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Impact of improved representation of volatile organic compound emissions and production of NO_x reservoirs on modeled urban ozone production

Katherine R. Travis et al.

Correspondence to: Katherine R. Travis (katherine.travis@nasa.gov)

Table S1. New species added to GEOS-Chem and their properties.

GEOS-Chem Species	Formula/Name	Molecular weight	Properties[1] Is_Gas: true (for all)
C4H6	C4H6/1,3-butadiene	54.09	Henry_CR: 4500.0 Henry_K0: 1.4e-2 Is_Advected: true
BUTO2	C4H7O3	103.10	Is_Gas: true
BUTN	C4H7NO4	133.1	DD_F0: 1.0 DD_Hstar: 5.0e+5 Henry_CR: 0.0 Henry_K0: 1.0e+3 Is_Advected: true Is_DryDep: true Is_WetDep: true WD_RetFactor: 2.0e-2
ACR	C3H4O/acrolein	56.06	DD_F0: 1.0 DD_Hstar: 7.3 Henry_CR: 5100.0 Henry_K0: 7.3 Is_Advected: true Is_DryDep: true Is_Photolysis: true
APAN	C3H3NO5/peroxyacrylic nitric anhydride	133.06	DD_F0: 1.0 DD_Hstar: 3.6 Henry_CR: 5700.0 Henry_K0: 2.94 Is_Advected: true Is_DryDep: true Is_Photolysis: true Is_WetDep: true WD_RetFactor: 2.0e-2
ACO3	C3H3O3	87.05	N/A
ACRO2	C3H5O4	105.07	N/A
STYR	C8H8/ styrene	104.15	Is_Advected: true
EBZ	C8H10/ethylbenzene	106.167	Is_Advected: true
TMB	C8H10/Trimethylbenzenes	106.167	Is_Advected: true
ALK6	C7H16/ ≥C6 alkanes	100.20	Is_Advected: true
R6O2	C7H15O2/peroxy radical from ALK6	131.19	N/A
R6N2	C7H15NO3/lumped alkyl nitrate	161.2	DD_F0: 1.0 DD_Hstar: 1.7e+4 Henry_CR: 6700.0 Henry_K0: 0.77 Is_Advected: true Is_DryDep: true Is_Photolysis: true Is_WetDep: true WD_RetFactor: 2.0e-2
R6N1	C7H13O3	145.18	
R6P	C7H16O2/peroxide from R4O2	132.2	DD_F0: 1.0 DD_Hstar: 2.94e+2 Henry_CR: 5200.0 Henry_K0: 2.94e+2 Is_Advected: true

GEOS-Chem Species	Formula/Name	Molecular weight	Properties[1] Is_Gas: true (for all)
			Is_DryDep: true Is_Photolysis: true Is_WetDep: true WD_RetFactor: 2.0e-2
PHAN	C2H3NO6/peroxyhydroxyacetic nitric anhydride	137.0483	DD_F0: 1.0 DD_Hstar: 3.6 Henry_CR: 5700.0 Henry_K0: 2.94 Is_Advected: true Is_DryDep: true Is_Photolysis: true Is_WetDep: true WD_RetFactor: 2.0e-2
GCO3	C2H3O4/peroxyacetyl radical for PHAN	91.04	N/A
HACTA	C2H4O3/hydroxyacetic acid/glycolic acid	76.05	DD_F0: 1.0 DD_Hstar: 2.83e+4 Henry_CR: 4000.0 Henry_K0: 2.83e+4 (Ka = 3.83) Is_Advected: true Is_DryDep: true Is_WetDep: true WD_RetFactor: 2.0e-2
RNO3	C7H9NO6/lumped aromatic alkyl nitrate	203.15	DD_F0: 1.0 DD_Hstar: 1.7e+4 Henry_CR: 5800.0 Henry_K0: 1.0 Is_Advected: true Is_DryDep: true Is_Photolysis: true Is_WetDep: true WD_RetFactor: 2.0e-2
TLFUONE	C5H6O2/ 5-Methyl-2(5H)-furanone	98.1	DD_F0: 1.0 DD_Hstar: 2.0e+6 Is_Advected: true Is_DryDep: true Is_WetDep: true Henry_CR: 7500.0 Henry_K0: 2.0e+6 WD_RetFactor: 2.0e-2
TLFO2	C5H7O5	147.1	N/A
AROMCHO	C5H6O4/ (ACCOMECHO from MCMV3.3.1)	130.1	DD_F0: 1.0 DD_Hstar: 2.0e+6 Formula: C5H6O2 FullName: C5 unsaturated dicarbonyl Is_Advected: true Is_DryDep: true Is_Gas: true Is_WetDep: true MW_g: 98.10 Henry_CR: 7500.0

