborrelli et al., 2012; Fuchs et al., 2013) indicate that the photooxidation of isoprene may contribute to appreciable amounts of HO recycling. In environments such as the rain forest, isoprene plays a central role in sustaining the oxidation capacity of the lower atmosphere by adjusting HO levels (Lelieveld et al., 2008; Nölscher et al., 2016).
Hence, it is necessary to estimate seasonal emission rates, ambient levels, and oxidation rates of isoprene in the tropical rain forest to establish regional SOA and HO budgets, and to develop an improved understanding of the role of rain forests in the Earth system.

Tropical rain forests experience year-round high temperature and PAR levels and may thus be assumed to support minor seasonality in isoprene emissions (Levis et al., 2003). However, strong seasonality in ambient isoprene levels is observed over the Amazon rain forest (Kesselmeier, 2002; Kuhn et al., 2004). Studies on tropical tree species show mature leaves exhibit higher isoprene emissions than new leaves (2 versus 30-40 nmole m$^{-2}$s$^{-1}$; Figure 4b in Jardine et al., 2016). Also, remote sensing studies (Barkley et al., 2008) in the Amazon basin demonstrate that variations in leaf area and enhanced vegetation indices (EVI) before the dry season are consistent with observed decreases in the slant atmospheric columns of formaldehyde (HCHO, Palmer et al., 2007), which is a high-yield product of isoprene oxidation and is assumed as a proxy for isoprene emissions (Palmer et al., 2006). Such results suggest large-scale reductions in isoprene biosynthesis due to new leaf growth prior to the dry season. While co-located seasonal isoprene and phenology measurements are not available for the Amazon rain forest, close links exist between phenology and photosynthesis (Wu et al., 2016), which would be consistent with the observed seasonality in isoprene emissions. Previous ecosystem-level studies in the tropical rain forest (Rinne et al., 2002; Greenberg et al., 2004; Karl et al., 2004; Kuhn et al., 2007; Rizzo et al., 2010; Jardine et al., 2012) were performed during brief periods and confirmed seasonal variations in isoprene emission activity deduced from forest canopy flux densities. Nonetheless, long-term studies are still needed in the tropics to constraint budgets of biogenic hydrocarbons and resulting sources and sinks of atmospheric oxidants and SOAs.

### 3.2 Research methods

#### 3.2.1 Study site

The field campaign took place at the Curaías Biological Reserve (N 2°36.11′, E 60°12.56′), in the central Amazon basin, Brazil from April 2014 to January 2015 as part of the GoAmazon 2014/5 project (Fuentes et al., 2016). The study site (called the K34 tower at ZF2, and designated as T0k, located about 120 km from T3 site during GoAmazon 2014/5 (Martin et al., 2016)) is approximately 60 km north-northwest of the city of Manaus, Amazonas,
Figure 3.1: Temporal variations of isoprene over the rain forest depend on emission, surface deposition, chemical transformation, and transport in (entrainment) and out (detrainment) of the atmospheric boundary layer. Each process differently contributes to ambient isoprene mixing ratios over the course of the day. After being emitted during the daytime, turbulence redistributes isoprene throughout the boundary layer while reactions with hydroxyl radicals (HO) decrease its concentration. Subsequent reaction pathways depend on nitric oxide (NO) levels. Under high NO conditions, ozone is generated while under low NO conditions notable amounts of HO can be recycled through isomerization of isoprene peroxy radicals (ISOPOO). Incomplete turbulent mixing slows down the reactions of isoprene with HO, and segregation of isoprene-HO can occur. Air entrainment from the free atmosphere into the mixed layer and deep boundary layer depths support rapid isoprene dilution, primarily during the morning when accelerated development of the convective boundary layer occurs. All these processes control the temporal patterns of isoprene mixing ratios above the rain forest. Figure modeled after (Stull, 1988).

Brazil and is part of the Large-Biosphere-Atmosphere (LBA) experiment (Araújo et al., 2002). The reserve covers approximately 230 km² of largely undisturbed lowland evergreen rain forest with a canopy height of about 35 m (Luizao, 1995) surrounding a 50-m tower that served as a platform to mount meteorological instruments and air samplers. The leaf area index (LAI) is estimated to be 5–6 m² m⁻² (McWilliam et al., 1993; Marques Filho
et al., 2005), with maximum LAI values reaching 7.3 m² m⁻² (Tóta et al., 2012). Myneni et al. (2007) reported LAI seasonal variations reaching 1 m² m⁻² in the Amazon basin. Due to prevailing easterly wind, the air masses arriving at the site mostly come from vast expanses of undisturbed rain forest. However, the site occasionally experiences the influences of biomass burning during the dry season when high NO (> 2 ppbv) and O₃ (> 50 ppbv) levels can be recorded (Artaxo et al., 2013; Gerken et al., 2016).

3.2.2 Trace gas and meteorological measurements

Mixing ratios of trace gases were measured at the fixed level of 40 m above the ground surface. Ozone (model 49i, Thermo Fisher Scientific Inc., Waltham, MA) and nitrogen oxides (NO and NO₂, model 48i, Thermo Fisher Scientific Inc.) were measured at the frequency of 1 Hz and reduced to generate half hourly averages. A Proton Transfer Reaction-Mass Spectrometer (PTR-MS, Ionicon Analytik Ges.m.b.H., Innsbruck, Austria) measured ambient levels of volatile organic compounds (VOCs), including isoprene and methanol (CH₃OH). The PTR-MS was purposely configured to make measurements in slow-response (1 Hertz) mode to optimize the reliable measurements of multiple gases. Therefore, eddy-covariance hydrocarbon fluxes did not exist for the field campaign. Pumps drew ambient air from the inlet at 40 m to a heated (to prevent condensation) manifold unit that was housed in an environmentally controlled hut, located 3 m away from the tower. The manifold unit had several outlet ports to allow the ambient air to pass through different gas analyzers. For isoprene measurements, the PTR-MS monitored the mass (m) and charge number of ions (z) ratio, m/z, of 69. The PTR-MS was calibrated before, during, and after the field studies. Commercial mixture gas standards in high-purity air (Apel-Riemer Environmental, Inc., Boulder, Colorado) contained 15 different compounds (including isoprene) at mixing ratios of ∼ 500 ppbv and diluted the standard mixtures using zero air that was created at the site via a catalytic converter (Restek, Inc., Bellefonte, PA) and a series of mass flow controllers. After subtracting zero air from the measured counts per second, the average normalized counts per second (ncps), which were normalized by both m/z 21 and 37, were plotted against the gas mixing ratio at four different levels. The calibration factor (ncps/ppbv ± uncertainty) was then applied to the field measurements after subtracting intermittent zeros in order to obtain final gas concentrations. Fuentes et al. (2016) and Freire et al. (2017) provide full details on air sampling procedures, and operation and calibration protocols of the gas
analyzers. In this study, air chemistry data for June, September, December, and January (2015), incorporating both wet and dry seasons, are presented and discussed.

Meteorological and air turbulence measurements provided contextual information to understand seasonal variations of isoprene. Nine sonic anemometers (model CSAT3, Campbell Scientific Inc, Logan, UT), deployed at 7.0, 13.5, 18.4, 22.1, 24.5, 31.6, 34.9, 40.4, 48.2 m above the ground, recorded the three components of the wind speed (u, v, and w) and virtual temperature ($T_v$) at the frequency of 20 Hz (Santos et al., 2016). Using the air turbulence data, the kinematic virtual heat flux ($\left( w' \theta'_V \right)_s$, $\theta_v$ is the virtual potential temperature derived from $T_v$) at 48.2 m above the ground were calculated to determine the depth ($z_i$) of the ABL (see details in Section 2.3). A quantum sensor (model Li190, LiCor Biosciences, Lincoln, NE) recorded PAR, and a thermometer/hygristor probe (model HMP-155, Väisälä, Vantaa, Finland) measured air temperature and relative humidity at 51.6 m and 32.0 m above the ground, respectively. Rain gauges (model RIMB500, McVan Instruments, Melbourne, Australia), deployed at a site located 3.1 km away from the flux tower, recorded rainfall amounts. Analyses also included rainfall data from the GoAmazon2014/5 T3 study site.

### 3.2.3 Modeling isoprene temporal variability

Isoprene mixing ratios in the ABL are governed by emissions, chemical reactions, surface deposition, and exchange processes between the ABL and the free atmosphere. In this study, a zero-dimensional model was employed to estimate the temporal evolution of isoprene in the mixed layer (ML), $\frac{\partial \langle \text{ISOP} \rangle_{\text{ML}}}{\partial t}$, under the assumption of surface homogeneity and instantaneous atmospheric mixing of isoprene and its reactants (it is hereby assumed that the bottom of the ML starts at the top of the forest canopy). The validity of the mixing assumption will be evaluated by incorporating the segregation of species (see below). Under the stated assumptions, the isoprene budget is thus given by

$$\frac{\partial \langle \text{ISOP} \rangle_{\text{ML}}}{\partial t} = \frac{E - F_e - D}{z_i} + f_{\text{Chem}}. \quad (3.1)$$

$E$ denotes isoprene emission rates, $F_e$ represents the isoprene flux at the top of the ML caused by entrainment and detrainment, $D$ is the isoprene surface deposition rate, and $f_{\text{Chem}}$ is the destruction rate of isoprene due to gas-phase reactions. The effect of a growing convective boundary layer is included via the variable $z_i$. 
Isoprene emission rates \( E \) in Equation 3.1) are estimated following established algorithms (the MEGAN model, Guenther et al. (2006, 2012) as shown in Equation 3.2.

\[
E = [\epsilon][\gamma][\rho] \quad (3.2)
\]

\( \epsilon \) is the basal isoprene emission rate (mg m\(^{-2}\) h\(^{-1}\)) defined at the standardized conditions of PAR level of 1000 \( \mu \text{mol (photons)} \) m\(^{-2}\) s\(^{-1}\) and leaf temperature of 300 K. The magnitude of \( \epsilon \) depends on plant types (Guenther et al., 2012). The \( \gamma \) factor (i.e., a ratio) accounts for emission changes due to deviation from normalized conditions. The \( \rho \) (normalized ratio) accounts for loss of isoprene within the forest canopy (in this study \( \rho \) is assumed = 1).

The algorithm considers the main processes influencing isoprene emissions such as the light response \( (\gamma_P) \) in acquiring the carbon substrate, temperature response based on enzymatic activity responsible for isoprene biosynthesis \( (\gamma_T) \), leaf age \( (\gamma_A) \), LAI, emission inhibition due to CO\(_2\) levels \( (\gamma_C) \), and soil moisture \( (\gamma_{SM}) \), as shown in Equation 3.3 (Guenther et al., 2012).

\[
\gamma = C_{CE}LAI\gamma_P\gamma_T\gamma_A\gamma_C\gamma_{SM} \quad (3.3)
\]

\( C_{CE} \) represents the type of canopy environment, and following previous studies (Guenther et al., 2006) the value of 0.57 is used. The CO\(_2\) response \( (\gamma_C) \) was set to 1. During the study period, for the volumetric soil moisture values (0.28 - 0.48 in m\(^3\) m\(^{-3}\)) recorded at the soil depths ranging from 10 to 75 cm, the forest most likely did not experience water-related stress. In the rain forest, water storage occurs in deep soil columns. Therefore, plant roots can access moisture stored in the soil at depths reaching up to about 10 m (Bruno et al., 2006). Even during the dry season when near-surface soil dries, trees can access deep soil water and as a result exhibit little evidence of stress (Nepstad et al., 1994). Therefore, the soil moisture \( (\gamma_{SM}) \) influences on emissions was set to 1. The isoprene emission algorithm was executed with the measured PAR levels and air temperature. Due to the incomplete canopy surface temperature \( (T_{sfc}) \) dataset, the air temperature \( (T_a) \) was used to determine isoprene emissions. Analyses of the limited \( T_{sfc} \) data for September showed that during 8:00-16:00 local hours the \( T_{sfc} \) was 1.6±0.4 \(^{\circ}\)C greater than \( T_a \) (for the other times, the canopy was cooler than the air). Small differences between \( T_a \) and \( T_{sfc} \) prevailed due to preponderance of cloudiness (which reduced the solar radiation loading on the foliage) and lack of soil moisture stress. For daytime conditions, the averaged temperature of forest crown canopies without soil moisture stress can be ordinarily within 3 °C (Fuentes et al., 1995; Gao
et al., 2008), although individual sunlit leaves reach temperatures as much as 15 °C above air temperature (Singsaas et al., 1999). To estimate the uncertainties associated with the differences between $T_a$ and $T_{sfc}$, several simulations were performed with temperature values that were 0.5, 1.0, 2.0, and 3.0 °C higher than air temperature. Results indicated that these higher temperature values (0.5, 1.0, 2.0, and 3.0 °C higher) resulted in 1 %, 3 %, 12 % and 21 % overestimates in isoprene emission rates, respectively.

