Supplement materials for

Kanaya et al., Comparisons of observed and modeled OH and HO_2 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 + 0.25ISOPACO2	$2.54\times10^{-11}\times\exp(410/T)$	1 (RACM R70 replaced), For Isom and Isom_a(HC8) runs, products and yields are 0.6ISOPBO2 + 0.3ISOPDO2 + 0.1ISOPEO2
A2	ISOPBO2 + NO → 0.928 (MVK + HO2 + NO2 + HCHO) + 0.072ISON	$2.54\times10^{-12}\times\exp(360/T)$	2
A3	ISOPDO2 + NO → 0.855 (MACR + HO2 + NO2 + HCHO) + 0.145ISON	$2.54\times10^{-12}\times\exp(360/T)$	2
A4	ISOPACO2 + NO → 0.952 (HALD5152 + HO2 + NO2 + HCHO) + 0.044ISON	$2.54\times10^{-12}\times\exp(360/T)$	2
A5	ISOPBO2 + HO2 → ISOPBOOH	$0.706\times2.91\times10^{-13}\times\exp(1300/T)$	2
A6	ISOPDO2 + HO2 → ISOPDOOH	$0.706\times2.91\times10^{-13}\times\exp(1300/T)$	2
A7	ISOPBOOH+OH → IEPOX + OH	$1.9\times10^{-11}\times\exp(390/T)$	4
A8	ISOPBOOH+OH → 0.7ISOPBO2 + 0.3HCOC5 + 0.3OH	$0.38\times10^{-11}\times\exp(200/T)$	4
A9	ISOPDOOH+OH → IEPOX + OH	$1.9\times10^{-11}\times\exp(390/T)$	4
A10	ISOPDOOH+OH → 0.7ISOPDO2 + 0.3HCOC5 + 0.3OH	$0.38\times10^{-11}\times\exp(200/T)$	4
A11	IEPOX+OH → IEPOXO2	$5.78\times10^{-11}\times\exp(-400/T)$	4
A12	IEPOXO2+ NO→ 0.725HKET + 0.275GLY + 0.275GLYALD + 0.275MGLY + 0.375HCHO + 0.074ORA1 + 0.125OH + 0.825HO2 + 0.251CO + NO2	$2.54\times10^{-12}\times\exp(360/T)$	4
A13	IEPOXO2+HO2 →0.725HKET + 0.275GLY + 0.275GLYALD + 0.275MGLY + 0.375HCHO + 0.074ORA1 + 1.125OH + 0.825HO2 + 0.251CO	$0.074\times10^{-11}\exp(700/T)$	4
A14	ISON+OH→HKET+NALD	1.30×10^{-11}	1
A15	MACR+OH →MACP	$1.86\times10^{-11}\times\exp(175/T)$	2 (RACM R82 replaced)
A16	MACR+O3→ 0.90MGLY+0.45ORA1+0.32HO2+0.22CO+0.19OH+0.10ACO3	$1.36\times10^{-15}\times\exp(-2112/T)$	2 (RACM R113 replaced)
A17	MACP+NO→NO2+0.25HKET+0.25CO+0.25ACO3+0.50MGLY+0.75HCHO+0.75HO2	$2.54\times10^{-12}\times\exp(360/T)$	1
A18	MACP + HO2→ MAHP	$1.82\times10^{-13}\times\exp(1300/T)$	1
A19	MACP + NO2 → MPAN	$k_0 = 9.7\times10^{-29}\times(T/300)^{-5.6}$ $k_\infty = 9.3\times10^{-12}\times(T/300)^{-1.5}$ $k=\{k_0\times[M]/(1+k_0\times[M]/k_\infty)\}\times0.6^{\{1+[\log10(k0[M]/k\infty)]2\}-1}$	1
A20	MPAN → MACP + NO2	$k = k(260)/(9.0\times10^{-29}\times\exp(14000/T))$	1
A21	MPAN + OH → HKET + NO2	3.60×10^{-12}	1

