Turbulent mixing and removal of ozone within an Amazon rainforest canopy

L. S. Freire1, T. Gerken1,2, J. Ruiz-Plancarte1, D. Wei1, J. D. Fuentes1, G. G. Katul3, N. L. Dias4, O. C. Acevedo5, and M. Chamecki6

1Department of Meteorology and Atmospheric Science, Pennsylvania State University, University Park, Pennsylvania, USA, 2Department of Land Resources and Environmental Sciences, Montana State University, Bozeman, Montana, USA, 3Nicholas School of the Environment, Duke University, Durham, North Carolina, USA, 4Universidade Federal do Paraná, Curitiba, Brazil, 5Universidade Federal de Santa Maria, Santa Maria, Rio Grande do Sul, Brazil, 6Department of Atmospheric and Oceanic Sciences, University of California, Los Angeles, California, USA

Abstract  Simultaneous profiles of turbulence statistics and mean ozone mixing ratio are used to establish a relation between eddy diffusivity and ozone mixing within the Amazon forest. A one-dimensional diffusion model is proposed and used to infer mixing time scales from the eddy diffusivity profiles. Data and model results indicate that during daytime conditions, the upper (lower) half of the canopy is well (partially) mixed most of the time and that most of the vertical extent of the forest can be mixed in less than an hour. During nighttime, most of the canopy is predominantly poorly mixed, except for periods with bursts of intermittent turbulence. Even though turbulence is faster than chemistry during daytime, both processes have comparable time scales in the lower canopy layers during nighttime conditions. Nonchemical loss time scales (associated with stomatal uptake and dry deposition) for the entire forest are comparable to turbulent mixing time scale in the lower canopy during the day and in the entire canopy during the night, indicating a tight coupling between turbulent transport and dry deposition and stomatal uptake processes. Because of the significant time of day and height variability of the turbulent mixing time scale inside the canopy, it is important to take it into account when studying chemical and biophysical processes happening in the forest environment. The method proposed here to estimate turbulent mixing time scales is a reliable alternative to currently used models, especially for situations in which the vertical distribution of the time scale is relevant.

1. Introduction

The significance of the Amazon rainforest on climate and global biogeochemical cycling is rarely disputed. Current subjects of discussion and inquiry are the role of biogenic volatile organic compounds (BVOCs) [e.g., Kesselmeier et al., 2000; Jardine et al., 2015] that undergo rapid photochemical oxidation and their contribution to driving ozone dynamics in the lower atmosphere. These hydrocarbon species represent a large sink for the hydroxyl radical (OH), which is deemed crucial for the regional oxidation capacity of the atmosphere. Ozone is reactive and substantially contributes to the oxidation of terpenes [e.g., Paulson and Orlando, 1996; Aschmann et al., 2002]. In the Amazon, the oxidation of BVOCs leads to numerous reaction pathways and thus influences the forest environment photoxidative capacity through the OH generation [Lelieveld et al., 2008; Gerken et al., 2016; Lelieveld et al., 2016].

Ozone mixing ratio in the atmospheric boundary layer (ABL) over the Amazon shows pronounced diurnal cycles in response to source and sink processes. Daytime increases are governed by entrainment of ozone into the ABL, efficient vertical mixing promoted by convective turbulence, and photochemical production [Gregory et al., 1988; Kirchhoff, 1988; Sigler et al., 2002]. Ozone deposition onto the forest and chemical reaction with biogenic hydrocarbons dominate the dynamics of nighttime ozone mixing ratios. These nocturnal ozone sinks can be sufficiently strong to promote complete ozone depletion in the ABL [Kirchhoff, 1988]. Given that most of the ozone available for oxidation originates above the forest and the hydrocarbon emissions occur within the forest canopy, the mixing of gases promoted by turbulence plays an important role in the chemical processes occurring both within and above the forest.

The wide ranges of time scales associated with ABL and canopy turbulence, on one hand, and chemistry, on the other hand, invariably lead to overlaps in time scales and strong coupling between physical and
chemical processes. In the absence of advection and/or deposition, if the chemical time scales are large compared to those associated with turbulent mixing, the system is mostly well mixed and its bulk evolution is determined by the chemistry. Conversely, if turbulent mixing time scales are larger, strong segregation of chemical species occurs, reactions take place in relatively thin layers where limited mixing occurs (in this case near the top of the canopy), and the evolution of the system is determined by turbulent mixing [Hill, 1976; McRae et al., 1982; Stockwell, 1995]. These processes are usually recast in terms of a dimensionless number, the Damköhler number $Da = \tau_{mix}/\tau_{chem}$ [Damköhler, 1940], with $\tau_{mix}$ and $\tau_{chem}$ being time scales characterizing turbulent transport (or mixing) and chemical reactions, respectively. In the specific case of interest here, ozone removal by nonchemical processes (stomatal uptake and dry deposition) with their own characteristic time scale $\tau_{nu,de}$ is also important, and the ozone dynamics within the canopy is then dependent on the relationships between these three time scales.

One issue that typically arises is the choice of time scale associated with the turbulent mixing in dense and tall forests such as the Amazon. Trumbore et al. [1990] estimated the flushing time for the entire vertical extent of the Amazon forest during the night using measurements of radon (222Rn) and carbon dioxide (CO$_2$), obtaining 3.4 and 5.5 h, respectively (the difference being attributed to the production of CO$_2$ in the canopy). Martens et al. [2004] used the same approach based on radon measurements at a different site (with slightly larger canopy height) and obtained nighttime estimates between 2 and 10 h (even though they also show estimates of daytime flushing times and cite those to reach values as small as a few minutes, no detailed analysis or discussion is presented). Simon et al. [2005] combined 222Rn and the localized near-field model [Raupach, 1989a] to predict height-dependent turbulence exchange for another site in the Amazon forest. For a height of 15 m ($z/h = 0.375$, where $z$ is the variable representing height and $h = 40$ m is the canopy height), they obtained exchange times of 40 min for nighttime and 11 min for daytime conditions. Simon et al. [2005] conclude that convective mixing inside the canopy during nighttime is important and that typical values of exchange time scales are 10 min for daytime and 1 h for nighttime conditions.

In the present study, two research objectives are addressed. The first one is the definition and estimation of a turbulent mixing time scale representing the ability of turbulence in creating a well-mixed environment in the region inside the forest. This is accomplished by combining a simple one-dimensional turbulent diffusion model with a large data set of turbulence statistics inside and above the canopy. The second goal is to compare the obtained values of turbulent mixing time scales with those for chemical and nonchemical sinks of ozone inside the forest, allowing an assessment of the importance of each process to ozone mixing ratio during different periods of the diurnal cycle. Results from the current investigation can help the understanding of the impact of turbulence on the distribution of reactive gases such as ozone and biogenic hydrocarbons in the forest environment.

2. Methods
2.1. Data Set
The data set used was collected during a field campaign at the Cuiéiras Biological Reserve, commonly referred to as ZF2, located 60 km north-northwest of the city of Manaus, Amazonas, Brazil. The experiment was part of the GoAmazon (Observations and Modeling of the Green Ocean Amazon) 2014/2015 project [Martin et al., 2016], and it is described in detail elsewhere [Fuentes et al., 2016]. In summary, data were collected between March 2014 and January 2015 at the 50 m tall tower (2°36’33”S, 60°12’33”W, 130 m ASL, labeled as T0 for the GoAmazon campaign) located on top of a plateau and surrounded by a dense primary forest. Canopy height at the measurement site varied between 30 and 40 m, with leaf area index estimated to be between 5.7 and 7.3 m$^2$ m$^{-2}$ [McWilliam et al., 1993; Marques Filho et al., 2005; Tóta et al., 2012]. Hereafter, $h = 35$ m is used as the mean canopy height and LAI = 6.0 is adopted as a representative value. At the site, the prevailing wind direction was from the northeast, a direction covered mostly by undisturbed forest. High-frequency time series of the three wind velocity components within and immediately above the canopy were continuously measured by 10 triaxial sonic anemometers (model CSAT3, Campbell Scientific Inc, Logan, UT) from 23 March 2014 to 16 January 2015. Measurement frequency was 20 Hz, and all sensors were facing the east direction on the 50 m tower. The sensors were vertically deployed in an array designed to sample the vertical structure of turbulence inside the canopy (see Table 1).

Ozone mixing ratios (and other trace gases) above the canopy were continuously measured throughout the experiment. An air inlet was placed at a height of 40 m above the ground ($z/h = 1.15$) on the tower. A pump
November, and December 2014, several days were selected to perform vertically resolved measurements of mean ozone mixing ratios within the canopy. A roving sampling system was designed to carry the air inlet up and down along the 50 m tower. At the beginning of a profile measurement, the intake was moved to the top position (at 50 m height), and measurements were sequentially taken at every descending 5 m until the bottom position located at 5 m above the ground was reached. Ambient air was sampled for 5 min at each level, and the movement of the intake to each subsequent height required about 10–15 s. The measurements were recorded at 1 Hz frequency, and the start and end times were logged from each level. Seventy ozone profiles were obtained between 5 October and 6 December 2014.

