Differences in BVOC oxidation and SOA formation above and below the forest canopy

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Received: 8 June 2016 – Discussion started: 14 June 2016
Revised: 18 November 2016 – Accepted: 22 December 2016 – Published: 7 February 2017

Abstract. Gas-phase biogenic volatile organic compounds (BVOCs) are oxidized in the troposphere to produce secondary pollutants such as ozone (O3), organic nitrates (RONO2), and secondary organic aerosol (SOA). Two coupled zero-dimensional models have been used to investigate differences in oxidation and SOA production from isoprene and α-pinene, especially with respect to the nitrate radical (NO3), above and below a forest canopy in rural Michigan. In both modeled environments (above and below the canopy), NO3 mixing ratios are relatively small (<0.5 pptv); however, daytime (08:00–20:00 LT) mixing ratios below the canopy are 2 to 3 times larger than those above. As a result of this difference, NO3 contributes 12% of total daytime α-pinene oxidation below the canopy while only contributing 4% above. Increasing background pollutant levels to simulate a more polluted suburban or peri-urban forest environment increases the average contribution of NO3 to daytime below-canopy α-pinene oxidation to 32%. Gas-phase RONO2 produced through NO3 oxidation undergoes net transport upward from the below-canopy environment during the day, and this transport contributes up to 30% of total NO3-derived RONO2 production above the canopy in the morning (~07:00). Modeled SOA mass loadings above and below the canopy ultimately differ by less than 0.5 µg m⁻³, and extremely low-volatility organic compounds dominate SOA composition. Lower temperatures below the canopy cause increased partitioning of semi-volatile gas-phase products to the particle phase and up to 35% larger SOA mass loadings of these products relative to above the canopy in the model. Including transport between above- and below-canopy environments increases above-canopy NO3-derived α-pinene RONO2 SOA mass by as much as 45%, suggesting that below-canopy chemical processes substantially influence above-canopy SOA mass loadings, especially with regard to monoterpene-derived RONO2.
1 Introduction

Globally, organic compounds account for a substantial fraction of total atmospheric aerosol mass (Zhang et al., 2007; Jimenez et al., 2009) and therefore have significant implications for health, visibility, and climate. Rather than being emitted directly, nearly 70% of this material is thought to be secondary organic aerosol (SOA) formed from the oxidation of volatile organic compounds (VOCs) (Hallquist et al., 2009). Many of the relevant VOCs are biogenic in origin, causing naturally emitted compounds to contribute substantially to tropospheric aerosol burdens (Seinfeld and Pankow, 2003). Isoprene (C$_3$H$_8$) and monoterpenes (C$_{10}$H$_{16}$) are important biogenic VOCs (BVOCs) due to their significant rates of emission and reactivity. Studies suggest that together they comprise 55–65% of non-methane VOC emissions globally (Guenther et al., 1995, 2012; Hallquist et al., 2009) with estimated yearly emissions of 535 and 157 Tg for isoprene and monoterpenes, respectively (Arndt et al., 2011; Guenther et al., 2012). Thus, characterizing the oxidation chemistry and subsequent formation of SOA from BVOCs, especially isoprene and monoterpenes, is critical. Despite continual progress, many questions remain regarding the mechanisms of SOA production, and current large-scale atmospheric models often underpredict organic aerosol (OA) mass loadings (Heald et al., 2005; Volkamer et al., 2006; Pye and Seinfeld, 2010).

Forests represent a major source of BVOC emissions and therefore heavily influence processes related to ozone (O$_3$) and SOA formation on a global scale. As a result, major efforts have recently been undertaken to better understand the dynamics of chemical processing in forest environments and the related exchange with the atmosphere (Pugh et al., 2010; Steiner et al., 2011; Wolfe et al., 2011; Bryan et al., 2012; Ashworth et al., 2015). These studies have improved understanding of in-canopy gas-phase chemical processing, revealed current problems associated with BVOC degradation schemes, and highlighted the relevance of atmospheric turbulence within the canopy layer; however, aerosol formation processes within forests have thus far received less attention (Ashworth et al., 2015; VanReken et al., 2015). Observed differences in photolysis rates, temperature, and mixing ratios of BVOCs and other trace gases above and below the canopy, combined with measurements that indicate above- and below-canopy environments frequently experience atmospherically decoupled conditions, suggest that chemical processes occurring above and below the forest canopy may be substantially different (Foken et al., 2012; Wallace, 2013), implying the potential for different SOA formation and loss processes.

While differences in major daytime oxidants O$_3$ and hydroxyl radical (OH) mixing ratios above and below the forest canopy have been better characterized, the effect of the forest canopy on the nitrate radical (NO$_3$), a known significant nighttime oxidant of BVOCs, has received less study (Fuentes et al., 2007; Bryan et al., 2012; Ashworth et al., 2015). Ambient NO$_3$ concentrations depend strongly on anthropogenic combustion processes, as the compound is formed from the reaction of O$_3$ and nitrogen dioxide (NO$_2$) and lost, either directly or indirectly, through reaction with nitric oxide (NO) and NO$_2$. Daytime NO$_3$ concentrations are generally assumed to be negligible, as rapid photolysis and reaction with NO result in midday lifetimes as low as 5 s (Monks, 2005). However, recent work has highlighted the potential for relevant daytime NO$_3$ concentrations (Geyer et al., 2003a; Brown et al., 2005; Fuentes et al., 2007; Pratt et al., 2012). For example, the shade provided by a forest canopy and the corresponding reduction in photolysis rates may result in elevated concentrations near the ground relative to the mixed boundary layer above (Brown et al., 2005; Fuentes et al., 2007).

Differences in oxidant mixing ratios above and below the canopy may lead to above-/below-canopy differences in the production pathway of organic nitrates (RONO$_2$), which form either through NO$_3$ oxidation of BVOCs or through OH oxidation followed by reaction with NO. Organic nitrates, many of which have volatilities low enough to partition to the aerosol phase, depend on both BVOCs (biogenic) and NO$_x$ (primarily anthropogenic) for their formation, causing these products to often be particularly important to aerosol production in regions subject to high biogenic and anthropogenic emissions (Hallquist et al., 1999; Fry et al., 2009, 2011, 2013, 2014; Rollins et al., 2013; Xu et al., 2014, 2015; B. H. Lee et al., 2016). As it has recently become apparent that RONO$_2$ produced through NO$_3$ oxidation of monoterpenes are a particularly important source of SOA (e.g., Fry et al., 2009, 2013; Rollins et al., 2013; Ayres et al., 2015), underestimating formation through this pathway may partially contribute to the current underprediction of SOA in large-scale models. In addition, by serving as nitrogen oxide (NO$_x = NO + NO_2$) reservoirs, RONO$_2$ species influence O$_3$ production and the oxidative capacity of the atmosphere (Wu et al., 2007; Farmer et al., 2011; Paulot et al., 2012). As a result, modifications to their production could have cascading effects on other aspects of atmospheric chemistry. While gas-phase RONO$_2$ have been previously modeled above a forest canopy layer (Giacopelli et al., 2005; Pratt et al., 2012), the effect of physical and chemical differences above and below the forest canopy on their formation and their contribution to SOA has yet to be specifically investigated.

In addition to RONO$_2$ chemistry, recent work has highlighted pathways for SOA formation other than reversible partitioning of gas-phase oxidation products that may also be impacted by light and chemical gradients produced by forest canopies. For example, O$_3$ oxidation of monoterpenes has been observed to produce extremely low-volatility oxidation products that condense irreversibly onto existing aerosol, and these products may be a dominant relative contributor to SOA at low total mass loadings (Ehn et al., 2014; Jokinen
et al., 2015). In addition, reactive uptake of isoprene epoxydiols, glyoxal, and methylglyoxal onto aerosol surfaces to produce non-volatile SOA has been shown to constitute a substantial fraction of total SOA mass loadings in isoprene-dominated environments (Li et al., 2015).