The LAI data are obtained from the Moderate Resolution Imaging Spectroradiometer (MODIS) onboard the National Aeronautics and Space Administration’s (NASA’s) Terra satellite. Datasets are provided at the 1 km × 1 km resolution. The best-quality daily retrievals are averaged over an 8-day period. The MODIS data have been reprocessed several times with the latest available algorithms, calibration, and geolocation information. In this study, the collection-5 MODIS Terra LAI products are used (Yang et al., 2006). The 8-day LAI products were further processed into monthly averages in the study. The MODIS-derived LAI can have uncertainties reaching 20 %, mostly due to the overestimates of absorbed PAR (Fensholt et al., 2004). The leaf age emission activity factor $\gamma_A$ is estimated as:

$$\gamma_A = F_{new}A_{new} + F_{mat}A_{mat} + F_{old}A_{old}$$

where $A_{new} (=0.05)$, $A_{mat} (=1)$, and $A_{old} (=0.9)$ are empirical coefficients that describe the relative emission rates for new, mature, and old leaves, respectively (Guenther et al., 2012). $F_{new}$, $F_{mat}$, and $F_{old}$ represent leaf age fractions estimated by Wu et al. (2016). Estimates of leaf demographic dynamics (i.e., $F_{new}$, $F_{mat}$, and $F_{old}$) were constrained by three sets of observations, including the total LAI, the litter fall LAI, and the new leaf production (Wu et al., 2016). Guenther et al. (2006, 2012) provide additional details about the isoprene emission algorithm.

Dry deposition is an efficient sink for gaseous chemical species in tropical forests (Fan et al., 1990; Sigler et al., 2002; Rummel et al., 2007; Nguyen et al., 2015). The deposition flux of isoprene to the forest canopy and ground surface ($D$ in Equation 3.1) is estimated as the product of $\langle ISOP \rangle_{ML}$ and a deposition velocity ($V_{d,ISOP}$)

$$D = \langle ISOP \rangle_{ML} V_{d,ISOP}.$$  

Direct determinations of isoprene deposition to soil are rare and none exists, to our knowledge, for tropical forests. A nighttime $V_{d,ISOP}$ of 0.25 cm s$^{-1}$ is used in this study,
following numerical studies (Karl et al., 2004) for a tropical forest canopy. The daytime deposition was estimated by the resistance analogue model (Equation 3.6) following earlier studies (e.g., Wesely, 2000).

\[
V_{d,ISOP} = \frac{1}{R_a + R_b + R_c}. \tag{3.6}
\]

\(R_a\) is the aerodynamic resistance and \(R_b\) the quasi-laminar sublayer resistance. The expressions for \(R_a\) and \(R_b\) can be found in Equation (2) and (4) in the article by Wesely et al. (2002). The results of \(R_a\) and \(R_b\) are shown in Table 3.2.

<table>
<thead>
<tr>
<th></th>
<th>June</th>
<th>September</th>
<th>December</th>
<th>January</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_a)</td>
<td>11±6</td>
<td>8±3</td>
<td>13±12</td>
<td>13±9</td>
</tr>
<tr>
<td>(R_b)</td>
<td>14±6</td>
<td>14±5</td>
<td>15±7</td>
<td>15±6</td>
</tr>
</tbody>
</table>

The canopy resistance \(R_c\) can be separated into two parallel paths as shown in Equation 3.7 (Nguyen et al., 2015).

\[
\frac{1}{R_c} = \frac{1}{R_s + R_m} + \frac{1}{R_{cut}}. \tag{3.7}
\]

\(R_s\), \(R_m\), and \(R_{cut}\) are stomatal, mesophyll and cuticle resistances respectively. During the daytime when leaf-level isoprene emission occurs through the stomata, the stomatal and mesophyll resistances are assumed to be infinite for isoprene. Therefore, the canopy resistance \(R_c\) is equal to the cuticle resistance \(R_{cut}\). Due to the lack of information for estimating \(R_{cut}\), the well-documented cuticle resistance for ozone (e.g., Fuentes, 1992; Zhang et al., 2003) was used as an analog (\(R_{cut,ozone}\)) to isoprene. The values of \(R_{cut,ozone}\) range from 400 to 6000 s m\(^{-1}\), yielding small daytime deposition velocity \(V_{d,ISOP}\) of 0.02 – 0.2 cm s\(^{-1}\). By applying this range of \(V_{d,ISOP}\) to Equation (5) and (1), we found that the daytime deposition only accounts for less than 4 % of the emitted isoprene (i.e., \(\frac{D}{E} \leq 4\) % in Equation 1). Therefore, the daytime deposition of isoprene is neglected in this study (Verver et al., 2000; Hurst et al., 2001). Deposition for other highly reactive gases are not considered in the numerical model. The zero-dimensional model also requires the value of \(O_3\) dry deposition (\(V_{d,O3}\)) to foliage and ground surface. Tropical forests contribute to the \(O_3\) sink via the surface deposition process (Fan et al., 1990; Sigler et al., 2002; Rummel et al., 2007). In this study, the \(V_{d,O3}\) values of 1.53 cm s\(^{-1}\) and 0.57 cm s\(^{-1}\) for daytime and nighttime, respectively, are used (Freire et al., 2017).
The entrainment of air from the residual layer or free atmosphere to the mixed layer can influence the temporal variability of isoprene (Figure 1). The entrainment flux \( F_e \) in Equation 3.1 is estimated following previous studies (Nappo and van Dop, 1994).

\[
F_e = \frac{\partial z_i}{\partial t} (\langle \text{ISOP} \rangle_{\text{ML}} - \langle \text{ISOP} \rangle_{\text{RL}})
\]  

(3.8)

At 18:00 hours local time (LT) a fraction of isoprene stays in the residual layer where isoprene remains decoupled to the surface until the next morning when it is transported into the shallow mixed layer by entrainment (Verver et al., 2000). Therefore, the \( \langle \text{ISOP} \rangle_{\text{RL}} \) is assumed to be the observed isoprene at 18:00 hours and thereafter remains invariant with time. Due to the zero-dimensional modeling approach, the effect of convective detrainment cannot be explicitly included. The \( z_i \) in Equation 3.1 is determined using (Stull, 1988)

\[
z_i = \sqrt{\frac{2(2C + 1)}{\gamma_{\theta_V}}} \int_0^t \overline{(w'\theta'_V)}_s.
\]  

(3.9)

The entrainment parameter \( C \), defined as the ratio of kinematic heat fluxes at the mixed layer top to the surface \( \left( \overline{(w'\theta'_V)}_s / \overline{(w'\theta'_V)}_s \right) \), is set to 0.2 (Strong et al., 2005). The environmental lapse rate \( \gamma_{\theta_V} \) in the free atmosphere is assigned the value of 0.004 K m\(^{-1}\). Calculations of \( z_i \) start when \( \overline{(w'\theta'_V)}_s \) becomes a positive quantity, typically around 8:00 hours, and end when \( \overline{(w'\theta'_V)}_s \) turns negative, usually close to sunset (17:30 hours). In the absence of measurements, the initial value of \( z_i \) is assumed to be 100 m. The convective velocity scale \( w_* = \left[ \left( g/\theta_V \right) \overline{(w'\theta'_V)}_s z_i \right]^{1/3} \), \( g \) is the acceleration due to gravity) was estimated to determine the overturning time scales in the boundary layer.

Influences of chemical reactions \( \left( f_{\text{chem}} \right) \) on the temporal changes in isoprene levels are investigated using a photochemical module, known as the Regional Atmospheric Chemistry Mechanism, version 2 (RACM2, Goliff et al., 2013). The RACM2 includes 117 chemical species and 356 chemical reactions. The mechanism incorporates 17 stable inorganic species, 4 inorganic intermediates, 54 stable organic species, and 42 organic intermediates. Chemical species with similar molecular structures are aggregated into one model species. For example, the RACM2 species API represents \( \alpha \)-pinene and other cyclic terpenes with one double bond, and LIM represents d-limonene and other cyclic diene-terpenes. However, RACM2 explicitly considers the chemistry of isoprene. Thirty three molecules undergo photolysis in RACM2 and their photolysis frequencies are calculated using tested algorithms (Madronich
The cross section and quantum yields are taken from previous studies (Sander et al., 2006).

The zero-dimensional model (Equation 3.1) is executed with monthly averaged E and depths of the nocturnal stable boundary layer (nighttime) and \( z_i \) (daytime) to reproduce the mean diel variations of isoprene for months when isoprene measurements are available. Monthly averages of \textit{in situ} isoprene and O\(_3\) concentration measurements, made at 00:00 hours, are used to initialize the model for each month (Table 3.3). During the rainy season at the study site, NO mixing ratios remain predominantly less than 0.4 ppbv (Fuentes et al., 2016). Therefore, the initial NO mixing ratio of 0.2 ppbv is used for June and December. Initial NO mixing ratios for September and January are then adjusted to match O\(_3\) observations (Table 3.3). Emissions of NO are assumed to be \( 1.0 \times 10^{-5} \) ppb min\(^{-1}\) for June, December and January and are adjusted to \( 1.0 \times 10^{-4} \) ppb min\(^{-1}\) to match O\(_3\) observations in September. These initial levels and emissions of NO result in the modeled layer-averaged NO mixing ratios at 12:00 hours of approximately 0.05 ppbv which is the prevailing value observed in the undisturbed rain forest (Torres and Buchan, 1988; Liu et al., 2016). For other chemical species, reported values from previous studies are used for the initialization of the zero-dimensional model (see Supplement I).

Table 3.3: Initial mixing ratios (in ppbv) of isoprene, ozone and nitric oxide (NO) during the months considered in the numerical simulations.

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>June</th>
<th>September</th>
<th>December</th>
<th>January</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoprene</td>
<td>1.5</td>
<td>3.0</td>
<td>3.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Ozone</td>
<td>8.0</td>
<td>11.3</td>
<td>8.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>0.2</td>
<td>0.35</td>
<td>0.2</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The model was executed at a time step of 30 minutes to produce concentrations of all chemical species. The emission term \( (E(t) - F_e(t)) \), the chemical sink \( (f_{Chem}) \), and the resultant temporal changes in isoprene \( (\frac{\partial \langle ISOP \rangle_{RL}}{\partial t}) \) in Equation 3.1 are then used to investigate the relative contribution of each process to the total rate of change of isoprene (Figure 1). Mean diel cycles of isoprene concentrations are simulated using the zero-dimensional model with monthly averages of E and \( z_i \). It is therefore necessary to assess the uncertainties associated with the day-to-day variations in E and \( z_i \). Following previous methods (de Arellano et al., 2009), several experiments were done to determine the likely influences of each variable (E, \( z_i \) and \( \langle ISOP \rangle_{RL} \)) on isoprene cycles by varying only one variable within its expected range.
Chemical processes such as HO recycling, segregation of isoprene-HO, and NO levels can also influence isoprene concentrations. Reactions of O$_3$ with isoprene and monoterpenes can generate HO (Paulson and Orlando, 1996) whose yields depend on ambient NO levels (Stone et al., 2012). In low NO-environments, isoprene oxidation generates isoprene peroxy radicals (ISOPOOH) which can subsequently react and contribute to the recycling of HO, with suggested values ranging from 30 to 50 % HO yields (Paulot et al., 2009a; Taraborrelli et al., 2012; Fuchs et al., 2013). To estimate the influences of the regenerated HO on the inferred isoprene levels, sensitivity analyses are performed. As the exact nature of these reactions still remains under investigation, additional HO-recycling is enforced a priori in the existing chemical mechanism as shown in reactions 3.10 and 3.11.

\[
\text{ISOP} + \text{HO} \overset{k_{10}}{\rightarrow} \text{ISOPOOH} \tag{3.10}
\]

\[
\text{ISOPOOH} + \text{HO}_2 \overset{k_{11}}{\rightarrow} \chi \text{HO} + \text{Products} \tag{3.11}
\]

The \(\chi\) denotes the fraction of additional HO recycling, which in the current study varies from 0 to 20, 40, 60, 80, and 100 %. The interplay and the interaction of upward- and downward-moving eddies can produce incomplete mixing of chemical species within the ABL. Segregation of chemical reactants results in response to different spatial distribution of sources and sinks of isoprene and oxidants, and is hypothesized to affect isoprene oxidation within the ABL (e.g., Krol et al., 2000; Verver et al., 2000). The intensity of segregation (I$_s$) for two chemical species (A, B) can be estimated using Equation 3.12 (Brodkey, 1981).

\[
I_{s,A+B} = \frac{\overline{AB'}}{\overline{A\overline{B}}} \tag{3.12}
\]

Covariances between the chemical species (\(\overline{AB'}\)), averaged over a given time period (the over bar denotes temporal averages), serve as measures of the segregation of the gases compared to their averaged quantities (\(\overline{A}, \overline{B}\)). Spatial segregation of chemical species can lead to negative I$_s$ while colocation of their source distribution causes I$_s$ to be positive. In the context of the zero-dimensional modeling, effects of segregation are typically included (e.g., Ouwersloot et al., 2011) through the introduction of effective reaction rate coefficients (k$_{\text{eff}, I_s}$). The method uses I$_s$ to reduce the default reaction rate coefficient. In the case of the reaction of
isoprene with HO, from the second-order reaction

\[ \text{ISOP} + \text{HO} \xrightarrow{k_{13}} \text{Products} \]  

(3.13)

the effective reaction rate \( R \) can be determined as

\[ R = k_{13}(1 + I_{s,\text{ISOP+HO}}) \langle \text{ISOP} \rangle_{\text{ML}} \langle \text{HO} \rangle_{\text{ML}} = k_{\text{eff},I_s} \langle \text{ISOP} \rangle_{\text{ML}} \langle \text{HO} \rangle_{\text{ML}}. \]  

(3.14)

In the tropical convective boundary layer, previous studies reported isoprene and HO segregation intensities of 7–13 % based on large eddy simulation results (Ouwersloot et al., 2011), 13–43 % from aircraft profile measurements, and up to 50 % from regional chemical model calculations (Karl et al., 2007; Butler et al., 2008). \textit{Ad hoc} \( I_{s,\text{ISOP+HO}} \) values of -0.1, -0.2, -0.3, -0.4 and -0.5 are used in this study to estimate the potential impacts of segregation effects and incomplete air mixing on the temporal variability of ambient isoprene levels.

