Supplement of Geosci. Model Dev., 10, 609–638, 2017
http://www.geosci-model-dev.net/10/609/2017/
doi:10.5194/gmd-10-609-2017-supplement
© Author(s) 2017. CC Attribution 3.0 License.

Geoscientific Model Development
Open Access

Supplement of

Description and evaluation of the Multiscale Online Nonhydrostatic AtmospheRe CHemistry model (NMMB-MONARCH) version 1.0: gas-phase chemistry at global scale

Alba Badia et al.

Correspondence to: Oriol Jorba (oriol.jorba@bsc.es)

The copyright of individual parts of the supplement might differ from the CC-BY 3.0 licence.

S1 Statistical Measures

There are several metrics that are used by the modeling community to evaluate performances of AQMs (U.S.EPA, 1991; Cox and Tikvart, 1990; Russell and Dennis, 2000). The statistical indicators selected in this study are: Correlation coefficient (r: Eq. 1) , Mean Bias (MB: Eq. 2) and Root Mean Square Error (RMSE: Eq.3).

$$r = \frac{1}{N} \frac{\sum_{i=1}^{N} (O_i - \overline{O}) \Delta (P_i - \overline{P})}{\sigma_O \Delta \sigma_P} \tag{1}$$

$$MB = \frac{\sum_{i=1}^{N} (P_i - O_i)}{N} \tag{2}$$

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (P_i - O_i)^2} \tag{3}$$

where σ is the standard deviation and P and O denote the vector of model output and the vector observations, respectively. No threshold has been applied in the computation of the statistics.

S2 Figures

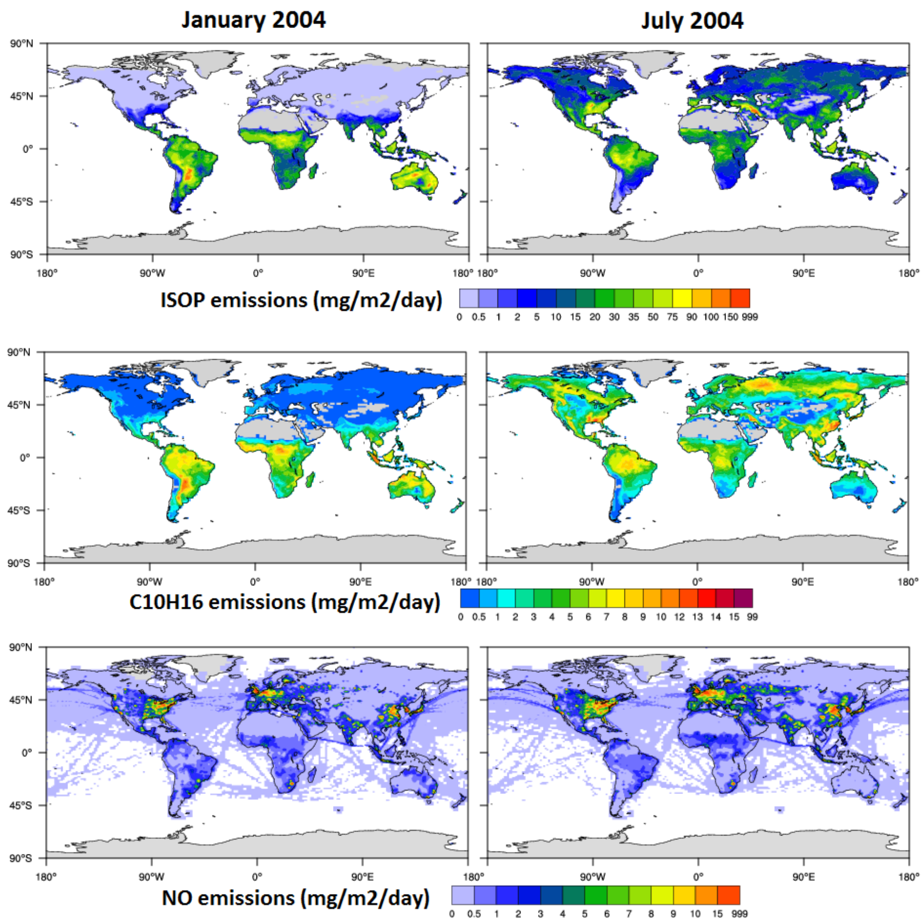

Figure S1: Biogenic emisions of isoprene (upper panel) and monoterpene (middle panel), from the on-line model MEGAN, and anthropogenic emissions of NO (lower panel), from ACCMIP inventory, for January and July 2004 used in this model simulation.

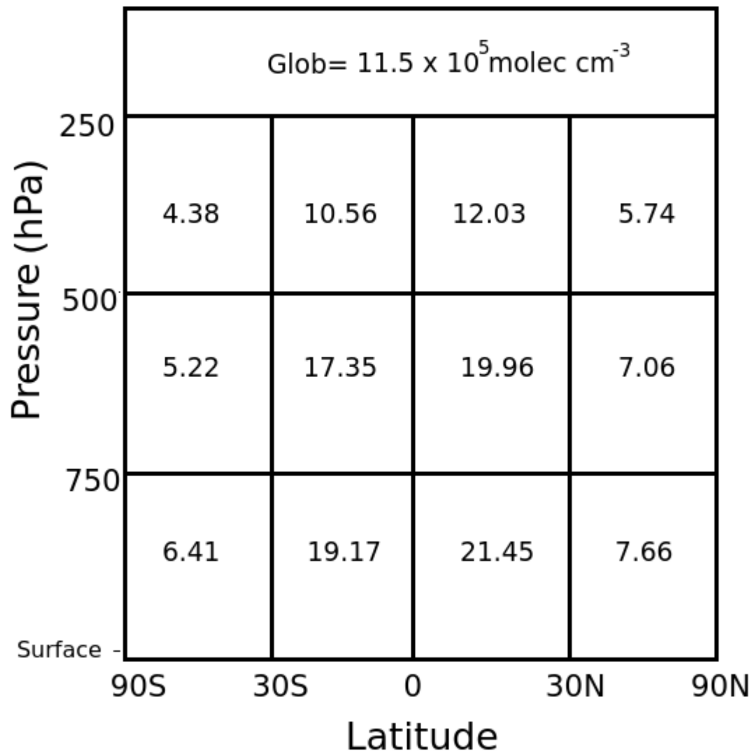

Figure S2: NMMB-MONARCH regional annual mean airmass-weighted OH concentrations (x 10^5 molecule cm^{-3}).

