

1 **Supporting Information:**

2 **Contributions of individual reactive biogenic volatile organic compounds to organic**  
3 **nitrates above a mixed forest**

4  
5 K. A. Pratt<sup>1</sup>, L. H. Mielke<sup>1\*</sup>, P. B. Shepson<sup>1,2,3</sup>, A. M. Bryan<sup>4</sup>, A. L. Steiner<sup>4</sup>, J. Ortega<sup>5†</sup>, R.  
6 Daly<sup>5‡</sup>, D. Helmig<sup>5</sup>, C. S. Vogel<sup>6</sup>, S. Griffith<sup>7</sup>, S. Dusanter<sup>7-9</sup>, P. S. Stevens<sup>7,10</sup>, M. Alaghmand<sup>1</sup>  
7

8 <sup>1</sup>Department of Chemistry, Purdue University, West Lafayette, IN USA

9 <sup>2</sup>Department of Earth and Atmospheric Sciences, Purdue University, West Lafayette, IN USA

10 <sup>3</sup>Purdue Climate Change Research Center, Purdue University, West Lafayette, IN USA

11 <sup>4</sup>Department of Atmospheric, Oceanic and Space Sciences, University of Michigan, Ann Arbor,  
12 MI USA

13 <sup>5</sup>Institute of Arctic and Alpine Research, University of Colorado, Boulder, CO USA

14 <sup>6</sup>University of Michigan Biological Station, Pellston, MI USA

15 <sup>7</sup>School of Public and Environmental Affairs, Indiana University, Bloomington, IN USA

16 <sup>8</sup>Université Lille Nord de France, Lille, France

17 <sup>9</sup>École des Mines de Douai, Douai, France

18 <sup>10</sup>Department of Chemistry, Indiana University, Bloomington, IN USA  
19

20 \*Now at: School of Public and Environmental Affairs, Indiana University, Bloomington, IN USA

21 †Now at: Atmospheric Chemistry Division, Earth System Laboratory, National Center for  
22 Atmospheric Research, Boulder, CO USA

23 ‡Now at: Air Pollution Prevention and Control Division, National Risk Management Research  
24 Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC USA

25  
26 *Correspondence to:* K.A. Pratt ([kapratt@purdue.edu](mailto:kapratt@purdue.edu))  
27  
28

29 **2.2 One-dimensional model description**

30 ***Future forest composition***

31 Stem density of aspen trees at UMBS and relative proportions of hardwood and pine  
32 species and size were estimated in a 1.4 km<sup>2</sup> area of the UMBS forest in 2010 by measuring tree  
33 diameter at breast height (DBH, 1.37 m) of all trees with a DBH  $\geq$  8.0 cm in 101 – 800 m<sup>2</sup> plots.  
34 For this exercise, all aspen trees were assumed to be replaced by either northern hardwood or  
35 upland pine assemblages of like DBH and stem density. Dry leaf mass of each of the  
36 replacement species was estimated from biomass equations developed in the Great Lake States  
37 or northeastern U.S. in the form  $M = aD^b$ , where M is foliage dry mass, D is DBH, and a and b  
38 are species/site specific parameters (Ribe, 1973; Pastor and Bockheim, 1981; Young et al., 1981;  
39 Crow and Erdmann, 1983; Hocker and Early, 1983; Perala and Alban, 1994; Ter-Michaelian and  
40 Korzukhin, 1997). From the 2010 census at UMBS we found the mean DBH of aspen trees was  
41 25.0 cm at a density of 22300 stems km<sup>-2</sup> or 32% of the trees in the forest. The proportions of  
42 species in the pine and northern hardwood assemblages were determined from the 2010 census  
43 and foliage biomass estimated assuming a complete replacement of aspen with either pine or  
44 northern hardwood assemblages (Table S2). For scaling emission rates for temperature, average  
45  $\beta$ -factors for the two future forest scenarios were based on the projected forest composition and  
46 associated individual BVOC emissions. For the upland pines future forest scenario,  
47 monoterpenene (MT) and sesquiterpene (SQT)  $\beta$ -factors were calculated to be 0.19 K<sup>-1</sup> and 0.14 K<sup>-1</sup>  
48 respectively. For the northern hardwoods future forest scenario, the SQT  $\beta$ -factor was  
49 calculated to be 0.15 K<sup>-1</sup>; due to uncertainties in the measured aspen MT  $\beta$ -factor, the average  
50 MT  $\beta$ -factor (0.14 K<sup>-1</sup>) was used.

51

52

53 **BVOC emissions**

54 Normalized fluxes, measured during branch-enclosure sampling, for the three emission  
55 scenarios (base, maximum, and minimum) are shown in Table S3. For the base scenario, the  
56 emission rates of all BVOCs were scaled to account for measurement uncertainties. For  
57 isoprene, emission rates were scaled by -30% for the base production rate scenario, with no  
58 scaling for the maximum production rate scenario and scaling by -66% for the minimum  
59 production rate scenario. Previously, Pressley et al. (2005) reported an uncertainty in isoprene  
60 eddy covariance measurements at UMBS of  $\pm 32\text{-}66\%$ . However, similar to the modeling study  
61 of Ortega et al. (2007), morning (5:30-10:30 EST) isoprene emissions were overestimated;  
62 therefore, for all production rate scenarios, isoprene emission rates during this time period were  
63 also scaled (by -9% to -83%, with 0.5 h resolution) according to previously documented average  
64 overestimations by Ortega et al. (2007); this adjustment is not reflected in Table S3.

65 For MTs and other BVOCs, the base production rate scenario included scaling emission  
66 rates by +107%; for the maximum and minimum production rate scenarios, scaling by +107%  
67 and +10%, respectively, was completed. For these species, Ortega et al. (2007; 2008) previously  
68 reported a measurement uncertainty of 27%, as well as reported average sampling losses of  $\sim 20\text{-}30\%$   
69 [range of 10-80%]. For SQTs, the base production rate scenario included scaling emission  
70 rates by +130%, with scaling by +130% and +10% for the maximum and minimum production  
71 rate scenarios, respectively. This accounts for the previously reported a measurement  
72 uncertainty of 50% for SQTs, as well as reported average sampling losses of  $\sim 20\text{-}30\%$  [range of  
73 10-80%] (Ortega et al., 2007; 2008). In addition, for temperature dependence scaling of the  
74 MTs, SQTs, and other BVOCs, upper and lower quartile  $\beta$ -factors were applied for the minimum  
75 and maximum production rate scenarios. Also, for the MTs, SQTs, and other BVOCs, the

76 maximum and minimum production rate scenarios account for tree-to-tree variability during  
77 branch enclosure measurements, as well as 95% confidence intervals associated with  
78 measurements of mean green-leaf dry mass of the various tree species. Thus, the production rate  
79 scenarios account for uncertainty and variability in emission rate measurements.

80

81 ***Calculated NO<sub>3</sub> concentrations***

82 Nitrate radicals are primarily produced by reaction of NO<sub>2</sub> with O<sub>3</sub> and generally  
83 removed by photolysis and reaction with NO, as described by reactions 1-3:



88 The NO<sub>3</sub> production and loss reactions included in the box model are described in Table S4 with  
89 their corresponding rate constants. Total sesquiterpene (SQT) concentrations were estimated  
90 using the noontime average [SQT]/[MT] ratio measured by Kim et al. (2009) at the PROPHET  
91 site (July-August 2005) and the measured total MT concentration for July-August 2008 (PTR-  
92 LIT). NO<sub>3</sub> photolysis rates were calculated using the National Center for Atmospheric Research  
93 (NCAR) tropospheric ultraviolet and visible (TUV) radiation model  
94 (<http://cprm.acd.ucar.edu/Models/TUV/>) with total column ozone obtained from the Ozone  
95 Monitoring Instrument (OMI) on the Aura spacecraft  
96 ([http://jwocky.gsfc.nasa.gov/teacher/ozone\\_overhead.html](http://jwocky.gsfc.nasa.gov/teacher/ozone_overhead.html)). NO<sub>3</sub> reached steady state within  
97 ~0.5-8 min in the box model calculations, which were repeated to create an average 0.5 hr  
98 resolution NO<sub>3</sub> diurnal profile for sunny days in July-August 2008.

