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	10608	12372
Number of Species	3443	3476	3592
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 Σ$C_4H_7NO_5$ 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), comprehensive two dimensional gas chromatography with flame ionisation detection (GC×GC), 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	i-pentane	IC5H12	DC-GC
α-pinene	APINENE	GC×GC	n-hexane	NC6H14	DC-GC
limonene	LIMONENE	GC×GC	n-heptane	NC7H16	DC-GC
ethene	C2H4	DC-GC, SIFT	n-octane	NC8H18	DC-GC
propene	C3H6	DC-GC, SIFT,	n-nonane	NC9H20	GC×GC
trans-2-butene	TBUT2ENE	DC-GC	n-decane	NC10H22	GC×GC
1-butene	BUT1ENE	DC-GC	n-undecane	NC11H24	GC×GC
i-butene	MEPROPENE	DC-GC	n-dodecane	NC12H26	GC×GC
cis-2-butene	CBUT2ENE	DC-GC	benzene	BENZENE	DC-GC, SIFT, PTR
trans-2-pentene	TPENT2ENE	DC-GC	Ethylbenzene	EBENZ	GC×GC, DC-GC, SIFT, PTR
cis-2-pentene	CPENT2ENE	DC-GC	propylbenzene	PBENZ	GC×GC, SIFT, PTR
1,3-butadiene	C4H6	DC-GC, SIFT	isopropylbenzene	IPBENZ	GC×GC
acetylene	C2H2	DC-GC, SIFT	1,3,5-trimethylbenzene	TM135B	GC×GC
methanol	CH3OH	DC-GC, SIFT	1,2,3-trimethylbenzene	TM123B	GC×GC
ethanol	C2H5OH	DC-GC, SIFT	1,2,4-trimethylbenzene	TM124B	GC×GC
ethane	C2H6	DC-GC	toluene	TOLUENE	DC-GC, SIFT, PTR
propane	C3H8	DC-GC, SIFT	m-ethyltoluene	METHTOL	GC×GC
n-butane	NC4H10	DC-GC	p-ethyltoluene	PETHTOL	GC×GC
i-butane	IC4H10	DC-GC	o-ethyltoluene	OETHTOL	GC×GC
n-pentane	NC5H12	DC-GC	o-xylene	OXYL	GC×GC, 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

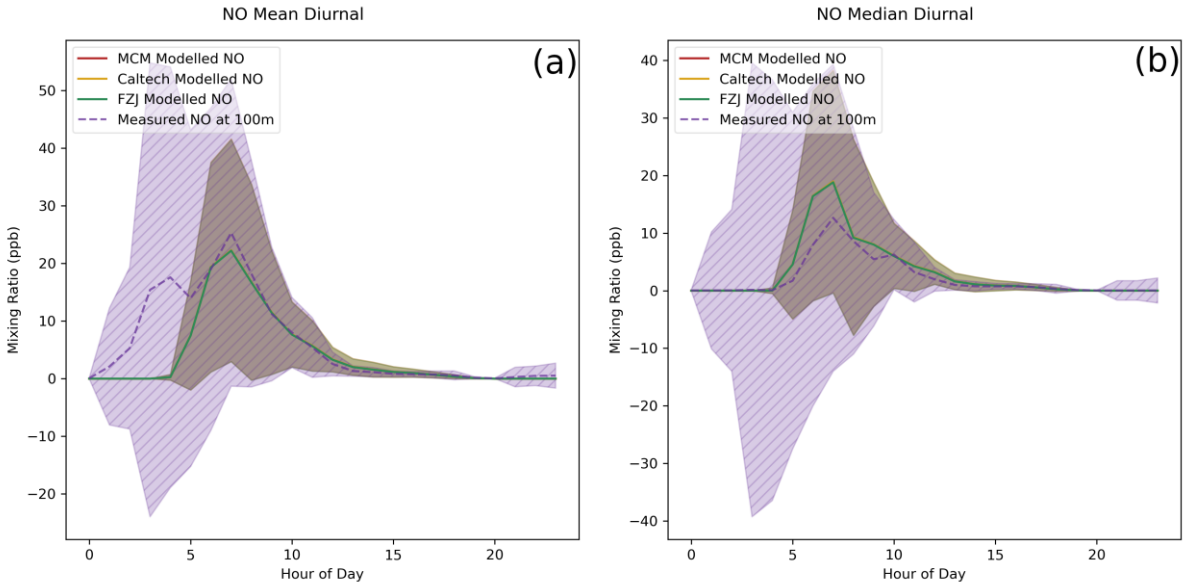


Figure S1. Measured NO at 100m and modelled NO in each model. The mean values (a) show a peak before sunrise due to large spikes in the measurements in the morning on some days, so the median diurnal (b) is also shown.

