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Evaluation of isoprene nitrate chemistry in detailed chemical mechanisms

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Description of SMPS Instrument

Two scanning mobility particle sizer (SMPS) instruments measured particle size distributions at 15 min time resolution, with one long SMPS with an inlet flowrate of 0.3 L min-1 (TSI 3080 EC, 3082 long DMA, 3775 CPC, TSI, USA) and one nano SMPS with an inlet flowrate of 1.5 L min-1 (3082 EC, 3082 nano DMA, 3776 CPC, TSI, USA) measuring the ranges 14–615 and 4–65 nm respectively. A particle size magnifier (A10, Airmodus, FN) linked to a CPC (3775, TSI, USA) measured the sub-3 nm size fraction with an inlet flowrate of 2.5 L min-1. The PSM was run in stepping mode, operating at four different saturator flows to vary the lowest size cut-off of particles that it will grow (this cut-off is technically a point of 50 % detection efficiency) of < 1.30, 1.36, 1.67, and 2.01 nm. The instrument switched between saturator flows per 2.5 min, giving a sub2.01 nm size distribution every 10 min. The data were treated with a moving-average filter to account for jumps in total particle count, and due to the similar behaviour of the two upper and two lower size cuts, these have been averaged to two size cuts at 1.30 and 1.84 nm. No drying was performed on the inlet air.

Table S1. Summary of the properties of each mechanism used in this work. Note that the statistics for the "Caltech Mechanism" and "FZJ Mechanism" apply to the mechanisms in the form used in this work, i.e. with the incorporated MCM subset for non-isoprene VOCs and with RO_2 reactions lumped as described in the main text for the Caltech Mechanism.

Property	MCM	Caltech Mechanism	FZJ Mechanism
Number of Reactions	10371	10435	11046
Number of Species	3443	3589	3730
Number of INO_2 Isomers	1	4	8
Number of IPN Isomers	1	4	4
Number of ΣIPN Isomers	6	11	13
Number of IHN Isomers	5	8	8
Number of ΣIHN Isomers	9	12	12
Number of ICN Isomers	1	3	3
Number of ΣICN Isomers	1	3	3
Number of $C_4H_7NO_5$ Isomers	4	4	4
Number of $\Sigma C_4H_7NO_5$ Isomers	10	10	10

Table S2. List of VOCs (and their names in the MCM) constrained to measured concentrations in the models. The "Measurement(s) Used" column indicates which instrument's measurements were used to constrain each species in model runs: proton transfer mass spectrometry (PTR), selected ion flow tube mass spectrometry (SIFT), and dual-channel gas chromatography with flame ionization detection (DC-GC).

Compound	MCM Name	Measurement(s) Used	Compound	MCM Name	Measurement(s) Used
isoprene	C5H8	DC-GC, SIFT, PTR	ethane	C2H6	DC-GC
monoterpenes	APINENE, LIMONENE	SIFT, PTR	propane	C3H8	DC-GC, SIFT
ethene	C2H4	DC-GC, SIFT	n-butane	NC4H10	DC-GC
propene	C3H6	DC-GC, SIFT,	i-butane	IC4H10	DC-GC
trans-2-butene	TBUT2ENE	DC-GC	n-pentane	NC5H12	DC-GC
1-butene	BUT1ENE	DC-GC	i-pentane	IC5H12	DC-GC
i-butene	MEPROPENE	DC-GC	n-hexane	NC6H14	DC-GC
cis-2-butene	CBUT2ENE	DC-GC	n-heptane	NC7H16	DC-GC
trans-2-pentene	TPENT2ENE	DC-GC	n-octane	NC8H18	DC-GC

cis-2-pentene	CPENT2ENE	DC-GC	benzene	BENZENE	DC-GC, SIFT, PTR
1,3-butadiene	C4H6	DC-GC, SIFT	ethylbenzene	EBENZ	DC-GC, SIFT, PTR
acetylene	C2H2	DC-GC, SIFT	propylbenzene	PBENZ	SIFT, PTR
methanol	CH3OH	DC-GC, SIFT	toluene	TOLUENE	DC-GC, SIFT, PTR
ethanol	C2H5OH	DC-GC, SIFT	o-xylene	OXYL	DC-GC

Table S3. Deposition rates used in the models depending on functionality. All values are taken from Nguyen et al. 2015.

Functionality	Deposition Velocity (cm s^{-1})
H2O2	5.2
HNO3	3.8
O3	0.1
Organic Hydroperoxide (R-OOH)	1.8
Organic Nitrate (R-ONO2)	2.0
Formic Acid and All Carboxylic Acids (R-COOH)	1.0
Oxidised Volatile Organic Compound (OVOC)	1.2

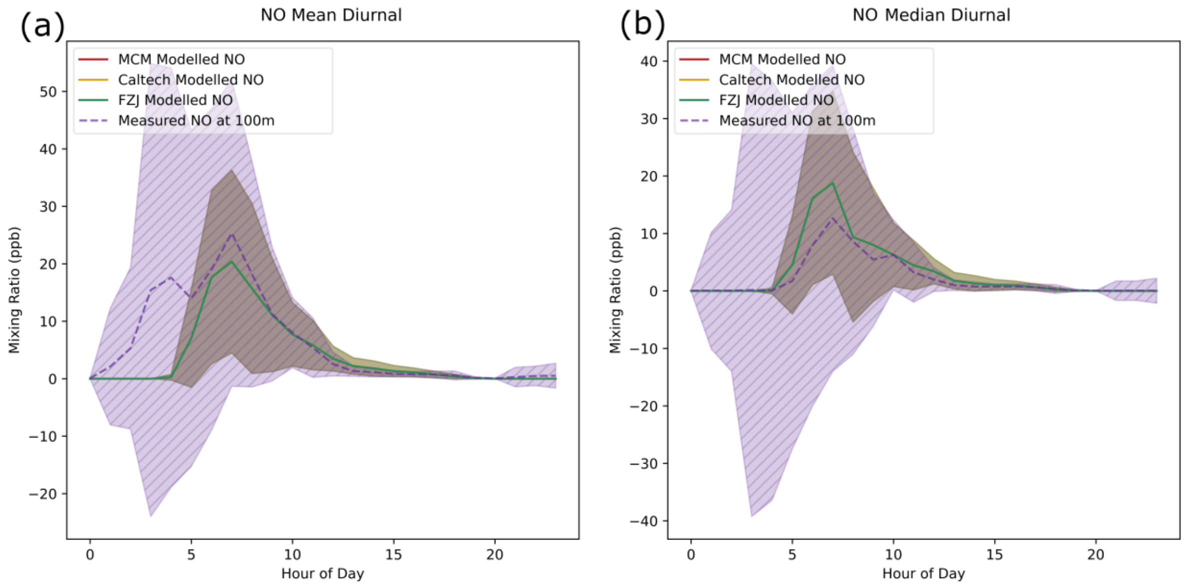


Figure S1. Measured NO at 100m and modelled NO in each model. The mean values (a) show a peak before sunrise due to large spikes in the measurements in the morning on some days, so the median diurnal (b) is also shown.