Numerous studies have utilized one-dimensional models to investigate BVOC and radical chemistry within and above forests (Fuentes et al., 2007; Wolfe et al., 2011; Pratt et al., 2012; Rinne et al., 2012; Mogensen et al., 2015); however, to our knowledge only one study has used such a model to investigate SOA production (Ashworth et al., 2015), and the influence of chemical and physical differences above and below the forest canopy was not explicitly investigated. In addition, it was noted that SOA mass loadings were underpredicted within the canopy space. Furthermore, the majority of forest–atmosphere exchange models have considered relatively remote locations, encouraging an evaluation of the sensitivity of modeled results to elevated background pollutant concentrations that may exist in suburban (or even urban), forested locations.

Understanding differences in atmospheric chemistry above and below the forest canopy is important for two reasons. First, as people living within or nearby forested environments breathe air under the canopy, substantial differences in mass loadings above and below the forest may lead to incorrect conclusions in regional air quality models on the outer edges of suburban metropolitan areas. Second, while vertical transport is suppressed within the forest layer relative to conditions without trees, exchange between the sub-canopy environment and the atmospheric boundary layer does occur, suggesting that products formed in the low-light conditions below the canopy affect above-canopy chemical processes and aerosol formation once transported, a phenomenon that may be particularly relevant for NO3-derived RONO2. To investigate these possibilities, we applied two coupled zero-dimensional (0-D) models describing BVOC–NO3–SOA chemistry with highly detailed chemical mechanisms to observations made above and below a forest canopy in a rural, deciduous forest environment during the intensive Community Atmosphere-Biosphere Interactions Experiments (CABINEX) 2009 field campaign.

2 Methods

2.1 Description of the model

The modeling structure used in this study incorporates the coupling of two 0-D models designed to investigate detailed differences in chemical processing and SOA formation above and below the forest canopy layer. MATLAB computing software (v. R2014a) was used to perform a diel analysis of each environment (above and below the canopy) with output every second. The model uses a variable-order ordinary differential equation solver (MATLAB ODE solver ode15s) to solve the underlying system of differential equations. One day of model spin-up was used for each analysis (Pratt et al., 2012). The oxidation mechanisms of α-pinene and isoprene were obtained directly from the Master Chemical Mechanism (MCM v3.2, via the website: http://mcm.leeds.ac.uk/MCM; Jenkin et al., 1997; Saunders et al., 2003), as well as the standard gas-phase inorganic reactions included in the MCM, resulting in a system of 2260 chemical reactions with 2012 chemical species. These two BVOCs were chosen because of their relatively high emission rates as well as differences in their reactivity and SOA formation potential. For instance, isoprene is known to react predominately with OH, while α-pinene reacts substantially with all three major oxidants within forests (Fuentes et al., 2007). The SOA yields measured during low-NOx OH oxidation of isoprene are generally lower than those from α-pinene; however, their SOA yields from NO3 oxidation are similar (Table 1).

Chemical species within each 0-D box (above and below the canopy) react in the gas phase via mechanisms dictated by the MCM, partition between the gas and aerosol phases if of sufficiently low volatility, undergo dry deposition, and are transported between environments. While the gas-phase chemical mechanism has been briefly introduced above, the remaining model processes are described in the sections below.

2.2 Modeling of aerosol processes

2.2.1 Equilibrium gas-particle partitioning

The equilibrium gas-particle partitioning model developed by Colville and Griffin (2004) was used to quantify SOA production from individual isoprene and α-pinene oxidation products. Assuming that OA exists as a liquid, an equilibrium partitioning coefficient (K_{om,i}, m^3 μg^{-1}) for each oxidation product can be expressed as (Pankow, 1994a, b; Odum et al., 1996)

\[ K_{om,i} = \frac{A_i}{G_i M_o} = \frac{RT}{MW_{om} N_a p_o^{L,i}}, \] (1)

Table 1. Overview of SOA mass yields from previous chamber experiments on isoprene, α-pinene, β-pinene, and limonene.

<table>
<thead>
<tr>
<th>BVOC</th>
<th>SOA mass yield (low-NOx OH oxidation)</th>
<th>SOA mass yield (NO3 oxidation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>isoprene</td>
<td>0.01–0.053</td>
<td>0.04–0.238</td>
</tr>
<tr>
<td>α-pinene</td>
<td>0.24–0.36</td>
<td>~0–0.13</td>
</tr>
<tr>
<td>β-pinene</td>
<td>0.14–0.17</td>
<td>0.46–0.53</td>
</tr>
<tr>
<td>limonene</td>
<td>0.09–0.34</td>
<td>0.45</td>
</tr>
</tbody>
</table>

where $A_i$ is the mass concentrations of species $i$ in the aerosol phase (µg m$^{-3}$), $G_i$ is the mass concentration of species $i$ in the gas phase (µg m$^{-3}$), $M_o$ is the total mass concentration of the absorbing phase (µg m$^{-3}$), $R$ is the ideal gas constant (8.206 × 10$^{-5}$ m$^3$ atm mol$^{-1}$ K$^{-1}$), $T$ is the temperature (K), $MW_{om}$ is the average molecular weight of the absorbing phase (g mol$^{-1}$), $\alpha_i$ is the activity coefficient of oxidation product $i$ in the aerosol phase (here assumed ideal, $\alpha_i = 1$), and $p_{L,L}^0$ is the temperature-dependent sub-cooled liquid vapor pressure of the species (atm). The sub-cooled liquid vapor pressure of each oxidation product was determined using the SIMPOL.1 group contribution method (Pankow and Asher, 2008).

Considering this definition in conjunction with the total species concentration (µg m$^{-3}$), $C_i$ (based on the chemical mechanism described above), and a mass balance for the phase distribution,

$$\sum_{i=1}^{N} \frac{K_{om,i}C_i}{1 + K_{om,i}M_o} + \frac{POA}{M_o} - 1 = 0,$$

where POA represents any initially present OA. Using $C_i$ values determined by the gas-phase mechanism, this equation is solved for $M_o$ at every model time step, from which the value of $A_i$ for each of the $N$ species can be determined. It should be noted that this partitioning model fails to account for any effects related to the liquid water content (LWC) of SOA or any particle-phase reactions, which, in the case of non-oxidative accretion reactions, have the potential to significantly lower the volatility of the resulting SOA (Kroll and Seinfeld, 2008). As these particle-phase reactions can rapidly produce high MW, low-volatility compounds, often more aerosol mass is produced in the environment than equilibrium partitioning of the gas-phase species would predict (Johnson et al., 2005; Kroll and Seinfeld, 2008).

Furthermore, as increases in relative humidity (RH), and subsequent increases in the water content of SOA, are known to enhance the partitioning of organic species to the aerosol phase, the omission of this process also potentially leads to underestimation of the total amount of SOA formed (Hennigan et al., 2008). However, as water uptake is generally driven by inorganic aerosol components (Hennigan et al., 2008; Carlton and Turpin, 2013), which only comprised a small fraction of total aerosol mass during CABINEX, the overall effect of RH is predicted to be small for the conditions of this study (VanReken et al., 2015).

Therefore, the primary uncertainty in aerosol formation is related to the production of high MW compounds through particle-phase reactions, but these compounds are partially accounted for through the parameterization of extremely low-volatility organic compound (ELVOC) formation described below. Following Ashworth et al. (2015), our model utilizes a POA value of 0.5 µg m$^{-3}$ for calculation of SOA partitioning.

### 2.2.2 Production of ELVOCs

Recent studies have indicated that ELVOCs contribute substantially to monoterpane SOA mass loadings (Ehn et al., 2014; Jokinen et al., 2015). As a result, despite the MCM being the most complete chemical mechanism available, sole modeling of the partitioning of MCM oxidation products may result in an underprediction of SOA formation. After initial oxidation by O$_3$ (or OH to a lesser extent), monoterpane peroxy radicals have the potential to undergo sequential H-shifts and O$_2$ additions that very rapidly produce ELVOCs with multiple hydroperoxide moieties (Jokinen et al., 2015; Mentel et al., 2015). Isoprene is also known to produce ELVOCs; however, measured yields are much smaller than those of monoterpenes (Jokinen et al., 2015). In SOA formation experiments with low total aerosol mass loadings, a characteristic similar to the relatively pristine environment near the CABINEX site used in this study, irreversible condensation of these ELVOCs represents a dominant fraction of total aerosol mass (Ehn et al., 2014).

