The role of boundary layer dynamics on the diurnal evolution of isoprene and the hydroxyl radical over tropical forests

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[1] We investigate diurnal variability of isoprene and related chemical species in the Amazonian region. The dynamics and chemistry of an atmospheric boundary layer are studied with a large-eddy simulation code and a mixed-layer model which are guided by observations available for the same area. The main features of isoprene and related species are reproduced well, but their evolution raises questions regarding the physical and chemical processes responsible for the observed diurnal behaviors. To address these questions, we systematically examine the role of (1) the exchange of chemical species between the free troposphere and the atmospheric boundary layer (entrainment), (2) surface isoprene and nitric oxide emissions, and (3) new chemical pathways to recycle the hydroxyl radical. The entrainment flux of isoprene is shown to be equally important as surface isoprene emissions in determining the isoprene temporal evolution. Varying the relationship between the initial isoprene mixing ratio in the boundary layer and that in the overlying free troposphere in the early morning results in an 50% increase/decrease in isoprene mixing ratio or more within the atmospheric boundary layer at noon. Entrainment of free tropospheric nitrogen oxides creates changes of similar magnitude to the boundary layer isoprene mixing ratio. These effects of entrainment and surface emissions on isoprene are found for two different chemical regimes. The introduction of an OH recycling pathway in the chemical mechanism increases midday OH. Our findings show that atmospheric dynamics and chemistry are equally important for interpreting the diurnal observation of reactants and for including in regional-scale modeling efforts where turbulence is parameterized.


1. Introduction

[2] The reactivity of key compounds like ozone, isoprene, and the hydroxyl radical is controlled by physical and chemical processes occurring in the lower part of the troposphere, namely the atmospheric boundary layer (ABL), where these species can directly interact with the land surface. During a diurnal cycle, the ABL experiences a large height variation in response to time-dependent buoyancy forcing (ranging from heights as small as 100 m or smaller at night up to more than 2 km during midday). This height variation has two key implications for ABL chemistry: (1) as the ABL grows during the morning, free tropospheric (FT) air is entrained into the ABL which is typically characterized by mixing ratios of atmospheric compounds different than those within the ABL, and (2) surface-emitted or entrained species are mixed into a growing volume throughout the day and then into a smaller volume after the buoyancy forcing shuts down and the convective boundary layer collapses. The entrainment process is often not quantified adequately in studies focusing on soil and vegetation exchanges of reactants and turbulent mixing within the atmospheric surface layer. Therefore the aim here is to quantify the importance of ABL growth and the subsequent FT-ABL exchange relative to surface sources/sinks.

[3] By conducting numerical experiments using both the large-eddy simulation technique [Heus et al., 2010] and mixed-layer theory [Vilà-Guerau de Arellano et al., 2009] which are guided by observations taken during the Tropical Forest and Fire Emission Experiment (TROFFEE) campaign [Karl et al., 2007; Yokelson et al., 2008], we study the interplay between turbulent dynamics and the O₃-NOₓ-VOC-HOₓ
chemistry in the Amazonian boundary layer. The reasons to select Amazonia are fourfold: (1) the chemistry is characterized by high biogenic emissions and the role of dynamics is not yet well understood [Butler et al., 2008; Gansleveld et al., 2008; Pugh et al., 2009], (2) tropical systems are globally significant in regulating atmospheric composition [Karl et al., 2007; Lelieveld et al., 2008], (3) the Amazon is undergoing rapid changes in surface vegetation characteristics through deforestation and Amazonian ABL dynamics and chemistry is potentially very sensitive to these modifications [e.g., Fan et al., 1990; Keller et al., 1991], and (4) disagreements between measured and modeled OH have been observed, and a variety of different chemical reaction pathways that form and destroy OH have been proposed [e.g., Lelieveld et al., 2008; Peeters et al., 2009].

The role of entrainment on heat and moisture budgets has been previously investigated for clear [e.g., Tennekes, 1973] and stratocumulus boundary layers [e.g., Lilly, 1968]. Large-eddy simulation has enabled investigations into the dynamics determining entrainment in free convective situations [Sullivan et al., 1998; Jonker et al., 1999] and into the influence of wind shear on entrainment [Pinto et al., 2003; Conzemius and Fedorovich, 2006]. For moisture and carbon dioxide, observation and modeling [Martin et al., 1988; Davis et al., 1994; Vilà-Guerau de Arellano et al., 2004; Casso-Torralba et al., 2008; van Heerwaarden et al., 2009] studies showed that entrainment is as important as the surface exchange process in estimating the diurnal budget of water vapor and CO₂. For atmospheric reactants, Martin et al. [1988] suggested the importance of the FT-ABL exchange in regulating the diurnal cycle of reactants in the Amazonian region; however, to our knowledge no further attempt has been made to quantify the role of entrainment on diurnal reactant variation.

The research in this current manuscript therefore aims to determine which processes control the diurnal evolution of reactants in the O₂–NO₂–VOC–HO₂ system, and consequently to determine which processes need to be included in boundary layer parameterization schemes to adequately reproduce their diurnal characteristics. Since we have observations of isoprene and its major byproducts available from TROFFEE, we mainly focus our analysis on those species but extend that analysis to the OH radical due to its oxidizing relevance above tropical forests [Zimmerman et al., 1988; Guenther et al., 1996; Fuentes et al., 2000; Karl et al., 2007; Lelieveld et al., 2008].

Systematic numerical experiments are carried out to determine and quantify the roles of (1) FT-ABL exchange, (2) isoprene and NO surface emissions, and (3) OH production rates in modulating reactant diurnal evolution. In consequence, these numerical experiments enable us to establish the different contribution from each process and to determine their importance at different stages of the boundary layer evolution. A final investigation studies the relationship between surface isoprene emission flux and the atmospheric mixing ratio for other observational campaigns in the tropics.

This study also permits assessment of the turbulence-resolving large-eddy simulation technique for studying complex chemical systems and establishes expected relationships between LES and predictions using zeroth-order mixed-layer (MXL) theory applied to ABL chemistry. Models based on MXL theory allow incorporation of surface and entrainment flux relationships into a simple conceptual model of boundary layer dynamics and its interaction with chemistry while maintaining similar computational expense to box model simulations. The mixed-layer model representation of the convective boundary layer is similar to parameterizations implemented in large-scale chemistry-transport models; this close relationship consequently enables identification of the key processes needing inclusion or improvement within such boundary layer schemes.

The structure of this article is as follows: Section 2 describes the design of the numerical experiments and the sensitivity studies. The dynamical and chemical evolution of the boundary layer obtained through large-eddy simulation and through the mixed-layer model are evaluated against observations and discussed in section 3. Section 4 focuses on determining and comparing the main processes driving diurnal variability of isoprene and the hydroxyl radical, namely: (1) FT-ABL exchange, (2) surface emissions, and (3) chemical reactivity associated to OH-reincycling and fast chemical pathways. Section 5 extends this investigation by looking at the relationship between the isoprene emission and atmospheric mixing ratio by analyzing data collected during a variety of Amazonian observational campaigns characterized by different biogenic surface fluxes. Section 6 closes the paper by summarizing the main conclusions and emphasizing the need for an appropriate balance between ABL dynamics and chemistry when investigating ABL chemistry from either a modeling or an observational perspective.