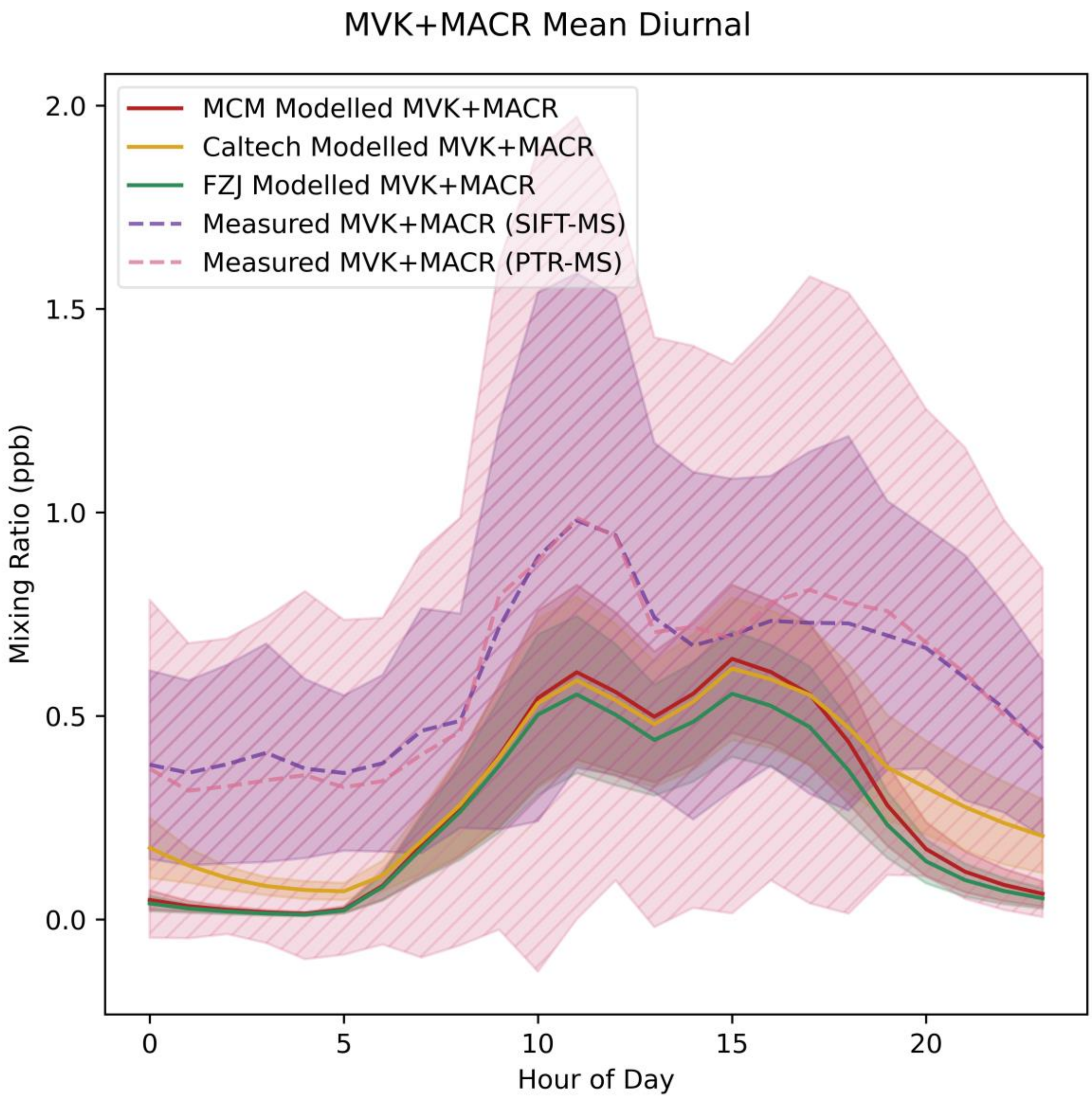


Figure S2. Measured and modelled MVK+MACR mixing ratios. Each line shows the mean value for each dataset, with the shaded area indicating one standard deviation above and below the mean.