99

100 **Table S1.** BVOCs identified during branch-enclosure emission measurements for UMBS tree  
 101 species. Corresponding reaction rate constants (units of  $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ) for OH,  $\text{O}_3$ , and  $\text{NO}_3$  at  
 102 298 K ( $k_{\text{OH}}$ ,  $k_{\text{O}_3}$ , and  $k_{\text{NO}_3}$ , respectively) and  $\text{RONO}_2$  yields for reactions with OH and  $\text{NO}_3$  ( $\gamma_{\text{OH}}$   
 103 and  $\gamma_{\text{NO}_3}$ , respectively) are included for each BVOC identified. Individual BVOCs are displayed  
 104 in order of simulated  $\text{RONO}_2$  contribution; BVOCs contributing  $>0.5$  ppt  $\text{RONO}_2$  (at  $\sim 12$  m  
 105 above forest canopy) at any time are shown in Table 1.

BVOC	Structure	$k_{\text{OH}}$ $k_{\text{O}_3}$ $k_{\text{NO}_3}$ ( $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ )	$\text{RONO}_2:$ $\gamma_{\text{OH}}$ $\gamma_{\text{NO}_3}$
$\beta$ -linalool ( $\text{C}_{10}\text{H}_{18}\text{O}$ )		$1.59 \times 10^{-10}$ a) $4.3 \times 10^{-16}$ a) $1.12 \times 10^{-11}$ a)	0.30 b) 0.31 c)
camphene ( $\text{C}_{10}\text{H}_{16}$ )		$5.30 \times 10^{-11}$ d) $9.0 \times 10^{-19}$ d) $6.6 \times 10^{-13}$ d)	0.23 e) 0.31 c)
$\alpha$ -farnesene ( $\text{C}_{15}\text{H}_{24}$ )		$2.19 \times 10^{-10}$ f) $5.94 \times 10^{-16}$ f) $2.1 \times 10^{-11}$ g)	0.29 h) 0.31 c)
$\beta$ -phellandrene ( $\text{C}_{10}\text{H}_{16}$ )		$1.68 \times 10^{-10}$ d) $4.7 \times 10^{-17}$ d) $8.0 \times 10^{-12}$ d)	0.18 h) 0.31 c)
$\alpha$ -phellandrene ( $\text{C}_{10}\text{H}_{16}$ )		$3.13 \times 10^{-10}$ d) $3.0 \times 10^{-15}$ d) $7.3 \times 10^{-11}$ d)	0.18 h) 0.31 c)
terpinolene ( $\text{C}_{10}\text{H}_{16}$ )		$2.25 \times 10^{-10}$ d) $1.9 \times 10^{-15}$ d) $9.7 \times 10^{-11}$ d)	0.18 h) 0.31 c)
<i>allo</i> -ocimene ( $\text{C}_{10}\text{H}_{16}$ )		$2.36 \times 10^{-10}$ i) $4.16 \times 10^{-16}$ i) $1.1 \times 10^{-11}$ g)	0.18 h) 0.31 c)
dimethylnonatriene ( $\text{C}_{11}\text{H}_{18}$ )		$2.32 \times 10^{-10}$ i) $7.50 \times 10^{-16}$ i) $9.6 \times 10^{-12}$ g)	0.20 h) 0.31 c)
$\alpha$ -terpineol ( $\text{C}_{10}\text{H}_{18}\text{O}$ )		$1.9 \times 10^{-10}$ j) $3.0 \times 10^{-16}$ j) $1.60 \times 10^{-11}$ k)	0.30 b) 0.31 c)
$\alpha$ -terpinene ( $\text{C}_{10}\text{H}_{16}$ )		$3.63 \times 10^{-10}$ d) $2.1 \times 10^{-14}$ d) $1.4 \times 10^{-11}$ d)	0.18 h) 0.31 c)
$\beta$ -selinene ( $\text{C}_{15}\text{H}_{24}$ )		$1.17 \times 10^{-10}$ i) $2.40 \times 10^{-17}$ i) $6.5 \times 10^{-13}$ g)	0.29 h) 0.31 c)

$\beta$ -caryophyllene (C <sub>15</sub> H <sub>24</sub> )		1.97 x 10 <sup>-11</sup> d) 1.16 x 10 <sup>-14</sup> d) 1.9 x 10 <sup>-11</sup> d)	0.29 h) 0.31 c)
$\delta$ -cadinene (C <sub>15</sub> H <sub>24</sub> )		2.11 x 10 <sup>-10</sup> i) 1.63 x 10 <sup>-15</sup> i) 5.2 x 10 <sup>-11</sup> g)	0.29 h) 0.31 c)
$\beta$ -bourbonene (C <sub>15</sub> H <sub>24</sub> )		6.19 x 10 <sup>-11</sup> i) 1.2 x 10 <sup>-17</sup> i) 3.5 x 10 <sup>-13</sup> g)	0.29 h) 0.31 c)
$\alpha$ -copaene (C <sub>15</sub> H <sub>24</sub> )		9.00 x 10 <sup>-11</sup> d) 1.60 x 10 <sup>-16</sup> d) 1.60 x 10 <sup>-11</sup> d)	0.29 h) 0.31 c)
4-carene (C <sub>10</sub> H <sub>16</sub> )		5.81 x 10 <sup>-11</sup> i) 2.00 x 10 <sup>-16</sup> i) 8.9 x 10 <sup>-13</sup> g)	0.18 e) 0.31 f)
4-terpineol (C <sub>10</sub> H <sub>18</sub> O)		1.04 x 10 <sup>-10</sup> i) (<)1 x 10 <sup>-20</sup> i) 1.4 x 10 <sup>-16</sup> g)	0.30 b) 0.31 c)
$\alpha$ -selinene (C <sub>15</sub> H <sub>24</sub> )		1.51 x 10 <sup>-10</sup> i) 4.42 x 10 <sup>-16</sup> i) 5.8 x 10 <sup>-12</sup> g)	0.29 h) 0.31 c)
camphor (C <sub>10</sub> H <sub>16</sub> O)		4.30 x 10 <sup>-12</sup> d) (<)7 x 10 <sup>-20</sup> l) (<)3.00 x 10 <sup>-16</sup> d)	0.31 m) 0.31 c)
3-carene (C <sub>10</sub> H <sub>16</sub> )		8.80 x 10 <sup>-11</sup> d) 3.7 x 10 <sup>-17</sup> d) 9.1 x 10 <sup>-12</sup> d)	0.18 h) 0.31 c)
$\beta$ -elemene (C <sub>15</sub> H <sub>24</sub> )		1.40 x 10 <sup>-10</sup> i) 2.6 x 10 <sup>-17</sup> i) 6.3 x 10 <sup>-11</sup> g)	0.29 h) 0.31 c)
$\alpha$ -cubebene (C <sub>15</sub> H <sub>24</sub> )		1.00 x 10 <sup>-10</sup> i) 4.30 x 10 <sup>-16</sup> d) 7.9 x 10 <sup>-12</sup> g)	0.29 h) 0.31 c)
1,8-cineole (C <sub>10</sub> H <sub>18</sub> O)		1.11 x 10 <sup>-11</sup> n) (<)1.5 x 10 <sup>-19</sup> o) 1.7 x 10 <sup>-16</sup> n)	0.52 p) 0.31 c)