GEOS-Chem Species	Formula/Name	Molecular weight	Properties[1] Is_Gas: true (for all)
			Henry_K0: 2.0e+6
AROMPN	C5H5NO8/ (ACCOMEPAN from MCMV3.3.1)	207.1	DD_F0: 1.0 DD_Hstar: 3.6 Henry_CR: 5700.0 Henry_K0: 2.94 Is_Advected: true Is_DryDep: true Is_WetDep: true WD_RetFactor: 2.0e-2
AROMCO3	C5H5O6	161.09	N/A
MEKPN	C3H5NO6/hydroxypropanonyl peroxy nitrate (C3PAN1 from MCMV3.3.1)	151.07	DD_F0: 1.0 DD_Hstar: 3.6 Henry_CR: 5700.0 Henry_K0: 2.94 Is_Advected: true Is_DryDep: true Is_WetDep: true WD_RetFactor: 2.0e-2
MEKCO3	C3H5O4	105.07	N/A
ZRO2	C7H9O5	173.16	N/A
RCOOH (currently in GEOS-Chem as a 'dead' species)	C3H6O2 > C2 organic acids	74.08	DD_F0: 1.0 DD_Hstar: 1.52e+3 Henry_CR: 6800.0 Henry_K0: 1.52e+3 Is_Advected: true Is_DryDep: true Is_WetDep: true WD_RetFactor: 2.0e-2
APINP	C10H18O3/hydroperoxide from APIN	186.28	DD_F0: 1.0 DD_Hstar: 1.0e+5 Henry_CR: 6039.0 Henry_K0: 1.0e+5 Is_Advected: true Is_DryDep: true Is_Gas: true Is_WetDep: true WD_RetFactor: 2.0e-2
APINN	C10H17NO4/1st gen organic nitrate from APIN	215.28	DD_F0: 1.0 DD_Hstar: 2.0e+6 Henry_CR: 9200.0 Henry_K0: 1.7e+4 Is_Advected: true Is_DryDep: true Is_Gas: true Is_Photolysis: true Is_WetDep: true WD_RetFactor: 2.0e-2
PINAL	C10H16O2/pinonaldehyde	186.28	DD_F0: 1.0 DD_Hstar: 1.0e+3 Henry_CR: 6039.0 Henry_K0: 1.0e+3 Is_Advected: true Is_DryDep: true Is_Gas: true Is_WetDep: true