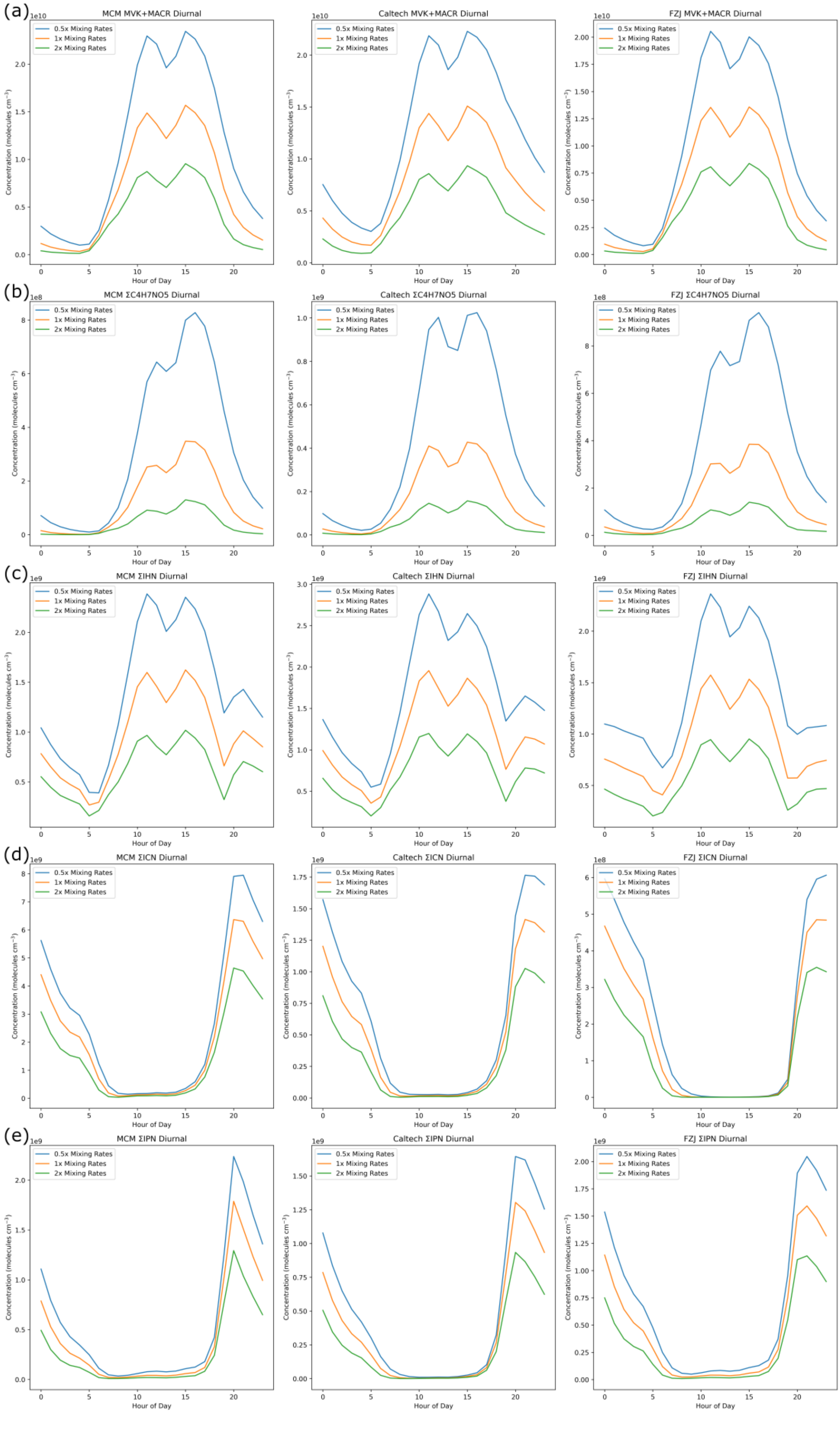


Figure S3. Impact on MVK+MACR (a), $\Sigma C_4H_7NO_5$ (b), ΣIHN (c), ΣICN (d), and ΣIPN (e) of varying the ventilation rate used in each model by 0.5 times and 2 times from the base mixing lifetime.

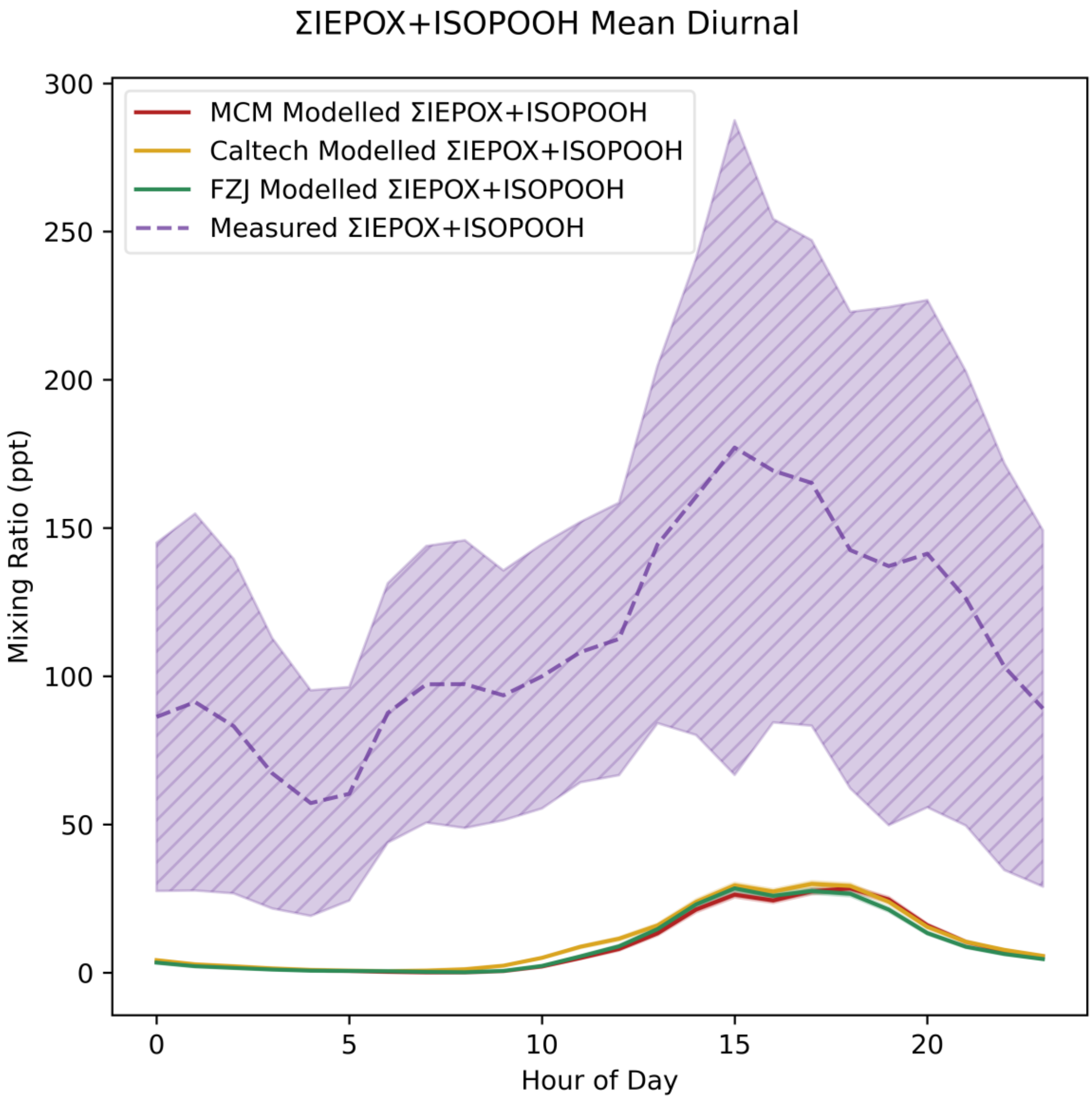


Figure S4. Measured and modelled ΣIEPOX+ISOPOOH mixing ratios. Each line shows the mean value for each dataset, with the shaded area indicating one standard deviation above and below the mean.

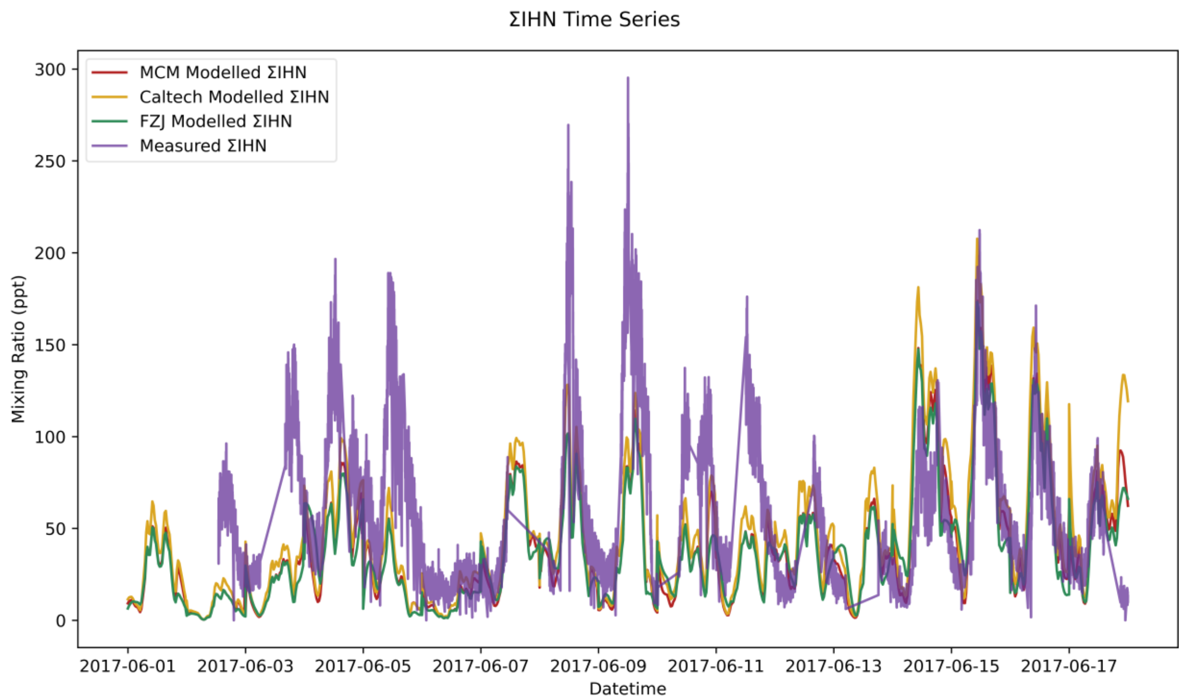


Figure S5. Time series for measured and modelled ΣIHN.