Concurrent to ozone observations, nitric oxide (NO) measurements (model 43i-TLE, Thermo Fisher Scientific, Waltham, MA) were made at 40 m above ground. In the absence of biomass burning, the NO levels at the study site remained below 0.4 ppb (similar NO levels were recorded in another study where mean NO mixing ratios were 0.035 ± 0.032 ppb [Liu et al., 2016]). In addition, a Proton Transfer Reaction-Mass Spectrometer (PTR-MS, Ionicon Analytik Ge.m.b.H., Innsbruck, Austria) measured ambient levels of hydrocarbon compounds, including isoprene and methanol. The PTR-MS only characterizes compounds and fractions of compounds by molecular weight, and the identities of the hydrocarbons measured should be considered putative with the exception of isoprene, with mass (m) and charge number of ions (c) ratio (m/c) of 69. A dynamic dilution technique allowed the PTR-MS calibration for the measured compounds that was applied before, during, and after the measurement campaign.

To complement the ozone profile measurements, profiles of monoterpenes and sesquiterpenes measured during the BrazilianAir 2010 Field Campaign and reported by Jardine et al. [2011, Figures 3a and 3b] are also used here. Measurements were taken at six levels (z = 2, 11, 17, 24, 30, and 40 m) at a site less than 2 km away from the K34 tower between the months of September and December, 2010. Profiles of isoprene from the same experiment were obtained from Alves et al. [2016, Figure 2a]. In addition to these profiles, vertically averaged mixing ratios inside the forest were independently estimated from their data and are presented in Table 2.

### 2.2. Data Analysis

Turbulence data were divided into 30 min blocks and error flags produced by the sonic anemometer were monitored. Blocks with more than 1 s of consecutive error flags were eliminated from further analysis. These error flags occurred frequently due to precipitation or obstruction of the sonic path by plant elements. Only blocks corresponding to the sensors impacted by error flags were removed, producing an uneven distribution in the number of “acceptable” blocks with height. In the remaining data set, the rare cases of measurements flagged with error were replaced by the previous acceptable measurement. To avoid contaminating turbulence statistics with flow distortion caused by the presence of the tower, data blocks with mean wind direction with a western component were discarded (i.e., only blocks corresponding to mean wind directions with an

<table>
<thead>
<tr>
<th>Height (z m)</th>
<th>z/h</th>
<th>Number of 30 min Data Blocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.04</td>
<td>5138</td>
</tr>
<tr>
<td>7.0</td>
<td>0.20</td>
<td>5801</td>
</tr>
<tr>
<td>13.5</td>
<td>0.39</td>
<td>5820</td>
</tr>
<tr>
<td>18.4</td>
<td>0.52</td>
<td>5537</td>
</tr>
<tr>
<td>22.1</td>
<td>0.63</td>
<td>5757</td>
</tr>
<tr>
<td>24.5</td>
<td>0.70</td>
<td>7076</td>
</tr>
<tr>
<td>31.6</td>
<td>0.90</td>
<td>6875</td>
</tr>
<tr>
<td>34.9</td>
<td>1.00</td>
<td>7014</td>
</tr>
<tr>
<td>40.4</td>
<td>1.15</td>
<td>7694</td>
</tr>
<tr>
<td>48.2</td>
<td>1.38</td>
<td>7633</td>
</tr>
</tbody>
</table>

*Canopy height h = 35 m is used.*
angle within ±90° of the instrument axis were used). For this purpose, the wind direction at the highest measurement (z/h = 1.38) was used and the blocks from all heights were discarded when the criterion was not satisfied. The total number of blocks remaining for each height is presented in Table 1. Finally, the vertical velocity time series were filtered using a Gaussian filter with a window of 3 min to eliminate low-frequency nonturbulent oscillations that can be significant during nighttime periods [e.g., Campos et al., 2009; Santos et al., 2016] and can lead to large integral time scales that are not associated with turbulence.

In prior work, the degree of mixing inside the canopy has been empirically correlated to the friction velocity ($u_*$) at the top of the canopy [e.g., Pleijel, 2008] and the vertical velocity variance, $\sigma_w^2$ [Thomas et al., 2013]. The premise is that $u_*$ at the canopy top is related to the mechanical production of turbulent kinetic energy ($\sim u_*^3$) whereas $\sigma_w$ is related to the turbulent kinetic energy component directly responsible for vertical mixing. Here the eddy diffusivity ($K(z)$) is used as a proxy for the vertical mixing capacity of turbulence. While different estimates of eddy diffusivity exist [e.g., $l_m^2 |\partial \bar{u}/\partial z|$], where $l_m$ is a mixing length and $|\partial \bar{u}/\partial z|$ is the mean velocity gradient), the expression

$$K(z) = \sigma_w^2(z) T_l(z)$$

is selected here as derived for the far-field diffusion regime defined by Taylor [1922], where $T_l(z)$ is a characteristic time scale representing the coherency of the momentum transporting eddies. This description of $K(z)$ ensures that turbulent diffusivity is positive within the canopy and can readily accommodate the zero mean gradient flow conditions ubiquitous to canopy flows. However, the definition of $T_l(z)$ requires further clarification. In the original Lagrangian diffusion theory, $T_l(z)$ must be interpreted as a Lagrangian turbulence time scale. One commonly used estimate suggests that $T_l(z) \approx h/\bar{u}_*$ is a constant within the canopy but increases linearly above the canopy [Raupach, 1989a; Poggie et al., 2006]. This estimate partly shows that $K(z) \sim (\sigma_w(z)/u_*) \sigma_u(z) h$ accommodates both $u_*$ and $\sigma_w$ as flow variables when establishing the degree of mixing. Other estimates of $T_l(z)$ employ well-established relations between Eulerian and Lagrangian integral time scales [Corryn, 1963; Angell et al., 1971; Hanna, 1981; Koeltzsch, 1999; Anfossi et al., 2006; Poggie et al., 2008].

The Eulerian integral time scale of $w$, $T_e(z)$, is computed by numerically integrating the autocorrelation function of $w$ up to its first zero crossing [e.g., see Sreenivasan et al., 1978; Lenschow and Stankov, 1986; Chamecki, 2013]. Here a simplified relation obtained from Lagrangian and Eulerian expressions for second-order structure functions based on the approach outlined by Poggie et al. [2008] is used and yields

$$T_l(z) = \frac{C_2^{3/2}}{\sqrt{2C_0}} \frac{\bar{u}(z)}{\sigma_w(z)} T_e(z),$$

where $C_2 \approx 2.8$ and $C_0 \approx 5.5$ are universal constants (see Appendix A for a derivation of this relation).

Last, it is to be noted that ozone is a reactive gas and that for application to ozone exchange the eddy diffusivity may be different from that for a passive tracer. As noted by Lamb [1973], the issue is well characterized by the time scales of turbulence and chemistry. This correction can be incorporated by introducing a Schmidt number $Sc$, and its importance can be estimated using the simple modeling framework developed by Hamba [1993] which yields $ScO_3 = K/K_{O_3} = (1 + \tau_{\text{eddy}}/\tau_{\text{chem}})$. It is important to realize that $\tau_{\text{eddy}}$ is different from $\tau_{\text{mix}}$, as the former is the turbulent time scale associated with eddies that contribute the most to the turbulent fluxes.

### Table 2. Approximate Values of Vertically Averaged Mixing Ratios of Isoprene, Monoterpenes, and Sesquiterpenes Obtained From Jardine et al. [2011] and Alves et al. [2016]

<table>
<thead>
<tr>
<th>Species</th>
<th>Symbol</th>
<th>Approximate Mixing Ratio</th>
<th>Daytime (ppbv)</th>
<th>Nighttime (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoprene</td>
<td>ISOP</td>
<td>$k_{[ISOP]} \approx 1.28 \times 10^{-12}$</td>
<td>2.820</td>
<td>0.815</td>
</tr>
<tr>
<td>Monoterpenes</td>
<td>MTavg</td>
<td>$k_{[MT]} \approx 1.82 \times 10^{-16}$</td>
<td>0.750</td>
<td>0.200</td>
</tr>
<tr>
<td>Sesquiterpenes</td>
<td>SQTavg</td>
<td>$k_{[SQT]} \approx 1.00 \times 10^{-14}$</td>
<td>0.160</td>
<td>0.220</td>
</tr>
</tbody>
</table>

*Atkinson [1997] for temperature of 300 K.