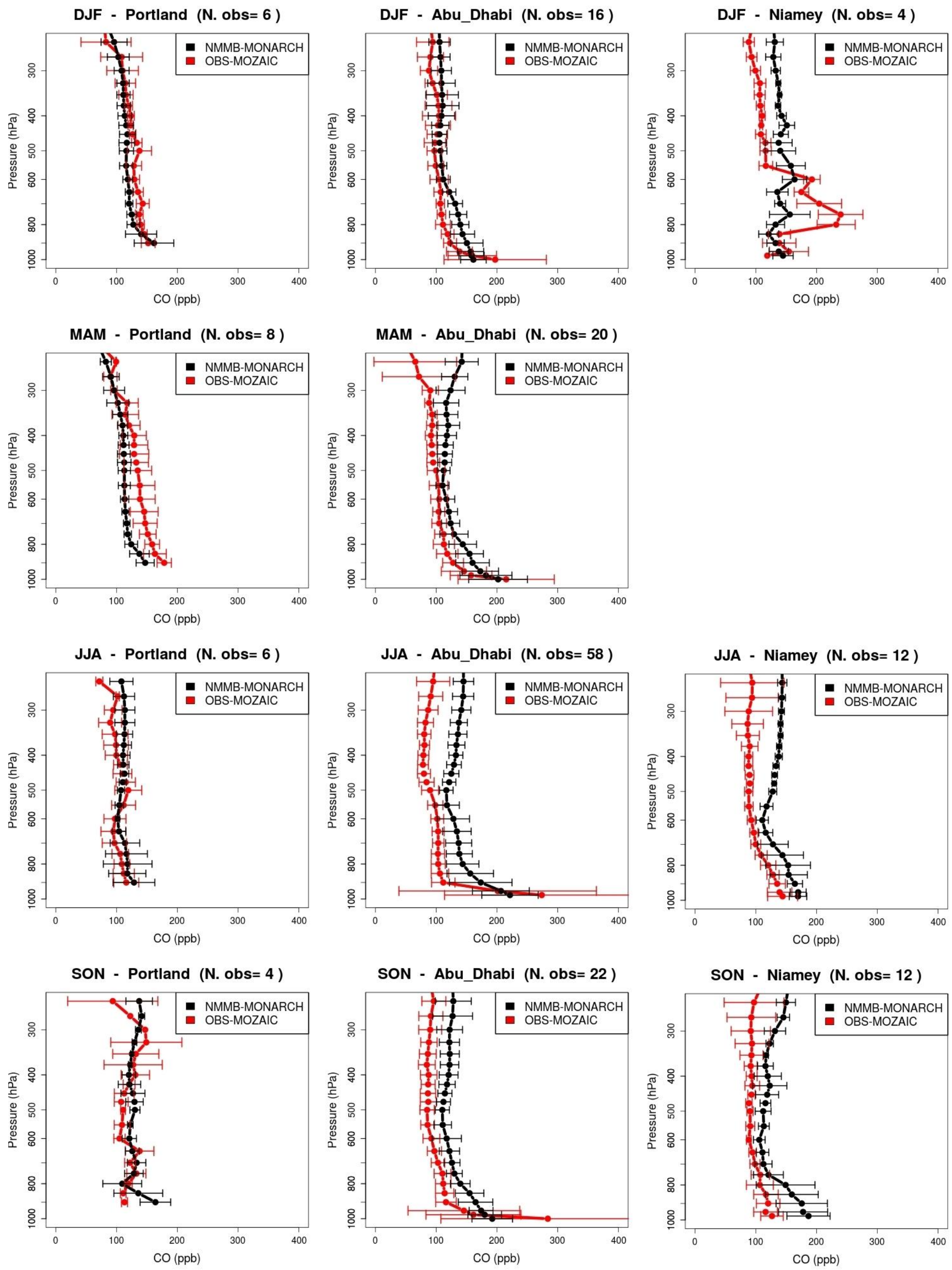

Figure S3: CO vertical profile seasonal averages over Portland, Abu Zabi and Niamey (from left to right) for year 2004. Observations depicted with a solid red line and model with a solid black line. The number of flights is provided on the top of each plot.

