Journal of Geophysical Research: Atmospheres

Supporting Information for

Reconciling Observed and Predicted Tropical Rainforest OH Concentrations using a Chemical Ionization Mass Spectrometer during the GoAmazon2014/5 Field Campaign

Daun Jeong[1,a], Roger Seco[1,b], Louisa Emmons[2], Rebecca Schwantes[2,c], Yingjun Liu[3,d], Karena A. McKinney3, Scot T. Martin[3,4], Frank N. Keutsch[3,5,6], Dasa Gu[1,e],d, Alex B. Guenther[1], Oscar Vega[7], Julio Tota[8], Rodrigo A. F. Souza[9], Stephen R. Springston[10], Thomas B. Watson[10], Saewung Kim[1]

[1]Department of Earth System Science, School of Physical Sciences, University of California, Irvine, California, USA.

[2]Atmospheric Chemistry Observations and Modeling Laboratory, National Center for Atmospheric Research, Boulder, Colorado, USA.

[3]John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, USA.

[4]Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA.

[5]Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin, USA.

[6]Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts, USA.

[7]Instituto de Pesquisas Energéticas e Nucleares, Cidade Universitaria, São Paulo, Brazil.

[8]Universidade Federal do Oeste do Pará, Santarém, Brazil.

[9]Escola Superior de Tecnologia, Universidade do Estado do Amazonas, Manaus, Amazonas, Brazil.

[10]Department of Environmental and Climate Sciences, Brookhaven National Laboratory, Upton New York, USA.

[a]Now at Department of Chemistry, University of Michigan, Ann Arbor, Michigan, USA.

[b]Now at Department of Biology, University of Copenhagen, Copenhagen, Denmark.

[c]Now at Chemical Sciences Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado, USA

[d]Now at College of Environmental Sciences and Engineering, Peking University, Beijing, China.

[e]Now at Hong Kong University of Science and Technology, Hong Kong, China

Corresponding author: Saewung Kim (saewung.kim@uci.edu)