D germacrene (C <sub>15</sub> H <sub>24</sub> )		2.40 x 10 <sup>-10</sup> i) 6.10 x 10 <sup>-16</sup> i) 6.4 x 10 <sup>-12</sup> g)	0.29 h) 0.31 c)
<i>o</i> -cymene (C <sub>10</sub> H <sub>14</sub> )		8.54 x 10 <sup>-12</sup> i) (<5 x 10 <sup>-20</sup> q) 9.9 x 10 <sup>-16</sup> q)	0.03 r) 0.31 c)
<i>allo</i> - aromadendrene (C <sub>15</sub> H <sub>24</sub> )		6.25 x 10 <sup>-11</sup> i) 1.20 x 10 <sup>-17</sup> i) 3.5 x 10 <sup>-13</sup> g)	0.29 h) 0.31 c)
$\gamma$ -muurolene (C <sub>15</sub> H <sub>24</sub> )		1.56 x 10 <sup>-10</sup> i) 4.42 x 10 <sup>-16</sup> i) 5.9 x 10 <sup>-12</sup> g)	0.29 h) 0.31 c)
$\beta$ -cubebene (C <sub>15</sub> H <sub>24</sub> )		6.54 x 10 <sup>-11</sup> i) 1.20 x 10 <sup>-17</sup> i) 3.5 x 10 <sup>-13</sup> g)	0.29 h) 0.31 c)
$\alpha$ -muurolene (C <sub>15</sub> H <sub>24</sub> )		1.90 x 10 <sup>-10</sup> i) 8.6 x 10 <sup>-16</sup> i) 1.1 x 10 <sup>-11</sup> g)	0.29 h) 0.31 c)
$\beta$ -gurjunene (C <sub>15</sub> H <sub>24</sub> )		6.01 x 10 <sup>-11</sup> i) 1.20 x 10 <sup>-17</sup> i) 3.5 x 10 <sup>-13</sup> g)	0.29 h) 0.31 c)
borneol (C <sub>10</sub> H <sub>18</sub> O)		1.14 x 10 <sup>-11</sup> i) (<1 x 10 <sup>-20</sup> d) 4.6 x 10 <sup>-15</sup> s)	0.52 p) 0.31 c)
$\beta$ -farnesene (C <sub>15</sub> H <sub>24</sub> )		2.88 x 10 <sup>-10</sup> f) 6.86 x 10 <sup>-16</sup> f) 9.3 x 10 <sup>-12</sup> g)	0.29 h) 0.31 c)
$\alpha$ -humulene (C <sub>15</sub> H <sub>24</sub> )		2.93 x 10 <sup>-10</sup> d) 1.17 x 10 <sup>-14</sup> d) 3.90 x 10 <sup>-11</sup> d)	0.29 h) 0.31 c)
<i>cis</i> - and <i>trans</i> - linalool oxide (C <sub>10</sub> H <sub>18</sub> O <sub>2</sub> )		6.68 x 10 <sup>-11</sup> i) 1.75 x 10 <sup>-18</sup> i) 4.6 x 10 <sup>-14</sup> g)	0.30 b) 0.31 c)
$\beta$ -bisabolene (C <sub>15</sub> H <sub>24</sub> )		2.4 x 10 <sup>-11</sup> i) 8.7 x 10 <sup>-16</sup> i) 9.2 x 10 <sup>-12</sup> g)	0.29 h) 0.31 c)

<i>p</i> -cymene (C <sub>10</sub> H <sub>14</sub> )		1.51 x 10 <sup>-11</sup> h) (<5 x 10 <sup>-20</sup> o) 9.9 x 10 <sup>-16</sup> n)	0.03 r) 0.31 c)
germacrene B (C <sub>15</sub> H <sub>24</sub> )		2.90 x 10 <sup>-10</sup> i) 2.06 x 10 <sup>-15</sup> i) 4.3 x 10 <sup>-11</sup> g)	0.29 h) 0.31 c)
aromadendrene (C <sub>15</sub> H <sub>24</sub> )		1.50 x 10 <sup>-10</sup> t) 6.50 x 10 <sup>-15</sup> u) 3.5 x 10 <sup>-13</sup> g)	0.29 h) 0.31 c)
$\alpha$ -cedrene (C <sub>15</sub> H <sub>24</sub> )		6.70 x 10 <sup>-11</sup> d) 2.80 x 10 <sup>-17</sup> d) 8.20 x 10 <sup>-12</sup> d)	0.29 h) 0.31 c)
tricyclene (C <sub>10</sub> H <sub>16</sub> )		2.66 x 10 <sup>-12</sup> i) (<1 x 10 <sup>-23</sup> d) 1.1 x 10 <sup>-15</sup> s)	0.31 m) 0.31 c)
$\alpha$ - <i>trans</i> -bergamotene (C <sub>15</sub> H <sub>24</sub> )		1.80 x 10 <sup>-10</sup> i) 8.60 x 10 <sup>-16</sup> i) 9.6 x 10 <sup>-12</sup> g)	0.29 h) 0.31 c)
camphene hydrate (C <sub>10</sub> H <sub>18</sub> O)		9.43 x 10 <sup>-12</sup> i) (<1 x 10 <sup>-20</sup> d) 6.4 x 10 <sup>-16</sup> s)	0.52 p) 0.31 c)
$\gamma$ -cadinene (C <sub>15</sub> H <sub>24</sub> )		1.56 x 10 <sup>-10</sup> i) 3.20 x 10 <sup>-14</sup> t) 5.9 x 10 <sup>-12</sup> g)	0.29 h) 0.31 c)
<i>para</i> -cymenene (C <sub>10</sub> H <sub>16</sub> )		5.7 x 10 <sup>-11</sup> i) 1.4 x 10 <sup>-16</sup> i) 1.5 x 10 <sup>-12</sup> v)	0.18 h) 0.31 c)
norbornene (C <sub>7</sub> H <sub>10</sub> )		1.0 x 10 <sup>-10</sup> d) 1.27 x 10 <sup>-17</sup> d) 7.0 x 10 <sup>-13</sup> d)	0.11 h) 0.31 c)
cyclofenchone (C <sub>10</sub> H <sub>16</sub> )		3.54 x 10 <sup>-12</sup> i) (<1 x 10 <sup>-23</sup> d) 1.4 x 10 <sup>-15</sup> s)	0.31 m) 0.31 c)

106

a) Atkinson et al. (1995)

107

b) Estimated based on Arey et al. (2001), Espada and Shepson (2005), and O'Brien et al. (1998)

108

c) Average of  $\alpha$ -pinene,  $\beta$ -pinene, and limonene yields

109 d) Atkinson and Arey (2003)  
110 e)  $\beta$ -pinene used as a proxy  
111 f) Kim et al. (2011)  
112 g) Estimated based on Pfrang et al. (2006)  
113 h) Estimated based on Arey et al. (2001) and O'Brien et al. (1998)  
114 i) Estimated using the Environmental Protection Agency's Estimation Program Interface Suite  
115 (USEPA, 2010)  
116 j) Wells (2005)  
117 k) Jones and Ham (2008)  
118 l) Reissell et al. (2001)  
119 m) Estimated based on Arey et al. (2001)  
120 n) Corchnoy and Atkinson (1990)  
121 o) Atkinson et al. (1990)  
122 p) Estimated based on Arey et al. (2001) and Espada and Shepson (2005)  
123 q) *p*-cymene used as a proxy  
124 r) *p*-xylene (Espada et al., 2005) used as a proxy  
125 s) Estimated based on Kerdouci et al. (2010)  
126 t) Ng et al. (2007)  
127 u) Pollmann et al. (2005)  
128 v) styrene (Atkinson and Arey, 2003) used as a proxy  
129

130 **Table S2.** Estimated leaf dry mass and species proportions for replacement of aspen in the  
131 future UMBS forest. Values in parentheses are  $\pm$  standard error.

Assemblage/species	Leaf dry mass ( $\text{g}\cdot\text{m}^{-2}$ )	Species proportions (%)
Northern Hardwoods		
<i>Acer rubrum</i>	102.8 (19.5)	70.5
<i>Acer saccharum</i>	28.3 (1.6)	15.5
<i>Fagus grandifolia</i>	26.1 (1.7)	14.0
Upland Pines		
<i>Pinus strobus</i>	233.4 (35.0)	89.0
<i>Pinus resinosa</i>	44.1 (4.4)	11.0

132

133

134 **Table S3.** Normalized fluxes ( $\mu\text{g C m}^{-2} \text{ h}^{-1}$ ) for three emission scenarios (base, maximum, and  
135 minimum production). Fluxes were normalized to a standard photosynthetic active radiation flux  
136 of  $1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$  and a standard temperature of 303.15 K.