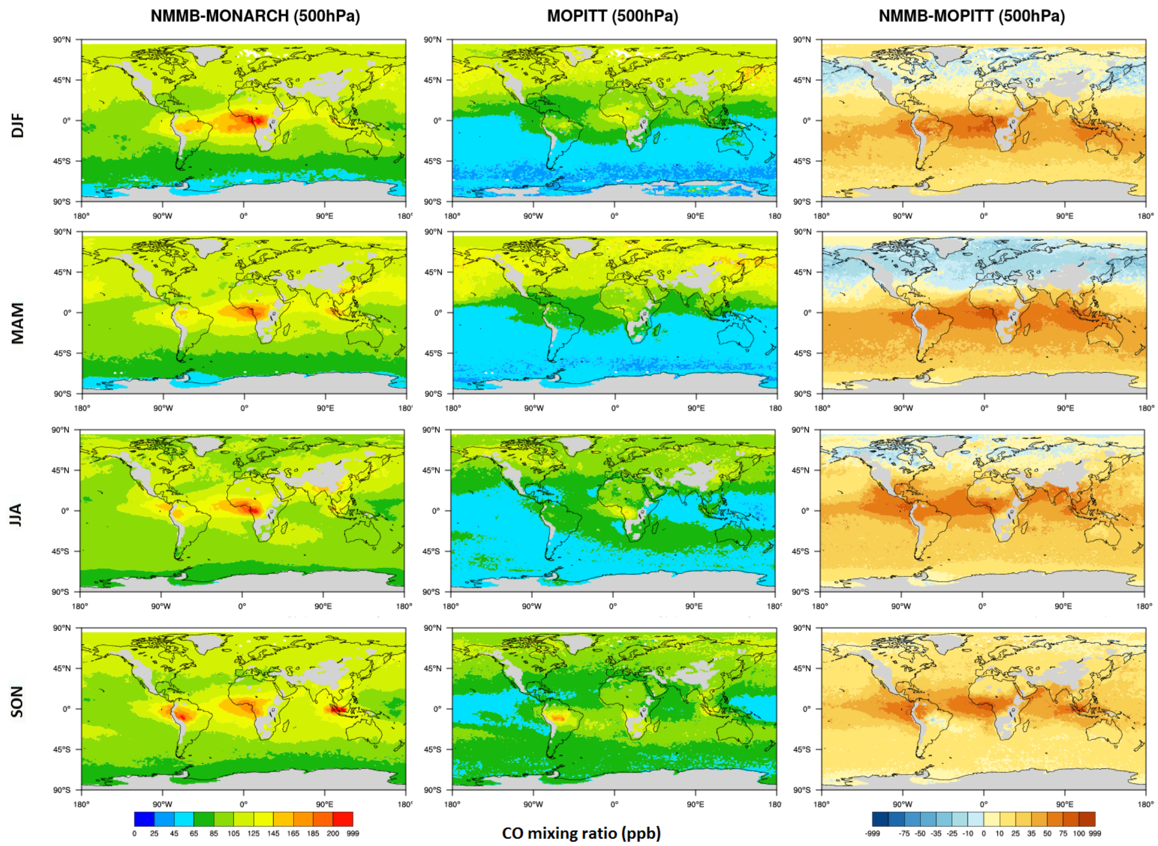

Figure S4: Comparison of modeled CO mixing ratio at 500 hPa against satellite data (MOPITT) in ppb. From top to bottom: DJF for December-January-February, MAM for March-April-May, JJA for June-July-August and SON for September-October-November for year 2004. NMMB-MONARCH data is displayed in the left panel, MOPITT data in the middle panel and the bias in the right panel.

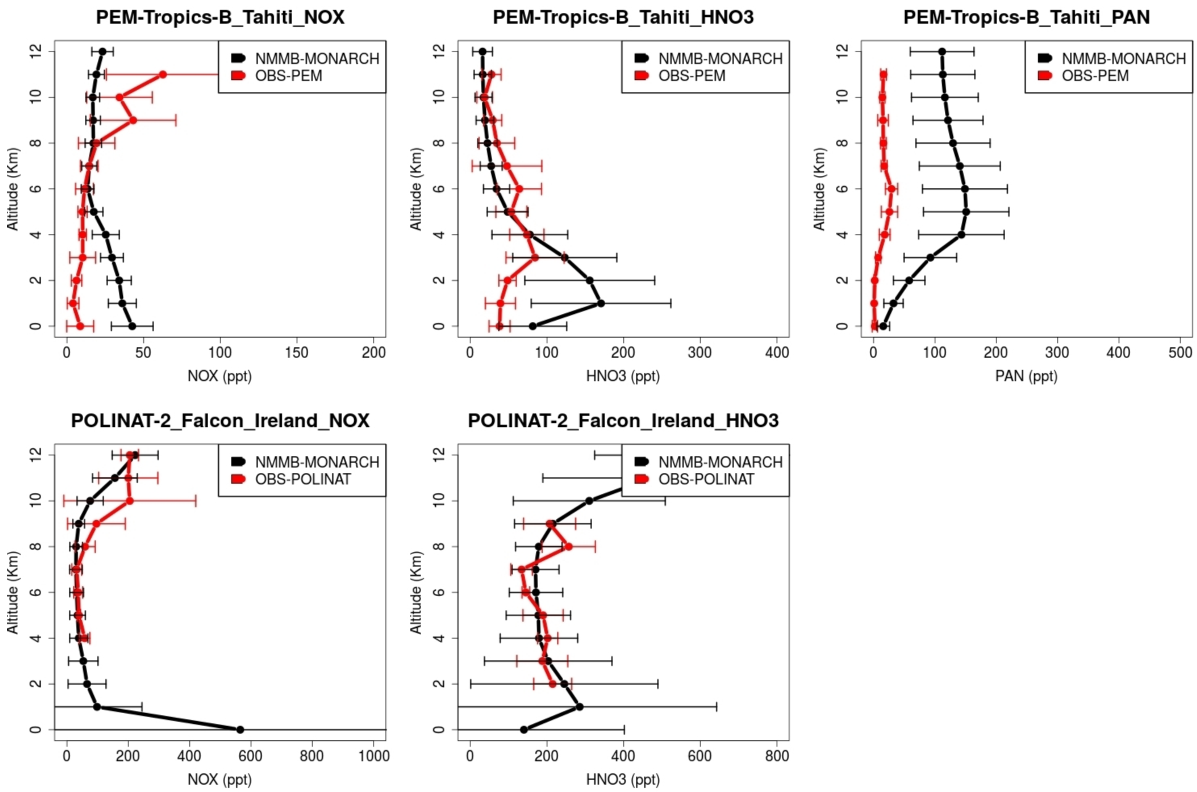

Figure S5: Comparison of modeled (black lines) and observed (red lines) vertical profiles of NO_x (first column), HNO_3 (second column) and PAN (third column) over Tahiti and Ireland.

