

## Additional model documentation

### Equations

To compute the NO<sub>x</sub> recycling efficiency (NRE) and RONO<sub>2</sub> lifetime ( $\tau_{\text{RONO}_2}$ ) we use Eq (1) and Eq (2):

$$\text{NRE} = \frac{P(\text{NO}_x)}{\text{Loss}(\text{NO}_x)} \quad (1)$$

$$\tau_{\text{RONO}_2} = \frac{[\text{RONO}_2]}{\text{Loss}(\text{RONO}_2)} \quad (2)$$

where P (NO<sub>x</sub>) and Loss (NO<sub>x</sub>) refer to the re-released NO<sub>x</sub> due to oxidation and photolysis of RONO<sub>2</sub>, and loss of NO<sub>x</sub> due to the production of RONO<sub>2</sub>, respectively. Loss (RONO<sub>2</sub>) is loss rate of RONO<sub>2</sub>. This lifetime does not include reactions that convert one nitrate into a different nitrate. In contrast, to calculate the lifetime of specific individual molecules we consider all reactions.

A simplified scheme, as an example, provides more detail on the approach used.

Reactants	Products	Species to track rates
BVOC + OH	RO <sub>2</sub>	
RO <sub>2</sub> + NO	$\alpha$ AN1 + (1- $\alpha$ ) NO <sub>2</sub>	+ $\alpha$ LNOX
AN1 + OH/O <sub>3</sub> /h $\nu$	$\gamma$ AN2 + (1- $\gamma$ ) NO <sub>2</sub>	+ (1- $\gamma$ ) PNOX1 + LAN1
AN2 + OH/h $\nu$	NO <sub>2</sub>	+ PNOX2 + LAN2

LAN1, LAN2, LNOX are used to track insatantanous loss of first- and second-generation RONO<sub>2</sub> (AN1 and AN2) and NO<sub>x</sub> at each time step. PNOX1 and PNOX2 track instantaneous re-released NO<sub>x</sub> due to loss of first- and second-generation RONO<sub>2</sub>. Thus, NO<sub>x</sub> recycling efficiency and lifetime of first- and total RONO<sub>2</sub> at each time step are calculated as:

$$\text{NRE} = \frac{((1 - \gamma) \text{PNOX1} + \text{PNOX2})}{(\alpha \text{LNOX})}$$

$$\tau_{\text{AN1}} = \frac{[\text{AN1}]}{(\text{LAN1})}$$

$$\tau_{\text{RONO}_2} = \frac{[\text{AN1}] + [\text{AN2}]}{((1 - \gamma) \text{PNOX1} + \text{LAN2})}$$

Reactants	Products	Rate	References	Status
ISOP+HO <sub>2</sub>	0.628 ISHPA+0.272 ISHPB+0.037 ISHPD+0.063 HO+0.063 HO <sub>2</sub> +0.063 HCHO+0.025 MACR+0.038 MVK	2.06D-13 exp(1300/T)	(Liu et al., 2013; St. Clair et al., 2015)	Modified
ISHPA+HO	0.75 ISOP+0.25 HC5 +0.125 HO+0.125 H <sub>2</sub> O	6.13D-12exp(200/T)	(St. Clair et al., 2015)	Added
ISHPB+HO	0.480 ISOP+0.520 HC5+0.26 HO+0.26 H <sub>2</sub> O	4.14D-12exp(200/T)	(St. Clair et al., 2015)	Modified
ISHPD+HO	0.250 ISOP+0.750 HC5+0.375 HO+0.375 H <sub>2</sub> O	5.11D-12exp(200/T)	(St. Clair et al., 2015)	Added
ISHPA+HO	0.578 IEPOXA+0.272 IEPOXB+0.850 HO+0.150 HC5P	1.7D-11exp(390/T)	(St. Clair et al., 2015)	Added
ISHPB+HO	0.68 IEPOXA+0.32 IEPOXB+1.00 HO	2.97D-11exp(390/T)	(St. Clair et al., 2015)	Modified
ISHPD+HO	0.50 IEPOXD+0.50 HC5P+0.50 HO	2.92D-11exp(390/T)	(St. Clair et al., 2015)	Added
IEPOXA+HO	IEPOXOO	3.73D-11exp(-400/T)	(Bates et al., 2016)	Added
IEPOXB+HO	IEPOXOO	5.79D-11exp(-400/T)	(Bates et al., 2016)	Modified
IEPOXD+HO	IEPOXOO	3.20D-11exp(-400/T)	(Bates et al., 2016)	Added
ISOP+NO	0.4 MVK+0.26 MACR+0.883 NO <sub>2</sub> +0.0117 ISOPND+0.1053 ISOPNB+0 .66 HCHO+0.143 UHC+0.08 DIBOO+0.803 HO <sub>2</sub>	2.7D-12exp(360/T)	(Peeters et al., 2014; Teng et al., 2017)	Modified
ISOPNB+O <sub>3</sub>	0.541 HCHO+0.506 CO+0.526 HO+0.327 NO <sub>2</sub> +0.179 HAC+0.102 H <sub>2</sub> O <sub>2</sub> +0.349 MACRN+0.112 IMONIT+0.128 CO <sub>2</sub> +0.327 HO <sub>2</sub> +0.068 ORA1+0.212 MVKN+0.14 8 MGLY	3.7D-19	(Lee et al., 2014)	Modified
ISOPND+O <sub>3</sub>	0.266 PROPNN+0.017 ORA2+0.249	2.9D-17	(Lee et al., 2014)	Modified