2. Design of the Numerical Experiment

2.1. Observations

The intent of our numerical experiments is to shed light on the relative importance of entrainment, surface fluxes, and chemistry on the variability of observations taken during TROFFEE, which took place 60 km NNW of Manaus in Central Amazonia (2.612 S, 60.91 W) during the dry season between 14 and 29 September 2004 [Karl et al., 2007]. The Manaus region is not heavily influenced by biomass burning due to the vast expanse of surrounding undisturbed forest upwind. TROFFEE focused mainly on measuring trace atmospheric compounds but also included observations of potential temperature and sensible heat flux. The canopy height was 30 m with a leaf area index ranging between 5 and 6. Isoprene flux and mixing ratio were measured at 40 m. In addition, we employed aircraft measurements of isoprene mixing ratio to establish a link between surface flux emission and isoprene levels within the ABL. The aircraft observations were taken at 675 m. Surface fluxes and upper atmospheric conditions observed during TROFFEE were combined with observations from previous Amazonian ABL studies [Martin et al., 1988; Garstang et al., 1990; Betts and Jacob, 2002; Andrae et al., 2002] to create a generic atmospheric situation reproducing a typical Amazonian boundary layer undisturbed by large-scale forcing. Similarly, hourly averaged atmospheric chemistry observations from the 15-day TROFFEE campaign are used to impose time-evolving surface isoprene and nitric oxide emission fluxes. Because NO or NO₂ mixing ratios were not available in TROFFEE, observed NO₂ from Andrae et al. [2002] measured in a pristine forest region of Rondonia, Brazil is used to constrain the initial mixing ratios of nitrogen compounds NO, NO₂.
2.2. Atmospheric Representation

[10] The study is based on the simulations carried out by two numerical tools: (1) the Dutch Atmospheric Large-Eddy Simulation (DALES) [Heus et al., 2010; Vilà-Guerau de Arellano et al., 2005] and (2) a much simpler dynamics model based on mixed-layer theory (MXLCH) [Tennekes, 1973; Vilà-Guerau de Arellano et al., 2009]. The large-eddy simulation technique solves the filtered three-dimensional thermodynamic equations and conservation equation for reactive species, and as a result produces three-dimensional time-evolving fields. In convective boundary layers, LES explicitly reproduces approximately 90% of the energy contained in the turbulent eddies. Therefore it is also able to account for the influence of large-scale turbulent structure on chemical reactivity and on entrainment.

[11] Although the LES is highly accurate, it is also computationally expensive. The MXLCH model allows for a less expensive method to reasonably represent key ABL processes and to conduct sensitivity tests as is done here. The MXLCH model assumes horizontal homogeneity and perfectly mixed convective boundary layer characteristics resulting in a one-dimensional representation producing vertical profiles which are constant with height within the mixed layer. On the basis of these characteristics, the governing equations of this conceptual model are therefore obtained by the vertical integration of the one-dimensional thermodynamic equations and conservation equation for reactive species.

[12] A relevant aspect to appreciate is that MXLCH is very similar to a box model where heat/moisture/reactant sources can be introduced into the box; these sources/sinks might be time-dependent but are generally specified a priori and are intended to mimic all possible sources/sinks to the box. Like a box model, MXLCH also includes a prescribed source; however, the imposed source is interpreted solely as a surface emission which is instantaneously mixed into the box. However, unlike a box model, MXLCH also incorporates a simple mechanism by which the boundary layer (the box) can grow vertically through the action of parameterized buoyancy-driven turbulent motions eating away at an infinitesimally sharp gradient at the top of the boundary layer (the box) thereby exchanging heat/moisture/reactants across that interface. If the mixing ratio above the box is higher (lower) than that within the box then there is an additional increase (decrease) of that quantity to (from) the box, where the magnitude of that increase (decrease) is assumed to be proportional to the growth rate of the box and the magnitude of the mixing ratio gradient across the interface. See Vilà-Guerau de Arellano et al. [2009] for further details. Although MXLCH represents entrainment in this simplified fashion, it captures the essential interplay between surface forcing, boundary layer dynamics, entrainment zone variations, and free tropospheric conditions that is not captured in box model simulations.

[13] While the fluid mechanics between DALES and MXLCH differ, they share an identical two-step chemical solver [Verwer, 1994; Verwer and Simpson, 1995]. This two-step chemical solver is an implicit method with second-order accuracy based on the two-step backward differentiation formula which is able to adjust the time step depending on the chemical reaction rate [Vilà-Guerau de Arellano et al., 2009; Heus et al., 2010].

[14] The LES calculations are carried out using a 12,800 m × 12,800 m horizontal and a 2550 m vertical domain resolved by 128 × 128 × 128 grid points. Periodic boundary conditions are imposed in the horizontal directions, and Monin-Obukhov similarity theory is used to relate quantities at the first grid point to the imposed surface fluxes at the ground. MXLCH uses the identical initial conditions and surface emissions as are imposed in the LES experiments.

[15] Fifteen-day averaged TROFFEE observations are prescribed as initial and boundary conditions in the numerical experiments (Table 1). The geostrophic wind is 0 m s⁻¹ (i.e., local free convective conditions). The roughness length is 0.035 m. We do not prescribe any large-scale forcing (zero horizontal heat or moisture, no subsidence, nor radiative tendencies). The simulation begins at 0500 local time (LT) and lasts 13 h (sunrise is at 0600 LT and sunset occurs at 1800 LT).

[16] ABLs above tropical forests are typically warm and moist and are capped by a free troposphere which is close to being conditionally unstable [Garstang et al., 1990; Betts and Jacob, 2002]. These conditions favor the formation of shallow cumulus during the day, which significantly complicates the relationships between surface/entrainment fluxes and mid-ABL mixing ratios. To simplify the interpretation of our results, we chose not to permit cloud formation in our simulations by not allowing condensation.

2.3. Chemistry Representation

[17] Simulating the interactions between turbulence and complex chemistry is computationally intensive. We therefore choose an approach that balances the costs between dynamics and chemistry while attempting to minimize any compromise for either component. We select a chemical mechanism which semiquantitatively reproduces the essential components of the O₃/NOₓ/VOC-HOₓ system while allowing a series of LES experiments with sufficient numerical resolution to reproduce the atmospheric fluid dynamics. The chemical mechanism is described in Table 2. In short, we use a highly condensed gas phase mechanism describing the basic features of isoprene-NOₓ-O₃ chemistry in the remote tropical atmosphere. Notice also that the chemical mechanism is acting in the ABL and FT.

