

Photolysis Controls Atmospheric Budgets of Biogenic Secondary Organic Aerosol

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Supplementary Methods

Chamber Actinometry Measurements. J_{NO_2} of the chamber was quantified in three different ways.

First, the spectrally-resolved actinic flux of the chamber was measured (Supplementary Figure S7) with the SaSHE spectral radiometer. It was then translated to J_{NO_2} using:¹

$$J_{NO_2} = \int \Phi_{NO_2}(\lambda, T) \sigma_{NO_2}(\lambda, T) F(\theta, \lambda) d\lambda$$

where $\Phi_{NO_2}(\lambda, T)$ is the quantum yield of NO_2 , $\sigma_{NO_2}(\lambda, T)$ is the absorption cross-section of NO_2 , and $F(\theta, \lambda)$ is the actinic flux of the chamber lights. Spectrally-resolved quantum yield and absorption cross-section values for NO_2 were obtained from the JPL recommendation.² The resulting spectrally-resolved J_{NO_2} is plotted in Supplementary Figure S7B and the integrated J_{NO_2} value was 0.14 min^{-1} .

Second, J_{NO_2} was also measured chemically, through the measured concentrations of NO , NO_2 , and ozone. A chamber was simultaneously filled with NO and excess ozone in dry ($<5\%$ RH), dark conditions, which immediately produced NO_2 . After the lights are turned on, J_{NO_2} can be calculated using:³

$$J_{NO_2} = \frac{k_{NO}[NO][O_3]_{ss}}{[NO_2]}$$

where $k_{NO} = 0.0275 \text{ ppb min}^{-1}$. An average of 0.14 min^{-1} was obtained from two replicate measurements.

Finally, a J_{NO_2} filter radiometer was deployed in the center of the chamber to provide a real-time measurement for each experiment. The average value across the measurements period was 0.16 min^{-1} . In summary, three independent measurements of J_{NO_2} agreed to within the experimental error.

Experimental uncertainties. To quantify uncertainty and account for any biases introduced by the AMS analysis, all experiments were also analyzed using the Scanning Mobility Particle Sizer (SMPS) mass loadings. In this case, $J_{\text{photolysis}}$ was derived by fitting a first-order exponential to $[SMPS_{\text{mass}}]/[SMPS_{\text{mass}}]_0$, defined analogously to equivalent AMS quantities, and correcting this quantity for particulate wall loss obtained by fitting a first-order exponential to $[SMPS_{\text{number}}]/[SMPS_{\text{number}}]_0$. The dark corrections were also performed analogously to AMS. Supplementary Figures S8 and S9 show the results of this comparative analysis. For isoprene, the SMPS photolysis rates were systematically higher than AMS and the average difference was 17%. For α -pinene, no systematic bias was found, and the average difference was 7%. For

wet β -caryophyllene, the average difference was 12%. For mixed isoprene - α -pinene SOA, the average difference was 9%, and for mixed isoprene - β -caryophyllene SOA, the average difference was 11%. These errors should be considered together with error bars reported in the rest of the paper (from exponential fitting uncertainties or 1σ standard deviations for multiple experiments, as noted in figure captions), for a complete picture of uncertainties associated with these measurements.

We have also quantified the error associated with using the SMPS number concentrations to derive the particle wall loss rates for SMPS-based analysis. Particle number can be lost due to both coagulation and wall deposition. The coagulation rate was estimated using the sectional aerosol box model MOSAIC (Model for Simulating Aerosol Interactions and Chemistry).⁴ The logarithmically spaced bin structure in the MOSAIC was configured to that of the particle size distribution data provided by the SMPS. Aerosol size distribution in the model was initialized using observations at the beginning of the photolysis. The aerosols were assumed to be composed of two organic species with user-specified volatilities. The model was then used to reproduce the observed evolution of the aerosol number size distribution by taking into account coagulation and by tuning the wall loss constant and the species volatilities to simulate particle evaporation caused by photolysis. Four experiments representing different SOA peak mass loadings were selected, as shown in Supplementary Figure S10. Wall loss rates were estimated both using AMS [SO_4], and using MOSAIC. While the percent differences in wall loss time constant estimates were as high as 60% in $70 \mu\text{g}/\text{m}^3$ α -pinene SOA experiment (Figure S11A), they translated into small differences in photolysis time constants (Figure S11B, 7% for α -pinene and 10% for β -pinene).

Chamber wall loss. Particle wall loss in the chamber is an important factor in translating chamber experiments into measurements of atmospheric lifetime. As mentioned above, this was quantified using both the high resolution AMS sulfate loading and SMPS particle number concentration. Measurements for all chamber experiments for both chambers are shown in Supplementary Figure S11. On average, the two independent measurements differ by 50%. Supplementary Figure S11 represents wall losses through the lifetime of the chambers (i.e. no new chambers were installed during these experiments). The outliers at the

beginning of the experiments and around November, 2018 indicate periods of chamber service, where contact between the chamber and operator increased static charge on the chamber walls. Note that the majority of photolysis experiments are batch mode and monodisperse, which simplifies wall loss corrections.⁵

Use of H₂O₂ for OH Production. We note that the condensed-phase OH oxidation initiated by photolysis of aqueous phase hydrogen peroxide is not likely to account for the mass loss observations. If the effect of aqueous H₂O₂ was significant, the photolysis rates would also be expected to always increase under higher RH, and this is not the case for isoprene and α -pinene OH photooxidation SOA. As an addition test, we performed experiments measuring the photolysis rate of isoprene SOA formed with 1.5 ppm H₂O₂ instead of 7.5 ppm used in the majority of experiments (Supplementary Figure S12). While particle-phase measurements in Supplementary Figure S12 show that there is five times less H₂O₂ dissolved into particle phase in the experiments with 1.5 ppm H₂O₂, the rate of the mass loss remains the same.

SOA Coating Experiments. We also performed a series of experiments in which we coated isoprene SOA with α -pinene or β -caryophyllene SOA. In these experiments, isoprene SOA was prepared in the chamber under dry conditions, as described in the Methods section. UV lights were turned off once isoprene SOA loading has reached maximum. The second VOC was injected, either α -pinene or β -caryophyllene. The lights were then tuned on for a short (~1 hour) time to coat the original SOA. Following the coating period, the lights were turned off, the scavenger was injected and allowed to equilibrate for 30 minutes, and the lights were turned back on. Results from the coating experiments are summarized in Supplementary Figure S4. Volume coating fractions were calculated using SMPS data. As described in the main text, photolysis rates observed in these experiments generally followed those predicted using a volume-weighted mixing rule and the photolysis rates of the individual constituents. These experiments show that the presence of viscous SOA does not impact photolysis of isoprene SOA.