Nitric oxide plays an essential role in the chemistry of biogenic hydrocarbons and can regulate the concentrations of \( \text{O}_3 \) and HO. In addition, NO levels to some extent dictate the pathway of isoprene photochemical reactions (Liu et al., 2016). Therefore, simulation experiments are executed with varying NO emission rates, ranging from \( 1 \times 10^{-5} \) to \( 4 \times 10^{-4} \) ppbv min\(^{-1}\), to examine the impacts of NO on the inferred isoprene levels.

### 3.3 Results and discussion

Observed isoprene mixing ratios along with the concurrent meteorological and phenology data are presented and discussed. Zero-dimensional model results are presented to investigate the processes controlling diel evolution of isoprene mixing ratio. Uncertainties associated with isoprene emission, boundary layer evolution, and chemistry are assessed.

#### 3.3.1 Influences of meteorological conditions on diurnal cycles of isoprene

During 2014, the study site experienced only small seasonal variations in air temperature, with averaged monthly oscillations of about 5 °C. Maximum ambient temperature (32.4 ± 1.7 °C) occurred at the end of the dry season in September (Figure 3.2a) when the highest averaged PAR levels reached 394 ± 76 W m\(^{-2}\) (Figure 2a) in response to reduced
cloudiness and storms. In contrast, the lowest radiation and temperature were observed in January 2015 (245 ± 124 W m⁻², 27.8 ± 2.7°C, respectively) (Figure 3.2a). June and July were transition months and they experienced mixed features of both wet and dry seasons with a notable reduction in monthly rainfall but similar light and temperature conditions compared to the preceding months (Figures 3.2a, b). The Amazon rain forest is characterized by high rainfall year round but is punctuated with reduced rainy periods when total monthly rainfall drops below 100 mm (Sombroek, 2001). The study site experiences considerable inter-annual rainfall variability (Malhi, 2002). In 2014, August and September were considered dry periods with total monthly rainfall of < 100 mm whereas October to May represented the peak of the rainy season with maximum monthly rainfall of 600 mm (Figure 3.2b). Kinematic heat fluxes, derived from eddy covariance measurements, exhibited strong diurnal variations with maximum values of 0.15 K m s⁻¹ generally attained during 11:00 to 13:00 hours (Figure 3.2d). During the morning hours, rapid increases in the kinematic heat fluxes occurred due to reduced cloudiness. Mean maximum heat fluxes exceeding 0.10 K m s⁻¹ prevailed during the dry season in response to the greater incoming solar irradiance and surface heating (Figures 3.2a,d). Utilizing knowledge of kinematic heat fluxes, the estimated depth of the ABL mixed layer exhibited pronounced diurnal and seasonal patterns, with z_i values ranging from 100 m up to 1300 m (Figure 3.2c). From 8:00 to 14:00 hours, the mixed layer rapidly developed with time in response to increasing surface heating (Figure 3.2d) and from 14:00 to 18:00 hours the mixed layer depth remained relatively stationary while the kinematic heat fluxes decreased, with the extra energy to support the CBL coming from entrainment. Although the modeling of mixed layer did not consider day-to-day variations in the advection or large-scale atmospheric dynamics, estimates of the mixed layer depth (Figure 3.2c) reasonably agreed with values derived from upper air soundings made over the rain forest in the southwest Amazonia (Fisch et al., 2004). Typical z_i values derived by Fisch et al. (2004) using rawinsondes are presented (Figure 2c) in order to compare them with the estimates obtained in this study.

Isoprene mixing ratios over the rain forest exhibited strong seasonal variability in response to meteorological conditions and plant phenology. Maximum averaged isoprene levels of about 10 ppbv prevailed during September (Figure 3.3b) and coincided with ambient temperature of > 30 °C that promoted enhanced emissions. Throughout the growing season, variations in leaf area and foliage phenology also influenced isoprene emissions (Figures 3.3a; see below). On daily time scales, isoprene mixing ratios showed well-defined diel cycles
with maximum levels observed in the early afternoon and minimum just before sunrise (Figures 3.3a-d) in response to daytime emissions from the rain forest. Isoprene mixing ratios increased with PAR levels (Figures 3.3e-l) due to the influences of light on isoprene biosynthesis. The relationship between isoprene levels and PAR (Figures 3.3e-h) exhibited some hysteresis in the variability of isoprene. In the morning hours, isoprene levels increased with PAR whereas in the afternoon isoprene mixing ratios declined along a different trajectory after PAR reached the daily maximum values. These PAR-isoprene patterns result partly owing to the thermodynamic characteristics of the local atmospheric boundary layer (Fuentes
and Wang, 1999). Diurnal hysteresis between evapotranspiration and vapor pressure deficit also prevail in many ecosystems (Zhang et al., 2014). In the morning hours, emissions occur when there are shallow boundary layers whose isoprene content is low (< 2 ppbv) due to the combined influences of surface deposition and no emissions from the previous night. Because of the weak convection in the morning, the emitted isoprene remains mixed in a relatively small atmospheric volume whose depth is defined by the shallow mixed layer. In contrast, during the afternoon isoprene emission takes place when the atmospheric boundary layer is deeper and remains relatively well mixed due to the strong convection. Consequently, isoprene levels tend to decreased with reducing PAR along a path exhibiting greater values compared to the morning quantities (Figures 3.3e-h). Isoprene mixing ratios correlated well with air temperature in both morning and afternoon hours (Figures 3.3i-l).

Figure 3.3: Top panel (a, b, c, d) shows mean diel cycles of isoprene mixing ratios for June, September, December and January (2015). Middle (e, f, g, h) and bottom (i, g, k, l) panels show diurnal cycles of isoprene mixing ratios versus those of PAR and temperature, respectively. The values are monthly averages. Squares denotes the period from 6:00 to 8:00 hours, stars 8:00 to 10:00 hours, crosses 10:00 to 12:00 hours, diamonds 12:00 to 14:00 hours, open circles 14:00 to 16:00 hours, and triangles 16:00 to 18:00 hours.
3.3.2 Influences of foliage phenology on isoprene seasonal patterns

Over the course of the 2014 growing season, MODIS-derived LAI varied from 4.5 to 6.5 m$^2$ m$^{-2}$ (Figure 3.4a). Based on in situ observations (Wu et al., 2016), the low LAI values obtained for June and July resulted due to the combination of high amounts of leaf senescence and abscission, and development of new foliage (Figure 3.4a). The leaf loss in June was greater than the new leaf production. Just before the onset of dry seasons in July, new leaf production exceeds the simultaneous litterfall, which resulted in the significant net increase of LAI from July to August. The significant reductions in LAI identified during June coincided with the onset of the dry season (Figure 3.2b) and indicated shifts of leaf age composition toward new leaves (Figure 3.4a). In addition, reductions in LAI and shifts toward young foliage corresponded with the observed lowest isoprene and highest methanol levels (Figure 3.4b). These results are consistent with the fact that young leaves ordinarily exhibit low isoprene (Monson et al., 1994; Fuentes and Wang, 1999) and high methanol emissions (Alves et al., 2014; Jardine et al., 2016). With the start of the rainy season in September (Figure 3.2b) new leaves expanded and matured throughout the growing season, resulting in larger LAI during September to January (Figure 3.4a). Wu et al. (2016) showed similar foliage patterns that new leaves emerge in June and mature during both the dry period (from August to September) and the beginning of the wet season (from September to November). Such simultaneous temporal patterns in foliage quantity and phenology seemed consistent with the seasonal isoprene levels observed in September, December and January (Figure 3.4b). Median isoprene mixing ratios, calculated for the period ranging from 10:00 to 14:00 hours, exhibited strong seasonal patterns, with maximum and minimum values observed in September and June, respectively (Figure 3.4b). Percentage changes in isoprene mixing ratios relative to June revealed major seasonal variations, ranging from 10 to 80% (Figure 3.4c). The percentage changes in the temperature response ($\gamma_T$) with respect to June were also plotted (Figure 3.4c) in order to quantitatively show the influences of temperature on the increased isoprene mixing ratios. In September, both meteorological factors and LAI contributed to the 80% increase in isoprene, with temperature being the predominant factor as shown by the 110% increase in $\gamma_T$. However, isoprene mixing ratios were 60% and 10% greater in December and January than in June despite the similar meteorological conditions observed during these months (Figure 3.4c). Therefore, temperature and PAR levels did not consistently drive isoprene mixing ratios. In fact, the increases in LAI invariably followed those in isoprene mixing ratios (Figure 3.4c), suggesting amount of foliage and phenology
consistently tracked the seasonality of isoprene mixing ratios.

In the rain forest, isoprene emission algorithms need to consider seasonal variations of active biomass and changes in constitutive basal emissions associated with foliage age. To quantify the effects of foliage amounts and leaf age on isoprene emissions, the information presented above (Figures 3.3 and 3.4) were included in the isoprene emission algorithm described in Section 2.3. Even though suitable environmental conditions and adequate amounts of active biomass prevailed in June, maximum isoprene emissions only reached 5 mg m\(^{-2}\) h\(^{-1}\) (Figure 3.5a). Highest emission rates of approximately 11 mg m\(^{-2}\) h\(^{-1}\) estimated for September (Figure 3.5a) resulted mainly due to temperature and PAR as well as greater amounts of foliage quantity and basal isoprene biosynthesis. The almost identical meteorological conditions observed during December and June (Figure 3.2a) indicated that the greater isoprene emissions estimated for December occurred in response to foliage attaining a greater capacity to emit isoprene. On the whole, these results (Figure 3.5a) illustrate that aggregate foliage phenology as expressed in the basal emission rates, considering the relatively small variability of environmental drivers in the rain forest, is one factor contributing to the isoprene seasonality. Estimates of isoprene emissions are in good agreement with previously reported canopy-scale isoprene fluxes (Rinne et al., 2002; Kuhn et al., 2007).

To corroborate the influences of foliage phenology on estimated isoprene emissions, three additional numerical simulations were performed. The first simulation included a constant LAI of 6 m\(^2\) m\(^{-2}\) and an unchanged leaf age while the second experiment involved the observed LAI (shown in Figure 3.4a). These two simulations indicated that isoprene emissions barely changed with amount of active biomass when LAI exceeded 4.5 m\(^2\) m\(^{-2}\) (Figure 3.5b). As shown in previous studies (Guenter et al., 2006), the emission algorithm provides nearly constant isoprene fluxes for LAI greater than 5 m\(^2\) m\(^{-2}\) due to the insufficient PAR levels reaching the lower forest canopy. The third simulation incorporated the observed LAI and variable isoprene basal emissions to reflect leaf age (as done in Figure 3.5a). Results indicated that the maximum isoprene emission rates decreased by 6 % in June and increased by 12 % in September, December and January when leaf phenology was considered in the emission algorithm. Results (Figure 5b) indicated that between June and September changes in maximum isoprene emission without leaf age increased from 4 mg m\(^{-2}\) h\(^{-1}\) to 8 mg m\(^{-2}\) h\(^{-1}\) while emission changes associated with the leaf age algorithm were small (from 8 mg m\(^{-2}\) h\(^{-1}\) to 9 mg m\(^{-2}\) h\(^{-1}\) ). Environmental conditions predominantly explained the large emission changes between June and September. Seasonal differences in emissions
Figure 3.4: (a) Monthly leaf area index (LAI) from the tile of h11v09 of the Terra MODIS (moderate-resolution imaging spectroradiometer) for the measurement period (dark green squares); dark green asterisk represents January 2015 LAI from Wu et al. (2016); New leaf production (blue circles) at the same site (ZF2) from Wu et al. (2016); (b) Median daytime (10:00-14:00 hours) isoprene and methanol mixing ratios for June, September, December and January; (c) Percentage increases in isoprene, PAR, temperature, gamma-temperature ($\gamma_T$), LAI, and methanol relative to June.

are linked to new leaves with low isoprene emission capacity in June, leaves grow mature in about six months and incrementally augment their photosynthetic capacity and isoprene biosynthesis, and leaves become old from January until next June which is just before the start of the dry season (Wu et al., 2016).
Figure 3.5: (a) Estimates of isoprene emission rates for June, September, December and January (2015). Solid lines denote the monthly averages of modeled emission rates and shaded areas represent the standard deviations. (b) The modeled responses of emission rates to leaf area index (LAI) and leaf age in the algorithm of isoprene emission.

3.3.3 Processes controlling the isoprene diel cycles

Once released from leaves, isoprene molecules can undergo chemical reactions, surface deposition, and turbulent transport in the atmospheric boundary layer. With the zero-dimensional model (Goliff et al., 2013), it was possible to investigate the influences of each aforementioned process on isoprene temporal variations. Model results closely matched isoprene (Figures 3.6a-d) and ozone (Figures 3.6e-h) levels for the chosen months of the simulations. Comparisons of the typical atmospheric lifetime of isoprene, which is in the order of 1–2 hours, with the convective boundary layer overturning timescales (typically
$z_i/w_* \sim 10 \text{ minutes}$ indicated that isoprene remained relatively well mixed in the ABL as demonstrated by previous field studies (Karl et al., 2007; Fuentes et al., 2016).