A gas-phase ELVOC formation mechanism is included within the model based on observed molar ELVOC yields from α-pinene + O$_3$ (3.4 %), α-pinene + OH (0.44 %), isoprene + O$_3$ (0.01 %), and isoprene + OH (0.04 %) (Jokinen et al., 2015). Laboratory experiments suggest that, in general, a distribution of monomer (C$_{10}$) and dimer (C$_{19-20}$) ELVOC oxidation products contributes to SOA mass from α-pinene oxidation (Ehn et al., 2014), while isoprene is thought to form primarily monomer (C$_3$) species (Jokinen et al., 2015); however, as monomers are generally observed with a mass spectral signal an order of magnitude higher than those of dimers, and in order to ensure that uncertainty in the modeling parameters results in underprediction rather than overprediction of ELVOC mass loadings, all ELVOC products in the model presented here are assumed to be monomers. Specifically, α-pinene is assumed to produce the species C$_{10}$H$_{16}$O$_3$, while isoprene is assumed to produce C$_{5}$H$_{10}$O$_3$. At a representative temperature of 20°C, these products have saturation vapor pressures of 1.03 × 10$^{-14}$ atm and 2.81 × 10$^{-11}$ atm, respectively, according to the SIMPOL.1 method. These specific products were selected based on their intensity in observed ELVOC mass spectra and the fact that their elemental ratios are generally representative of the average ELVOC product distributions observed (Ehn et al., 2014; Jokinen et al., 2015).

### 2.2.3 Reactive uptake of isoprene epoxides, glyoxal, and methylglyoxal

Another mechanism for aerosol formation known to be substantial in isoprene-dominated environments is the reactive uptake of isoprene epoxides, glyoxal, and methylglyoxal (Volkamer et al., 2007; Paulot et al., 2009; Li et al., 2015). Rather than reversibly partitioning between the gas and aerosol phases, these specific oxidation products are irre-
versely incorporated into SOA with rates controlled by particle acidity and the surface area of ambient OA. Isoprene epoxides (IEPOX) are formed through OH oxidation of isoprene hydroxyhydroperoxides and constitute a major fraction of SOA from isoprene oxidation in low-NO3 conditions (Paulot et al., 2009; Lin et al., 2012). Glyoxal (CHOCHO) and methylglyoxal (CH2C(O)CHO), the smallest dicarbonyl compounds, are formed from the oxidation of a variety of VOCs, and while they are known to have short atmospheric lifetimes due to photolysis and OH oxidation, their high water solubility results in substantial uptake onto aqueous surfaces (Fu et al., 2009). After being incorporated into the aerosol, aqueous-phase oxidation of these species results in the formation of non-volatile organic acids or oligomers, preventing partitioning back into the gas phase (Loeffler et al., 2006; Carlton et al., 2007; Lin et al., 2012). Previous measurements in Mexico City reported significantly lower concentrations of glyoxal and methylglyoxal than gas-phase pressure measurements in Mexico City reported significantly lower concentrations than gas-phase processes would predict, supporting the hypothesis of their reactive uptake into the particle phase (Volkamer et al., 2007). Isoprene epoxides have been identified in aerosol measurements at multiple locations (Chan et al., 2010; Froyd et al., 2010).

Following the method of Li et al. (2015), the surface-controlled uptake of these products can be expressed by

\[
\frac{dM_{air}}{dt} = -\left(\frac{1}{4} \gamma_i v_i A \right) G_i, \tag{3}
\]

where \(\gamma_i\) is the reactive uptake coefficient (not the activity coefficient used in Eq. 1), \(v_i\) is the thermal velocity of the gas species (m s\(^{-1}\)), \(A\) is the ambient aerosol surface area concentration (m\(^2\) m\(^{-3}\)), and \(G_i\) is the mass concentration of the species in the gas phase (µg m\(^{-3}\)) (the same quantity as \(G_i\) in Eq. 1). As the model does not explicitly calculate aerosol sizes, aerosol surface area concentrations were obtained from the study of VanReken et al. (2015) during CABINEX 2009. The reactive uptake coefficient represents the probability that any collision between a gas-phase molecule and the aerosol surface will result in irreversible uptake into the aerosol phase. Glyoxal and methylglyoxal were assigned a reactive uptake coefficient of \(2.9 \times 10^{-3}\), following the method of Fu et al. (2009). As this value is not adjusted for the LWC of aerosol measured at CABINEX, which is predicted to be low, our model may overpredict uptake of glyoxal and methylglyoxal to some extent; however, modeled mass loadings of both glyoxal and methylglyoxal SOA agree with simulations by Li et al. (2015) for northern Michigan. The reactive uptake coefficient of isoprene epoxides depends strongly on aerosol acidity, causing the value to vary substantially depending on the composition of the ambient aerosol (Wang et al., 2012). Using the Community Multi-Scale Air Quality (CMAQ) model, Li et al. (2015) calculated isoprene epoxide uptake coefficients based on particle acidity across the entire US and found a value of around \(0.5 \times 10^{-3}\) appropriate for conditions in northern Michigan. We utilized this value for this study.

### 2.2.4 Heterogeneous hydrolysis of organic nitrates

Organic nitrates have a large influence on atmospheric chemistry through their impacts on NO3, O3, and OA. It has been shown that RONO2 within the aerosol phase can be efficiently hydrolyzed, leading to the production of HNO3 and the removal of NO3 from the atmosphere (Day et al., 2010; Browne et al., 2013; Rindelaub et al., 2015; Bean and Hildebrandt Ruiz, 2016). Both field studies and chamber experiments have observed decreases in the RONO2 content of SOA under conditions of increased RH (Day et al., 2010; Bean and Hildebrandt Ruiz, 2016).

While many questions remain regarding the kinetics of the hydrolysis mechanism and the specific relationship with RH, chamber experiments have defined lifetimes of both isoprene and α-pinene nitrates within OA (Cole-Filipiak et al., 2010; Durer et al., 2011; Hu et al., 2011; Rindelaub et al., 2015; Bean and Hildebrandt Ruiz, 2016). For our study, both isoprene and α-pinene nitrate oxidation products are assumed to undergo first-order loss within the aerosol phase. Isoprene nitrate loss is parameterized using the average lifetimes found by Hu et al. (2011) for primary, secondary, and tertiary nitrate species. As primary and secondary nitrates only slowly hydrolyze even under the most acidic conditions observed (with a lifetime of \(\sim 500\) h at a pH of 0), which were not likely to occur during CABINEX, those products have an effective hydrolysis rate of zero within the model (Hu et al., 2011). However, tertiary nitrates, which are efficiently hydrolyzed even at neutral pH, have an effective lifetime of 0.67 h within the aerosol (Hu et al., 2011).

To our knowledge, only two chamber experiments have been performed regarding the hydrolysis of α-pinene nitrate oxidation products within OA (Rindelaub et al., 2015; Bean and Hildebrandt Ruiz, 2016). Of these, only the study by Bean and Hildebrandt Ruiz (2016) quantified hydrolysis rates. The overall hydrolysis rate was found to depend strongly on RH. For instance, experiments with an RH between 20 and 60 % produced a hydrolysis rate of \(2\) day\(^{-1}\), while those with RH above 70 % had rates around \(7\) day\(^{-1}\) (Bean and Hildebrandt Ruiz, 2016). As RH values measured during CABINEX were generally above 60 %, our model uses a rate of \(7\) day\(^{-1}\), corresponding to a lifetime of \(3.4\) h.

### 2.3 Deposition

Dry deposition of gases and aerosols is included within both the above- and below-canopy boxes. In the above-canopy model, deposition is assumed to occur onto the top of the canopy, and the resistance to deposition is determined using the method of Meyers and Baldocchi (1988). Deposition velocities for each chemical species are calculated based on resistances from the quasi-laminar boundary layer and
leave mesophyll, cuticular surfaces, and stomata. A thorough description of the particular equations used in this method can be found in Bryan et al. (2012). The specific parameter values used in the calculation of deposition velocities are listed in Table S1 in the Supplement. The above-canopy box height was assumed to vary diurnally based on the boundary layer values utilized in Giacopelli et al. (2005) for a previous model of the CABINEX location. As our model does not calculate aerosol sizes, size distribution data obtained from VanReken et al. (2015) were used to calculate a volume-weighted average settling velocity of aerosol particles.

