

1 **Supporting Information:**

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

4
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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 km² 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 m² 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⁻² 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 β -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 monoterpene (MT) and sesquiterpene (SQT) β -factors were calculated to be 0.19 K⁻¹ and 0.14 K⁻¹
48 ¹, respectively. For the northern hardwoods future forest scenario, the SQT β -factor was
49 calculated to be 0.15 K⁻¹; due to uncertainties in the measured aspen MT β -factor, the average
50 MT β -factor (0.14 K⁻¹) 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 ± 32 -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 ~20-
69 30% [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 ~20-30% [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 β -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 NO₃ concentrations*

82 Nitrate radicals are primarily produced by reaction of NO₂ with O₃ and generally
83 removed by photolysis and reaction with NO, as described by reactions 1-3:

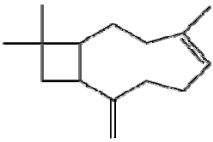
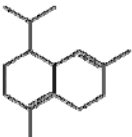
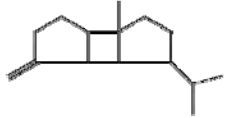
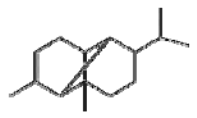
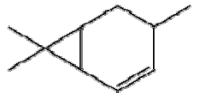
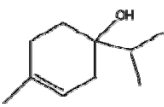
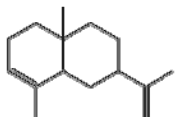
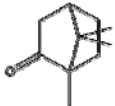
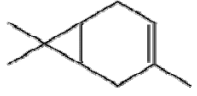
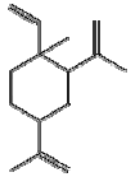
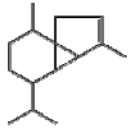



88 The NO₃ production and loss reactions included in the box model are described in Table S4 with
89 their corresponding rate constants. Total sesquiterpene (SQT) concentrations were estimated
90 using the noontime average [SQT]/[MT] ratio measured by Kim et al. (2009) at the PROPHET
91 site (July-August 2005) and the measured total MT concentration for July-August 2008 (PTR-
92 LIT). NO₃ 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). NO₃ 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 NO₃ diurnal profile for sunny days in July-August 2008.

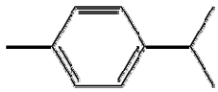
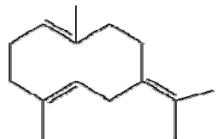
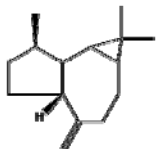
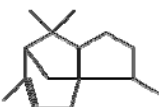

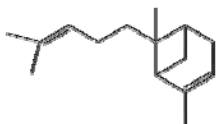
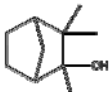
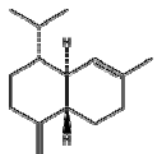
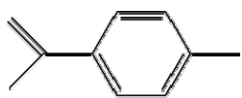


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100 **Table S1.** BVOCs identified during branch-enclosure emission measurements for UMBS tree
 101 species. Corresponding reaction rate constants (units of $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$) for OH, O_3 , and NO_3 at
 102 298 K (k_{OH} , k_{O_3} , and k_{NO_3} , respectively) and RONO_2 yields for reactions with OH and NO_3 (γ_{OH}
 103 and γ_{NO_3} , respectively) are included for each BVOC identified. Individual BVOCs are displayed
 104 in order of simulated RONO_2 contribution; BVOCs contributing >0.5 ppt RONO_2 (at ~ 12 m
 105 above forest canopy) at any time are shown in Table 1.