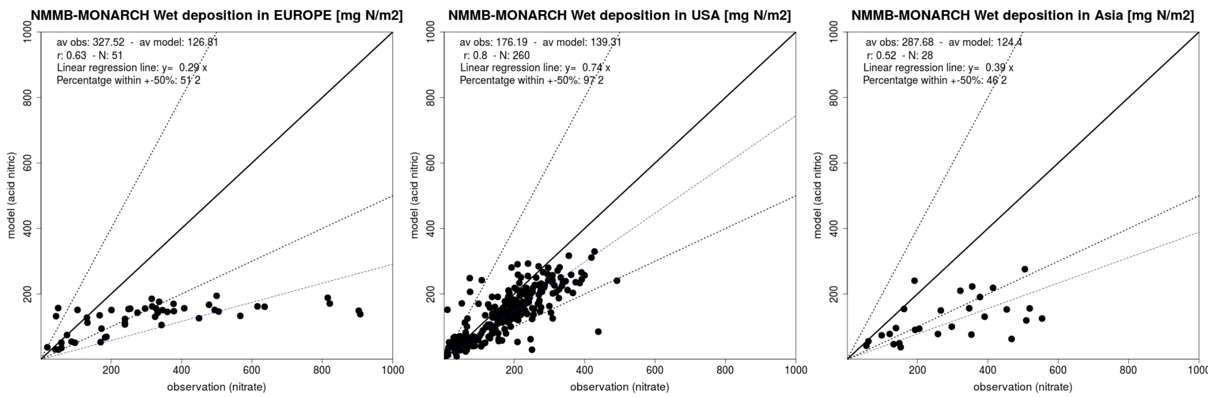

Figure S6: Scatter plots of the simulated HNO_3 versus nitrate measurements for three networks: Europe (left panel), USA (middle panel) and Asia (right panel). Dashed lines have slopes equal to 2 and 0.5. The dotted line is the result of the linear regression fitting through the origin.