Hydroxyl radicals, which serve as the main chemical sink of isoprene, were estimated based on the photolysis of ozone ($O_3 + \text{Light} \rightarrow O_2 + O^{(1D)}$) and reactions of the resulting electronically excited atomic oxygen ($O^{(1D)}$) with water vapor ($O^{(1D)} + H_2O \rightarrow HO + HO$; photolysis of chemical species such as nitric acid and formaldehyde also contributed to the HO formation). Simulated maximum HO concentrations and photolysis rates ($J_{NO_2}$) did not occur at the same time. Instead, estimated HO concentrations reached maximum values around 09:00 hours when ozone levels remained relatively low while maximum photolysis rates prevailed around noon time (Figures 3.6i-l). Early in the morning, abrupt increases in HO concentrations occurred due to rapid increases in solar irradiance, the preponderance of shallow atmospheric boundary layers, and low isoprene levels. Previous studies (Whalley et al., 2011; Taraborrelli et al., 2012) also found similar HO temporal trends. In this case (Figures 3.6i-l), temporal patterns in HO concentrations resulted from the combined effects of diurnal cycles of photolysis, isoprene emissions, and depth of the boundary layer. Highest and lowest HO concentrations happened in September ($1.1 \times 10^6 \text{ molecules cm}^{-3}$) and December ($6.4 \times 10^5 \text{ molecules cm}^{-3}$), respectively, consistent with the seasonality of ozone. Earlier studies (Whalley et al., 2011) reported averaged maximum HO concentrations of $\sim 2.5 \times 10^6$ molecules cm$^{-3}$ with a day-to-day variability of $\sim 1.5 \times 10^6$ molecules cm$^{-3}$ at 5 m above the ground in a clearing of a tropical rain forest. This underestimation of HO in the rain forest likely occurred as a consequence that the zero-dimensional model did not account for HO recycling from hydrocarbon oxidation (Taraborrelli et al., 2012; Fuchs et al., 2013) and segregation of isoprene-HO due to incomplete turbulent mixing (Kaser et al., 2015; Kim et al., 2016) (evaluations of these two processes on modeled HO concentrations are discussed in Section 3.4).

In the absence of biomass burning or anthropogenic pollution, the NO levels in central Amazonia exist in the parts per trillion (pptv) range (for the same study period, Liu et al. (2016) reported a mean value of 0.035 ± 0.032 ppbv). Soil emissions (Bakwin et al., 1990) in the zero-dimensional model were set to yield the range of NO mixing ratios measured at the study site. During the nighttime, the reaction of NO with $O_3$ produced $NO_2$ whose maximum mixing ratios reached 0.5 ppbv (Figures 3.6m-p). Modeled daytime (8:00–16:00 hours) mean NO levels (0.06 ppbv for June, 0.05 ppbv for December and January, and 0.07 ppbv for September) closely agreed with measured quantities (see below). In the early
morning the NO levels increased rapidly due to the photolysis of NO$_2$ (Jacob and Wofsy, 1988; Torres and Buchan, 1988). The results summarized in Figure 3.6 indicated that the zero-dimensional model adequately captured the principal reaction pathways responsible for the oxidation of isoprene.

Contributions of isoprene emissions, entrainment into the ABL ($E(t) - F_{e}(t)$), and chemical reactions ($f_{Chem}$) were examined to identify the most important controls on the diel cycles of isoprene mixing ratios (Figure 1). During the nighttime, isoprene emissions and reac-
tion with HO were negligible (Figures 3.7a-d) but dry deposition and reaction with nitrate radicals (NO$_3$) represented sinks. On average, dry deposition accounted for 78% of the total nighttime loss of isoprene (not shown) and NO$_3$ played a minor sink role due to its low concentrations. Before 15:00 hours, the rate of isoprene change ($\frac{\partial \langle \text{ISOP} \rangle_{\text{ML}}}{\partial t}$), due to the dominance of the emission term over the chemical reactions, resulted in a positive quantity. The emission term attained highest values around 7:00 hours when isoprene was emitted and entrained (which accounted for 34% of the emission at this time) into a shallow boundary-layer and chemical destruction was weak. In contrast, the chemical sink (mostly by HO) reached maximum values around 11:00 hours when both isoprene and HO were abundantly available. Around 15:00 hours, emissions and reactions almost reached a balance and gave rise to highest daily isoprene mixing ratios (Figures 3.7a-d). Thereafter, chemical consumption dominated as declining isoprene emissions coincided with high $z_i$. This budget method (Equation 1) failed to capture the precipitous declines of isoprene observed around sunset (Figures 3.7a-d), which have been ubiquitously reported for other forested ecosystems (Fuentes et al., 1999; Hurst et al., 2001) and urban sites (Doughty et al., 2015). Hurst et al. (2001) estimated that vertical mixing with isoprene-depleted air probably contributes to the rapid isoprene decay in unpolluted environments. Doughty et al. (2015) concluded that the abrupt isoprene declines depend on nitrate radicals. Altogether this budget analysis revealed that, integrated over the 6:00-to 18:00-hour period, on average 56% (4.8 ppbv), 77% (12.3 ppbv), 69% (6.2 ppbv), and 69% (6.2 ppbv) of the emitted isoprene was chemically consumed in June, September, December, and January, respectively (Figures 3.7e). These results highlight the necessity and the importance of having reliable knowledge of isoprene reaction pathways so that improved estimates of oxidant and SOA formation can be made for the Amazon rain forest.

### 3.3.4 Sensitivity analysis

Uncertainties associated with day-to-day variations in $E$, $z_i$, entrainment, HO recycling, and HO-isoprene segregation are estimated to ascertain the fidelity of simulated mean diel cycles of isoprene. The focus of this analysis is on the sensitivity of each process in influencing the ambient isoprene levels. Therefore, experiments only for June (Figure 3.6a) are considered as the control simulation. The estimated $z_i$ exhibited large day-to-day variations (Figure 3.8a) due to the variability of kinematic heat fluxes, assumed lapse rate in the free atmo-
Figure 3.7: Contributions of the emission term in Equation 3.1 and the chemical destruction in Equation 3.1 to layer-averaged isoprene mixing ratios. Upper panels (a, b, c, d) show observed (cyan) and modeled (black) rates of change of isoprene due to a combination of emission (blue) and chemical destruction (red). Lower panel (e) shows changes of air layer-averaged isoprene mixing ratios over the course of day (blue bar) due to chemical consumption (red bar) and emission (whole bar).

Modeled isoprene ambient levels increased by 77 % when hourly $z_i$ decreased one standard deviation from its averaged half values $z_i - \sigma_i$ (Figure 3.8a) whereas the corresponding increase to $z_i + \sigma_i$ reduced isoprene by 31 % (Figure 3.8b). These results indicated that in shallow mixed layers and hence smaller atmospheric mixing volume, isoprene levels can be overestimated. In contrast, in deeper mixed layers and thus greater atmospheric mixing volume, isoprene mixing ratios can be substantially underestimated. In the case of emissions, the simulations of $E + \sigma_E$ and $E - \sigma_E$ generated a 78 % increase and a 55 % decrease, respectively, in isoprene mixing ratios (Figure 3.8d) compared to the mean quantities. This sensitivity analysis (Figures 3.8c,d) illustrated that even small perturbations of $z_i$ and $E$ can engender substantial deviations in isoprene levels from averaged conditions.
Entrainment of air from the residual layer or the free atmosphere to the mixed layer can influence ambient isoprene levels in the air above the forest canopy. In this sensitivity analysis (Figure 3.9), it was assumed that the isoprene mixing ratio ($\langle$ISOP$\rangle_{RL}$) observed around 17:30 hours (when the onset of the stable boundary layer occurred and a fraction of isoprene remained in the residual layer (Verver et al., 2000)) could be employed to estimate the entrainment using Equation 3.8. The $\langle$ISOP$\rangle_{RL}$ could be construed as the upper bound of the isoprene mixing ratio because chemical sinks were not considered during the nighttime. As the mixed layer developed in the early morning, the computed fraction of entrainment flux to isoprene emission attained maximum values amounting to -34 %, indicating that entrainment enhanced the isoprene content of the mixed layer (Figure 3.9a). After 9:00 hours the ratios reached about 20 %, suggesting that entrainment contributed to the dilution of isoprene in the mixed layer (Figure 3.9a). It is sometimes assumed that the free troposphere is devoid of isoprene (de Arellano et al., 2009). Therefore, additional simulations were performed to assess the impact of entraining isoprene-depleted air into the mixed layer. Results (Figure
3.9b) showed that entrainment of isoprene-free air decreased the maximum isoprene mixing ratios by 32 % while the controlled case ($\langle \text{ISOP} \rangle_{\text{FA}} = 2.75 \text{ ppbv}$) consistently matched the observations. In summary, the sensitivity analysis (Figure 3.9) demonstrated that the temporal patterns of ambient isoprene levels were strongly coupled to the entrainment process as confirmed by earlier studies (Karl et al., 2007; de Arellano et al., 2009).

Figure 3.9: Diurnal variations of the ratio of isoprene entrainment flux to emission (a). Measured and calculated isoprene mixing ratios under different conditions of isoprene content in the residual layer (b).

Hydroxyl radicals exert control on the temporal patterns of isoprene above the rain forest. Recycling of HO from isoprene reactions (Taraborrelli et al., 2012; Fuchs et al., 2013) and segregation of isoprene-HO (Krol et al., 2000; Verver et al., 2000; Karl et al., 2007;
Ouwersloot et al., 2011; Kaser et al., 2015) are investigated for their potential influence on ambient isoprene levels. Because the photochemical mechanism to study isoprene chemistry did not include HO recycling, several \textit{a priori} \( \chi \) values were included in the simulations. As expected, the recycling of HO enhanced the HO concentrations but in general reduced isoprene mixing ratios (Figure 3.10a). Compared to the control simulations, the \( \chi \) value of 100\% contributed to 24\% increase in HO concentrations and 16\% underestimation of isoprene mixing ratios (Figure 3.10a). Simulated isoprene levels closely matched observations when the \( \chi \) value of 20\% was considered. As suggested in previous studies (Fuchs et al., 2013), the isomerization reactions associated with HO recycling need to be investigated as a function of NO concentrations. Slowing down the reaction rate of isoprene and HO (Reaction 3.13) tended to increase both isoprene and HO (Figure 3.10b). A 50\% reduction in the reaction rate caused the maxima of isoprene and HO to deviate from the control run by 16\% and 42\%, respectively. Deviations in the inferred isoprene mixing ratios (Figure 3.10) were lower than those associated with the physical processes described earlier (Section 3.3) and indicated that, within their likely ranges and as reported in other studies (Karl et al., 2007; Ouwersloot et al., 2011), isoprene-HO segregation played a lesser role in regulating ambient isoprene levels.

Isoprene reaction pathways and associated oxidant yields depend on the ambient NO levels. Several numerical model simulations were performed to examine the impacts of varying NO levels on isoprene and HO estimation. Initial levels and emissions of NO were prescribed in the zero-dimensional model to generate ambient NO levels that remained within the range of observations in the central Amazonia region (Torres and Buchan, 1988; Liu et al., 2016). Results (Figure 3.11) indicated that as NO increased from 0.04 to 0.36 ppbv then isoprene rapidly declined from its initial value of 4.0 to 0.2 ppbv while at the same time HO exponentially increased from \( 1 \times 10^6 \) to \( 13 \times 10^6 \) radicals per cm\(^3\). Part of the explanation for the increases in HO concentrations is that the oxidation of isoprene produces hydroperoxyl radicals (HO\(_2\)) which react with NO to form HO and NO\(_2\) (Fuentes et al., 2000; Paulot et al., 2009a). Therefore, environments with elevated concentrations of NO can experience sufficient HO levels to promote the oxidation of biogenic hydrocarbons within the atmospheric boundary layer. Chemistry of isoprene in air with NO greater than 0.1 ppbv is the salient process influencing the diel cycles of isoprene above the rain forest.
Figure 3.10: Calculated isoprene mixing ratios under different conditions of hydroxyl radical (HO) recycling (a) and segregation of isoprene-HO (b). Solid lines (green, red and black) denote modeled isoprene mixing ratios and dashed lines represent modeled hydroxyl radicals. Cyan lines denote measured mean isoprene mixing ratios and shaded areas represent the standard deviations.

3.3.5 Study limitations

Because of the lack of crucial measurements such as foliage- and ecosystem-based isoprene emissions, several limitations are acknowledged with this study. The comparison of the leaf phenology between September and December can not be made because these two months have similar LAI. Results from previous studies (Wu et al., 2016) were used to complement the statements about leaf age and the capacity to emit isoprene when comparing September
Figure 3.11: Variations of isoprene as a function of initial nitric oxide and hydroxyl radical. Photochemical model simulations included emissions of nitric oxide. Isoprene mixing ratio and hydroxyl radical concentration are daytime (10:00-14:00 hours, local time) averages. Values of isoprene mixing ratios within the shaded area represent the averages of the standard deviation calculated during 10:00 - 14:00 hours.

and December. Also, the MODIS-derived LAI data have up to 20 % uncertainties (Fensholt et al., 2004), which likely contributes to the variations in LAI estimated for August and December. The isoprene emission algorithm included multiple parameters to adjust for various climates and ecosystems. Without local foliage measurements, required parameters are challenging to adjust at the site level. The variability of foliage age as a function of canopy depth was not considered. In the tropics, it is likely that younger foliage can mostly remain in the forest crown. Isoprene and its reactants were assumed to stay well mixed within the ABL. Throughout the numerical model simulations, isoprene levels within the residual layer were kept constant with time. Daytime isoprene deposition velocity is calculated based on the reported cuticle resistances of ozone because of the lack of information for estimating the cuticle resistance for isoprene. Therefore, the deposition of isoprene remains a source of uncertainty. The assumed ABL thermodynamics and air chemistry applied to undisturbed conditions. Mesoscale convective systems frequently occur in the tropics and modify the thermodynamics of the lower atmosphere (e.g., $\gamma \theta_v$, $\Delta \theta_v$, $z_i$), the spatio-temporal distribution of $O_3$ and other reactive gases, and associated chemical cycles (Gerken et al.,
2016). Taken together, these assumptions carry certain levels of uncertainties which can be addressed in future investigations.