Supplementary Figures

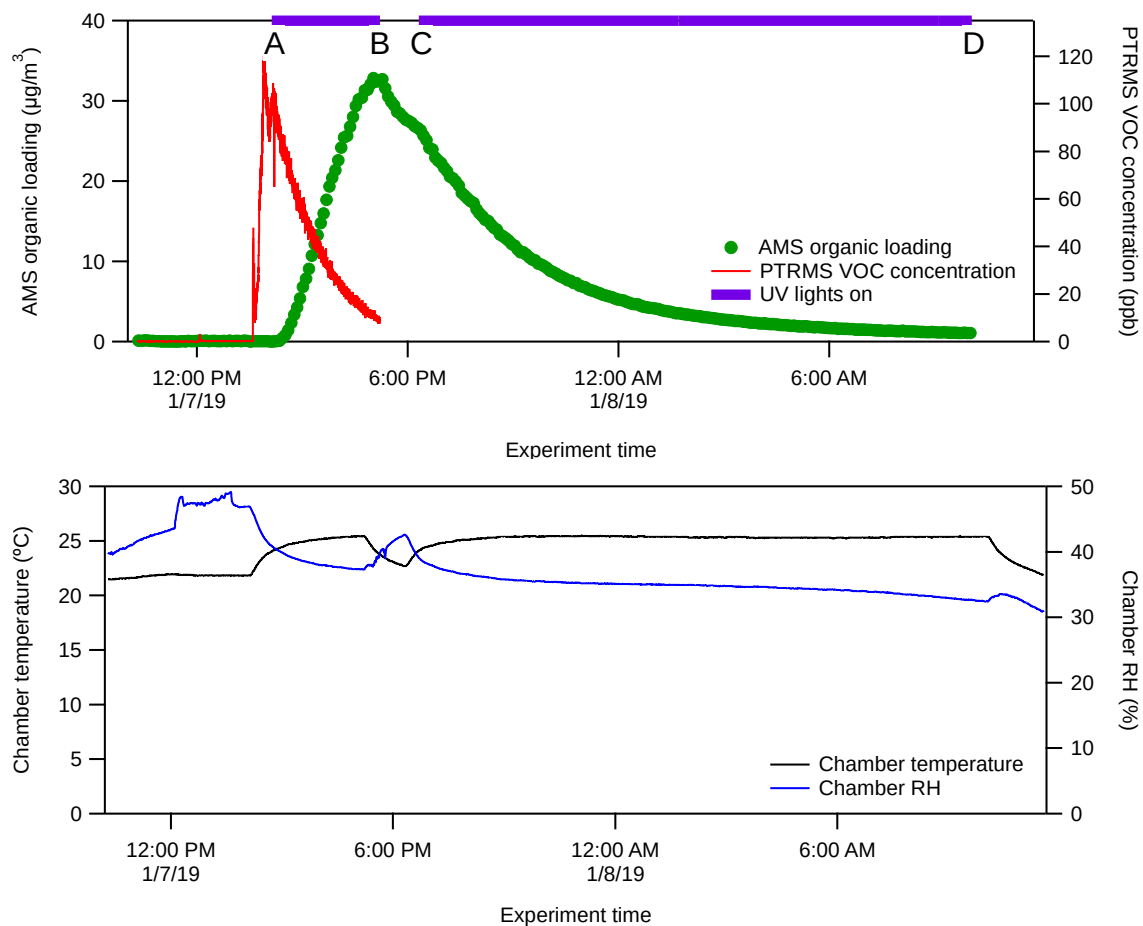


Figure S1. An example timeline for a photolysis experiment. Top panel: AMS organic loading and VOC (isoprene, in this case) concentration from PTR-MS. Bottom panel: Chamber temperature and RH. Points A, B, C and D are the key points of the experiment, see text.



Figure S2. Modeling domain used for the WRF-Chem model simulation of photolysis. The inset shows the model domain relative to geopolitical boundaries. The black dots represent surface measurement sites during GoAmazon 2014/5.⁶

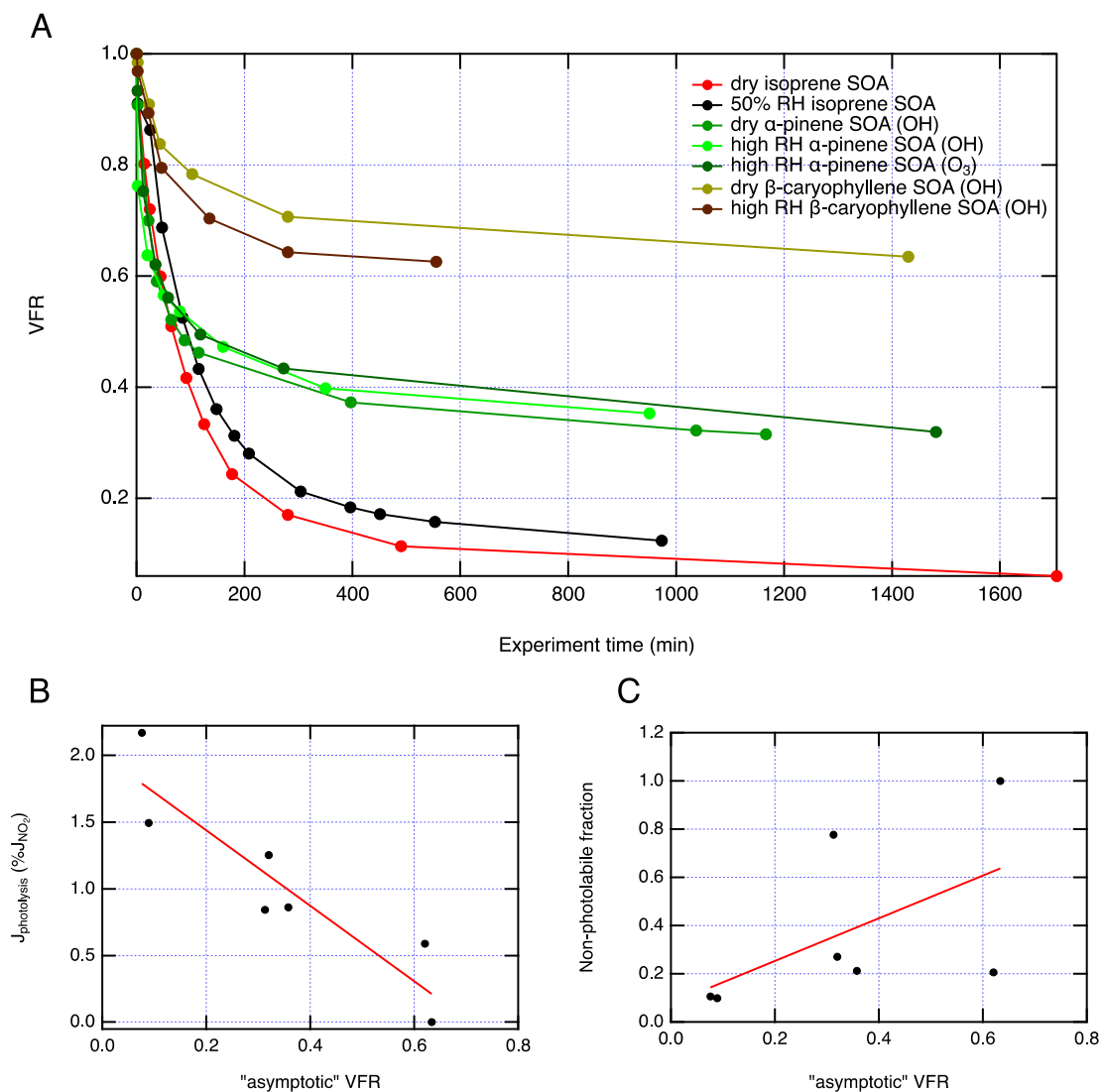


Figure S3. (A) Room-temperature evaporation kinetics plots for several SOA types generated in this study. (B) Correlation between the measured $J_{\text{photolysis}}$ values and asymptotic values of volume fraction remaining (VFR) at long evaporation times for seven types of SOA from (A). $R^2 = 0.83$. (C) Correlation between the measured non-photolabile fractions and asymptotic values of VFR at long evaporation times seven types of SOA from (A). $R^2 = 0.31$.

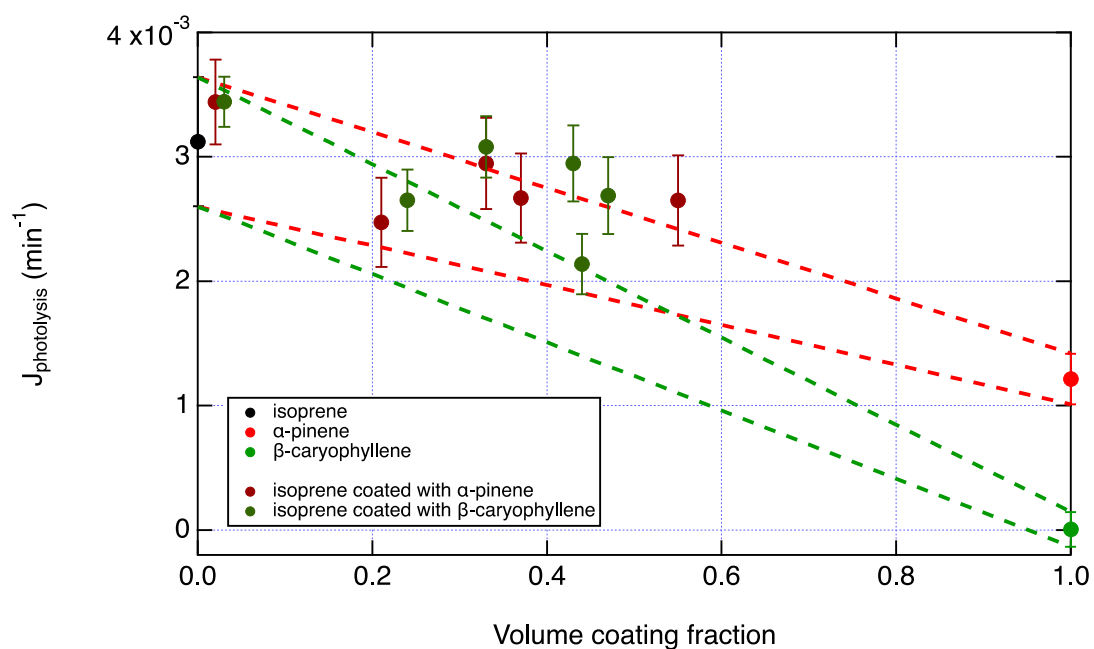


Figure S4. A study of the effects of mixed aerosols on photolysis. Isoprene SOA was coated with α -pinene or β -caryophyllene SOA and subsequently photolyzed. Dotted lines show "theoretical" mass loss rates for mixed particles, calculated based on volume fractions and photolysis rates of the two components.

