

Supplement materials for

**Kanaya et al., Comparisons of observed and modeled OH and HO₂
concentrations during the ambient measurement period of the
HOxComp field campaign**

Table S1. Revised isoprene degradation chemistry used in this study.

No.	Reaction	k (cm ³ s ⁻¹)	Note
A1	ISO+OH → 0.491ISOPBO2 + 0.259ISOPDO2 + 0.25ISOPEO2	2.54×10 ⁻¹¹ ×exp(410/T)	1 (RACM R70 replaced), for S1, S2, and S1_a(HC8) runs, product yields are 0.6ISOPBO2 + 0.3ISOPDO2 + 0.1ISOPEO2
A2	ISOPBO2 + NO → 0.928 (MVK + HO2 + NO2 + HCHO) + 0.072ISON	2.54×10 ⁻¹² ×exp(360/T)	2
A3	ISOPDO2 + NO → 0.855 (MACR + HO2 + NO2 + HCHO) + 0.145ISON	2.54×10 ⁻¹² ×exp(360/T)	2
A4	ISOPEO2 + NO → 0.952 (HALD5152 + HO2 + NO2 + HCHO) + 0.044ISON	2.54×10 ⁻¹² ×exp(360/T)	2
A5	ISOPBO2 + HO2 → ISOPBOOH	0.706×2.91×10 ⁻¹³ ×exp(1300/T)	2
A6	ISOPDO2 + HO2 → ISOPDOOH	0.706×2.91×10 ⁻¹³ ×exp(1300/T)	2
A7	ISOPBO2 → HPALD1 + HO2	4.06×10 ⁹ ×exp(-7302/T) (s ⁻¹)	3, 4, Only for S1, S2, and S1_a(HC8) runs
A8	ISOPBO2 → MVK + HCHO + OH	2.08×10 ¹¹ ×exp(-8993/T) (s ⁻¹)	3, 4, Only for S1, S2, and S1_a(HC8) runs
A9	ISOPDO2 → HPALD2 + HO2	8.5×10 ⁹ ×exp(-7432/T) (s ⁻¹)	3, 4, Only for S1, S2, and S1_a(HC8) runs
A10	ISOPDO2 → MACR + HCHO + OH	2.08×10 ¹¹ ×exp(-8993/T) (s ⁻¹)	3, 4, Only for S1, S2, and S1_a(HC8) runs
A11	ISOPBOOH+OH → IEPOX + OH	1.9×10 ⁻¹¹ ×exp(390/T)	4
A12	ISOPBOOH+OH → 0.7ISOPBO2 + 0.3HCOC5 + 0.3OH	0.38×10 ⁻¹¹ ×exp(200/T)	4
A13	ISOPDOOH+OH → IEPOX + OH	1.9×10 ⁻¹¹ ×exp(390/T)	4
A14	ISOPDOOH+OH → 0.7ISOPDO2 + 0.3HCOC5 + 0.3OH	0.38×10 ⁻¹¹ ×exp(200/T)	4
A15	IEPOX+OH → IEPOXO2	5.78×10 ⁻¹¹ ×exp(-400/T)	4
A16	IEPOXO2+ NO → 0.725HKET + 0.275GLY + 0.275GLYALD + 0.275MGLY + 0.375HCHO + 0.074ORA1 + 0.125OH + 0.825HO2 + 0.251CO + NO2	2.54×10 ⁻¹² ×exp(360/T)	4
A17	IEPOXO2+HO2 → 0.725HKET + 0.275GLY + 0.275GLYALD + 0.275MGLY + 0.375HCHO + 0.074ORA1 + 1.125OH + 0.825HO2 + 0.251CO	0.074×10 ⁻¹¹ exp(700/T)	4
A18	ISON+OH → HKET+NALD	1.30×10 ⁻¹¹	1
A19	MACR+OH → MACP	1.86×10 ⁻¹¹ ×exp(175/T)	2 (RACM R82 replaced)
A20	MACR+O3 → 0.90MGLY+0.45ORA1+0.32HO2+0.22CO+0.19OH+0.10ACO3	1.36×10 ⁻¹⁵ ×exp(-2112/T)	2 (RACM R113 replaced)
A21	MACP+NO → NO2+0.25HKET+0.25CO+0.25A	2.54×10 ⁻¹² ×exp(360/T)	1