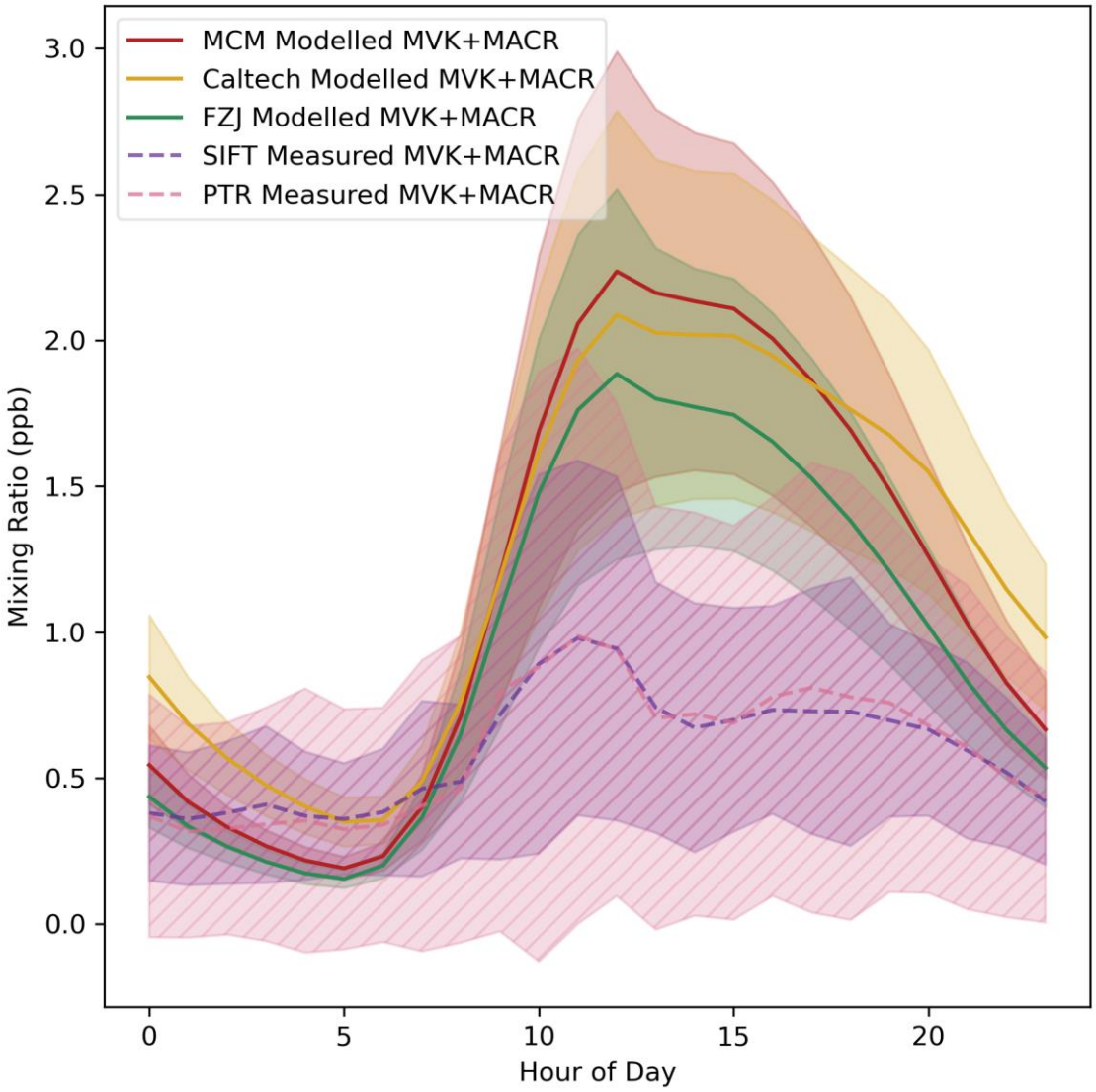


Figure S2. Measured and modelled MVK+MACR mixing ratios. Each line shows the mean value for each dataset, with the shaded area indicating one standard deviation above and below the mean.