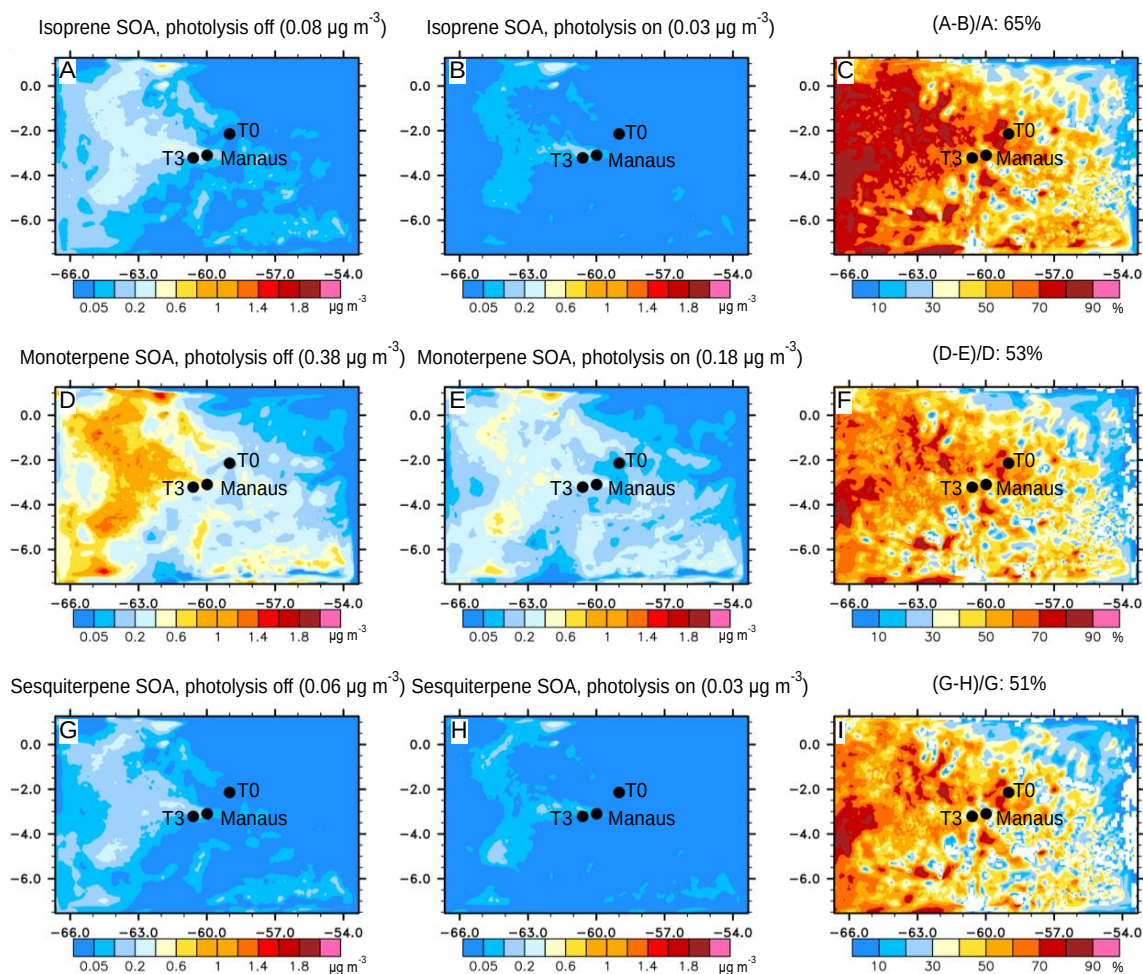


Figure S5. WRF-Chem simulations probing the impact of SOA photolysis on SOA loading, as in Figure 4. Simulations are for March 14, 16-20 UTC. Panels A, D and G represent the base “no photolysis” case as in Shrivastava et al.⁷ Panels B, E and H show simulations with the experimental photolysis rates included in the model. Panels C, F and I show the percent changes in average SOA budget due to photolysis. The black dots represent surface measurement sites during GoAmazon 2014/5.⁶

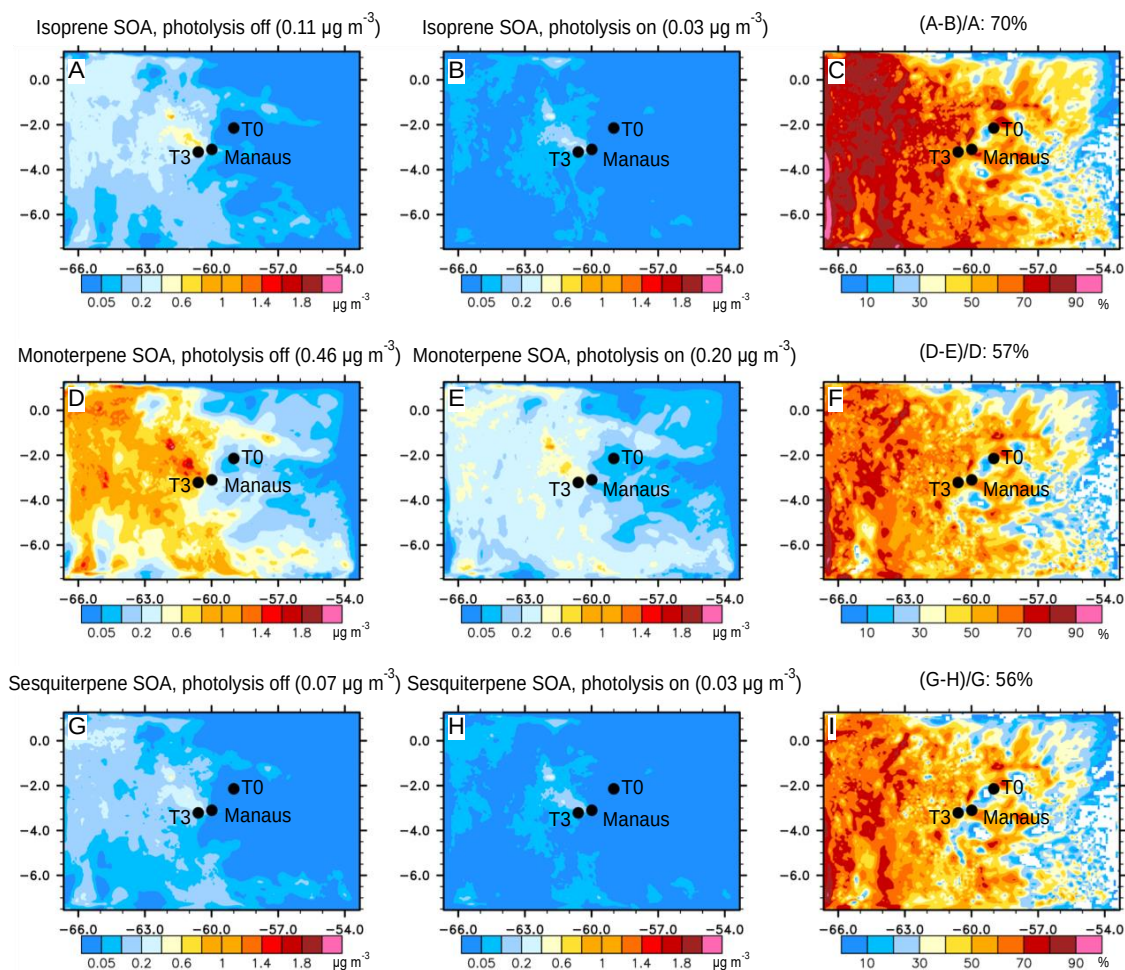


Figure S6. WRF-Chem simulations probing the impact of SOA photolysis on SOA loading, as in Figure 4. Simulations are for March 15, 16-20 UTC. Panels A, D and G represent the base “no photolysis” case as in Shrivastava et al.⁷ Panels B, E and H show simulations with the experimental photolysis rates included in the model. Panels C, F and I show the percent changes in average SOA budget due to photolysis. The black dots represent surface measurement sites during GoAmazon 2014/5.⁶

