



RESEARCH LETTER

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Key Points:

- LES with comprehensive chemistry is used for study of isoprene chemistry
- Turbulence can decrease or increase the isoprene-OH reaction rate
- NO_x levels influence the range of the effects of turbulence on the reactivity

Supporting Information:

- Supporting Information S1

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Impact of turbulent mixing on isoprene chemistry

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Abstract Isoprene, a volatile organic compound that is mainly emitted from trees, rapidly reacts with hydroxyl radical (OH) during daytime and subsequently forms ozone and aerosols in the troposphere. The isoprene-OH reaction can be affected by the interplay between chemistry and mixing because the two processes occur at a similar time scale. We investigate the impact of turbulent mixing on isoprene-OH reactivity with large eddy simulations (LES) coupled with comprehensive chemistry. Our results show that the covariance of isoprene and OH causes ~20% decrease to ~10% increase of the horizontal average reaction rate, depending on nitrogen oxides (NO_x = NO + NO₂) abundances, compared to the rate that neglects the covariance. This wide range of effects on reaction rates is caused by the primary production and loss reactions of OH in each NO_x regime. Our research promotes the use of LES for better understanding the role of turbulence in isoprene-OH reaction and parameterizations in large-scale models.

1. Introduction

Isoprene (C₅H₈), which is emitted mainly from deciduous trees in the sunlit atmosphere, is an important gas that affects ozone (O₃) and aerosol production in the troposphere [e.g., Guenther *et al.*, 2006; Carlton and Baker, 2011; Wolfe *et al.*, 2015]. Isoprene reacts with hydroxyl radical (OH), NO₃, and O₃, but its daytime loss is dominated by OH oxidation. In the summertime, the chemical lifetime of isoprene with respect to OH is similar to the typical turbulent mixing time scale within the convective boundary layer (10–30 min). Therefore, the interplay between chemistry and turbulent mixing may play an important role in the spatial distribution and abundance of isoprene and related chemical species.

For midday conditions, the chemical tendency of isoprene can be estimated following Reynolds decomposition as

$$\left. \frac{\partial C_5H_8}{\partial t} \right|_{\text{chemistry}} = -\bar{k} \left[\overline{C_5H_8} \overline{OH} + \overline{C_5H_8' OH'} \right], \quad (1)$$

where k is the C₅H₈ + OH reaction rate coefficient, the bars denote time and space averages, and the primes are deviations or fluctuations from the averages [e.g., Kaser *et al.*, 2015]. By discretizing the conservation equation on a grid, regional- and global-scale models implicitly average over all motions smaller than the grid size. In these models, chemical production and loss are typically calculated as the product of the rate coefficient and predicted reactant concentrations within each grid cell, where a well-mixed grid cell is assumed and the covariance term (e.g., $\overline{C_5H_8' OH'}$ in equation (1)) is ignored. In contrast, large eddy simulation (LES) models use a fine-resolution (<100 m) grid and resolve the energy containing turbulent eddies and clouds in the convective boundary layer [Moeng, 1984; Moeng and Sullivan, 1994; Sullivan *et al.*, 1996; Brown *et al.*, 2002; Patton *et al.*, 2005]. Therefore, LES coupled with chemistry can explicitly calculate the covariance of isoprene and OH.

Equation (1) can be rearranged as

$$\left. \frac{\partial C_5H_8}{\partial t} \right|_{\text{chemistry}} = -\bar{k} [1 + I_s] \overline{C_5H_8} \overline{OH}, \quad (2)$$

where the second term in the bracket is the intensity of segregation (I_s) between isoprene and OH or the normalized covariance between isoprene and OH turbulent fluctuations that is used to measure the validity of the well-mixed grid cell assumption. I_s for isoprene and OH in equation (2) is defined as

$$I_s = \frac{\overline{C_5H_8' OH'}}{\overline{C_5H_8} \overline{OH}}. \quad (3)$$

Table 1. Description of Experiments^a

Case	Nitrogen Oxide Emission ($\text{kg m}^{-2} \text{s}^{-1}$)
VERY LOW NO_x	5.0×10^{-12}
LOW NO_x	5.0×10^{-11}
HIGH NO_x	5.0×10^{-10}
VERY HIGH NO_x	2.5×10^{-9}

^aMaximum surface isoprene flux: 1.4×10^{-9} ($\text{kg m}^{-2} \text{s}^{-1}$) and maximum surface monoterpene flux: 8.4×10^{-11} ($\text{kg m}^{-2} \text{s}^{-1}$).

