Table S1 displays the photolytic reactions included in RACM and their associated parameterization factors.

Table S2 summarizes all the chemical reactions that were selected and grouped together to calculate the rates of radical fluxes. Note that peroxyacyl radicals (RCO_3) are differentiated from peroxy radicals (RO_2) since RCO_3 exhibit different sources (photolysis of methyl glyoxal and unsaturated dicarbonyl species) than RO_2 and can react with NO_2 to form peroxy acetyl nitrate (PAN) species. Radical initiation steps displayed in Table S2 are characterized by photolytic reactions (Photol) and ozonolysis reactions of unsaturated compounds (Unsat + O_3). The latter reactions are displayed with their associated radical yields in RACM (Stockwell et al., 1997). Termination mainly occurs through radical-NO_x reactions. Cross-reactions between radicals are negligible under the high NO_x conditions of MCMA but are included in the calculations for completeness. Through reactions with VOCs, OH directly propagates to RO_2 (alkanes, alkenes, ketones, esters, alcohols, acids, aromatics, peroxides), HO_2 (CO, HCHO, alcohols, aromatics, peroxides, unsaturated species) and RCO_3 (alcohols, acids, aldehydes, peroxides). RO_2 is propagated to HO_2 through its reaction with NO.

Table captions

Table S1: Photolytic reactions included in RACM. Reaction products are displayed as indicated in the RACM mechanism. J-values were calculated using the parameterization employed in MCM (Jenkin et al., 1997; Saunders et al., 2003). Calculated J-values are

scaled using measured $J(NO_2)$ or measured $J(O^1D)$ as indicated in the third column. Corresponding photolysis rates for MCM v3.1 are indicated in the forth column. SZA: Solar Zenith Angle.

Table S2: Initiation, termination and propagation pathways of OH, HO_2, RO_2 and RCO_3 selected in RACM to investigate the radical budget.

Table S3: Contribution of OH, HO_2, RO_2 and RCO_3 sources to the total initiation of RO_x radicals. Reported values are for the large set of VOCs and GLY/MGLY/DCB constrained.

Table S4: Contribution of OH, HO_2, RO_2 and RCO_3 sinks to the total termination of RO_x. Reported values are for the large set of VOCs and GLY/MGLY/DCB constrained.

Table S5: Lifetime comparison between radicals and long-lived chemical species that directly impact the radical chemistry.

Table S6: Model sensitivity to initial constraints.