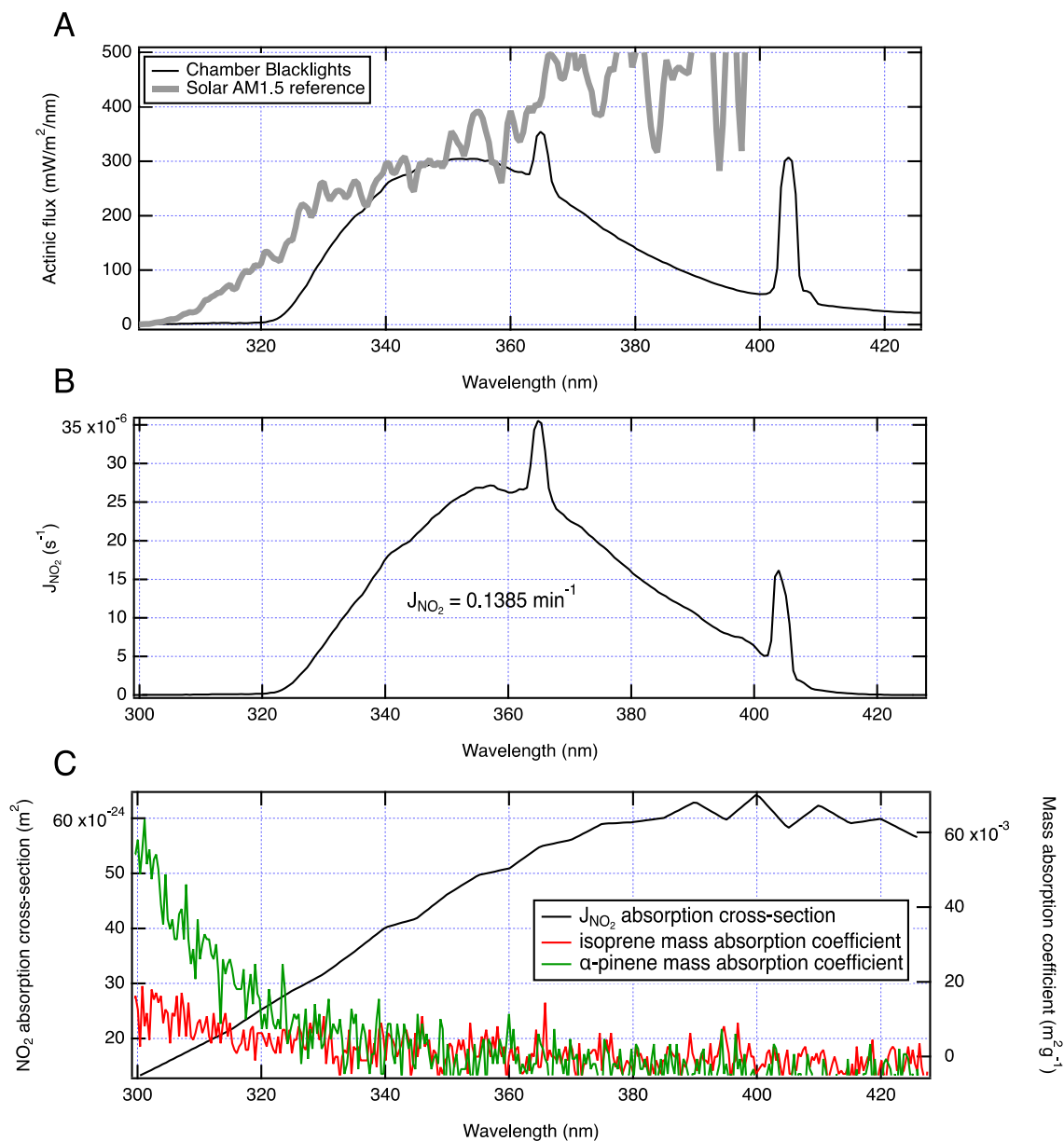


Figure S7. (A) Directly measured spectrally-resolved actinic flux inside the PNNL Environmental Chamber compared to the AM1.5 reference solar spectrum.⁸ (B) Spectrally-resolved J_{NO_2} obtained by convolving (A) with NO₂ absorption cross-section and quantum yield² (C) NO₂ absorption cross-section² and experimentally-derived⁹ mass absorption coefficients for isoprene and α-pinene photooxidation SOA.

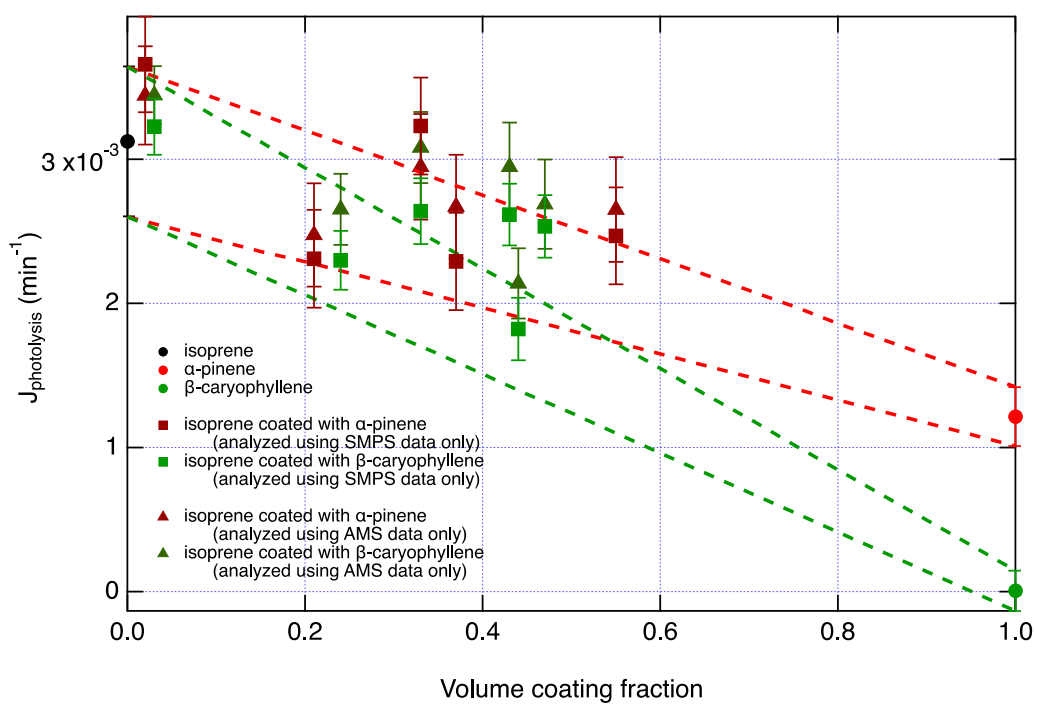


Figure S8. Uncertainty analysis for mixed SOA experiments using SMPS data analysis. AMS-analyzed data points are plotted as open triangles and SMPS-analyzed data points are plotted as solid rectangles.