GEOS-Chem Species	Formula/Name	Molecular weight	Properties[1] Is_Gas: true (for all)
			WD_RetFactor: 2.0e-2
PINONIC	C10H18O3/pinonic acid	186.28	DD_F0: 1.0 DD_Hstar: 3.14e+5 Henry_CR: 6039.0 Henry_K0: 3.14e+5 Is_Advected: true Is_DryDep: true Is_Gas: true Is_WetDep: true WD_RetFactor: 2.0e-2
PINO3H	C10H18O4/pinonic peracid	186.28	DD_F0: 1.0 DD_Hstar: 1.0e+5 Henry_CR: 6039.0 Henry_K0: 1.0e+5 Is_Advected: true Is_DryDep: true Is_Gas: true Is_WetDep: true WD_RetFactor: 2.0e-2
C96O2H	C9H16O3/peroxide from APIN 2nd gen	186.28	DD_F0: 1.0 DD_Hstar: 3.14e+5 Henry_CR: 6039.0 Henry_K0: 3.14e+5 Is_Advected: true Is_DryDep: true Is_Gas: true Is_WetDep: true WD_RetFactor: 2.0e-2
C96N	C9H15NO4/saturated 2nd gen monoterpene organic nitrate	215.28	DD_F0: 1.0 DD_Hstar: 2.0e+6 Henry_CR: 9200.0 Henry_K0: 1.7e+4 Is_Advected: true Is_DryDep: true Is_Gas: true Is_Photolysis: true Is_WetDep: true WD_RetFactor: 2.0e-2
BPINO	C9H14O/ketone from BPIN	186.28	DD_F0: 1.0 DD_Hstar: 1.0e+3 Henry_CR: 6039.0 Henry_K0: 1.0e+3 Is_Advected: true Is_DryDep: true Is_Gas: true Is_WetDep: true WD_RetFactor: 2.0e-2
BPINN	C10H17NO4/saturated 1st gen BPIN organic nitrate	215.28	DD_F0: 1.0 DD_Hstar: 2.0e+6 Henry_CR: 9200.0 Henry_K0: 1.7e+4 Is_Advected: true Is_DryDep: true Is_Gas: true Is_Photolysis: true Is_WetDep: true WD_RetFactor: 2.0e-2

GEOS-Chem Species	Formula/Name	Molecular weight	Properties[1] Is_Gas: true (for all)
BPINP	C10H18O3/peroxide from BPIN	186.28	DD_F0: 1.0 DD_Hstar: 1.0e+5 Henry_CR: 6039.0 Henry_K0: 1.0e+5 Is_Advected: true Is_DryDep: true Is_Gas: true Is_WetDep: true WD_RetFactor: 2.0e-2
BPINOOH	C9H14O3/2nd gen peroxide from BPIN	186.28	DD_F0: 1.0 DD_Hstar: 1.0e+5 Henry_CR: 6039.0 Henry_K0: 1.0e+5 Is_Advected: true Is_DryDep: true Is_Gas: true Is_WetDep: true WD_RetFactor: 2.0e-2
BIPINON	C9H13NO4/saturated 2nd gen BPIN organic nitrate	215.28	DD_F0: 1.0 DD_Hstar: 2.0e+6 Henry_CR: 9200.0 Henry_K0: 1.7e+4 Is_Advected: true Is_DryDep: true Is_Gas: true Is_Photolysis: true Is_WetDep: true WD_RetFactor: 2.0e-2
LIMAL	C10H16O2/aldehyde from limonene	186.28	DD_F0: 1.0 DD_Hstar: 1.0e+3 Henry_CR: 6039.0 Henry_K0: 1.0e+3 Is_Advected: true Is_DryDep: true Is_Gas: true Is_WetDep: true WD_RetFactor: 2.0e-2
LIMN	C10H17NO4/saturated 1st gen limonene organic nitrate	215.28	DD_F0: 1.0 DD_Hstar: 2.0e+6 Henry_CR: 9200.0 Henry_K0: 1.7e+4 Is_Advected: true Is_DryDep: true Is_Gas: true Is_Photolysis: true Is_WetDep: true WD_RetFactor: 2.0e-2
LIMKET	C10H16O2/ketone from limonene	186.28	DD_F0: 1.0 DD_Hstar: 1.0e+3 Henry_CR: 6039.0 Henry_K0: 1.0e+3 Is_Advected: true Is_DryDep: true Is_Gas: true Is_WetDep: true WD_RetFactor: 2.0e-2
LIMKB	C10H16O3/2nd gen ketone from limonene		DD_F0: 1.0 DD_Hstar: 1.0e+3