	CO3+0.50MGly+0.75HCHO+0.75HO2		
A22	MACP + HO2 → MAHP	$1.82 \times 10^{-13} \times \exp(1300/T)$	1
A23	MACP + NO2 → MPAN	$k_0 = 9.7 \times 10^{-29} \times (T/300)^{-5.6}$ $k_\infty = 9.3 \times 10^{-12} \times (T/300)^{-1.5}$ $k = \{k_0 \times [M] / (1 + k_0 \times [M] / k_\infty)\} \times 0.6^{\{1 + [\log_{10}(k_0[M]/k_\infty)]^2\} - 1}$	1
A24	MPAN → MACP + NO2	$k = k(260) / (9.0 \times 10^{-29} \times \exp(14000/T))$	1
A25	MPAN + OH → HKET + NO2	3.60×10^{-12}	1
A26	MAHP + OH → MACP	3.0×10^{-11}	1
A27	NALD + OH → HCHO + CO + NO2	$5.60 \times 10^{-12} \times \exp(270/T)$	1
A28	ISO + O3 → 0.39MACR + 0.26MVK + 0.58HCHO + 0.10MACP + 0.10ACO3 + 0.08MO2 + 0.28ORA1 + 0.14CO + 0.09H2O2 + 0.25HO2 + 0.25OH	$7.86 \times 10^{-15} \times \exp(-1913/T)$	1 (RACM R110 replaced)
A29	MVK + OH → MACP	$4.13 \times 10^{-12} \times \exp(452/T)$	2
A30	MVK + O3 → 0.90MGly + 0.45ORA1 + 0.32HO2 + 0.22CO + 0.19OH + 0.10ACO3	$7.51 \times 10^{-16} \times \exp(-1521/T)$	2
A31	MACR + hv → CO + HCHO + HO2 + ACO3	$2.192 \times 10^{-5} \times \cos(\text{sza})^{0.526} \times \exp(-0.227 \times \text{sec}(\text{sza}))$ (clear sky, s ⁻¹)	2 (RACM R22 replaced)
A32	MVK + hv → 0.5OLT + 0.5 ACO3 + 0.5 HCHO + CO + 0.5HO2	$3.672 \times 10^{-5} \times \cos(\text{sza})^{0.395} \times \exp(-0.296 \times \text{sec}(\text{sza}))$ (clear sky, s ⁻¹)	2
A33	NALD + hv → HCHO + CO + NO2 + HO2	=J(ALD) (s ⁻¹)	1
A34	MAHP + hv → 0.5HKET + 0.5CO + 0.5MGly + 0.5HCHO + OH + HO2	=J(OP2) (s ⁻¹)	1
A35	MPAN + hv → MACP + NO2	0 (s ⁻¹)	1
A36	HPALD1 + hv → mOH + HO2 + 0.5HKET + 0.5 MGly + 0.5 GLYALD + HCHO	=23×J(MACR) (s ⁻¹) (scaled to yield overhead sun value of $5 \times 10^{-4} \text{ s}^{-1}$)	3, 4, m = 3 (S1, S1_a(HC8)), m = 1 (S2)
A37	HPALD2 + hv → mOH + HO2 + 0.5HKET + 0.5 GLY + 0.5 GLYALD + HCHO	=23×J(MACR) (s ⁻¹) (scaled to yield overhead sun value of $5 \times 10^{-4} \text{ s}^{-1}$)	3, 4, m = 3 (S1, S1_a(HC8)), m = 1 (S2)
A38	ISON + hv → NO2 + MACR + HCHO + HO2	=J(ONIT) (s ⁻¹)	1
A39	HCOC5 + hv → 2ACO3 + HCHO	=J(MVK) (s ⁻¹)	2
A40	OH + HCOC5 → C59O2	3.81×10^{-11}	2
A41	C59O2 + NO → HKET + ACO3 + NO2	$2.54 \times 10^{-12} \times \exp(360/T)$	2
A42	C59O2 + HO2 → C59OOH	$0.706 \times 2.91 \times 10^{-13} \times \exp(1300/T)$	2
A43	OH + C59OOH → C59O2	9.70×10^{-12}	2
A44	C59OOH + hv → HKET + ACO3 + OH	$5.804 \times 10^{-6} \times \cos(\text{sza})^{1.092} \times \exp(-0.377 \times \text{sec}(\text{sza})) + J(OP2)$ (clear sky, s ⁻¹)	2
A45	HALD5152 + hv → HO2 + TCO3	$1.140 \times 10^{-5} \times \cos(\text{sza})^{0.396} \times \exp(-0.298 \times \text{sec}(\text{sza}))$ (clear sky, s ⁻¹)	2
A46	HALD5152 + hv → HKET + 2HO2 + 2CO	$1.140 \times 10^{-5} \times \cos(\text{sza})^{0.396} \times \exp(-0.298 \times \text{sec}(\text{sza}))$ (clear sky, s ⁻¹)	2
A47	HALD5152 + OH → 0.48TCO3 + 0.52C58O2	4.50×10^{-11}	2
A48	C58O2 + NO → HKET + GLY + HO2 + NO2	$2.54 \times 10^{-12} \times \exp(360/T)$	2
A49	C58O2 + HO2 → C58OOH	$0.706 \times 2.91 \times 10^{-13} \times \exp(1300/T)$	2
A50	OH + C58OOH → C58O2	3.16×10^{-11}	2