	GLYC+0.075 H2O2+0.89 HO+0.445 HO2+0.214 CO+0.214 HCHO+0.445 NO2+0.271 ETHLN+0.018 IMONIT+0.445 MGLY+0 .289 HAC+0.231 GLY			
ISOPNB+HO	0.88 ISOPNBO2+0.12 IEPOXA+0.12 NO2	2.4D-12exp(745/T)	(Jacobs et al., 2014; Lee et al., 2014)	Modified
ISOPND+HO	ISOPNDO2	1.2D-11exp(652/T)	(Lee et al., 2014)	Modified
ISOPNDO2+NO	0.15 PROPNN+0.44 HAC+0.07 MVKN+0.13 ETHLN+0.31 ORA1+0 .31 NO3+0.72 HCHO+0.15 GLYC+1.34 NO2+0.35 HO2+0.34 HKET	2.4D-12exp(360/T)	(Lee et al., 2014)	Modified
ISOPNBO2+NO	0.29 GLYC+0.29 HAC+0.71 HCHO+0.71 HO2+0.461 MACRN+0.249 MVKN+1.29 NO2	2.4D-12exp(360/T)	(Lee et al., 2014)	Modified
MVK+HO	MVKP	2.60D-12exp(610/T)	(Praske et al., 2015)	Modified
MVKP+NO	0.716 GLYC+0.716 ACO3+0.249 MGLY+0.249 HCHO+0.249 HO2+0.035 MVKN+0.965 NO2	2.7D-12exp(350/T)	(Praske et al., 2015)	Modified
MVKP+HO2	0.38 VRP+0.37 GLYC+0.37 ACO3+0.62 HO+0.13 KET+0.25 HO2+0.12 MGLY+0.12 HCHO	1.82D-13exp(1300/T)	(Praske et al., 2015)	Modified
ISO+NO3	INO2	3.15D-12exp(-450/T)	MCM v3.3.1	Modified
INO2+NO3	0.54 ICN+0.42 MVK+0.04 MACR+1.46 NO2+0.54 HO2+0.46 HCHO	2.30D-12	(Schwantes et al., 2015)	Added
INO2+INO2	0.39 INO+0.728 ICN+0.10 MACR+0.616	5.2D-12	(Schwantes et al., 2015)	Added