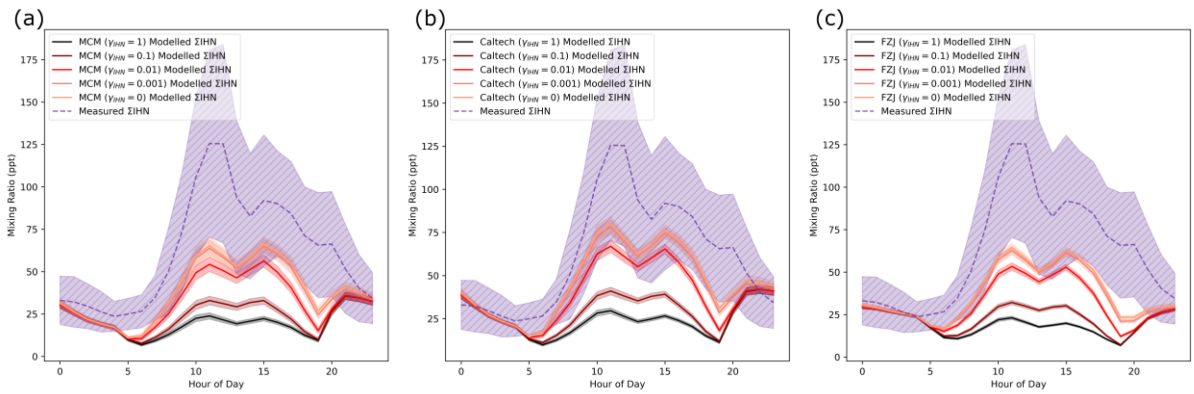


Figure S6. Measured and modelled ΣIHN mixing ratios for models using a range of γ_{IHN} values to account for the hydrolysis of 1,2-IHN. The mechanisms used in each model are as follows: (a) MCM, (b) Caltech Mechanism, (c) FZJ Mechanism. Each line shows the mean value for each dataset, with the shaded area indicating one standard deviation above and below the mean.

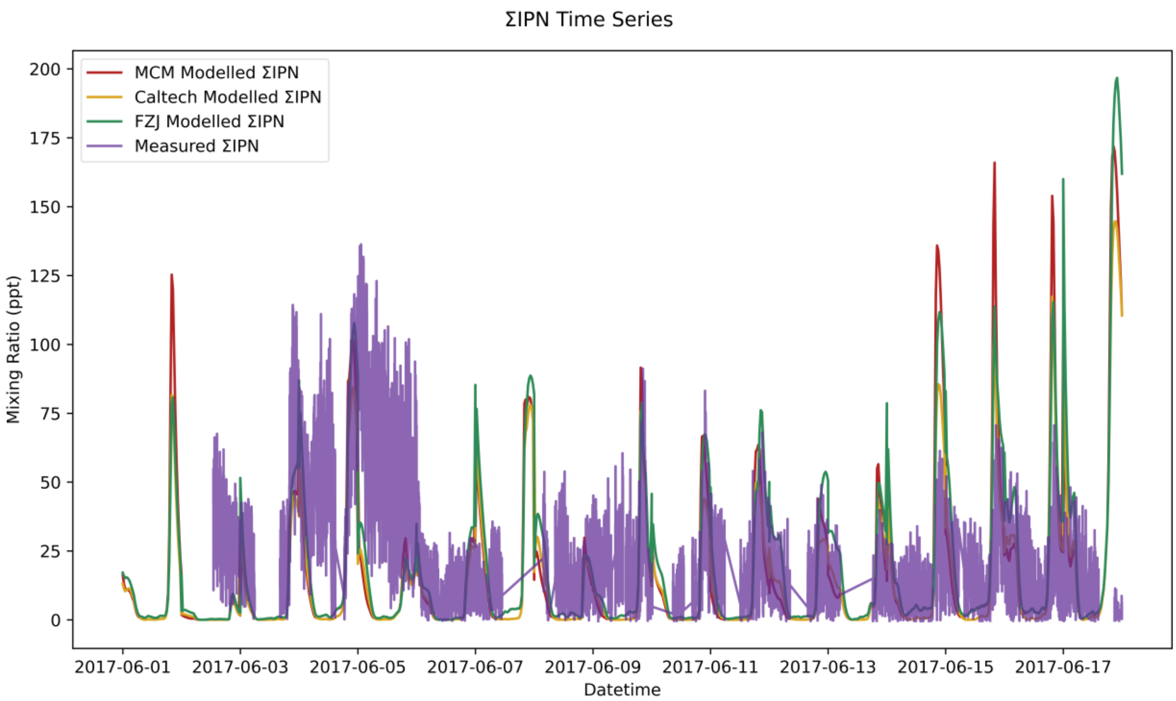


Figure S7. Time series for measured and modelled ΣIPN.