If I_s is negative or the fluctuations of the two reactants are negatively correlated, the effective reaction rate ($\bar{k}[1 + I_s]$) is slower than the rate that assumes a well-mixed condition within a grid (\bar{k}). Slowing down of the reaction due to this segregation effect was suggested as a possible cause for large OH observations that

cannot be explained with known sources/sinks in the tropics [Karl *et al.*, 2007; Butler *et al.*, 2008]. However, Ouwersloot *et al.* [2011] found that the segregation effect alone does not reconcile modeled and observed OH concentrations because reactant segregation in their LES modifies the reaction rate by less than 20%. In contrast, if I_s is positive or the fluctuations of the two reactants are positively correlated, the effective reaction rate is faster than the rate that assumes a well-mixed condition within a grid.

Previous studies have coupled LES models with conceptual or very simple chemistry to investigate I_s and have suggested that the impact of turbulent mixing on the chemical reactivity could be important [Schumann, 1989; Sykes *et al.*, 1992, 1994; Krol *et al.*, 2000; Patton *et al.*, 2001; Vila-Guerau de Arellano *et al.*, 2005; Vinuesa and Vila-Guerau de Arellano, 2005; Ouwersloot *et al.*, 2011]. For example, Krol *et al.* [2000] found $I_s = -20\%$ between OH and a generic hydrocarbon with an OH oxidation rate similar to isoprene using a simple chemistry mechanism with nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) mixing ratio of 0.73 ppbv. However, gas-phase photochemistry is a complex, nonlinear system that these previous studies did not fully represent. In this study, we investigate characteristics of I_s under various chemical scenarios using the LES model coupled with a chemical mechanism that is much more comprehensive than the previous LES studies. After describing the LES model, configuration and set of model simulations, the nonlinear relationships between isoprene and OH that are influenced by NO_x emission rates are examined. We then show that the intensity of segregation between isoprene and OH can vary from -20% to $+10\%$ depending on the NO_x regime. This wide range in segregation can be explained by the primary production and loss reactions of OH.

2. Description of the LES Experiments

The experiments in this study are the same as in Kim *et al.* [2012]. Here we provide a brief description of the model and experiments. The National Center for Atmospheric Research (NCAR) LES model used in this study is derived from Moeng [1984] and Moeng and Wyngaard [1984] with modifications described in Sullivan *et al.* [1994, 1996] and Patton *et al.* [2005]. A modified version of the model for ozone and related chemical tracers MOZART2.2 [Horowitz *et al.*, 2003; Kim *et al.*, 2012] chemistry is utilized. Gas-to-liquid partitioning and aqueous-phase chemistry are not included in this study. The dynamics, cloud physics, and chemistry are integrated, with a 1.5 s time step, over a model domain of $6.4 \times 6.4 \times 4.4 \text{ km}^3$ (96^3 grid points). The simulation is initialized for the meteorological conditions observed at the Southern Great Plains site of the Atmospheric Radiation Measurement program on 21 June 1997, which was intensively analyzed as part of an international LES intercomparison study [Brown *et al.*, 2002]. The LES experiments in this study are identical to the CLOUDY cases in Kim *et al.* [2012] that produce well-developed fair weather cumulus. The surface emissions of isoprene, monoterpene, and nitric oxide and list of experiments are given in Table 1. Isoprene emissions vary diurnally depending on the solar zenith angle; monoterpene emissions are higher during daytime and NO emissions are constant as in Kim *et al.* [2012]. Isoprene, monoterpene, and NO_x emissions are equally distributed in the domain.