A51	$C58OOH + hv \rightarrow HKET + GLY + HO_2 + OH$	$=J(OP2) (s^{-1})$	2
A52	$ISOPBOOH + hv \rightarrow MVK + 0.75 HCHO + 0.75HO_2 + 0.25 MO_2 + OH$	$=J(OP2) (s^{-1})$	2
A53	$ISOPDOOH + hv \rightarrow MACR + HCHO + HO_2 + OH$	$=J(OP2) (s^{-1})$	2
A54	$GLYALD + OH \rightarrow 0.8 ACO_3 + 0.2 GLY + 0.2 HO_2$	1.0×10^{-11}	2
A55	$GLYALD + hv \rightarrow 2HO_2 + HCHO + CO$	$2.792 \times 10^{-5} \times \cos(sza)^{0.805} \times \exp(-0.338 \times \sec(sza))$ (clear sky, s^{-1})	2
A56	$E\text{TEP} + NO \rightarrow 1.6HCHO + HO_2 + NO_2 + 0.2GLYALD$	9×10^{-12}	2 (RACM R136 replaced)
A57	$ISOPBO_2 + NO_3 \rightarrow 0.60MACR + 0.40OLT + 0.686HCHO + HO_2 + NO_2$	1.2×10^{-12}	2
A58	$ISOPDO_2 + NO_3 \rightarrow 0.60MACR + 0.40OLT + 0.686HCHO + HO_2 + NO_2$	1.2×10^{-12}	2
A59	$ISOPEO_2 + NO_3 \rightarrow 0.60MACR + 0.40OLT + 0.686HCHO + HO_2 + NO_2$	1.2×10^{-12}	2
A60	$HPALD1 + OH \rightarrow OH$	4.6×10^{-11}	3
A61	$HPALD2 + OH \rightarrow OH$	4.6×10^{-11}	3
A62	$ISOPEO_2 + HO_2 \rightarrow ISOPEOOH$	$0.706 \times 2.91 \times 10^{-13} \times \exp(1300/T)$	2
A63	$ISOPEOOH + OH \rightarrow HALD5152 + OH$	1.07×10^{-10}	2
A64	$ISOPEOOH + hv \rightarrow HALD5152 + HO_2 + OH$	$=J(OP2) (s^{-1})$	2

Notes: 1: Pöschl et al. (2000), 2: MCM ver. 3.1, 3: Peeters and Müller (2010), 4: Stavrou et al. (2010)

References to the Notes:

- Pöschl, U., von Kuhlmann, R., Poisson, N., and Crutzen, P. J.: Development and intercomparison of condensed isoprene oxidation mechanisms for global atmospheric modeling, *J. Atmos. Chem.*, 37, 29-52, 2000.
- Peeters, J. and Müller, J.-F.: HO_x radical regeneration in isoprene oxidation via peroxy radical isomerisations, II: Experimental evidence and global impact, *Phys. Chem. Chem. Phys.*, 12, 14227-14235, 2010.
- Stavrou, T., Peeters, J., and Müller, J.-F.: Improved global modelling of HO_x recycling in isoprene oxidation: evaluation against the GABRIEL and INTEX-A aircraft campaign measurements, *Atmos. Chem. Phys.*, 10, 9863-9878, doi:10.5194/acp-10-9863-2010, 2010.