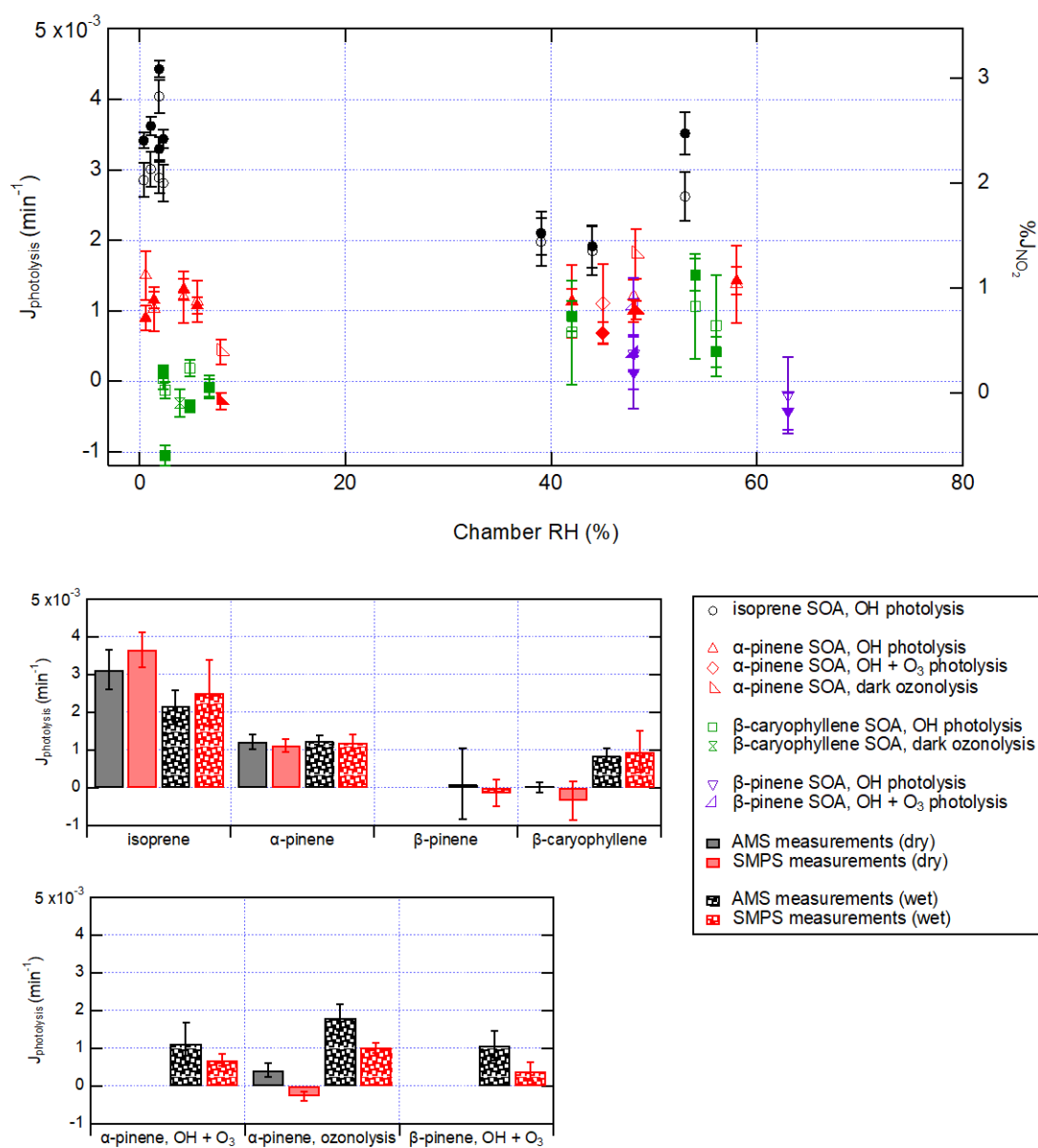


Figure S9. Comparison of SOA photolysis rates derived from AMS and SMPS measurements. In the top panel AMS-analyzed data points are plotted as open symbols and SMPS-analyzed data points are plotted as solid symbols. Bar plots showing the a comparison of the average photolysis rate derived from the AMS and SMPS data.

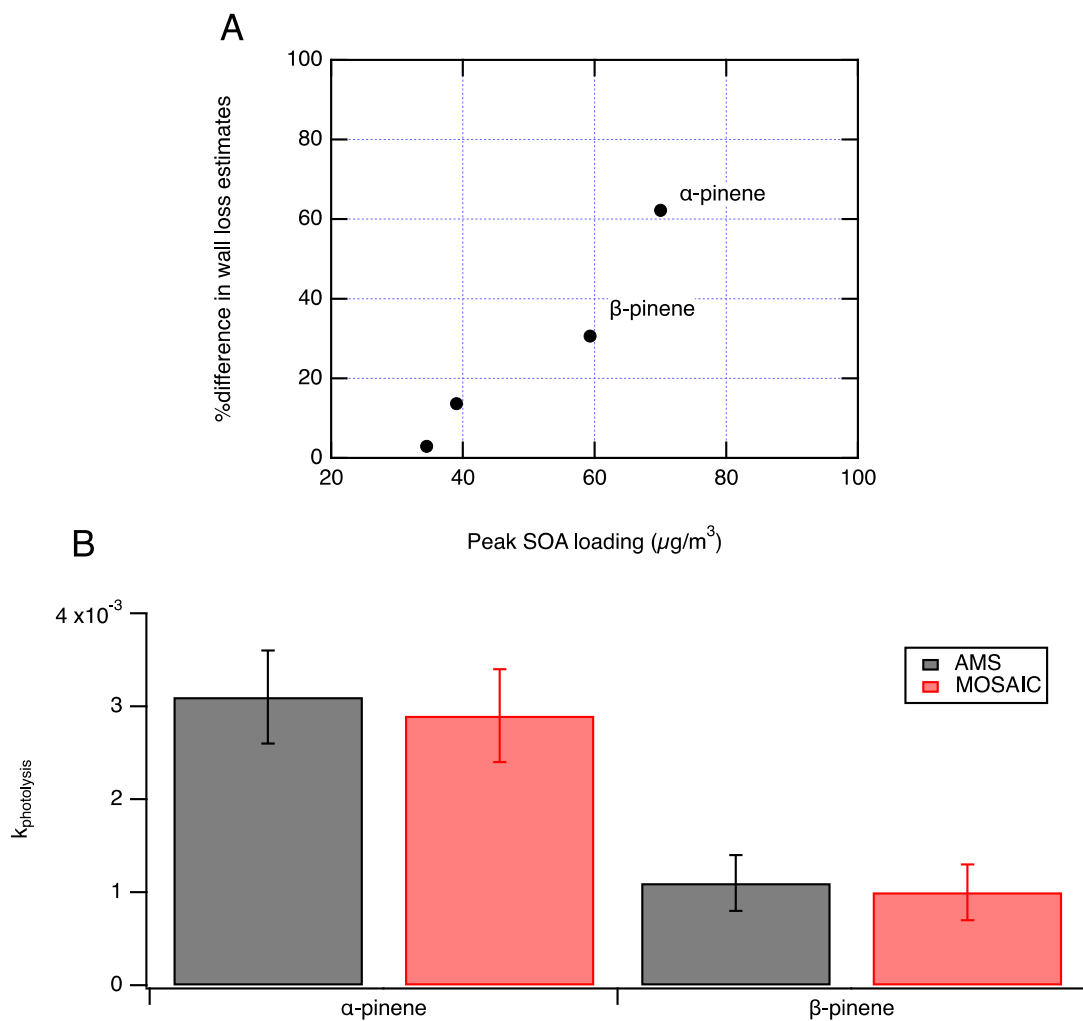


Figure S10. Wall loss analysis using both AMS (see Methods section) data and the MOSAIC model. (A) Percent difference in wall loss time constant estimates using the AMS [SO_4] method and MOSAIC for four different experiments at different peak SOA loadings. (B) Mass decay rate (not corrected for dark gas-phase wall loss) derived from α -pinene and β -pinene experiments from (A), as described in the Methods Section, assuming AMS-derived particle wall loss rates or MOSAIC-derived particle wall loss.