*Weighted geometric mean of monoterpane species reported by Jardine et al. [2015] and rates from Atkinson et al. [1999].

*Following Jardine et al. [2011] we use the rate constant for β-caryophyllene from Shu and Atkinson [1994].
and the latter is the time scale for the ozone profile to reach a well-mixed condition. Our estimates using \( \tau_{\text{eddy}} = h/(3u_*) \) \cite{Patton et al., 2001} suggest that \( 1.00 \leq Sc_{O_3} \leq 1.11 \) for conditions representative of more than 95% of our data. Hereafter, this effect is included in the analysis by using a constant Schmidt number \( Sc_{O_3} = 1.08 \) based on observational data of ozone fluxes under low \( NO_x \) concentrations by Launiainen et al. \cite{2013}. The final expression for estimating the ozone eddy diffusivity from field data is given by

\[
K_{O_3}(z) = \frac{C_2^{3/2} \bar{u}(z) T_f(z) \sigma_w(z)}{2C_0 Sc_{O_3}}.
\]

For simplicity in the notation used in this manuscript, hereafter, we refer to \( K_{O_3} \) as \( K \) and we emphasize that the difference between the eddy diffusivities for \( O_3 \) and a passive scalar is constant and much smaller than the variability of \( K \) and the errors associated with its estimation.

The mean ozone mixing ratios \([O_3] \) (henceforth the word mean is omitted) were obtained by averaging over 4.5 min at each level. The first 30 s at each level were discarded to avoid contaminating the mean values with air sampled while the air intake was in transit. Each profile was labeled with the time at which the profile measurement was initiated (i.e., the time when the sample at \( z/h = 1.43 \) was collected). Note that the true time for the lowest sample is about 1 h later. The averaging time of 4.5 min is short and the presence of random errors in the estimates of the mean mixing ratios is likely not negligible (we estimated relative random errors in the estimates of mean ozone concentrations to be within 10% based on measurements above the canopy top — see Text S2 in the supporting information). However, this is a reasonable compromise between required averaging time at each level and the total time needed for the execution of the entire profile sampling.

To accompany the analysis of the ozone profiles, a second set of vertical velocity statistics was calculated employing averaging periods consistent with the ozone sampling durations. An estimated eddy diffusivity was paired to each mean ozone mixing ratio measurement even though the heights were slightly different (ozone measurements at \( z/h = 0.29, 0.43, 0.57, 0.71, \) and 0.86 were paired with turbulence measurements at \( z/h = 0.39, 0.52, 0.63, 0.70, \) and 0.90, respectively). This eddy diffusivity was based on a 10 min block designed to end simultaneously with the 4.5 min block used for the ozone (note that here the true time of ozone sampling at each height was used in determining the appropriate window of time for averaging the turbulence). The choice of 10 min blocks for the turbulence was based on an assessment that the uncertainty in the integral scale was too large for shorter averaging times (and it was more reasonable to include turbulence data before the ozone sampling than after, since only the former can impact measured ozone mixing ratio).

### 2.3. Mass Balance of Ozone Inside the Canopy

A mass balance approach was employed to extract characteristic time scales associated with ozone transport and sources/sinks from the measurements described above. For simplicity and data limitations, the net result of chemical production and destruction \( (R_{\text{chem}}(z)) \), stomatal uptake \( (O_{su}(z)) \), and dry deposition \( (D_{dd}(z)) \) were lumped together into a single source/sink term \( S(z) \). Thus, upon assuming horizontal homogeneity, zero mean vertical velocity and negligible molecular diffusion, the mass balance for the ozone mixing ratio can be expressed as \cite[e.g., see Rummel et al., 2007; Launiainen et al., 2013]{}

\[
\frac{d[O_3]}{dt} = - \frac{\partial w'[O_3]}{\partial z} + S(z). \tag{4}
\]

If the eddy diffusivity model is invoked to parameterize the ozone kinematic turbulent flux, then

\[
\frac{d[O_3]}{dt} - K \frac{d^2[O_3]}{dz^2} - \frac{\partial K}{\partial z} \frac{d[O_3]}{dz} = S(z). \tag{5}
\]

This budget yields a nonhomogeneous partial differential equation for the mean ozone mixing ratio that can be solved for given \( K(z) \), a closure model linking \( S(z) \) to \([O_3] \), and appropriate initial and boundary conditions. The approach sought here is to employ two approximations to equation (5) as a means to obtain time scales associated with (i) turbulent mixing, (ii) chemical destruction, and (iii) vertically integrated nonchemical removal processes. A discussion of the applicability of the eddy diffusivity approach in the present application is deferred to section 2.3.4.
2.3.1. Turbulent Mixing Time Scale

The homogeneous solution to equation (5) (i.e., the one obtained when setting \( S = 0 \)) represents the time evolution of the ozone mixing ratio due to turbulent mixing in isolation. The turbulent mixing time scale can be obtained by solving the homogeneous equation for an idealized scenario in which an initial ozone mixing ratio is zero everywhere except at \( z/h = 1 \) (layer across which ozone enters the canopy volume), where it assumes a known fixed value \([O_3]_1\). It is to be noted that if this concentration value is set to unity, then the desired homogeneous solution becomes the well-known Green’s function of equation (5). For simplicity and analytical tractability, the term including the vertical variation of \( K(z) \) in equation (5) is neglected. To reconcile a solution using a constant eddy diffusivity with one impacted by vertical variations in \( K(z) \), an equivalent eddy diffusivity \( K_{eq}(z_1) \) may be defined. We define two equivalent diffusivities that we infer to represent upper and lower bounds on the solution with a varying \( K(z) \) (see Appendix B for more details). The first definition, which can be considered as an upper bound on the eddy diffusivity, simply uses the average eddy diffusivity between the target height \( z_1 \) and the top of the canopy

\[
K_{eq,1}(z_1) = \frac{1}{(h-z_1)} \int_{z_1}^{h} K(z) \, dz. \tag{6}
\]

The second definition, which is interpreted as a lower bound in the eddy diffusivity, makes use of a resistances-in-series analogy with the resistance to transport across an infinitesimal layer being given by \( dz/K(z) \). Thus, the average resistance between target height \( z_1 \) and the top of the canopy is

\[
\frac{1}{K_{eq,2}(z_1)} = \frac{1}{(h-z_1)} \int_{z_1}^{h} \frac{dz}{K(z)}. \tag{7}
\]

Thus, equation (5) is reduced to

\[
\frac{\partial [O_3]}{\partial t} = -K_{eq}(z_1) \frac{\partial^2 [O_3]}{\partial z^2}, \tag{8}
\]

where \( K_{eq}(z_1) \) can be \( K_{eq,1}(z_1) \) or \( K_{eq,2}(z_1) \). When equation (8) is integrated between the top of the canopy and the target height \( z_1 \), \( K_{eq}(z_1) \) is treated as a constant. This approach assumes a different value for each target height \( z_1 \). In this way, the vertical variation of \( K(z) \) is not completely neglected and some of its consequences are present in the final solution. Equation (8) is, in principle, defined in the domain \( z < h \) and a solution subject to the initial condition \([O_3](z, t = 0) = 0\) and boundary condition \([O_3](z = h, t) = [O_3]_b\) is sought. If a second boundary condition is set to be a zero ozone mixing ratio at \( z \to -\infty \), then the problem is analogous to the classical fluid mechanics solution for an impulsively started infinite plate in a fluid at rest often referred to as the Stokes’ first problem [e.g., see Batchelor, 2000; Kundu et al., 2012]. In the present case, it is more appropriate to set a zero ozone flux at \( z = 0 \) as the lower boundary condition (formally setting the domain of the solution to be \( 0 < z < h \)). In this case, the transient solution for the ozone mixing ratio inside the canopy can be expressed as [Liu, 2008]

\[
\frac{[O_3](z, t)}{[O_3]_b} = 1 - \sum_{n=0}^{\infty} \frac{4}{(2n+1)\pi} \exp \left\{ - \left[ \frac{(2n+1)\pi}{2} \right]^2 \frac{K_{eq}(z_1)t}{h^2} \right\} \sin \left[ \frac{(2n+1)\pi}{2} \frac{(h-z)}{h} \right], \tag{9}
\]

where \( z_1 \) is now replaced by a generic height \( z \) for convenience. A height-dependent turbulent mixing time scale \( \tau_{mix}(z) \) can be obtained from equation (9) by finding the time required for the ozone mixing ratio to reach a certain fraction of the imposed value at the top of the forest. In the present application, \( \tau_{mix}(z) \) is defined as the time required for \([O_3](z)/[O_3]_b\) to reach 0.86 (the choice of this value is justified in section 3.1).