Contents of this file

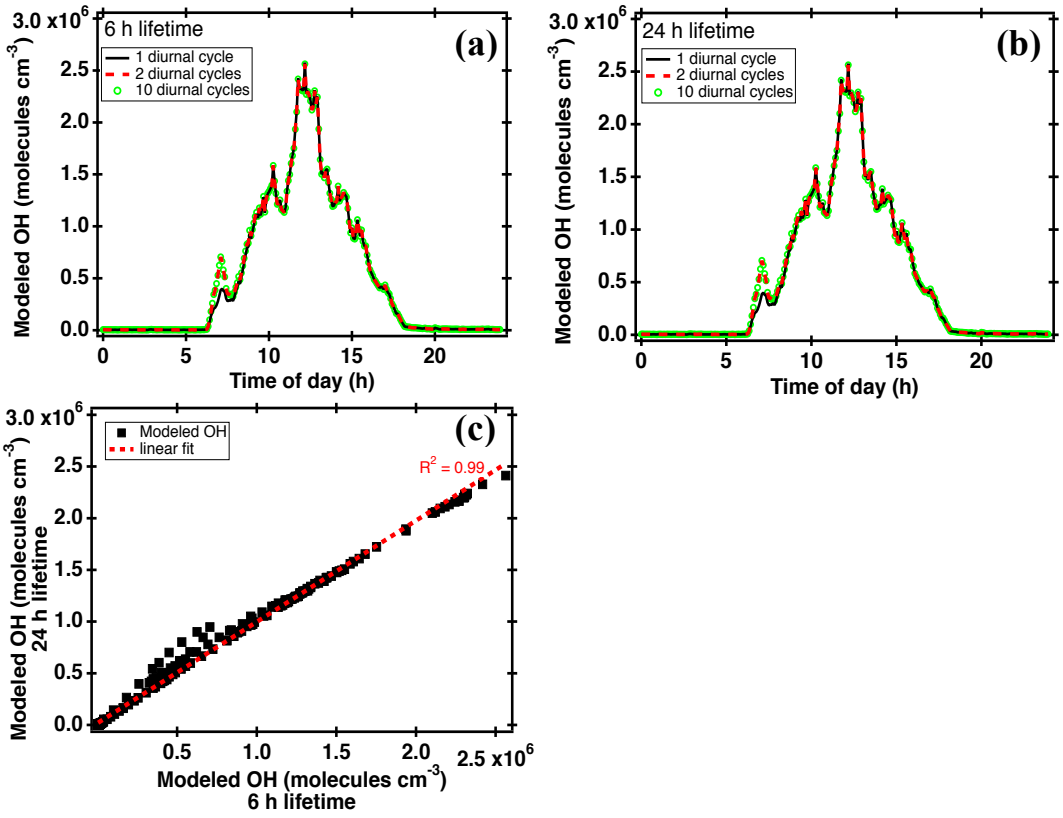

Figure S1. Sensitivity tests of dilution rate and spin-up days. The first, second, tenth day of model simulation are shown with a (a) 6 h lifetime and (b) 24 h lifetime. (c) Correlation between 6 h and 24 h lifetime on the second day of the simulation.

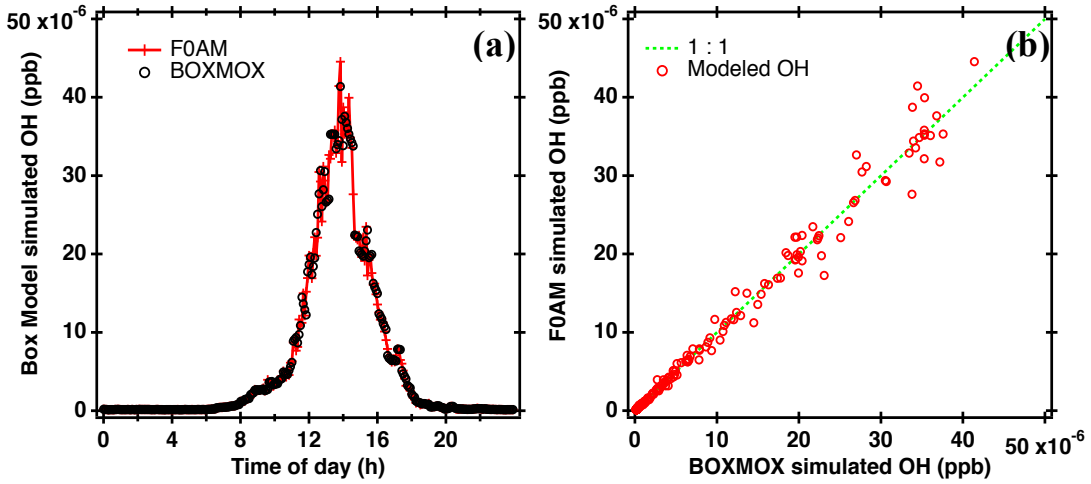

Figure S2. (a) Diurnal variation and (b) scatter plot of box model simulated OH between F0AMv3.2 and BOXMOX. Both model frameworks were constrained with the same meteorology and trace gas measurements from Mar 18th 2014 during the GoAmazon2014/5. For the purpose of comparing the two box models, only O_3, CO, NO_2, CH_4, isoprene, and methanol were constrained in the models.