GEOS-Chem Species	Formula/Name	Molecular weight	Properties[1] Is_Gas: true (for all)
			Henry_CR: 6039.0 Henry_K0: 1.0e+3 Is_Advected: true Is_DryDep: true Is_Gas: true Is_WetDep: true MW_g: 186.28 WD_RetFactor: 2.0e-2
LIMNB	C10H15NO4/saturated 1st gen LIMO organic nitrate	215.28	DD_F0: 1.0 DD_Hstar: 2.0e+6 Henry_CR: 9200.0 Henry_K0: 1.7e+4 Is_Advected: true Is_DryDep: true Is_Gas: true Is_Photolysis: true Is_WetDep: true WD_RetFactor: 2.0e-2
LIMO2H	C10H18O3/acid from LIMO	186.28	DD_F0: 1.0 DD_Hstar: 3.14e+5 Henry_CR: 6039.0 Henry_K0: 3.14e+5 Is_Advected: true Is_DryDep: true Is_Gas: true Is_WetDep: true WD_RetFactor: 2.0e-2
LIMO3H	C10H18O4/peracid from LIMO	186.28	DD_F0: 1.0 DD_Hstar: 1.0e+5 Henry_CR: 6039.0 Henry_K0: 1.0e+5 Is_Advected: true Is_DryDep: true Is_Gas: true Is_WetDep: true WD_RetFactor: 2.0e-2
MYRCO	C10H18O3/aldehyde or ketone from myrcene	186.28	DD_F0: 1.0 DD_Hstar: 1.0e+3 Henry_CR: 6039.0 Henry_K0: 1.0e+3 Is_Advected: true Is_DryDep: true Is_Gas: true Is_WetDep: true WD_RetFactor: 2.0e-2
PIN	C10H17NO4/saturated 1st gen monoterpene organic nitrate	215.28	DD_F0: 1.0 DD_Hstar: 2.0e+6 Henry_CR: 9200.0 Henry_K0: 1.7e+4 Is_Advected: true Is_DryDep: true Is_Gas: true Is_Photolysis: true Is_WetDep: true WD_RetFactor: 2.0e-2
APINO2	C10H17O3/peroxy radical from APIN	185.27	N/A

GEOS-Chem Species	Formula/Name	Molecular weight	Properties[1] Is_Gas: true (for all)
PINO3	C10H17O3/acylperoxy radical from APIN	185.27	N/A
C96O2	C10H17O3/2nd gen peroxy radical from APIN	185.27	N/A
BPINO2	C10H17O3/peroxy radical from BPIN	185.27	N/A
BPINOO2	C10H17O3/2nd gen peroxy radical from BPIN	185.27	N/A
LIMKO2	C10H17O3/ 2nd gen peroxy radical from	185.27	N/A
LIMO3	C10H17O3/acylperoxy radical from LIMO	185.27	N/A
PINPAN	215.28/α-Pinonyl peroxynitrate	C10H17NO4	DD_F0: 1.0 DD_Hstar: 2.0e+6 Henry_CR: 9200.0 Henry_K0: 1.7e+4 Is_Advected: true Is_DryDep: true Is_Gas: true Is_Photolysis: true Is_WetDep: true WD_RetFactor: 2.0e-2
LIMPAN	C10H17NO4/Limononyl peroxy nitrate	215.28	DD_F0: 1.0 DD_Hstar: 2.0e+6 Henry_CR: 9200.0 Henry_K0: 1.7e+4 Is_Advected: true Is_DryDep: true Is_Gas: true Is_Photolysis: true Is_WetDep: true WD_RetFactor: 2.0e-2

[1]DD_Hstar (M atm-1, T=298.15, pH=7).Henry_K0 = M atm-1, T=298.15, pH=4.5). Henry_K0 = DD_Hstar*(1+H^+/Ka). Where possible, DD_Hstar from http://www.henrys-law.org, and adjusted for pH using K_a from https://acp.copernicus.org/articles/21/13483/2021/.