In practice, equation (9) cannot be rearranged to yield an explicit solution for \( t = \tau_{mix} \). An iterative method is necessary and was applied with \( t \) being increased in increments of 0.1 s from zero until \([O_3]/[O_3]_b\) reached 0.86, yielding an estimate for \( \tau_{mix}(z) \). The truncation of the infinite summation was done so that inclusion of additional terms did not have a contribution larger than 0.1% in the value of \([O_3]/[O_3]_b\).

As a final note, the two equivalent eddy diffusivity models \( K_{eq,1}(z_1) \) and \( K_{eq,2}(z_1) \) are interpreted here as upper and lower bounds on the mixing produced by the vertically variable eddy diffusivity. Therefore, they yield lower and upper bounds on the mixing time scales, respectively (see Appendix B for more details).
2.3.2. Ozone Chemistry Time Scale

Due to the strong attenuation of actinic irradiance by the forest crown and the low nitrogen oxides ($\text{NO}_x = \text{nitric oxide (NO) + nitrogen dioxide (NO}_2)$) mixing ratios within the forest canopy, photochemical production of ozone is likely to be negligible. For typical mixing ratios of isoprene, monoterpenes, and sesquiterpenes in the Amazon forest, the oxidation of sesquiterpenes represents the largest ozone sink [Jardine et al., 2011]. Nevertheless, for the sake of completeness, oxidation of monoterpenes and isoprene are also included. Therefore, the chemical sink term is modeled as

$$R_{\text{chem}}(z) = -\left[k_{\text{ISOP}}^{\text{eff}}[\text{ISOP}](z) + k_{\text{MT}}^{\text{eff}}[\text{MT}](z) + k_{\text{SQT}}^{\text{eff}}[\text{SQT}](z)\right][\text{O}_3](z),$$

(10)

where $[\text{ISOP}]$, $[\text{MT}]$, and $[\text{SQT}]$ are the mean mixing ratios of isoprene, monoterpenes, and sesquiterpenes, respectively. Additionally, the effective reaction rate constant for the reaction of the chemical species $[A]$ with ozone is defined as

$$k_{[A]}^{\text{eff}} = k_{[A]}(1 + I_{[A]}),$$

(11)

where $k_{[A]}$ is the true reaction rate constant for the reaction and $I_{[A]} = [A][\text{O}_3]^T/([A][O_3])$ is the intensity of segregation between spatial distributions of ozone and $[A]$ [e.g., see Schumann, 1989; de Arellano et al., 1993]. The rate constants for the reactions of isoprene, monoterpenes, and sesquiterpenes with ozone are needed (see Table 2). Hereafter we use the notation $k_{\text{BVOC}}^{\text{eff}}(z)$ to represent the sum of the three terms inside square brackets in equation (10) and define a time scale associated with the ozone loss in the oxidation of the BVOCs as

$$\tau_{\text{chem}}(z) = \frac{1}{k_{\text{BVOC}}^{\text{eff}}(z)}.$$  

(12)

The intensity of segregation cannot be determined from the measurements available as this would require simultaneous, high-frequency measurements of the two species involved. While the intensity of segregation between isoprene and OH may be significant [e.g., Kaser et al., 2015], the reactivity between ozone and terpenes is much lower (due to the much lower ambient levels of terpenes compared to isoprene) and segregation effects are expected to be much smaller [e.g., see Ouwersloot et al., 2010]. These effects are neglected hereafter and the approximation $k_{[A]}^{\text{eff}} \approx k_{[A]}$ is employed.

2.3.3. Ozone Nonchemical Removal Time Scale

In addition to turbulent mixing and chemical destruction, the processes of stomatal uptake and dry deposition can be taken into account together in the estimation of a nonchemical ozone removal. For that, the mass balance of ozone within the canopy (equation (5)) is now considered. In principle, the profile of source/sink $S(z)$ can be estimated from data as the residual of the three terms on the left-hand side of equation (5). All the three terms can be estimated directly from mean ozone mixing ratio profiles and turbulence data, and the nonchemical sinks can be obtained by removing the chemical contribution to the residual. However, estimating the profile of $S(z)$ from observed mean mixing ratio profiles is difficult even for passive scalars [Siqueira et al., 2000]. For this reason, the present analysis follows a different approach limited to determine a time scale associated with the total sink integrated over the entire height of the forest. Vertical profiles of eddy diffusivity and mean ozone mixing ratio are used in the determination of a vertical ozone flux profile (see Appendix C for more details) and the mean ozone flux at the top of the canopy is then used in the calculation of a bulk deposition velocity at canopy top

$$V_s = -\frac{w'[\text{O}_3]^T_h}{[\text{O}_3]_h}.$$  

(13)

The bulk deposition velocity $V_s$ includes all sink processes, namely, chemical loss, stomatal uptake, and dry deposition. Here we split $V_s$ into the components associated with chemical loss ($V_{\text{chem}}$) and nonchemical removal processes (stomatal uptake plus dry deposition, $V_{\text{su,dd}}$)

$$V_s \approx V_{\text{su,dd}} + k_{\text{BVOC}}^{\text{avg}} h,$$

(14)

$$V_s \approx V_{\text{su,dd}} + h,$$

(15)
where $\bar{g}$ is an average canopy conductance, $\overline{[\text{BVOC}]_{\text{avg}}}$ is the mean mixing ratio of BVOCs averaged within the vertical extent of the canopy and by definition $\text{LAI} = \int_0^h a(z) \, dz$. More details related to the assumptions leading from (13) to (14) are given in Appendix C. Following Rannik et al. (2016), time scales can be defined from deposition velocities as $\tau = h/V$. The partitioning of the deposition velocity, given by equation (14), yields a time scale for the chemistry which is in agreement with (12) and a nonchemical removal time scale given by

$$\tau_{\text{su,dd}} = \frac{h}{V_{\text{su,dd}}}.$$  \hspace{1cm} (15)

Note that $\tau_{\text{su,dd}}$ is a time scale associated with the vertically integrated loss of ozone due to stomatal uptake and dry deposition. As equation (15) is used to estimate the order of magnitude of $\tau_{\text{su,dd}}$ rather than exact values, the assumptions required to progress from (13) to (15) are likely justifiable.

### 2.3.4. Applicability of the Eddy Diffusivity Model

The use of eddy diffusivity closures to model fluxes within plant canopies has received much criticism [e.g., Finnigan, 2000]. Its applicability is in fact dependent on the characteristics of the mean concentration profile for the scalar in question [Corrin, 1975], as well as the spatial distribution of sources and sinks. Second-order closure modeling suggests that in the present case, the magnitude of deviations from the eddy diffusivity model can be approximated by the dimensionless number (see Appendix D for more details)

$$N_{GD} \sim \frac{\tau_{\text{eddy}} \overline{[O_3]}_h}{h[O_3]_h} = \frac{V_S}{3u_*}.$$  \hspace{1cm} (16)

The equality follows from adopting $\tau_{\text{eddy}} = h/(3u_*)$ [Raupach, 1989b] and the definition of the deposition velocity by equation (13). The eddy diffusivity approach is expected to yield a reasonable model for the fluxes if $N_{GD} \ll 1$.

### 3. Results and Discussion

#### 3.1. Turbulent Mixing of Ozone Into the Forest

To establish the validity of eddy diffusivity as a proxy for mixing of ozone into the canopy, three days (30 October, 3 December, and 4 December 2014, with five profiles on each day) in which consecutive profiles of ozone mixing ratio were measured inside the forest were selected. In particular, the early morning evolution of ozone mixing ratios inside the canopy is evaluated. Early morning profiles are ideal to establish a connection between eddy diffusivities and mixing, because ozone mixing ratio and turbulence inside the forest before sunrise are typically low. During this early morning period, photochemical production of ozone is limited by the low levels of both radiation and NO	extsubscript{v}. Inside the forest, the main source of ozone is transport from the air layers above the canopy. Therefore, in the morning the onset of turbulence is key for increases in ozone mixing ratios inside the canopy, providing an ideal scenario for linkages between turbulence levels and mixing states. Profiles of $\sigma_w(z)$, $T(z)$, $K(z)$, $[O_3]_h(z)$, and $[O_3]_h/[O_3]_h$ for the three selected days are shown in Figure 1. Low levels of turbulence, characterized by low values of $\sigma_w(z)$ and $K(z)$ were observed before 07:00 h (local time). At these early morning times, not only ozone mixing ratios were low inside the forest but the mean ozone mixing ratio profiles exhibited large vertical gradients as evident in the $[O_3]_h/[O_3]_h$ shown in Figures 1j and 1o. As turbulence mixing increased, mixing ratio of ozone inside the forest increased and the shape of the ozone profiles became more uniform (i.e., the ozone mixing ratios became nearly constant with height). This is particularly clear in the upper region of the canopy, $0.4 \leq z/h < 1.0$. Note that $K(z)$ for $z/h < 0.4$ is always small compared with values observed in the upper canopy, a characteristic feature of many tall and dense forests.