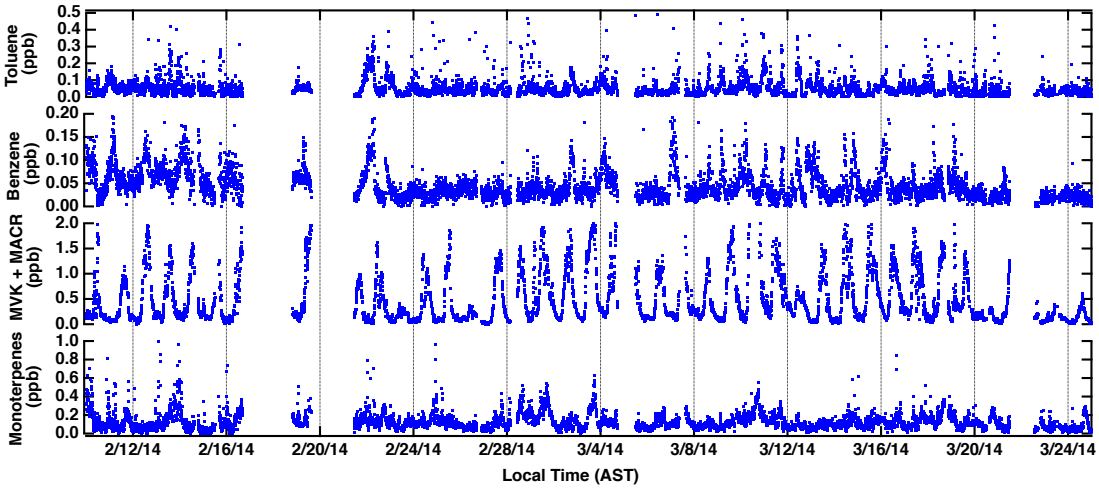

Figure S3. Time series of 5 minute averaged toluene, benzene, MVK and MACR, and monoterpenes, measured by PTR-MS during the GoAmazon2014/5 campaign.

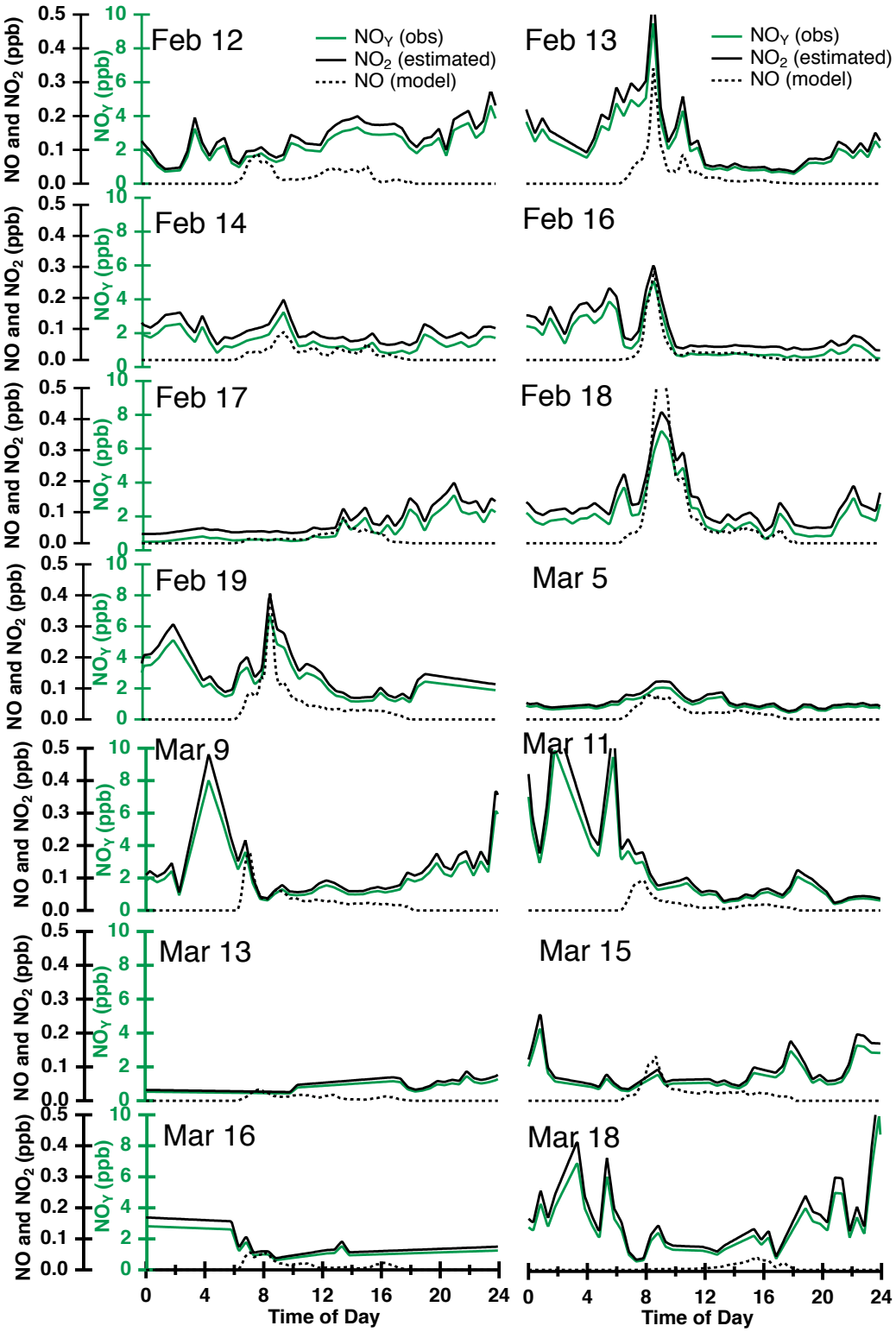

Figure S4. Diurnal variation of NO_Y, NO_2, and NO for the 14 days selected in this study. 30 minute averaged measured NOY is shown with interpolation as needed. NO_2 was estimated as 6 % of measured NO_Y and constrained in the model. NO was simulated from MCM v3.3.1 based on the constrained NO_2.