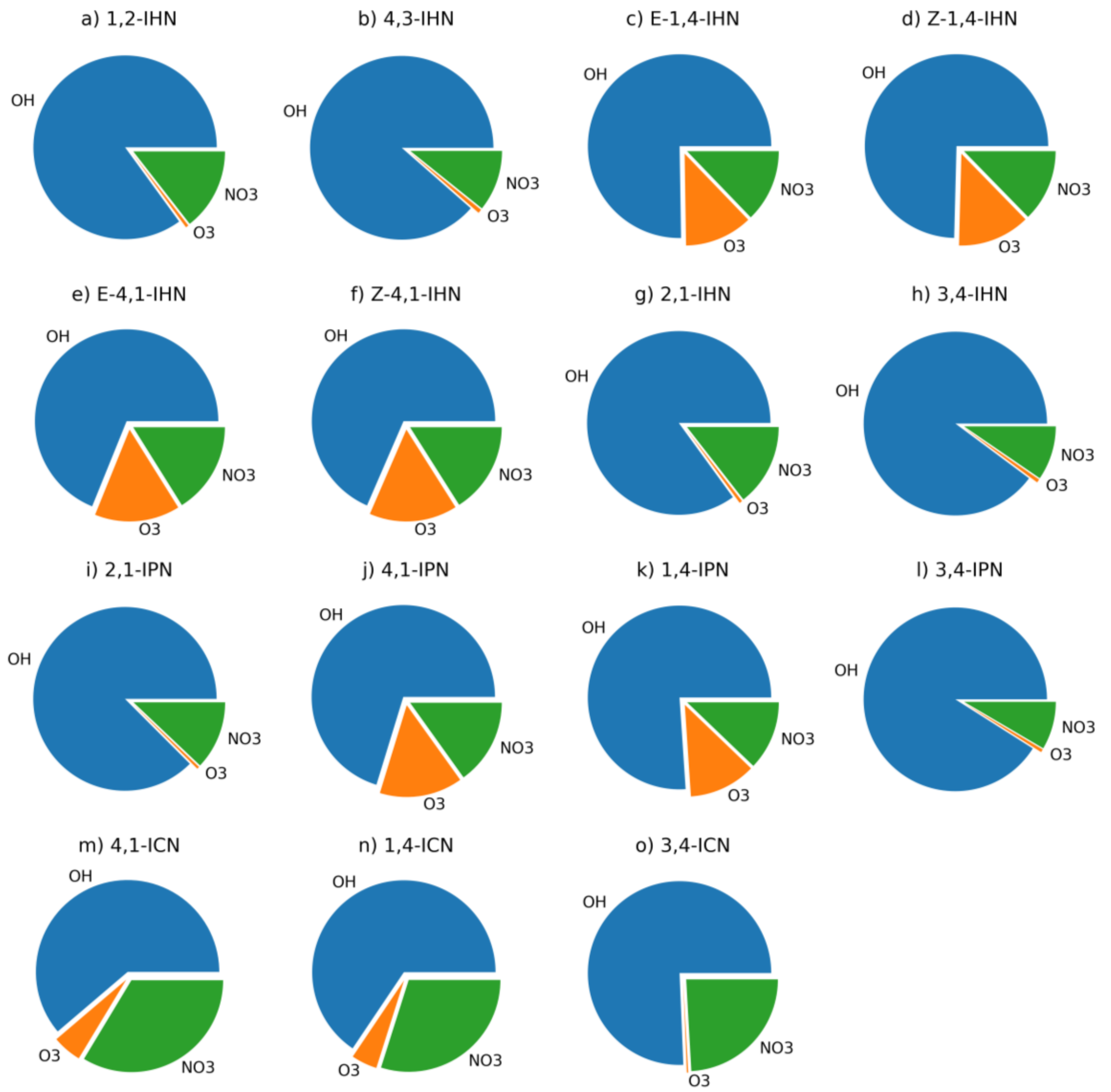
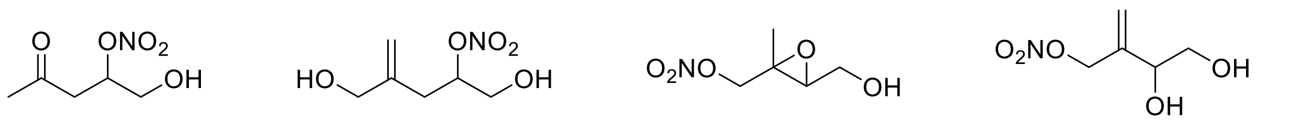


Figure S8. Proportional contribution of OH, O_3, and NO_3 to the night-time chemical loss (between 20:00 and 05:00) of IHN (a-h), IPN (i-l), and ICN (m-o) isomers. The loss rates are calculated using measured OH, O_3, and NO_3 concentrations and the rate constants listed in Wennberg et al. 2018.



C51NO3 **C524NO3** **ISOP1N23O4OH** **ISOP1N253OH4OH**

Figure S9. Structures of the three isomers of IPN that collectively comprise the majority of ΣIPN ($C_5H_9NO_5$) in the models.

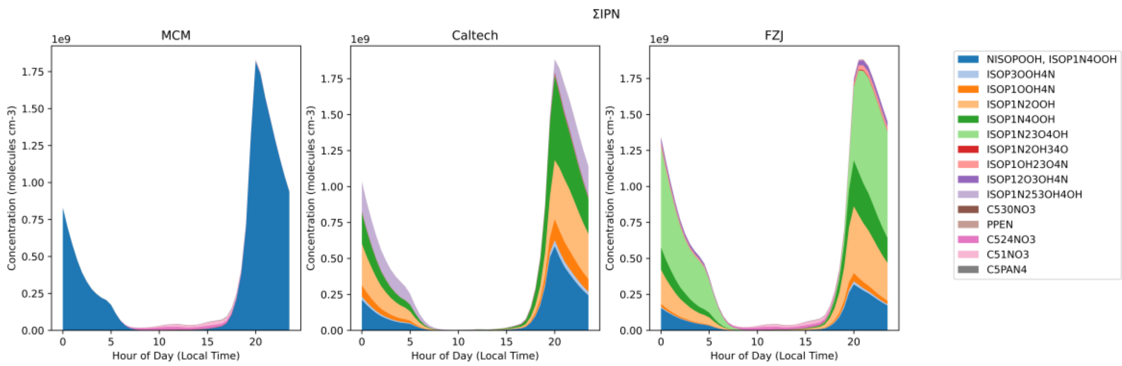


Figure S10. Isomer composition of the modelled ΣIPN.