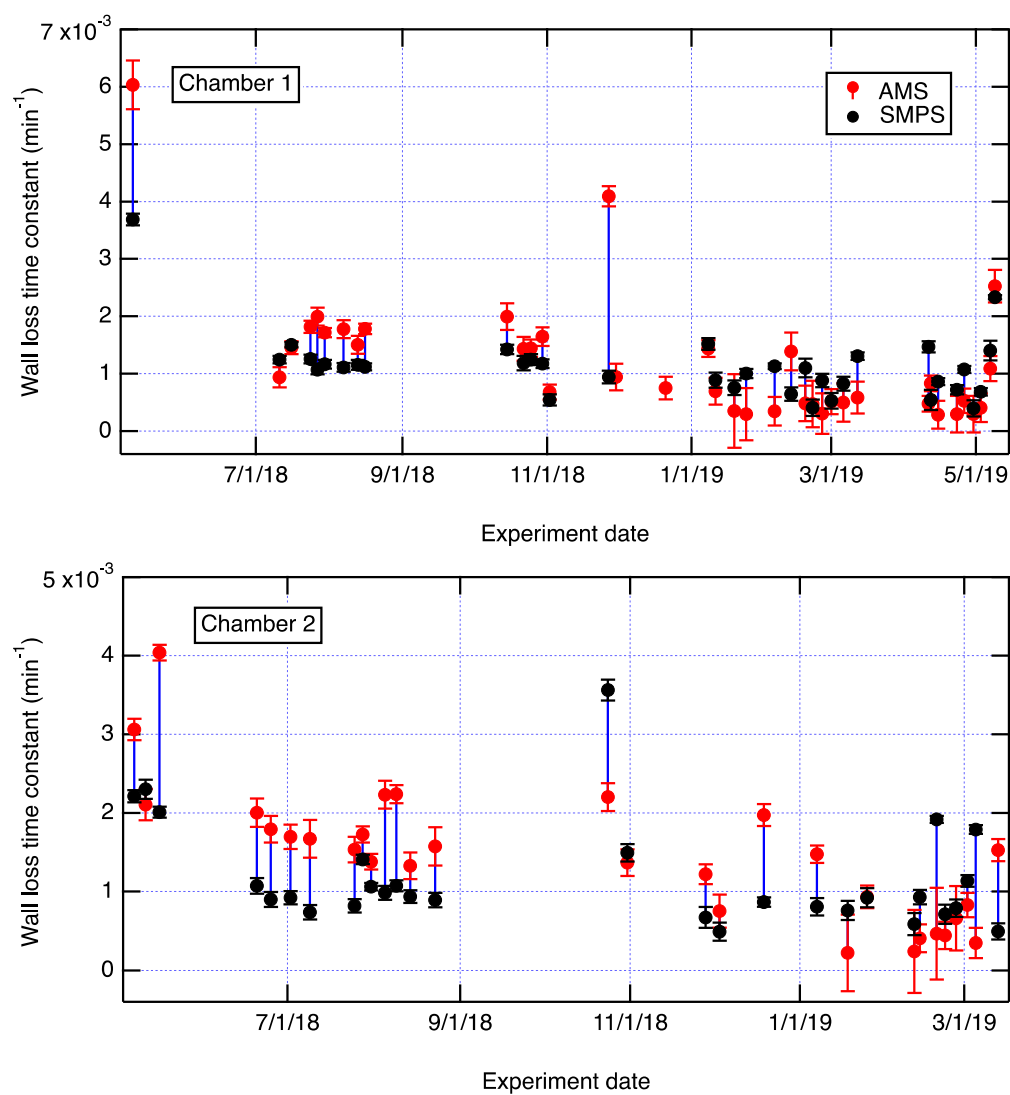


Figure S11. Measurements of chamber wall loss rates for both chambers throughout the duration of the experiments. Measurements derived using the AMS and SMPS data are both shown for comparison.

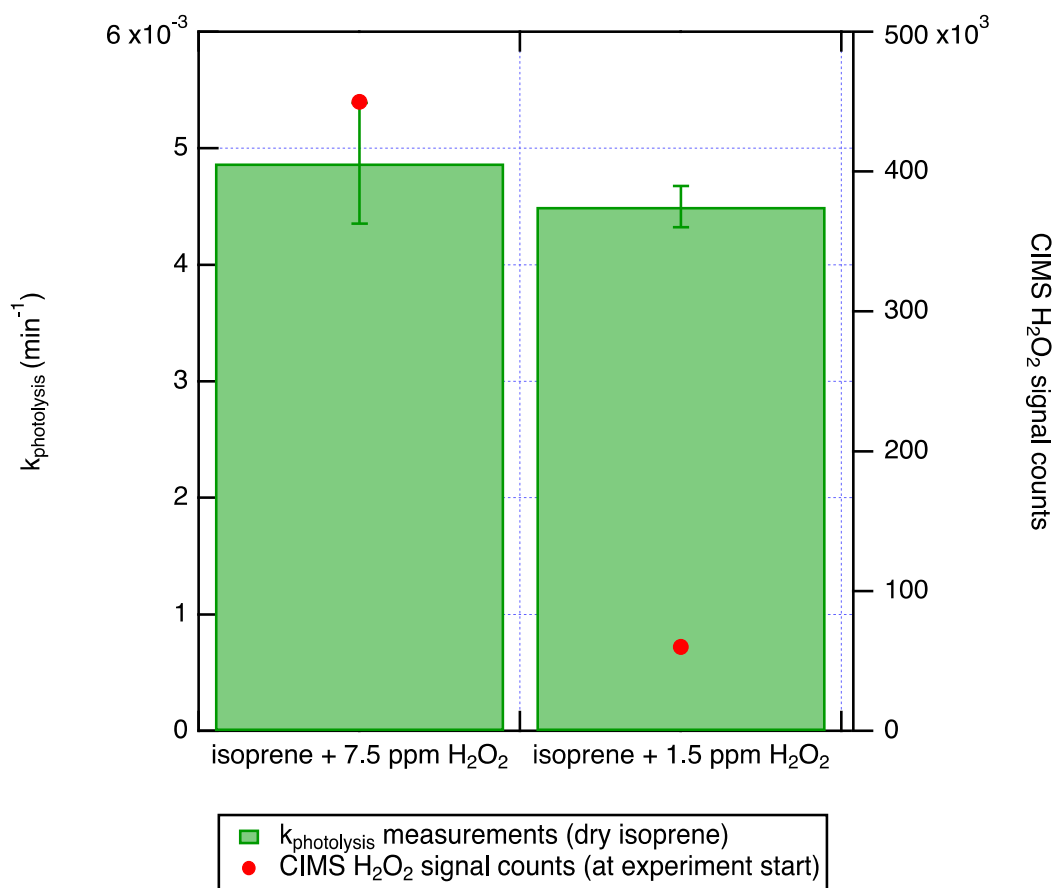


Figure S12. Mass decay rate ($k_{\text{photolysis}}$, uncorrected for dark gas-phase wall loss) was measured for isoprene photooxidation SOA formed using 1.5 ppmv and 7.5 ppmv H_2O_2 . This value is compared to the average of experiments described in the main text, where isoprene SOA was formed using ~ 7.5 ppm H_2O_2 . Additionally, relative H_2O_2 content of particles measured with FIGAERO-CIMS is shown.

Supplementary Tables

Table S1. Table of all chamber measurements and conditions used to derive photolysis rates in this paper. Points A, B, C and D are the key points of the experiment, see text.