<b>BVOC Class</b>	<b>Base</b>	<b>Maximum</b>	<b>Minimum</b>
<b>Isoprene</b>	8141	14375	3909
<b>Monoterpenes</b>	667	1357	148
<b>Sesquiterpenes</b>	94	274	7
<b>Other BVOCs</b>	61	119	14

137  
138

139 **Table S4.**  $\text{NO}_3$  production and loss reactions included in the box model with corresponding rate  
 140 constants.

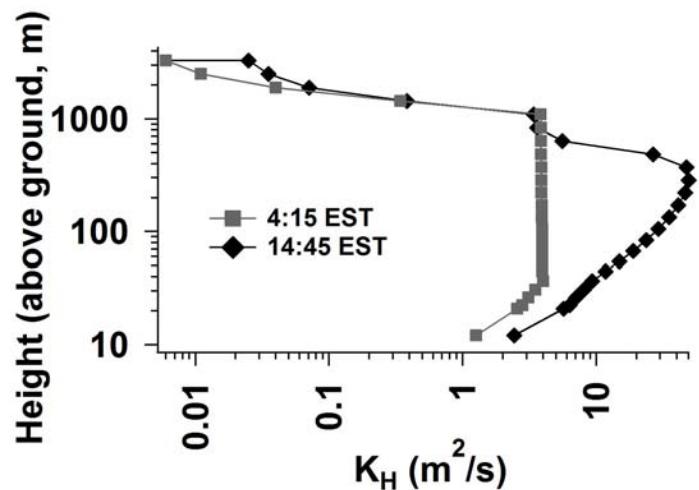
Reaction	$k (\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1})$	Reference
$\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2$	$2.6 \times 10^{-11}$	(Atkinson et al., 2004)
$\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5$	$1.9 \times 10^{-12}$	(Atkinson et al., 2004)
$\text{NO}_3 + \text{OH} \rightarrow \text{NO}_2 + \text{HO}_2$	$2.0 \times 10^{-11}$	(Atkinson et al., 2004)
$\text{NO}_3 + \text{HO}_2 \rightarrow \text{HNO}_3 + \text{O}_2$	$4.0 \times 10^{-12}$	(Atkinson et al., 2004)
$\text{NO}_3 + \text{RO}_2 \rightarrow \text{RO} + \text{NO}_2$	$4.0 \times 10^{-12}$	Assumed same as $\text{HO}_2$ reaction
$\text{NO}_3 + \text{Isoprene} \rightarrow \text{Products}$	$7.0 \times 10^{-13}$	(Atkinson and Arey, 2003)
$\text{NO}_3 + \text{MTs} \rightarrow \text{Products}$	$1.4 \times 10^{-11}$	Emission weighted average (see Table 1 for individual $k_{\text{NO}_3}$ )
$\text{NO}_3 + \text{SQTs} \rightarrow \text{Products}$	$1.7 \times 10^{-11}$	Emission weighted average (see Table 1 for individual $k_{\text{NO}_3}$ )
$\text{NO}_3 + \text{MACR} \rightarrow \text{Products}$	$3.4 \times 10^{-15}$	(Atkinson and Arey, 2003)
$\text{NO}_3 + \text{MVK} \rightarrow \text{Products}$	$(<)6 \times 10^{-15}$	(Atkinson and Arey, 2003)
$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	$3.5 \times 10^{-17}$	(Atkinson et al., 2004)
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	$1.8 \times 10^{-14}$	(Atkinson et al., 2004)
$\text{N}_2\text{O}_5 \rightarrow \text{NO}_3 + \text{NO}_2$	$6.9 \times 10^{-2} \text{ s}^{-1}$	(Atkinson et al., 2004)
$\text{NO}_3 \rightarrow \text{particles}$	$4.0 \times 10^{-3} \text{ s}^{-1}$	(Hurst et al., 2001)
$\text{N}_2\text{O}_5 \rightarrow \text{particles}$	$9.3 \times 10^{-4} \text{ s}^{-1}$	(Hurst et al., 2001)
$\text{NO}_3 + \text{hv} \rightarrow \text{NO}_2 + \text{O}$	variable	NCAR TUV model
$\text{NO}_3 + \text{hv} \rightarrow \text{NO} + \text{O}_2$	variable	NCAR TUV model

141  
 142

143 **Table S5.** First generation isoprene oxidation products with yields from isoprene oxidation,  
 144 oxidation rate constants (units of  $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ), and  $\text{RONO}_2$  yields. Methacrolein (MACR)  
 145 and methyl vinyl ketone (MVK) yields by OH oxidation are defined within the model based on  
 146 the availability of NO, as represented by  $\beta$  (defined in the text as the fraction of time  $\text{RO}_2$  reacts  
 147 with NO versus  $\text{HO}_2$  and  $\text{RO}_2$ ), using high and low  $\text{NO}_x$  chamber yields from Ruppert and  
 148 Becker (2000). The structures of  $\text{RONO}_2$  products from the oxidation of these first generation  
 149 isoprene oxidation products were estimated, and corresponding rate constants were estimated  
 150 (Atkinson and Arey, 2003; Kerdouci et al., 2010; USEPA, 2010) to predict the removal of the  
 151 nitrates.

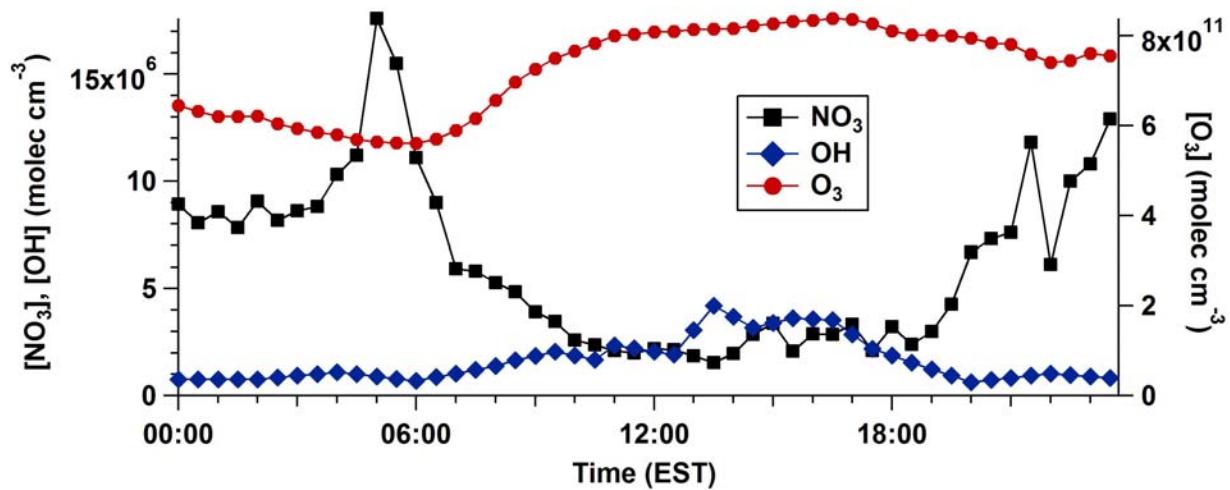
First Generation Isoprene Oxidation Product	Structure	Isoprene $\gamma_{\text{OH}}$ $\gamma_{\text{O}_3}$ $\gamma_{\text{NO}_3}$	$k_{\text{OH}}$ $k_{\text{O}_3}$ $k_{\text{NO}_3}$	$\text{RONO}_2:$ $\gamma_{\text{OH}}$ $\gamma_{\text{NO}_3}$
<b>MACR</b>		0.18-0.20 a) 0.39 b) 0.035 b)	$2.9 \times 10^{-11} \text{ c)}$ $1.2 \times 10^{-18} \text{ c)}$ $3.4 \times 10^{-15} \text{ c)}$	0.0705 d) 0.24 e)
<b>MVK</b>		0.15-0.31 a) 0.16 b) 0.035 b)	$2.0 \times 10^{-11} \text{ c)}$ $5.2 \times 10^{-18} \text{ c)}$ ( $<6.0 \times 10^{-16} \text{ c}$ )	0.11 d) 0.24 e)
<b>IP-HMY</b>		0.15 e) 0 e) 0 e)	$7.0 \times 10^{-11} \text{ f)}$ $1.0 \times 10^{-17} \text{ f)}$ $1.0 \times 10^{-13} \text{ f)}$	0.075 e) 0.20 e)
<b>IP-MHY</b>		0.13 e) 0 e) 0.32 f)	$7.0 \times 10^{-11} \text{ f)}$ $1.0 \times 10^{-17} \text{ f)}$ $1.0 \times 10^{-13} \text{ f)}$	0.075 e) 0.20 e)