Table S2. Uncertainty factors taken into account in the Monte-Carlo model simulations.

Species*	Uncertainty factor
O ₃	1.05
NO	1.1
NO ₂	1.15
HONO	1.12
CO	1.1
H ₂ O	1.1
H ₂	1.05
CH ₄	1.05
ETH	1.1
HC3	1.2
HC5	1.2
HC8	1.2
ETE	1.1
OLT	1.2
OLI	1.2
ISO	1.2
TOL	1.2
XYL	1.2
HCHO	1.2
ALD	1.3
KET	1.3
MACR	1.2
MVK	1.2

*See text and Stockwell et al. (1997) and Table S1 for the definition of model species.

Reference:

Stockwell, W. R., Kirchner, F., Kuhn, M., Seefeld, S.: A new mechanism for regional atmospheric chemistry modeling, *J. Geophys. Res.*, 102(D22), 25,847-25,880, 1997.

Table S3. Uncertainty factors taken into account in the Monte-Carlo model simulations.

No.	Reactions*	Uncertainty factor
R1	NO ₂ + hv	1.2
R2	O ₃ + hv → O ¹ D + O ₂	1.3
R4	HONO + hv	1.2
R5	HNO ₃ + hv	1.3
R6	HNO ₄ + hv	2
R7	NO ₃ + hv → NO + O ₂	1.5
R8	NO ₃ + hv → NO ₂ + O ₃ P	1.5
R9	H ₂ O ₂ + hv	1.3
R10	HCHO + hv → H ₂ + CO	1.4
R11	HCHO + hv → 2HO ₂ + CO	1.4
R12	ALD + hv	1.4
R13	OP1 + hv	1.5
R14	OP2 + hv	1.5
R15	PAA + hv	1.5
R16	KET + hv	1.5
R17	GLY + hv → 0.13HCHO + ...	1.5
R18	GLY + hv → 0.45HCHO + ...	1.5
R19	MGLY + hv	1.5
R20	DCB + hv	1.5
R21	ONIT + hv	1.5
R22	MACR + hv	1.5

R23	HKET + hv	1.5
R24	O3P + O2	1.1
R25	O3P + N2	1.15
R26	O1D + N2	1.1
R27	O1D + O2	1.2
R28	O1D + H2O	1.2
R29	O3 + OH	1.2
R30	O3 + HO2	1.15
R31	OH + HO2	1.3
R32	H2O2 + OH	1.15
R33	HO2 + HO2	1.3
R34	HO2 + HO2 + H2O	1.3
R35	O3P + NO	1.3
R36	O3P + NO2 → NO + O2	1.1
R37	O3P + NO2 → NO3	1.3
R38	OH + NO	1.3
R39	OH + NO2	1.3
R40	OH + NO3	1.5
R41	HO2 + NO	1.15
R42	HO2 + NO2	2
R43	HNO4	5
R44	HO2 + NO3	1.5
R45	OH + HONO	1.5
R46	OH + HNO3	1.2
R47	OH + HNO4	1.3
R48	O3 + NO	1.1
R49	O3 + NO2	1.15
R51	NO3 + NO	1.3
R52	NO3 + NO2 → NO + NO2 + O2	1.5
R53	NO3 + NO2 → N2O5	1.2
R54	N2O5	1.2
R55	NO3 + NO3	1.5
R56	OH + H2	1.1
R57	OH + SO2	1.3
R58	OH + CO	1.3
R59	ISO + O3P	1.3
R60	MACR + O3P	1.3
R61	CH4 + OH	1.1
R62	ETH + OH	1.2
R63	HC3 + OH	1.3
R64	HC5 + OH	1.3
R65	HC8 + OH	1.3
R66	ETE + OH	1.3
R67	OLT + OH	1.3
R68	OLI + OH	1.4
R69	DIEN + OH	1.3
R71	API + OH	1.2
R72	LIM + OH	1.2
R73	TOL + OH	1.3
R74	XYL + OH	1.4
R75	CSL + OH	1.3
R76	HCHO + OH	1.2
R77	ALD + OH	1.2
R78	KET + OH	1.3
R79	HKET + OH	1.3
R80	GLY + OH	1.3
R81	MGLY + OH	1.3
R83	DCB + OH	1.3