[18] This simple mechanism has been compared with a more complete mechanism (that of MOZART-4, Enmons et al., 2010), using a box model software package Acuchem [Braun et al., 1988] and in limited tests using MXLCH. The box model comparisons show that in general, the MOZART-4 mechanism results in lower steady state OH levels than does the simple mechanism, owing to the existence of NOₓ sinks in MOZART-4 that are not included in the simple model. Thus for the control case described below, [OH] is about 30% lower in MOZART than in the simple mechanism. On the other hand, in case studies in which OH recycling is included in the mechanism (n = 1.5 in (R17) of Table 2, see section 4.3.2), OH levels are essentially identical in the two models despite the differences in NOₓ, due to the dominant role of the recycling in the production of OH. Thus despite its limitations, the simple mechanism is capable of semiquantitatively representing OH levels when compared to a more complete mechanism, thus providing an adequate representation of the inherent chemical timescales. Note also that the range of OH levels explored in the various case studies that follow (about a factor of 5) is much larger than the model/model variations just discussed.
Table 1. Initial and Prescribed Values Used for the Large-Eddy Simulation (DALES) and the Mixed-Layer Model (MXLCH) Numerical Experiments

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Boundary Layer Properties</strong></td>
<td></td>
</tr>
<tr>
<td>Initial boundary layer height</td>
<td>200</td>
</tr>
<tr>
<td>$h$ (m)</td>
<td></td>
</tr>
<tr>
<td>Large scale subsidence velocity, $w_z$ (m s$^{-1}$)</td>
<td>0</td>
</tr>
<tr>
<td>Imposed geostrophic wind, ($U_p$, $V_p$) (m s$^{-1}$)</td>
<td>(0, 0)</td>
</tr>
<tr>
<td>Surface roughness length, $z_c$ (m)</td>
<td>0.035</td>
</tr>
<tr>
<td><strong>Heat</strong></td>
<td></td>
</tr>
<tr>
<td>Surface sensible heat flux (from 0725 to 1525 LT) (K m s$^{-1}$)</td>
<td>1990</td>
</tr>
<tr>
<td>Entrainment to surface sensible flux ratio, $\beta_{MXLCH}$</td>
<td>0.2</td>
</tr>
<tr>
<td>Potential temperature profile (K)</td>
<td></td>
</tr>
<tr>
<td>$z &lt; 200.0$ m</td>
<td>299.0</td>
</tr>
<tr>
<td>$200.0$ m $&lt; z &lt; 212.5$ m</td>
<td>300.0</td>
</tr>
<tr>
<td>$z &gt; 212.5$ m</td>
<td>300.0 + 6 · 10$^{-3}$ · $z$</td>
</tr>
<tr>
<td><strong>Moisture</strong></td>
<td></td>
</tr>
<tr>
<td>Latent heat flux (from 0600 to 1650 LT) (g kg$^{-1}$ m s$^{-1}$)</td>
<td>1.00</td>
</tr>
<tr>
<td>Specific moisture profile (g kg$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>$z &lt; 200.0$ m</td>
<td>0.2</td>
</tr>
<tr>
<td>$200.0$ m $&lt; z &lt; 212.5$ m</td>
<td>0.2</td>
</tr>
<tr>
<td>$z &gt; 212.5$ m</td>
<td>2.00</td>
</tr>
</tbody>
</table>

*All initial conditions are imposed at 0500 LT and $t$ is the time in seconds. The subscripts $s$ and $e$ indicate values at the surface and the entrainment zone, respectively.

[19] Last, it should be noted that all first generation products of isoprene oxidation are lumped into a single species (referred to as MVK in (R13)) which is assumed to be formed in 100% yield. In the TROFFEE observations to which we compare, the PTR-MS instrument cannot discern between species exhibiting the same molecular weight. Therefore the reported PTR-MS values for species with molecular weight 70.09 (g mol$^{-1}$) include both methyl vinyl ketone (MVK) and methacrolein (MACR). In combination, MVK and MACR also represent only 60% of the isoprene oxidation products [Tiuazon and Atkinson, 1990]. Therefore our chemical mechanism should overestimate MVK production. It is important to stress that we use the reduced mechanism described in Table 2 so that the MXLCH predictions can be compared with results from the computationally demanding three-dimensional turbulence resolving LES calculations using DALES.

[20] All the reactions rates are specified in Table 2, except for (R15), where we assume the following reaction rate:

$$k = (k_1 + k_2) \cdot k_3$$  \hspace{1cm} \text{(1)}

where,

$$k_1 = 2.2 \cdot 10^{-13} \cdot e^{\theta_1}$$  \hspace{1cm} \text{(2)}

$$k_2 = 1.9 \cdot 10^{-33} \cdot e^{\theta_2} \cdot [M]$$  \hspace{1cm} \text{(3)}

$$k_3 = 1 + 1.4 \cdot 10^{-21} \cdot e^{\theta_3} \cdot [H_2O]$$  \hspace{1cm} \text{(4)}

[M] and [H$_2$O] are the local concentration of air and water vapor molecules in molec cm$^{-3}$, respectively. The reaction rate coefficients are from the International Union of Pure and Applied Chemistry (IUPAC) Subcommittee for Gas Kinetic Data Evaluation (http://www.iupac-kinetic.ch.cam.ac.uk/). For the sake of simplicity, the photolysis rates are adapted from empirical expressions suggested by Wiegand and Bofinger [2000], which were previously compared with the Tropospheric Ultraviolet and Visible (TUV) radiation transfer code. The tails of the photolysis function of O$_3$ (R1) differ at dawn and at dusk, however our results are not sensitive to these different values.

[21] In (R17), a variable stoichiometric coefficient $n$ has been introduced to study the sensitivity of the system to the OH-recycling. In the Control case $n = 0$; variations of $n$ are studied and discussed in section 4.3.

[22] Table 3 lists the initial profiles and surface fluxes imposed in the Control experiment carried out using both DALES and MXLCH. As mentioned, the time-evolving surface isoprene emission is derived from the 15-day averaged observations as are the initial boundary layer mixing-ratio profiles. Initial NO$_2$ is taken from Andreea et al. [2002]. While initial NO$_2$ is fairly high, mixed layer values of NO$_x$ during the simulation are ~200 pptv. It should be noted that chemistry in the Amazonian region is characterized by relatively low levels of NO$_x$ and relatively high surface isoprene emission. Owing to the absence of trace species observations above the ABL (a typically difficult observation to obtain), all initial trace species profiles are assumed constant throughout the domain. The sensitivity of the simulation results to these initial profiles are discussed at length in section 4. In the LES and MXLCH experiments, mass conservation is preserved within 1%.