Table S2. New reactions added to GEOS-Chem.

Reaction	Rate	Reference
New Peroxynitrates (precursor)		
PHAN (glycoaldehyde)		
GLYC + OH = 0.200GLYX + 0.200HO2 + 0.800GCO3	1E-11	MCMV3.3.1
GLYC + NO3 = GCO3 + HNO3	1.44E-12*exp(-1862/T)	MCMV3.3.1
GCO3 + NO2 {+M} = PHAN	Same as PAN	MCMV3.3.1
GCO3 + NO = NO2 + HO2 + CH2O	7.5E-12*exp(290/T)	MCMV3.3.1
GCO3 + HO2 = 0.44HO2 + 0.44CH2O + 0.44OH + 0.560HACTA + 0.15O3 +0.44CO2	5.2E-13*exp(980/T)	MCMV3.3.1

GCO3 + NO3 = CH2O + HO2 + NO2	4E-12	MCMV3.3.1
HACTA + OH = CH2O + HO2	2.73E-12	MCMV3.3.1
PHAN = GCO3 + NO2	Same as PAN	MCMV3.3.1
PHAN + OH = CH2O + CO + NO2	1.12E-12	MCMV3.3.1
AROMPN (aromatics)		
TLFUONE + OH → TLFO2	6.9E-11	MCMV3.3.1
TLFO2 + NO = NO2 + HO2 + AROMCHO	2.70E-12*exp(360/T)	MCMV3.3.1
TLFO2 + HO2 = AROMCHO	2.05E-13*exp(1300/T)	MCMV3.3.1
AROMCHO + OH → AROMCO3	7.09E-11	MCMV3.3.1
AROMCHO + jv^1 → HO2 + CO + MCO3 + CH2O	Same as RCHO	MCMV3.3.1
AROMCO3 + NO2 {+M}→ AROMPN	same as BZPAN	MCMV3.3.1
AROMCO3 + NO → NO2 + RCO3 + 2CO2	7.5E-12*EXP(290/T)	MCMV3.3.1
AROMCO3 + HO2 = 0.15O3 + 0.15RCOOH + 0.44CO2 + 0.44OH + 0.44RCO3+ 0.41RP	5.2e-13*exp(980/T)	MCMV3.3.1 for rate, estimated products
AROMPN = AROMCO3 + NO2	same as BZPAN	
AROMPN + OH = 2CO +NO2 + MCO3 + HCHO	1E-14	MCMV3.3.1 for ACCOMEPAN
MEKPN (MEK)		
MEK + OH = KO2	1.30E-12*exp(-25.0/T)	currently in GEOS-Chem
KO2 + NO = 0.070R4N2 + 0.930 NO2 + 0.62ALD2 + 0.62MCO3 + 0.31MEKCO3 + 0.31CH2O	same rate as GEOS-Chem	branching for A vs. B from Cox et al, 1981
MEKCO3 + NO2 {+M}→MEKPN	Same as PAN	C3PAN1 from MCMV3.3.1
MEKCO3 + NO = NO2 + ETOO + CO2	7.5E-12*exp(290/T)	MCMV3.3.1
MEKCO3 + HO2 = 0.15O3 + 0.15RCOOH + 0.44CO2 + 0.44OH + 0.44ETOO + 0.41RP	5.2e-13*exp(980/T) ;	MCMV3.3.1 for rate, estimated products
MEKPN = MEKCO3 + NO2	Same as PAN	
MEKPN + OH = GLYC + CO + NO2	4.51E-12	MCMV3.3.1
APAN (1,3 butadiene)		
C4H6 + OH = BUTO2	1.48E-11*exp(448/T)	MCMV3.3.1
C4H6 + NO3 = ACR + HCHO + NO2	1.03E-13	
C4H6 + O3= ACR + HCHO	1.34E-14*exp(-2283/T)	
BUTO2 + HO2 = 0.659GLYC + 0.894RCHO	1.82E-13*exp(1300/T)	MCMV3.3.1
BUTO2 + NO = 0.058BUTN + 0.730ACR + 0.603CH2O + 0.513HO2 + 0.942NO2+0.326RCHO	2.70E-12*exp(360/T)	MCMV3.3.1 – all pathways
BUTN + OH = GLYC + NO2 + CH2O + HO2 + CO	3.59E-11	MCMV3.3.1
ACR + OH = 0.680ACO3 + 0.255ACRO2 + 0.065CH2O + 0.065GLYX + 0.425HO2	2.0E-11	MCMV3.3.1
ACRO2 + NO = GLYC + NO2 + HO2 + CO	2.7E-12*exp(360/T)	MCMV3.3.1
ACRO2 + HO2 = GLYC + HO2 + CO	1.51E-13*exp(1300/T)	MCMV3.3.1
ACO3 + HO2 = CO + CH2O + 0.500GLYC + 0.250HO2 + 0.250OH	5.2E-13*exp(980/T)	MCMV3.3.1
ACO3 + NO = HO2 + CO + CH2O + NO2	7.5E-12*exp(290/T)	MCMV3.3.1
ACO3 + NO2 {+M} = APAN	Same as for PAN	MCMV3.3.1
APAN = ACO3 + NO2	Same as for PAN	MCMV3.3.1
APAN + OH = GLYC + CO + NO3	1.47E-11	MCMV3.3.1
ACR + jv^1 = 0.3ACO3 + 0.4C2H4 + 0.7CO + 0.3HCHO+ 0.3HO2	Same as MACR	MCMV3.3.1
APAN + jv^1 = ACO3 + NO2	Same as for PAN	MCMV3.3.1
New Alkylnitrates		