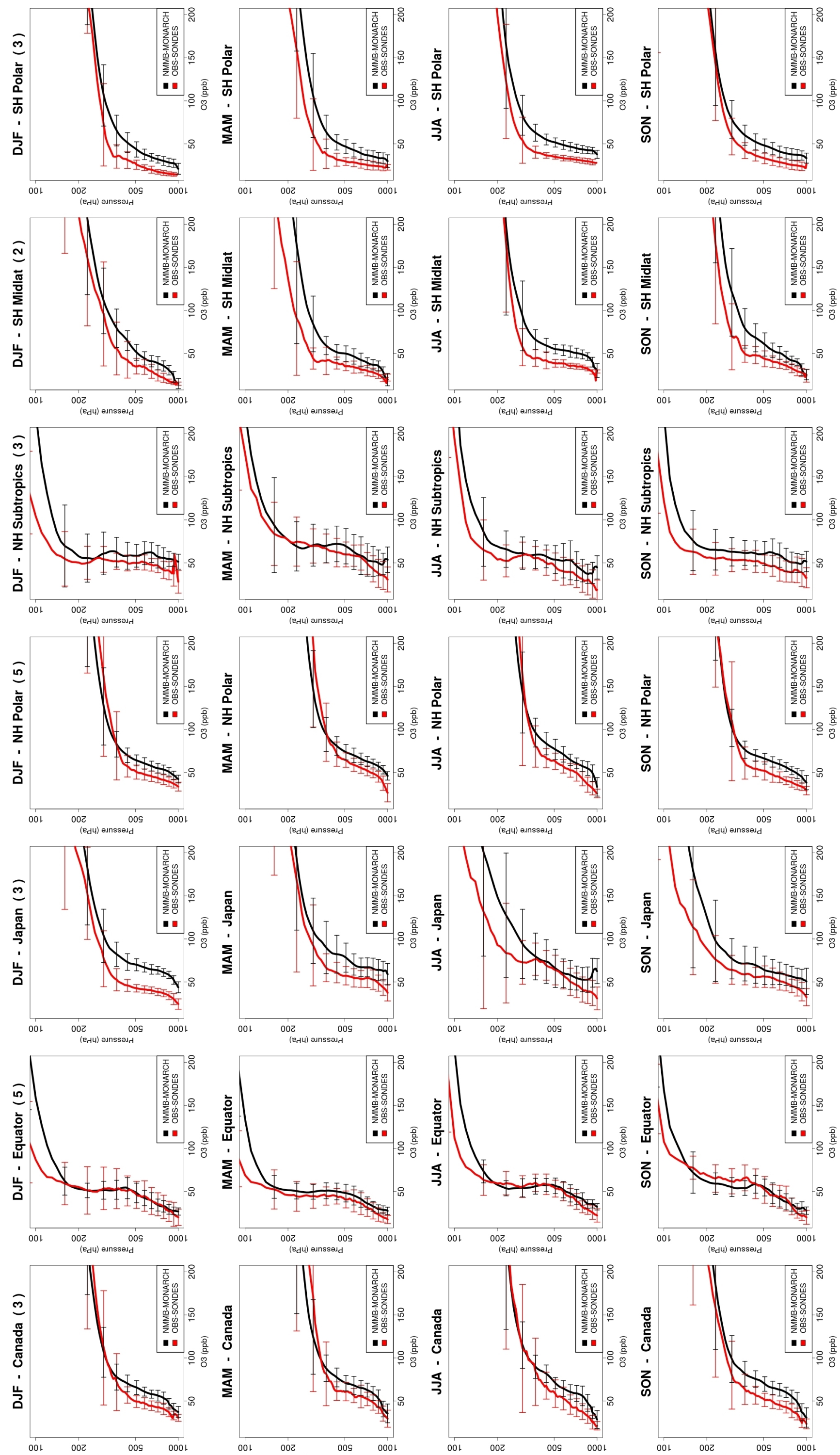

Figure S7: Comparison of ozonesonde measurements (red lines) and simulated (black lines) seasonal vertical profiles of O_3 (ppb) and standard deviations (horizontal lines). The region name and the number of stations are given above each plot between brackets.

S3 Tables

Table S1: The chemical trace species for the CB05 chemical mechanism included in gas-phase tropospheric chemistry version of NMMB-MONARCH.

Species name	**Description**	**Species name**	**Description**
NO	Nitric oxide	SO_2	Sulfur dioxide
NO_2	Nitrogen dioxide	MEO_2	Methylperoxy radical
O_3	Ozone	MEOH	Methanol
O	Oxygen atom in the O^3(P) electronic state	MEPX	Methylhydroperoxide
O^1D	Oxygen atom in the O^1(D) electronic state	FACD	Formic acid
OH	Hydroxyl radical	ETHA	Ethane
HO_2	Hydroperoxy radical	ROOH	Higher organic peroxide
H_2O_2	Hydrogen peroxide	AACD	Acetic and higher carboxylic acids
NO_3	Nitrate radical	PACD	Peroxyacetic and higher peroxycarboxylic acids
N_2O_5	Dinitrogen pentoxide	PAR	Paraffin carbon bond (C-C)
HONO	Nitrous acid	ROR	Secondary alkoxy radical
HNO_3	Nitric acid	ETH	Ethene
PNA	Peroxynitric acid (HNO_4)	OLE	Terminal olefin carbon bond (R-C=C)
CO	Carbon monoxide	IOLE	Internal olefin carbon bond (R-C=C-R)
FORM	Formaldehyde	ISOP	Isoprene
ALD2	Acetaldehyde	ISPD	Isoprene product (lumped methacrolein, methyl vinyl ketone, etc.)
C_2O_3	Acetylperoxy radical		
PAN	Peroxyacetyl nitrate	TERP	Terpene
ALDX	Propionaldehyde and higher aldehydes	TOL	Toluene and other monoalkyl aromatics
CXO_3	C3 and higher acylperoxy radicals	XYL	Xylene and other polyalkyl aromatics
PANX	C3 and higher peroxyacyl nitrates	CRES	Cresol and higher molecular weight phenols
XO_2	NO to NO_2 conversion from alkylperoxy (RO_2) radical	TO_2	Toluene-hydroxyl radical adduct
XO_2N	NO to organic nitrate conversion from alkylperoxy (RO_2) radical	OPEN	Aromatic ring opening product
NTR	Organic nitrate (RNO_3)	CRO	Methylphenoxy radical
ETOH	Ethanol	MGLY	Methylglyoxal and other aromatic products
SULF	Sulfuric acid (gaseous)		

Table S2: The gas-phase CB05 chemical mechanism reactions applied in the NMMB-MONARCH. The first column describes the reactants, the second the products and the third displays the coefficients to compute the full rate expressions for each reaction.

Reactants		**Products**	**Rate expression**
$O + O_2 + M$	→	$O_3 + M$	6.0E-34*(300/T)$^{2.4}$
$O_3 + NO$	→	NO_2	3.0E-12*exp(T/1500)
$O + NO_2$	→	NO	5.6E-12*exp(180/T)
$O + NO_2$	→	NO_3	K_0= 2.5E-31*exp(300/T)$^{1.8}$ K_∞=2.2E-11*exp(300/T)$^{0.7}$
O + NO	→	NO_2	K_0=9.0E-32*exp(300/T)$^{1.5}$ K_∞=3.0E-11
$NO_2 + O_3$	→	NO_3	1.2E-13*exp(T/2450)
$O(^1)D + M$	→	O + M	2.1E-11*exp(102/T)
$O(^1)D + H_2O$	→	2.000*OH	2.2E-10
$O_3 + OH$	→	HO_2	1.7E-12*exp(T/940)
$O_3 + HO_2$	→	OH	1.0E-14*exp(T/490)
$NO_3 + NO$	→	2.000*NO_2	1.5E-11*exp(170/T)
$NO_3 + NO_2$	→	$NO + NO_2$	4.5E-14*exp(T/1260)
$NO_3 + NO_2$	→	$N2O_5$	K_0= 2.0E-30 *(300/T)$^{4.4}$ K_∞= 1.4E-12*(300/T)$^{0.7}$
$N_2O_5 + H_2O$	→	2.000*HNO_3	2.5E-22
$N_2O_5 + H_2O + H_2O$	→	2.000*HNO_3	1.8E-39
N_2O_5	→	$NO_3 + NO_2$	K_0= 1.0E-03*exp(11000/T)$^{3.5}$ K_∞= 9.7E+14*exp(T/11080)$^{0.1}$ F_c= 0.45 n= 1.0
$NO + NO + O_2$	→	2.000*NO_2	3.3E-39*exp(530/T)
$NO + NO_2 + H_2O$	→	2.000*HONO	5.0E-40
NO + OH	→	HONO	7.0E-31*exp(300/T)$^{2.6}$ 3.6E-11*exp(300/T)−0.1
OH + HONO	→	NO_2	1.8E-11*exp(T/390)
HONO + HONO	→	$NO + NO_2$	1.0E-20
$NO_2 + OH$	→	HNO_3	K_0=2.0E-30*exp(300/T)$^{3.0}$ K_∞=2.5E-11
$OH + HNO_3$	→	NO_3	K_0=2.4E-14*exp(460/T) K_2= 2.7E-17*exp(2199/T) K_3= 6.5E-34*exp(1335/T)
$HO_2 + NO$	→	$OH + NO_2$	K_0=3.5E-12*exp(250/T)
$HO_2 + NO_2$	→	PNA	K_0=1.8E-31*exp(300/T)$^{3.2}$ K_∞=4.7E-12 F_c=0.6
PNA	→	HO_2+NO_2	K_0=4.1E-5*exp(T/10650) K_∞=4.8E15*exp(T/11170) F_c=0.6
OH + PNA	→	NO_2	1.3E-12*exp(380/T)
$HO_2 + HO_2$	→	H_2O_2	K_1=2.3E-13*exp(600/T) K_2=1.7E-33*exp(1000/T)
$HO_2+HO_2+H_2O$	→	H_2O_2	K_1=3.22E-34*exp(2800/T) K_2=2.38E-54*exp(3200/T)