To understand I_s between isoprene and OH under different chemical conditions, the cases have four different NO emission scenarios classified as VERY LOW, LOW, HIGH, and VERY HIGH NO_x cases (Table 1). A factor of 10 increase of surface NO emissions between the cases is applied from the VERY LOW to HIGH NO_x case and a factor of 5 increase is applied from the HIGH to VERY HIGH NO_x case. The domain-averaged NO_x mixing ratios at $\sim 500 \text{ m}$ height are 0.14 ppbv in VERY LOW case, 0.30 ppbv in LOW case, 1.38 ppbv in HIGH case, and 8.17 ppbv in VERY HIGH case at 14 local time (LT). The NO_x levels in the simulations were set to represent the rural to urban conditions in the U.S., rather than pristine conditions (e.g., Amazon forests). However,

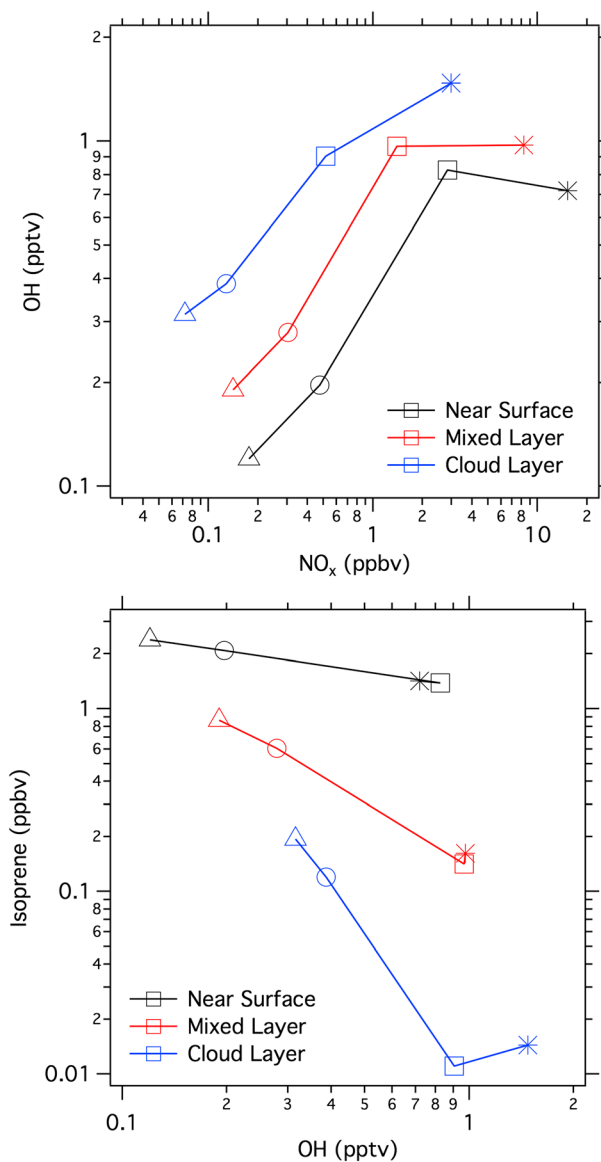


Figure 1. Relationship between (top) OH and NO_x and (bottom) isoprene and OH at different vertical levels from the LES horizontal averages for 1330 LT–1430 LT. Symbols of triangle, circle, square, and asterisk denote VERY LOW, LOW, HIGH, and VERY HIGH NO_x cases, respectively. Black, red, and blue colors represent near surface (~20 m), mixed layer (~500 m), and cloud layer (~1500 m), respectively.

owing to a relatively diluted NO_x concentration favoring OH production instead of forming HNO₃. The chemical mechanism in the LES does not include the recent updates in isoprene chemistry and OH recycling [e.g., Paulot *et al.*, 2009, 2012]. However, a photochemical box model test with these updates shows that the relationship between NO_x and OH behaves consistently for the chemical mechanism used in here and the chemical mechanism with updated isoprene chemistry (see supporting information Figure S2).

The isoprene level is determined by the emission rates and the loss via reaction with OH. Note that the isoprene emission is the same for all of the cases in this study. Figure 1 shows the isoprene–OH relationship in the LES results. Near the surface, the isoprene concentration is anticorrelated with the OH concentration: higher OH results in lower isoprene. In contrast, in the mixed layer and the cloud layer, the isoprene concentration increases as the OH concentration increases from the HIGH to VERY HIGH NO_x case, which was not

several studies [Jacob and Wofsy, 1988; Garcia-Montiel *et al.*, 2003; Keller *et al.*, 2005] reported strong soil NO_x emissions in the Amazon forests that are greater than the emission in our VERY LOW NO_x case. Isoprene emission is kept the same for all cases with a maximum emission during the day of $1.4 \times 10^{-9} \text{ kg m}^{-2} \text{ s}^{-1}$.