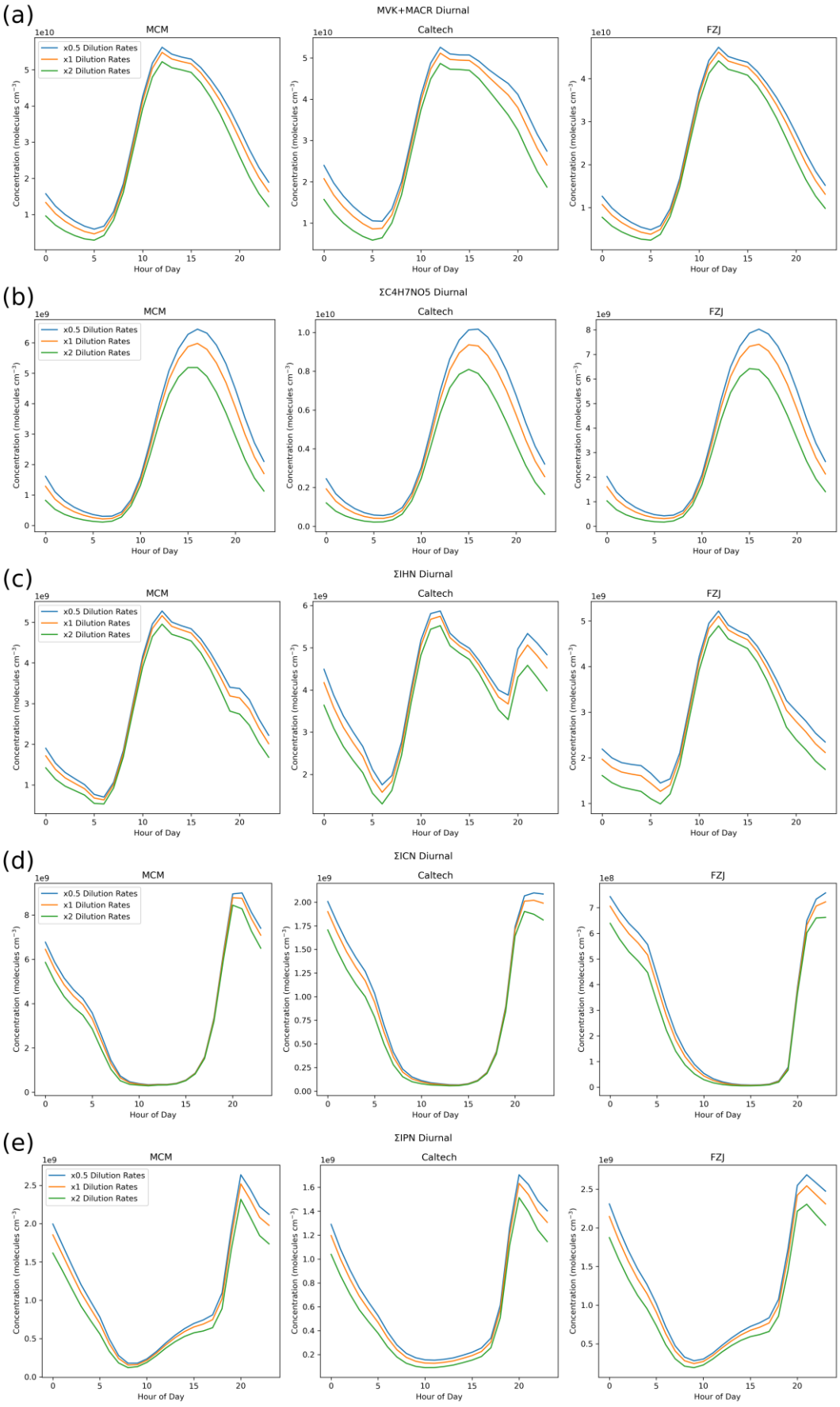


Figure S3. Impact on MVK+MACR (a), $\Sigma C_4H_7NO_5$ (b), ΣIHN (c), ΣICN (d), and ΣIPN (e) of varying the ventilation rate used in each model by 0.5 times and 2 times from the base mixing lifetime of 24 hours (a rate of 1.157×10^{-5} s^{-1}).

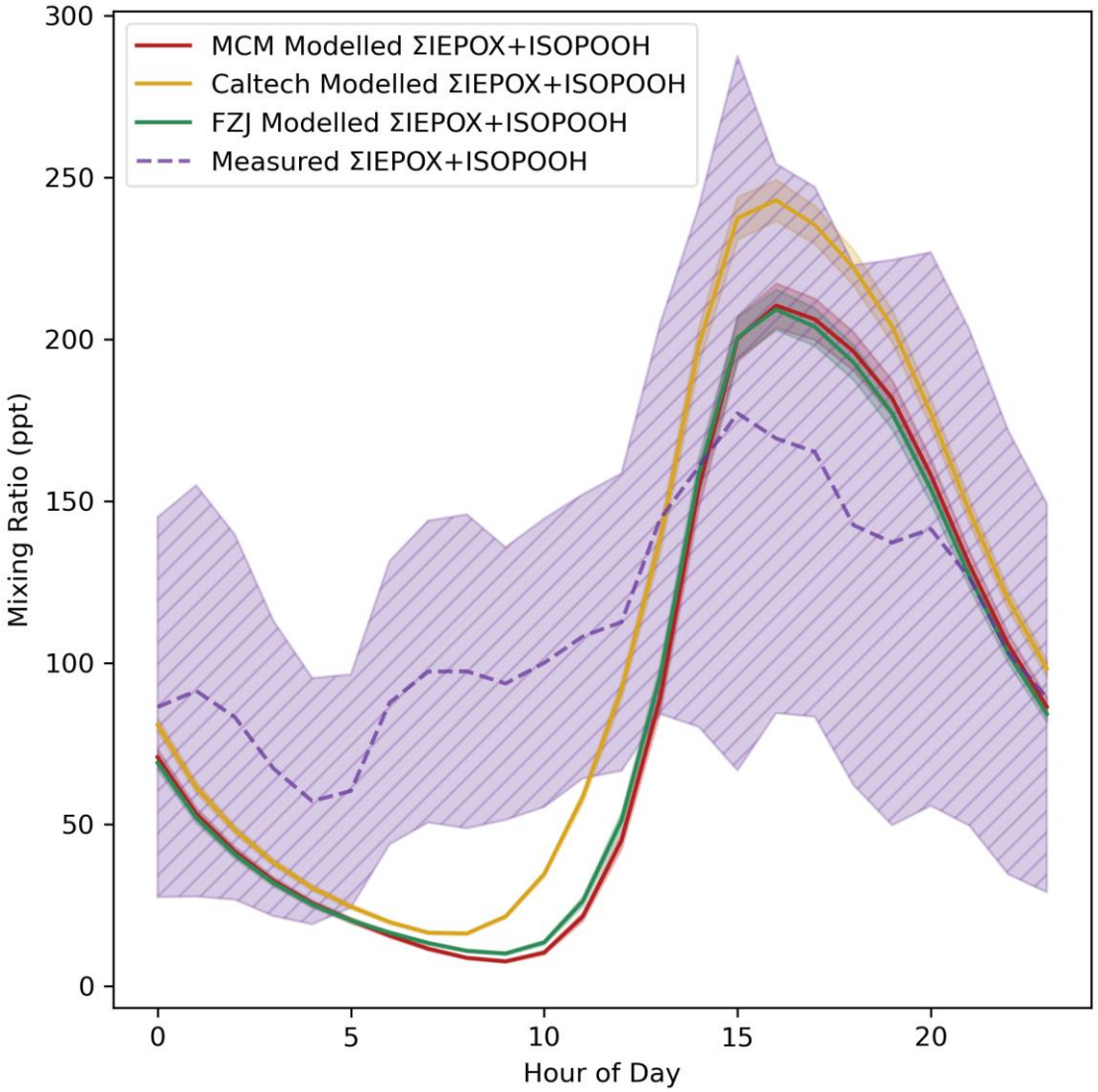


Figure S4. Measured and modelled ΣIEPOX+ISOPOOH mixing ratios. Each line shows the mean value for each dataset, with the shaded area indicating one standard deviation above and below the mean.