BVOC	Structure	k_{OH} k_{O_3} k_{NO_3} ($\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$)	RONO_2 : γ_{OH} γ_{NO_3}
β -linalool ($\text{C}_{10}\text{H}_{18}\text{O}$)		1.59×10^{-10} a) 4.3×10^{-16} a) 1.12×10^{-11} a)	0.30 b) 0.31 c)
camphene ($\text{C}_{10}\text{H}_{16}$)		5.30×10^{-11} d) 9.0×10^{-19} d) 6.6×10^{-13} d)	0.23 e) 0.31 c)
α -farnesene ($\text{C}_{15}\text{H}_{24}$)		2.19×10^{-10} f) 5.94×10^{-16} f) 2.1×10^{-11} g)	0.29 h) 0.31 c)
β -phellandrene ($\text{C}_{10}\text{H}_{16}$)		1.68×10^{-10} d) 4.7×10^{-17} d) 8.0×10^{-12} d)	0.18 h) 0.31 c)
α -phellandrene ($\text{C}_{10}\text{H}_{16}$)		3.13×10^{-10} d) 3.0×10^{-15} d) 7.3×10^{-11} d)	0.18 h) 0.31 c)
terpinolene ($\text{C}_{10}\text{H}_{16}$)		2.25×10^{-10} d) 1.9×10^{-15} d) 9.7×10^{-11} d)	0.18 h) 0.31 c)
<i>allo</i> -ocimene ($\text{C}_{10}\text{H}_{16}$)		2.36×10^{-10} i) 4.16×10^{-16} i) 1.1×10^{-11} g)	0.18 h) 0.31 c)
dimethylnonatriene ($\text{C}_{11}\text{H}_{18}$)		2.32×10^{-10} i) 7.50×10^{-16} i) 9.6×10^{-12} g)	0.20 h) 0.31 c)
α -terpineol ($\text{C}_{10}\text{H}_{18}\text{O}$)		1.9×10^{-10} j) 3.0×10^{-16} j) 1.60×10^{-11} k)	0.30 b) 0.31 c)
α -terpinene ($\text{C}_{10}\text{H}_{16}$)		3.63×10^{-10} d) 2.1×10^{-14} d) 1.4×10^{-11} d)	0.18 h) 0.31 c)
β -selinene ($\text{C}_{15}\text{H}_{24}$)		1.17×10^{-10} i) 2.40×10^{-17} i) 6.5×10^{-13} g)	0.29 h) 0.31 c)

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

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

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

- 109 d) Atkinson and Arey (2003)
- 110 e) β -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 (g·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.

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

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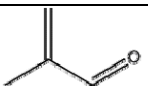
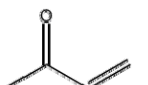
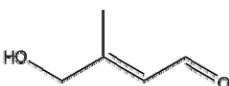
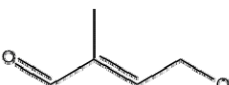
138

139 **Table S4.** NO₃ production and loss reactions included in the box model with corresponding rate
 140 constants.

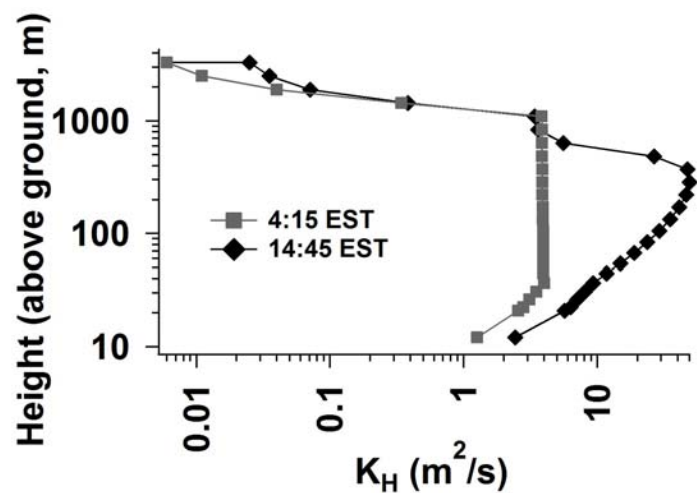
Reaction	k (cm ³ molec ⁻¹ s ⁻¹)	Reference
NO ₃ + NO → 2NO ₂	2.6 × 10 ⁻¹¹	(Atkinson et al., 2004)
NO ₃ + NO ₂ → N ₂ O ₅	1.9 × 10 ⁻¹²	(Atkinson et al., 2004)
NO ₃ + OH → NO ₂ + HO ₂	2.0 × 10 ⁻¹¹	(Atkinson et al., 2004)
NO ₃ + HO ₂ → HNO ₃ + O ₂	4.0 × 10 ⁻¹²	(Atkinson et al., 2004)
NO ₃ + RO ₂ → RO + NO ₂	4.0 × 10 ⁻¹²	Assumed same as HO ₂ reaction
NO ₃ + Isoprene → Products	7.0 × 10 ⁻¹³	(Atkinson and Arey, 2003)
NO ₃ + MTs → Products	1.4 × 10 ⁻¹¹	Emission weighted average (see Table 1 for individual k _{NO3})
NO ₃ + SQTs → Products	1.7 × 10 ⁻¹¹	Emission weighted average (see Table 1 for individual k _{NO3})
NO ₃ + MACR → Products	3.4 × 10 ⁻¹⁵	(Atkinson and Arey, 2003)
NO ₃ + MVK → Products	(<)6 × 10 ⁻¹⁵	(Atkinson and Arey, 2003)
NO ₂ + O ₃ → NO ₃ + O ₂	3.5 × 10 ⁻¹⁷	(Atkinson et al., 2004)
NO + O ₃ → NO ₂ + O ₂	1.8 × 10 ⁻¹⁴	(Atkinson et al., 2004)
N ₂ O ₅ → NO ₃ + NO ₂	6.9 × 10 ⁻² s ⁻¹	(Atkinson et al., 2004)
NO ₃ → particles	4.0 × 10 ⁻³ s ⁻¹	(Hurst et al., 2001)
N ₂ O ₅ → particles	9.3 × 10 ⁻⁴ s ⁻¹	(Hurst et al., 2001)
NO ₃ + hv → NO ₂ + O	variable	NCAR TUV model
NO ₃ + hv → NO + O ₂	variable	NCAR TUV model