### 3.4 Conclusions

Isoprene mixing ratios over the rain forest canopy exhibited substantial seasonality, with diurnal values in December reaching levels approximately 70% higher than those in June. Incoming photosynthetically active radiation and temperature, the two environmental variables modulating emissions, were almost identical in June and December but did not correspondingly explain the observed seasonality in isoprene levels. Instead, leaf phenology and quantity consistently followed the seasonality of isoprene. The dry months of August and September had the highest estimated isoprene emission rates, with averaged maximum flux densities of 11 mg m\(^{-2}\) hour\(^{-1}\) prevailing due to the concomitant influences of high temperature (> 30 °C) and incoming insolation, and high quality and quantity of foliage. New foliage, developed at the start of the wet season, had to accrue competency to emit isoprene. Therefore, aggregate foliage phenology and associated variations in putative basal emissions became important controls on isoprene seasonality. Not all seasonal variability in observed isoprene levels could be ascribed to changes in basal emissions. For instance, convective boundary layer depths, which exhibit clear seasonal cycles in the Amazon region, can also substantially influence ambient isoprene levels. Model results show that a 30% deeper boundary layer can lead to 31% reduction in estimated isoprene mixing ratios.

Several boundary layer processes influenced the diel cycles of isoprene and each processes contributed differently at different times of day. Dry deposition represented the main sink of isoprene during the nighttime. During the daytime, a significant amount of the emitted isoprene was chemically consumed via reactions involving HO, with more than 50% of isoprene variability owing to oxidation.

Sensitivity analysis revealed that the air layer-averaged NO levels became the predominant factor promoting the isoprene oxidation through the reaction with HO. Several chemical pathways explain the NO-isoprene-HO relationship. The isoprene oxidation produces HO\(_2\) which combines with NO to form additional HO. Also, the rain forest emits large amounts of monoterpenes and sesquiterpenes whose reactions with O\(_3\) generate organic peroxyl radicals (RO\(_2\)). The RO\(_2\) subsequently reacts with NO to form NO\(_2\), which is a direct O\(_3\) precursor. In the presence of water vapor, the photolysis of O\(_3\) produces HO. Therefore, the accurate
determination of NO concentrations is crucially important for the reliable estimation of isoprene levels under low-NO and high-VOC conditions. Given that the Amazon rain forest frequently experiences enhanced levels of nitrogen oxides due to human activities such as biomass burning or urban polluted plumes, the atmospheric chemistry of isoprene can be greatly modified and thus impact its seasonal patterns.
### 3.5 Supplement A

Table 3.4: Initial mixing ratios of other chemical species included in the photochemical module during the months considered in the numerical simulations.

<table>
<thead>
<tr>
<th>Model species</th>
<th>Definition</th>
<th>Initial values (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>API</td>
<td>$\alpha$-pinene and other cyclic terpenes with one double bond</td>
<td>0.2$^*$</td>
</tr>
<tr>
<td>LIM</td>
<td>d-limonene and other cyclic diene-terpenes</td>
<td>0.5$^*$</td>
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<td>OLT</td>
<td>Terminal alkenes</td>
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<td>OLI</td>
<td>Internal alkenes</td>
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<td>HC3</td>
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<tr>
<td>HC5</td>
<td>Alkanes, alcohols, esters, and alkynes with HO rate constant between $3.4 \times 10^{-12}$ and $6.8 \times 10^{-12}$ cm$^3$s$^{-1}$</td>
<td>0.39</td>
</tr>
<tr>
<td>HC8</td>
<td>Alkanes, alcohols, esters, and alkynes with HO rate constant greater than $6.8 \times 10^{-12}$</td>
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</tr>
<tr>
<td>DIEN</td>
<td>Butadiene and other anthropogenic dienes</td>
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<td>TOL</td>
<td>Toluene and less reactive aromatics</td>
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</tr>
<tr>
<td>XYL</td>
<td>Xylene and more reactive aromatics</td>
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<td>Ethene</td>
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<td>Ethane</td>
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<td>MVK</td>
<td>Methyl vinyl ketone</td>
<td>1.8$^{**}$</td>
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<td>MACR</td>
<td>Methacrolein and other unsaturated monoaldehydes</td>
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<td>BEN</td>
<td>Benzene</td>
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<td>Peroxyacetyl nitrate and higher saturated PANs</td>
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<td>Methanol</td>
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</tr>
<tr>
<td>ACE</td>
<td>Acetylene</td>
<td>2.0</td>
</tr>
<tr>
<td>CH4</td>
<td>Methane</td>
<td>1800</td>
</tr>
<tr>
<td>HCHO</td>
<td>Formaldehyde</td>
<td>1.0</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
<td>100</td>
</tr>
</tbody>
</table>

$^*$: Jardine et al. (2015)

$^{**}$: Hu et al. (2015)
Chapter 4

Evaluation of turbulent mixing and gas-phase chemistry in a one dimensional canopy-chemistry model

4.1 Introduction

Biogenic volatile organic compounds (BVOCs) in the forested environments play important roles in atmospheric chemistry and regional climate. The oxidation of BVOCs, in the presence of reactive nitrogen oxides \( \text{NO}_x = \text{nitric oxide (NO)} + \text{nitrogen dioxide (NO}_2) \) and sunlight, can lead to ozone \( \text{O}_3 \) formation and oxidation products that can yield secondary organic aerosols (SOA) (Claeys, 2004; Hallquist et al., 2009; Krechmer et al., 2015). In addition, the oxidation of BVOCs influences the abundance of hydroxyl radicals (OH) (Lelieveld et al., 2008; Peeters and Müller, 2010; Crounse et al., 2011; Taraborrelli et al., 2012; Peeters et al., 2014), which is deemed crucial for the regional oxidation capacity of the atmosphere. The tropical rain forest contributes to nearly half the global BVOCs budget (Guenther et al., 1995). The Amazon rain forest, which experiences year-round high temperature, insolation, and humidity, is a major source of BVOCs and OH, thereby playing an important role in the global OH and SOA budgets.

In order to affect these chemical budgets in the troposphere, BVOC and their oxidation products must be mixed effectively in the forest canopy and transported to the overlying atmosphere. However, differences in meteorological and chemical conditions prevail within the canopy compared to the air layers above the forest, resulting in atmospherically decoupled
conditions (Freire et al., 2017). Furthermore, the temporal turbulent transport scales are similar to the lifetimes of BVOCs due to reactions with OH, O₃ and nitrate radical, NO₃ (Karl et al., 2007; Butler et al., 2008; Ouwersloot et al., 2011). Therefore, it is necessary to evaluate the turbulent mixing and BVOC chemistry within the forest canopy.

The OH is the key oxidant in the Earth’s atmosphere and is responsible for the degradation of BVOCs. As a simplified set of reactions, the OH is formed through the reaction of water vapor with oxygen atoms O(^1D), which are produced from the photolysis of O₃. Reaction of BVOCs with OH produce organic peroxy radicals (RO₂). In the presence of oxygen (O₂), the reaction of OH with carbon monoxide (CO) forms hydroperoxy radicals (HO₂) and carbon dioxide (CO₂, Figure 4.1a). Nitrogen oxides have two roles regarding ambient OH concentrations (Ehhalt, 1999). On one hand, the HO₂ can react with NO to yield OH and NO₂ (Figure 4.1b). On the other hand, at higher NOₓ concentrations, the reaction of NO₂ with OH produces nitric acid (HNO₃) which is a OH sink as HNO₃ can be readily deposited to the surface (Nguyen et al., 2015). Previous analyses (Rohrer et al., 2014) of the OH-NOₓ chemistry, involving observations made in environments ranging from forests (Tan et al., 2001; Lelieveld et al., 2008; Hofzumahaus et al., 2009; Whalley et al., 2011; Mao et al., 2012) to polluted cities (Ren, 2003; Kanaya et al., 2007; Dusanter et al., 2009; Lu et al., 2013), showed that the measured OH concentrations decrease with NO in high NOₓ environments whereas OH concentrations seem to be independent on NOₓ levels under high-VOC and low-NOₓ conditions. However, there are two uncertainties related to the study of Rohrer et al. (2014) for the low-NOₓ regime: the possible interference in the OH measurement technique (Mao et al., 2012) and the small range in NOₓ concentrations. Liu et al. (2018) showed that OH concentrations were significantly amplified due to enhanced reactive nitrogen oxides (NO_y) in the Amazon rain forest. Therefore, there is a disagreement in the OH dependence on NOₓ under high-VOC and low-NOₓ conditions. The Amazon rain forest experiences increasing human encroachment and the prevailing low-NO conditions frequently shift to higher NOₓ conditions due to biomass burning and urban emissions. Few studies exist on the OH yields over the wide range of NOₓ levels experienced in the Amazon rain forest due to natural processes (e.g., soil emissions of NO) and anthropogenic activity. In this study, we investigate how the OH concentrations and vertical distributions change with a broad range of NOₓ levels using a one-dimensional (1-D) model (Forkel et al., 2006), paying particular attention to the performances of different chemical mechanisms in simulating the OH-NOₓ relationship.
The importance of turbulent transport within and above the canopy has long been recognized (Finnigan, 2000). A central problem for the parameterization of turbulent transfer in plant canopies is to relate mean concentrations of a scalar to its sources so that a measurement or prediction of one can be used to infer the other. Among the most common parameterization is the first-order flux-gradient relationship, also known as K-theory, in which atmospheric transport occurs by turbulent diffusion (K) along the mean concentration gradient of the scalar. However, K-theory has been found to break down completely within forest canopies, which is shown by frequent observations of counter-gradient fluxes (or negative K values) in forests (Denmead, 1984; Denmead and Bradley, 1985, 1987; Thurtell, 1988; Gao et al., 1989). The origin of the problem is that the vertical length scale of turbulence in the canopy is comparable with the canopy height, so that the mixing process cannot be calculated at higher resolution than the source density profiles (Finnigan, 2000; Raupach, 1989b). However, the K-theory continues to be used in many models due to its computational efficiency (Forkel et al., 2006; Wolfe and Thornton, 2011a; Bryan et al., 2012; Pratt et al., 2012; Hu et al., 2013). A modified K-theory (Makar et al., 1999), where the eddy diffusivity (K) is modified by a correction factor to account for the near-field effects (Raupach, 1989b), have been shown to improve modeled in-canopy and above canopy turbulence (Stroud et al., 2005; Wolfe and Thornton, 2011b; Bryan et al., 2012). Many canopy models do not contain higher-order turbulence to simulate the effects of canopy-scale organized turbulence such as coherent structures. Though large-eddy simulation models (Patton et al., 2001) can capture these dynamics, it is computationally expensive to incorporate the detailed chemical mechanisms in them (Kim et al., 2012). Therefore, using a computationally efficient 1-D model with detailed chemical mechanism is preferred over a model with a
detailed turbulence parameterization.

One-dimensional models can be used to investigate BVOCs chemistry and turbulent mixing within and above forests (Forkel et al., 2006; Wolfe and Thornton, 2011a; Bryan et al., 2012; Pratt et al., 2012; Hu et al., 2013; Saylor, 2013; Ashworth et al., 2015). Such models divide the plant environment into air layers with known amount of active biomass and allow for the determination of BVOC emissions, the turbulent transport, radiative transfer, surface deposition, and chemical reactions in each air layer. Chemical mechanisms used in 1-d models vary from simple representations of the chemical reactions (Gao et al., 1993; Makar et al., 1999; Stroud et al., 2005), highly condensed photochemical mechanisms (Forkel et al., 2006; Wolfe and Thornton, 2011a; Bryan et al., 2012; Pratt et al., 2012; Hu et al., 2013) that include the the Regional Atmospheric Chemistry Mechanism (Stockwell et al., 1997), to detailed and explicit photochemical mechanisms (Boy et al., 2011; Saylor, 2013; Ashworth et al., 2015) that use subsets of Master Chemical Mechanism (MCMv3.3) (Saunders et al., 2003). Detailed chemical mechanisms are desirable to include in 1-d models if the goal is to estimate all sinks and sources of OH associated with the oxidation of BVOCs. For example, the isoprene oxidation produces high yields of formaldehyde (CH$_2$O) (Palmer, 2003) which can undergo photolysis to generate OH as a function of NO. In the current study, the highly condensed RACM2 (Goliff et al., 2013) and nearly explicit MCMv3.3 mechanisms are included in a 1-d model to determine the the vertical OH distribution in the rain forest where BVOC emissions are copious. In addition, in most 1-D models, the turbulent mixing within the canopy is based on K-theory, which is known to have limitations, and thus these models need to be improved. Bryan et al. (2012) showed that the observation-based eddy diffusivity parameterization improves the prediction of in-canopy BVOC concentrations and gradients. However, the absence of lower canopy micrometeorological measurements is a typically limiting factor in estimating in-canopy mixing. For the GoAmazon 2014/5 field campaign, the ten levels of turbulence measurements provided the necessary information to evaluate the performance of the turbulent mixing formulation included in the 1-d model used in the present study.