The averages from our LES agree with the observational data acquired during the Southern Oxidant Study 1999 (SOS99) field campaign in reproducing the relationship between isoprene and NO_x: isoprene decreases as NO_x increases up to ~10 ppbv, while isoprene starts to increase as NO_x exceeds ~10 ppbv in the mixed boundary layer (supporting information Figure S1). Here the OH level responds to the abundance of NO_x and it in turn affects the isoprene level. In section 3, more discussions about the role of NO_x in production and destruction of OH and the relationship between OH and isoprene are provided.

3. Results

The horizontal domain-averaged OH at 14 LT (1330–1430 LT) increases as the NO_x emission increases for the VERY LOW, LOW, and HIGH NO_x cases (Figure 1). In contrast, the OH decreases as the NO_x emission increases from the HIGH to VERY HIGH NO_x case near the surface (altitude $z \sim 20 \text{ m}$) and in the mixed layer ($z \sim 500 \text{ m}$) because of enhanced OH depletion via formation of HNO₃ [Logan *et al.*, 1981; Trainer *et al.*, 1987; McKee *et al.*, 1997; Rohrer *et al.*, 2014]. In the cloud layer ($z \sim 1500 \text{ m}$), the OH increases as the NO_x emission increases from the HIGH to VERY HIGH NO_x case

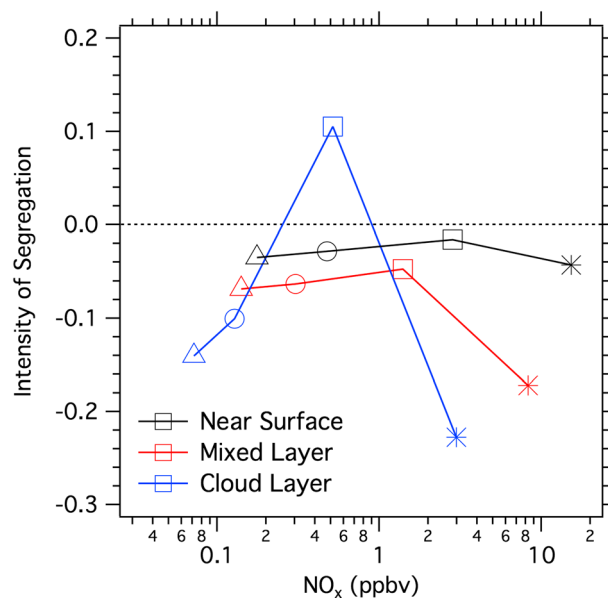


Figure 2. Variation of intensity of segregation I_s between isoprene and OH fluctuations with respect to NO_x . Meaning of symbols and colors is the same as in Figure 1. Here I_s is horizontally averaged for the domain and also time averaged for 1330–1430 LT.

expected. This unexpected positive correlation between isoprene and OH is explained below, based on the interaction between turbulent mixing and chemistry [Kim *et al.*, 2012].

Figure 2 exhibits the intensity of segregation between isoprene and OH fluctuations for the different NO_x cases. In general, I_s is negative and increases from the VERY LOW to HIGH NO_x case then decreases from the HIGH to VERY HIGH NO_x case. Near the surface the intensity of segregation is close to 0 and indicates less than 5% decrease of reaction rate. In the mixed layer, more than 5% decrease of reaction rate is found for all cases. The VERY LOW and the VERY HIGH NO_x cases in the mixed layer have 7% and 17% reduction of reaction rates, respectively. Krol *et al.* [2000] found about 20% segregation between a highly reactive hydrocarbon and OH for NO_x levels of 0.73 ppbv in the mixed layer, which is between our LOW and HIGH NO_x cases.

We find about 5–6% segregation between isoprene and OH for similar conditions. Differences between our findings and Krol *et al.* [2000] are likely due to the chemistry producing radicals that a comprehensive chemistry mechanism represents (our work) but not a simplified mechanism [Krol *et al.*, 2000]. Ouwersloot *et al.* [2011] found 7%–12% segregation between isoprene and OH for the conditions similar to our LOW NO_x case. Our results are similar giving confidence that the condensed scheme that Ouwersloot *et al.* [2011] employed captures the main segregation effects. However, Ouwersloot *et al.* [2011] did not examine a range of NO_x regimes, as our study does. In the cloud layer, I_s is negative except for the HIGH NO_x case. In the cloud layer, the VERY LOW and the VERY HIGH NO_x cases have the largest reduction of reaction rate of 14% and 23%, respectively. In contrast, the HIGH NO_x case has an 11% increase of reaction rate in the cloud layer. We next discuss why I_s varies from one NO_x regime to another.