A strong relation between ozone mixing (characterized by $[O_3]/[O_3]_h$) and $K(z)$ exists in the upper canopy (Figure 2). The relation with $K(z)$ is even clearer than the one obtained by plotting normalized ozone mixing ratio against $\sigma_w$ alone (not shown). This result lends support to the assertion that the main source of ozone in this morning period is entrainment from the region above the canopy. The pattern of the scatter in Figure 2 suggests an exponential form

$$\frac{[O_3]}{[O_3]_h} = 1 - \exp \left( - \frac{K(z)}{K_c} \right).$$  \hspace{1cm} (17)
Figure 1. Profiles of (a, f, and k) standard deviation of vertical wind velocity ($\sigma_w$), (b, g, and l) Lagrangian integral time scale of the vertical velocity ($T_L$), (c, h, and m) eddy diffusivity ($K$), (d, i, and n) ozone mixing ratio ([O$_3$]), and (e, j, and o) normalized ozone mixing ratio ([O$_3$/O$_3$]$_h$) for the morning transition of 30 October (Figures 1a–1e), 3 December (Figures 1f–1j), and 4 December 2014 (Figures 1k–1o).

where $K_e = 0.09$ m$^2$ s$^{-1}$ is the best fit e-folding eddy diffusivity. This e-folding eddy diffusivity is used to set the limits between three distinct regimes of ozone turbulent mixing within the forest. The value 0.5$K_e = 0.045$ m$^2$ s$^{-1}$ is henceforth used as the limit between poorly mixed and partially mixed regimes and 2$K_e = 0.18$ m$^2$ s$^{-1}$ is used as the limit between partially mixed and well-mixed regimes. The only motivation for the curve fitting is to provide an objective determination of these regime transition limits, which are expected to be canopy dependent. A summary of the basic characteristics of the three regimes defined here is presented in Table 3. Note that the threshold $[O_3]/[O_3]_h = 0.86$ used for the definition of $\tau_{\text{mix}}$ in section 2.3.1 is the mixing corresponding to 2$K_e$ in the fit given by equation (17). Thus, the mixing time scale is, by definition, the time needed to achieve a well-mixed condition according to the analytical model used to represent turbulence mixing.

The large spread for the poorly mixed regimes in Figure 2 originates mostly from early morning profiles measured on 4 December, which were more mixed than the early morning profiles observed on 3 December 2014. This result can be understood when the entire nighttime evolution of the eddy diffusivity is considered (Figure 3). The three selected mornings were preceded by different nighttime mixing patterns. October 30 was characterized by significant mixing in the upper canopy and extremely small eddy diffusivities below $z/h = 0.6$. The lower measurement heights of the ozone profile labeled as 7:12 were actually sampled closer to 8:00 h, when mixing was much more pronounced. Interestingly, the first morning profile of 3 December was sampled in the middle of a period of extremely low eddy diffusivity, while on 4 December a significant
event of enhanced diffusivity spanning the entire vertical extent of the forest took place right before the ozone measurements. This was likely the cause for a more mixed profile despite low diffusivities computed for 4 December. All three days were characterized by strong mixing during the daytime, but large differences in mixing were evident after sunset, providing an example of large day-to-day variability of turbulent mixing within the Amazon forest (much stronger contrasts were observed in the data set). Analysis of the kinematic heat flux profiles within the canopy (see Text S3) suggests that enhanced nighttime mixing on 3 and 4 December (as compared to the very weak mixing on 30 October) is associated with positive heat fluxes and, consequently, unstable thermal stratification below $z/h = 0.7$. This convective mixing is likely caused by longwave radiative cooling in the upper canopy [Kruijt et al., 2000; Santos et al., 2016].

A general average picture of the diurnal cycle of turbulent mixing within the Amazon forest is presented in Figure 4, where $\langle K \rangle$ is the yearly averaged eddy diffusivity. Between 6:30 and 18:00 h, a period starting 30 min after sunrise and ending at sunset, the upper half of the canopy was in the well-mixed regime while most of the lower half was still partially mixed. Conversely, during nighttime, the uppermost 40% of the canopy (above $z/h \approx 0.6$) was in the partially mixed regime while the rest was poorly mixed. An interesting region of slightly enhanced mixing was present in the lower canopy during the night (around $z/h \approx 0.2$). This region was coincident with the location where a secondary peak in the mean velocity forms at night [e.g., see Santos et al., 2016]. Even though this increased mixing likely diluted trace gases locally, it was decoupled from the top of the canopy and therefore unlikely to cause significant exchanges of trace gases with the air above the forest. Based on the average diurnal cycle alone, one can expect that on average, trace gases emitted by the forest may accumulate inside the canopy during nighttime. Gases are thereafter transported out of the forest, though not as a spatially uniform diffusive front (assumed here) but as spatially intermittent plumes (not considered here). Also, on average, gases present above the canopy undertake significant levels of mixing within the entire vertical extent of the forest during the period between sunrise and sunset. The day-to-day variability in eddy diffusivity was quantified via $\sigma_K$ (the standard deviation around the yearly averaged eddy diffusivity; not shown). Values of $\sigma_K/\langle K \rangle$ tend to be larger than unity in the lower canopy (below $z/h \leq 0.4$) during the entire diurnal cycle. In the upper canopy, the values are much smaller during daytime ($\sigma_K/\langle K \rangle < 0.5$), but they are still slightly larger than unity during most of the night.

A better measure of the variability in the data set can be gained from Figure 5, which shows the fraction of the time spent in each of the three mixing regimes as a function of height. Results were separated into three periods: nighttime (18:00–24:00 and 00:00–6:30 h), sunrise and sunset transitions (6:30–9:00 and 16:00–18:00 h), and daytime (9:00–16:00 h). Daytime periods exhibited little variability, and the average results shown

<table>
<thead>
<tr>
<th>Table 3. Three Mixing Regimes Defined for the Amazon Rainforest Canopy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Regime</strong></td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>Poorly mixed</td>
</tr>
<tr>
<td>Partially mixed</td>
</tr>
<tr>
<td>Well-mixed</td>
</tr>
</tbody>
</table>
Figure 3. Eddy diffusivity ($K$) as a function of local time and height. (a) 30 October 2014, (b) 3 December 2014, and (c) 4 December 2014. Blue and red lines indicate the limits $K = 0.5K_e$ and $K = 2K_e$, respectively. The arrows at the bottom indicate the times of the profiles presented in Figure 1.

in Figure 4 were dominant throughout the year. Conversely, nighttime periods displayed more variability, specially in the upper canopy layers where most of the time was evenly distributed between partially mixed and poorly mixed. This variability was likely associated with the distinct behaviors of calm nights with weak turbulence, fully turbulent nights, and intermediate cases in which intermittent turbulence was present at the site [Santos et al., 2016]. A summary of these results is also presented in Table 4.

3.2. Time Scales for Turbulent Mixing
The proposed model (equation (9)) can now be used to translate eddy diffusivity estimates into time scales associated with a chosen level of mixing. Here $\tau_{\text{mix}}$ is defined as the time required to reach $[\text{O}_3]/[\text{O}_3]_h = 0.86$. This time scale illustrates the significance of the large space-time differences in eddy diffusivity observed.
within the Amazon forest as the day progresses. As a first example, consider two hypothetical situations in which \( K \) is constant within the entire depth of the canopy and equal to the two limits used to separate the three mixing regimes defined in the previous section (see Table 3). The time evolution of normalized ozone mixing ratios inside the forest obtained from equation (9) is shown for these two cases in Figure 6. After 2 h, the entire depth of the canopy is well mixed for the larger \( K = 2 K_e \), while the well-mixed region only encompasses the uppermost 15% of the canopy for the lower \( K = 0.5 K_e \). Thus, a rough interpretation of the mixing limits inferred from Figure 2 in terms of how much mixing can be accomplished in 2 h can be established. For the poorly mixed regime, only the uppermost 15% of the canopy is mixed within 2 h, while for the well-mixed regime the entire canopy becomes mixed within 2 h or less. Other cases fall into the partially mixed regime.