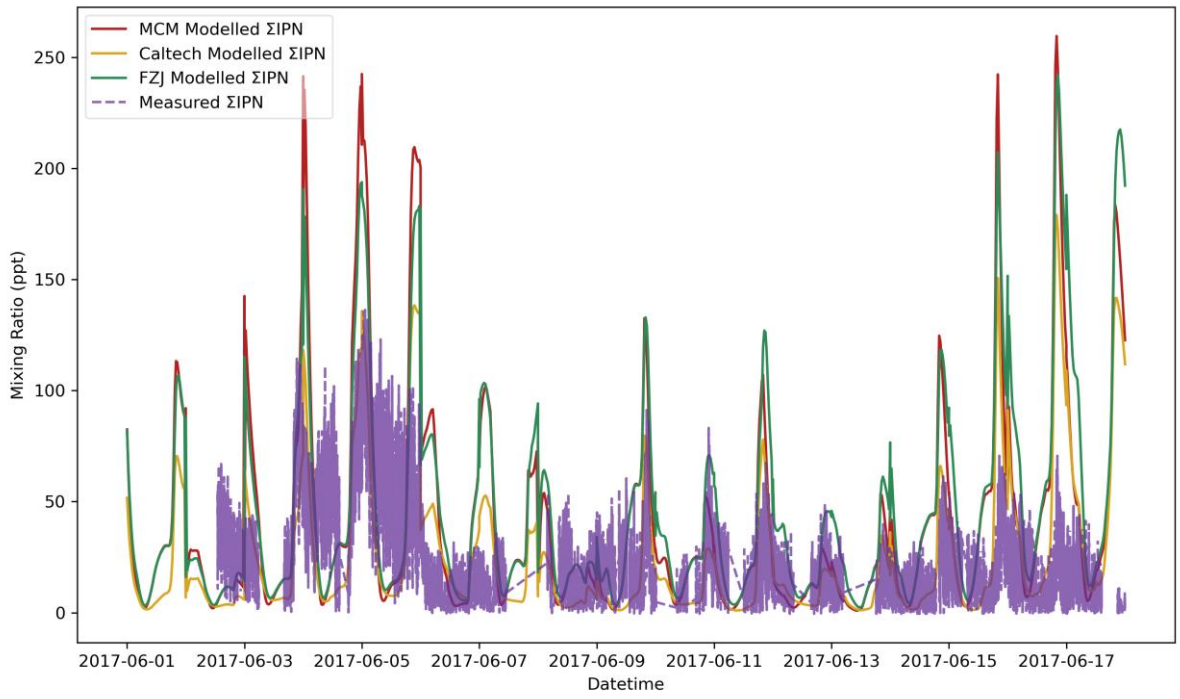


Figure S5. Time series for measured and modelled ΣIPN.

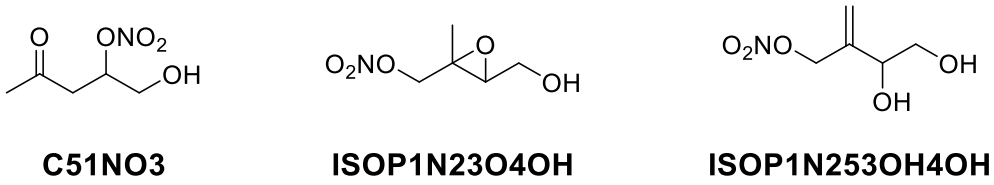


Figure S6. Structures of the three isomers of IPN that collectively comprise the majority of ΣIPN ($C_5H_9NO_5$) in the models.

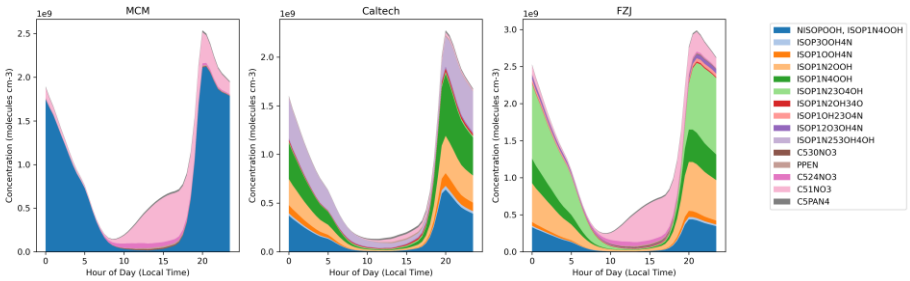


Figure S7. Isomer composition of the modelled ΣIPN.