3. Evaluation of the Numerical Experiments

[23] The time evolution of key atmospheric bulk quantities characterizing the simulated Amazonian boundary layer

Table 2. Chemical Reaction Scheme Used in the Numerical Experiments of DALES and MXLCH

<table>
<thead>
<tr>
<th>Number</th>
<th>Reaction</th>
<th>Reaction Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>O$_3$ + hv → O(1D) + O$_2$</td>
<td>6.62 · 10$^{-5}$ · e$^{-\theta_1}$</td>
</tr>
<tr>
<td>R2</td>
<td>O(1D) + H$_2$O → OH + OH</td>
<td>1.63 · 10$^{-18}$ · e$^{-\theta_2}$</td>
</tr>
<tr>
<td>R3</td>
<td>O(1D) + N$_2$ → O$_3$</td>
<td>2.15 · 10$^{-11}$ · e$^{-\theta_3}$</td>
</tr>
<tr>
<td>R4</td>
<td>O(1D) + O$_2$ → O$_3$</td>
<td>3.30 · 10$^{-11}$ · e$^{-\theta_4}$</td>
</tr>
<tr>
<td>R5</td>
<td>NO$_2$ + hv → NO + O$_3$</td>
<td>1.67 · 10$^{-2}$ · e$^{-\theta_5}$</td>
</tr>
<tr>
<td>R6</td>
<td>CH$_3$O + hv → HO$_2$</td>
<td>5.88 · 10$^{-11}$ · e$^{-\theta_6}$</td>
</tr>
<tr>
<td>R7</td>
<td>OH + CO → HO$_2$ + CO$_2$</td>
<td>2.40 · 10$^{-13}$</td>
</tr>
<tr>
<td>R8</td>
<td>OH + CH$_4$ → CH$_3$O</td>
<td>2.45 · 10$^{-12}$ · e$^{-\theta_8}$</td>
</tr>
<tr>
<td>R9</td>
<td>OH + ISO → RO$_2$</td>
<td>1.00 · 10$^{-10}$</td>
</tr>
<tr>
<td>R10</td>
<td>OH + MVK → HO$_2$ + CH$_3$O</td>
<td>2.40 · 10$^{-14}$</td>
</tr>
<tr>
<td>R11</td>
<td>HO$_2$ + NO → OH + NO$_2$</td>
<td>3.50 · 10$^{-12}$ · e$^{-\theta_{11}}$</td>
</tr>
<tr>
<td>R12</td>
<td>CH$_2$O$_2$ + NO → HO$_2$ + NO$_2$ + CH$_3$O</td>
<td>2.80 · 10$^{-13}$ · e$^{-\theta_{12}}$</td>
</tr>
<tr>
<td>R13</td>
<td>RO$_2$ + NO → HO$_2$ + NO$_2$ + CH$_3$O + MVK</td>
<td>1.00 · 10$^{-11}$</td>
</tr>
<tr>
<td>R14</td>
<td>OH + CH$_3$O → HO$_2$</td>
<td>5.50 · 10$^{-12}$ · e$^{-\theta_{14}}$</td>
</tr>
<tr>
<td>R15</td>
<td>HO$_2$ + HO$_2$ → H$_2$O$_2$</td>
<td>(see equations 1–4)</td>
</tr>
<tr>
<td>R16</td>
<td>CH$_2$O + HO$_2$ → PRODUCT</td>
<td>4.10 · 10$^{-15}$</td>
</tr>
<tr>
<td>R17</td>
<td>R12 + HO$_2$ → product</td>
<td>1.50 · 10$^{-10}$</td>
</tr>
<tr>
<td>R18</td>
<td>OH + NO$_2$ → HNO$_3$</td>
<td>3.50 · 10$^{-12}$ · e$^{-\theta_{18}}$</td>
</tr>
<tr>
<td>R19</td>
<td>NO + O$_3$ → NO$_2$ + (O$_2$</td>
<td>3.00 · 10$^{-12}$ · e$^{-\theta_{19}}$</td>
</tr>
</tbody>
</table>

*In the reaction rate functions, $T$ is the absolute temperature and $\chi$ is the solar zenith angle. First-order reaction rates are in s$^{-1}$ and second-order reactions are in cm$^{-3}$ molecule$^{-1}$ s$^{-1}$. In the control experiment, $n = 0$ in reaction (R17).
are shown in Figure 1, where $h$ is the boundary layer height, $\langle \theta \rangle$ is the ABL-averaged potential temperature, and $\langle q \rangle$ is the ABL-averaged specific humidity. To maintain consistency with mixed-layer theory, the height of the minimum horizontally averaged buoyancy flux is taken as the boundary layer height in the LES calculations.

The two models predict similar ABL depth evolution, albeit with the LES code predicting slightly larger boundary layer growth compared to MXLCH. Turbulence is explicitly calculated in the LES and breaks down the temperature inversion at the ABL top 30 minutes prior to MXLCH (i.e., at 0700 LT compared to 0730 LT). In DALES, the entrainment rate (boundary layer growth rate) is a result of the simulations and depends on (1) the initial profiles (e.g., temperature, wind, and moisture), (2) the imposed forcing (e.g., geostrophic wind, surface energy balance, free tropospheric lapse rate), (3) the grid resolution, and (4) the numerical methods used to solve the equations. MXLCH does not explicitly calculate entrainment; rather, it uses a zeroth-order approach to represent entrainment. In MXLCH, the potential temperature jump across the inversion at the ABL top is parameterized as a sharp discontinuity determined by a theoretical and prescribed relationship between entrainment and surface buoyancy fluxes ($\beta_{\text{MXLCH}}$); in this study, we assume $\beta_{\text{MXLCH}} = -0.2$ (Table 1). This value is larger in magnitude than the value predicted by DALES (where, $\beta_{\text{DALES}}$ averaged between 0800 LT and 1500 LT equaled $-0.15$). As such, one of the consequences of using the mixed-layer approach is that the larger value of

<table>
<thead>
<tr>
<th>Initial scalar value (ppbv)</th>
<th>O$_3$</th>
<th>NO</th>
<th>NO$_2$</th>
<th>ISO</th>
<th>MVK</th>
<th>CH$_4$</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial mixing ratio</td>
<td>10.0</td>
<td>0.0</td>
<td>1.0</td>
<td>2.0</td>
<td>1.3</td>
<td>1724</td>
<td>124</td>
</tr>
<tr>
<td>Initial mixing ratio</td>
<td>10.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.0</td>
<td>1.3</td>
<td>1724</td>
<td>124</td>
</tr>
<tr>
<td>Initial mixing ratio</td>
<td>10.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Reacts in Table 2 that are not included in the table have zero initial concentrations and zero surface emissions. For the molecules O$_3$ and N$_2$ we have imposed the values $2 \cdot 10^8$ and $8 \cdot 10^8$ ppbv, respectively. For the surface emission of isoprene the $\zeta$ function is $\zeta = \left((t + 18,000) - 42,705\right)/7999$ with a conversion factor from ppbv m s$^{-1}$ to mg m$^{-2}$ h$^{-1}$ equal to 11.5. This function has been fitted to the TROFFEE isoprene observations emissions averaged during the period 14–29 September 2004. Here $t$ is the simulation time starting at 0500 LT. No deposition fluxes are imposed.