A22	MAHP + OH → MACP	3.0×10^{-11}	1
A23	NALD + OH → HCHO + CO + NO2	$5.60\times10^{-12}\times\exp(270/T)$	1
A24	ISO + O3→ 0.39MACR + 0.26MVK + 0.58HCHO + 0.10MACP + 0.10ACO3 + 0.08MO2 + 0.28ORA1 + 0.14CO + 0.09H2O2 + 0.25HO2 + 0.25OH	$7.86\times10^{-15}\times\exp(-1913/T)$	1 (RACM R110 replaced)
A25	MVK + OH → MACP	$4.13\times10^{-12}\times\exp(452/T)$	2
A26	MVK + O3→ 0.90MGLY + 0.45ORA1 + 0.32HO2 + 0.22CO + 0.19OH + 0.10ACO3	$7.51\times10^{-16}\times\exp(-1521/T)$	2
A27	MACR + hν → CO + HCHO + HO2 + ACO3	$2.192\times10^{-5}\times\cos(sza)^{0.526}\times\exp(-0.227\times\sec(sza))$ (clear sky, s^{-1})	2 (RACM R22 replaced)
A28	MVK + hν →0.5OLT + 0.5 ACO3 + 0.5 HCHO + CO + 0.5HO2	$3.672\times10^{-5}\times\cos(sza)^{0.395}\times\exp(-0.296\times\sec(sza))$ (clear sky, s^{-1})	2
A29	NALD + hν → HCHO + CO + NO2 + HO2	=J(ALD) (s^{-1})	1
A30	MAHP + hν → 0.5HKET + 0.5CO + 0.5MGLY + 0.5HCHO + OH + HO2	=J(OP2) (s^{-1})	1
A31	MPAN + hν → MACP + NO2	0 (s^{-1})	1
A32	ISON + hν → NO2 + MACR + HCHO + HO2	=J(ONIT) (s^{-1})	1
A33	HCOC5 +hν →2ACO3 + HCHO	=J(MVK) (s^{-1})	2
A34	OH + HCOC5 → C59O2	3.81×10^{-11}	2
A35	C59O2 + NO→ HKET + ACO3 + NO2	$2.54\times10^{-12}\times\exp(360/T)$	2
A36	C59O2 + HO2→ C59OOH	$0.706\times2.91\times10^{-13}\times\exp(1300/T)$	2
A37	OH + C59OOH → C59O2	9.70×10^{-12}	2
A38	C59OOH + hν→ HKET + ACO3 + OH	$5.804\times10^{-6}\times\cos(sza)^{1.092}\times\exp(-0.377\times\sec(sza))$+J(OP2) (clear sky, s-1)	2
A39	HALD5152 + hν →HO2 + TCO3	$1.140\times10^{-5}\times\cos(sza)^{0.396}\times\exp(-0.298\times\sec(sza))$ (clear sky, s^{-1})	2
A40	HALD5152 + hν → HKET + 2HO2 + 2CO	$1.140\times10^{-5}\times\cos(sza)^{0.396}\times\exp(-0.298\times\sec(sza))$ (clear sky, s^{-1})	2
A41	HALD5152 + OH → 0.48TCO3 + 0.52C58O2	4.50×10^{-11}	2
A42	C58O2 + NO → HKET + GLY + HO2 + NO2	$2.54\times10^{-12}\times\exp(360/T)$	2
A43	C58O2 + HO2 → C58OOH	$0.706\times2.91\times10^{-13}\times\exp(1300/T)$	2
A44	OH + C58OOH → C58O2	3.16×10^{-11}	2
A45	C58OOH + hν → HKET + GLY + HO2 + OH	=J(OP2) (s^{-1})	2
A46	ISOPBOOH + hν→ MVK+ 0.75 HCHO + 0.75HO2 + 0.25 MO2 + OH	=J(OP2) (s^{-1})	2
A47	ISOPDOOH + hν→ MACR + HCHO + HO2 + OH	=J(OP2) (s^{-1})	2
A48	GLYALD + OH→ 0.8 ACO3 + 0.2 GLY + 0.2 HO2	1.0×10^{-11}	2
A49	GLYALD + hν → 2HO2 + HCHO + CO	$2.792\times10^{-5}\times\cos(sza)^{0.805}\times\exp(-0.338\times\sec(sza))$ (clear sky, s^{-1})	2
A50	ETEP + NO→ 1.6HCHO + HO2 + NO2 + 0.2GLYALD	9×10^{-12}	2 (RACM R136 replaced)
A51	ISOPBO2 + NO3→0.60MACR + 0.40OLT + 0.686HCHO + HO2 + NO2	1.2×10^{-12}	2
A52	ISOPDO2 + NO3→ 0.60MACR + 0.40OLT + 0.686HCHO + HO2 + NO2	1.2×10^{-12}	2