	IHND+0.154 IHNB			
INO{+O2}	0.88 ICN+0.88 HO2+0.12 NO2+0.12 HCHO+0.12 MACR	2.5D-14exp(-300/T)	(Schwantes et al., 2015)	Added
ICN+NO3	NH4CO3+HNO3	6.3D-12exp(-1860/T)	MCM v3.3.1	Added
NH4CO3+NO	PROPNN+CO+HO2+NO2	7.5D-12exp(-690/T)	MCM v3.3.1	Added
NH4CO3+NH4CO3	0.3 R4N+0.7 PROPNN +0.7 HO2+0.7 CO	1.0D-11	MCM v3.3.1	Added
ICN+HO	0.52 R4NO+ CO+0.52 HO2+0.48 R4N+0.48 HO	4.1D-11	MCM v3.3.1 & Schwantes(2015)	Added
IHND+HO	0.92 IDHNO2D+0.08 IEPOXD+0.08 NO2	1.1D-10	(Schwantes et al., 2015)	Added
IHNB+HO	IDHNO2B	4.2D-11	(Schwantes et al., 2015)	Added
IDHNO2D+NO3	HO2+NO2+0.12 HAC+0.12 ETHLN+0.8 GLYC+0.80 PROPNN+0.08 R4N+0.08 HCHO	2.3D-12	(Schwantes et al., 2015)	Added
IDHNO2B+NO3	HO2+NO2+0.76 HAC+0.76 ETHLN+0.23 R4N+0.23 HCHO	2.3D-12	(Schwantes et al., 2015)	Added
INO2+HO2	0.22 MVK+0.015 MACR+0.235 NO2+0.235 HO+0.235 HCHO+0.54 INPD+0.23 INPB	2.06D-13exp(1300/T)	(Schwantes et al., 2015)	Added
INPD+HO	HO2+INO2	6.9D-12	(Schwantes et al., 2015; St. Clair et al., 2015)	Added
INPB+HO	HO2+INO2	6.9D-12	(Schwantes et al., 2015; St. Clair et al., 2015)	Added
INPD+HO	0.37 INHED+0.37 HO+0.63 INPHO2D	1.1D-10	(Lee et al., 2014; Schwantes et al., 2015)	Added

INPB+HO	0.78 INHEB+0.78 HO+0.22 INPHO2B	4.2D-11	(Lee et al., 2014; Schwantes et al., 2015)	Added
INPHO2B+NO3	NO2+HO2+HCHO+R4NO	2.3D-12	(Schwantes et al., 2015)	Added
INPHO2D+NO3	NO2+HO2+0.92 PROPNN+0.92 GLY+0.08 HAC+0.08 ETHLN	2.3D-12	(Schwantes et al., 2015)	Added
INHED+HO	0.27 HAC+0.73 CO+0.27 NO2+0.27 HCHO+0.27 PROPNN+0.27 GLY+0.46 R4N	8.4D-12	(Bates et al., 2016; Schwantes et al., 2015)	Added
INHEB+HO	0.30 PROPNN+0.30 GLY+0.31 GLYC+0.31 MGLY+0.09 HAC+0.43 NO2+0.39 HCHO+0.01 ETHLN+0.01 HAC+0.12 KET+0.26 R4N	1.25D-11	(Bates et al., 2016; Schwantes et al., 2015)	Added
R4N+HO	PROPNN+HO2+CO	1.7D-11	(Schwantes et al., 2015)	Added
R4NO+HO	PROPNN+HO+CO	1.7D-11	(Schwantes et al., 2015)	Added
INPD+hv	INO+HO	j(Pj_ch3o2h)	MCM v3.3.1 Schwantes et al. (2015)	Added
INPB+hv	INO+HO	j(Pj_ch3o2h)	MCM v3.3.1 Schwantes et al. (2015)	Added
ICN+hv	PROPNN+CO+CO+HO2+ HO2	10*j(Pj_noa)	(Müller et al., 2014; Schwantes et al., 2015)	Added
R4N+hv	NO2+ACO3+0.5 ETHP+0.5 MO2	j(Pj_ch3coc2h5)	MCM v3.3.1 Schwantes et al. (2015)	Added
R4NO+hv	HO+MGLY+HCHO+NO2	j(Pj_ch3coc2h5)	MCM v3.3.1 Schwantes et al. (2015)	Added
IHND+hv	HO2+NO2+UHC+DIBOO	j(Pj_onit1)	Same as	Added