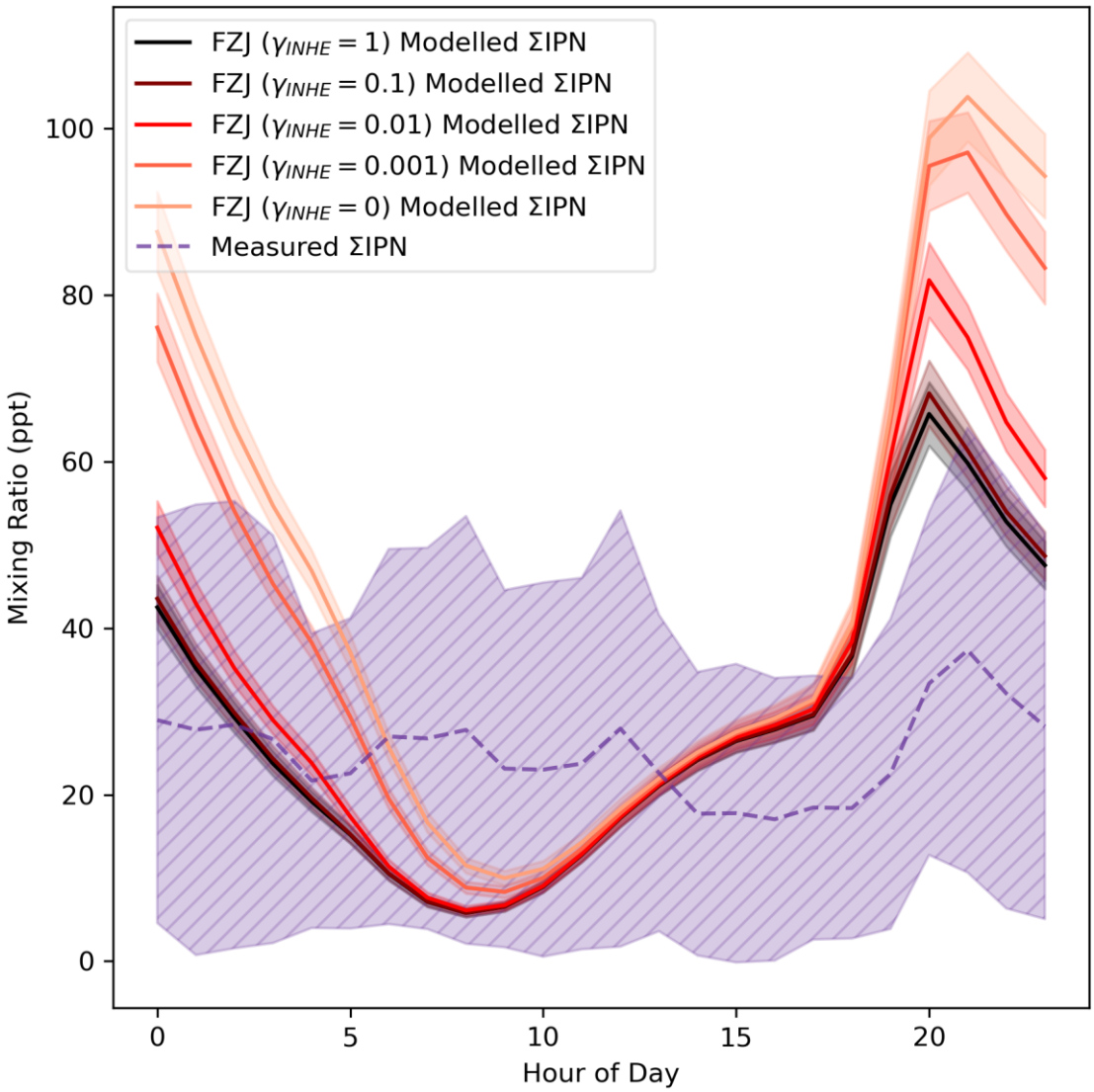


Figure S8.Measured and modelled ΣIPN mixing ratios for FZJ models using a range of γ_{INHE} values to account for the reactive uptake of INHE. Each line shows the mean value for each dataset, with the shaded area indicating one standard deviation above and below the mean.

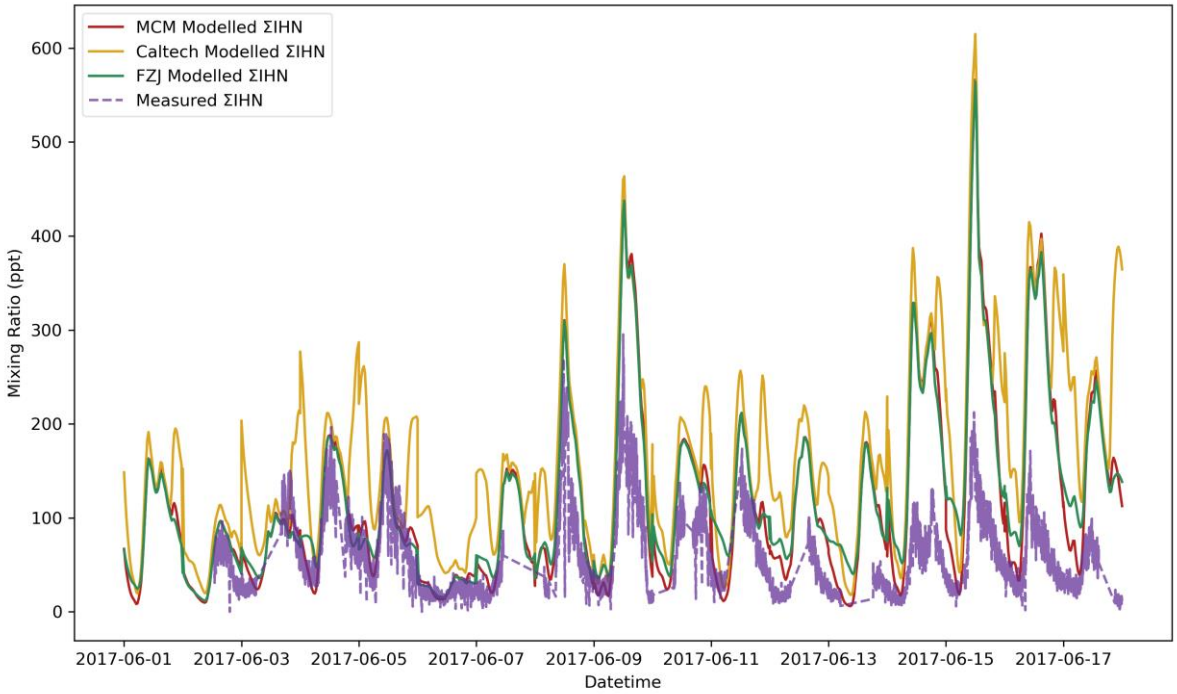


Figure S9. Time series for measured and modelled ΣIHN.