A53	ISOPACO2 + NO3→0.60MACR + 0.40OLT + 0.686HCHO + HO2 + NO2	1.2×10^{-12}	2
A54	ISOPACO2 + HO2 → ISOPACOOH	$0.706\times2.91\times10^{-13}\times\exp(1300/T)$	2
A55	ISOPACOOH + OH → HALD5152 + OH	1.07×10^{-10}	2
A56	ISOPACOOH + hν→ HALD5152 + HO2 + OH	=J(OP2) (s^{-1})	2
A57	ISOPBO2 → HPALD1 + HO2	$4.06\times10^{9}\times\exp(-7302/T)$ (s^{-1})	3, 4, Only for Isom and Isom _a(HC8) runs
A58	ISOPBO2 → MVK + HCHO + OH	$2.08\times10^{11}\times\exp(-8993/T)$ (s^{-1})	3, 4, Only for Isom and Isom _a(HC8) runs
A59	ISOPDO2 → HPALD2 + HO2	$8.5\times10^{9}\times\exp(-7432/T)$ (s^{-1})	3, 4, Only for Isom and Isom _a(HC8) runs
A60	ISOPDO2 → MACR + HCHO + OH	$2.08\times10^{11}\times\exp(-8993/T)$ (s^{-1})	3, 4, Only for Isom and Isom _a(HC8) runs
A61	HPALD1 + hν →OH + HO2 + PACALD1	=23×J(MACR) (s^{-1}) (scaled to yield overhead sun value of 5×10^{-4} s^{-1})	3, 4
A62	HPALD2 + hν →OH + HO2 + PACALD2	=23×J(MACR) (s^{-1}) (scaled to yield overhead sun value of 5×10^{-4} s^{-1})	3, 4
A63	PACALD1+ hν→ 2OH + 0.5HKET + 0.5 MGLY + 0.5 GLYALD + HCHO	=2×J(HPALD1) (s^{-1})	3
A64	PACALD2+ hν→ 2OH + 0.5HKET + 0.5 MGLY + 0.5 GLYALD + HCHO	=2×J(HPALD2) (s^{-1})	3
A65	HPALD1 + OH → OH	4.6×10^{-11}	3
A66	HPALD2 + OH → OH	4.6×10^{-11}	3
A67	ISOPEO2 + NO → 0.952 (CAR + HO2 + NO2 + HCHO) + 0.044ISON	$2.54\times10^{-12}\times\exp(360/T)$	2
A68	CAR + hν →HO2 + TCO3	$1.140\times10^{-5}\times\cos(sza)^{0.396}\times\exp(-0.298\times\sec(sza))$ (clear sky, s^{-1})	2
A69	CAR + hν → HKET + 2HO2 + 2CO	$1.140\times10^{-5}\times\cos(sza)^{0.396}\times\exp(-0.298\times\sec(sza))$ (clear sky, s^{-1})	2
A70	CAR + OH → 0.48TCO3 + 0.52C58O2	4.50×10^{-11}	2
A71	ISOPEO2 + NO3→0.60MACR + 0.40OLT + 0.686HCHO + HO2 + NO2	1.2×10^{-12}	2
A72	ISOPEO2 + HO2 → ISOPEOOH	$0.706\times2.91\times10^{-13}\times\exp(1300/T)$	2
A73	ISOPEOOH + OH → CAR + OH	1.07×10^{-10}	2
A74	ISOPEOOH + hν→ CAR + HO2 + OH	=J(OP2) (s^{-1})	2

Notes: 1: Pöschl et al. (2000), 2: MCM ver. 3.1, 3: Peeters and Müller (2010), 4: Stavrakou 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.: HOx radical regeneration in isoprene oxidation via peroxy radical isomerisations, II: Experimental evidence and global impact, Phys. Chem. Chem. Phys., 12, 14227-14235, 2010.