			ISOPND	
IHNB+hv	HO2+NO2+UHC+DIBOO	j(Pj_onitOH3)	Same as ISOPNB	Added
PROPNN+hv	NO2+ACO3+HCHO	10*j(Pj_noa)	Müller et al. (2014)	Modified
ETHLN+hv	HO2+CO+HCHO+NO2	10*j(Pj_noa)	(Müller et al., 2014)	Modified
MACRN+hv	NO2+CO+HAC+HO2	10*j(Pj_ibutald)	(Müller et al., 2014)	Modified
MVKN+hv	GLYC+NO2+ACO3	10*j(Pj_noa)	(Müller et al., 2014)	Modified
API+NO3	0.10 TOLNN+0.90 TOLND	8.33D-13exp(490/T)	MCM v3.3.1	Modified
UTONIT+NO3	HONIT	3.15D-13exp(-448/T)	(Fisher et al., 2016)	Added
UTONIN+NO3	HONIT	3.15D-13exp(-448/T)	(Fisher et al., 2016)	Added
TONIN+NO3	HONIT	3.15D-13exp(-448/T)	(Fisher et al., 2016)	Added
TONIT+NO3	HONIT	3.15D-13exp(-448/T)	(Fisher et al., 2016)	Added
TONIH+NO3	HONIT	3.15D-13exp(-448/T)	(Fisher et al., 2016)	Added

**Table S1: Isoprene and Monoterpene reactions added to/revised from RACM2\_Berkeley.**

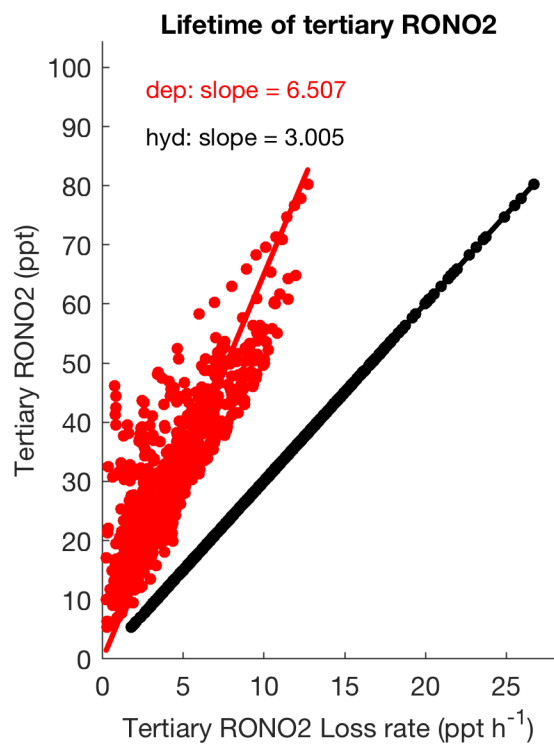
Species	Description	Species	Description
ISHPA	(1,2) hydroxy hydro peroxides	INO2	Isoprene nitrooxy peroxy radical
ISHPB	(4,3) hydroxy hydro peroxides	ICN	C5 carbonyl nitrate
ISHPD	delta (1,4 and 4,1) hydroxy hydro peroxides	INO	C5 nitrooxyalkoxy radical
IEPOXA	trans- $\beta$ isoprene-derived dihydroxy epoxide	IHND	C5 hydroxy nitrate – $\beta$ isomer
IEPOXB	cis- $\beta$ isoprene-derived dihydroxy epoxide	IHNB	C5 hydroxy nitrate – $\delta$ isomer
IEPOXD	delta isoprene-derived dihydroxy epoxide	NH4CO3	Radical from ICN
R4N	C4 carbonyl hydroxynitrate	INPB	C5 nitrooxy hydroperoxide – $\beta$ isomer
R4NO	C4 nitrooxycarbonyl hydroperoxide	INPHO2B	C5 nitrooxy hydroperoxy hydroxy peroxy radical (From $\beta$ isomers)
IDHNO2D	C5 dihydroxy nitrooxyperoxy radical – $\delta$ isomer	INPHO2D	C5 nitrooxy hydroperoxy hydroxy peroxy radical (From $\delta$ isomers)
IDHNO2B	C5 dihydroxy nitrooxyperoxy radical – $\beta$ isomer	INHED	C5 nitrooxy hydroxy epoxide – $\delta$ isomer
INPD	C5 nitrooxy hydroperoxide – $\delta$ isomer	INHEB	C5 nitrooxy hydroxy epoxide – $\beta$ isomer

Table S2: New chemical species that are introduced in RACM2\_Berkeley2 mechanism.