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 142

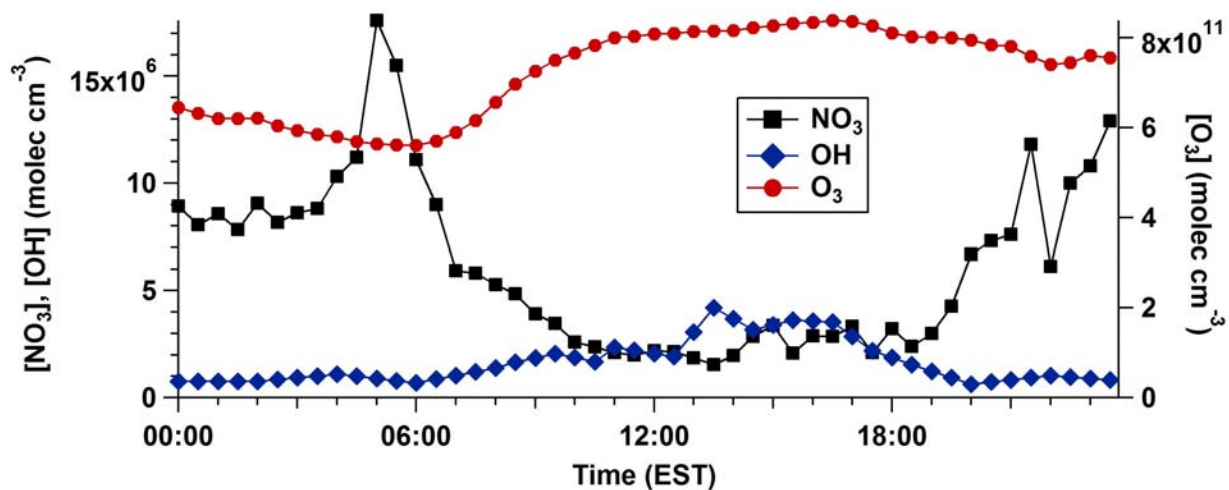
143 **Table S5.** First generation isoprene oxidation products with yields from isoprene oxidation,
 144 oxidation rate constants (units of $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$), and RONO_2 yields. Methacrolein (MACR)
 145 and methyl vinyl ketone (MVK) yields by OH oxidation are defined within the model based on
 146 the availability of NO, as represented by β (defined in the text as the fraction of time RO_2 reacts
 147 with NO versus HO_2 and RO_2), using high and low NO_x chamber yields from Ruppert and
 148 Becker (2000). The structures of 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			RONO_2 :				
		Y_{OH}	Y_{O_3}	Y_{NO_3}	k_{OH}	k_{O_3}	k_{NO_3}	Y_{OH}	Y_{NO_3}
MACR		0.18-0.20 a)			2.9×10^{-11} c)			0.0705 d)	
		0.39 b)			1.2×10^{-18} c)			0.24 e)	
		0.035 b)			3.4×10^{-15} c)				
MVK		0.15-0.31 a)			2.0×10^{-11} c)			0.11 d)	
		0.16 b)			5.2×10^{-18} c)			0.24 e)	
		0.035 b)			$(<)6.0 \times 10^{-16}$ c)				
IP-HMY		0.15 e)			7.0×10^{-11} f)			0.075 e)	
		0 e)			1.0×10^{-17} f)			0.20 e)	
		0 e)			1.0×10^{-13} f)				
IP-MHY		0.13 e)			7.0×10^{-11} f)			0.075 e)	
		0 e)			1.0×10^{-17} f)			0.20 e)	
		0.32 f)			1.0×10^{-13} f)				