Stavrakou, 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_2O	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	NO2 + hν	1.2
R2	O3 + hν → O1D + O2	1.3
R4	HONO + hν	1.2
R5	HNO3 + hν	1.3
R6	HNO4 + hν	2
R7	NO3 + hν→ NO + O2	1.5
R8	NO3 + hν→ NO2 + O3P	1.5
R9	H2O2 + hν	1.3
R10	HCHO + hν→ H2 + CO	1.4
R11	HCHO + hν→ 2HO2 + CO	1.4
R12	ALD + hν	1.4
R13	OP1 + hν	1.5
R14	OP2 + hν	1.5
R15	PAA + hν	1.5
R16	KET + hν	1.5
R17	GLY + hν→ 0.13HCHO + ...	1.5
R18	GLY + hν→ 0.45HCHO + ...	1.5
R19	MGLY +hν	1.5
R20	DCB + hν	1.5
R21	ONIT + hν	1.5
R22	MACR + hν	1.5

R23	HKET + hν	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	ISOPACO2 + NO	2
A5	ISOPBO2 + HO2	2
A6	ISOPDO2 + HO2	2
A7	ISOPBOOH+OH → IEPOX + OH	2
A8	ISOPBOOH+OH → 0.7ISOPBO2 + 0.3HCOC5 + 0.3OH	1.4
A9	ISOPDOOH+OH → IEPOX + OH	2
A10	ISOPDOOH+OH → 0.7ISOPDO2 + 0.3HCOC5 + 0.3OH	1.4
A11	IEPOX+OH	2
A12	IEPOXO2+ NO	2
A13	IEPOXO2+HO2	2
A14	ISON+OH	1.5
A15	MACR+OH	1.3
A16	MACR+O3	1.3
A17	MACP+NO	2
A18	MACP + HO2	2
A19	MACP + NO2	2
A20	MPAN	2
A21	MPAN + OH	1.4
A22	MAHP + OH	1.4
A23	NALD + OH	1.2
A24	ISO + O3	1.3
A25	MVK + OH	1.3

A26	MVK + O3	1.3
A27	MACR + hν	1.5
A28	MVK + hν	1.5
A29	NALD + hν	1.5
A30	MAHP + hν	1.5
A31	MPAN + hν	1.5
A32	ISON + hν	1.5
A33	HCOC5 +hν	1.5
A34	OH + HCOC5	1.5
A35	C59O2 + NO	2
A36	C59O2 + HO2	2
A37	OH + C59OOH	1.4
A38	C59OOH + hν	1.5
A39	HALD5152 + hν →HO2 + TCO3	1.5
A40	HALD5152 + hν → HKET + 2HO2 + 2CO	1.5
A41	HALD5152 + OH	1.5
A42	C58O2 + NO	2
A43	C58O2 + HO2	2
A44	OH + C58OOH	1.4
A45	C58OOH + hν	1.5
A46	ISOPBOOH + hν	1.5
A47	ISOPDOOH + hν	1.5
A48	GLYALD + OH	1.3
A49	GLYALD + hν	1.5
A50	ETEP + NO	2
A51	ISOPBO2 + NO3	2
A52	ISOPDO2 + NO3	2
A53	ISOPACO2 + NO3	2
A54	ISOPACO2 + HO2	2
A55	ISOPACOOH + OH	1.4
A56	ISOPACOOH + hν	1.5
A57	ISOPBO2 → HPALD1 + HO2	1
A58	ISOPBO2 → MVK + HCHO + OH	1
A59	ISOPDO2 → HPALD2 + HO2	1
A60	ISOPDO2 → MACR + HCHO + OH	1
A61	HPALD1 + hν	1.5
A62	HPALD2 + hν	1.5
A63	PACALD1 + hν	1.5
A64	PACALD2 + hν	1.5
A65	HPALD1 + OH	1.5
A66	HPALD2 + OH	1.5
A67	ISOPEO2 + NO	2
A68	CAR + hν →HO2 + TCO3	1.5
A69	CAR + hν → HKET + 2HO2 + 2CO	1.5
A70	CAR + OH	1.5
A71	ISOPEO2 + NO3	2
A72	ISOPEO2 + HO2	2
A73	ISOPEOOH + OH	1.4
A74	ISOPEOOH + hν	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.