Table S2: Continued from previous page

Reactants		Products	Rate expression
$OH + H_2O_2$	→	HO_2	2.9E-12*exp(T/160)
$O^1D + H_2$	→	$OH + HO_2$	1.1E-10
$OH + H_2$	→	HO_2	5.5E-12*exp(T/2000)
OH + O	→	HO_2	2.2E-11*exp(120/T)
OH + OH	→	O	4.2E-12*exp(T/240)
OH + OH	→	H_2O_2	K_0=6.9E-31*exp(300/T)$^{1.0}$ K_∞=2.6E-11
$OH + HO_2$	→		4.8E-11*exp(250/T)
HO_2 + O	→	OH	3.0E-11*exp(200/T)
H_2O_2 + O	→	$OH + HO_2$	1.4E-12*exp(-2000/T)
NO_3 + O	→	NO_2	1.0E-11
NO_3 + OH	→	HO_2+ NO_2	2.2E-11
$NO_3 + HO_2$	→	HNO_3	3.5E-12
$NO_3 + O_3$	→	NO_2	1.0E-17
$NO_3 + NO_3$	→	2.000*NO_2	8.5E-13*exp(T/2450)
XO_2 + NO	→	NO_2	2.6E-12*exp(365/T)
XO_2N + NO	→	NTR	2.6E-12*exp(365/T)
$XO_2 + HO_2$	→	ROOH	7.5E-13*exp(700/T)
$XO_2N + HO_2$	→	ROOH	7.5E-13*exp(700/T)
$XO_2 + XO_2$	→		6.8E-14
$XO_2N + XO_2N$	→		6.8E-14
$XO_2 + XO_2N$	→		6.8E-14
NTR + OH	→	HNO_3+ HO_2 + 0.330*FORM+ 0.330*ALD2+ 0.330*ALDX- 0.660*PAR	5.9E-13*exp(360/T)
ROOH + OH	→	XO_2+ 0.500*ALD2 + 0.500*ALDX	3.01E-12*exp(190/T)
OH + CO	→	HO_2	K_1= 1.44E-13 K_2=3.43E-33
OH + CH4	→	MEO_2	2.45E-12*exp(T/1775)
MEO_2 + NO	→	FORM + HO_2+ NO_2	2.8E-12*exp(300/T)
$MEO_2 + HO_2$	→	MEPX	4.1E-13*exp(750/T)
$MEO_2 + MEO_2$	→	1.370*FORM+ 0.740*HO_2+ 0.630*MEOH	9.5E-14*exp(390/T)
MEPX + OH	→	0.700*MEO_2+ 0.300*XO_2+ 0.300*HO_2	3.8E-12*exp(200/T)
MEOH + OH	→	FORM + HO_2	7.3E-12*exp(T/620)
FORM + OH	→	HO_2 + CO	9.0E-12
FORM + O	→	OH + HO_2 + CO	3.4E-11*exp(T/1600)
FORM + NO_3	→	HNO_3+HO_2+ CO	5.8E-16
FORM + HO_2	→	HCO_3	9.7E-15*exp(625/T)
HCO_3	→	FORM + HO_2	2.4E+12*exp(T/7000)
HCO_3 + NO	→	FACD+ NO_2 + HO_2	5.6E-12
$HCO_3 + HO_2$	→	MEPX	5.6E-15*exp(2300/T)
FACD + OH	→	HO_2	4.0E-13
ALD2 + O	→	C_2O_3 + OH	1.8E-11*exp(T/1100)
ALD2 + OH	→	C_2O_3	5.6E-12*exp(270/T)
ALD2 + NO_3	→	C_2O_3+ HNO_3	1.4E-12*exp(T/1900)
C_2O_3 + NO	→	$MEO_2 + NO_2$	8.1E-12*exp(270/T)
PAN	→	$C_2O_3 + NO_2$	K_0= 4.9E-3*exp(12100/T) K_∞= 5.4E16*exp(T/13830) F_c=0.3
$C_2O_3 + HO_2$	→	0.800*PACD+ 0.200*AACD+ 0.200*O_3	4.3E-13*exp(1040/T)
$C_2O_3 + MEO_2$	→	0.900*MEO_2+ 0.900*HO_2+ FORM+ 0.100*AACD	2.0E-12*exp(500/T)