![Figure 1](image-url)  

Figure 1. Diurnal evolution of (a) boundary layer height ($h$), (b) ABL-averaged potential temperature ($\langle \theta \rangle$), and (c) ABL-averaged specific humidity ($\langle q \rangle$) predicted by DALES and MXLCH.
\( \beta_{\text{MXLCH}} = -0.2 \) is compensated by the fact that in the LES entrainment occurs over a larger depth [Pino et al., 2006]. To determine the entrainment flux for the other compounds (i.e., specific moisture or reactants), MXLCH assumes that the entrainment flux of each quantity is proportional to the product of the entrainment velocity (the growth rate of the ABL, \( \partial h/\partial t \)) multiplied by the mixing ratio jump of that quantity across the ABL–FT interface [Vilà-Guerau de Arellano et al., 2009].

Figure 1b reveals the increase of ABL-averaged potential temperature due to heat introduced through surface and entrainment buoyancy fluxes; the time evolution of \( h/C_18 \) between the models compares well. In contrast, Figure 1c shows distinct differences in ABL-averaged specific humidity between the models, suggesting that \( h_q \) is more sensitive to differences in boundary layer growth and FT-ABL exchange than is \( h/C_18 \).

The increased ABL growth predicted by the LES means higher entrainment rate of low water vapor mixing ratio air from aloft that leads to a dilution of the ABL in the LES compared to that in MXLCH during the early morning hours. This dilution process in the LES leads to a smaller ABL-averaged water vapor mixing ratio peak at 0700 LT and to a more rapid rate of decrease of \( h_q \) in time compared to MXLCH. The LES reproduces the same process, but with a slight time delay. However after 1000 LT, the \( h_q \) evolution calculated from MXLCH and DALES compare satisfactorily. When analyzing the diurnal evolution of the reactants we will refer to this difference between the LES and MXLCH during the morning transition.

It is important to mention here that we advocate solving dynamics and chemistry simultaneously, in contrast to box model studies using either an imposed constant boundary layer height or an imposed constant growth rate. We purport that doing so ensures consistency in calculating not only the ABL dilution and FT-ABL exchange rate, but also the absolute temperature and specific humidity which are key variables in the calculation of the reaction rates (Table 2).

The time evolution of isoprene and MVK mixing ratio observed during TROFFEE are used to evaluate the model predictions. The three-dimensional reactant fields calculated by the LES are first horizontally averaged, and then time-averaged over five minutes. Lastly, the profiles are vertically integrated from the surface to the boundary layer height (defined again as the height of minimum buoyancy flux), which ensures consistency with the assumptions made in MXLCH permitting direct comparison between the two numerical results.

Figure 2 shows the time evolution of ABL-averaged isoprene (ISO) and MVK. To evaluate the model against the observations, the model results at \( z = 40 \) m are used which corresponds to the observation height. Since isoprene is
surface-emitted, the largest isoprene values are found in the surface layer, hence the better agreement with the 40 m observations. However, the ABL-averaged isoprene mixing ratio from the simulations with simple chemistry reproduce the observed temporal evolution reasonably well, although both simulations underestimate the 15-day averaged observed isoprene mixing ratio by about 2 to 2.5 ppbv during daytime hours. The comparison of the isoprene temporal evolution between MXLCH with limited chemistry and MOZART-4 chemistry shows that our limited chemical mechanism reproduces the tendency but slightly underestimates the isoprene temporal evolution (by less than 0.5 ppbv) in the hours of maximum growth of the boundary layer (from 0800 to 1300 LT).

The models reproduce the observed MVK mixing ratio during the morning hours but then diverge from the observations between 1000 and 1400 LT (recall the discussion in section 2.3 where the differences between our modeled MVK and that measured by the PTR-MS are presented). During this late-morning to midday period, the observed MVK mixing ratio is essentially constant whereas the ABL-averaged modeled MVK mixing ratio increases. Identical MXLCH simulations but using the MOZART-4 mechanism instead of our simple chemical mechanism are similar, but with a 1–2 ppbv negative bias. In section 4, we will analyze and discuss potential reasons for the variability seen in the observations by investigating contributions from a variety of processes. Other possible key processes, such as wet deposition, should not be important for the conditions that we are simulating. Dry deposition may be important and will be discussed in section 4.

The time evolution of the ABL-averaged ISO and MVK values calculated by the two different dynamics models (DALES and MXLCH) also agree reasonably well. Explicit calculation of the intensity of segregation (defined as $I_s = \frac{\sigma^2}{\bar{a}^2}$, the ratio of the covariance of species to the product of the horizontal averages where an instantaneous quantity $a = \bar{a} + a'$ [e.g., Schumann, 1989]) from DALES reveals that $I_s < 8\%$ for the ISO+OH reaction (R9) averaged within the ABL [Ouwersloot et al., 2010] and is no greater than 12\%, which occurs at $z/h = 0.05$. These relatively low values of $I_s$ indicate efficient reactant mixing, which suggests MXLCH’s instantaneous and homogeneous mixing assumption is reasonable for the chemical mechanism and the uniformly imposed surface source distribution considered here. However, Vilà-Guerau de Arellano et al. [1990], Krol et al. [2000], and Patton et al. [2001] showed that greater segregation between reactants is expected when the species are not premixed and when species are emitted nonuniformly in space, i.e., plume emission, heterogeneous surfaces, or intermittent canopy emissions. These findings therefore disagree with those who purport using intensity of segregation to explain the model results underestimation of isoprene concentrations above tropical forests [e.g., Butler et al., 2008; Pugh et al., 2009].

To complete the intercomparison, Figures 3 and 4 show DALES and MXLCH predicted vertical profiles of isoprene and nitric oxide (NO) mixing ratio and flux at...
1200 LT. The mixing ratio profiles (Figures 3a and 4a) are remarkably well reproduced by MXLCH in the region from 100 m ≤ z ≤ 900 m, i.e., the mixed layer. The surface layer (z ≤ 100 m) and entrainment zone (900 m ≤ z ≤ 1500 m) reveal strong ISO- and NO-vertical gradients in the LES; these gradients are not reproduced by MXLCH. These differences result from MXLCH’s assumption that the reactants are instantaneously mixed, while DALES solves the full set of filtered nonlinear equations governing the interactions between dynamics and chemistry and is therefore able to simulate the nonlinear behavior near the interfaces.