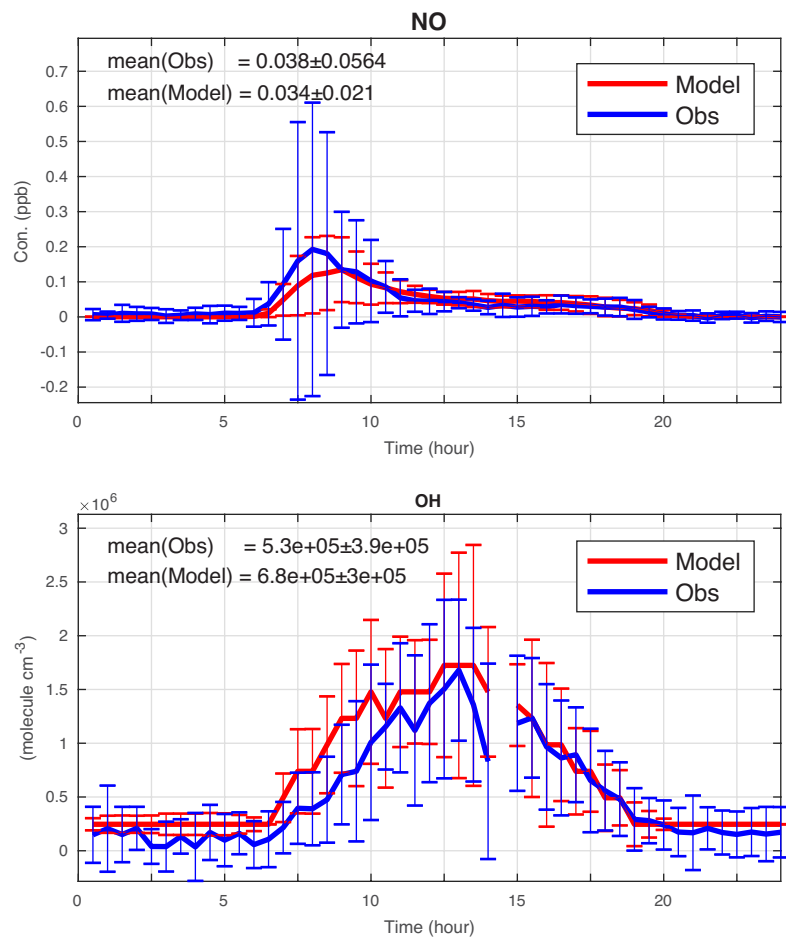
Species	H* (M atm <sup>-1</sup> )	f0
ISOPND, ISOPNB, IMONIT, MACRN, MVKN, INPD, INPB, ICN, R4N, R4NO, IHND, IHNB, TONIT, UTONIT, TONIN, UTONIN, TONIH	2.00E+06	1
PROPNN	5.0E+5	1
ISHPA, ISHPB, ISHPD	1.0E+14	0
IEPOXA, IEPOXB, IEPOXD, INHEB, INHED	8.0E+7	1
GLYC	2.00E+7	1
HAC	1.4E+6	1
H2O2	5.0E+7	1

**Table S3: Changes to dry deposition parameters for isoprene chemistry species and organic nitrate species as recommended by Nguyen et al. (2015). H\* is the Henry's law coefficient and f0 is the reactivity factor as defined in Wesely (1989).**