In the below-canopy model, deposition was assumed to occur to the ground and was modeled following the method of Gao et al. (1993). This method assumes that the deposition velocity is based on the combination of aerodynamic resistance near the ground and a species-specific resistance to deposition to the forest floor. The box height was set to 6 m (the assumed bottom of the canopy layer or top of the trunk space) for the entire diurnal period.

2.4 Vertical transport

Recent modeling studies have revealed that in-canopy vertical mixing substantially influences overall forest chemistry (Bryan et al., 2012). Mixing is often parameterized in one-dimensional (1-D) models using traditional K-theory, which quantifies the transport of chemical species by eddy diffusion at a rate corresponding to the heat exchange coefficient (Wolfe et al., 2011; Bryan et al., 2012). While one of the most accurate turbulence parameterization methods available, such a process is computationally sophisticated and is better suited to 1-D modeling of an environment. In order to simplify the quantification of mixing, we have implemented the concept of in-canopy residence lifetimes to determine mixing rates. Measured and modeled in-canopy residence times vary substantially depending on the forest environment studied. For instance, Fuentes et al. (2007) report average residence times of ~8 min for a parcel emitted near the ground, during the day, in a forest with a 26 m high canopy, while Farmer and Cohen (2008) calculate residence times of 1–7 min for a forest with a canopy height of only 5.7 m. Maximum residence times of up to 50 min have been reported in tall forests (Strong et al., 2004). Transport back into the canopy is an even more complicated process, as coherent structures (i.e., sweeps of air downward), rather than simple turbulence, often produce the majority of scalar fluxes (Steiner et al., 2011).

For our model, a minimum residence time of 10 min in each location is assumed to apply midday, in agreement with previous measurements, and residence times vary diurnally based on the modeled turbulent heat exchange coefficient produced by the CACHE model (Bryan et al., 2012). In addition, we have included a diurnal above-canopy vertical dilution rate based on the average of methanol and acetaldehyde above-canopy vertical loss calculated by the FORCAsT 1-D model for summertime conditions (Ashworth et al., 2016).

The inclusion of a mixing process, vertical dilution, and dry deposition results in relatively good agreement between measured and modeled concentrations of the sum of the isoprene oxidation products methacrolein and methyl vinyl ketone (MACR + MVK) (Supplement Fig. S1). These photooxidation products of isoprene are often significantly overestimated in low NOx conditions modeled in forests (Bryan et al., 2012; Ashworth et al., 2015). The validity of the mixing process specifically is supported by the agreement between the measured and modeled differences in MACR + MVK mixing ratios above and below the canopy (Fig. S1c), as this comparison removes the influence of errors in the chemical mechanism that may produce overpredictions or underpredictions of the overall mixing ratios. While the comparison of differences in mixing ratios above and below the canopy indicates that we likely overpredict mixing in the early morning and underpredict mixing in the late evening, this study is primarily focused on daytime conditions, during which the differences are within a few percent. Different minimum transport lifetimes above and below the canopy (from 10 to 30 min) were analyzed to determine whether better agreement between measured and modeled MACR + MVK profiles could be attained; however, this ultimately produced little variation in the overall agreement, and the use of a 10 min lifetime in each location was found to produce minimum error between measured and modeled MACR + MVK mixing ratios (Fig. S1d).

2.5 Input data

The CABINEX campaign took place in northern Michigan near the University of Michigan Biological Station (UMBS) in August 2009 and utilized the Program on Oxidants: Photochemistry, Emissions, and Transport (PROPHET) tower to perform gas-phase measurements throughout the canopy. A deciduous forest with a canopy height of around 22.5 m surrounds the PROPHET tower and consists of tree species that emit significant quantities of both isoprene (aspen and oak) and monoterpenes (pine and birch). Above-canopy measurements were made at a height of 34 m, while those below the canopy occurred at a height of 6 m (Fig. S2). More detailed descriptions of both the PROPHET tower and the surrounding environment can be found in the literature (Carroll et al., 2001; Ortega et al., 2007; Griffith et al., 2013).

The primary goal of the campaign was to examine the effect of forest succession on atmospheric chemistry. The majority of studies resulting from the CABINEX campaign have focused on improving understanding of the linkage between gas-phase radical and BVOC chemistry through measurements and modeling (Kim et al., 2011; Bryan et al., 2012; Griffith et al., 2013; Hansen et al., 2014), while two have investigated aerosol concentrations at the site (Ashworth et al., 2015; VanReken et al., 2015). Aerosol size and composi-
tion vary widely based on ambient wind direction, but show a stronger anthropogenic influence when air masses come from populated areas to the east and south (VanReken et al., 2015). Accurate modeling of diel changes in SOA mass loadings using a 1-D model has thus far proven difficult (Ashworth et al., 2015).

The model was constrained by diel median values of hydroxyl radicals (HO\(_x\) = OH + hydroperoxy radical (HO\(_2\))), NO, NO\(_2\), O\(_3\), α-pinene (monoterpenes), isoprene, formaldehyde (HCHO), and the photolysis rate of NO\(_2\). Each of these species was therefore assigned a median measured value at every hour, and values used for each model time step (e.g., 08:03) were determined by linear interpolation between hourly values. Values taken from the National Center for Atmospheric Research (NCAR) Tropospheric Ultraviolet and Visible (TUV) Model (TUV Model 4.1, via the website: http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUVT/). In order to correct for non-clear-sky conditions, above-canopy photolysis frequencies were scaled to represent differences between the measured NO\(_2\) photolysis frequency and that predicted by the TUV model. Below-canopy frequencies were then calculated by scaling by the ratio of the below-to-above-canopy NO\(_2\) photolysis frequencies measured during CABINEX. This ratio is time-of-day dependent, with a maximum around noon, and varies over the range of 0.05 to 0.17 during daylight hours (Fig. S3d). Model input data are shown in the SI (Fig. S3).

At CABINEX, O\(_3\) levels were relatively consistent throughout the day, reaching a maximum in the afternoon (Fig. S3). Median mixing ratios were consistently ~5 to 10 ppbv larger above the canopy than below (~30–35 ppbv above, ~20–30 ppbv below). While NO\(_2\) concentrations peaked at night (~1 ppbv), likely due to both O\(_3\) oxidation of local NO and transport from non-local air masses, they were larger below the canopy in the early morning. Concentrations of NO were below the detection limit of the instrument (6.7 ppbv) for much of the night and were therefore held at 6.7 ppbv for modeling purposes during these periods. Maximum daytime NO mixing ratios reached ~0.2 ppbv in the early morning, largely the result of NO\(_2\) photolysis (Seok et al., 2013). Monoterpene (-pinene) concentrations were consistent at around 0.3 ppbv, although they exhibited slight diel variability with maxima occurring at night, whereas the isoprene profile displayed strong emission dependence on sunlight and temperature and reached a maximum mixing ratio of ~1.6–1.7 ppbv mid-afternoon.

### 2.6 Modification of the gas-phase RONO\(_2\) chemical mechanism

Without any changes to the MCM, predicted gas-phase RONO\(_2\) concentrations (~400 pptv) are much larger than those modeled by Pratt et al. (2012) (~20–70 pptv), implying that gas-phase RONO\(_2\) is overpredicted by the MCM. Dry deposition rates of both isoprene and α-pinene nitrates (~1.5–2.5 cm s\(^{-1}\)) are similar to the values used in Pratt et al. (2012), and the vertical dilution rate used in our model is comparable to the value used by Giacopelli et al. (2005) for nitrates at UMBS, suggesting that physical processes are not the reason for the modeled difference.