[33] The ISO- and NO-flux profiles predicted by the LES versus MXLCH reveal a different behavior with height (Figures 3b and 4b). The vertical isoprene flux profile is linear with height indicating that the chemical term in the conservation equation for vertical isoprene flux is small compared to the transport terms [Gao and Wesely, 1994; Vinuesa and Vilà-Guerau de Arellano, 2003]; i.e., for isoprene, the turbulent mixing timescale \( \tau_t \) (defined as \( \tau_t = \frac{h}{w_*} \), which is about 20 min) is smaller than the chemical reaction timescale \( \tau_c \) (defined as \( \tau_c = \frac{1}{k_{R9}(OH)} \), which is for the Control case approximately 1.4 h). In contrast, the 1-h averaged NO-flux profile calculated by DALES departs from linearity (where \( \tau_c = \frac{1}{k_{R19}(O_3)} \)) and is approximately 200 s). This departure is most notable near the interfaces with the surface and the entrainment zone, where NO chemistry is more rapid than the turbulent mixing process. As shown by Figure 4b, this nonlinear behavior is not reproduced by the mixed-layer model since it assumes a linear flux profile for all species. NO-flux measurements taken within the atmospheric surface layer (z ≤ ~100 m) are clearly influenced by chemistry as indicated by the large curvature of the NO-flux profile [Gao and Wesely, 1994].

[34] In summary, by comparing the DALES results with observations at 40 m, we show that MXLCH predicts isoprene well and overpredicts MVK by ~1 ppbv. By comparing the MXLCH model results with the ABL-averaged DALES results, we show that the MXLCH represents turbulence and therefore chemical mixing ratios similarly to the more accurate DALES results. This comparison also indicates that for the conditions simulated, the MXLCH assumption of a well-mixed ABL is reasonable. It is important to emphasize that compared to typical box model chemistry studies (where turbulence and entrainment are generally ignored), MXLCH incorporates the coupling between atmospheric dynamics and chemistry associated with a convective boundary layer and its diurnal variation while retaining much of a box model’s simplicity.

4. Processes Determining the Time Evolution of ABL-Averaged Species

[35] The evaluation of MXLCH presented in section 3 provides sufficient confidence to embark upon a systematic sensitivity study using MXLCH to investigate factors affecting the diurnal variations observed in the measurements. An important factor is the role of exchange between the free troposphere and the ABL in determining the diurnal variability of ABL-averaged isoprene, MVK, and OH. This sensitivity study will also answer the question whether the diurnal variability of ABL-averaged isoprene induced by entrainment is of similar magnitude to variability induced by variations of isoprene and NO surface emissions.

Figure 4. Same as Figure 3 but for nitric oxide (NO).
The diurnal evolution of bulk ISO, MVK mixing ratio and the OH concentration emphasizes the importance of FT-ABL exchange (Figure 5); Figure 5 shows the control case compared with cases 1 and 2. For ISO (Figure 5a), the dashed line shows the enhancement of isoprene mixing ratio resulting from entrainment of isoprene rich air (case 1). The dotted line shows the dilution of ABL-averaged isoprene mixing ratio resulting from entrainment of isoprene-poor air from aloft (case 2). As a consequence, when the convectively driven ABL growth begins at 0800 LT, (ISO) and (MVK) both depart significantly from the control case. The magnitude of the modulation is proportional to the initial isoprene mixing ratio jump across the FT-ABL interface.

In Figure 5, variations in entrainment produce variations in predicted (ISO) and (MVK) mixing ratios that generally encapsulate the observations. These variations of (ISO) and (MVK) mixing ratios due solely to entrainment support our suggestion that properly accounting for entrainment is an O(1) effect when discussing diurnal variations of boundary layer chemistry.

The ABL-averaged hydroxyl radical concentration ([OH]) is also sensitive to the sign and magnitude of FT-ABL exchange (Figure 5c) of ISO and MVK. In case 1, entrainment increases ABL-averaged isoprene and MVK mixing ratio, [OH] thereby decreases by about 22% at 1000 LT. For case 2, the [OH] concentration increases 39% at 1000 LT due to entrainment of isoprene- and MVK-poor air originating above the boundary layer in the overlying residual layer or free troposphere. The [OH] concentration peak at approximately 0800 LT occurs because the high initial NO2 mixing ratio coupled with low, early morning isoprene emissions produces OH until the FT-ABL exchange of NOx reduces the [OH] in the ABL thus diminishing OH production.

A combination of the inversion strength at the top of the boundary layer and the imposed surface buoyancy flux forcing the convection could also control the [OH] peak. To determine the sensitivity of this [OH] peak to the inversion strength, we carried out a separate experiment increasing the potential temperature gradient across the inversion (the inversion strength) from the initial prescribed Δθ = 1 K (control case, Table 1) to Δθ = 4 K (not shown). Keeping all other conditions the same, an increase in Δθ delays and reduces the growth rate of the ABL and the entrainment of FT air into the ABL. In this experiment where the initial Δθ is set to 4 K, the [OH] maximum increases by 24% and is delayed by 30 min compared to the control case. For surface emitted species, the reduced exchange between the free troposphere and the ABL enhances ABL mixing ratios of those species (in particular NO), which yields higher OH concentrations as the Sun rises and photolysis reactions become important. In addition to this dynamical process, the timing of the [OH] peak is also very sensitive to the onset of isoprene emission occurring during the morning transition from stable to unstable stratification. Delaying the onset of surface isoprene emission by 1 h (experiment not shown) increases the [OH] peak in the control case from 1.7 × 1010 molec cm⁻³ to 2.7 × 1010 molec cm⁻³. When investigating the role of ozone dry deposition (using a deposition velocity equal to 0.5 cm s⁻¹), we did not find a significant influence on the OH peak. Other processes, e.g., entrainment of free tropospheric NOx (case 3) can create an OH diurnal evolution that does not substantially decrease after 0800 LT.

Case 3 examines the influence of NOx entrainment on ABL-averaged isoprene, MVK, and OH mixing ratios. NOx entrainment increases [NOx] from 128 ppbv to 540 ppbv (at 1200 LT), which results in an increase in [OH]; its peak increases to 2.2 · 10⁶ molec cm⁻³ and remains >1.5 · 10⁶ molec cm⁻³ until 1500 LT (Figure 5). The OH increase leads to a decrease in the isoprene mixing ratio by >50% (~3 ppbv), while only increasing (MVK) mixing ratios by 0.5 ppbv. These results again show the importance of entrainment on ABL-averaged isoprene and OH concentrations.

These investigations emphasize the need to obtain information regarding the vertical variation of reactants during the morning transition in order to assess the impact of
entrainment on mixed-layer species. Therefore to accurately predict diurnal mixed-layer reactant evolution, we strongly advocate for profile observations (within the boundary layer up to heights above the mixed-layer) of mean thermodynamic and reacting variables on tall towers or via tethered balloon.

4.2. Surface Emissions and Initial Mixing Ratio Conditions

[45] An important question arises after discussing the role of the FT-ABL exchange on the ISO, MVK, and OH-diurnal variability: What is the relative importance of surface emission to entrainment of FT air in determining observed near-surface mixing ratios? To address this question, in this second experiment case 4 (case 5) imposes a 35% larger (smaller) surface isoprene emission flux than the control case, respectively; this percentage variation is similar to the variability found in the isoprene surface measurements [Karl et al., 2007]. Cases 6 and 7 investigate the influence of NO emission variations and initial NO mixing ratios in the ABL.