Precursor VOC	VOC concentration (A) (ppb)	Oxidant (A-B)	Ozone concentration (A) (ppb)	H ₂ O ₂ concentration (A) (ppm)	peak SOA concentration (B) (μg/m ³)	Coating	Scavenger	UV lights on/off (C-D)	Chamber RH (A-B) (%)	Chamber temperature (A-B) (°C)	Chamber RH (C-D) (%)	Chamber temperature (C-D) (°C)
isoprene	57 ± 5	OH	0	7.5	22.6 ± 0.2	no	2-butanol	on	1.9 ± 0.1	25.4 ± 0.9	2.9 ± 0.6	26.1 ± 0.3
isoprene	66 ± 4	OH	0	7.5	22 ± 1	no	2-butanol	on	2.3 ± 0.2	24.4 ± 0.9	2.8 ± 0.5	25.3 ± 0.3
isoprene	58 ± 4	OH	0	7.5	21.9 ± 0.6	no	2-butanol	on	1.1 ± 0.1	24.1 ± 0.9	1.8 ± 0.4	25.1 ± 0.3
isoprene	72 ± 4	OH	0	7.5	28.1 ± 0.3	no	2-butanol	on	0.4 ± 0.1	24.2 ± 0.9	2.0 ± 0.9	25.2 ± 0.2
isoprene	118 ± 3	OH	0	7.5	34.5 ± 0.7	no	2-butanol	on	1.9 ± 0.1	25.0 ± 0.7	2.7 ± 0.5	25.5 ± 0.3
isoprene	100 ± 4	OH	0	7.5	30.8 ± 0.5	no	2-butanol	on	44 ± 1	25.3 ± 0.5	40 ± 2	25.3 ± 0.1
isoprene	95 ± 6	OH	0	7.5	31.2 ± 0.5	no	2-butanol	on	39 ± 2	24.7 ± 0.9	35 ± 1	25.3 ± 0.3
isoprene	66 ± 4	OH	0	7.5	17.5 ± 0.3	no	2-butanol	on	53 ± 3	24.9 ± 0.8	47 ± 2	25.6 ± 0.4
isoprene	77 ± 3	OH	0	1.5	3.82 ± 0.07	no	2-butanol	on	2.8 ± 0.2	24.6 ± 0.5	3.4 ± 0.2	24.7 ± 0.5
isoprene	62 ± 5	OH	0	7.5	35 ± 1	α-pinene	2-butanol	on	1.5 ± 0.2	24.7 ± 0.8	3 ± 1	25.3 ± 0.3
isoprene	50 ± 4	OH	0	7.5	26.9 ± 0.4	α-pinene	2-butanol	on	6.4 ± 0.2	25.0 ± 0.6	8.2 ± 0.6	24.7 ± 0.3
isoprene	46 ± 4	OH	0	7.5	21.0 ± 0.2	α-pinene	2-butanol	on	2.6 ± 0.2	24.6 ± 0.9	4 ± 1	25.4 ± 0.3
isoprene	51 ± 4	OH	0	7.5	34.0 ± 0.4	α-pinene	2-butanol	on	6.7 ± 0.2	24.7 ± 0.6	7.7 ± 0.6	24.5 ± 0.2
isoprene	43 ± 4	OH	0	7.5	37.3 ± 0.7	α-pinene	2-butanol	on	2.6 ± 0.1	24.7 ± 0.7	5 ± 1	25.3 ± 0.4
isoprene	44 ± 4	OH	0	7.5	21.3 ± 0.2	β-caryophyllene	2-butanol	on	6.7 ± 0.2	24.7 ± 0.6	7.5 ± 0.7	24.6 ± 0.2
isoprene	52 ± 4	OH	0	7.5	38.7 ± 0.7	β-caryophyllene	2-butanol	on	3.6 ± 0.3	24.5 ± 0.6	3.8 ± 0.2	24.6 ± 0.2

isoprene	71 ± 9	OH	0	7.5	30.0 ± 0.8	β-caryophyllene	2-butanol	on	2.9 ± 0.1	24.9 ± 0.5	3.5 ± 0.2	24.9 ± 0.2
isoprene	85 ± 4	OH	0	7.5	41.4 ± 0.4	β-caryophyllene	2-butanol	on	4.5 ± 0.2	25.0 ± 0.6	6.5 ± 0.3	25.2 ± 0.3
isoprene	84 ± 4	OH	0	7.5	32.4 ± 0.1	β-caryophyllene	2-butanol	on	3.4 ± 0.1	25.0 ± 0.5	4.5 ± 0.5	25.1 ± 0.2
isoprene	81 ± 4	OH	0	7.5	31.7 ± 0.5	β-caryophyllene	2-butanol	on	1.7 ± 0.1	25.2 ± 0.8	2.7 ± 0.3	25.8 ± 0.4
isoprene	70 ± 10	OH	0	7.5	23.0 ± 0.3	no	none	off	1.7 ± 0.1	25.2 ± 0.8	4 ± 1	22.6 ± 0.4
isoprene	39 ± 3	OH	0	7.5	16.9 ± 0.1	no	none	off	7.0 ± 0.1	24.9 ± 0.5	9.3 ± 0.6	22.1 ± 0.3
isoprene	58 ± 4	OH	0	7.5	24.5 ± 0.5	no	none	off	2.8 ± 0.3	24.7 ± 0.9	5 ± 2	22.0 ± 0.7
isoprene	74 ± 7	OH	0	7.5	23 ± 1	no	none	off	51 ± 3	24.1 ± 0.9	57 ± 2	21.5 ± 0.5
isoprene	55 ± 3	OH	0	7.5	19.3 ± 0.5	no	none	off	50 ± 3	24.4 ± 0.9	58 ± 2	21.5 ± 0.5
isoprene	91 ± 4	OH	0	7.5	21.1 ± 0.2	no	none	off	53 ± 1	26.0 ± 0.5	64 ± 2	22.8 ± 0.4
isoprene	70 ± 5	OH	0	1.5	2.81 ± 0.04	no	none	off	3.3 ± 0.2	25.9 ± 0.7	5.1 ± 0.4	22.7 ± 0.3
isoprene	72 ± 3	OH	0	7.5	32.7 ± 0.4	no	none	on	5.1 ± 0.2	24.9 ± 0.5	5.73 ± 0.08	25.14 ± 0.05
α-pinene	37 ± 5	OH	0	7.5	62.6 ± 0.5	no	2-butanol	on	4.3 ± 0.2	24.5 ± 0.5	3.7 ± 0.2	24.7 ± 0.2
α-pinene	33 ± 7	OH	0	7.5	39.8 ± 0.3	no	2-butanol	on	5.6 ± 0.2	24.6 ± 0.7	6.7 ± 0.6	24.8 ± 0.3
α-pinene	33 ± 5	OH	0	7.5	50 ± 1	no	2-butanol	on	1.4 ± 0.1	24.5 ± 0.8	3 ± 1	25.3 ± 0.3
α-pinene	58 ± 4	OH	0	7.5	90 ± 1	no	2-butanol	on	0.6 ± 0.1	24.5 ± 0.8	1.1 ± 0.3	25.2 ± 0.4
α-pinene	39 ± 2	OH	0	7.5	69 ± 2	no	2-butanol	on	42 ± 2	24.9 ± 0.8	39 ± 1	25.6 ± 0.3
α-pinene	38 ± 2	OH	0	7.5	64.4 ± 0.9	no	2-butanol	on	58 ± 3	24.2 ± 0.9	50 ± 3	25.1 ± 0.4
α-pinene	23 ± 2	OH	0	7.5	36 ± 1	no	2-butanol	on	48 ± 3	24.3 ± 0.9	43 ± 2	25.3 ± 0.5
α-pinene	19 ± 5	O ₃	40.6 ± 0.3	0	31.9 ± 0.3	no	2-butanol	on	7.9 ± 0.1	22.3 ± 0.1	8.0 ± 0.6	24.8 ± 0.3
α-pinene	15 ± 3	O ₃	103 ± 2	0	38.5 ± 0.3	no	2-butanol	on	48.2 ± 0.5	22.7 ± 0.1	39 ± 1	25.4 ± 0.2
α-pinene	29 ± 2	O ₃ + OH	62 ± 2	7.5	70 ± 1	no	2-butanol	on	45 ± 2	24.9 ± 0.5	42 ± 1	25.0 ± 0.3