The discrepancy in total RONO\(_2\) concentrations therefore likely stems from inappropriately large RONO\(_2\) yields or inappropriately small loss rates within the MCM. While monoterpene nitrate concentrations modeled in previous studies are generally less than 50 pptv (Pratt et al., 2012; Fisher et al., 2016), without applying any changes to the chemical mechanism obtained from the MCM, two first-generation α-pinene hydro-hydroxynitrates, produced from NO\(_3\) oxidation followed by RO\(_2\) + HO\(_2\) reaction, have a cumulative concentration of over 100 pptv for the majority of the day (Fig. S4a). Within the MCM, the first-generation RONO\(_2\) + HO\(_2\) reaction that forms these products has a 100% hydro-hydroxynitrate yield; however, laboratory experiments have indicated that while such a yield may be suitable for small peroxy radicals such as methyl peroxy, larger peroxy...
The final concentrations, while still larger than those modeled by Pratt et al. (2012), show much better agreement with previous findings. Second-generation isoprene nitrate concentrations (∼100 pptv) appear to be overpredicted relative to previous observations, which report concentrations of 20–50 pptv (Pratt et al., 2012; Fisher et al., 2016). Similarly, to the first-generation α-pinene nitrate concentrations, modeled second-generation isoprene nitrate mixing ratios are dominated by two species, methyl vinyl ketone nitrate (MVKN) and methacrolein nitrate (MACRN). The MCM does not assume these products react with NO$_3$ or O$_3$, as has been recently suggested (Kerdouci et al., 2010), and the reaction rate of each species with OH is 5–10 times larger in the model used by Pratt et al. (2012) than in the MCM. Adding reactions with NO$_3$ and O$_3$ and modifying the reaction rate with OH to match that used in Pratt et al. (2012) improves agreement (Fig. S4); however, the implications of the remaining differences are discussed in Sect. 3.3. Ultimately, as will be discussed, the RONO$_2$ fraction of SOA agrees well with previous measurements, indicating that the possible remaining errors in gas-phase RONO$_2$ concentrations should not unduly influence the conclusions related to SOA mass loadings.

2.7 Model evaluation

Measured OH and HO$_2$ profiles above the canopy were compared to those predicted by our model when leaving HO$_x$ concentrations unconstrained, which gives an indication of the validity of both the modeled oxidation processes and photolysis frequencies, as both have a large effect on HO$_x$ chemistry (Fig. S5). The model tends to underpredict nighttime OH concentrations, similarly to previous model comparisons (Carslaw et al., 2001; Ren et al., 2006; Pugh et al., 2010). On average, nighttime (22:00–06:00 local time) modeled OH concentrations are ∼2.5 × 10$^5$ mol cm$^{-3}$ below those observed (∼60 % difference). As the model only incorporates α-pinene (for all monoterpenes) and isoprene, the absence of OH-producing ozonolysis reactions with other VOCs likely contributes to this nighttime discrepancy. These reactions have been shown to produce up to ∼64–72 % of nighttime OH in rural environments (Bey et al., 1997; Geyer et al., 2003b). Daytime concentrations are also generally underpredicted, especially during the late morning, when the measured OH concentration peaks. Despite the observed difference in the two profiles, only two measured points (11:00, 19:00) fail to capture modeled concentrations within their 68 % confidence intervals. A linear regression of measured versus modeled OH concentrations highlights the ability of the model to capture the diel trend of OH concentrations ($r^2$ = 0.82) (Fig. S6).

While modeling studies have generally found better performance for HO$_2$ than for OH, many models involving HO$_x$ cycling in forested environments tend to underestimate HO$_2$ levels (Lelieveld et al., 2008; Pugh et al., 2010; Stavrakou et al., 2010). Interferences involved in the operation of the IU-FAGE instrument can lead to conversion of isoprene-derived peroxy radicals into HO$_2$, resulting in a positive artifact (Fuchs et al., 2011). Tests indicate that ∼90 % of isoprene-based hydroxyalkylperoxy radicals are converted into HO$_2$ in the sampling cell through reaction with NO and subsequent decomposition (Griffith et al., 2013). As a result, IU-FAGE measurements represent both ambient HO$_2$ and a fraction of isoprene peroxy radicals chemically converted to HO$_2$ within the instrument itself. Griffith et al. (2013) noted that HO$_2$ concentrations measured during CABINEX are similar to previously reported concentrations of HO$_2$ + RO$_2$ (Mihele and Hastie, 2003). To account for this, simulated isoprene peroxy radical concentrations were added to simulated HO$_2$ concentrations when performing a regression analysis, and the discussion of the agreement between measurements and model output focuses on simulated HO$_2$ + isoprene RO$_2$ rather than simply HO$_2$.

While the model results successfully represent the overall diel HO$_2$ profile and show good agreement at night, modeled concentrations of HO$_2$ + isoprene RO$_2$ overestimate measured concentrations midday by about 30 %, suggesting either a missing isoprene RO$_2$ loss mechanism, a HO$_2$ loss mechanism, or a combination of both. Nevertheless, good agreement is observed between measured and modeled concentrations with and without the addition of isoprene RO$_2$ ($r^2$ = 0.94, slope = 0.68 with RO$_2$, $r^2$ = 0.9, slope = 1.2 without). The observation that adding isoprene RO$_2$ improves the coefficient of determination supports the notion of an isoprene-derived interference (Fig. S6). Ultimately, the agreement observed between measured and modeled HO$_2$ concentrations relative to previously published atmospheric chemistry models supports the validity of the modeling process.

3 Results and discussion

3.1 Nitrate radical concentrations

Air surrounding the PROPHET tower is free from major NO$_x$ sources, causing soil emissions and long-range trans-
Numerous studies have investigated NO$_3$ oxidation of BVOCs and highlighted that such oxidation is especially important at night (Golz et al., 2001; Brown et al., 2005, 2011; Stutz et al., 2010; Brown and Stutz, 2012). Certain classes of BVOCs also show appreciable daytime oxidation rates by NO$_3$ (Geyer et al., 2003a; Brown et al., 2005). The prediction of elevated daytime NO$_3$ concentrations below the forest canopy implies an increased rate of BVOC oxidation in that environment. Oxidation rates (and fractional contributions of the total) by each oxidant are determined by

\[ \text{oxidation rate (ppbw h}^{-1}\text{)} = k[\text{oxidant}][\text{VOC}] \]  

(4)
Difference in the NO$_3$ oxidation of isoprene, and oxidation of α-pinene above and below the forest canopy. Figure 2. (a) Difference in individual NO$_3$ loss rates ($L$(NO$_3$)) from photolysis, reaction with NO, oxidation of isoprene, and oxidation of α-pinene above and below the forest canopy. Ambient CABINEX results (Figs. 3 and 4) show that overall rates of α-pinene oxidation above and below the canopy are similar (∼0.06–0.1 ppbv h$^{-1}$), while the fractional plots indicate that, in both cases, O$_3$ is the most consistent oxidant, contributing over 40% of total oxidation. Hydroxyl radical oxidation reaches maximum contributions of 67% above the canopy and 62% below the canopy near midday (Fig. 4). The NO$_3$ oxidation rates largely reflect the NO$_3$ concentration profile, as α-pinene concentrations are relatively consistent throughout the 24 h period, with above-canopy rates displaying more diel variation than those below, due to the substantial effect of NO$_3$ photolysis. Oxidation by NO$_3$ contributes 17% of the total above the canopy on average and 18% below. This similarity in averages is due to the fact that daytime NO$_3$ concentrations are elevated below the canopy relative to above, whereas at night the opposite occurs. The most substantial difference between the two environments occurs from around 08:00 to 20:00, as NO$_3$ contributes on average only 4% of total α-pinene oxidation above the canopy, but as much as 12% below.

Increasing the concentration of background pollutants to simulate a suburban environment raises the fractional amount of NO$_3$ oxidation to as high as 32% during the day (08:00–20:00) below the canopy, similar to the model results of Fuentes et al. (2007) for a forest with 40–60 ppbv of O$_3$ and maximum NO$_x$ mixing ratios of 6–8 ppbv. Even during midday when NO$_3$ concentrations are minimized, the contribution of NO$_3$ to total α-pinene oxidation below the canopy is ∼18% in this simulated polluted environment (Fig. 5).

Isoprene oxidation is only briefly discussed, as the total rates and fractional oxidant contributions are similar above and below the canopy (Figs. 3 and 4). In both locations, OH dominates isoprene oxidation, especially during the day when oxidation rates are most substantial. Peak below-canopy oxidation rates are generally smaller than those above, as expected, largely due to increased photolytic activity and OH concentrations above the canopy. Even in the highly polluted conditions, NO$_3$ oxidation accounts for only ∼3% of the total near midday (Fig. 5).