Photolytic reaction	$J = l \times (COS(sza))^m \times EXP[-n \times SEC(sza)]$			Scaling Factor	Corresponding J-Values in MCM v3.1	Median value 1:00 pm CST (s^{-1})
	l	m	n			
$NO_2 \rightarrow NO+O(^3P)$	Measured				J<4>	8.6×10^{-3}
$O_3 \rightarrow O(^1D)+O_2$	Measured				J<1>	3.9×10^{-5}
$O_3 \rightarrow O(^3P)+O_2$	4.775E-04	0.298	0.08	$J(NO_2)$	J<2>	4.3×10^{-4}
$HONO \rightarrow HO+NO$	Measured				J<7>	1.9×10^{-3}
$HNO_3 \rightarrow OH+NO_2$	9.312E-07	1.23	0.307	$J(O^1D)$	J<8>	7.5×10^{-7}
$HO_2NO_2 \rightarrow$ $0.65HO_2+0.65NO_2+0.35OH+0.35NO_3$	Calculated from TUV			$J(O^1D)$	NA	5.7×10^{-6}
$NO_3 \rightarrow NO+O_2$	2.485E-02	0.168	0.108	$J(NO_2)$	J<5>	2.2×10^{-2}
$NO_3 \rightarrow NO_2+O(^3P)$	1.747E-01	0.155	0.125	$J(NO_2)$	J<6>	1.5×10^{-1}
$H_2O_2 \rightarrow OH+OH$	1.041E-05	0.723	0.279	$J(NO_2)$	J<3>	7.4×10^{-6}
$HCHO \rightarrow HO_2+HO_2+CO$	Measured				J<11>	3.7×10^{-5}
$HCHO \rightarrow CO+H_2$	Measured				J<12>	8.3×10^{-5}
$ALD \rightarrow CH_3O_2+HO_2+CO$	7.344E-06	1.202	0.417	$J(O^1D)$	J<13>	5.2×10^{-6}
$CH_3OOH \rightarrow HO_2+OH+HCHO$	7.649E-06	0.682	0.279	$J(O^1D)$	J<41>	6.6×10^{-6}
$OP2 \rightarrow HO_2+OH+ALD$	7.649E-06	0.682	0.279	$J(O^1D)$	J<41>	6.6×10^{-6}
$PAA \rightarrow CH_3O_2+OH$	7.649E-06	0.682	0.279	$J(O^1D)$	J<41>	6.6×10^{-6}
$KET \rightarrow ETHP+ACO_3$	7.992E-07	1.578	0.271	$J(O^1D)$	J<21>	6.5×10^{-7}
$GLY \rightarrow HCHO+CO$	1.032E-05	0.13	0.201	$J(NO_2)$	J<32>	8.3×10^{-6}
$GLY \rightarrow CO+H_2$	6.845E-05	0.13	0.201	$J(NO_2)$	J<31>	5.5×10^{-5}
$GLY \rightarrow HO_2+HO_2$	3.802E-05	0.644	0.312	$J(NO_2)$	J<33>	2.6×10^{-5}
$MGLY \rightarrow HO_2+ACO_3+CO$	1.537E-04	0.17	0.208	$J(NO_2)$	J<34>	1.2×10^{-4}
$DCB \rightarrow TCO_3+HO_2$	5.710E-04	0.256	0.159	$J(NO_2)$	J<4> x 0.2 x 0.6	4.7×10^{-4}
$ONIT \rightarrow HO_2+NO_2+0.2ALD+0.8KET$	2.772E-06	1.183	0.348	$J(O^1D)$	J<51, 52, 53>	2.1×10^{-6}
$MACR \rightarrow CO+HO_2+ACO_3+HCHO$	1.140E-05	0.396	0.298	$J(O^1D)$	J<18>	2.0×10^{-5}
$HKET \rightarrow HO_2+ACO_3+HCHO$	7.992E-07	1.578	0.271	$J(O^1D)$	J<21>	6.5×10^{-7}