Aromatic Nitrates from TOLU, XYLE, EBZ, TMB		
TOLU + OH = TRO2 + 0.19CSL + 0.19HO2 + 0.81AROMRO2 0.75AROMRO2 + 0.06BALD 0.06ZRO2 + 0.12GLYX + 0.12MGLY + 0.27CO + 0.04MVK + 0.3AROMP5 0.18AROMP5 + 0.12TLFUONE + 0.68AROMP4	1.8E-12*exp(340/T)	Modified from Bates et al., 2021
XYLE + OH = XRO2 + 0.15CSL + 0.15HO2 + 0.85AROMRO20.79AROMRO2+ 0.06BALD 0.06ZRO2+ 0.1GLYX + 0.2MGLY + 0.3CO + 0.04MVK + 0.56AROMP50.39AROMP5 + 0.17TLFUONE + 0.28AROMP4 + 0.45RCOOH :	1.7E-11	Modified from Bates et al., 2021
EBZ + OH = 0.820AROMRO2 0.813AROMRO2 + 0.250CH2O + 0.07BALD 0.07ZRO2 + 0.180CSL + 0.400ALD2 + 0.400AROMP5 + 0.800AROMP4 + 0.1800HO2	7E-12	Modified from Bates et al., 2021
TMB + OH = 0.970AROMRO2 0.930AROMRO2 + 0.120CH2O + 0.05BALD 0.05ZRO2 + 0.030CSL + 0.750AROMP50.600AROMP5 + 0.15TLFUONE + 0.375AROMP4 + 0.250MGLY + 0.100GLYX + 0.500RCOOH + 0.120CO + 0.030HO2	3.92E-11	Modified from Bates et al., 2021
ZRO2 + NO = 0.11RNO3 + 0.89BALD + 0.89NO2 + HO2	2.7E-12*exp(360/T)	MCMV3.3.1 (from TLBIPERO2) making RNO
ZRO2 + HO2 = BALD + OH	1.5E-13*exp(1310/T)	MCMV3.3.1
RNO3 + OH = BALD + NO2 + HO2	7.16E-11	MCMV3.3.1
RNO3 + jv^1 = BALD + NO2 +HO2?	Same as R4N2	
ALK6 mechanism		
ALK6 + OH = R6O2 + H2O	2.00E-11*exp(-359/T)	Lurmann et al., 1986
R6O2 + NO = 0.750RCHO + 0.250R4O2 + 0.250MEK +0.750HO2	GC_RO2NO_B2_aca(2.7E-12,350,7)	Lurmann et al., 1986 Adjust nitrate yield for weighted avg. of observed >C6 ANs
R6O2 + NO = R6N2	GC_RO2NO_A2_aca(2.7E-12,350,7)	Lurmann et al., 1986
ALK6 + NO3 = HNO3 + R6O2	6.0E-17	Lurmann et al., 1986
R6N2 + OH = R6N1 + H2O	4.00E-12	Lurmann et al., 1986
R6N2 + jv^1 = NO2 + 0.348ALD2 + 1.558 RCHO + 0.326 MCO3 + 0.326 RCO3 + 0.326 HO2	Same as R4N2	Lurmann et al., 1986
R6N1 + NO = 2.00NO2 + 1.240RCHO + 0.650ALD2 + 0.980CH2O	4.20E-12*exp(180.0/T)	Lurmann et al., 1986
R6O2 + HO2 = R6P	3.00E-12	Lurmann et al., 1986
OH + R6P = 0.500R6O2 + 0.500RCHO + 0.500OH	1.00E-11	
R6N1 + HO2 = R6N2	GCARR(7.4E-13, 700)	Lurmann et al., 1986
Styrene (C8H8) mechanism		
STYR + NO3 = AROMRO2 + NO2 + CH2O + BALD	1.5E-12	Bates et al., 2021
STYR + OH = 0.7AROMRO2 +0.7 HO2 + CH2O + 0.7BALD+ 0.3ZRO2	5.8E-11	Bates et al., 2021