Turbulent mixing time scales obtained from the yearly averaged diurnal patterns of eddy diffusivity are shown in Figure 7 for the two equivalent eddy diffusivities. These time scales can be interpreted as lower and upper bounds on the “response time scale” associated with turbulent mixing. It is the time it would take for a given level within the forest to respond to changes in ozone concentration above the forest. Between 10:00 and 13:00 h, most of the forest responded to such ozone concentration changes, on average, in less than 60 min. This may be surprisingly fast given how stagnant air flow may be inside the forest on an average day. In contrast to daytime conditions, during most of the night only the upper 20% of the forest responded within an hour or so as a consequence of the weak turbulence associated with the nighttime calm conditions.

The case of 3 December 2014 is shown in Figure 8, as an example of the possible variability of individual days instead of an ensemble averaged day (where ensemble averaging is applied across the hour of the day). The nighttime evolution for this day presented patterns of effective atmospheric mixing. During nighttime, mixing was slow with time scales much longer than 2 h throughout most of the forest depth and most of the time. However, this pattern was interrupted by events of enhanced turbulence that lasted 1 or 2 h (during this specific night) in which significant mixing can occur (because a significant portion of the canopy has a mixing time scale shorter than the duration of the events). These events, which are associated with bursts of intermittent turbulence, have the capability of mixing ozone into the forest and, more importantly, promoting the transport of gases emitted by the forest during nighttime that would, otherwise, be accumulating until morning hours.

Table 4. Summary of Occurrence of the Three Mixing Regimes

<table>
<thead>
<tr>
<th>Canopy Region</th>
<th>Nighttime Periods</th>
<th>Transition Periods</th>
<th>Daytime Period</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0:00–6:30</td>
<td>6:30–9:00</td>
<td>9:00–16:00</td>
</tr>
<tr>
<td>Uppercanopy</td>
<td>z/h &gt; 0.5</td>
<td>0.40; 0.43; 0.17</td>
<td>0.09; 0.33; 0.58</td>
</tr>
<tr>
<td>Lower canopy</td>
<td>z/h &lt; 0.5</td>
<td>0.79; 0.20; 0.01</td>
<td>0.58; 0.38; 0.04</td>
</tr>
</tbody>
</table>

*Numbers represent fraction of time in poorly mixed, partially mixed, and well-mixed regimes.
Average profiles of turbulent mixing time scales for nighttime and daytime are shown in Figure 9 (sunrise and sunset transitions fall in between and are not shown). The entire vertical extent of the forest is mixed in 1 h or less during daytime, with the exception of the lowermost levels where the uncertainty in the estimates is quite large. During nighttime, between 3.5 and 6.5 h are required to accomplish the same level of mixing. These values seem to be in reasonable agreement with the 3.4 h estimated by Trumbore et al. [1990] and within the large range of 2 to 10 h suggested by Martens et al. [2004], both based on $^{222}$Rn measurements. Note that at $z/h \approx 0.375$, $\tau_{\text{mix}} > 2.5$ h, which is significantly larger than the 40 min estimate of Simon et al. [2005], despite the fact that the data set used here also presents cases of convective mixing inside the canopy produced by nighttime radiative cooling in the upper canopy [Santos et al., 2016].
3.3. Time Scales for Ozone Sink Within the Forest

The bulk deposition velocities at the canopy top obtained from the ozone mass balance were compared to those reported by Fan et al. [1990] for the Ducke Forest and by Rummel et al. [2007] for a site in the Reserva Biológica Jarú (90 km north of the city of Ji-Paraná, approximately 900 km southwest of ZF2 site). The values reported by Fan et al. [1990] and Rummel et al. [2007] were obtained using eddy covariance estimates of the ozone flux and are more reliable than those obtained from the ozone budget model employed here. Comparisons between different experiments must take into account the time of the year, as the lower specific humidity in the dry season leads to a reduction in stomatal activity and ozone deposition in the Amazon [Rummel et al., 2007]. Data from the other experiments correspond to average values for wet or dry seasons, and our comparison here hinges on the assumption that variations in atmospheric and surface conditions are dominated by the seasonal cycle between wet and dry seasons. The ozone profiles presented here were obtained at the beginning of the wet season (October–December), whereas the data presented by Fan et al. [1990] correspond to the end of the wet season (April–May, which is the peak of rainfall near Manaus). Therefore, it is reasonable that the data from the GoAmazon field campaign fall between the wet period of Fan et al. [1990] and the dry period of Rummel et al. [2007]. The reasonable agreement with deposition velocity inferred from eddy covariance measurements (Figure 10a) serves as a partial verification of the fidelity of the ozone budget model outcome.

Values of the dimensionless number $N_{GD} = V_s/(3u_*)$ are never larger than 0.06, satisfying the criteria $N_{GD} < 1$ (see Figure 10b). This result lends some support to the validity of eddy diffusivity model for estimating ozone fluxes. At first, it seems to be at odds with the general idea that eddy diffusivity models fail in the canopy region. Differently from heat or CO$_2$, in the present case ozone has no net sources inside...
Figure 10. (a) Deposition velocity ($V_D$) as a function of time. Black line corresponds to results presented by Fan et al. [1990] for a similar site in the Amazon forest, dashed lines correspond to results presented by Rummel et al. [2007] for wet (yellow) and dry (red) in the Amazon forest. (b) Values of the criteria $N_{GD} = V_D/(3u_*)$ for applicability of the eddy diffusivity model.

The canopy and the time scales associated with the sink processes are in general quite large. This combination leads to monotonic and fairly smooth ozone profiles within the canopy, being more amenable to the application of eddy diffusivity models.

The daytime and nighttime average values of ozone deposition velocity are summarized in Table 5. These results suggest that the chemical sink is responsible for about 10% of the total sink into the canopy during the day, and 39% during the night. As expected from the dominant role of sesquiterpenes in the chemical sink, these values of $V_{chem}$ are not impacted by concentrations of monoterpane and isoprene (deposition velocities due to reactions with isoprene and monoterpenes are between 10 and 300 times smaller than those associated with sesquiterpene oxidation). The larger chemical deposition during nighttime is caused by the inverse relationship between ambient mixing ratios of ozone and sesquiterpene [Jardine et al., 2011]. Due to smaller nighttime $O_3$ mixing ratios, nighttime ozone fluxes due to sesquiterpene oxidation may still be smaller than daytime fluxes. The bulk time scale at canopy top resulting from chemical sink is equal to $\tau_{chem} = 6.1$ h for daytime and $\tau_{chem} = 4.4$ h for nighttime. For the nonchemical loss, values of $V_{su,dd}$ were estimated by inserting these estimates of $V_S$ and $V_{chem}$ into equation (14), which when combined with equation (15) yields a rough estimate of the bulk time scale associated with nonchemical processes of $\tau_{su,dd} = 0.71$ h for daytime and $\tau_{su,dd} = 2.8$ h for nighttime.

Perhaps at this point, a caveat in this analysis must be discussed. The definition of chemical lifetimes as a characterization of the canopy chemical environment must be based on the true ambient concentration of the reactive species. However, the mixing ratios of isoprene, monoterpenes, and sesquiterpenes obtained from the measurements and used in the estimates of $V_{chem}$ (and indirectly in the estimates of $\tau_{su,dd}$) already include effects of ozone oxidation. Ideally, concentration of these gases before oxidation should be used, as the oxidation can be quite significant for the most reactive sesquiterpenes [Stroud et al., 2005]. The concentrations of BVOCs used in the calculation of the $V_{chem}$ likely represent the lower bound values, and therefore, the ozone chemical sink could be greater than the ones estimated here and consequently the values of $\tau_{su,dd}$ could be smaller.

Table 5. Values of Bulk Sink Deposition Velocity $V_S$, Chemical Deposition Velocity $V_{chem}$ and Nonchemical Deposition Velocity $V_{su,dd}$

<table>
<thead>
<tr>
<th></th>
<th>$V_S$ (cm s$^{-1}$)</th>
<th>$V_{chem}$ (cm s$^{-1}$)</th>
<th>$V_{su,dd}$ (cm s$^{-1}$)</th>
<th>$V_{chem}/V_S$</th>
<th>$V_{su,dd}/V_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daytime</td>
<td>1.53</td>
<td>0.16</td>
<td>1.37</td>
<td>0.10</td>
<td>0.90</td>
</tr>
<tr>
<td>Nighttime</td>
<td>0.57</td>
<td>0.22</td>
<td>0.35</td>
<td>0.39</td>
<td>0.61</td>
</tr>
</tbody>
</table>
Figure 11. Time scales for turbulent mixing ($\tau_{\text{mix}}$), chemical reaction with BVOCs ($\tau_{\text{chem}}$), and nonchemical removal processes ($\tau_{\text{su,dd}}$) for (a) daytime and (b) nighttime conditions.