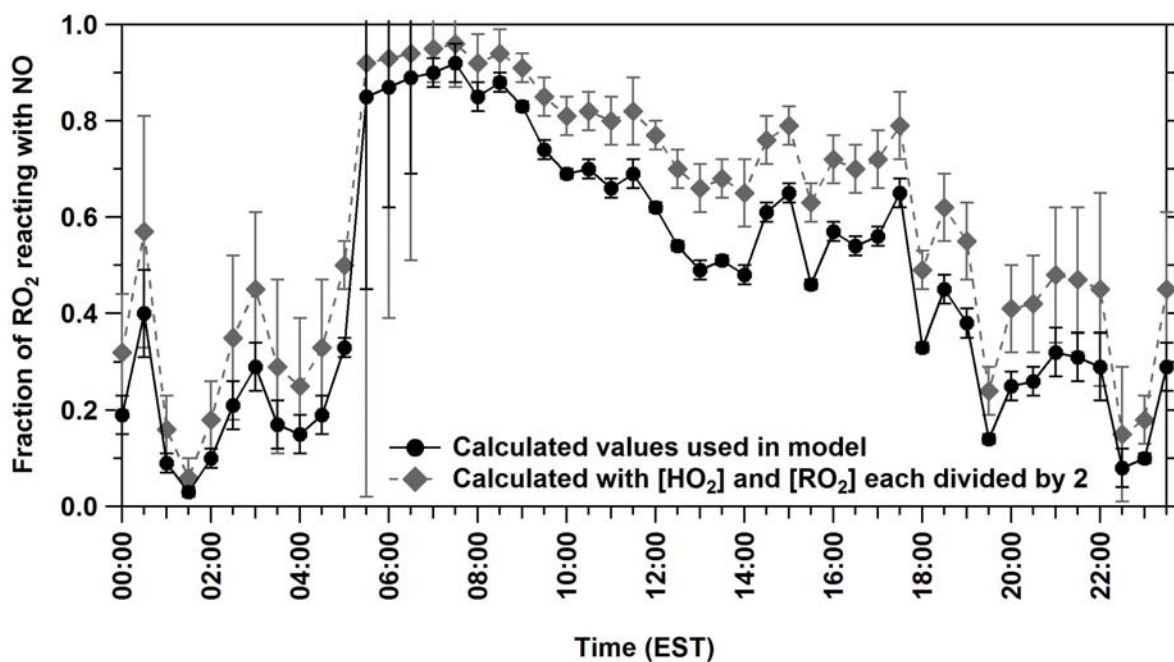
152 a) (Ruppert and Becker, 2000)
 153 b) (Atkinson and Arey, 1998)
 154 c) (Atkinson et al., 2006)
 155 d) (Paulot et al., 2009)
 156 e) Estimation by Costa (2011)
 157 f) (Carter and Atkinson, 1996)
 158