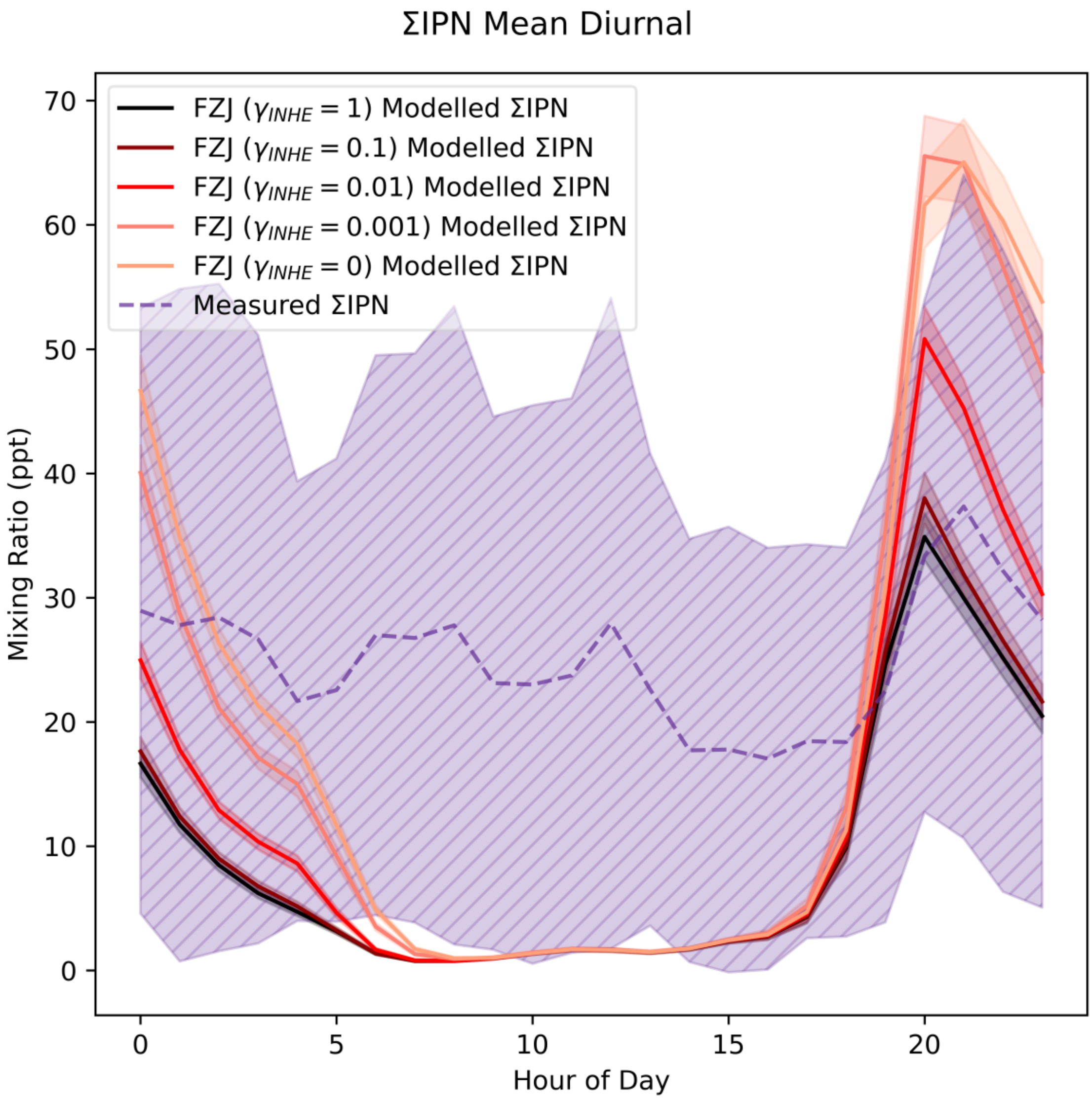


Figure S11.Measured and modelled ΣIPN mixing ratios for FZJ models using a range of γ_{INHE} values to account for the reactive uptake of INHE. Each line shows the mean value for each dataset, with the shaded area indicating one standard deviation above and below the mean.

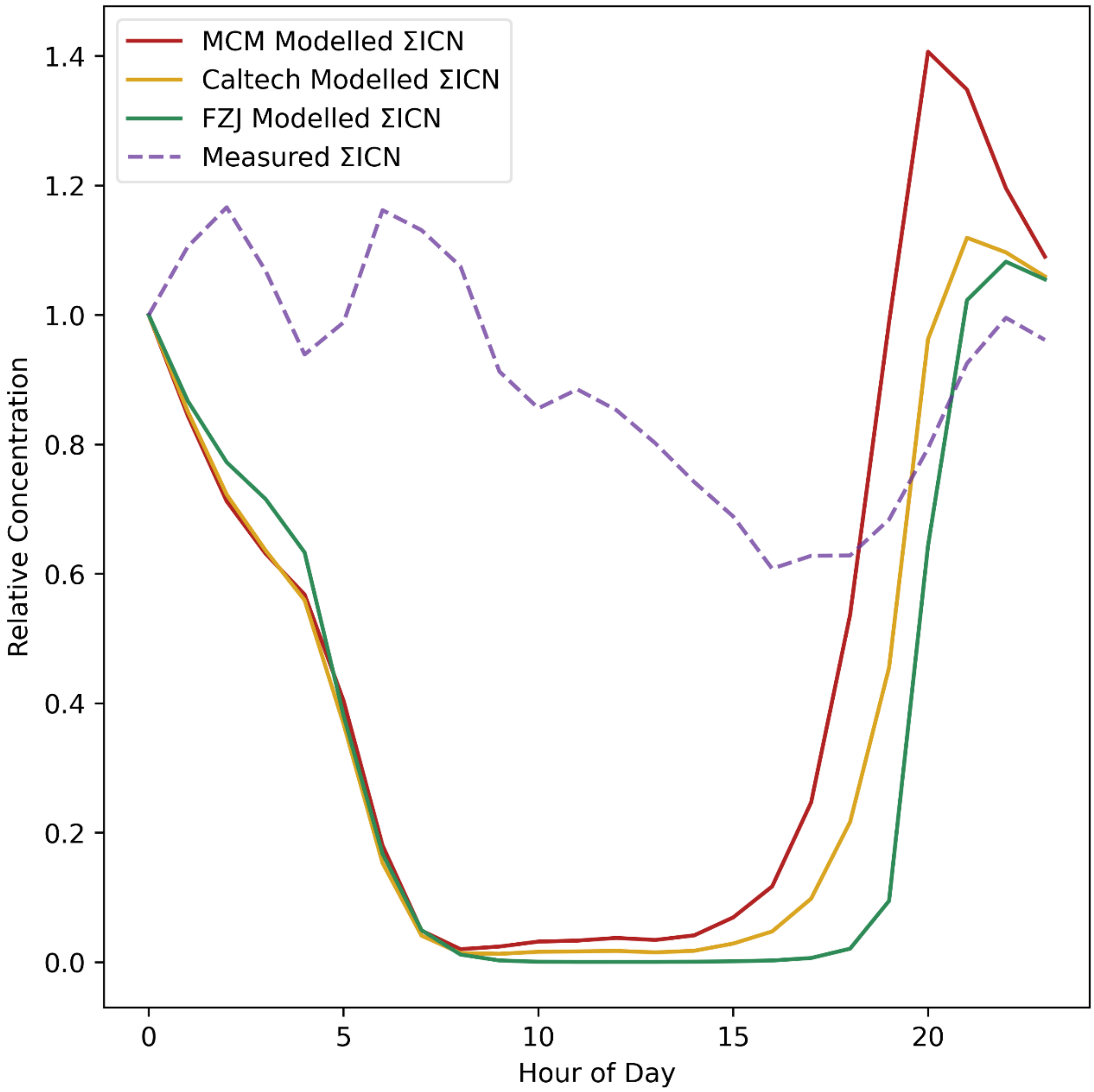


Figure S12. Measured and modelled ICN relative to the concentration at 00:00.