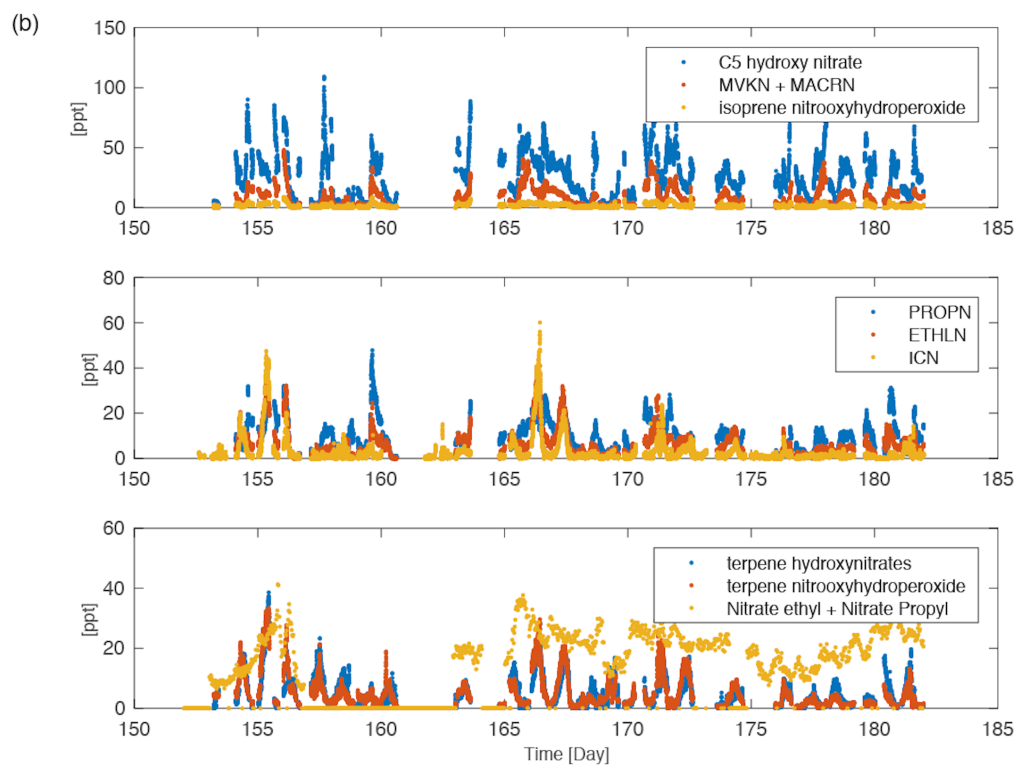
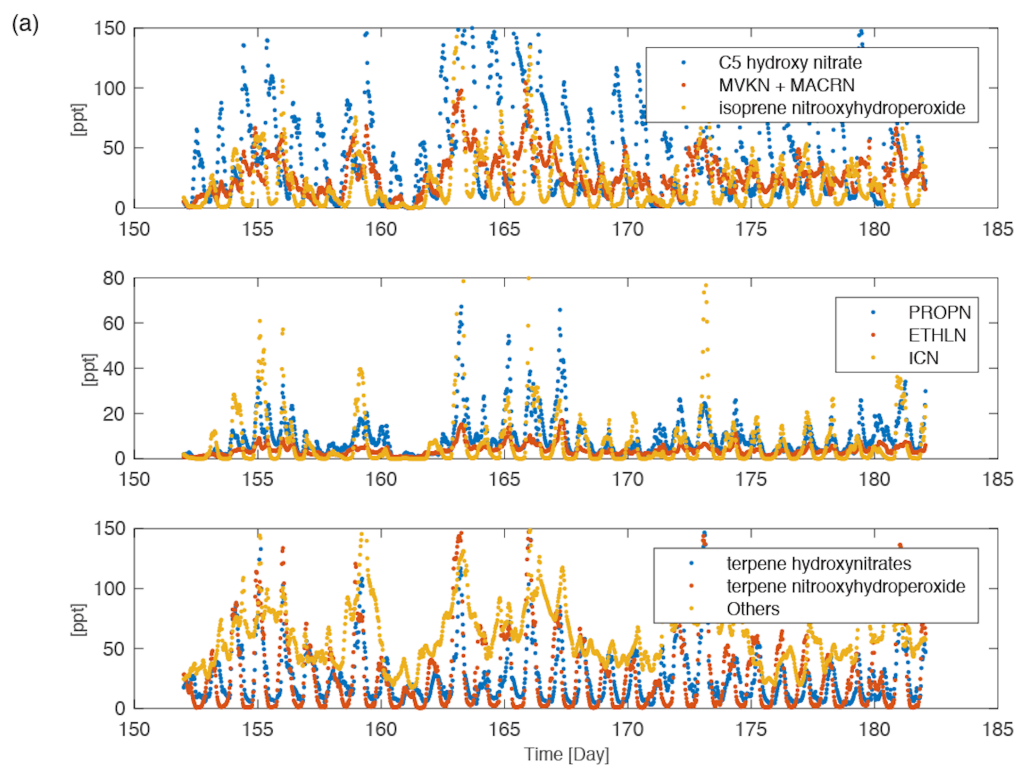