The three time scales representing turbulent mixing, chemical reaction, and nonchemical loss are shown in Figure 11 for daytime and nighttime conditions. During the day, turbulent mixing is clearly much faster than chemical reactions for the entire canopy, indicating that the well-mixed assumption is a good representation for modeling chemical reactions of ozone inside the forest. During the night, turbulent mixing time scales remain much smaller than the chemistry in the upper canopy (where the eddy diffusivity remains large). However, deeper in the canopy, turbulence becomes weak and the time scales of turbulence and chemistry become similar (i.e., the Damköhler number is of order unity), suggesting a strong link between physical and chemical processes.

Some care is needed in comparing the nonchemical removal time scale to chemistry and turbulent mixing, as this is a bulk time scale for the entire canopy and it is not vertically resolved as the others. Nevertheless, as it represents an integration through the canopy height, this bulk time scale can be seen as an average value of the profile observed in the forest. In this case, the nonchemical loss time scale can have values comparable to the turbulence time scale during both daytime and nighttime periods, whereas it is likely much smaller than the chemical time scale during the day.

4. Summary and Conclusions

The analysis of profiles of ozone mixing ratio within and above the Amazon forest suggested a dependency on local eddy diffusivity, indicating an impact of turbulent mixing on the evolution of ozone concentration. This observed relationship was used to establish threshold values in eddy diffusivity that define regimes of poorly, partially, and well-mixed turbulence conditions. Based on a 10 month period for which turbulence data are available, it was observed that the upper half of the forest is well mixed 94% of the time during the day and it is either partially or poorly mixed (43% and 40% of the time, respectively) during the night. For the lower half of the forest, prevailing conditions are partially mixed during the day (50% of the time with well-mixed conditions occurring 18% of the time) and poorly mixed (79% of the time) during the night. This scenario describes the average conditions in which chemical and physical processes happen in the Amazon.

A simplified model was developed to convert the eddy diffusivity data into a meaningful turbulent mixing time scale as a function of canopy depth and time of day. The values of turbulent mixing time scales can assist in interpreting the potential impact of turbulence on other processes happening in the forest environment. In the case of the Amazon forest, on average, the entire vertical extent of the forest responds to changes above the canopy in less than 60 min during the hours around local noon. During nighttime, only the uppermost 20% of the forest responds to changes within an hour or so and 3.5 to 6.5 h are needed for the entire forest to respond to changes above the canopy. At a given height inside the canopy, $\tau_{\text{mix}}$ presented not only a significant diurnal cycle but also great variability among individual nights, depending on the episodic nature of intermittent turbulence that exerts a dominant role in nighttime mixing. Results also showed that in the morning transition the change in turbulent mixing can be quite fast, creating a transient scenario that limits the use of equilibrium or steady state models and well-mixed assumptions when representing chemical and physical processes happening in the forest environment during the first hours of the day. The mixing time
scales estimated here can be used as a reference for comparison with other processes happening within the Amazon rainforest. In addition, the new methodology applied here can be a useful tool for the estimation of mixing time scales in other types of canopy.

Ozone sinks inside the canopy were estimated using a one-dimensional ozone mass balance and typical values of BVOCs observed in the Amazon forest. While dry deposition and stomatal uptake dominate the daytime ozone sink, the oxidation of sesquiterpenes is responsible for some 40% of the nighttime ozone loss, highlighting the importance of within-canopy chemical reactions. Results also showed that turbulence is much faster than ozone chemistry during daytime, whereas chemistry and turbulence are comparably slow in the lower half of the canopy during nighttime. Time scales of nonchemical removal processes are comparable to mixing time scales, indicating that stomatal uptake and dry deposition of ozone is possibly dependent on the efficiency of turbulence on transporting ozone to the canopy environment. These ozone results exemplify the important role of turbulent mixing in the air chemistry of a forest.

Appendix A: A Simplified Relation Between Eulerian and Lagrangian Time Scales

A simplified relation between Eulerian \((T_E)\) and Lagrangian \((T_L)\) time scales can be obtained following the approach proposed by Poggi et al. [2008]. Here the Eulerian and Lagrangian second-order structure functions of vertical velocity \((D^E_{33}(r))\) and \((D^L_{33}(τ))\), respectively) are used to link these two time scales. At the crossover from production to inertial, it is assumed that the largest scales populating the inertial subrange follow their respective Kolmogorov scaling [e.g., see Monin and Yaglom, 1975]

\[
D^E_{33}(r) = C_2 \epsilon^{2/3} r^{2/3}, \tag{A1}
\]

\[
D^L_{33}(τ) = C_0 \epsilon \tau, \tag{A2}
\]

where \(r\) and \(τ\) are space and time lags, \(\epsilon\) is the mean turbulent kinetic energy (TKE) dissipation rate, and \(C_2\) and \(C_0\) are universal constants. For simplicity, it is also assumed that both formulations already yield most of the vertical velocity variance at the crossover point from production to inertial (indicated by \(R_E\) and \(T_L\)) so that

\[
D^E_{33}(R_E) = D^L_{33}(T_L) = 2σ_w^2. \tag{A3}
\]

If Taylor’s frozen turbulence hypothesis is used to define \(R_E = \overline{UT}_E\), then we can rewrite (A3) as

\[
T_L = \frac{C_2}{C_0} \epsilon^{1/3} \overline{(UT)_E}^{2/3}. \tag{A4}
\]

However, using (A3) the rate of TKE dissipation can be expressed in terms of the vertical velocity variance \(\epsilon = 2σ_w^2/(C_T T_L)\), which yields the desired relation between the aforementioned time scales

\[
T_L = \frac{C_2^{1/2}}{\sqrt{2C_0}} \frac{\overline{U}}{σ_w} T_E. \tag{A5}
\]

Finally, the constants \(C_2\) and \(C_0\) must be specified. The constant \(C_2\) can be related to the Kolmogorov constant for the energy spectrum \(C_2 \approx 0.53\) [Sreenivasan, 1995] via \(C_2 \approx (4/3) \times 4 \times C_v\), where the factor \(4/3\) arises from the assumption of isotropy in the inertial subrange and the factor \(4\) is a conversion between constants in the energy spectrum and the second-order structure function [Pope, 2000]. As for \(C_0\), a wide range of estimates is available in the literature (e.g., see values listed by Lien and D’Asaro [2002] and Poggi et al. [2008]). Recent high resolution Lagrangian experiments performed by Ouellette et al. [2006] in anisotropic turbulence suggest that the value is impacted by anisotropy and it varies between 5.0 and 6.2 for their largest Reynolds numbers. We adopt an intermediate value of \(C_0 \approx 5.5\), which is in agreement with the classic value of Pope and Chen [1990] and the experimental value for model canopies reported by Poggi and Katul [2006].

Appendix B: Equivalent Eddy Diffusivity

Consider a system with two homogeneous layers with thicknesses \(z_1 = z_2 = h/2\) and eddy diffusivities \(K_1\) and \(K_2\). To make the argument clearer, we consider an extreme case in which \(K_2 \gg K_1\) with \(K_2 \sim 1\) m\(^2\) s\(^{-1}\) and \(K_1 \ll 1\) m\(^2\) s\(^{-1}\) (note in Figure 4 that typical values of \(K\) are of order 1 m\(^2\) s\(^{-1}\) at the top of canopy and 10\(^{-2}\) m\(^2\) s\(^{-1}\)}
deeper into the canopy). As in the ozone transport into the canopy, assume that the scalar of interest must first travel through the layer with higher diffusivity to reach the layer with lower diffusivity. Given that $K_2 \gg K_1$, transport across layer 2 occurs efficiently and the time for transport across the entire layer is approximately the diffusion time across layer 1. We seek to replace $K_1$ and $K_2$ by an equivalent eddy diffusivity $K_\text{eq}$ that can be used uniformly through the entire depth $h$. An arithmetic average estimate yields $K_\text{eq} = (K_1 + K_2)/2 \approx K_2/2$. This is equivalent to $K_\text{eq,1}$ given by equation (6). Transport across layer 2 will still be very fast, but the transport time across layer 1 will be strongly underestimated. Therefore, using the average $K$ will yield a lower bound on the diffusion time across the entire layer. Alternatively, one can use an electrical circuit analogy and consider $K_1$ and $K_2$ as conductivities across each layer. Thus, the resistances across the layers are $h/(2K_1)$ and $h/(2K_2)$.

Given that the two pathways are in series (in the sense that the scalar must first travel across layer 2 and then across layer 1), the equivalent resistance is $h/K_\text{eq} = h/(2K_1) + h/(2K_2)$ and yields $K_\text{eq} = 2K_1K_2/(K_1 + K_2) \approx 2K_1$. This model is equivalent to $K_\text{eq,2}$ given by equation (7). This model will provide a reasonable estimate of transport time across layer 1, but it will overestimate the transport time across layer 2, yielding an upper bound on the diffusion time across the entire layer. Finally, a geometric mean between $K_1$ and $K_2$ would yield an intermediate transport time and it could be written in a general form using the product integral, but it is not clear that the results would be an upper or lower bound on the transport time.