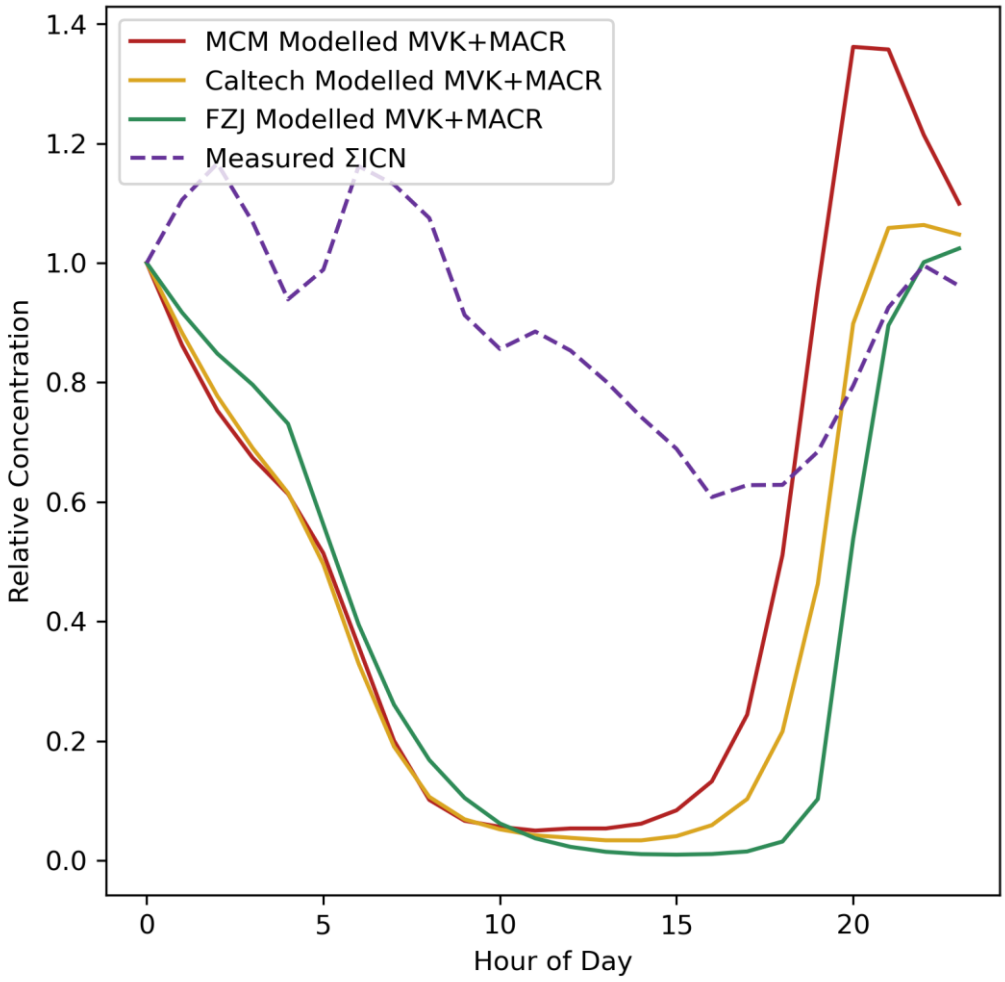


Figure S10. Measured and modelled ICN relative to the concentration at 00:00.

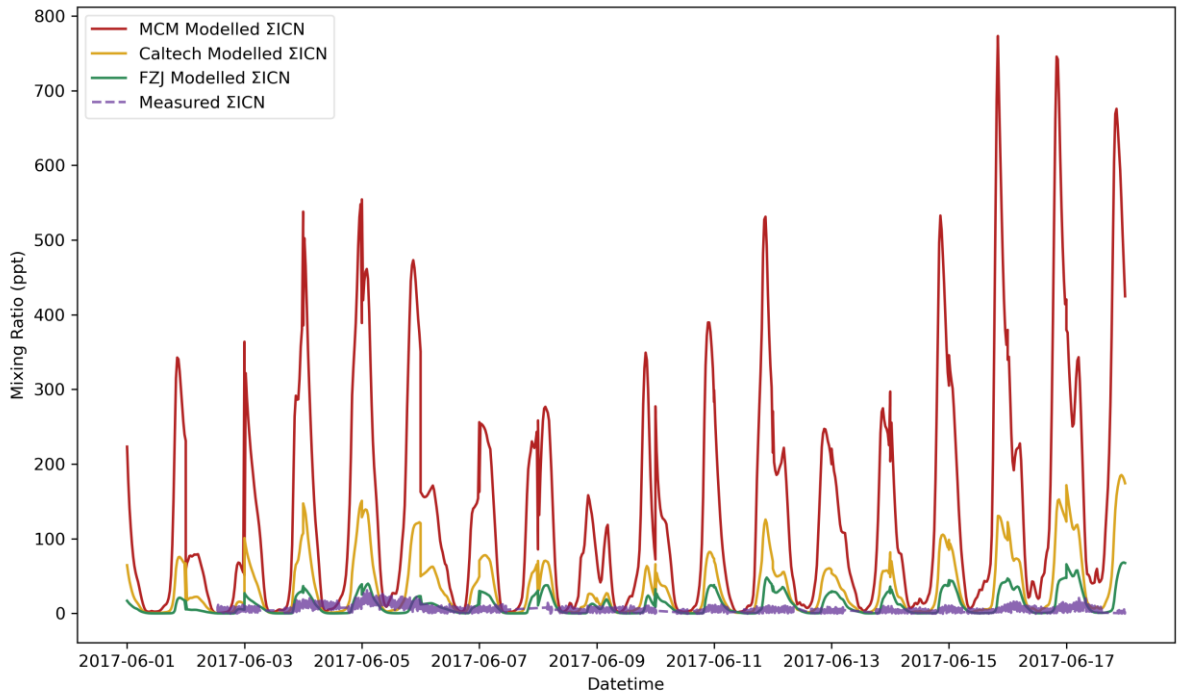


Figure S11. Time series for measured and modelled ΣICN.