152 a) (Ruppert and Becker, 2000)  
 153 b) (Atkinson and Arey, 1998)  
 154 c) (Atkinson et al., 2006)  
 155 d) (Paulot et al., 2009)  
 156 e) Estimation by Costa (2011)  
 157 f) (Carter and Atkinson, 1996)  
 158



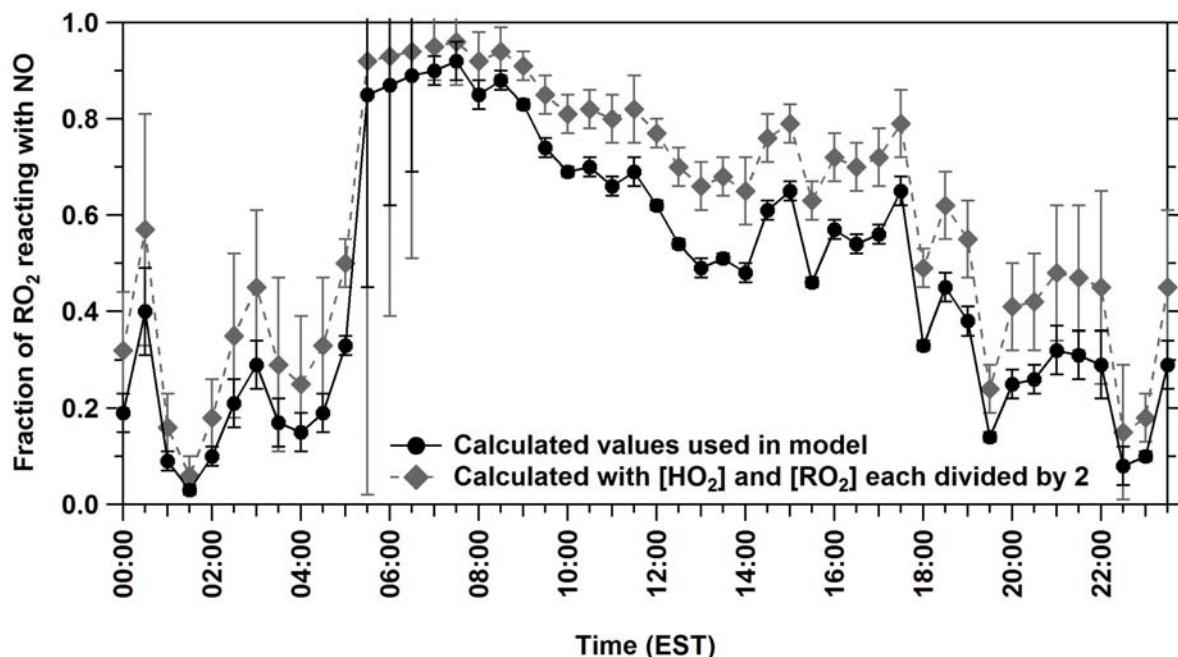
159  
160  
161  
162

**Figure S1.** Modeled thermal eddy diffusivity ( $K_H$ ) profiles for UMBS in the summer at 4:15 and 14:45 EST.

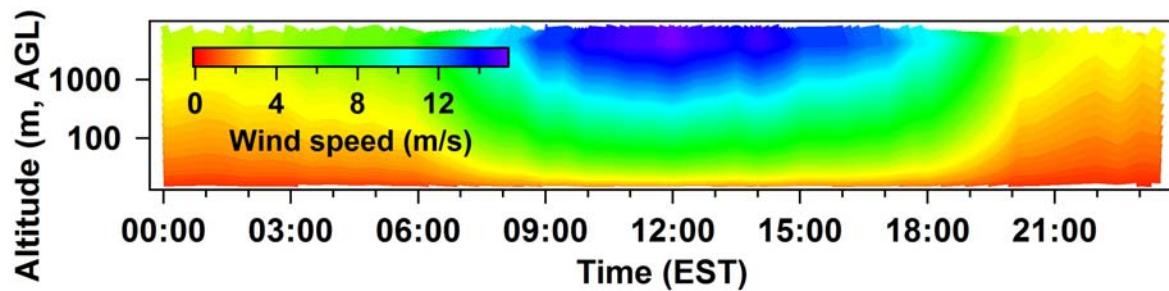


163  
164  
165

**Figure S2.** Diurnal cycles of the average concentrations of  $NO_3$  (modeled),  $OH$  (measured), and  $O_3$  (measured), used in the model, for 32 m above ground (10 m above canopy).

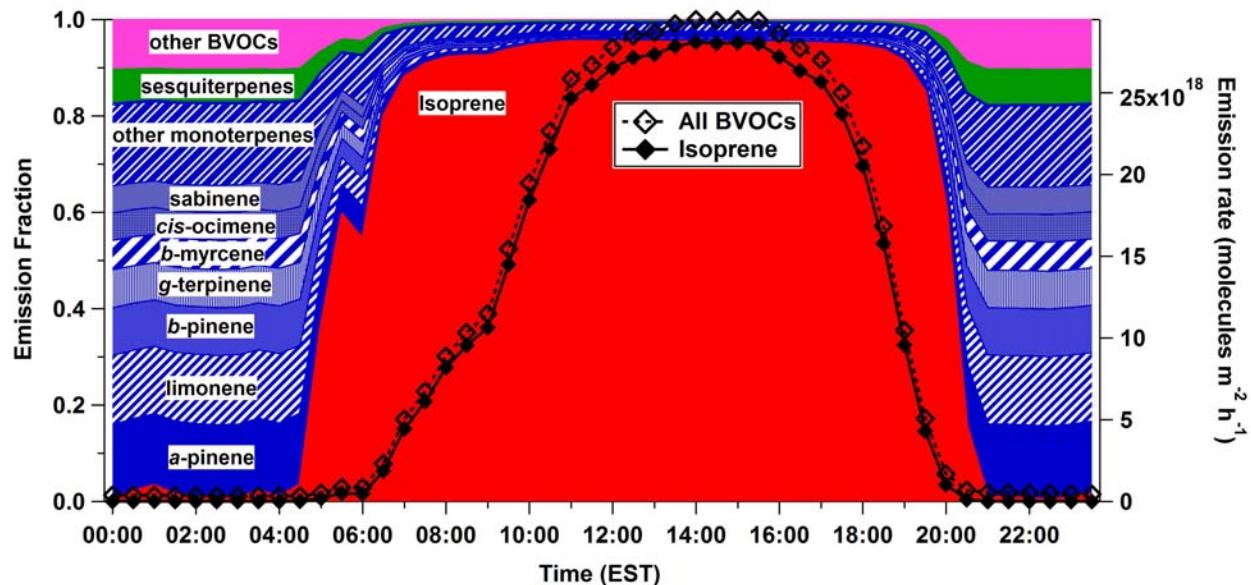


166  
 167 **Figure S3.** Calculated average diurnal cycle of  $\delta$ , used in the model and defined in Section 2.2.4  
 168 as the fraction of time  $\text{RO}_2$  reacts with NO versus  $\text{HO}_2$  and  $\text{RO}_2$ . If we assume that the actual  
 169 “ $\text{HO}_2$ ” concentrations were half the measured values due to an interference from isoprene  $\text{RO}_2$ ,  
 170 this translates to an average diurnal increase in  $\delta$  of 0.12 (range of 0.02-0.17); as shown here, the  
 171 primary effect would be a relative increase in  $\text{RONO}_2$  production in the mid-day and nighttime.  
 172