Table S2: Continued from previous page

Reactants		Products	Rate expression
C_2O_3 + XO_2	→	0.900*MEO_2+ 0.100*AACD	4.4E-13*exp(1070/T)
C_2O_3 + C_2O_3	→	2.000*MEO_2	2.9E-12*exp(500/T)
PACD + OH	→	C_2O_3	4.0E-13*exp(200/T)
AACD + OH	→	MEO_2	4.0E-13*exp(200/T)
ALDX + O	→	CXO_3 + OH	1.3E-11*exp(T/870)
ALDX + OH	→	CXO_3	5.1E-12*exp(405/T)
ALDX + NO_3	→	CXO_3 + HNO_3	6.5E-15
CXO_3 + NO	→	ALD2+ NO_2+ HO_2+XO_2	6.7E-12*exp(340/T)
CXO_3 + NO_2	→	PANX	K_0=2.7E-28*exp(300/T)$^{7.1}$ K_∞=1.2E-11*exp(300/T)$^{0.9}$ F_c=0.3
PANX	→	CXO_3 + NO_2	
PANX + OH	→	ALD2 + NO_2	3.0E-13
CXO_3 + HO_2	→	0.800*PACD+ 0.200*AACD+ 0.200*O_3	4.3E-13*exp(1040/T)
CXO_3 + MEO_2	→	0.900*ALD2+ 0.900*XO_2+ HO_2+ 0.100*AACD+ 0.100*FORM	2.0E-12*exp(500/T)
CXO_3 + XO_2	→	0.900*ALD2+ 0.100*AACD	4.4E-13*exp(1070/T)
CXO_3 + CXO_3	→	2.000*ALD2 + 2.000*XO_2+ 2.000*HO_2	2.9E-12*exp(500/T)
CXO_3 + C_2O_3	→	MEO_2+ XO_2+ HO_2+ ALD2	2.9E-12*exp(500/T)
PAR + OH	→	0.870*XO_2+ 0.130*XO_2N+ 0.110*HO_2+ 0.060*ALD2- 0.110*PAR+ 0.760*ROR+ 0.050*ALDX	8.1E-13
ROR	→	0.960*XO_2+ 0.600*ALD2+ 0.940*HO_2- 2.100*PAR+ 0.040*XO_2N+ 0.020*ROR+ 0.500*ALDX	1.E+15*exp(T/8000)
ROR	→	HO_2	1.6E+3
ROR + NO_2	→	NTR	1.5E-11
O + OLE	→	0.200*ALD2+ 0.300*ALDX+ 0.300*HO_2+ 0.200*XO_2+ 0.200*CO+ 0.200*FORM+ 0.010*XO_2N+ 0.200*PAR+ 0.100*OH	1.E-11*exp(T/280)
OH + OLE	→	0.800*FORM+ 0.330*ALD2+ 0.620*ALDX + 0.800*XO_2+ 0.950*HO_2- 0.700*PAR	3.2E-11
O_3 + OLE	→	0.180*ALD2+ 0.740*FORM+ 0.320*ALDX+ 0.220*XO_2+ 0.100*OH+ 0.330*CO+ 0.440*HO_2 - 1.000*PAR	6.5E-15*exp(T/1900)
NO_3 + OLE	→	NO_2+ FORM+ 0.910*XO_2+ 0.090*XO_2N+ 0.560*ALDX+ 0.350*ALD2- 1.000*PAR	7.0E-13*exp(T/2160)
O + ETH	→	FORM+ 1.700*HO_2+ CO+ 0.700*XO_2+ 0.300*OH	1.04E-11*exp(T/792)
OH + ETH	→	XO_2+ 1.560*FORM+ 0.220*ALDX+ HO_2	K_0=1.0E-28*exp(300/T)$^{0.8}$ K_∞=8.8E-12
O_3 + ETH	→	FORM+ 0.630*CO+ 0.130*HO_2+ 0.130*OH+ 0.370*FACD	1.2E-14*exp(T/2630)
NO_3 + ETH	→	NO_2+ XO_2+ 2.0*FORM	3.3E-12*exp(T/2880)
IOLE + O	→	1.240*ALD2+ 0.660*ALDX+ 0.100*HO_2+ 0.100*XO_2+ 0.100*CO+ 0.100*PAR	2.3E-11
IOLE + OH	→	1.300*ALD2 + 0.700*ALDX + HO_2 + XO_2	1.0E-11*exp(550/T)
IOLE + O_3	→	0.650*ALD2 + 0.350*ALDX + 0.250*FORM + 0.250*CO + 0.500*O + 0.500*OH + 0.500*HO_2	8.4E-15*exp(T/1100)