[46] All other parameters being the same as those in the control case, the diurnal variability of \( \langle \text{ISO} \rangle \), \( \langle \text{MVK} \rangle \) and \( \langle \text{OH} \rangle \) reveals a significant influence from variations in the magnitude of the surface isoprene flux (Figure 6). A 35% isoprene emission increase (case 4, dashed line) leads to an increase of ABL-averaged ISO (34% increase at 1000 LT), which yields increases in \( \langle \text{MVK} \rangle \) (6% increase at 1000 LT) and depletes \( \langle \text{OH} \rangle \) (26% decrease at 1000 LT). Lower isoprene emissions (case 5, dotted line) produces the opposite behavior; namely, a 33% decrease, 9% decrease, and 35% increase at 1000 LT for ISO, MVK, and OH, respectively. Comparing the shaded regions of Figures 5 and 6, we find that entrainment and ISO surface emissions can have similar influence on ABL-averaged mixing ratios.

[47] This result has repercussions for regional scale isoprene studies. It is common practice when modeling isoprene at larger scales to reduce isoprene emission levels up to 50% in order to obtain agreement with OH observations [e.g., Ganzeveld et al., 2008]. The analysis presented here shows that FT-ABL exchange driven by the dynamic growth of the ABL (i.e., entrainment) and the reactant's
initial distribution at sunrise has similar influence as surface emission. Therefore we purport that improper representation of entrainment in the large-scale chemistry transport models could explain some of the OH disagreement between the observations and predictions by large-scale models.

[48] The daily evolution of \( \langle \text{ISO}_i \rangle \), \( \langle \text{MVK}_i \rangle \) and \( \langle \text{NO}_i \rangle \) is also sensitive to surface NO emission variations and the initial concentration of NO\(_x\) (Figure 7). A factor of ten increase in surface NO emission (case 6, dashed line) yields a 46% increase in daytime OH. At 1800 LT, the ozone mixing ratio in the control and case 6 is 18.0 ppbv and 22.4 ppbv, respectively. For NO\(_x\) the mixing ratios at 1800 LT are: 0.14 ppbv (control) and 0.26 ppbv (case 6). Notice how the \( \langle \text{OH} \rangle \) increase gradually decreases the isoprene levels throughout the day (via (R9)) and increases \( \langle \text{MVK} \rangle \) levels (mainly through (R13)).

[49] Closely related to the previous experiment, it is interesting to determine the influence of the initial NO\(_x\) mixing ratio (prior to sunrise). The initial NO\(_x\) profiles for the control case were inspired by the observations reported by Andreae et al. [2002]. However, it is useful to establish the impact of a lower initial NO\(_x\) mixing ratio on our model results: case 7 (dotted line in Figure 7). As shown, \( \langle \text{OH} \rangle \) decreases considerably (by a factor 0.6 at 0800 LT) and therefore less isoprene is consumed by the hydroxyl radical and MVK production is similarly diminished.

4.3. Chemical Pathways

[50] Here we investigate the influence of chemical reactivity on the isoprene and OH diurnal variability. First, we use the control simulation to examine the role of a chemical OH recycling pathway on ABL mixing ratios. Second, we examine the influence of ABL dynamics, emissions, and OH recycling in a faster chemistry regime.

4.3.1. Recycling of OH

[51] Recent literature has suggested a OH recycling pathway for low NO\(_x\) conditions [e.g., Lelieveld et al., 2008; Butler et al., 2008; Pugh et al., 2009; Peeters et al., 2009]. To investigate whether recycling of OH impacts isoprene, MVK and OH, we modified the products and stoichiometry in (R17) following Lelieveld et al. [2008]:

\[
\text{RO}_2 + \text{HO}_2 \rightarrow n\text{OH} + \text{PRODUCT}
\]

where reaction of \( \text{RO}_2 \) and \( \text{HO}_2 \) occurs with a rate coefficient of \( 1.50 \cdot 10^{-11} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1} \), and yields OH with a stoichiometric coefficient \( n \) equal to 0, 1, or 1.5. As expected, OH production increases dramatically for both \( n = 1 \) and \( n = 1.5 \) (Figure 8); at 1200 LT, the OH concentration is \( 1.0 \cdot 10^6 \text{ mole cm}^{-3} \) and \( 1.6 \cdot 10^6 \text{ mole cm}^{-3} \), respectively. The increased OH subsequently depletes ISO to values much lower than the TROFFEE observations. This OH increase is not uniform through the day, where a post-
sunrise OH maximum is controlled by the morning evolution of the ABL’s thermodynamic characteristics and the subsequent influence of boundary layer growth on FT-ABL exchange, and also by the onset of isoprene surface emission.

The chemical production and loss terms in the conservation equation for OH provide further evidence for the importance of boundary layer dynamics and entrainment on OH reactivity. Figure 9 presents the chemical production (P) and loss (L) terms normalized by the total production (TP) or loss (TL) for the case where $n = 1.5$ in reaction (R17); only loss reactions with larger than 10% contribution are shown. Notice that the production terms are sensitive to the boundary layer and UV-B radiation evolution. The morning OH maximum (i.e., between 0600 and 0900 LT) is clearly dominated by OH produced by NO$_2$ + HO$_2$ (R11). As discussed in section 4.1, the magnitude of this peak depends on the evolution of both thermodynamics and chemistry during the morning transition. Near 1200 LT when isoprene emissions are maximized, the recycling reaction RO$_2$ + HO$_2$ (R17) becomes the main OH source because NO levels have fallen off, and RO$_2$ and HO$_2$ levels have both reached a maximum. In contrast to production (P), the loss reactions (L) reveal very little diurnal variability and are dominated by OH destruction through reactions with isoprene and MVK.

4.3.2. Faster Chemistry Regime

One might ask: Is the relative importance of entrainment, emissions, and OH recycling in determining diurnal ABL mixing ratio variations maintained across different chemistry regimes? To shed light on this question, we configured a set of simulations representing faster radical photochemistry. To create this faster chemical regime, we include OH recycling by setting $n = 1.5$ in (R17). We also add a source of OH and HO$_2$ to represent ozonolysis of terpenes at a rate of $10^6$ molec cm$^{-3}$ s$^{-1}$. This source of OH and HO$_2$ occurs in both the ABL and FT. For consistency with the MOZART-4 chemistry mechanism, we also add a RO$_2$ + NO reaction to represent formation of isoprene nitrates using a rate coefficient of $8 \times 10^{-13}$ cm$^3$ molec$^{-1}$ s$^{-1}$. Because isoprene nitrates are not explicitly represented, this reaction simply forms an end product, namely:

$$\text{RO}_2 + \text{NO} \rightarrow \text{PRODUCT}$$

In addition to these two changes, the model is configured with an initial NO$_2$ of 1 ppbv in the ABL and 0.35 ppbv in the FT, NO emissions are set to $5 \times 10^{-3}$ ppbv m s$^{-1}$, and initial ISO and MVK and ISO emissions are the same as in the control simulation.