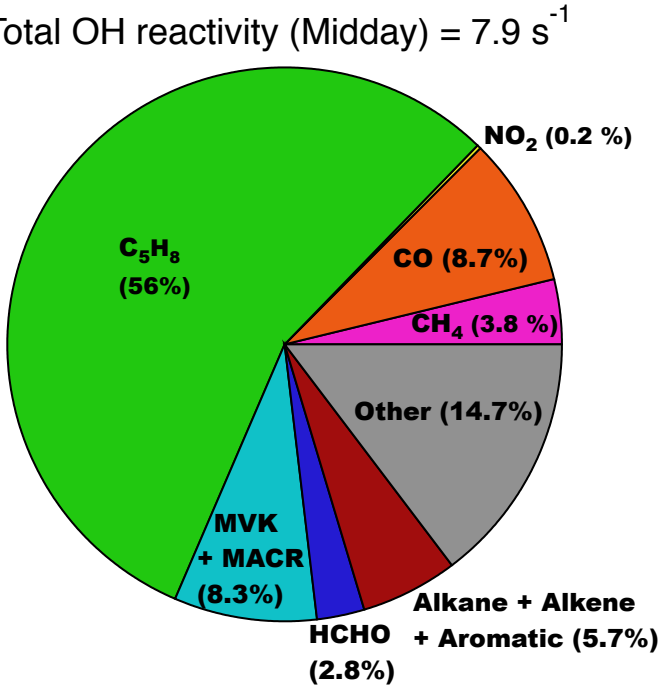

Figure S5. OH reactivity from box model simulations embedded with MCM 3.3.1. Midday (11:00 – 13:00) OH reactivity averaged over the 14 days selected in this study are shown. Category 'Alkane + Alkene + Aromatic' consists of only trace gases (i.e., ethane, propane, n-butane, iso-butane, n-pentane, iso-pentane, hexane, heptane, ethene, propene, toluene, and benzene) constrained in the model runs from observations or previous literature.

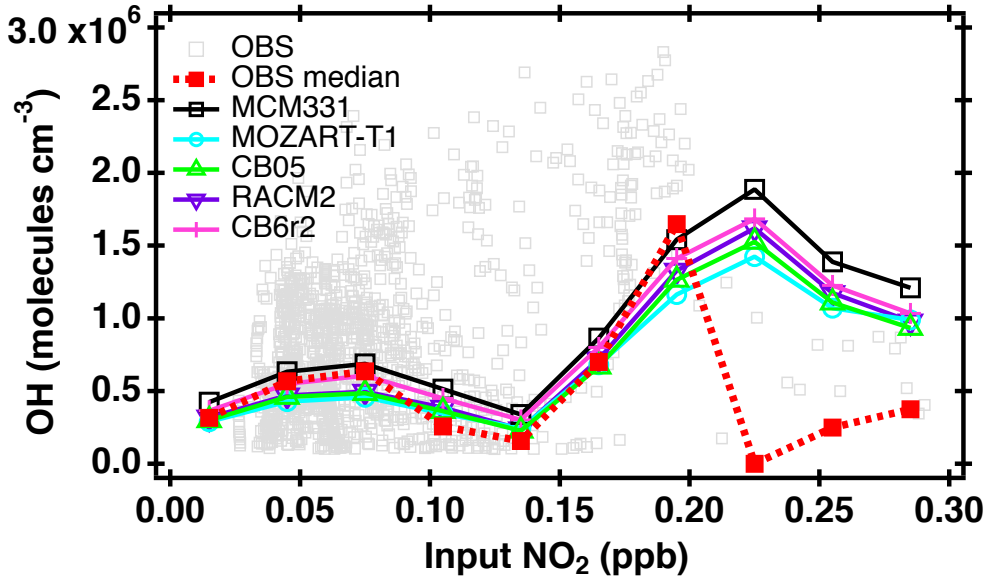

Figure S6. Correlation between input NO_2 and observed and modeled OH. Markers are 5 minute averaged OH measurements and lines are median of observed or modeled OH for each NO_2 bin.