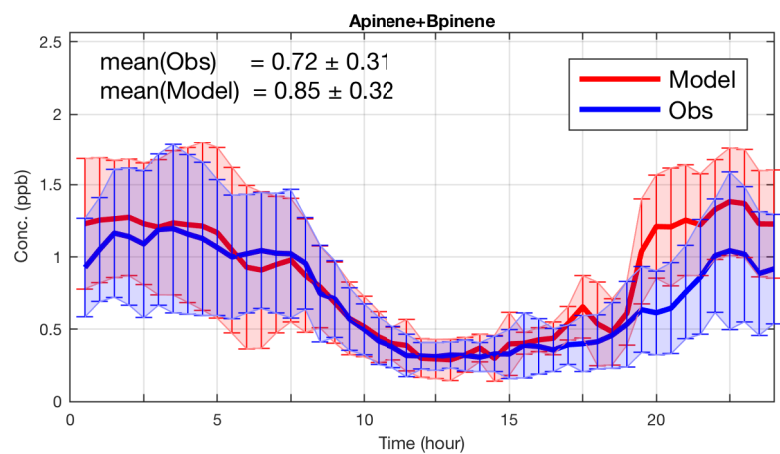
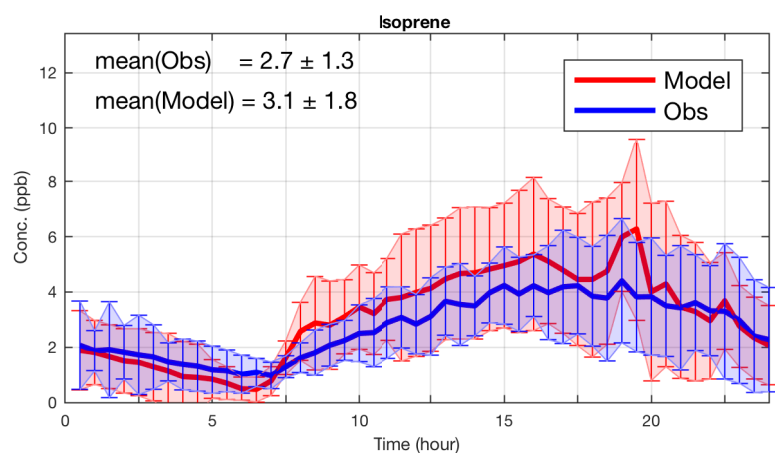
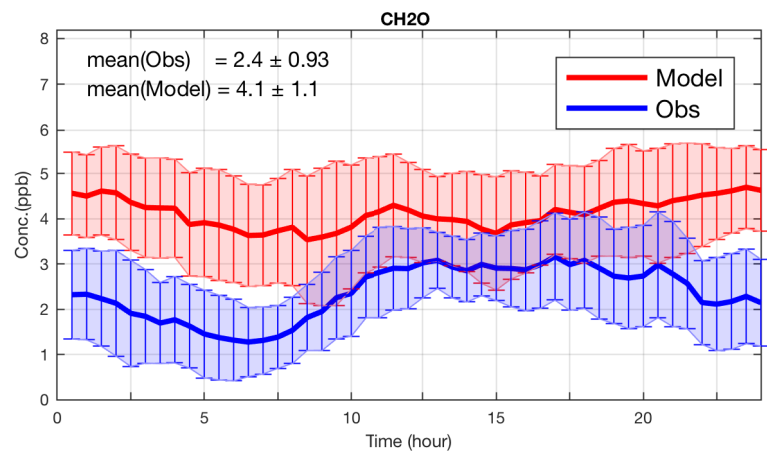
**Figure S1: The concentration of tertiary organic nitrates versus their loss rates through deposition and hydrolysis during SOAS. Slopes of the linear fit give the lifetimes against deposition and hydrolysis of tertiary organic nitrates.**