α -pinene	39 $\pm$ 4	OH	0	7.5	72 $\pm$ 1	no	none	off	4.3 $\pm$ 0.1	25.2 $\pm$ 0.6	6.4 $\pm$ 0.5	22.3 $\pm$ 0.3
α -pinene	20 $\pm$ 1	OH	0	7.5	62.5 $\pm$ 0.9	no	none	off	2.7 $\pm$ 0.1	24.6 $\pm$ 0.4	3.5 $\pm$ 0.2	21.7 $\pm$ 0.7
α -pinene	26 $\pm$ 3	OH	0	7.5	55.6 $\pm$ 0.7	no	none	off	4.9 $\pm$ 0.1	25.2 $\pm$ 0.5	5.7 $\pm$ 0.2	22.3 $\pm$ 0.2
α -pinene	22 $\pm$ 2	OH	0	7.5	37.9 $\pm$ 0.4	no	none	off	50 $\pm$ 2	24.6 $\pm$ 0.4	55 $\pm$ 2	21.8 $\pm$ 0.7
α -pinene	23 $\pm$ 2	OH	0	7.5	33 $\pm$ 1	no	none	off	53 $\pm$ 3	24.3 $\pm$ 0.9	59 $\pm$ 2	21.4 $\pm$ 0.4
α -pinene	20 $\pm$ 1	OH	0	7.5	33 $\pm$ 1	no	none	off	50.3 $\pm$ 0.5	24.5 $\pm$ 0.1	56 $\pm$ 2	21.7 $\pm$ 0.8
α -pinene	22 $\pm$ 3	O ₃	102 $\pm$ 3	0	53.6 $\pm$ 0.4	no	none	off	3.1 $\pm$ 0.1	22.3 $\pm$ 0.1	3.8 $\pm$ 0.3	22.3 $\pm$ 0.2
α -pinene	N/A	O ₃	103 $\pm$ 4	0	80.8 $\pm$ 0.7	no	none	off	49.2 $\pm$ 0.3	22.9 $\pm$ 0.1	47 $\pm$ 2	22.7 $\pm$ 0.2
α -pinene	26 $\pm$ 4	O ₃ + OH	62 $\pm$ 2	7.5	45.0 $\pm$ 0.3	no	none	off	52 $\pm$ 2	25.6 $\pm$ 0.5	57 $\pm$ 1	22.7 $\pm$ 0.4
α -pinene	39 $\pm$ 2	OH	0	7.5	137.4 $\pm$ 0.7	no	none	on	4.7 $\pm$ 0.1	25.0 $\pm$ 0.5	5.5 $\pm$ 0.6	25.0 $\pm$ 0.1
β -pinene	46 $\pm$ 2	OH	0	7.5	80 $\pm$ 1	no	2-butanol	on	48 $\pm$ 1	24.9 $\pm$ 0.4	44 $\pm$ 2	24.9 $\pm$ 0.2
β -pinene	28 $\pm$ 2	OH	0	7.5	30.3 $\pm$ 0.7	no	2-butanol	on	63 $\pm$ 2	24.7 $\pm$ 0.5	60 $\pm$ 2	24.7 $\pm$ 0.2
β -pinene	29 $\pm$ 2	O ₃ + OH	63 $\pm$ 3	7.5	35.7 $\pm$ 0.5	no	2-butanol	on	48 $\pm$ 1	24.9 $\pm$ 0.4	43 $\pm$ 2	24.9 $\pm$ 0.2
β -pinene	21 $\pm$ 2	OH	0	7.5	39.1 $\pm$ 0.6	no	none	off	52 $\pm$ 1	24.7 $\pm$ 0.4	58 $\pm$ 2	21.8 $\pm$ 0.7
β -pinene	33 $\pm$ 4	O ₃ + OH	63 $\pm$ 2	7.5	59.3 $\pm$ 0.4	no	none	off	52 $\pm$ 2	25.6 $\pm$ 0.5	57 $\pm$ 1	22.5 $\pm$ 0.4
limonene	17 $\pm$ 3	OH	0	7.5	120.7 $\pm$ 0.9	no	2-butanol	on	51 $\pm$ 2	25.9 $\pm$ 0.7	47 $\pm$ 2	25.7 $\pm$ 0.3
limonene	5 $\pm$ 2	OH	0	7.5	26.1 $\pm$ 0.4	no	2-butanol	on	51 $\pm$ 2	25.8 $\pm$ 0.7	48 $\pm$ 1	25.7 $\pm$ 0.4
limonene	5.0 $\pm$ 0.9	OH	0	7.5	26.8 $\pm$ 0.2	no	none	off	52 $\pm$ 2	25.6 $\pm$ 2	57.4 $\pm$ 0.8	22.8 $\pm$ 0.2
β -caryophyllene	5	OH	0	7.5	34.3 $\pm$ 0.6	no	2-butanol	on	4.9 $\pm$ 0.2	24.8 $\pm$ 0.7	5.2 $\pm$ 0.9	25.0 $\pm$ 0.3
β -caryophyllene	5	OH	0	7.5	28.8 $\pm$ 0.5	no	2-butanol	on	6.8 $\pm$ 0.3	24.3 $\pm$ 0.8	8.1 $\pm$ 0.2	24.8 $\pm$ 0.3
β -caryophyllene	10	OH	0	7.5	29.2 $\pm$ 0.4	no	2-butanol	on	2.5 $\pm$ 0.1	24.0 $\pm$ 0.5	4 $\pm$ 1	25.3 $\pm$ 0.4
β -caryophyllene	10	OH	0	7.5	62 $\pm$ 1	no	2-butanol	on	2.3 $\pm$ 0.1	24.8 $\pm$ 0.7	3.1 $\pm$ 0.5	25.6 $\pm$ 0.4
β -caryophyllene	5	OH	0	7.5	28.5 $\pm$ 0.2	no	2-butanol	on	42 $\pm$ 2	24.8 $\pm$ 0.6	39 $\pm$ 1	24.8 $\pm$ 0.3
β -caryophyllene	5	OH	0	7.5	25.4 $\pm$ 0.4	no	2-butanol	on	56 $\pm$ 3	24.0 $\pm$ 0.9	48 $\pm$ 2	25.2 $\pm$ 0.4

β -caryophyllene	5	OH	0	7.5	20.2 ± 0.1	no	2-butanol	on	54 ± 1	25.5 ± 0.5	53.2 ± 0.8	25.1 ± 0.2
β -caryophyllene	15	O ₃	100 ± 1	0	65.0 ± 0.6	no	2-butanol	on	3.9 ± 0.2	22.17 ± 0.04	3.7 ± 0.1	24.8 ± 0.3
β -caryophyllene	10	OH	0	7.5	39 ± 1	no	none	off	1.4 ± 0.2	24.5 ± 0.9	2.6 ± 0.5	22.3 ± 0.5
β -caryophyllene	2	OH	0	7.5	24.9 ± 0.4	no	none	off	1.3 ± 0.2	23.8 ± 0.9	1.9 ± 0.2	21.4 ± 0.5
β -caryophyllene	2	OH	0	7.5	44 ± 1	no	none	off	53 ± 3	24.2 ± 0.9	60 ± 2	21.5 ± 0.5
β -caryophyllene	5	OH	0	7.5	22.9 ± 0.2	no	none	off	40 ± 2	24.6 ± 0.5	43 ± 1	21.7 ± 0.6
β -caryophyllene	20	O ₃	105 ± 4	0	77.0 ± 0.4	no	none	off	3.3 ± 0.3	22.8 ± 0.2	6 ± 1	22.8 ± 0.3

Table S2. Best estimates of photolysis rates for various SOA systems investigated in this paper.

Precursor VOC	Oxidant	Best estimate of $J_{\text{photolysis}}$ (% of J_{NO_2})	Best estimate range of photolysis minimum value (% of initial SOA)	Number of scavenger experiments	Number of dark controls
	RH < 10% (dry)				
isoprene	OH	2.2 ± 0.4	7% - 15%	5	3
α -pinene	OH	0.8 ± 0.2	60% - 84%	4	3
α -pinene	O ₃	0.3 ± 0.1	N/A	1	1
β -caryophyllene	OH	0	N/A	4	2
β -caryophyllene	O ₃	0	N/A	1	1
	40% < RH < 60%				
isoprene	OH	1.5 ± 0.3	7% - 13%	3	3
α -pinene	OH	0.9 ± 0.1	20% - 23%	3	3
α -pinene	O ₃	1.3 ± 0.3	24% - 30%	1	1
α -pinene	O ₃ + OH	0.8 ± 0.4	25% - 29%	1	1
β -pinene	O ₃ + OH	0.7 ± 0.3	27% - 54%	1	1
limonene	OH	0.6 ± 0.5	8% - 9%	2	1
β -caryophyllene	OH	0.6 ± 0.1	18% - 23%	3	2

Table S3. WRF-Chem model configuration.

WRF domain	10 km resolution outer domain covering and 2 km resolution nested domain.
Simulation period	March 10-17, 2014
Boundary layer	YSU scheme
Surface	Community Land Model (CLM v4)
Cloud microphysics	Morrison (2 moments) ^{10, 11}
Radiation	RRTMG scheme (both longwave and shortwave)
Gas-phase chemistry	SAPRC-99
Aerosol chemistry	MOSAIC for inorganic aerosols Modified Volatility basis set (VBS) for organic aerosols.
Land use	Community land model (CLM) with US Geological Survey (USGS) dataset. CLM is run at the same resolution as WRF-Chem.
Boundary conditions	NCEP CFS reanalysis for meteorology and quasi-global WRF for aerosols and trace gases. ¹²

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