The spatial distribution of isoprene and OH fluctuations demonstrates whether the two are colocated or segregated. Figure 3 exhibits the distribution of the two reactants fluctuations in the clouds for the different NO_x cases. Because the VERY LOW and the LOW NO_x cases show a similar distribution, the VERY LOW NO_x case is omitted in the figure. For the VERY LOW and LOW NO_x cases, large positive isoprene fluctuation and negative OH fluctuation are found over strong updrafts in association with the clouds, which in turn leads to negative covariance of isoprene and OH fluctuations. On average, photolysis of O_3 is the largest source of OH in these NO_x cases (supporting information Figure S3). Additional production of OH originating from $\text{NO} + \text{HO}_2$ is larger in the LOW NO_x case than the VERY LOW NO_x case. Consequent lower OH mean in the VERY LOW NO_x case leads to higher isoprene mean and fluctuations and more segregation than the LOW NO_x case.

As the NO_x emission increases by a factor of 10 from the LOW NO_x case, there is a substantial change in the sign of OH fluctuations within the clouds (HIGH NO_x case in Figure 3). $\text{NO} + \text{HO}_2$ is the dominating OH production reaction for the HIGH NO_x case [Kim *et al.*, 2012] (supporting information Figure S3). In this case, as isoprene is transported by the updrafts, NO_x is also transported, producing OH efficiently enough to change the sign of the OH fluctuation to be positive. Positive isoprene and positive OH fluctuations generate positive intensity of segregation (i.e., acceleration of the reaction of isoprene + OH). In the HIGH NO_x case, isoprene is strongly depleted due to the enhanced OH and it has smaller fluctuations than other cases.

Increasing the NO_x emission by a factor of 5 from the HIGH NO_x case, the sign of OH fluctuations is reversed again to a negative value within the clouds (VERY HIGH NO_x case in Figure 3). OH destruction by NO_2 to form HNO_3 is substantial in the VERY HIGH NO_x case (Figure S3 in supporting information) and causes negative OH