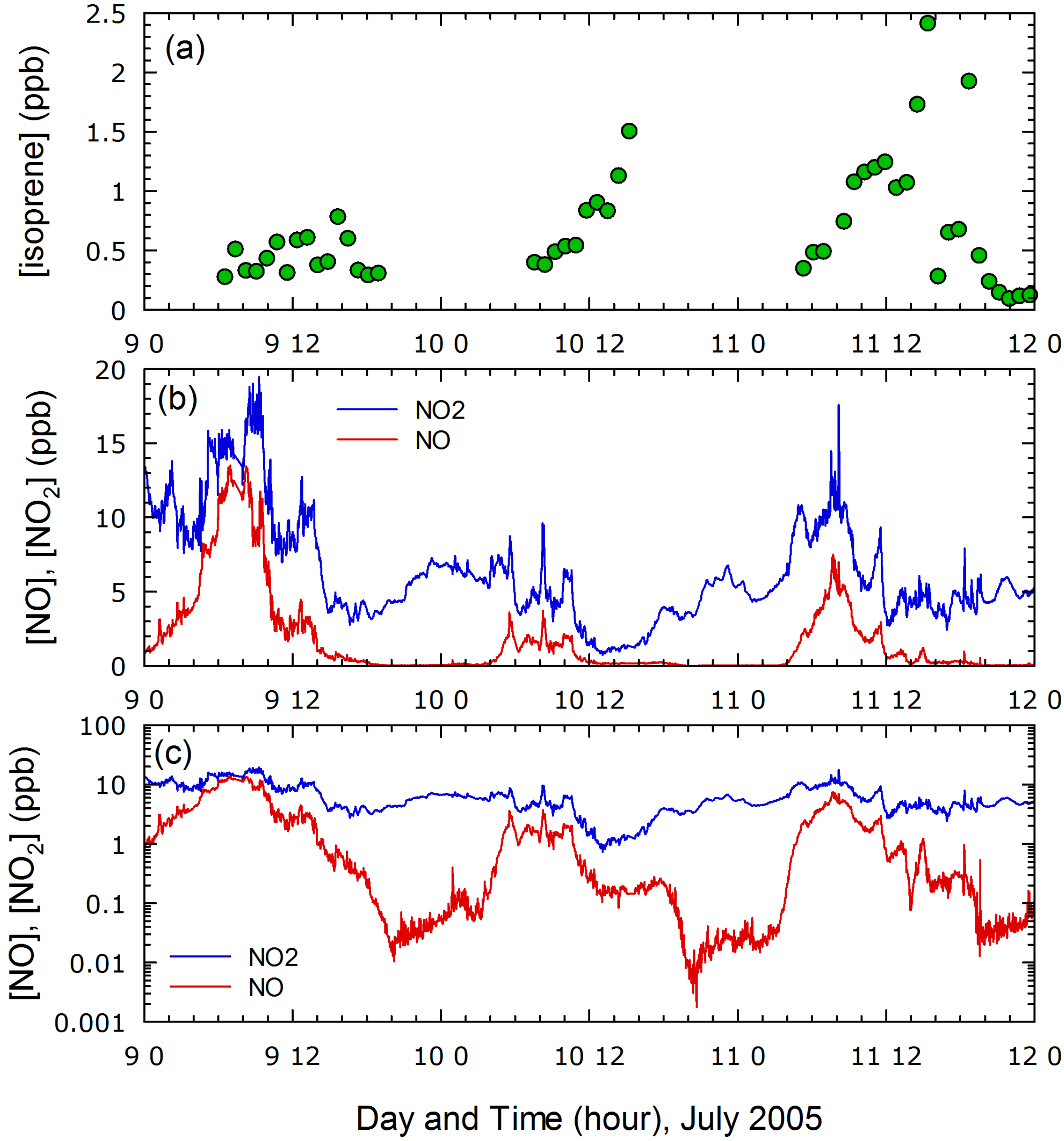

Figure S1. Temporal variations of the observed (a) isoprene, and (b) and (c) NO and NO_2 concentrations (in linear and logarithmic scales).

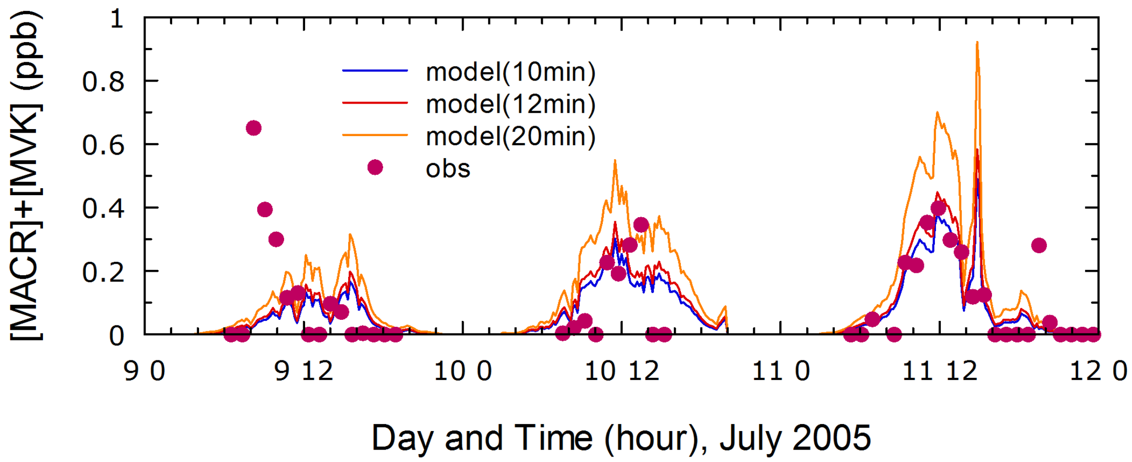

Figure S2. Time series of observed MACR + MVK concentrations and modeled concentrations for different time periods (10, 12, and 20 min), for which