**Appendix C: Determination of the Deposition Velocity**

A partitioning of the deposition velocity into chemical and nonchemical removal processes can be obtained using the ozone mass balance. The storage term ($\partial[O_3]/\partial t$) was always the smallest term in the mean ozone budget, being more than 1 order of magnitude smaller than the other terms during the day. This result is similar to the ozone budget estimated by Jacob and Wofsy [1990] for the Ducke Forest (a different site less than 60 km away from the ZF2), and it implies an approximate equilibrium between the sink term and the flux divergence. Therefore, the reduction in the flux must be approximately balanced by chemical loss, stomatal uptake, and dry deposition. Neglecting the storage term and the ozone deposition to the ground surface ($\overline{w}^h[O_3] \approx 0$), integration of equation (4) over the entire canopy height yields

$$\overline{w}^h[O_3] = \int_0^h S(z) \, dz. \quad (C1)$$

At this point, additional information about the nature of $S(z)$ is required. Following Launiainen et al. [2013], the stomatal uptake ($D_{\text{st}}$) and dry deposition ($D_{\text{dd}}$) can be modeled using

$$D_{\text{st}}(z) = -a(z)g_{\text{eff}}(z)[O_3](z), \quad (C2)$$

$$D_{\text{dd}}(z) = -a(z)g_{\text{cut,}}(z)[O_3](z), \quad (C3)$$

where $a(z)$ is the leaf area density and $g_{\text{eff}}(z)$ and $g_{\text{cut,}}(z)$ are conductances associated with stomatal uptake and dry deposition, respectively (see Launiainen et al. [2013] for more details).

Thus, the overall bulk sink term can be expressed as

$$S(z) = -a(z)[g(z)[O_3](z) - k[BVOC](z)[O_3](z)]. \quad (C4)$$

with $g(z) = g_{\text{eff}}(z) + g_{\text{cut,}}(z)$. It is of interest to obtain approximate expressions for the two components of $S(z)$ in terms of the ozone concentration at the top of the canopy so that the result can be recast in terms of the deposition velocity. We choose to rewrite (C4) as

$$S(z) \approx -a(z)[\overline{g}[O_3]h - k[BVOC]_{\text{avg}}[O_3]h], \quad (C5)$$

where $\overline{g}$ is an average conductance. Inserting (C5) into (C1) yields

$$\overline{w}^h[O_3] \approx -\overline{g}[O_3]h \cdot \text{LAI} - k[BVOC]_{\text{avg}}[O_3]h. \quad (C6)$$

Here $[BVOC]_{\text{avg}}$ is the mean mixing ratio of BVOCs averaged within the vertical extent of the canopy and by definition $\text{LAI} = \int_0^h a(\xi) \, d\xi$. Dividing by $-\overline{[O_3]}h$ allows for a partitioning of the deposition velocity into chemical and nonchemical sinks given by equation (14).
Appendix D: Criteria for Validity of Eddy Diffusivity Model

We consider the turbulent flux budget equation for a generic scalar $C$ that can be derived using conventional approaches. Assuming steady state, planar homogeneous flow with no subsidence, and negligible molecular terms (i.e., large Reynolds number), the mean scalar flux budget equation in the vertical direction is given as

$$ \frac{\partial w'C'}{\partial t} = 0 = -\overline{w'w''C'} - \frac{\partial \overline{w'w'C'}}{\partial z} + \frac{1}{\rho} C_i \frac{\partial \rho'}{\partial z} + \frac{g}{\gamma} \overline{\theta' C'}. $$  \tag{D1}$$

On the right-hand side, the first term is the production of turbulent flux due to the interaction between turbulence and the mean concentration gradient; the second represents a triple-moment term interpreted as a transport of the flux by turbulence; the third is the pressure–scalar interaction term (i.e., destruction term), which acts to decorrelate $w'$ from $C'$; and the fourth is the buoyancy term (can be a source or sink) induced by the covariance between temperature and scalar concentration turbulent fluctuations. To proceed further, the destruction term for the scalar flux is modeled similar to the destruction term for momentum flux and is given as

$$ \frac{1}{\rho} C_i \frac{\partial \rho'}{\partial z} = -C_R \frac{w'C'}{\tau} + C_i \sigma_w^2 \frac{\partial C}{\partial z}. $$  \tag{D2}$$

where $C_R$ is the Rotta constant, $C_i = 3/5$ (derived from Rapid Distortion Theory), and $\tau(z)$ is a relaxation time scale. Combining the above two equations, the scalar flux can be expressed as

$$ \overline{w'C'} = -\frac{\tau}{C_R} \left( 1 - C_i \overline{w'w'} \frac{\partial C}{\partial z} \right) + \frac{\partial \overline{w'w'C'}}{\partial z} - \frac{g}{\gamma} \overline{\theta' C'}. $$  \tag{D3}$$

Formulated in this manner, the necessary conditions leading to the validity of the eddy diffusivity approach become evident. When the sum of the flux transport term and buoyancy terms is small compared to the production, the eddy diffusivity model is recovered with $K = \left( \frac{1 - C_i}{C_R} \right) \frac{\tau \sigma_w^2}{w_s}$. Therefore, it is possible to derive a dimensionless number $N_{GD}$ to represent the modeled expected deviation from the eddy diffusivity model, given by

$$ N_{GD} = \left| \frac{\overline{w'w'C'}}{\overline{w'w'}} - \frac{\frac{g}{\gamma} \overline{\theta' C'}}{w_s} \right| \left( 1 - C_i \overline{w'w'} \frac{\partial C}{\partial z} \right). $$  \tag{D4}$$

The use of an eddy diffusivity closure is acceptable when $N_{GD} \ll 1$. However, determining $N_{GD}$ from data is difficult as it requires fast-response sensors to measure $\overline{w'w'C'}$ and multilevel flux measurements to determine $\overline{w'w'C'}$. For operational purposes, these measurements are rarely available in canopy studies necessitating additional approximations. For the purposes of evaluating $N_{GD}$, the buoyancy term is ignored and the flux transport term is modeled as

$$ \overline{w'w'C'} = -C_2 \tau \sigma_w^2 \frac{\partial \overline{w'C'}}{\partial z}. $$  \tag{D5}$$

where $C_2$ is a closure constant. Hence, when combined with the mass balance equation (4), $\overline{w'w'C'}$ scales as $\tau \sigma_w^2 S(z)$ (this is analogous to the near-field effect arising in Lagrangian models). To a first approximation, $N_{GD}$ scales as

$$ N_{GD} = C_2 \frac{\tau \sigma_w^2 S(z)}{1 - C_i} \left| \frac{\partial}{\partial z} \left( \frac{\sigma_w^2 S(z)}{w'_w} \right) \right| \sim \frac{\tau S_{avg}}{\overline{w'C'}}. $$  \tag{D6}$$

Here $\overline{w'C}$ may be estimated from the overall change in mean concentration across the entire canopy depth, and $\tau$ may be estimated from $T_e$ or $h/(3u_*)$. Assuming that $S_{avg}$ scales as $w'_w C_s h$ and taking $C(0) = 0$ leads to equation (16).
Acknowledgments

L.S.F. was funded by the program Science Without Borders (CNPq, Brazil). The U.S. Department of Energy supported the field studies as part of the GoAmazon 2014/5 project (grant SC001075). Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and Fundação de Amparo à Pesquisa do Estado do Amazonas (FAPEAM) funded the Brazilian component of the field studies. The Large-scale Biosphere-Atmosphere Experiment in Amazonia (LBA) provided logistic support and made the flux tower and housing unit available to complete the field studies. We thank the support from the LBA central office that operated at INPA. We acknowledge logistical support from the ARM Climate Research Facility. J.D.F. acknowledges support from the U.S. National Science Foundation (grant 1417914). The data needed for reproducing the figures are available from the authors upon request (chamecki@ucla.edu). We thank three anonymous reviewers for comments that greatly improved the manuscript.

References

Jacob, D. J., and S. C. Wofsy (1990), Budgets of reactive nitrogen, hydrocarbons, and ozone over the Amazon forest during the wet season, J. Geophys. Res., 95(D10), 16,737–16,754.
Lamb, R. G. (1973), Note on the application of K-theory to diffusion processes involving nonlinear chemical reactions, Atmos. Environ., 7(3), 257–263.


Trumbore, S., M. Keller, S. Wofsy, and J. Da Costa (1990), Measurements of soil and canopy exchange rates in the Amazon rain forest using 222 Rn, *J. Geophys. Res.*, 95(D10), 16,865–16,873.