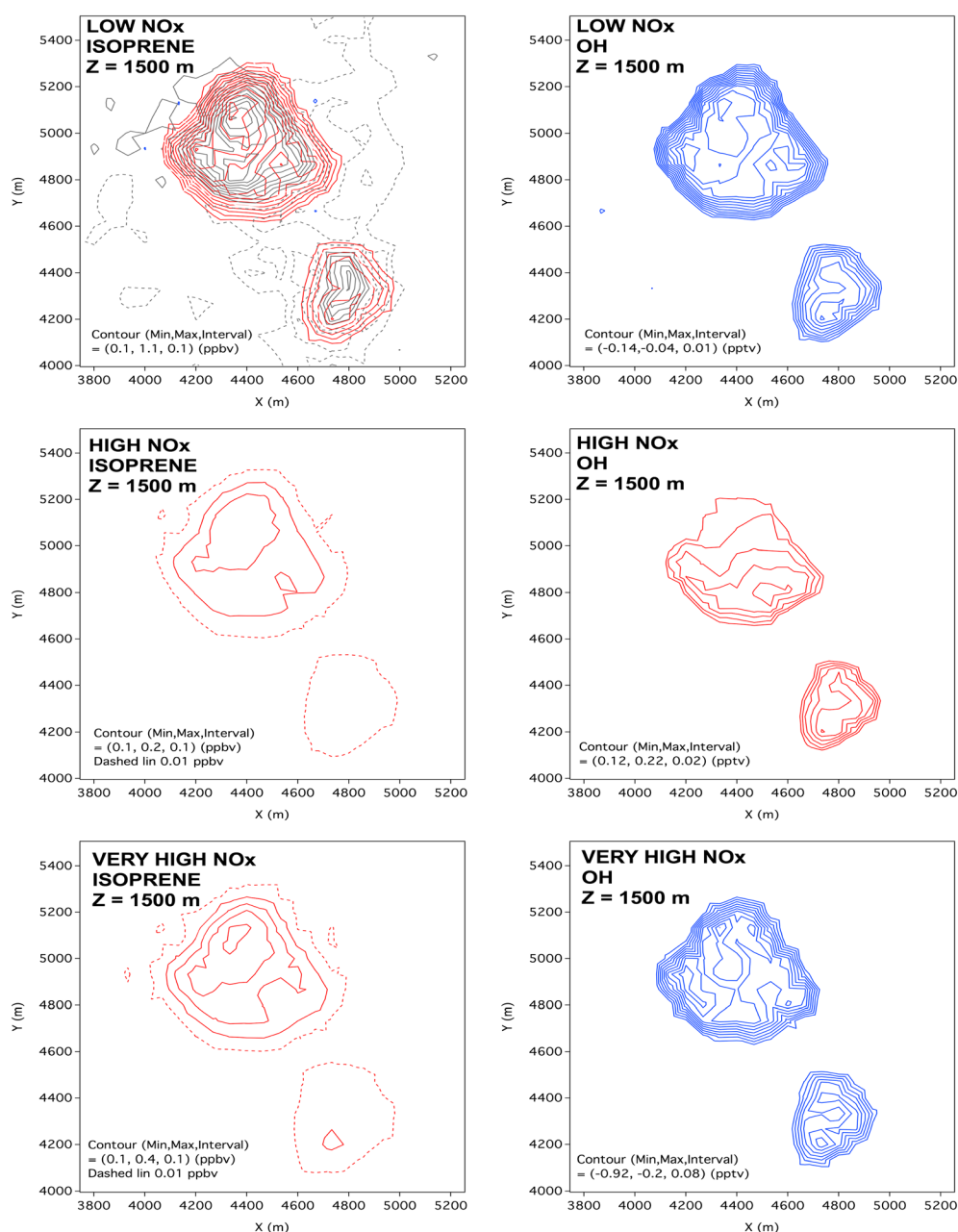


Figure 3. Instantaneous fluctuations of isoprene and OH in a portion of the domain at the altitude of 1500 m for the (top row) LOW, (middle row) HIGH, and (bottom row) VERY HIGH NO_x cases. Contour minimum, maximum, and interval are given in the plots. Red and blue contours denote positive and negative fluctuations, respectively. Red dashed lines are contours representing 0.01 ppbv. Vertical velocity is shown in gray line (updraft and downdraft in solid and dashed lines, respectively, with 0.5 m s^{-1} interval) in Figure 3 (top left).

fluctuation within the clouds where positive isoprene fluctuation occurs. Therefore, intensity of segregation in this case is negative causing more than 20% retardation of reaction between isoprene and OH. The segregation behavior in this study mimics the behavior of OH as a function of NO_x, which has been shown in previous studies [e.g., Logan *et al.*, 1981; Rohrer *et al.*, 2014].

The present study is an idealized scenario with uniform isoprene and NO_x emissions across the domain. Krol *et al.* [2000] found that the volume-averaged generic reactive hydrocarbon (RH) destruction by OH, (where the reaction rate is three times slower than the isoprene + OH reaction rate) can slow down by as much as 30% compared to a box model if RH is emitted nonuniformly at the surface. In their study, a uniform emission

assumption resulted in a much smaller segregation (3% reduction of reaction rate relative to a box model) compared to nonuniform emission scenario. The recent studies by *Kaser et al.* [2015] and *Ouwensloot et al.* [2011] also highlight the importance of inhomogeneous isoprene emissions in enhancement of segregation. Therefore, the spatial distribution of isoprene and NO emissions in the model will affect I_s between isoprene and OH reported in this study. In the future, improved knowledge on isoprene chemical mechanisms [e.g., *Paulot et al.*, 2009, 2012] can be included within the LES model developed in this study. Tests with a photochemical box model including updated isoprene chemical mechanisms show increases of OH by $< 100\%$ for VERY LOW and LOW NO_x cases (see Figure S2 in supporting information) compared to the values in this manuscript. It still supports the relationship between OH and NO_x seen in Figure 1. An enhancement of OH by the recycling mechanism may reduce the lifetime of isoprene (reacting with OH) for the VERY LOW and LOW NO_x cases compared to the results in this study by weakening segregation effects. It will be important to conduct the LES with the updated isoprene chemistry in order to assess the impact quantitatively.