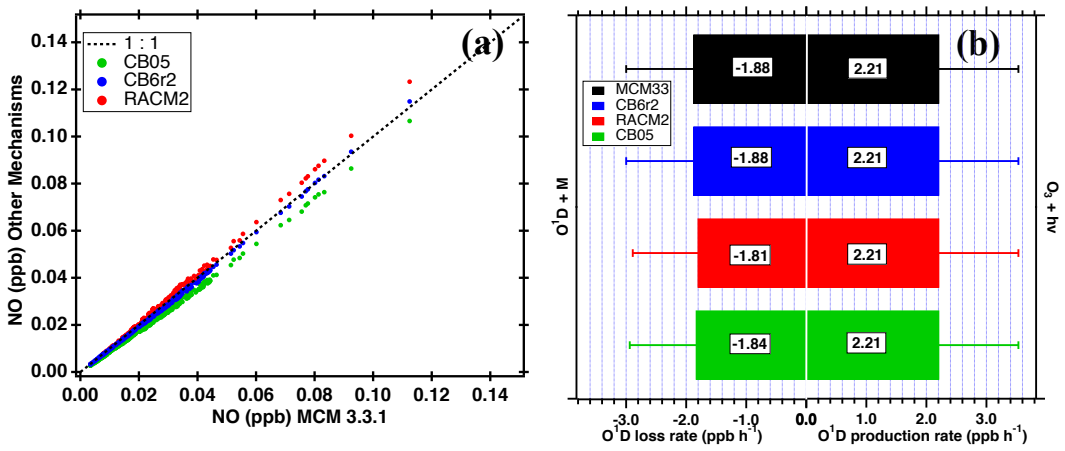

Figure S7. (a) Correlation of midday (11:00 – 13:00) modeled NO between MCM 3.3.1 and other mechanisms. Frequency of the modeled data is 5 min. (b) Production and Loss rates of O1D averaged over midday (11:00 – 13:00) . Rate coefficients of $O^1D + M$ at 298 K are : MCM v3.3.1 = 3.255 x 10^{-11} cm^3 $molecules^{-1}$ s^{-1},CB6r2 = 3.280 x 10^{-11} cm^3 $molecules^{-1}$ s^{-1}, RAMC2 = 3.250 x 10^{-11} cm^3 $molecules^{-1}$ s^{-1}, CB05 = 2.957 x 10^{-11} cm^3 $molecules^{-1}$ s^{-1}.

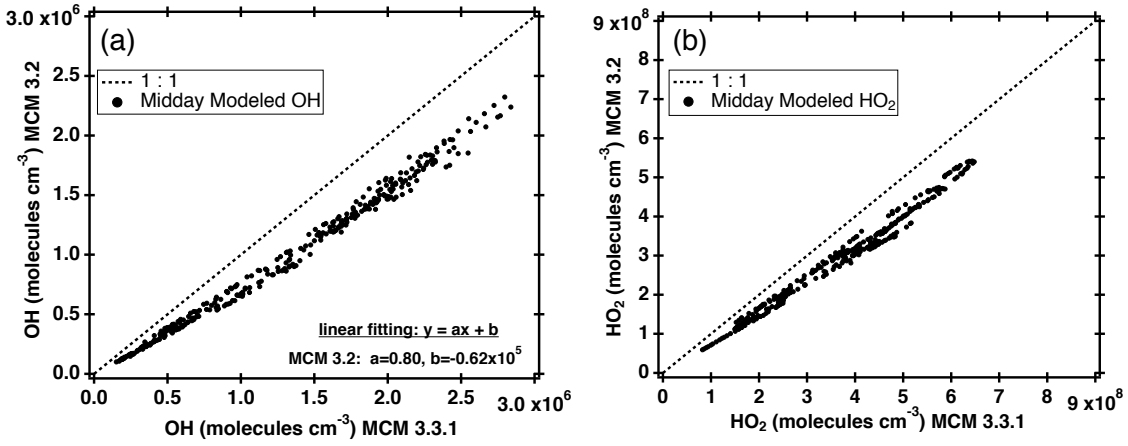

Figure S8. (a) Correlation of midday (11:00 – 13:00) modeled (a) OH and (b) HO_2 between MCM 3.2 and 3.3.1.