3.3 Gas-phase RONO$_2$ concentrations

The diurnal profile of the sum of isoprene- and α-pinene-derived gas-phase RONO$_2$ is shown in Fig. 6 for both above- and below-canopy environments. Isoprene is the major precursor of total RONO$_2$ (∼70–85%), following from its larger mixing ratios and much faster daytime oxidation rates than α-pinene. This is in agreement with other isoprene-dominated environments (Pratt et al., 2012; Fisher et al., 2016; Romer et al., 2016). First-generation nitrates produced from NO$_3$ oxidation of both BVOCs have much larger concentrations than the comparable second-generation products, which have virtually negligible concentrations, implying that further oxidation tends to remove the nitrate functional group, after which point further reaction with NO or NO$_3$ and regeneration of the nitrate group is unlikely, as suggested by Lee et al. (2014) and Xiong et al. (2016). As a result, despite the fact that OH only contributes around 20% of nighttime α-pinene oxidation, RONO$_2$ products formed from OH oxidation of α-pinene constitute over half of nighttime α-pinene RONO$_2$ concentrations.

The efficient mixing process parameterized within the model results in very similar overall concentrations above and below the canopy (within 9%), despite the modeled differences in BVOC oxidation. While this appears to imply that the canopy exerts little influence on RONO$_2$ production, midday (11:00–15:00) above-canopy mixing ratios of NO$_3$-derived RONO$_2$ products formed from α-pinene and isoprene are 15.2 and 33.7% larger on average than if the mixing process is turned off and the dilution rate is reduced by one-half (to partially account for the lack of oxidation product transport from below the canopy). Therefore, near midday, the below-canopy environment appears to act as a source of NO$_3$-derived nitrates above the canopy, a finding that is further explored subsequently. We use the term “NO$_3$-derived” extensively throughout the remainder of this paper to indicate products formed from initial oxidation of BVOCs by NO$_3$. 

Figure 3. Modeled diurnal oxidation rates of (a) α-pinene above canopy, (b) α-pinene below canopy, (c) isoprene above canopy, and (d) isoprene below canopy by OH, O$_3$, and NO$_3$.

Figure 4. Modeled fractional contribution to oxidation rates of (a) α-pinene above canopy, (b) α-pinene below canopy, (c) isoprene above canopy, and (d) isoprene below canopy by OH, O$_3$, and NO$_3$. 

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regional O3 and SOA formation rates may be significantly affected by such an error, as NOx reservoirs such as RONO2 can limit O3 production, and first- and second-generation RONO2 products are thought to have different deposition velocities, saturation vapor pressures, and tendencies to release NOx upon oxidation (Lee et al., 2014; Fisher et al., 2016).

3.4 RONO2 production, loss, and net transport

While modeled RONO2 mixing ratios above and below the canopy are similar due to efficient daytime mixing within the forest canopy, the physical and chemical differences described previously suggest that production and loss rates differ between locations. The diurnal profiles of simulated RONO2 production rates above and below the canopy are shown in Fig. 7. The total midday production rate of RONO2 above the canopy (∼100 pptv) and the dominance of isoprene-derived RONO2 production agree with summertime results obtained for the southeastern US in another deciduous forest (Romer et al., 2016).

In both locations, a large increase in production rates occurs around 06:00, corresponding to the rapid increase in OH, NO, and isoprene concentrations. Production of RONO2 through NO3 oxidation is faster below the canopy than above during the day; however, the difference, factors of 2.75 for α-pinene and 1.35 for isoprene, is slightly lower than the difference in oxidation rates. Following initial oxidation by NO3, the produced RO2 must react with HO2 or RO2 in order to form a stable nitrate, both of which have higher concentrations above the canopy than below (production through NO reaction after NO3 oxidation is negligible). As a result, while daytime oxidation by NO3 is much more rapid below the canopy, the differences in mixing ratios of species involved in secondary reactions slightly offset the difference in NO3 concentrations. Overall, NO3 accounts for ∼10 % of total RONO2 production above the canopy and 17 % below near midday (11:00–15:00).

In the more polluted environment, the fraction of total daytime RONO2 produced by NO3 oxidation increases to 14 % above the canopy and 20–25 % below the canopy (Fig. 8). Therefore, while NO3 chemistry becomes more relevant during the day under more polluted conditions, the relative difference between above- and below-canopy production through NO3 oxidation (6–11 %) stays relatively constant.

Loss rates of both α-pinene and isoprene RONO2 are shown in Fig. 9. On average, photolysis and gas-phase oxidation, processes that tend to release NOx, account for approximately half of α-pinene RONO2 loss both above and below the canopy (41 % above and 47 % below) and an even higher fraction of isoprene loss (65 % above and 48 % below), with loss due to photolysis displaying a strong difference between above- and below-canopy environments. Depositional losses are relatively consistent above and below the canopy, as a larger box height above the canopy (the boundary layer

Figure 5. Sensitivity of average fractional oxidation of (a) α-pinene and (b) isoprene by NO3 below the canopy from 11:00 to 15:00 to changes in O3 and NO concentrations. The term “scaling factor” specifies changes to the diurnal profiles of O3 and NO, while “mixing ratios” refer to the resulting average mixing ratios of these species between 11:00 and 15:00.

Overall RONO2 accounts for ∼7–12 % of total NOx in both environments, which, while somewhat smaller than observations in the eastern US by Perring et al. (2009) (∼18 %), nevertheless suggests that RONO2 fate is highly relevant to overall NOx cycling within this environment. However, inconsistencies between studies of RONO2 chemistry underscore the need for continued study of the oxidation pathways involved in RONO2 production and agreement between published mechanisms and laboratory results. For instance, despite our changes to the chemical mechanism, our MCM-based model predicts over twice as much total gas-phase RONO2 as the model of Pratt et al. (2012). Furthermore, second-generation products constitute 50–60 % of total RONO2 (predominantly from the OH–NO pathway) in our model, while models based on laboratory yields, such as that of Pratt et al. (2012), predict almost entirely first-generation products. Observations of isoprene nitrates suggest second-generation products comprise somewhere between 20 and 50 % of the total (Fisher et al., 2016).

In a rural area where RONO2 formation is limited, mischaracterizing RONO2 composition may have a negligible effect on predicting subsequent aspects of atmospheric chemistry; however, in more polluted areas both local and
Figure 6. Modeled gas-phase RONO$_2$ concentrations from (a) $\alpha$-pinene above canopy, (b) $\alpha$-pinene below canopy, (c) isoprene above canopy, and (d) isoprene below canopy. Species produced from NO$_3$ oxidation are blue, while those produced through OH + NO oxidation are red. Darker colors indicate first-generation products; lighter colors indicate second-generation products.

Figure 7. RONO$_2$ production through oxidation of (a) $\alpha$-pinene above canopy, (b) $\alpha$-pinene below canopy, (c) isoprene above canopy, and (d) isoprene below canopy by NO$_3$, O$_3$, OH, and a mix of oxidants. Each color represents the sum of the production rates of each RONO$_2$ species formed through initial oxidation of the parent VOC (isoprene or $\alpha$-pinene) by the specified oxidant. The “Mix” category represents later-generation RONO$_2$ products formed through initial oxidation by NO$_3$, O$_3$, or OH followed by secondary oxidation by a different oxidant.
their measurements nevertheless suggest a large fraction of somewhat if photolysis were included in their analysis, measurements of Romer et al. (2016) would be reduced have had to reduce gas-particle partitioning coefficients by previous studies using the MCM to predict SOA composition of the fraction of RONO$_2$ likely leading to an overprediction of hydrolysis rates for a nitrate species hydrolyze at the same rate as tertiary nitrates,ing study of Fisher et al. (2016) assumes all isoprene organic pinene and isoprene nitrates near midday, while the model-predicted nitrate species hydrolyze at the same rate as tertiary nitrates, likely leading to an overprediction of hydrolysis rates for a given fraction of RONO$_2$ within the aerosol phase in their model.