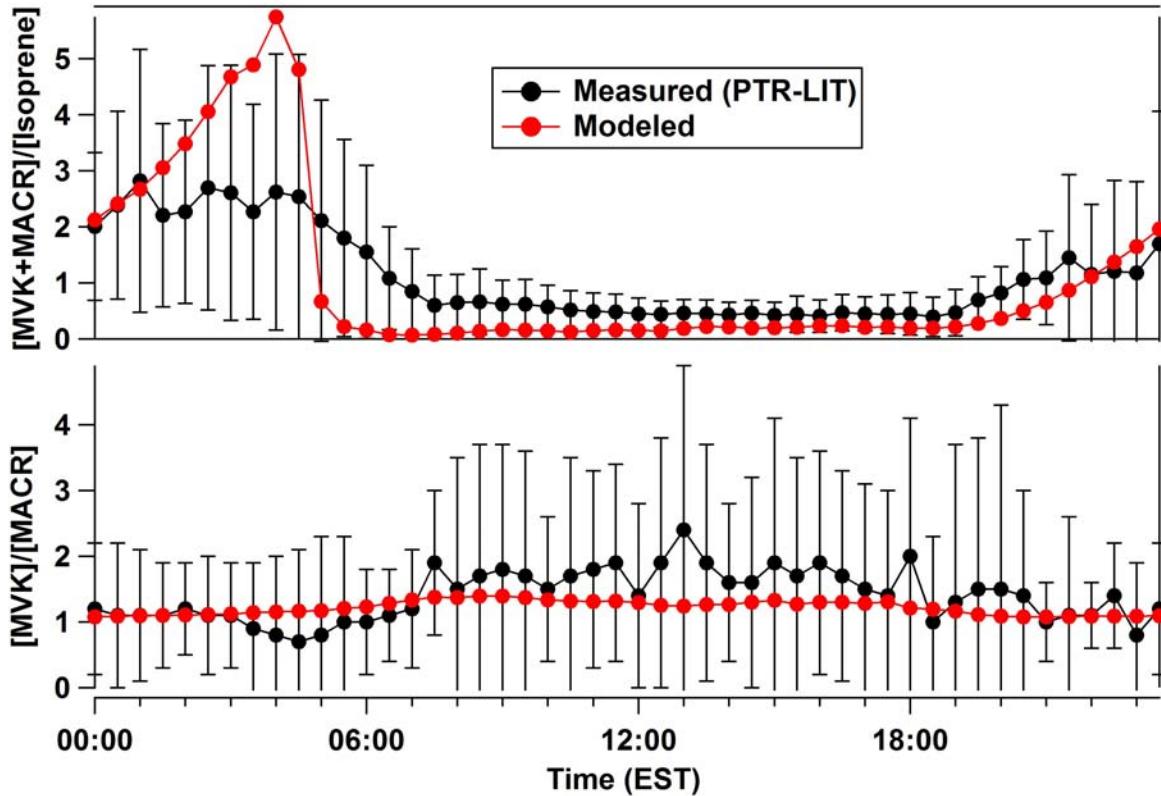
173  
174  
175  
176  
177

**Figure S4.** Diurnal cycle of calculated wind speed (0.5 hour time resolution) versus altitude. The logarithmic wind profile scaling (equation XII) does not account for atmospheric stability and may underestimate nighttime winds, particularly above 100 m.

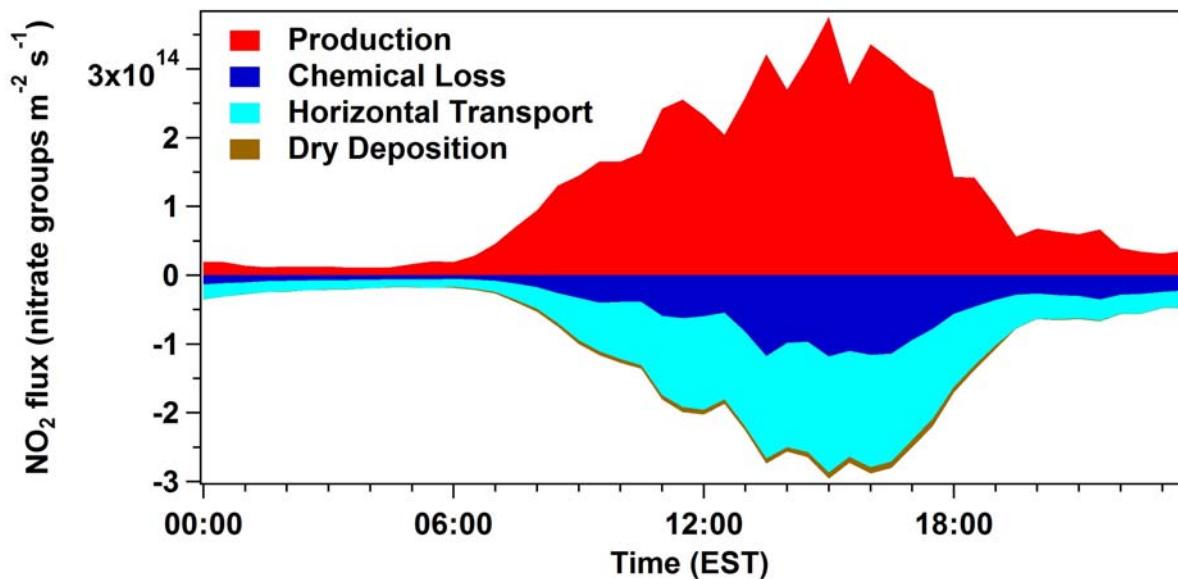


178  
179  
180  
181

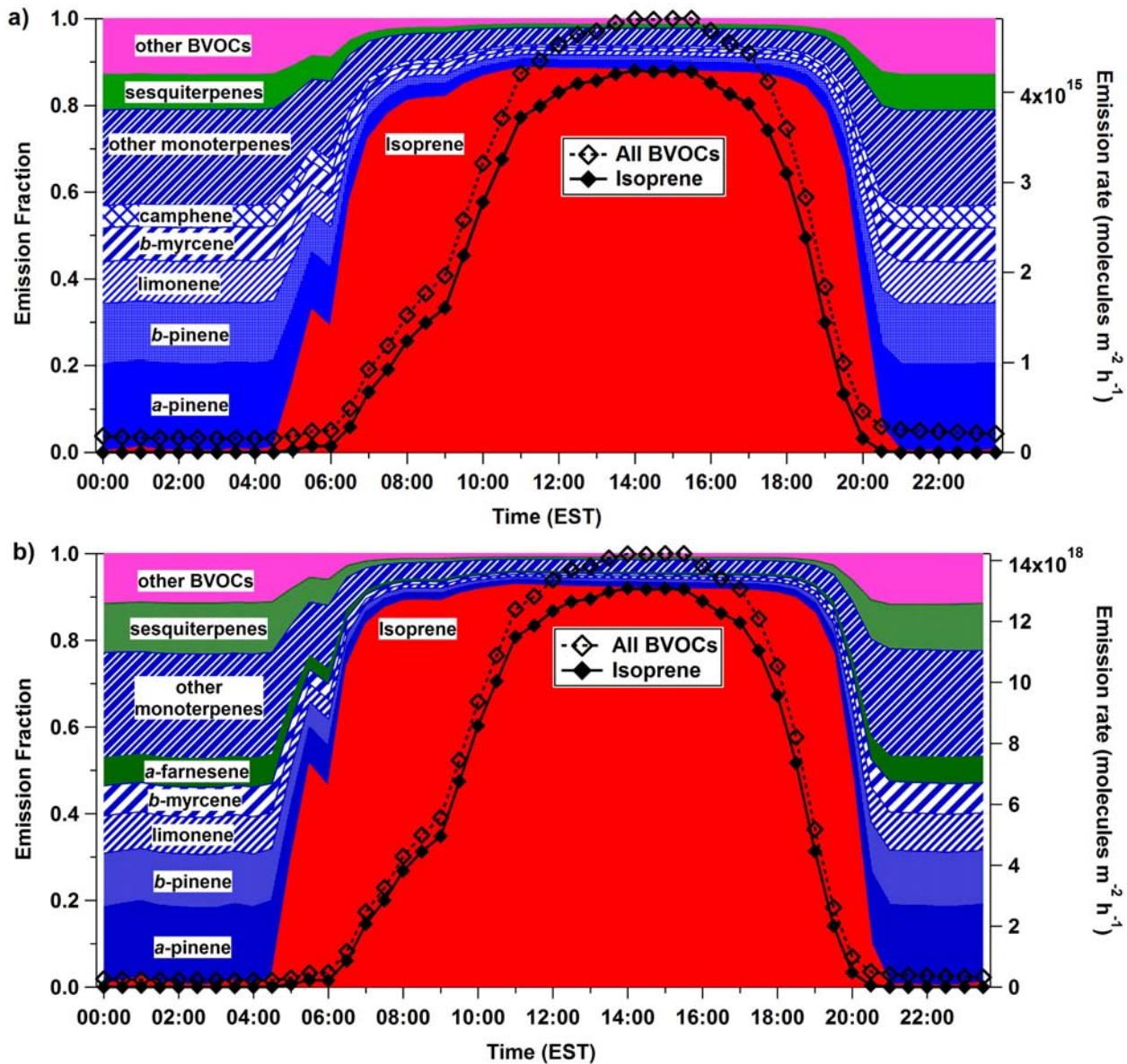
**Figure S5.** Diurnal cycle of calculated absolute (lines, right axis) and fractional (colors, left axis) emission rates (base scenario) of BVOCs at UMBS.