The objectives of this study are to (1) determine the influences of the eddy diffusivity formulation included in the 1-D model on in-canopy chemistry; (2) ascertain whether a condensed or an explicit chemical mechanism is more realistic in simulating the chemistry of BVOCs, key BVOC oxidation products (e.g., formaldehyde, MVK+MACR), and HO$_X$; (3) investigate the nature of the OH-NO$_X$ relationship and its implications for the oxidative
capacity in the Amazon rain forest where BVOCs are abundantly produced and low NO\textsubscript{X} levels prevail.

4.2 Methodology

4.2.1 Model description

The one-dimensional canopy-chemistry model (CACHE) predicts profiles of temperature, water vapor, and chemical compounds by solving the prognostic equations for the potential temperature ($\theta$) and the mixing ratios of water vapor and chemical compounds ($c_i$) within and above the forest canopy. Under the assumption of horizontally homogeneous conditions, the conservation of heat and mass of the chemical species of interest can be defined as:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} (K_H \frac{\partial \theta}{\partial z}) + S_H \tag{4.1}$$

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial z} (K_H \frac{\partial c_i}{\partial z}) + S_c + C \tag{4.2}$$

Equations (1) and (2) are solved for each model layer, where $K_H$ denotes the turbulent exchange coefficient for heat (also referred to as eddy diffusivity), $S_H$ and $S_c$ denote sources and sinks for heat and mass, respectively, and $C$ denotes chemical transformation. Turbulent exchange, chemistry, emissions, deposition, and advection are described in subsequent sections.

4.2.2 Model setup for the Amazon site

4.2.2.1 Study site

Details about the 2014/5 GoAmazon project, the study site ZF2, and the measurements of BVOC mixing ratios and meteorological factors are described in Chapter 1 and Chapter 2.

For the application to the 35 m high rain forest with a leaf area index (LAI) of 5–6 m\textsuperscript{2} m\textsuperscript{−2} in the central Amazonian (Figure 4.2, Fuentes et al. (2016)), CACHE was set up with 40 levels, 13 layers within the canopy, including 3 layers in the trunk space. The vertical resolution was 0.93 m for the lowest layer and 475 m for the uppermost layer. The model top
was located at 3.04 km above the ground. The time step of the simulations was 1 minute.
Initial conditions are provided to the model for vertical profiles of chemical concentrations
based on observed near-canopy concentrations at the start of the simulation. The model is
constrained by observed PAR and O₃. In addition, we prescribe a total leaf area index (LAI)
of 7.3 m²m⁻² (Tóta et al., 2012). The model is constrained by the observed O₃ at the height
of 41 m. The initial values for the chemical species are described in Table 4.1 and 4.2. After
24 hours, model results are not very sensitive to the initial values that are chose. Therefore,
the initial values for a given chemical species at all levels are set to be the same.

4.2.2.2 Turbulent mixing

Vertical transport is parameterized in CACHE using a first-order flux-gradient relationship,
or K-theory, in which heat and mass are transported by eddy diffusion at a rate
proportional to the turbulent exchange coefficient for heat, K₄. Vertical fluxes of heat and
mass are computed at each model time step as follows:
\[ w' \theta' = -K_H \frac{\partial \theta}{\partial z} \]  
(4.3)

\[ w' c'_i = -K_H \frac{\partial c'_i}{\partial z} \]  
(4.4)

Modeled \( K_H \) (hereinafter denoted \( K_{H,\text{mod}} \)) is derived empirically according to Forkel et al. (1990) given a length scale \( l \), the vertical wind shear \( |\frac{\partial u}{\partial z}| \), and a stability parameter \( f \):

\[ K_H = l^2 |\frac{\partial u}{\partial z}| f \]  
(4.5)

\( l \) varies within and above the canopy according to the following parameterization:

\[ l = \frac{\kappa(z - d)}{1 + \kappa(z - d)/\lambda} \]  
(4.6)

where \( \kappa \) is the von Karman constant (0.4), \( d \) is the zero-plane displacement height (0.85 \( h \) for \( z \geq h \) and zero for \( z < h \)), and \( \lambda \) is the maximum mixing length (given by Forkel et al. (1990, Eq. (10)) for \( z \geq h \) and set constant at 2 m for \( z < h \)). The vertical wind profile for computing \( |\frac{\partial u}{\partial z}| \) derives from the common logarithmic expression for the PBL (Stull, 1988); within the canopy, winds dissipate as a function of \( u_* \) and canopy structure according to a modified logarithmic wind equation following Baldocchi (1988, Eq. 6). The stability parameter \( f \) is a function of the Richardson number (Ri):

\[ f = 1.35 \sqrt{1 - Ri} \frac{1 - 5.5Ri}{1 - 3Ri}, \quad Ri < 0 \]  
(4.7)

\[ f = 1.35(1 + 6Ri)^{\frac{1}{2}}(1 + 6Ri), \quad Ri \geq 0 \]  
(4.8)

In the original model configuration—hereafter referred to as the “Control” – the vertical turbulent mixing is driven solely by Equation (4.5 - 4.6).

To evaluate the sensitivity of BVOC gradients to in-canopy vertical mixing, we apply a modified K-theory parameterization in a modeling scheme hereafter referred to as the “MIX” simulation. We first define “observed” \( K_H \) (hereafter denoted by \( K_{H,\text{obs}} \)) following Taylor [1922]:

\[ K_{H,\text{obs}} = \sigma_u^2 T_L \]  
(4.9)
$T_L$ is a characteristic time scale representing the coherency of the momentum transporting eddies and $\sigma_w$ is the standard deviation of the vertical velocity ($w$). This description of $K_{H,\text{obs}}$ ensures that turbulent diffusivity is positive within the canopy and can readily accommodate the zero mean gradient flow conditions ubiquitous to canopy flows (Freire et al., 2017). In the original Lagrangian diffusion theory, $T_L$ must be interpreted as a Lagrangian turbulence time scale. One commonly used estimate suggests that $T_L \sim h/u_*$ is a constant within the canopy but increases linearly above the canopy (Raupach, 1989a; Poggi et al., 2006). This estimate partly shows that $T_L \sim \sigma_w^2 h/u_*$ accommodates both $u_*$ and $\sigma_w$ as flow variables when establishing the degree of mixing. Other estimates of $T_L$ employ well-established relations between Eulerian and Lagrangian integral time scales (Corrsin, 1963; Poggi et al., 2006). The Eulerian integral time scale of $w$, $T_E$, is computed by numerically integrating the autocorrelation function of $w$ up to its first zero crossing (Raupach, 1989a). In this study a simplified relation obtained from Lagrangian and Eulerian expressions for second-order structure functions based on the approach outlined by (Poggi and Katul, 2008) is used and yields:

$$T_L = \frac{C_3^{3/2} u}{\sqrt{2} C_0 \sigma_w} T_E$$

(4.10)

where $C_2 \approx 2.8$ and $C_0 \approx 5.5$ are universal constants (Freire et al., 2017).

In the MIX simulations, we adjust the modeled turbulence profile (i.e. the Control case) to match the near-surface observations estimated in Equation 4.9 as follows. At each time step, we first compute a full vertical profile of $K_{H,\text{mod}}$ using Equation 4.5. Then, we linearly interpolate between $K_{H,\text{mod}}$ at the canopy base and $K_{H,\text{obs}}$ at measurement levels. Above 41 m, modeled values are adjusted to remove any discontinuity between the measured and modeled values.

### 4.2.2.3 Chemical mechanisms

Gas-phase chemical transformation in the original CACHE model implements the Regional Atmospheric Chemistry Mechanism (Stockwell et al., 1997), which includes a suite of 77 chemical species and 237 reactions. In this study, we use the RACM2 (Goliff et al., 2013) in the Control simulation. The RACM2 mechanism includes 115 species and 365 reactions, representing a more detailed treatment of aromatic products, alkanes, and alkenes. The mechanism includes explicit treatment of three BVOC categories: isoprene (denoted by
the RACM surrogate, ISO), monoterpenes with one double bond (i.e. α-pinene; denoted API), and monoterpenes with two double bonds (i.e. d-limonene; denoted LIM). We perform a sensitivity test (hereafter referred to as the “MCM” simulation) comparing RACM2 against the Master Chemical Mechanism (version 3.3) (Jenkin et al., 1997; Saunders et al., 2003). The MCM is a near-explicit chemical mechanism, including a base set of 45 inorganic reactions and more than 15,000 possible organic reactions based on the oxidation of 142 primary VOCs. The key BOVCs in the MCM are isoprene, α-pinene, d-limonene, and β-caryophyllene.

Photolysis rate constants at the top of the canopy are calculated using tested algorithms (Madronich and Flocke, 1999; Seefeld and Stockwell, 1999), and required cross section and quantum yields as a function of wavelength (\( \lambda \)), \( \sigma(\lambda) \) and \( \phi(\lambda) \), respectively, are taken from previous studies (Sander et al., 2006). Measured canopy top PAR values were directly implemented into the canopy model. The attenuation of PAR at each height level within the canopy was modeled by Beer–Lambert law (Stroud et al., 2005) (Eq. 4.11). The profiles of the photolysis rate constants within the canopy were estimated by scaling the photolysis rate constants at the top of the canopy based on the PAR profiles within the canopy.

\[
PAR(z) = PAR_o \exp[-\Omega \frac{G}{\cos(\phi)} \text{LAI}(z)]
\]  

(4.11)

where \( PAR_o \) is the PAR at the top of the canopy, \( G \) is the leaf orientation function, \( \Omega \) is the leaf clumping factor, \( \phi \) is the solar zenith angle, and LAI(z) is the leaf area index vertical profile.

### 4.2.2.4 Emission

Emissions of monoterpenes and isoprene are modelled according to Guenther et al. (1995), taking into account the predicted leaf temperatures and observed PAR in the canopy:

\[
e(T, PAR) = e_{pool} f_1(T) + e_{syn} f_2(T, PAR)
\]

(4.12)

with

\[
f_1(T) = \exp[0.09(T - 303.15)]
\]

(4.13)
\begin{equation}
    f_2(T, PAR) = \frac{1.066\alpha PAR}{\sqrt{1 + \alpha^2 PAR^2}} \frac{e^{\beta(T-303)}}{303 RT} \frac{1}{1 + e^{\gamma(T-314)}} \frac{303}{RT}
\end{equation}

where \( \alpha = 0.0027 \), \( \beta = 9.6 \times 10^4 \) J mol\(^{-1}\), \( \gamma = 2.3 \times 10^5 \), \( R = 8.314 \) J mol\(^{-1}\) K\(^{-1}\) (Guenther et al., 1995). The first term of Equation (4.12) describes the emission of BVOC from pools, i.e. material stored in resin vessels, and the second term the emission of newly synthesized BVOC. \( e_{\text{pool}} \) and \( e_{\text{syn}} \) are plant specific emission factors at 30 °C and PAR level of 1000 \( \mu \)Em\(^{-2}\)s\(^{-1}\). Steinbrecher et al. (1999) considered not only emissions from pools, but also emissions due to new synthesis of the monoterpenes. The emission factors for API and LIM followed (Forkel et al., 2006). Hakola et al. (2006) reported an emission factor of \( \beta \)-caryophyllene of 150-400 ng g\(^{-1}\) h\(^{-1}\). In the case of MCM, the emission factor for API was scaled by a factor of \( 10^{-4} \) as the emission factor of \( \beta \)-caryophyllene. The emission of oxygenated VOC (OVOC) is still less well known than the emission of isoprenoids. As a standard option CACHE considers the emission of OVOC as described by Grell et al. (2000), assuming that the emission of OVOC depends only on temperature. Soil NO emissions are parameterised by \( e_{\text{NO}} = a \times \text{EXP}(bT_{\text{soil}}) \) with the soil surface temperature \( T_{\text{soil}} \) in °C, where \( a = 5 \) ng m\(^{-2}\) s\(^{-1}\) and \( b = 0.14 \) °C\(^{-1}\) (Forkel et al., 2006).

### 4.2.2.5 Dry deposition

Dry deposition of gases to the surface is modeled using an Ohm’s law analogy, which considers multiple resistances to account for transport of scalars through discrete layers between the leaf surface and atmosphere (Wesely, 1989, 2000). Following the notation of (Forkel et al., 2006), the gas deposition rate is represented as:

\begin{equation}
    S_{i,\text{deposit}}(z) = -d LAI(z)c_i(z)\left(\frac{1}{r_{i,b}(z) + r_{i,m} + r_s\delta} + \frac{2}{r_{i,b}(z) + r_{i,c}}\right)
\end{equation}

where \( r_b \), \( r_s \), \( r_m \), and \( r_c \) are the resistances for the boundary layer, stomata, mesophyll, and cuticle, respectively. The stomatal resistance for water vapor, \( r_s \), obtained from biophysical module \( (r_s = 1/g_{sv}) \) is scaled for different gases using the ratio of their diffusivities in air, \( \delta \) (Wesely, 1989). The mesophyll and cuticle resistance terms are empirical functions based on the compound’s solubility (Henry constant, \( H \)) and reactivity factor, \( f_0 \) (Wesely, 1989; Forkel et al., 2006). Nguyen et al. (2015) proposed a modified formula to estimate the dry deposition velocity, which was tested in Chapter 3 against the old one (Eqn. 4.15). No
significant improvements in the surface deposition estimates was observed.