While the difference between our results and previous measurements of Romer et al. (2016) would be reduced somewhat if photolysis were included in their analysis, their measurements nevertheless suggest a large fraction of RONO$_2$ is lost to hydrolysis even in low-light conditions (06:00–07:00), implying an underprediction by our model of the fraction of RONO$_2$ mass in the aerosol phase. Previous studies using the MCM to predict SOA composition have had to reduce gas-particle partitioning coefficients by factors as high as 500 in order to reproduce observed mass loadings (Johnson et al., 2004, 2006a, b). Essentially this reduction accounts for particle-phase reactions (not captured by modeling simple semi-volatile partitioning) and particle viscosity that decrease the probability of repartitioning into the gas phase. Decreasing the vapor pressures of all BVOC oxidation products by a factor of 100 increases hydrolysis rates substantially, causing hydrolysis to account for a minimum of 40–50% of $\alpha$-pinene RONO$_2$ loss above-canopy and 60–70% below-canopy (Fig. S8). The fraction of isoprene RONO$_2$ lost through this mechanism also increases, but only to a maximum of 10–15% at night, as only tertiary nitrates undergo hydrolysis. The uncertainty with respect to hydrolysis loss rates highlights the importance of more accurately characterizing gas-particle partitioning when quantifying the lifetime and fate of NO$_3$ within an environment.

As we are focused primarily on highlighting differences between the above- and below-canopy locations rather than precisely determining production and loss rates, this uncertainty does not affect our major conclusions regarding the increased relevance of NO$_3$ chemistry below the canopy. In addition, we are primarily focused on daytime conditions, when higher temperatures shift partitioning to the gas phase and reduce overall hydrolysis rates. Nevertheless, future versions of this model will look to improve the characterization of hydrolysis by more accurately describing both hydrolysis rates within the aerosol (when more precise data are available) and more accurately partitioning the suite of BVOC oxidation products between the gas and particle phases. In addition, the choice of $\alpha$-pinene to represent all monoterpenes can impact these findings due to changes in product distribution that would occur if other monoterpenes were considered.

When considering all relevant losses, midday RONO$_2$ loss rates below the canopy are less than one-half of those above the canopy for $\alpha$-pinene products and are around 66% of those above the canopy for isoprene products. As daytime production rates of NO$_3$-derived RONO$_2$ below the canopy are larger than those above the canopy, our results suggest possible net transport of NO$_3$-derived products upward from the below-canopy environment. The net transport of both total RONO$_2$ and NO$_3$-derived RONO$_2$ is shown in Fig. 10.

While net transport of total RONO$_2$ is generally from the above-canopy environment to the below-canopy environment (downward), in agreement with previous NO$_3$ flux measurements at UMBS (Geddes and Murphy, 2014), the below-canopy environment acts as a substantial source of NO$_3$-derived RONO$_2$ above the canopy during the day ($\sim$ 25%). The largest contribution from net transport ($\sim$ 30% of the total) occurs around 07:00. Recent modeling work indicates that the mass loading of particulate RONO$_2$ is maximized around this time in the southeastern US (Pye et al., 2015). As NO$_3$-derived products are known to be major constituents of SOA in monoterpane-rich areas such as the southeastern US, neglecting below-canopy chemistry could therefore lead to...
an underprediction of RONO$_2$ SOA mass above the canopy during the day (Ayres et al., 2015; Xu et al., 2015).

While decreasing the vapor pressures of all oxidation products by a factor of 100 decreases the fraction of RONO$_2$ loss caused by photolysis and OH oxidation, the total contribution of net transport to above-canopy NO$_3^-$-derived RONO$_2$ production is still 14.5% on average from 06:00 to 18:00 (Fig. S9). Under more polluted conditions, the contribution of transport to total production remains substantial (between 7 and 25% from 11:00 to 15:00), but is highly dependent on the ratio of O$_3$ to NO (Fig. S10). Our assumption of no depositional losses during transport likely leads to an overprediction of the total amount of net transport that occurs; however, our model underpredicts concentrations of MACR + MVK above and below the canopy during the morning when mixing is beginning (Fig. S1), suggesting that losses during transport may be captured in the parameterization of deposition. Such underprediction could also be the result of errors in the chemical mechanism.

Precise determination of the influence of transport on above-canopy NO$_3^-$-derived RONO$_2$ production requires more accurate characterization of both hydrolysis losses and deposition during transport than our model can currently achieve. However, our results suggest that NO$_3^-$-derived products and total RONO$_2$ may undergo net transport in opposite directions. Because of the known relevance of NO$_3^-$-derived products to SOA production, this possibility should be the focus of further investigation.

3.5 Secondary organic aerosol production

Figure 11 displays the simulated diurnal SOA mass loadings modeled above and below the canopy at UMBS. As with gas-phase RONO$_2$, efficient daytime mixing results in a relatively small difference in total SOA mass loading between locations, with an average difference of 6% at night (21:00–06:00) (higher mass loadings below-canopy) and 7% near midday (11:00–15:00) (higher mass loadings above-canopy). The similarity above and below the canopy agrees with the results of the 1-D FORCAsT model (Ashworth et al., 2015), which predicts little change in aerosol mass loadings within 100 m from the ground.

To our knowledge, the composition of ambient aerosol at UMBS has only been characterized once before. Aerosol mass spectrometer measurements from 2001 indicate that OA mass loadings varied from $\sim 0.5$ to 2 µg m$^{-3}$, with values reaching 3 µg m$^{-3}$ during peak pollution events (Delia, 2004), in relatively good qualitative agreement with our results. However, more recent data from CABINEX 2009 indicate that water-soluble organic mass loadings were around 4 µg m$^{-3}$ on average (VanReken et al., 2015). As a result, while our model predicts more aerosol mass than recent results from the FORCAsT model (Ashworth et al., 2015), total SOA mass loadings may still be somewhat underpredicted.

In terms of SOA composition, ELVOCs comprise a consistent majority of total SOA in the model ($\sim 77$% above-canopy and $\sim 72$% below-canopy), which follows from the nearly constant rate of O$_3$ oxidation of $\alpha$-pinene. The dominance of these products agrees with laboratory studies that
find that SOA composition is almost entirely composed of ELVOC species at low total SOA mass loadings (Ehn et al., 2014). However, as the molar yield of ELVOCs varies substantially based on monoterpene studied (Jokinen et al., 2015), and as ELVOCs are not included in major chemical mechanisms such as the MCM, the modeled relevance of this type of oxidation product to SOA mass loadings suggests future studies should look to improve characterization of ELVOC formation processes and update published mechanisms.

Similar amounts of SOA are produced by reactive surface uptake of isoprene products (IEPOX, GLYOX, and METHYLGLYOX) and semi-volatile oxidation product partitioning (ROOH and RONO₂). The average mass loadings of isoprene epoxidiols (∼ 0 µg m⁻³), glyoxal (0–0.1 µg m⁻³), and methylglyoxal (0.1–0.25 µg m⁻³) are comparable to modeled mass loadings of these products in northern Michigan by Li et al. (2015). The composition of semi-volatile SOA is split between hydroperoxides (ROOH), predominately formed by OH oxidation followed by reaction with HO₂, and RONO₂. Organic nitrates constitute 6 % of total SOA above the canopy and 7 % below the canopy, in good agreement with results in both the southeastern US (3–8 %) (B. H. Lee et al., 2016) and a Colorado front-range forest (6–20 %) (Fry et al., 2013). Other oxidation products (alcohols, peroxyacetyl nitrates, etc.) contribute a negligible amount of aerosol.

Ultimately, SOA mass loadings above and below the canopy are within 0.5 µg m⁻³ of each other, and this similarity is caused by efficient mixing and different influences on aerosol production partially offsetting each other. For instance, lower temperatures below the canopy cause increased partitioning of semi-volatile oxidation products (ROOH and RONO₂) to the particle phase relative to above the canopy, resulting in nighttime mass loadings as much as 35 % larger.
below the canopy than above (when temperature differences are maximized). However, as the majority of semi-volatile products with volatilities low enough to partition appreciably to the aerosol phase contain peroxide functional groups, even in the case of RONO$_2$, lower HO$_3$ concentrations below the canopy partially offset the effect of temperature. This is highlighted by the fact that if temperatures above and below the canopy are assumed to be the same, more SOA mass is produced above the canopy than below (Fig. S11).