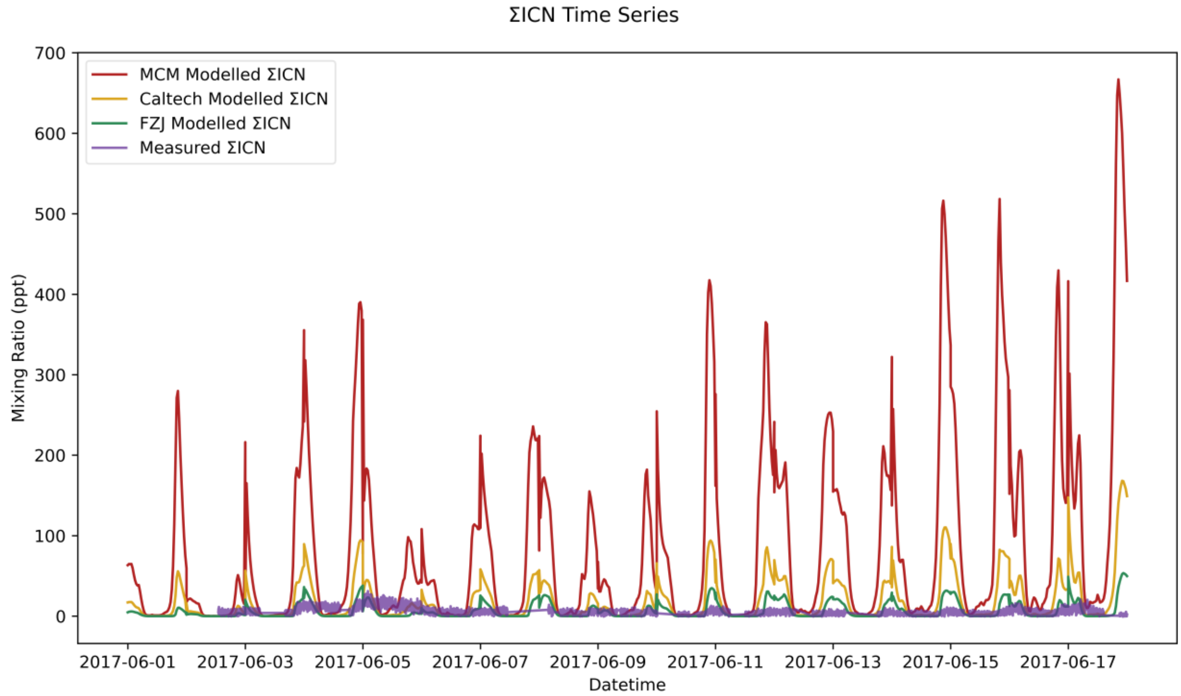


Figure S13. Time series for measured and modelled ΣICN.

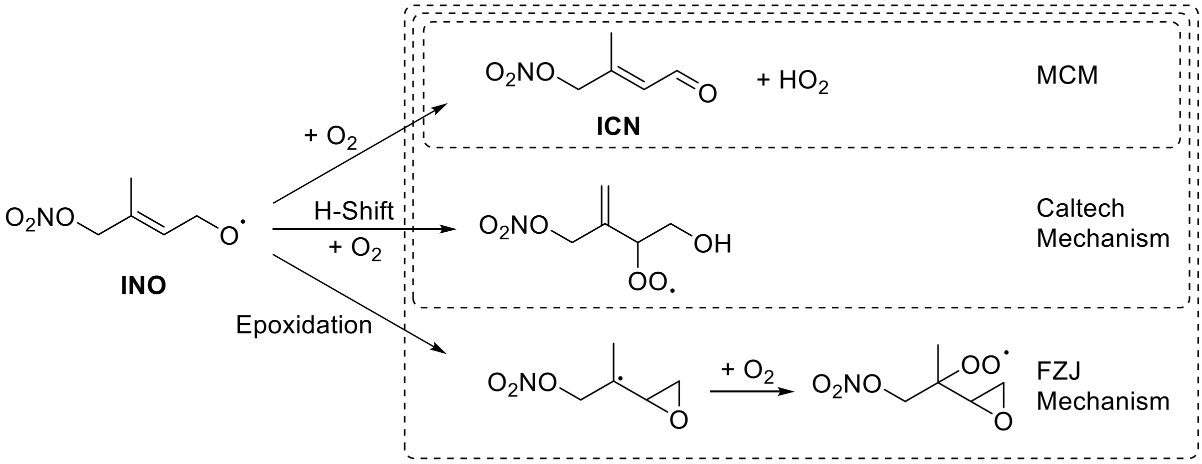


Figure S14. Examples of INO loss routes in each of the three mechanisms. Only one isomer is shown here, other isomers are present in the Caltech and FZJ Mechanisms. Additional reaction pathways are also possible in the Caltech and FZJ Mechanisms.

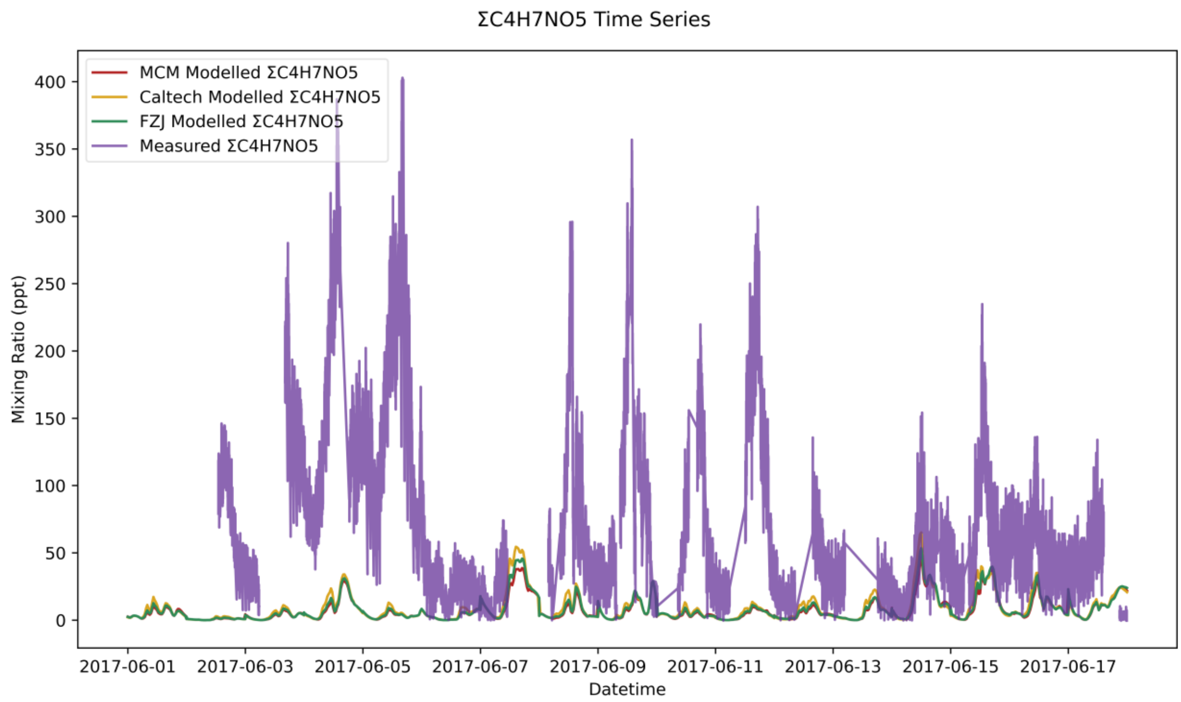
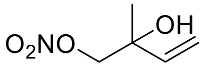
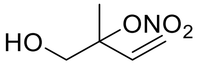
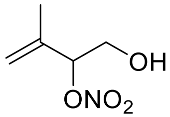
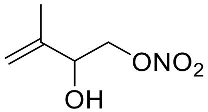
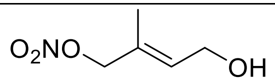
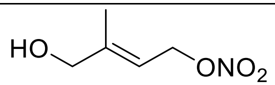
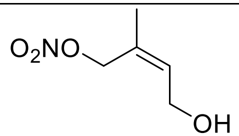
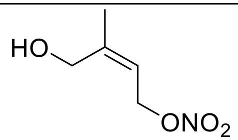
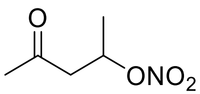
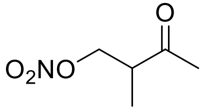
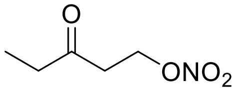
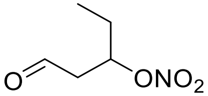
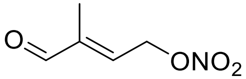
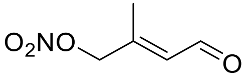
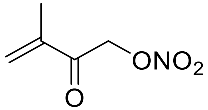
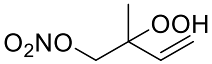
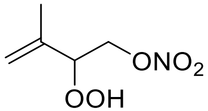
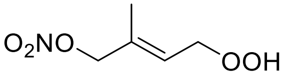
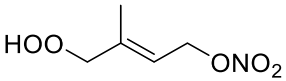
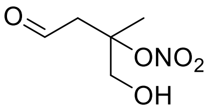
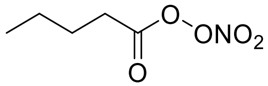
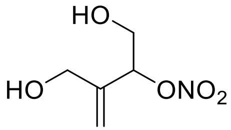
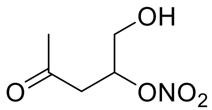
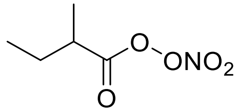
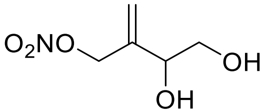
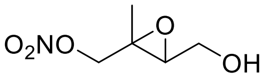
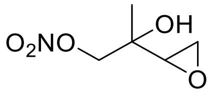
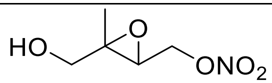
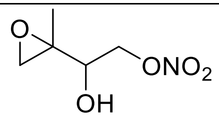
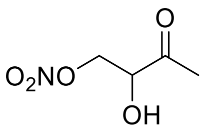