4.2.2.6 Model simulations

Three sets of model simulations were performed to address the research objectives of this study. First, the **Control** simulations entailed the turbulent transport as expressed by Equation 4.5 ($K_{H,mod}$) and the chemical reactions were determined with RACM2. Second, the **MIX** simulations included the turbulent transport as denoted by Equation 4.9 ($K_{H,obs}$) alone and the chemical reactions were evaluated with RACM2. Third, the **MIX-MCM** simulations involved the turbulent transport as formulated by Equation 4.9 ($K_{H,obs}$) alone and the chemical reactions were computed with the MCM. The performances of the modified mixing parameterization were evaluated by comparing the **Control** simulations against the **MIX** model runs as described in Section 4.3.1. The influences of chemical mechanisms were assessed, in terms of modeling $O_3$, BVOCs, key oxidation products, and HO$_X$, by comparing **MIX** values with the **MIX-MCM** quantities as explained in Section 4.3.2. Model results were contrasted with the field observations to verify the fidelity of the model results. In Section 4.3.3, the OH-NO$_X$ relationships are evaluated using results obtained from **MIX** and **MIX-MCM** simulations.

4.3 Results

4.3.1 Evaluation of the modified mixing scheme

We calculate observed eddy diffusivity ($K_{H,obs}$, Figure 4.3) from sonic anemometer measurements (Equation 4.9) at ten heights on the tower (0.04 h, 0.2 h, 0.4 h, 0.5 h, 0.6 h, 0.7 h, 0.9 h, 1.0 h, 1.1 h, and 1.4 h) for the 13-15 September 2014 case study as well as for all September 2014. Above the canopy at the height of 41 m (Figure 4.3c), the $K_{H,obs}$ showed a strong diurnal variation ranging from approximately zero at night to 4 m$^2$ s$^{-1}$ at midday. In the upper canopy at the height of 29 m (Figure 4.3a), the daytime $K_{H,obs}$ was only 1.0 m$^2$ s$^{-1}$. In addition, the daytime standard deviations for September above the canopy were approximately twice those in the upper canopy. The standard deviations during the night time were smaller than those during the daytime. The original CACHE parameterization of $K_{H,mod}$ was below one standard deviation of $K_{H,obs}$ at the top of the canopy (35 m) and in the upper canopy (29 m) 95% of the simulation time during the daytime (Figure 4.3). For
example, the daytime $K_{H,mod}$ was underestimated by a factor of two at 35 m. The daytime $K_{H,obs}$ above the canopy was reasonably reproduced by the model. The nighttime eddy diffusivity within the canopy was well captured by the model while it was overestimated above the canopy. Note that, at 29 m, the modeled onset of the mixing occurred 2 hours later than the observed, while the modeled onset of the stable nocturnal boundary layer happened 2 hours earlier compared to the observations. This suggests that the empirical stability function that is based on Richardson number may inadequately capture the formation of the stable layer. This phenomenon was also reported by Bryan et al. (2012).

We also compared vertical profiles of the $K_{H,mod}$ with the $K_{H,obs}$ for the 13-15 September 2014 case study (Figure 4.4). The $K_{H,obs}$ increased with height throughout the canopy. Below 0.4 h the $K_{H,obs}$ was less than 0.2 m$^2$ s$^{-1}$, indicating weak mixing in the lower canopy. According to Figure 4.2, the leaf area density was relatively large between 0.2 h to 0.5 h, which might have contributed to the small $K_{H,mod}$. Above 0.5 h, the $K_{H,obs}$ increased with height rapidly from 0.2 m$^2$ s$^{-1}$ to 5 m$^2$ s$^{-1}$, suggesting a well-mixed upper canopy. On average, the $K_{H,mod}$ was below one standard deviation of the $K_{H,obs}$ for September throughout
Figure 4.4: Profiles of observed ($K_{H,\text{obs}}$, solid blue lines) and modeled ($K_{H,\text{mod}}$, dashed blue lines) eddy diffusivity at 10:00 hours local time for September 13 (a), 14 (b) and 15 (c). The error bars (solid red) denote the standard deviations of measured eddy diffusivity for September.

the canopy. For the 13-15 September, the largest model-measurement differences occurred at the height of 0.2 h and 1.0 h. The underestimation of eddy diffusivity may lead to incomplete mixing of chemical species within the canopy and thus influencing the chemistry there.

We evaluate the MIX turbulence scheme by comparing the CONTROL and MIX model simulations against observed time series of near-canopy temperatures (Figure 4.5). We also compare the CONTROL and MIX for midday vertical profiles of eddy diffusivity, primary BVOC (isoprene and monoterpenes), BVOC oxidation products (formaldehyde), and OH (Figure 4.6). Daytime near-canopy temperatures are reproduced by the model, especially in the MIX simulation (Figure 4.5). This indicates that the PAR-driven heating source and vertical exchange of heat at the surface are captured well by the model. However, the control was in better agreement with the observed temperature at night. The eddy diffusivity in the MIX case was twice as large as the CONTROL turbulence from 0.7 h to 1.0 h, and an order of magnitude larger at 0.2 h (Figure 4.6a). Overall, in-canopy mixing is weak in the CONTROL simulation, indicating the original K-theory parameterization may not be adequate to capture the turbulence within the canopy.

Enhanced turbulence in the MIX case effectively reduced in-canopy concentrations and weakened the vertical gradient for reactive BVOCs such as isoprene, API, and LIM (Figure 4.6). For the longer-lived species such as formaldehyde, gradients decreased while concentr-
tions in the lower canopy actually increased, indicating more formaldehyde was mixed into the lower canopy. The OH, similar to formaldehyde, also showed increased concentrations in the lower canopy and reduced gradients throughout the entire canopy. On average, the OH gradient throughout the canopy decreased by 30% in the MIX simulation. The gradients of isoprene, API, and LIM decreased by 60% compared to the CONTROL run. For formaldehyde which has a longer chemical lifetime, the gradient decreased by 40%. Bryan et al. (2012) reported nearly uniform modeled vertical profiles for the main BVOCs and formaldehyde with a eddy diffusivity of 3 m$^2$ s$^{-1}$ at 0.5 h in a temperate forest. The eddy diffusivity at 0.5 h in this study was 0.2 m$^2$ s$^{-1}$, indicating less effective in-canopy mixing.

4.3.2 Evaluation of the chemical mechanisms

In this section, we compare model results from the MIX and the MIX-MCM runs to evaluate the performances of the chemical mechanisms in simulating the in-canopy chemistry. We compare the model against the observations when they are available.

We assess the performance of the model in simulating near-canopy O$_3$, NO$_2$, and NO during the 13-14 September case period (Figure 4.7). Since the model is constrained by observed O$_3$ at the height of 40 m, it reproduced ozone well at 40 m (Figure 4.7a). During the early morning of September 13, a storm passed by the study site and transported O$_3$ from
aloft to the surface. The in-canopy O$_3$ show similar patterns, indicating O$_3$ is well mixed into the canopy. The MIX and MIX-MCM produced similar O$_3$ mixing ratios at 41 m, 29 m, and 13 m. The modeled NO showed a distinct diurnal pattern that was observed by many other studies in the forested environments (Bryan et al., 2012). Overall, the modeled NO are in agreement with the observations that ranged from 0.04 to 0.4 in the Amazon rain forest (Liu et al., 2018). The NO concentrations decrease with increasing canopy depth as a result of light attenuation lowering the NO yields from NO$_2$ photolysis. The MIX-MCM predicted higher daytime NO mixing ratios than the MIX run, with a peak value of 0.15 ppbv and 0.04 ppbv for 13-14 September, respectively. Since the NO emission was the same for both simulations, the difference in NO mixing ratios were then attributed to the differences in the chemical mechanism. A budget analysis for NO is needed to find the additional sources of
Figure 4.7: Modeled time series for $O_3$ (a, d, g), NO (b, e, h), and NO$_2$ (c, f, i) at 41 m, 29 m, and 13 m for the 13-14 September 2014 (the canopy height is 35 m). Black circles in (a) represent the observed $O_3$. The blue lines denote model results from the simulation with modified eddy diffusivity parameterization and the RACM2 (MIX); the red lines denote model results with modified eddy diffusivity parameterization and the MCM (MIX-MCM).

NO in the MIX-MCM run. The MIX and MIX-MCM predicted similar NO$_2$ mixing ratios.

We assess the performance of the model in simulating near-canopy isoprene, $\alpha$-pinene, and limonene during the 13-14 September case period (Figure 4.8). Observations of isoprene show a strong diurnal cycle ranging from 2 ppbv at night to up to 9 ppbv at midday above the canopy (Figure 4.8a). The MIX simulations show slightly higher concentrations of isoprene over the MIX-MCM simulation, owing to lower OH availability. A storm passed by in the early afternoon of September 13 and the isoprene decreased rapidly during the passage of the storm. The CONTROL and MIX-MCM model scenarios have difficulty reproducing this diurnal pattern for isoprene. To account for cloud/storm effects, the observed PAR above the canopy was used as input here. However, the storm and the rapid decrease in isoprene cannot be simulated by solely using PAR. An attempt can be made to extend the simulation.
after the onset of storm on 13 September by adding the observed temperature drop of 6 °C during 1 h (Figure 4.5) together with an increase of the O₃ mixing ratio (Figure 4.7a) and a rise of humidity as external forcing. For the afternoon of 14 September, the MIX-MCM captured the isoprene decrease better than MIX because it had higher OH concentrations (Figure 4.11a).

Monoterpenes (C₁₀H₁₆) are grouped together as a total monoterpene concentration by the PTR-MS. Previous studies reported a different diurnal cycle for monoterpenes than for isoprene, with an early morning peak and a late evening peak for pine and boreal forests (Bouvier-Brown et al., 2009; Bryan et al., 2012). For this study, the observed monoterpene mixing ratios showed a similar diurnal cycle as isoprene with the maximum around noon (Figure 4.8c). However, the modeled limonene (which represents d-limonene and other cyclic diene-terpenes in MIX) show an early morning peak and higher concentrations at night than during the day (Figure 4.8c). This can be attributed to high photooxidation during the daytime and an accumulation at night as these temperature-dependent emissions continue in the absence of sunlight. The modeled limonene during the daytime was lower because the observations in Figure 4.8c represent the total monoterpenes. MIX-MCM simulated terpene concentrations to be smaller (approximately by 20-40%) the MIX(RACM2).

Formaldehyde (CH₂O) is an important VOC oxidation product and is typically produced in relatively large quantities from the oxidation of isoprene. Concentrations of CH₂O in rural locations are typically in the 0.1–4 ppb range (Munger et al., 1995; Lee et al., 1998; Heikes, 1992; Lowe and Schmidt, 1983), with much higher mixing ratios (up to 29 ppb) in urban locations (Possanzini et al., 2002; Grosjean, 1991). Measurements of CH₂O above a pine forest in the US Sierra Nevada showed elevated levels of 15–20 ppb at midday attributed to abundant emissions of very reactive volatile organic compounds (Choi et al., 2010). Mac-Donald et al. (2012) reported a range of 1.5-3.0 ppbv CH₂O with a maximum value of 4.5 ppbv in a tropical forest. Model results in this study are in general agreement with previous observations. The MCM and RACM2 predicted similar CH₂O mixing ratios even though the predicted isoprene in MIX-MCM is 20-40% smaller, indicating an additional source of CH₂O in the MIX-MCM simulation (Figure 4.9b). This may be attributed to the isoprene peroxy self-reaction and the new methacrolein peroxy radicals in MCM.

Other key BVOC oxidation products are the lumped species MACR+MVK (or C₄H₆O). These compounds are detected at the same nominal mass on the PTR-MS and are also lumped in the RACM2 mechanism. In the MCM mechanism, they are treated separately.
Figure 4.8: Modeled time series for isoprene (a, d, g), α-pinene (b, e, h), and limonene (c, f, i) at 41 m, 29 m, and 13 m for the 13-14 September 2014 (the canopy height is 35 m). Black diamonds represent the observed isoprene (a) and the total monoterpenes (c). The blue lines denote model results from the simulation with modified eddy diffusivity parameterization and the RACM2 (MIX); the red lines denote model results with modified eddy diffusivity parameterization and the MCM (MIX-MCM).