Table S1

		OH	HO$_2$	RO$_2$	RCO$_3$
Initiation	Photol	2 O$_3$ (O^{1}D+H$_2$O), HONO, 2 H$_2$O$_2$, HNO$_3$ CH$_3$OOH , OP2, PAA, 0.35 HO$_2$NO$_2$	2 HCHO[a], ALD, CH$_3$OOH, OP2, 2 GLY[a], MGLY, DCB, ONIT, MACR, HKET 0.65 HO$_2$NO$_2$	ALD, PAA, KET	KET, MGLY, DCB, MACR, HKET
	Unsat + O$_3$	0.12 ETE, 0.40 OLT, 0.63 OLI, 0.28 DIEN, 0.28 ISO, 0.85 API, 0.85 LIM, 0.07 MACR 0.21 DCB, 0.04 TPAN	0.26 ETE, 0.25 OLT, 0.22 OLI, 0.30 DIEN, 0.30 ISO, 0.10 API, 0.10 LIM, 0.29 MACR 0.29 DCB, 0.08 TPAN	0.32 OLT, 0.53 OLI, 0.05 DIEN0.05 ISO, 0.62 API, 0.58 LIM	0.15 DIEN 0.15 ISO, 0.13 MACR 0.28 DCB, 0.70 TPAN
Termination		NO$_2$, NO, PAN, 0.60 TPAN	HO$_2$, RO$_2$, RCO$_3$	HO$_2$, RO$_2$, RCO$_3$ NO: 0.06 HC3P, 0.12 HC5P, 0.26 HC8P, 0.15 ISOP 0.20 APIP, 0.35 LIMP, 0.05 TOLP 0.05 XYLP	HO$_2$, RO$_2$, RCO$_3$, NO$_2$
Propagation to	OH		NO, O$_3$, 0.70 NO$_3$		
	HO$_2$	O$_3$, NO$_3$, H$_2$, CO, H$_2$O$_2$, SO$_2$, HCHO HKET, GLY, UDD 0.38 HC3, 0.25 HC5, 0.05 HC8 0.10 TOL, O.10 XYL, 0.05 CSL 0.49 MACR, 0.50 DCB, 0.35 PAA 0.40 TPAN		NO: CH$_3$O$_2$, ETHP, 0.74 HC3P, 0.60 HC5P 0.61 HC8P, ETEP, OLTP, OLIP 0.85 ISOP, 0.80 APIP, 0.65 LIMP 0.95 TOLP, 0.95 XYLP, CSLP 0.77 KETP	
	RO$_2$	CH4, ETH, ETE, OLT, OLI, DIEN, ISO, API, LIM, KET, ONIT 0.58 HC3, 0.75 HC5, 0.95 HC8 0.90 TOL, 0.90 XYL, 0.95 CSL 0.65 CH$_3$OOH , 0.44 OP2		NO: 0.20 HC3P, 0.28 HC5P, 0.13 HC8P	NO : CH$_3$O$_2$
	RCO$_3$	ALD, MGLY 0.51 MACR, 0.50 DCB, 0.65 PAA		NO: 0.23 KETP	

Table S2: [a] from the photolytic channel leading to the production of radicals

Contribution (%)	Photolytic processes												Non-photolytic processes			
	HONO [a]	DCB		GLY / MGLY		HCHO / ALD		O(^{1}D) + H$_2$O	Others				O$_3$ + alkene			
	RO$_x$	RO$_x$		RO$_x$		RO$_x$		RO$_x$	RO$_x$				RO$_x$			
	OH	HO$_2$	RCO$_3$	HO$_2$	RCO$_3$	HO$_2$	RO$_2$	OH	OH [b]	HO$_2$ [c]	RCO$_3$ [d]	RO$_2$ [e]	OH	HO$_2$	RCO$_3$	RO$_2$
Morning	45.0	4.5		1.0 / 3.9		24.2 / 2.2		3.9	4.7				10.7			
(8:40-11:50)	80.3	6.7	45.9	2.9 / 5.7	0 / 39.2	71.5 / 3.2	0 / 20.9	6.9	4.1	4.7	13.2	4.2	8.6	5.3	1.7	74.9
Early afternoon	23.6	3.4		1.0 / 3.4		26.4 / 2.0		8.9	6.9				24.4			
(12:00-15:50)	50.2	4.5	38.5	2.6 / 4.4	0 / 38.0	69.0 / 2.6	0 / 9.8	18.9	7.3	6.1	17.5	2.8	23.6	10.8	5.9	87.3
Late afternoon	21.2	2.1		0.4 / 1.9		13.3 / 0.7		2.4	2.5				55.5			
(16:00-18:40)	42.6	4.0	37.8	1.4 / 3.5	0 / 33.1	50.3 / 1.3	0 / 1.7	4.9	1.8	3.9	17.9	0.5	50.8	35.6	11.2	97.8
Averaged day	34.5	3.9		1.0 / 3.5		24.4 / 2.0		5.9	5.4				19.3			
(8:40-18:40)	66.6	5.6	42.6	2.7 / 5.0	0 / 38.5	69.3 / 2.9	0 / 12.1	11.4	5.3	5.3	15.1	2.9	16.9	9.3	3.8	85.0