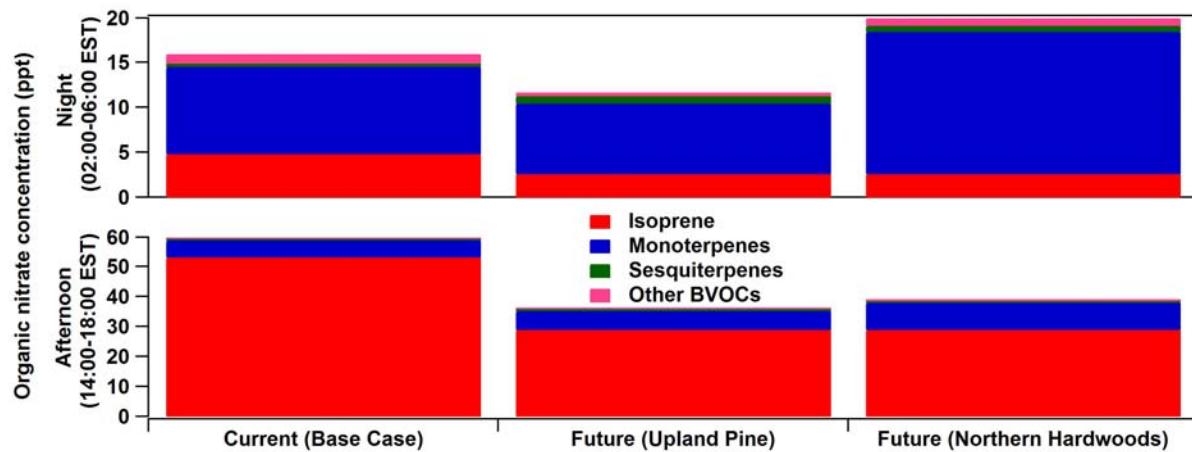


182  
 183 **Figure S6.** Diurnal cycles of modeled and measured [methyl vinyl ketone (MVK) +  
 184 methacrolein (MACR)]/[isoprene] and [MVK]/[MACR] at ~12 m above the forest canopy.  
 185 July-August 2008 measurements were completed using a proton-transfer reaction linear ion trap  
 186 mass spectrometer (PTR-LIT) (Mielke et al., 2010). For nighttime periods when few PTR-LIT  
 187 MS/MS measurements of [MVK] and [MACR] were made, PTR-LIT [MVK+MACR] data were  
 188 utilized to obtain estimated [MVK] and [MACR] by applying 0.5 h average [MVK]/[MACR]  
 189 from the previous UMBS study by Apel et al. (2002). Sensitivity to uncertainties and variability  
 190 are indicated by error bars.  
 191



192  
193 **Figure S7.** Modeled diurnal cycle of total column nitrate flux due to addition (organic nitrate  
194 production) and loss processes (chemical reaction, horizontal advection, and dry deposition).  
195 Loss of individual primary and secondary nitrates are shown, as well as the production of  
196 secondary nitrates, with dinitrate fluxes multiplied by two to represent the two nitrate groups  
197 present within these molecules.  
198





205  
206 **Figure S9.** Comparison of simulated biogenic organic nitrate concentrations at ~12 m above the  
207 forest canopy for the current forest (base case), compared to the two future forest scenarios  
208 (upland pine and northern hardwoods).

209 **References**

210 Apel, E. C., Riemer, D. D., Hills, A., Baugh, W., Orlando, J., Faloona, I., Tan, D., Brune, W.,  
211 Lamb, B., Westberg, H., Carroll, M. A., Thornberry, T., and Geron, C. D.: Measurement  
212 and interpretation of isoprene fluxes and isoprene, methacrolein, and methyl vinyl ketone  
213 mixing ratios at the PROPHET site during the 1998 Intensive, *J. Geophys. Res.*, 107,  
214 doi:10.1029/2000JD000225, 2002.

215 Arey, J., Aschmann, S. M., Kwok, E. S. C., and Atkinson, R.: Alkyl nitrate, hydroxy nitrate, and  
216 hydroxycarbonyl formation from the  $\text{NO}_x$ -air photooxidations of  $\text{C}_5\text{-C}_8$  *n*-alkanes, *J.*  
217 *Phys. Chem. A*, 105, 1020-1027, 2001.

218 Atkinson, R., Hasegawa, J., and Aschmann, S. M.: Rate constants for the gas-phase reactions of  
219  $\text{O}_3$  with a series of monoterpenes and related compounds at  $296 \pm 2$  K, *Int. J. Chem.*  
220 *Kinet.*, 22, 871-887, 1990.

221 Atkinson, R., Arey, J., Aschmann, S. M., Corchnoy, S. B., and Shu, Y.: Rate constants for the  
222 gas-phase reactions of *cis*-3-hexen-1-ol, *cis*-3-hexenylacetate, *trans*-2-hexenal, and  
223 linalool with OH and  $\text{NO}_3$  radicals and  $\text{O}_3$  at  $296 \pm 2$  K, and OH radical formation yields  
224 from the  $\text{O}_3$  reactions, *Int. J. Chem. Kinet.*, 27, 941-955, 1995.

225 Atkinson, R., and Arey, J.: Atmospheric chemistry of biogenic organic compounds, *Acc. Chem.*  
226 *Res.*, 31, 574-583, 1998.

227 Atkinson, R., and Arey, J.: Atmospheric degradation of volatile organic compounds, *Chem.*  
228 *Rev.*, 103, 4605-4638, 2003.

229 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin,  
230 M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for  
231 atmospheric chemistry: Volume I - gas phase reactions of  $\text{O}_x$ ,  $\text{HO}_x$ ,  $\text{NO}_x$  and  $\text{SO}_x$  species,  
232 *Atmos. Chem. Phys.*, 4, 1461-1738, 2004.

233 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin,  
234 M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for  
235 atmospheric chemistry: Volume II - gas phase reactions of organic species, *Atmos.*  
236 *Chem. Phys.*, 6, 2006.

237 Carter, W. P. L., and Atkinson, R.: Development and evaluation of a detailed mechanism for the  
238 atmospheric reactions of isoprene and NO<sub>x</sub>, *Int. J. Chem. Kinet.*, 28, 497-530, 1996.