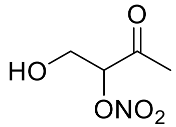
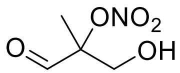
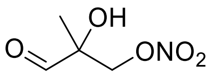
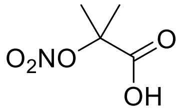
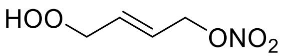
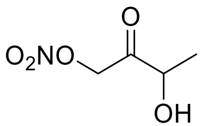
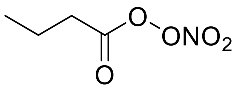
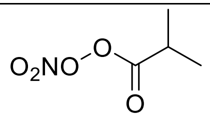
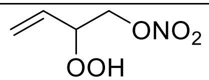
Figure S15. Time series for measured and modelled $\Sigma C_4H_7NO_5$.

Table S4. Glossary of nitrate species and their names

Species Group		Structure	Wennberg et al. 2018 Nomenclature	MCM Name	Caltech Mechanism Name	FZJ Mechanism Name
ΣIHN	IHN		2,1-IHN	-	ISOP1N2OH	ISOP1N2OH
			1,2-IHN	ISOPBNO3	ISOP1OH2N	ISOP1OH2N
			3,4-IHN	ISOPDNO3	ISOP3N4OH	ISOP3N4OH
			4,3-IHN	ISOP34NO3	ISOP3OH4N	ISOP3OH4N
			E-4,1-IHN	ISOPCNO3	ISOP1N4OHt	EISOP1N4OH
			E-1,4-IHN	ISOPANO3	ISOP1OH4Nt	EISOP1OH4N
			Z-4,1-IHN	-	ISOP1N4OHc	ZISOP1N4OH
			Z-1,4-IHN	-	ISOP1OH4Nc	ZISOP1OH4N
			-	MPRKNO3	MPRKNO3	MPRKNO3

Species Group		Structure	Wennberg et al. 2018 Nomenclature	MCM Name	Caltech Mechanism Name	FZJ Mechanism Name
			-	MIPKBNO3	MIPKBNO3	MIPKBNO3
			-	DIEKBNO3	DIEKBNO3	DIEKBNO3
			-	C4CHOBNO3	C4CHOBNO3	C4CHOBNO3
ΣICN			1,4-ICN	NC4CHO	ISOP1CO4N	ISOP1CO4N
			4,1-ICN	-	ISOP1N4CO	ISOP1N4CO
			3,4-ICN	-	ISOP3CO4N	ISOP3CO4N
ΣIPN	IPN		2,1-IPN	-	ISOP1N2OOH	ISOP1N2OOH
			3,4-IPN	-	ISOP3OOH4N	ISOP3OOH4N
			4,1-IPN	NISOPOOH	ISOP1N4OOH	ISOP1N4OOH
			1,4-IPN	-	ISOP1OOH4N	ISOP1OOH4N
			-	C530NO3	-	C530NO3

Species Group		Structure	Wennberg et al. 2018 Nomenclature	MCM Name	Caltech Mechanism Name	FZJ Mechanism Name
			-	PPEN	PPEN	PPEN
			-	C524NO3	-	C524NO3
			-	C51NO3	C51NO3	C51NO3
			-	C5PAN4	C5PAN4	C5PAN4
			-	-	ISOP1N253OH4OH	-
			-	-	ISOP1N23O4OH	ISOP1N23O4OH
			-	-	ISOP1N2OH34O	ISOP1N2OH34O
			-	-	ISOP1OH23O4N	ISOP1OH23O4N
			-	-	ISOP12O3OH4N	ISOP12O3OH4N
$\Sigma C_4H_7NO_5$	$C_4H_7NO_5$		-	HMVKANO3	MVK3OH4N	HMVKANO3

Species Group		Structure	Wennberg et al. 2018 Nomenclature	MCM Name	Caltech Mechanism Name	FZJ Mechanism Name
			-	MVKNO3	MVK3N4OH	MVKNO3
			-	MACRNO3	MACR2N3OH	MACRNO3
			-	MACRNB	MACR2OH3N	MACRNB
			-	MPRNO3CO2H	MPRNO3CO2H	MPRNO3CO2H
			-	NBUTDBOOH	NBUTDBOOH	NBUTDBOOH
			-	CO3C4NO3OH	CO3C4NO3OH	CO3C4NO3OH
			-	PBN	PBN	PBN
			-	PIPN	PIPN	PIPN
			-	NBUTDAOOH	NBUTDAOOH	NBUTDAOOH