R84	UDD + OH	1.3
R85	OP1 + OH	1.4
R86	OP2 + OH	1.4
R87	PAA + OH	1.4
R88	PAN + OH	1.4
R89	TPAN + OH	1.4
R90	ONIT + OH	1.5
R91	HCHO + NO3	1.3
R92	ALD + NO3	1.3
R93	GLY + NO3	1.3
R94	MGLY + NO3	1.3
R95	MACR + NO3	1.3
R96	DCB + NO3	1.3
R97	CSL + NO3	1.3
R98-105	olefins + NO3	1.3
R106-115	olefins + O3	1.3
R116-126	PHO, ADDT, ADDX, ADDC reactions	1.3
R127	ACO3 + NO2	1.5
R128	PAN	1.5
R129	TCO3 + NO2	2
R130	TPAN	2
R131-149	RO2 + NO	2
R150-170	RO2 + HO2	2
R171-191	RO2 + MO2	2
R192-209	RO2 + ACO3	2
R210-212	OLNN and OLND self and cross reactions	2
R213-231	NO3 + RO2	2
R232	XO2 + HO2	2
R233	XO2 + MO2	2
R234	XO2 + ACO3	2
R235	XO2 + XO2	2
R236	XO2 + NO	2
R237	XO2 + NO3	2
A1	ISO+OH	1.2
A2	ISOPBO2 + NO	2
A3	ISOPDO2 + NO	2
A4	ISOPEO2 + NO	2
A5	ISOPBO2 + HO2	2
A6	ISOPDO2 + HO2	2
A7	ISOPBO2 → HPALD1 + HO2	1
A8	ISOPBO2 → MVK + HCHO + OH	1
A9	ISOPDO2 → HPALD2 + HO2	1
A10	ISOPDO2 → MACR + HCHO + OH	1
A11	ISOPBOOH+OH → IEPOX + OH	2
A12	ISOPBOOH+OH → 0.7ISOPBO2 + 0.3HCOC5 + 0.3OH	1.4
A13	ISOPDOOH+OH → IEPOX + OH	2
A14	ISOPDOOH+OH → 0.7ISOPDO2 + 0.3HCOC5 + 0.3OH	1.4
A15	IEPOX+OH	2
A16	IEPOXO2+ NO	2
A17	IEPOXO2+HO2	2
A18	ISON+OH	1.5
A19	MACR+OH	1.3
A20	MACR+O3	1.3
A21	MACP+NO	2
A22	MACP + HO2	2
A23	MACP + NO2	2
A24	MPAN	2
A25	MPAN + OH	1.4

A26	MAHP + OH	1.4
A27	NALD + OH	1.2
A28	ISO + O3	1.3
A29	MVK + OH	1.3
A30	MVK + O3	1.3
A31	MACR + hv	1.5
A32	MVK + hv	1.5
A33	NALD + hv	1.5
A34	MAHP + hv	1.5
A35	MPAN + hv	1.5
A36	HPALD1 + hv	1.5
A37	HPALD2 + hv	1.5
A38	ISON + hv	1.5
A39	HCOC5 + hv	1.5
A40	OH + HCOC5	1.5
A41	C59O2 + NO	2
A42	C59O2 + HO2	2
A43	OH + C59OOH	1.4
A44	C59OOH + hv	1.5
A45	HALD5152 + hv → HO2 + TCO3	1.5
A46	HALD5152 + hv → HKET + 2HO2 + 2CO	1.5
A47	HALD5152 + OH	1.5
A48	C58O2 + NO	2
A49	C58O2 + HO2	2
A50	OH + C58OOH	1.4
A51	C58OOH + hv	1.5
A52	ISOPBOOH + hv	1.5
A53	ISOPDOOH + hv	1.5
A54	GLYALD + OH	1.3
A55	GLYALD + hv	1.5
A56	ETEP + NO	2
A57	ISOPBO2 + NO3	2
A58	ISOPDO2 + NO3	2
A59	ISOPEO2 + NO3	2
A60	HPALD1 + OH	1.5
A61	HPALD2 + OH	1.5
A62	ISOPEO2 + HO2	2
A63	ISOPEOOH + OH	1.4
A64	ISOPEOOH + hv	1.5

*See text and Stockwell et al. (1997) and Table S1 for definitions.