239 Corchnoy, S. B., and Atkinson, R.: Kinetics of the gas-phase reactions of OH and NO<sub>3</sub> radicals  
240 with 2-carene, 1,8-cineole, *p*-cymene, and terpinolene, *Environ. Sci. Technol.*, 24, 1497-  
241 1502, 1990.

242 Costa, A. W.: Coupling between the carbon and nitrogen cycles in a forested environment,  
243 Ph.D., Chemistry, Purdue University, West Lafayette, IN, 279 pp., 2011.

244 Crow, T. R., and Erdmann, G. G.: Weight and volume equations and tables for red maples in the  
245 Lake States, U.S. Forest Service Research Paper, NC-242, 14, 1983.

246 Espada, C., Grossenbacher, J. W., Ford, K., Couch, T., and Shepson, P. B.: The production of  
247 organic nitrates from various anthropogenic volatile organic compounds, *Int. J. Chem.*  
248 *Kinet.*, 37, 675-685, 2005.

249 Espada, C., and Shepson, P. B.: The production of organic nitrates from atmospheric oxidation of  
250 ethers and glycol ethers, *Int. J. Chem. Kinet.*, 37, 686-699, 2005.

251 Hocker, H. W., and Early, D. J.: Biomass and leaf area equations for northern forest species,  
252 New Hampshire Agricultural Experiment Station University of New Hampshire Research  
253 Report, 102, 27, 1983.

254 Hurst, J. M., Barket, D. J., Herrera-Gomez, O., Couch, T. L., Shepson, P. B., Faloona, I., Tan,  
255 D., Brune, W., Westberg, H., Lamb, B., Biesenthal, T., Young, V., Goldstein, A.,

256 Munger, J. W., Thornberry, T., and Carroll, M. A.: Investigation of the nighttime decay  
257 of isoprene, *J. Geophys. Res.*, 106, 24335-24346, 2001.

258 Jones, B. T., and Ham, J. E.:  $\alpha$ -Terpineol reactions with the nitrate radical: Rate constant and  
259 gas-phase products, *Atmos. Environ.*, 42, 6689-6698, 2008.

260 Kerdouci, J., Picquet-Varrault, B., and Doussin, J. F.: Prediction of rate constants for gas-phase  
261 reactions of nitrate radical with organic compounds: A new structure-activity  
262 relationship, *Chem. Phys. Chem.*, 11, 3909-3920, 2010.

263 Kim, D., Stevens, P. S., and Hites, R. A.: Rate constants for the gas-phase reactions of OH and  
264 O<sub>3</sub> with  $\beta$ -ocimene,  $\beta$ -myrcene, and  $\alpha$ - and  $\beta$ -farnesene as a function of temperature, *J.*  
265 *Phys. Chem. A*, 115, 500-506, 2011.

266 Kim, S., Karl, T., Helmig, D., Daly, R., Rasmussen, R., and Guenther, A.: Measurement of  
267 atmospheric sesquiterpenes by proton transfer reaction-mass spectrometry (PTR-MS),  
268 *Atmos. Meas. Tech.*, 2, 99-102, 2009.

269 Mielke, L. H., Pratt, K. A., Shepson, P. B., McLuckey, S. A., Wisthaler, A., and Hansel, A.:  
270 Quantitative determination of biogenic volatile organic compounds in the atmosphere  
271 using proton-transfer reaction linear ion trap mass spectrometry, *Anal. Chem.*, 82, 7952-  
272 7957, 2010.

273 Ng, N. L., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Kroll, J. H., Kwan, A. J., McCabe, D.  
274 C., Wennberg, P. O., Sorooshian, A., Murphy, S. M., Dalleska, N. F., Flagan, R. C., and  
275 Seinfeld, J. H.: Effect of NO<sub>x</sub> level on secondary organic aerosol (SOA) formation from  
276 the photooxidation of terpenes, *Atmos. Chem. Phys.*, 7, 5159-5174, 2007.

277 O'Brien, J. M., Czuba, E., Hastie, D., Francisco, J. S., and Shepson, P. B.: Determination of the  
278 hydroxy nitrate yields from the reaction of C<sub>2</sub>-C<sub>6</sub> alkenes with OH in the presence of NO,  
279 J. Phys. Chem. A, 102, 8903-8908, 1998.

280 Ortega, J., Helmig, D., Guenther, A., Harley, P., Pressley, S., and Vogel, C.: Flux estimates and  
281 OH reaction potential of reactive biogenic volatile organic compounds (BVOCs) from a  
282 mixed northern hardwood forest, Atmos. Environ., 41, 5479-5495, 2007.

283 Ortega, J., Helmig, D., Daly, R. W., Tanner, D. M., Guenther, A. B., and Herrick, J. D.:  
284 Approaches for quantifying reactive and low-volatility biogenic organic compound  
285 emissions by vegetation enclosure techniques - Part B: Applications, Chemosphere, 72,  
286 365-380, 2008.

287 Pastor, J., and Bockheim, J. G.: Biomass and production of an aspen-mixed hardwood-spodosol  
288 ecosystem in northern Wisconsin, Can. J. For. Res., 11, 132-138, 1981.

289 Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kroll, J. H., Seinfeld, J. H., and Wennberg, P. O.:  
290 Isoprene photooxidation: new insights into the production of acids and organic nitrates,  
291 Atmos. Chem. Phys., 9, 1479-1501, 2009.

292 Perala, D. A., and Alban, D. H.: Allometric biomass estimators for aspen-dominated ecosystems  
293 in the Upper Great Lakes, U.S. Forest Service Research Paper, NC-134, 38, 1994.

294 Pfrang, C., King, M. D., Canosa-Mas, C. E., and Wayne, R. P.: Structure-activity relations  
295 (SARs) for gas-phase reactions of NO<sub>3</sub>, OH and O<sub>3</sub> with alkenes: An update, Atmos.  
296 Environ., 40, 1180-1186, 2006.

297 Pollmann, J., Ortega, J., and Helmig, D.: Analysis of atmospheric sesquiterpenes: Sampling  
298 losses and mitigation of ozone interferences, Environ. Sci. Technol., 39, 9620-9629,  
299 2005.

300 Pressley, S., Lamb, B., Westberg, H., Flaherty, J., Chen, J., and Vogel, C.: Long-term isoprene  
301 flux measurements above a northern hardwood forest, *J. Geophys. Res.*, 110,  
302 doi:10.1029/2004JD005523, 2005.

303 Reissell, A., Arey, J., and Atkinson, R.: Atmospheric chemistry of camphor, *Int. J. Chem. Kinet.*,  
304 33, 56-63, 2001.

305 Ribe, J. H.: Puckerbrush weight tables, *Miscellaneous Report 152*, Life Sciences and  
306 Agricultural Experiment Station. University of Maine. Orono, ME, 92 pp., 1973.

307 Ruppert, L., and Becker, K. H.: A product study of the OH radical-initiated oxidation of  
308 isoprene: formation of C5-unsaturated diols, *Atmos. Environ.*, 34, 1529-1542, 2000.

309 Ter-Michaelian, M. T., and Korzukhin, M. D.: Biomass equations for sixty-five North American  
310 tree species, *Forest Ecol. Manage.*, 97, 1-24, 1997.

311 USEPA: *Estimation Programs Interface Suite<sup>TM</sup>* for Microsoft<sup>®</sup> Windows, v 4.0, United State  
312 Environmental Protection Agency, Washington, DC, USA, 2010.

313 Wells, J. R.: Gas-phase chemistry of  $\alpha$ -terpineol with ozone and OH radical: Rate constants and  
314 products, *Environ. Sci. Technol.*, 39, 6937-6943, 2005.

315 Young, H. E., Ribe, J. H., and Wainwright, K.: Weight tables for tree and shrub species in  
316 Maine, *Miscellaneous Report 230*, Life Sciences and Agriculture Experiment Station.  
317 University of Maine. Orono, ME, 84 pp., 1981.

318

319