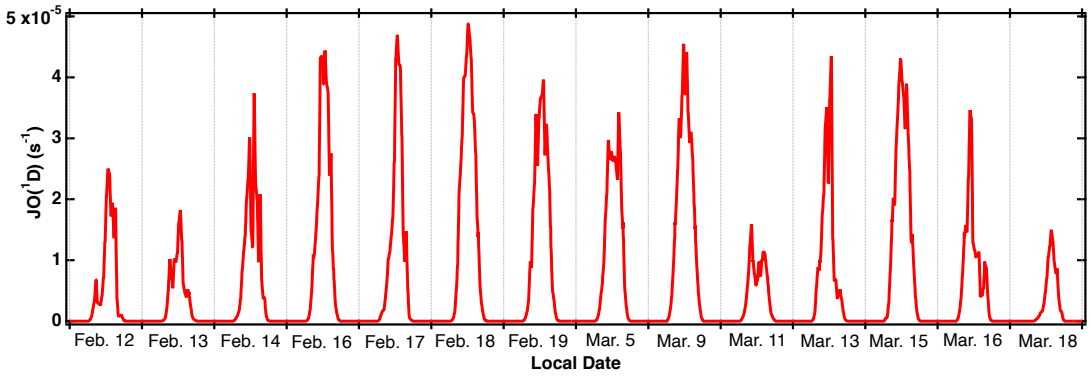

Figure S9. Ozone photolysis rate constants (JO^1D) of the 14 days selected for this study, calculated by the F0AM box model.

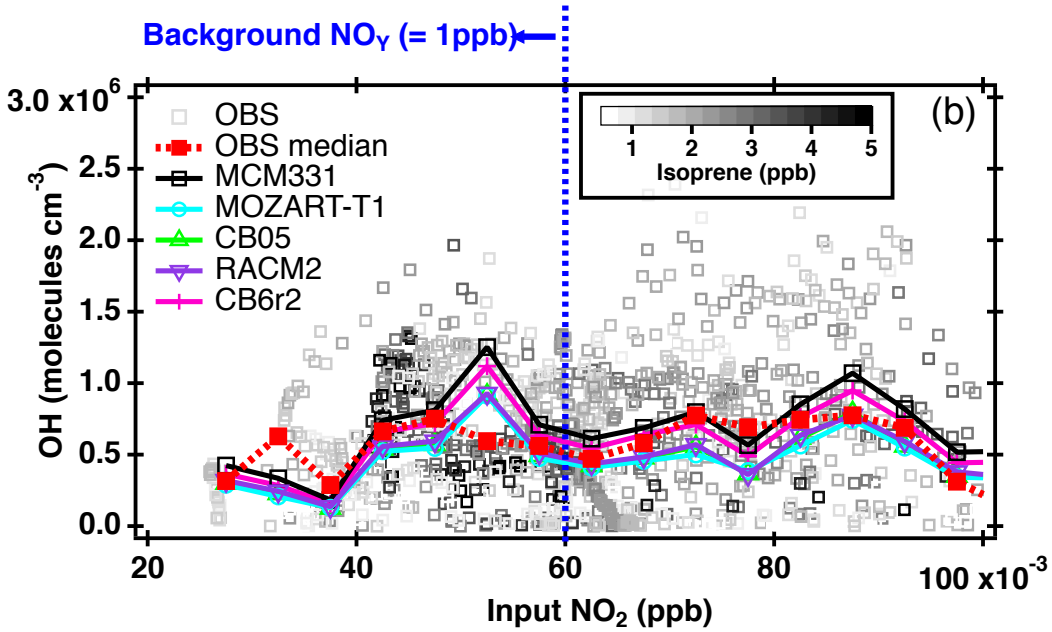

Figure S10. Correlation between input NO2 and observed and modeled OH color coded with measured isoprene.