Observed concentrations peak in the early afternoon above the canopy (Figure 4.9b), following a similar pattern as isoprene. The MIX produced higher MACR+MVK mixing ratios than the MIX-MCM by 25% at the height of 41 m due to isoprene oxidation (Figure 4.9b). The differences between MIX and MIX-MCM decreased within the canopy (Figure 4.9d, f). We plotted the daytime (8:00–16:00 local time) ratios of (MACR+MVK)/isoprene to evaluate the ability of the mechanisms to reproduce observed BVOC oxidation. Over September, the observed (MACR+MVK)/isoprene ratio is 0.23 (Figure 4.10a), smaller than the value of 0.44 observed by Karl et al. (2009) in a nearby study site. The MIX showed a higher ratio than the MIX-MCM (Figure 4.10b). However, both modeled ratios were higher than the observations. In summary, MIX produced higher MVK+MACR values than MIX-MCM,
Figure 4.9: Modeled time series for formaldehyde $\text{CH}_2\text{O}$ (a, c, e), the sum of methyl vinyl ketone (MVK) and methacrolein (MACR) ($\text{C}_4\text{H}_6\text{O}$) (b, d, f) at 41 m, 29 m, and 13 m for the 13-14 September 2014 (the canopy height is 35 m). Black diamonds in (b) represent the sum of observed MVK and MACR. The blue lines denote model results from the simulation with modified eddy diffusivity parameterization and the RACM2 (MIX); the red lines denote model results with modified eddy diffusivity parameterization and the MCM (MIX-MCM).

while both chemical mechanisms overestimated yields of MVK+MACR from isoprene oxidation during the daytime compared to observations. In addition, both simulations failed to capture the observed diurnal cycles of MVK+MACR, showing overestimated mixing ratios during the nighttime. The higher nighttime MVK+MACR mixing ratios suggest that dry deposition rates for MACR+MVK may be underestimated (Pugh et al., 2010; Bryan et al., 2012).

Modeled OH concentrations showed a clear diurnal cycles which have been observed in many previous studies covering from remote to urban sites. For the Amazon rain forest, very limited measurements of OH are available (Lelieveld et al., 2008) and the instruments are believed to suffer interference (Feiner et al., 2016). Saewung et al. (2019, in preparation)
Figure 4.10: Measured (a) and modeled (b) correlations between daytime (8:00-16:00 local time) MVK+MACR and isoprene.

measured OH concentrations at a nearby study site (T3, see details in Chapter 1) from February to March 2014 using the Chemical Ionization Mass Spectrometry (CIMS) which does not have an interference. They reported the average diurnal variation of OH peaked with a midday maximum of $1.2(\pm 0.6) \times 10^6$ radicals cm$^{-3}$, substantially lower than those previously reported in similar tropical forest by Lelieveld et al. (2008). Liu et al. (2018) inferred noon OH concentrations using the observed isoprene and isoprene oxidation products, suggesting a noon OH of $0.6 \times 10^6$ radicals cm$^{-3}$ in the Amazon rain forest experiencing NO$_y$ levels of approximately 0.35 ppbv. The MIX-MCM successfully reproduced the noon OH concentration of $7.5 \times 10^5$ radicals cm$^{-3}$ while the MIX case underestimated the OH concentrations by 30% for September 13 and by 50% for September 14 (Figure 4.11a). The higher OH concentration simulated with MIX-MCM might be associated with the higher NO prediction.

4.3.3 Influences of nitric oxide on hydroxyl radical concentrations

The dependence of OH formation on NO levels were reproduced by both MIX and MIX-MCM simulations, with a threshold NO$_X$ value of 1.0 ppbv obtained at 41 m and 29 m above the ground. In the Amazon rain forest, the background ambient level of NO is mostly below 0.5 ppbv (Liu et al., 2016). This indicated that OH formation increased rapidly with NO as the the OH-NO$_X$ chemistry operated in the left region of the relationship shown in Figure 4.12a. The MIX-MCM case predicted a slightly narrower bell curve than the
Figure 4.11: Modeled time series for hydroxyl radicals OH (a, c, e), hydroperoxyl radicals HO$_2$ (b, d, f) at 41 m, 29 m, and 13 m for the 13-14 September 2014 (the canopy height is 35 m).

The blue lines denote model results from the simulation with modified eddy diffusivity parameterization and the RACM2 (MIX); the red lines denote model results with modified eddy diffusivity parameterization and the MCM (MIX-MCM).

MIX case, with higher OH at the left end of the bell curve and a smaller OH maximum (Figure 4.12). In addition, the CH$_2$O formation showed dependence on NO levels with a threshold value of 1 ppbv. The threshold NO level for HO$_2$ formation was not captured by the simulations. In summary, as NO mixing ratios increased from 0.2 ppbv to 1.0 ppbv, the OH formation above the canopy increased by 150% (from $0.8 \times 10^6$ to $2.0 \times 10^6$ radicals cm$^{-3}$) and 70% (from $1.1 \times 10^6$ to $1.8 \times 10^6$ radicals cm$^{-3}$) as predicted by MIX and MIX-MCM simulations, respectively. These results (Figures 4.12a, d) reinforced the important role of NO$_X$ in sustaining OH concentrations in environments dominated by plant-emitted hydrocarbons.
4.4 Summary and conclusions

One of the main objectives of this study is to evaluate the eddy diffusivity parameterization in the CACHE model. The original formulation of the eddy diffusivity underestimated its values within the canopy and, as expected, reasonably reproduced the eddy diffusivity values above the canopy. The observed eddy diffusivity was twice as large as the modeled eddy diffusivity from 0.7 h to 1.0 h, and an order of magnitude larger at 0.2 h. In summary, in-canopy mixing is weak in the original model, indicating the original K-theory parameterization may not be adequate to capture the turbulence within the canopy. The model with the observed eddy diffusivity enhanced turbulence within the canopy and effectively reduced
in-canopy concentrations and weakened the vertical gradient for OH, isoprene, α-pinene, limonene, and formaldehyde by 30%, 60%, 60%, 60%, and 40%, respectively.

Another goal of this study is to evaluate the performances of the condensed RACM2 and nearly-explicit MCM in simulating the BVOC oxidation. Both RACM2 and MCM can realistically reproduce above-canopy O₃ because the simulations were constrained by observed O₃. Both RACM2 and MCM predicted similar monoterpene mixing ratios (i.e. α-pinene and limonene) within and above the canopy. The MCM predicted 20% lower isoprene mixing ratios than RACM2 at the top of the canopy. Both RACM2 and MCM overestimated the nighttime MVK+MACR by 110% at the top of the canopy, indicating an underestimation of the dry deposition velocities. The MCM predicted 50% higher OH concentrations than RACM2 at the top of the canopy, which may be due to the reaction of RO₂ with NO which was also predicted to be higher in the case of MCM.Summarily, both RACM2 and MCM show similar predictions of O₃, isoprene, monoterpenes, and formaldehyde. However, they produced different results for OH and NO, indicating that the OH-NOₓ chemistry is sensitive to the choice of chemical mechanisms in the forested environment.

The last objective of this study is to assess the dependence of OH on the ambient levels of NO. The MIX-MCM successfully reproduced the observed OH concentrations in the Amazon rainforest. The classical dependence of OH on NO were reproduced by both RACM2 and MCM, with a threshold NO value of 1.0 ppbv above the canopy. Accompanying the increase of NO concentration from 0.2 ppbv to 1.0 ppbv, the OH concentrations above the canopy increased by 150% (from $0.8 \times 10^6$ to $2.0 \times 10^6$) and 70% (from $1.1 \times 10^6$ to $1.8 \times 10^6$) predicted by the 1-d model with RACM2 and with MCM, respectively, highlighting the important role of NOₓ in sustaining OH concentrations under low-NO conditions.
4.5 supplement
Table 4.1: Initial mixing ratios (in ppbv) of chemical species included in CACHE with RACM2.

<table>
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<tr>
<th>Model species</th>
<th>Definition</th>
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<tr>
<td>ISOP</td>
<td>Isoprene</td>
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<td>O3</td>
<td>Ozone</td>
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<tr>
<td>NO</td>
<td>Nitric oxide</td>
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<td>Nitrogen dioxide</td>
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<td>CH4</td>
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<td>Toluene and less reactive aromatics</td>
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<td>Alpha-pinenenes and other cyclic terpenes with one double bond</td>
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<td>LIM</td>
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Table 4.2: Initial mixing ratios (in ppbv) of chemical species included in CACHE with MCM.

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<tr>
<td>NO</td>
<td>Nitric oxide</td>
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<tr>
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<td>Nitrogen dioxide</td>
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<tr>
<td>CO</td>
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<tr>
<td>CH4</td>
<td>Methane</td>
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<tr>
<td>HCHO</td>
<td>Formaldehyde</td>
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<td>Hydrogen peroxide</td>
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<td>MVK</td>
<td>Methyl vinyl ketone</td>
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<tr>
<td>BENZENE</td>
<td>Benzene</td>
<td>0.031</td>
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<td>HCOOH</td>
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Chapter 5

Conclusions

In this work, we focus on (i) the characterization of the meteorological and chemical background conditions in the Amazon rainforest using field data; (ii) the environmental and biological controls on the temporal variations in the most abundant BVOC species − isoprene; (iii) the link between turbulence and chemistry to evaluate the in-canopy mixing and chemical processes using a one-dimensional canopy model.

The atmospheric conditions at ZF2 during the wet season, as well as at T3 when NOX is less than 0.5 ppbv, can be considered as the regional background conditions in the central Amazon rain forest. Due to low NO levels, O3 production in the Amazon rain forest is NOX-limited with a observed O3 production efficiency of about 10-20 ppbv ppbv$^{-1}$. The urban plume enhanced the O3 and NOz mixing ratios by 30-50% and 40-90%, respectively. However, the NOX levels at the T3 site were increased by less than 20%, indicating the majority of NOX were chemically converted to O3 and NOz during transport. Model results show that an injection of 8 ppbv NOX into the rain forest can cause up to 260% and 150% increases in O3 and OH levels compared to the background conditions, suggesting NOX can significantly modify the air quality and oxidative capacity in the Amazon rain forest.

O3 mixing ratios showed significant linear correlations with temperature on half hourly and daily time scales. The rate of change of the O3-temperature slope with respect to NOz was approximately twice higher than that with respect to NOX, suggesting the NOz produced during transport contributed significantly to the O3 production at T3 under hot weather conditions. In summary, pollution plumes from the city of Manaus were the main source of NOX for the downwind rain forest, and largely influence the air quality and oxidative capacity in the aid of BVOCs and hot weather conditions in the central Amazon rain forest.
Isoprene mixing ratios over the rain forest canopy exhibited substantial seasonality, with diurnal values in December reaching levels approximately 70% higher than those in June. Incoming photosynthetically active radiation and temperature, the two environmental variables modulating emissions, were almost identical in June and December but did not correspondingly explain the observed seasonality in isoprene levels. Instead, leaf phenology and quantity consistently followed the seasonality of isoprene. The dry months of August and September had the highest estimated isoprene emission rates, with averaged maximum flux densities of 11 mg m$^{-2}$ hour$^{-1}$ prevailing due to the concomitant influences of high temperature ($>30^\circ$C) and incoming insolation, and high quality and quantity of foliage. New foliage, developed at the start of the wet season, had to accrue competency to emit isoprene. Therefore, aggregate foliage phenology and associated variations in putative basal emissions became important controls on isoprene seasonality.

Sensitivity analysis revealed that the air layer-averaged NO levels became the predominant factor promoting the isoprene oxidation through the reaction with OH. Therefore, the accurate determination of NO concentrations is crucially important for the reliable estimation of isoprene levels under low-NO and high-VOC conditions. The Amazon rain forest frequently experiences enhanced levels of nitrogen oxides due to human activities such as biomass burning or urban polluted plumes, the atmospheric chemistry of isoprene can be greatly modified and thus impact its seasonal patterns.

In-canopy mixing is weak in the original CACHE model, indicating the original K-theory parameterization may not be adequate to capture the turbulence within the canopy. The CACHE model with the observed eddy diffusivity enhanced turbulence within the canopy and effectively reduced in-canopy concentrations and weakened the vertical gradient for OH, isoprene, α-pinene, limonene, and formaldehyde.

The MCM is nearly-explicit chemical mechanism that has over 15,000 reactions. The RACM2 mechanism is a highly condensed mechanism that only has 365 reaction. The first-generation reactions of isoprene in MCM and RACM2 are similar. However, the MCM has more detailed reactions for the isoprene oxidation products. Both CACHE with RACM2 and CACHE with MCM predicted similar O$_3$, isoprene, monoterpenes, and formaldehyde mixing ratios. However, they produced different results for OH and NO, indicating that the OH-NO$_X$ chemistry is sensitive to the choice of chemical mechanisms in the forested environment. The classical dependence of OH on NO was reproduced by both RACM2 and MCM, with a threshold NO value of 1.0 ppbv above the canopy. Accompanying the increase
of NO concentration from 0.2 ppbv to 1.0 ppbv, the OH concentrations above the canopy increased by 150% and 70% predicted by CACHE with RACM2 and CACHE with MCM, respectively, highlighting the important role of NO\textsubscript{X} in sustaining OH concentrations in the remote Amazon rainforest.

In summary, this study call attention to the susceptibility of the atmospheric oxidation capacity over the forest to anthropogenic influence and reinforcing the important role of NO\textsubscript{X} in sustaining OH concentrations. Also, the CACHE model with modified eddy diffusivity parameterization and detail MCM can be a useful tool to study the forest-atmosphere exchanges and BVOC chemistry.
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Poggi, D., Katul, G., Albertson, J., 2006. Scalar dispersion within a model canopy: Measure-


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2018

Wei, D; Fuentes, JD; Gerken, T; Chamecki, M; Trowbridge, AM; Stoy, PC; Katul, GG; Fisch, G; Acevedo, O; Manzi, A; von Randow, C; Nascimento dos Santos, R: Environmental and biological controls on seasonal patterns of isoprene above a rainforest in central Amazonia, Agricultural and Forest Meteorology, 256–257, 391-406

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