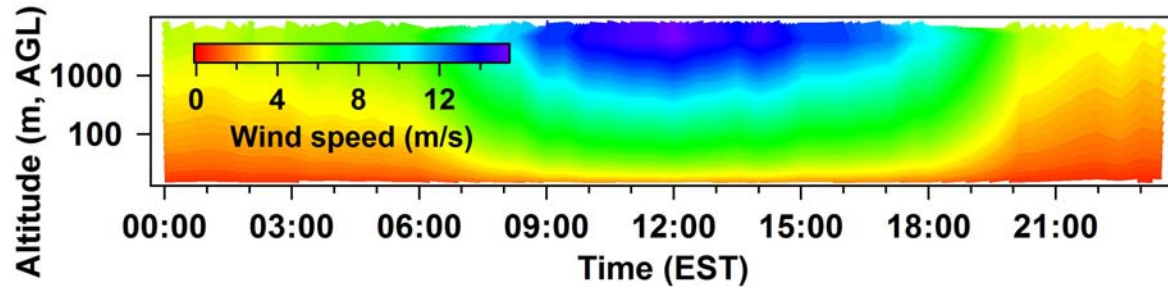
159
 160 **Figure S1.** Modeled thermal eddy diffusivity (K_H) profiles for UMBS in the summer at 4:15 and
 161 14:45 EST.
 162



163
 164 **Figure S2.** Diurnal cycles of the average concentrations of NO₃ (modeled), OH (measured), and
 165 O₃ (measured), used in the model, for 32 m above ground (10 m above canopy).

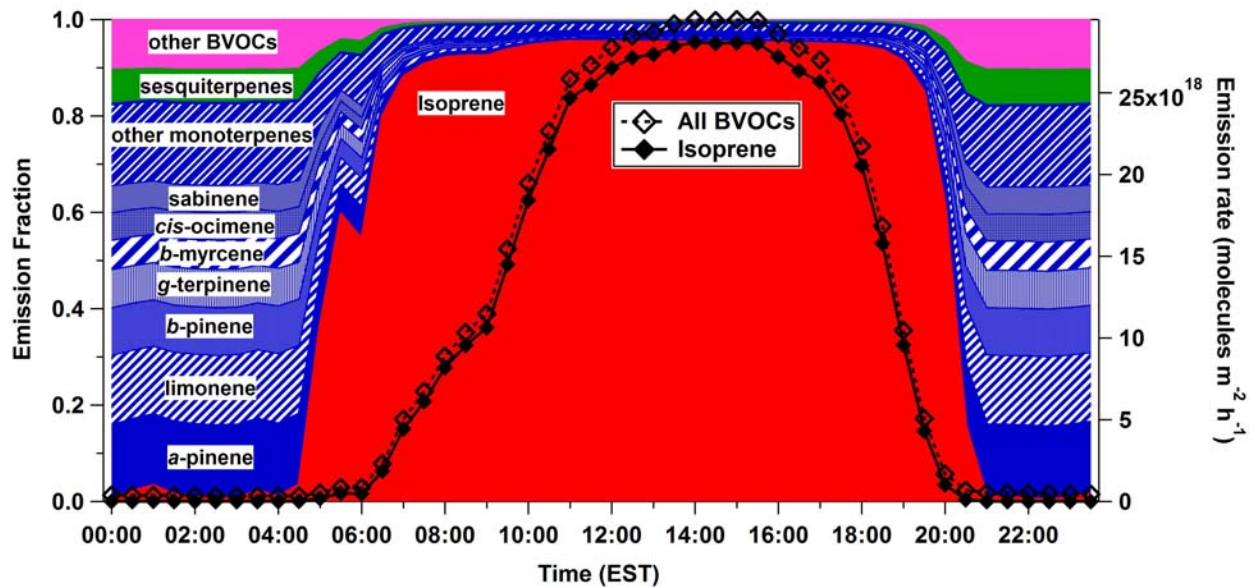


166
 167 **Figure S3.** Calculated average diurnal cycle of δ , used in the model and defined in Section 2.2.4
 168 as the fraction of time RO_2 reacts with NO versus HO_2 and RO_2 . If we assume that the actual
 169 “ HO_2 ” concentrations were half the measured values due to an interference from isoprene RO_2 ,
 170 this translates to an average diurnal increase in δ of 0.12 (range of 0.02-0.17); as shown here, the
 171 primary effect would be a relative increase in RONO_2 production in the mid-day and nighttime.
 172