This faster chemistry regime was simulated with both the DALES and MXLCH models and produced similar
behavior to the results shown in Figures 2–4. Most importantly, isoprene and NO are sufficiently well-mixed in the ABL, suggesting that using the MXLCH model for further investigations remains reasonable. We also compared this simplified faster chemistry regime to MOZART-4 chemistry using similarly configured Acuchem box model calculations [Braun et al., 1988]. This box model comparison between the mechanisms showed good agreement (<15%) for O₃, ISO, and OH. While NOₓ mixing ratios agree less favorably, the OH mixing ratios are not affected because the primary source of OH is from the recycling reaction (R17). Results from this fast chemistry simulation produce quite low isoprene and MVK mixing ratios, but much higher OH concentrations than the control simulation. The chemical timescale of isoprene at noon is 50 min. The ozone mixing ratio increases to 22 ppbv and NOₓ is 105 pptv at 1200 LT.

Sensitivity simulations using this faster chemistry case as the basis reveal that the changes in ISO, MVK, and OH were found to be of similar magnitude to those found for the cases discussed in sections 4.1 and 4.2. That is, the entrainment of FT ISO and MVK has a similar yet somewhat smaller effect on isoprene and MVK ABL mixing ratios. Entrainment of NOₓ-rich or NOₓ-poor FT air affected ABL-averaged isoprene by 30% but hardly influences MVK. Changes to the ISO surface emissions produced effects similar to those shown in Figure 6. However, changes to NO emission rates had <0.5 ppbv effect on isoprene mixing ratios. Reduced initial NO₂ in both the ABL and FT created only small differences, while the OH-recycling simulations produced variations similar to those described in section 4.3.1. Thus the relative importance of entrainment, surface emissions, and OH recycling on determining ABL ISO, and MVK mixing ratio variations are similar for two different chemical regimes, which strengthens our thesis that entrainment is important for large-scale models to represent.

5. The Relationship Between Surface Isoprene Flux and its Mixing Ratio

[56] Extending our findings in sections 3 and 4 to a wider range of isoprene surface emissions, we now incorporate additional observations from (1) [Kuhn et al., 2004] where observations were taken at 20 m in a primary tropical rain forest (canopy height: 8–10 m) in the Amazonian region (10 S, 62W) during September/October 1999 (end of the dry season), (2) the AMAZE-08 campaign [Karl et al., 2009] also in a forest with similar characteristics at 40 m (canopy height: 30 m) during February 2008, and (3) Costa Rica (CR).
in an old growth tropical forest with a 25 m canopy height [Karl et al., 2004]. Comparing our MXLCH predictions against this broad set of observations permits estimation of the combined roles of FT-ABL exchange, surface emission, and OH reactivity on isoprene mixing ratios above tropical forests.

Figure 10 shows 1-h averaged isoprene mixing ratio versus surface isoprene emissions for these observations and for MXLCH, where we present 1-h averages valid at 1200 LT. To calculate the MXLCH results, we use the dynamical and chemical conditions for three of the cases previously discussed: control case, case 1, and case 2 (Table 4), and then each of these cases is repeated with midday surface isoprene emissions varying from 1 to 7 mg m$^{-2}$ h$^{-1}$. The difference between the thin and thick lines in Figure 10 arises from (R17), where the thin lines are calculated with $n=0$ and the thick with $n=1.5$. We are aware that the measurements were taken under specific meteorological and chemistry conditions which are not exactly those used in our numerical experiments; however, our intention is simply to show the dependence of the surface isoprene flux and isoprene mixing ratio, and the variation of their relationship with boundary layer dynamics (entrainment) and reactivity (recycling).

Two important points come from Figure 10: (1) chemical mechanism differences (i.e., $n=0$ or $n=1.5$ in (R17)) determine the mean slope and curvature of the lines depicting surface isoprene flux and isoprene mixing ratio, and (2) the intercept with the ordinate varies with the importance of entrainment (i.e., FT-ABL exchange); displacement of the intercept can determine whether we find satisfactory agreement between observed surface emission and its respective mixing ratio evolution. Entrainment apparently plays an important role, comparable to surface emission or chemical pathway, and needs to be accounted for when interpreting the observations.

6. Conclusions

The daily cycle of isoprene, methyl-vinyl-ketone, and the hydroxyl radical above tropical forests is studied through numerical experiments guided by observations. Emphasis is placed on using an approach which incorporates a balance of the essential boundary layer dynamics and some basic chemical reactions of the O$_3$-NO$_x$-VOC-HO$_x$ system. By doing so, we are able to reproduce and study key contributions to the isoprene budget and their impact on diurnal variability of isoprene and other related species.

We conclude that the FT-ABL exchange (entrainment) is as important as the surface isoprene emission in determining isoprene mixing ratios. The FT-ABL exchange is controlled by the evolution of boundary layer dynamics, the vertical structure of temperature and moisture, and by the initial mixing ratio of isoprene or NO$_x$ in and above the atmospheric boundary layer at sunrise. Comparisons with the 15-day average mixing ratio observations suggest that the noon-time behavior of ISO and MVK is dependent on the FT-ABL exchange of these two reactants. By combining
measurements from widely varying observational campaigns with numerical experiments, the relationship between surface isoprene emission and isoprene mixing ratio is further studied; at noon, we find a relationship between these variables where the mean slope and curvature are determined by the chemical mechanism and the intercept is dependent on the FT-ABL exchange. Sensitivities of ABL-averaged OH to an OH recycling mechanism are also discussed, where strong recycling of OH is found to deplete ISO to values less than normally measured above tropical forests.

These numerical results demonstrate the ability of large-eddy simulation in studying the interplay between boundary layer processes and complex chemistry. It has to be mentioned that although our model results do not yet explain the discrepancies between modeled and observed OH, they indicate the need to account for the dynamic effects in order to improve the fate of VOC and the related oxidative capacity above tropical forests. Other processes in the O$_3$-NO$_x$-VOC-HO$_x$ system (e.g., dry deposition, boundary layer cloud venting, and surface heterogeneity effects) still remain to be investigated with systematic LES experiments in concert with available and forthcoming measurements.

As a tool that sits between box models and turbulence-resolving LES, a mixed-layer model coupled to a chemical solver can serve as a very useful instrument to analyze observations taken during convective diurnal conditions. Because the mixed-layer model makes similar assumptions to those made in parameterizations which are currently implemented in larger-scale chemistry transport models to represent turbulence/chemistry interactions, our results point to the need to revisit the parameterizations of FT-ABL exchange and their impact on reactant diurnal variability. As such, MXLCH results can be used to support the interpretation of more complex chemistry transport models. The MXLCH is available from the authors upon request.

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