In addition, ELVOC products have vapor pressures low enough that virtually all of their mass exists within the particle phase, causing temperature to have little to no effect on their partitioning between gas and aerosol. Therefore, higher rates of O$_3$ oxidation of $\alpha$-pinene above the canopy further offset the effect of increased partitioning of semi-volatile products below the canopy. Isoprene epoxide, glyoxal, and methylglyoxal mass loadings are only slightly larger below the canopy than above for the majority of the day (within 5–10% of each other) because of lower rates of aerosol deposition and similar gas-phase concentrations in each location (due to mixing), despite the fact that gas-phase epoxide production is more rapid above the canopy.

Overall, NO$_3$-derived products contribute little to total RONO$_2$ SOA mass, causing production of RONO$_2$ SOA to be driven primarily by the OH + NO pathway, even at night (Fig. S12). The small mass loading of NO$_3$-derived products is primarily the result of our assumption that all monoterpenes are $\alpha$-pinene. As NO$_3$ oxidation of $\alpha$-pinene produces first-generation nitrates, which have relatively high volatilities, almost exclusively (Berkemeier et al., 2016), the SOA mass yield of NO$_3$ oxidation is relatively small (Table 1). However, previous modeling with a variety of monoterpenes suggests as much as 0.2–0.4 µg m$^{-3}$ of SOA is produced from monoperoxynitrate in northern Michigan (Pye et al., 2015), in agreement with the much higher mass yields of other monoterpenes such as $\beta$-pinene and limonene. Adding this mass to the total amount of SOA would suggest RONO$_2$ contribute 16–24% of total SOA mass, on the upper end of estimates from previous measurements (Fry et al., 2013; B. H. Lee et al., 2016).

Assuming that this amount of monoperoxynitrate SOA mass is present, and assuming that the fraction of RONO$_2$ mass derived from NO$_3$ oxidation is the same as we have modeled for $\alpha$-pinene (~45–80%) (Fig. S13), NO$_3$ oxidation could be expected to contribute around 4–12% of total SOA mass in this environment. This contribution is reasonable, as A. K. Y. Lee et al. (2016) recently found that RONO$_2$ produced from NO$_3$ oxidation contribute around 22–33% of biogenic SOA in a remote coniferous forest in Canada. The sensitivity of RONO$_2$ SOA and SOA from NO$_3$-derived oxidation products to background pollutant loads is shown in Fig. S14. Both total RONO$_2$ SOA and NO$_3$-derived SOA increase by a factor of 3–4 under increased pollutant loadings. Interestingly, increases in NO$_3$-derived RONO$_2$ SOA mass are almost solely dependent upon increased O$_3$ mixing ratios, implying that NO$_3$ SOA production is essentially O$_3$-limited for the conditions modeled in the sensitivity analysis.

The preceding analysis serves as an indicator of the potential relevance of NO$_3$ to total aerosol mass in this location; however, our model results also suggest the possibility of net transport of NO$_3$-derived RONO$_2$ from the below-canopy environment through the canopy, potentially resulting in more NO$_3$-derived RONO$_2$ SOA mass than would be assumed if transport were neglected. Indeed, similarly to gas-phase RONO$_2$ concentrations, including in-canopy mixing results in a substantial increase in both isoprene and $\alpha$-pinene NO$_3$-derived OA above the canopy. This is shown in Fig. 12, where positive values indicate increased amounts of SOA mass above the canopy when mixing is included within the model. Ultimately our results suggest a 20–50% increase in NO$_3$-derived $\alpha$-pinene RONO$_2$ mass in the afternoon, which can be thought of as a surrogate for monoperoxynitrate nitrate mass, and an even larger increase from isoprene products. While we assume no loss of products during transport, which would reduce this effect, these results highlight the potential relevance of the below-canopy environment to above-canopy SOA mass. Because the contribution of NO$_3$-derived RONO$_2$ to total SOA is predicted to be high in areas such as the southeastern US (Ayres et al., 2015), the potential influence of net transport of NO$_3$-derived products and the associated effect on SOA mass warrants further study.

Figure 12. Diurnal profile of the net change in NO$_3$-derived RONO$_2$ SOA above the canopy as a result of including transport between the above- and below-canopy environments.

4 Conclusions

A detailed 0-D model was used to investigate $\alpha$-pinene and isoprene oxidation chemistry and SOA production above and below a forest canopy. Specific focus was placed on the contribution of NO$_3$ to BVOC processes, as shade provided by the canopy was assumed to reduce NO$_3$ photolysis rates. While NO$_3$ mixing ratios are relatively low due to the ru-
eral nature of the site (<0.5 pptv), daytime mixing ratios are 2 to 3 times larger below the canopy than above. Reduced photolysis frequencies are found to be the primary factor behind elevated daytime below-canopy NO$_3$ concentrations. Higher NO$_3$ mixing ratios below the canopy lead to a substantially higher contribution of NO$_3$ to daytime oxidation of α-pinene below the canopy (∼12 %) than above the canopy (∼4 %), and this contribution increases to 32 % below the canopy under hypothetical conditions meant to represent a polluted suburban environment. While the efficient mixing process parameterized within the model results in similar gas-phase RONO$_2$ concentrations above and below the canopy, our results suggest that daytime net transport of NO$_3$-derived products upward from the below-canopy environment constitutes as much as 30 % of total NO$_3$-derived RONO$_2$ production above the canopy in the morning. However, differences between the predictions of gas-phase RONO$_2$ by our MCM-based model, predictions from previous modeling of RONO$_2$ at the same site using laboratory yields (Pratt et al., 2012), and RONO$_2$ measurements (Romer et al., 2016) underscore the need for continued improvement of our understanding of RONO$_2$ chemistry.

Similarly to gas-phase RONO$_2$ mixing ratios, total SOA mass loadings are comparable above and below the canopy. The fact that ELVOCs constitute a majority of SOA mass implies the need for further study of these compounds, as they are not yet included in major chemical mechanisms such as the MCM but are likely highly relevant to SOA formation in rural areas. Lower temperatures below the canopy lead to increased partitioning of oxidation products to the particle phase and therefore higher mass loadings of semi-volatile products; however, the total contribution of these products to SOA mass is relatively low (∼10–25 %) under the simulated conditions.

Ultimately, substantially more NO$_3$-derived SOA mass from both α-pinene and isoprene oxidation products is modeled above the canopy when transport from the below-canopy environment is included. While our model results predict a small mass loading of NO$_3$-derived products due to the use of α-pinene as the sole monoterpane, Ayres et al. (2015) calculate that 23–44 % of NO$_3$ lost to reaction with monoterpenes becomes aerosol-phase RONO$_2$, and it has been estimated that RONO$_2$ contribute as much as 5–25 % of total OA in the southeastern US (Xu et al., 2015). Therefore, our results, when combined with the results of previous studies highlighting the relevance of NO$_3$ to total OA mass loadings, suggest that regional 3-D models that lack the near-ground resolution to account for effects of the forest canopy may be missing a substantial source of OA.

5 Code availability

The MATLAB code associated with this paper is available upon request.

6 Data availability

The compiled datasets used to produce each figure within this paper are available as Igor Pro files upon request.

The Supplement related to this article is available online at doi:10.5194/acp-17-1805-2017-supplement.

Author contributions. Benjamin C. Schulze developed the model, performed simulations and data analysis, and wrote the manuscript. Henry W. Wallace and Robert J. Griffin assisted heavily with model development, data analysis, and manuscript editing. Henry W. Wallace, James H. Flynn, Barry L. Lefer, Matt H. Erickson, B. Tom Johnson, Sebastien Dusanter, Stephen M. Griffith, Robert F. Hansen, Timothy VanReken, and Philip S. Stevens performed atmospheric measurements during CABINEX that were used as model inputs. James H. Flynn, Philip S. Stevens, Sebastien Dusanter, Stephen M. Griffith, and Robert F. Hansen provided helpful comments and edits.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements. We would like to acknowledge the National Science Foundation for funding this work with grant numbers AGS-0904214 and AGS-0904167.

Edited by: R. MacKenzie
Reviewed by: two anonymous referees

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