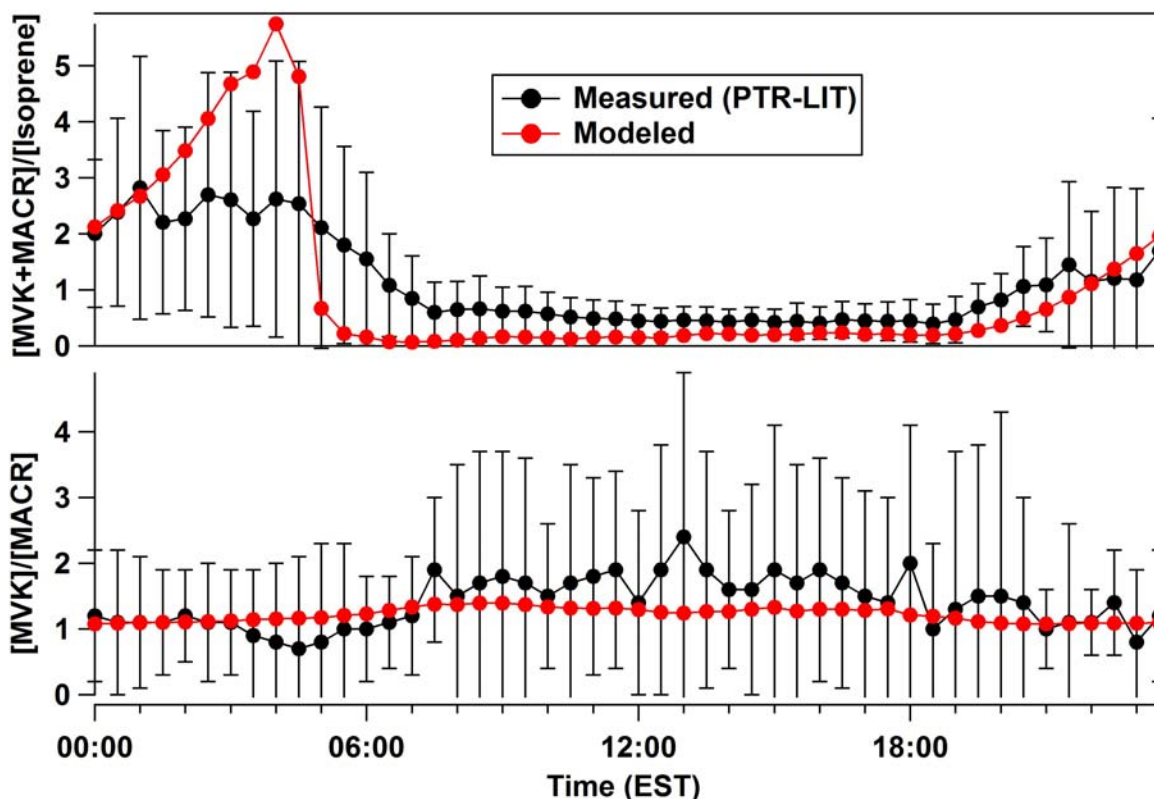


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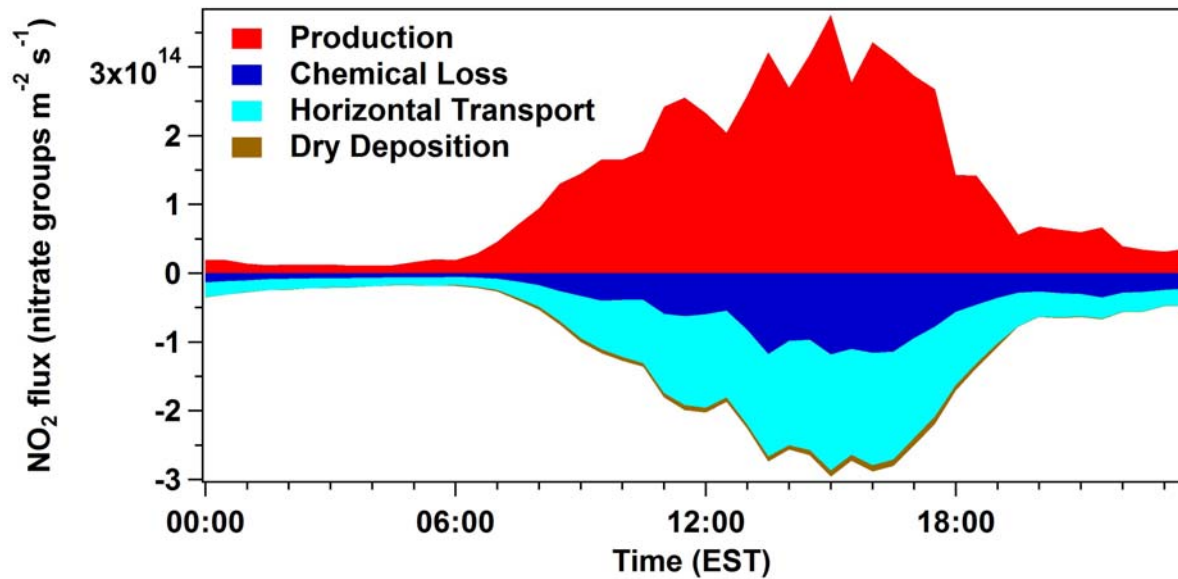
Figure S4. Diurnal cycle of calculated wind speed (0.5 hour time resolution) versus altitude. The logarithmic wind profile scaling (equation *XII*) does not account for atmospheric stability and may underestimate nighttime winds, particularly above 100 m.