Trace Gas and Meteorology	Techniques	Manufacturer/Reference
Carbon monoxide (CO)	Cavity Ring Down Spectroscopy	Los Gatos Research, Inc
Nitrogen oxides (NO_x and NO_Y)	Chemiluminescence	Thermo Scientific 42i-TL
Ozone (O_3)	UV photometry	Thermo Scientific 49i
Acetone (CH_3COCH_3) Benzene (C_6H_6) Toluene ($C_6H_5(CH_3)$) Isoprene (C_5H_8) Monoterpenes [a]Methyl vinyl ketone (MVK) [a]Methacrolein (MACR)	Proton Transfer Reaction-Time of Flight-Mass Spectrometer (PTR-TOF-MS)	Graus et al. (2010); Jordan et al. (2009)
[b]Ethane (C_2H_6) [b]Propane(C_3H_8) [b]n-Butane (n-C_4H_{10}) [b]i-Butane (i-C_4H_{10}) [b]n-Pentane (n-C_5H_{12}) [b]i-Pentane (i-C_5H_{12}) [b]n-Hexane (n-C_6H_{14}) [b]n-Heptane (n-C_7H_{16}) [b]Ethylene (C_2H_4) [b]Propene (C_3H_6)	Gas Chromatography-Flame Ionization Detection (GC-FID)	Greenberg and Zimmerman (1984); Zimmerman et al. (1988)
Solar Radiation (0.4 – 4 μm)	Shortwave Array Spectroradiometer	Flynn (2016)
Ambient Temperature Relative Humidity	Aerosol Observing System Surface Meteorology (AOSMET)	Chen et al. (2015)

[a] The sum of MVK and MACR was measured

[b] Mixing ratios used in box model simulations were taken from Zimmerman et al. (1988) and were: ethane = 0.98 ppb, propane = 0.37 ppb, n-butane = 0.09 ppb, i-butane = 0.08 ppb, n-pentane = 0.07 ppb, i-pentane = 0.13 ppb, n-hexane = 0.02 ppb, n-heptane = 0.03 ppb, ethylene = 0.97 ppb, propene = 0.31 ppb

Table S1. Summary of the analytical techniques and references of trace gases and meteorological data used in this study

Trace Gases Constrained in the Box Model	Nomenclature and Lumping of each Mechanism				
	MCM v3.3.1	**MOZART-T1**	**RACM2**	**CB05**	**CB6r2**
Ozone	O_3	O_3	O_3	O_3	O_3
Carbon Monoxide	CO	CO	CO	CO	CO
Nitrogen Dioxide	NO_2	NO_2	NO_2	NO_2	NO_2
Methane	CH_4	CH_4	CH_4	CH_4	CH_4
Methyl Vinyl Ketone	MVK	MVK	MVK	ISPD	ISPD
Methacrolein	MACR	MACR	MACR	ISPD	ISPD
Isoprene	C_5H_8	ISOP	ISO	ISOP	ISOP
Monoterpene	APINENE	APIN	API	TERP	TERP
Ethane	C_2H_6	C_2H_6	ETH	ETHA	ETHA
Propane	C_3H_8	C_3H_8	HC3	1.5 PAR, 1.5 NR	PRPA
n-Butane	NC4H10	BIGALK	HC3	4 PAR	4 PAR
iso-Butane	IC4H10	BIGALK	HC3	4 PAR	4 PAR
n-Pentane	NC5H12	BIGALK	HC5	5 PAR	5 PAR
Iso-Pentane	IC5H12	BIGALK	HC5	5 PAR	5 PAR
n-Hexane	NC6H14	BIGALK	HC5	6 PAR	6 PAR
n-Heptane	NC7H16	BIGALK	HC8	7 PAR	7 PAR
Ethene	C_2H_4	C_2H_4	ETE	ETH	ETH
Propene	C_3H_6	C_3H_6	HC8	1 PAR, 1 OLE	1 PAR, 1 OLE
Toluene	TOLUENE	TOLUENE	TOL	TOL	TOL
Benzene	BENZENE	BENZENE	BEN	1 Par, 5 NR	BENZ
Acetone	CH_3COCH_3	CH_3COCH_3	ACT	3 PAR	ACET
Methanol	CH_3OH	CH_3OH	MOH	MEOH	MEOH
Acetaldehyde	CH_3CHO	CH_3CHO	ACD	ALD2	ALD2

Table S2. Summary of the trace gases constrained in the box model simulations in this study and their lumping in each mechanism.