isoprene chemistry is active in the model (for details see text).

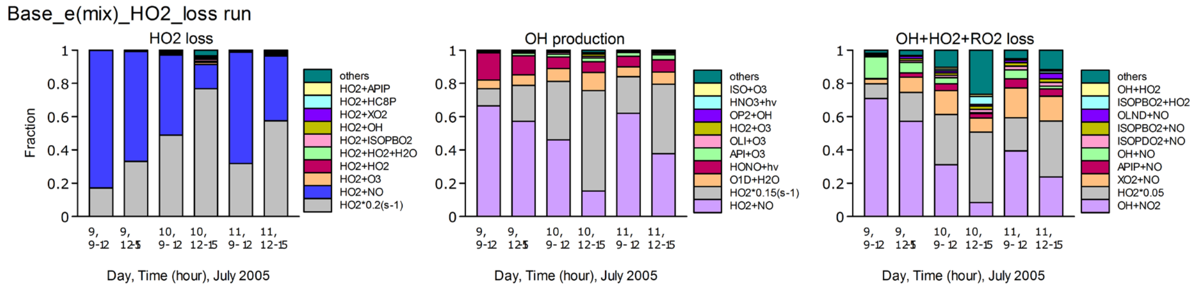

Figure S3. Breakdown of HO_2 loss, OH production, and radical (OH + HO_2 + RO_2) loss processes in the Base_e(mix)_HO_2_loss run. Gray bars indicate large contributions needed to be explained by the hypothetical HO_2 loss processes introduced in the model runs.