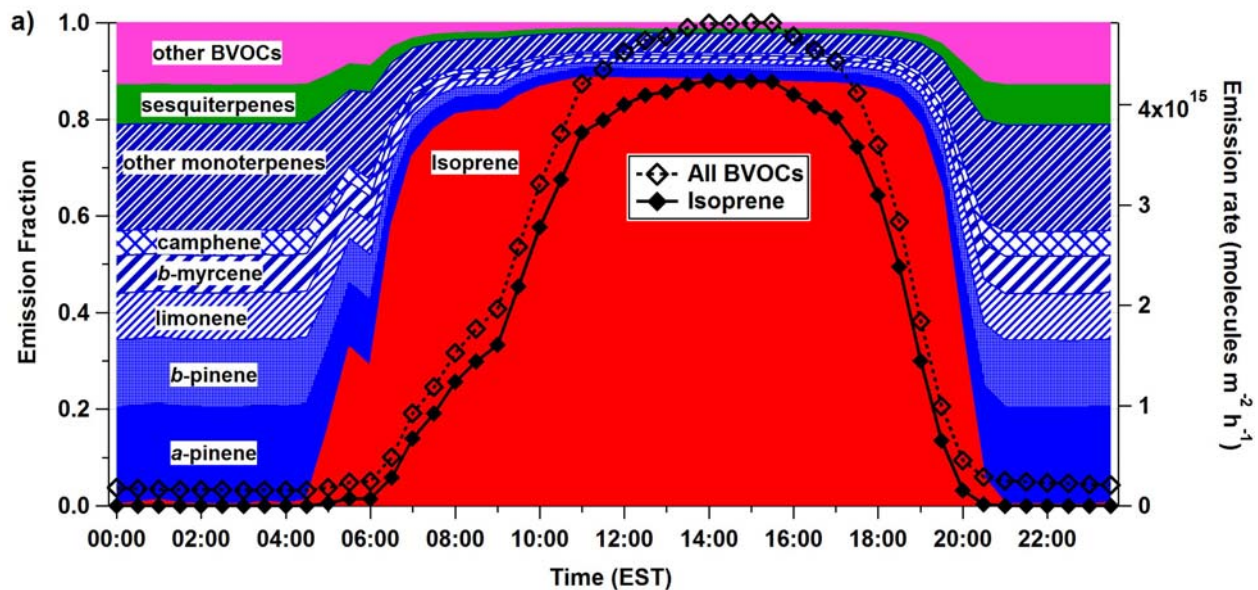
178
 179 **Figure S5.** Diurnal cycle of calculated absolute (lines, right axis) and fractional (colors, left axis)
 180 emission rates (base scenario) of BVOCs at UMBS.
 181