Reference:

Stockwell, W. R., Kirchner, F., Kuhn, M., Seefeld. S.: A new mechanism for regional atmospheric chemistry modeling, *J. Geophys. Res.*, 102(D22), 25,847-25,880, 1997.

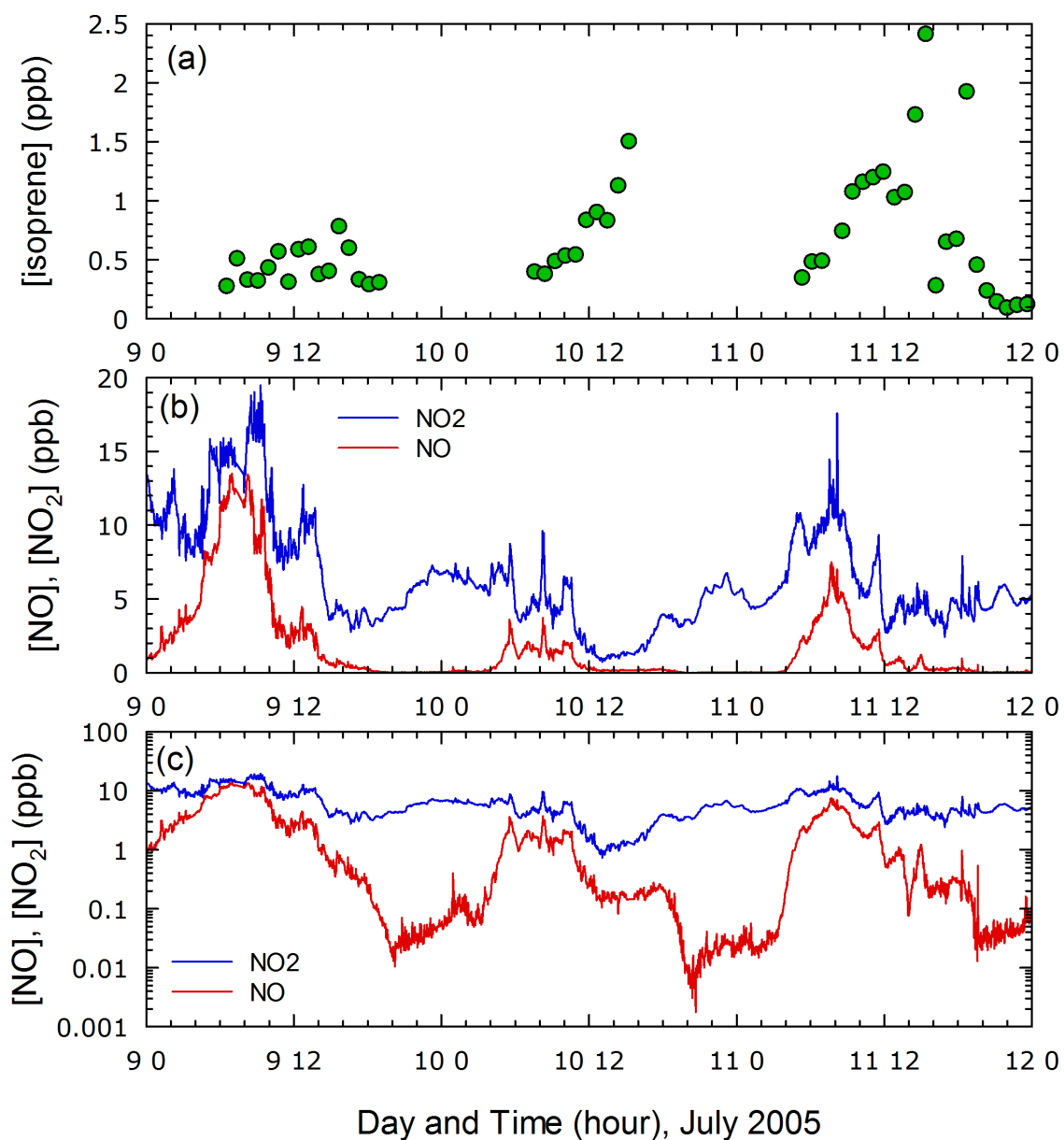


Figure S1. Temporal variations of the observed (a) isoprene, and (b) and (c) NO and NO₂ concentrations (in linear and logarithmic scales).

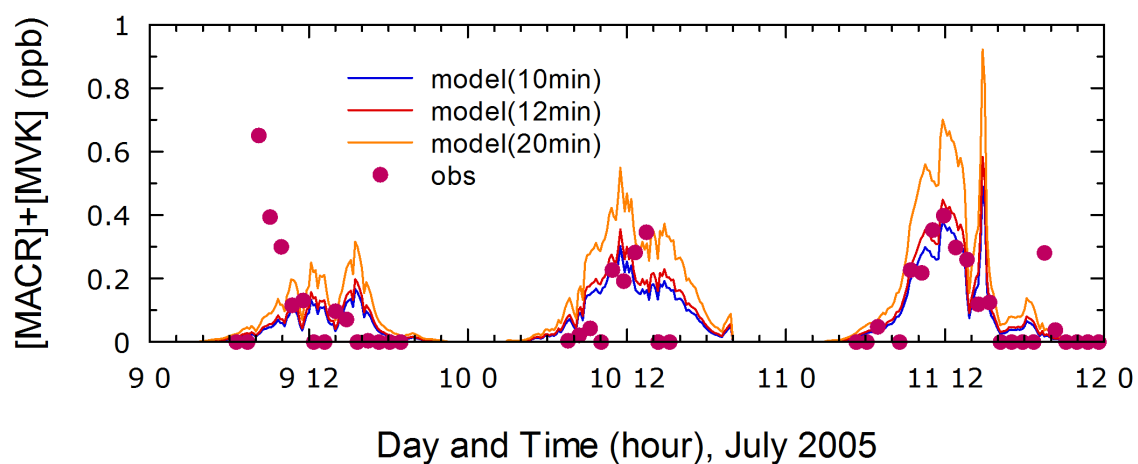


Figure S2. Time series of observed MACR + MVK concentrations and modeled concentrations for different time periods (10, 12, and 20 min), for which isoprene chemistry is active in the model (for details see text).