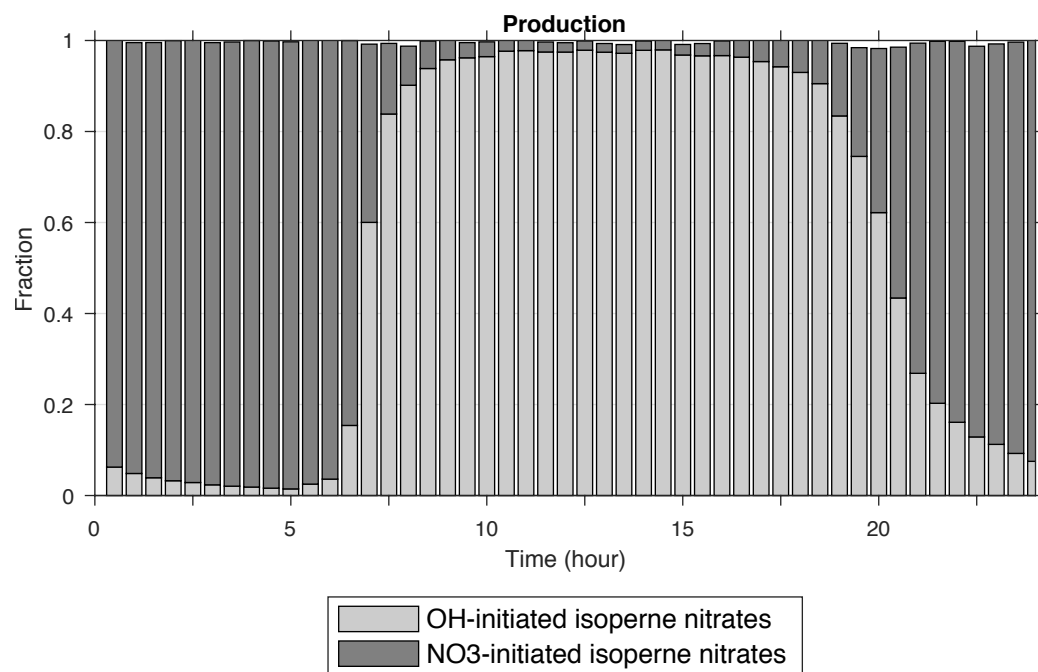
**Figure S2: Median diurnal cycles of observed and simulated NO and OH concentrations at Centreville (CTR) during the 2013 SOAS campaign. The vertical bars show the interquartile range of the hourly data. The panel includes mean of the simulated and observed concentrations.**



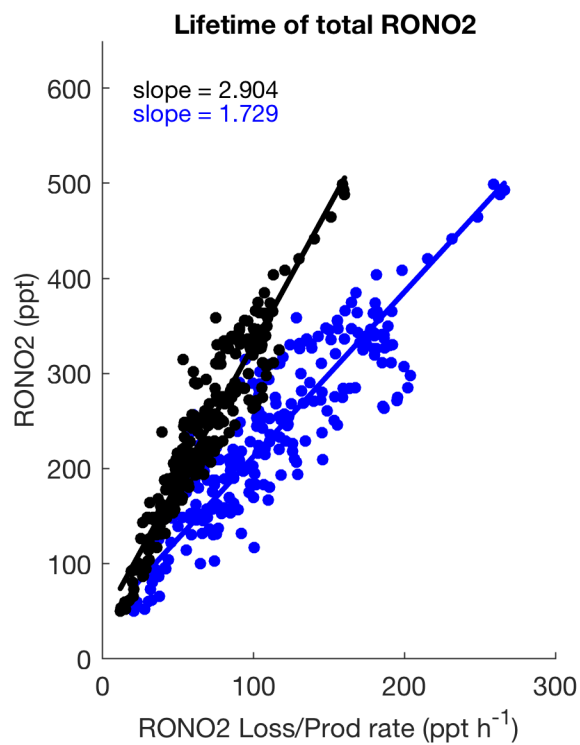
**Figure S3: The (a) simulated and (b) observed concentration of C5 hydroxy nitrate, MVKN+MACRN, C5 nitrooxy hydroperoxide [first panel], Propanone nitrate (PROPNN), Ethanal nitrate (ETHLN), C5 carbonyl nitrate (ICN) [second panel], and terpene hydroxynitrates, terpene nitrooxy hydroperoxide, and anthropogenic organic nitrates (Others) [3rd panel] in June 2013 during the SOAS field campaign. At the figure (b) on 3rd panel, observed ethyl Nitrate + propyl Nitrate is shown.**



**Figure S4: Median diurnal cycles of observed and simulated CH<sub>2</sub>O, isoprene and monoterpenes at Centreville during the 2013 SOAS campaign. The vertical bars show the interquartile range of the hourly data. The panel includes mean of the simulated and observed values.**



**Figure S5: Fraction of isoprene nitrates from OH and NO<sub>3</sub> oxidations to total isoprene nitrate production at boundary layer at the CTR site during SOAS.**



**Figure S6:** The concentrations of organic nitrates versus their loss rates (black) and production rates (blue) at 12:00-16:00 during SOAS. Slopes of the linear fit give lifetime of organic nitrates.

## References

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