4. Summary and Conclusions

Isoprene, which is emitted from deciduous trees, acts as an important precursor for tropospheric ozone and aerosol. Quantifying isoprene emissions and understanding isoprene chemical reactions (mainly with OH) have been difficult tasks for atmospheric chemistry and air quality research scientists. Observed isoprene mixing ratio in the atmosphere has often been used to infer the isoprene emissions from vegetation. Underlying assumptions in this approach is that OH levels in the atmosphere and chemical reaction rate between isoprene and OH are known/accurately parameterized. OH levels are often strongly influenced by NO_x levels in the atmosphere, which in turn directly modulate isoprene abundance. NO_x in the boundary layer, another important precursor of ozone and aerosol is released from fossil fuel combustions (e.g., mobile sources and power plants) as well as soil by uses of fertilizers and natural processes. In addition, isoprene chemical reactivity is affected by interplay between turbulence and chemistry because of the chemical lifetime of isoprene with respect to OH is similar to turbulent turnover time in convective boundary layer. To investigate complicated coupling of isoprene chemistry and turbulent motions, a numerical model that includes explicit treatments of turbulence and boundary layer clouds as well as complex chemistry is necessary. In this study, we adopt a LES model coupled with complex chemistry to investigate the sensitivity of isoprene reactivity to environmental NO_x conditions ensuring good model representations of boundary layer dynamics in association with turbulence and clouds.

The LES results reveal that segregation effects exist for all of the cases in this study. The intensity of segregation (I_s) between isoprene and OH, a measure of the extent to which reaction rates are modified by covariance between the two reactants, is nonzero and either negative or positive. For very high NO_x conditions (~ 10 ppbv of NO_x in the boundary layer) when NO_x mainly depletes OH, 17–23% reductions of reaction rate for isoprene + OH in the mixed and cloud layer are derived compared to the case ignoring covariance of the two reactants. Similarly, for low NO_x conditions (0.1–0.3 ppbv of NO_x) when NO_x produces OH, but it is still not a dominating source of OH, 6–14% decreases of reaction rate are found. For moderately high NO_x conditions (1–2 ppbv of NO_x) when the highest OH is expected (due to NO_x acting as a dominating source of OH), just 5% decrease to 11% increase of reaction rate is discovered. Fair weather cumulus cloud transport causes more segregation between isoprene and OH as updraft plumes rich in isoprene and NO_x are brought into a region with a different chemical environment. In general, we found weak segregation (close to zero) near the surface because NO_x and isoprene are coemitted at the surface in our study and balances between OH production and loss are reached. As suggested by *Krol et al.* [2000] and *Ouwensloot et al.* [2011], heterogeneous emissions of isoprene and NO_x can increase segregation even near the surface, especially for the NO_x < 1 –2 ppbv (NO_x at OH maximum). Our investigation did not consider spatially heterogeneous emissions or transport of urban/industrial plumes to biogenic source regions [e.g., *Ryerson et al.*, 2001; *Kuhn et al.*, 2010]. These more realistic scenarios including the forest canopy model [*Patton et al.*, 2001] should be studied in the future in order to give guidance for implementing the effect of isoprene-OH covariance into regional and global models. Abovementioned recent updates in isoprene chemistry and OH recycling for low NO_x cases [*Paulot et al.*, 2009, 2012; *Rohrer et al.*, 2014] can be included in our LES to test assumptions in the new chemical mechanisms and uncertainties in the measurements and their impacts on I_s between isoprene and OH. In addition, gas-to-liquid partitioning and aqueous-phase chemistry are processes that need to be considered in the

LES modeling. Gas-to-liquid partitioning will separate HO₂ and NO from each other, reducing its production of OH. Furthermore, aqueous chemistry will reduce OH concentrations in the interstitial cloud regions, consequently reducing gas-phase oxidation rates [Leleiveld and Crutzen, 1990; Barth et al., 2003]. Thus, cloud chemistry may cause additional segregation between isoprene and OH.

Even without heterogeneous emission distributions, our LES shows significant impacts of segregation on the lifetime of isoprene and OH under various environmental NO_x conditions. With consideration of heterogeneity, the segregation impacts are expected to increase, which has important implications for global isoprene chemistry, potentially providing guidance in interpreting observations and model results at various temporal and spatial scales. Our study emphasizes an important role of NO_x in changing effective reaction rate for isoprene + OH (either increase or decrease). Therefore, measuring NO_x along with isoprene and OH will be essential for investigation of covariance of isoprene and OH.

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