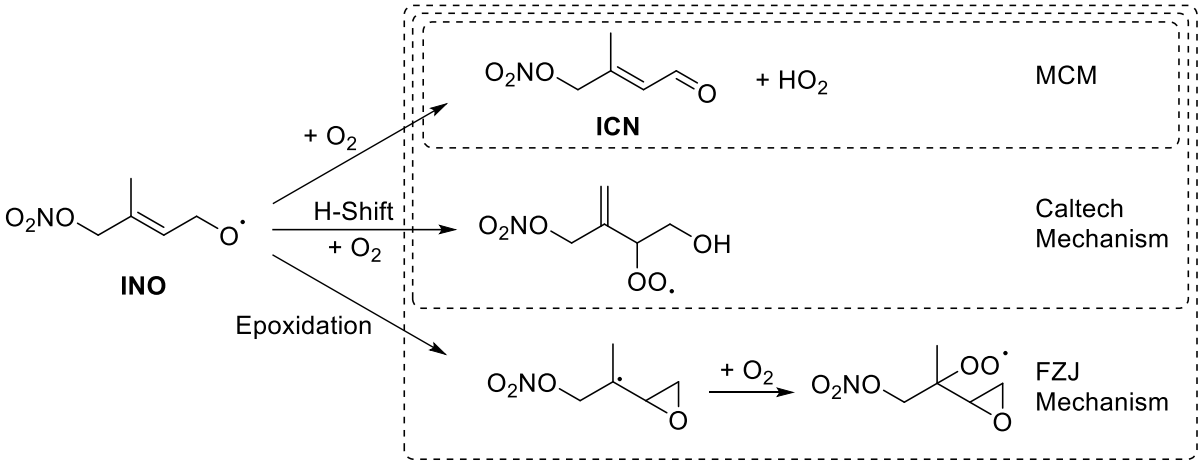


Figure S12. Examples of INO loss routes in each of the three mechanisms. Only one isomer is shown here, other isomers are present in the Caltech and FZJ Mechanisms. Additional reaction pathways are also possible in the Caltech and FZJ Mechanisms.

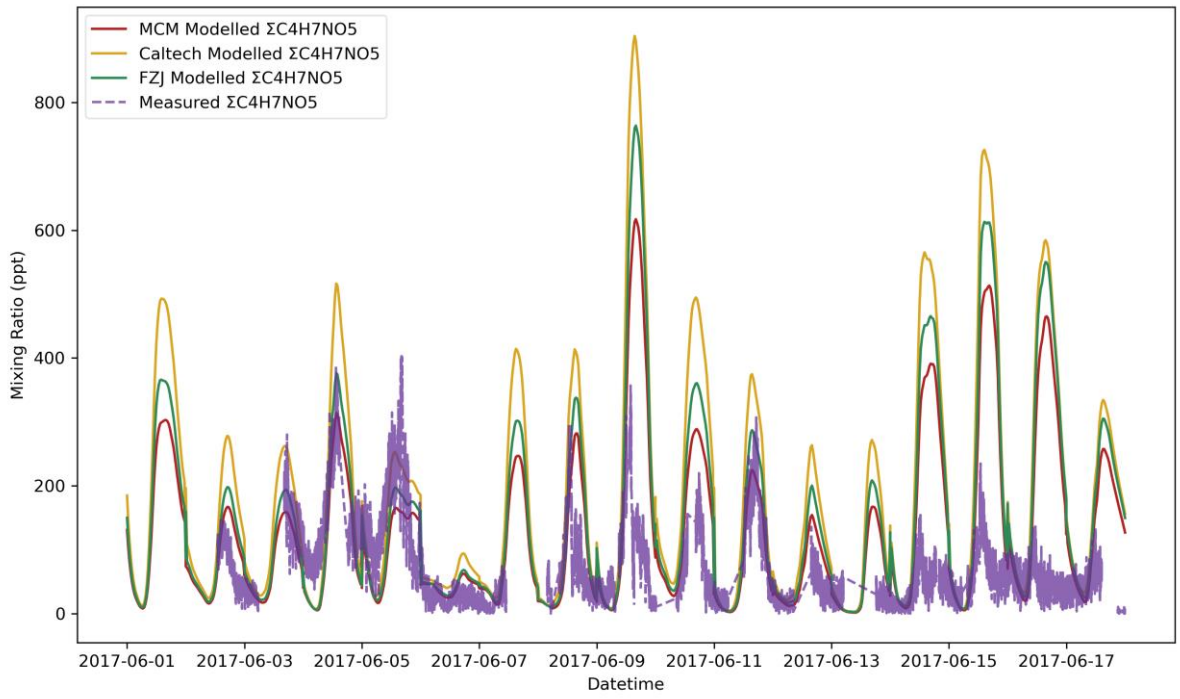


Figure S13. Time series for measured and modelled $\Sigma C_4H_7NO_5$.