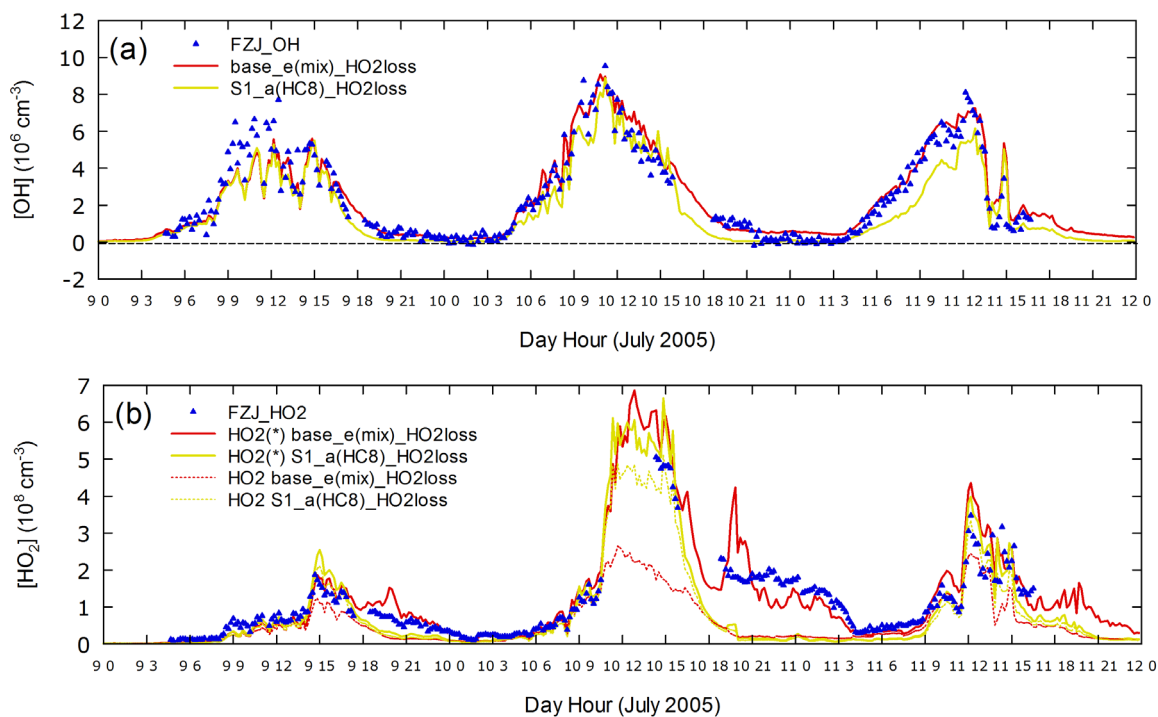


Figure S3. Time series of observed OH and HO₂ by FZJ instrument, and modeled OH, HO₂, and HO₂(*) in the Base_e(mix)_HO₂_loss and S1_a(HC8)_HO₂_loss runs.

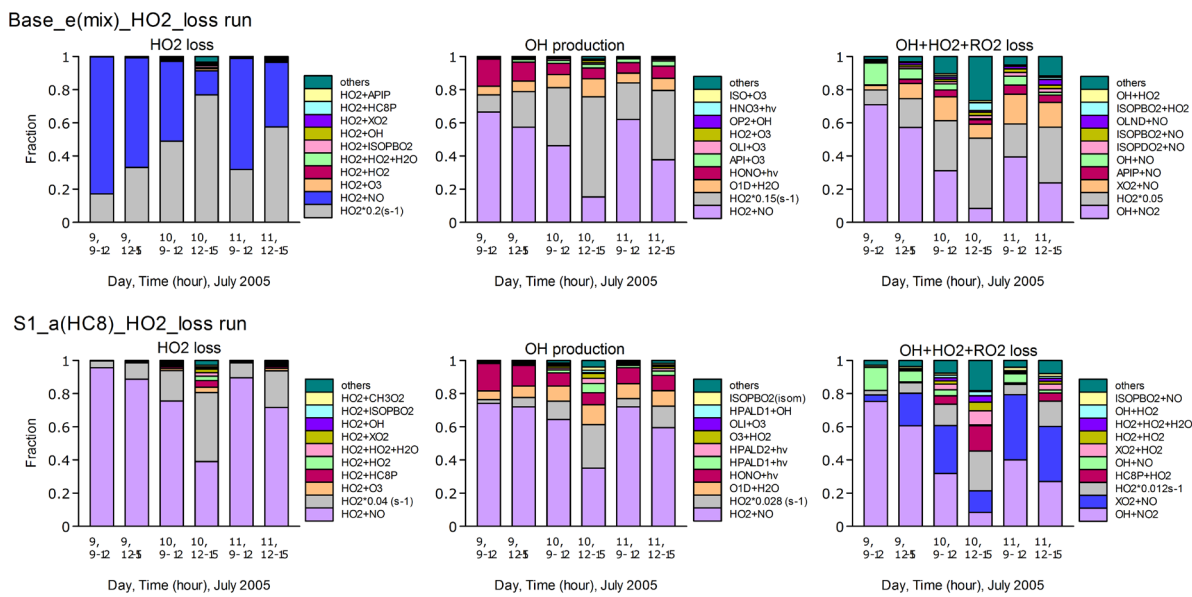


Figure S4. Breakdown of HO₂ loss, OH production, and radical (OH + HO₂ + RO₂) loss processes in the Base_e(mix)_HO₂_loss and S1_a(HC8)_HO₂_loss runs. Gray bars indicate large contributions needed to be explained by the hypothetical HO₂ loss processes introduced in the model runs.