Table S2: Continued from previous page

Reactants		Products	Rate expression
IOLE + NO_3	→	1.180*ALD2 + 0.640*ALDX + HO_2 + NO_2	9.6E-13*exp(T/270)
TOL + OH	→	0.440*HO_2 + 0.080*XO_2 + 0.360*CRES + 0.560*TO_2 + 0.765*TOLRO$_2$	1.8E-12*exp(355/T)
TO_2 + NO	→	0.900*NO_2 + 0.900*HO_2 + 0.900*OPEN + 0.100*NTR	8.1E-12
TO_2	→	CRES + HO_2	4.2
OH + CRES	→	0.400*CRO + 0.600*XO_2 + 0.600*HO_2 + 0.300*OPEN	4.1E-11
CRES + NO_3	→	CRO + HNO_3	2.2E-11
CRO + NO_2	→	NTR	1.4E-11
CRO + HO_2	→	CRES	5.5E-12
OPEN + OH	→	XO_2 + 2.000*CO + 2.000*HO_2 + C_2O_3 + FORM	3.0E-11
OPEN + O_3	→	0.030*ALDX + 0.620*C_2O_3 + 0.700*FORM + 0.030*XO_2 + 0.690*CO + 0.080*OH + 0.760*HO_2 + 0.200*MGLY	5.4E-17*exp(T/500)
OH + XYL	→	0.700*HO_2 + 0.500*XO_2 + 0.200*CRES + 0.800*MGLY + 1.100*PAR + 0.300*TO_2 + 0.804*XYLRO$_2$	1.7E-11*exp(116/T)
OH + MGLY	→	XO_2 + C_2O_3	1.8E-11
O + ISOP	→	0.750*ISPD + 0.500*FORM + 0.250*XO_2 + 0.250*HO_2 + 0.250*CXO_3 + 0.250*PAR	3.6E-11
OH + ISOP	→	0.912*ISPD + 0.629*FORM + 0.991*XO_2 + 0.912*HO_2 + 0.088*XO_2N + ISOPRXN	2.54E-11*exp(407.6/T)
O_3 + ISOP	→	0.650*ISPD + 0.600*FORM + 0.200*XO_2 + 0.066*HO_2 + 0.266*OH + 0.200*CXO_3 + 0.150*ALDX + 0.350*PAR + 0.066*CO	7.86E-15*exp(T/1912)
NO_3 + ISOP	→	0.200*ISPD + 0.800*NTR + XO_2 + 0.800*HO_2 + 0.200*NO_2 + 0.800*ALDX + 2.400*PAR	3.03E-12*exp(T/448)
OH + ISPD	→	1.565*PAR + 0.167*FORM + 0.713*XO_2 + 0.503*HO_2 + 0.334*CO + 0.168*MGLY + 0.252*ALD2 + 0.210*C_2O_3 + 0.250*CXO_3 + 0.120*ALDX	3.36E-11
O_3 + ISPD	→	0.114*C_2O_3 + 0.150*FORM + 0.850*MGLY + 0.154*HO_2 + 0.268*OH + 0.064*XO_2 + 0.020*ALD2 + 0.360*PAR + 0.225*CO	7.1E-18
NO_3 + ISPD	→	0.357*ALDX + 0.282*FORM + 1.282*PAR + 0.925*HO_2 + 0.643*CO + 0.850*NTR + 0.075*CXO_3 + 0.075*XO_2 + 0.150*HNO_3	1.0E-15
TERP + O	→	0.150*ALDX + 5.12*PAR + TRPRXN	3.6E-11
TERP + OH	→	0.750*HO_2 + 1.250*XO_2 + 0.250*XO_2N + 0.280*FORM + 1.66* PAR + 0.470*ALDX + TRPRXN	1.5E-11*exp(449/T)
TERP + O_3	→	0.570*OH + 0.070*HO_2 + 0.760*XO_2 + 0.180*XO_2N + 0.240*FORM + 0.001*CO + 7.000*PAR + 0.210*ALDX + 0.390*CXO_3 + TRPRXN	1.2E-15*exp(T/821)
TERP + NO_3	→	0.470*NO_2 + 0.280*HO_2 + 1.030*XO_2 + 0.250*XO_2N + 0.470*ALDX + 0.530*NTR + TRPRXN	3.7E-12*exp(175/T)

Table S2: Continued from previous page

Reactants		Products	Rate expression
SO_2 + OH	→	SULF + HO_2 + SULRXN	K_0= 3.0E-31*exp(300/T)$^{3.3}$ K_∞= 1.5E-12
OH + ETOH	→	HO_2 + 0.900*ALD2 + 0.050*ALDX + 0.100*FORM + 0.100*XO_2	6.9E-12*exp(T/230)
OH + ETHA	→	0.991*ALD2 + 0.991*XO_2 + 0.009*XO_2N + HO_2	8.7E-12*exp(T/1070)
NO_2 + ISOP	→	0.200*ISPD + 0.800*NTR + XO_2 + 0.800*HO_2 + 0.200*NO + 0.800*ALDX + 2.400*PAR	1.5E-19

Table S3: Photolysis reactions applied in the NMMB-MONARCH.

Reactants		Products
NO_2 +hv	→	NO + O
O_3 +hv	→	O
O_3 +hv	→	O^1D
NO_3 +hv	→	NO_2 + O
NO_3 +hv	→	NO
HONO +hv	→	NO + OH
H_2O_2 +hv	→	2.000*OH
PNA +hv	→	0.610*HO_2 + 0.610*NO_2 + 0.390*OH+ 0.390*NO_3
HNO_3 +hv	→	OH + NO_2
N_2O_5 +hv	→	NO_2+ NO_3
NTR +hv	→	NO_2+ HO_2+ 0.330*FORM+ 0.330*ALD2+ 0.330*ALDX- 0.660*PAR
FORM +hv	→	2.000*HO_2 + CO
FORM +hv	→	CO
ALD2 +hv	→	MEO_2 + CO + HO_2
PAN +hv	→	C_2O_3 + NO_2
PANX +hv	→	CXO_3 + NO_2
PACD +hv	→	MEO_2 + OH
ALDX +hv	→	MEO_2 + CO+ HO_2

References

W. M. Cox and J. A. Tikvart. A statistical procedure for determining the best performing air quality simulation model . *Atmospheric Environment. Part A. General Topics*, 24(9): 2387 – 2395, 1990. ISSN 0960-1686. doi: http://dx.doi.org/10.1016/0960-1686(90)90331-G.

A. Russell and R. Dennis. NARSTO critical review of photochemical models and modeling . *Atmospheric Environment*, 34(12–14):2283 – 2324, 2000. ISSN 1352-2310. doi: http://dx.doi.org/10.1016/S1352-2310(99)00468-9.

U.S.EPA. Guideline for Regulatory Application of the Urban Airshed Model. Technical report, EPA-450/4-91-013. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC., 1991.