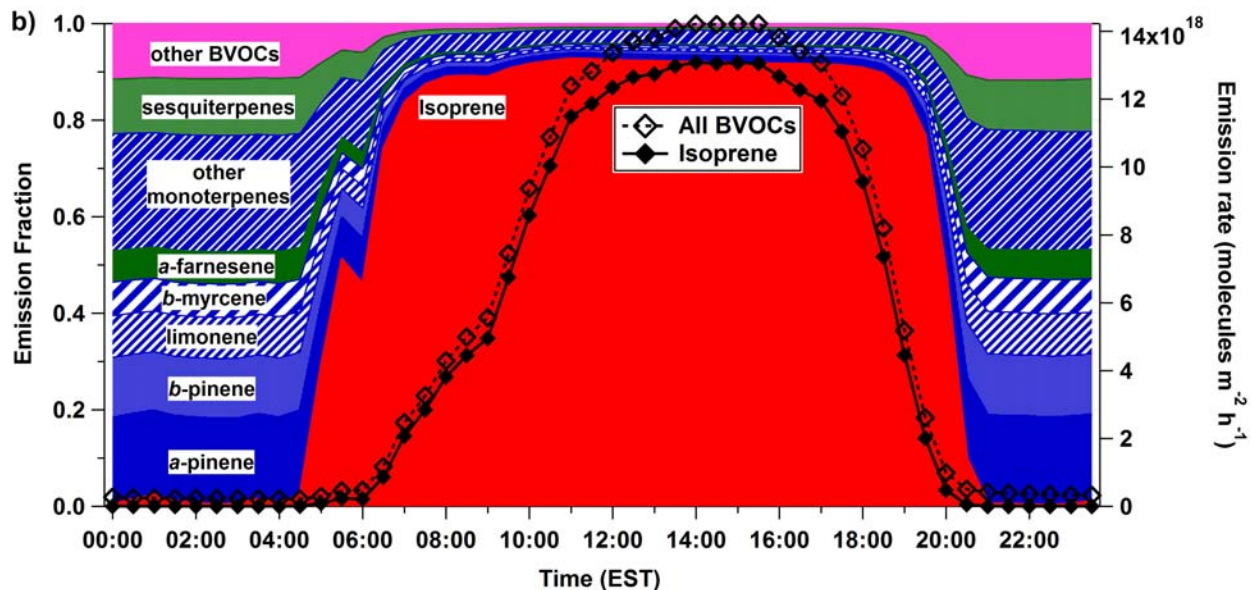
182
 183 **Figure S6.** Diurnal cycles of modeled and measured [methyl vinyl ketone (MVK) +
 184 methacrolein (MACR)]/[isoprene] and [MVK]/[MACR] at ~12 m above the forest canopy.
 185 July-August 2008 measurements were completed using a proton-transfer reaction linear ion trap
 186 mass spectrometer (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



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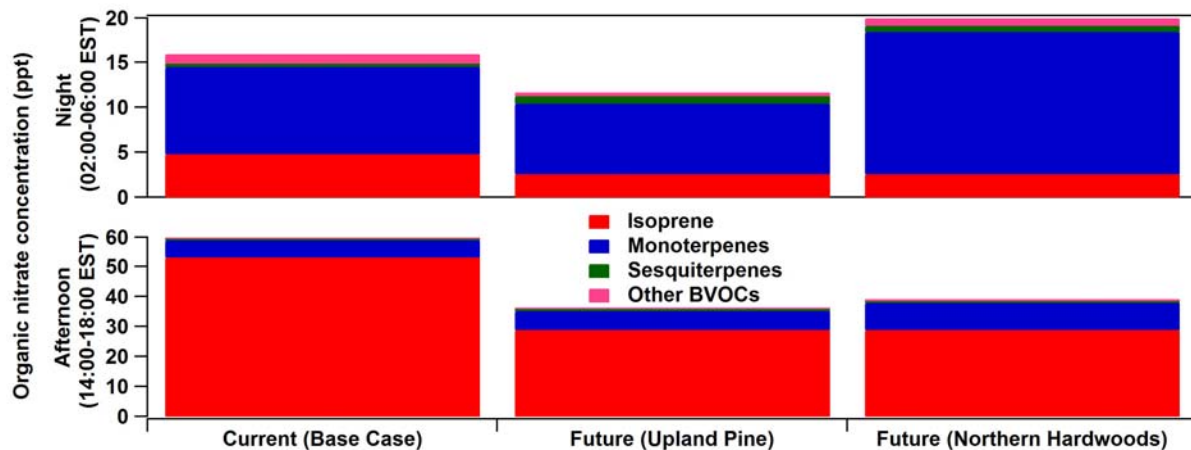
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Figure S8. Diurnal cycles of calculated absolute (lines, right axis) and fractional (colors, left axis) emission rates (base scenario) of BVOCs at UMBS following replacement of aspen by a) northern hardwoods or b) upland pine.



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).

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