Table S3: [a] These calculations are based on a gross initiation rate of OH from HONO photolysis. The contribution of HONO photolysis to the total rate of RO$_x$ initiation would be smaller on a net basis. [b] HNO$_3$, H$_2$O$_2$, organic peroxides, PAA, [c] organic peroxides, organic nitrates, methacrolein, hydroxyl ketones, [d] ketones, hydroxyl ketones, methacrolein, [e] PAA, ketones

Contribution (%)	OH + NO_2	OH + NO	RO_2 + NO	Others [a]
Morning (8:40-11:50)	55.5	29.6	11.2	3.7
Early afternoon (12:00-15:50)	63.7	9.9	17.0	9.5
Late afternoon (16:00-18:40)	69.3	5.6	18.0	7.1
Averaged day (8:40-18:40)	59.8	19.8	14.1	6.3

Table S4: [a] OH + PAN, OH + TPAN, OH + HNO_3, OH + HONO, OH + HNO_4, radical + radical

Species	Lifetime (h)		
	Photolysis [a]	Reaction with OH [b]	Total
OH			40 ms [c]
HO$_2$			0.9 s [d]
HONO	0.15	15.4	0.14
DCB	0.6	1.4	0.4
MGLY	2.3	4.1	1.5
GLY	3.1	6.0	2.1
KET	427.3	106.8	85.5

Table S5: [a] using the median J-values displayed in Table S1. [b] using the median OH concentration of 4 x 10^6 cm^{-3} measured at 1pm and the rate constants at 298K from Sander et al. (Sander et al., 2006) for HONO+OH and GLY+OH. The rate constants for OH+MGLY, OH+DCB and OH+KET are from Stockwell et al. (Stockwell et al., 1997). OH and HO$_2$ lifetime were calculated using measured median concentrations of chemical species at 1 pm CST. [c] OH lifetime calculated from total OH reactivity. [d] HO$_2$ lifetime calculated for the rate of HO$_2$ + NO.

Model constraints	[OH] ($\times 10^6$ cm^{-3})		[HO$_2$] ($\times 10^7$ cm^{-3})	
	8:40 am - noon	noon – 6:40 pm	8:40 am - noon	noon – 6:40 pm
Median base modeling Large VOC dataset Dicarbonyls constrained	3.61	3.90	3.3	11.9
Dicarbonyls unconstrained	6.48 +79.5%	6.00 +53.9%	6.9 +109.1%	21.4 +79.8%
HONO unconstrained	2.90 -19.7%	3.32 -14.9%	2.8 -15.2%	10.3 -13.5%
NO$_2$ unconstrained	3.19 -11.6%	3.96 +1.5%	3.0 -9.1%	12.2 +2.5%
[KET] x 2	3.63 +0.6%	3.92 +0.5%	3.3 +0.0%	12.0 +0.8%
[OLI + OLT] x 2	4.00 +10.8%	4.80 +23.1%	4.0 +21.2%	16.3 +37.0%
[HC3 + HC5 + HC8] x 2	3.32 -8.0%	3.40 -12.8%	3.9 +18.2%	13.5 +13.5%
[CO] x 2	3.60 -0.3%	3.89 -0.3%	3.4 +3.0%	12.4 +4.2%
[ALD] x 3	3.76 +4.2%	3.99 +2.3%	4.0 +21.2%	13.8 +16.0%
[HCHO] x 2	4.51 +24.9%	4.76 +22.1%	4.6 +39.4%	15.8 +32.8%
[HCHO] / 2	3.15 -12.7%	3.44 -11.8%	2.7 -18.2%	10.0 -16.0%
[NO$_x$] / 2	6.09 +68.7%	5.15 +32.1%	10.3 +212.1%	29.6 +148.7%
[NO$_x$] x 2	1.96 -45.7%	2.28 -41.5%	1.0 -69.7%	3.8 -68.1%
J(HONO) / 1.5	3.12 -13.6%	3.61 -7.4%	3.0 -9.1%	11.1 -6.7%

Table S6: Dicarbonyls = GLY + MGLY + DCB

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