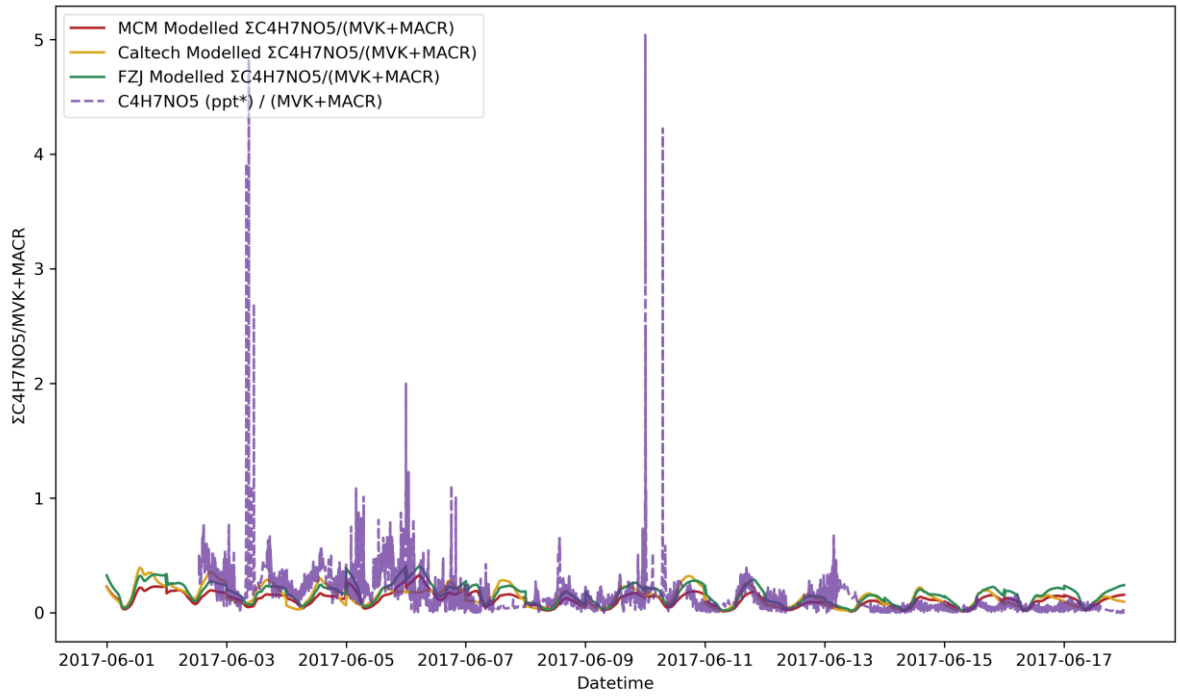
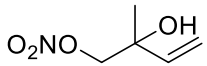
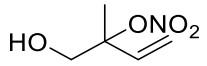
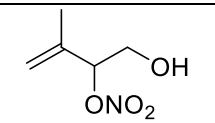
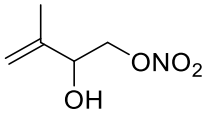
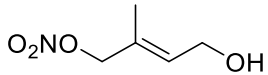
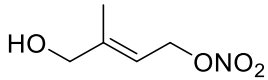
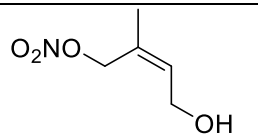
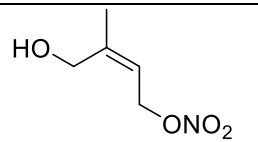
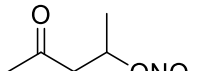
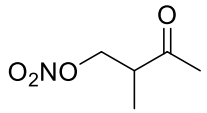
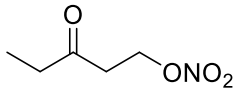
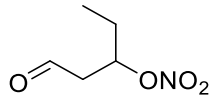
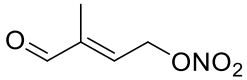
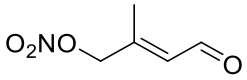
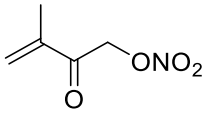
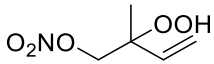
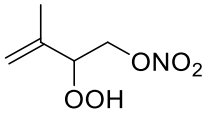
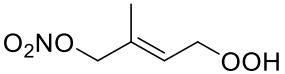
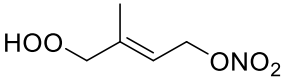
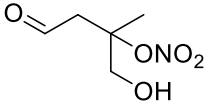
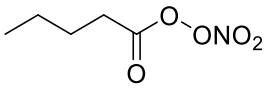
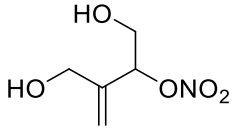
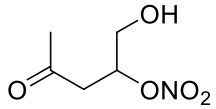
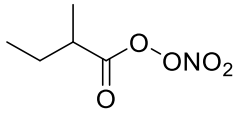
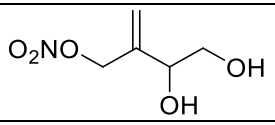
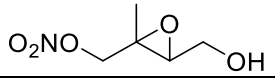
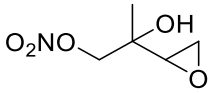
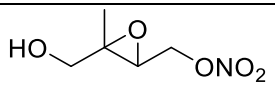
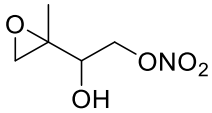
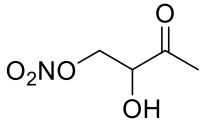


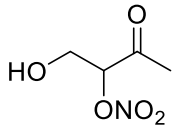
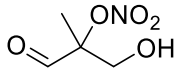
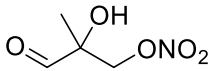
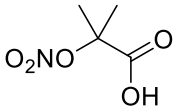
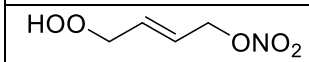
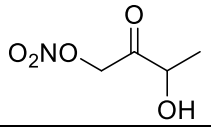
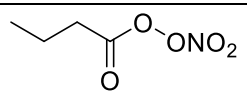
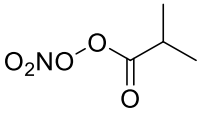
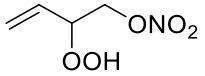
Figure S14. Time series for measured and modelled $\Sigma C_4H_7NO_5$/(MVK+MACR).

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
			-	MIPKBNO3	MIPKBNO3	MIPKBNO3

Species Group		Structure	Wennberg et al. 2018 Nomenclature	MCM Name	Caltech Mechanism Name	FZJ Mechanism Name
			-	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
			-	PPEN	PPEN	PPEN

Species Group		Structure	Wennberg et al. 2018 Nomenclature	MCM Name	Caltech Mechanism Name	FZJ Mechanism Name
			-	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