STYR+ O3 = 0.5SCI + 0.5CH2O + 0.62BALD + 0.1BENZ + 0.28BENZO2 + 0.18CO + 0.18OH + 0.1HO2	1.7E-17	Bates et al., 2021
Other new chemistry		
RCOOH (>C2 organic acids) chemistry		
RCOOH + OH = ETO2 + CO2 + H2O	1.2E-12	Propionic acid from MCMV3.3.1
Monoterpene chemistry		
LIMO + OH = LIMO2	4.20E-11*exp(401.0/T)	Modified from MCMV3.3.1
LIMO + O3 = 0.865OH + 0.15CO + 0.15AROMRO2 + 0.27LIMAL + 0.715LIMO3	2.95E-15*exp(-783.0/T)	Modified from MCMV3.3.1
MTPO + OH = 0.15APINO2 + 0.15BPINO2 + 0.2LIMO2 + 0.5PIO2	1.21E-11*exp(440.0/T)	Modified from MCMV3.3.1
MTPO + O3 = 0.5ACET + 0.8OH + 0.1CH2O + 0.5MEK + 0.15MVK + 0.4MYRCO + 0.5AROMRO2 + 0.05HO2 + 0.3KO2 + 0.3RCHO	2.7E-15*exp(-520.0/T)	Modified from MCMV3.3.1
MTPA + OH = 0.075LIMO2 + 0.67APINO2 + 0.255BPINO2	1.34E-11*exp(410.0/T)	Modified from MCMV3.3.1
MTPA + O3 = 0.65OH + 0.5APINO2 + 0.1BPINOO2 + 0.2BPINO + 0.2PINAL + 0.1CH2OO + 0.1CO + 0.1CH2O	8.22E-16*exp(-640.0/T)	Modified from MCMV3.3.1
APINO2 + HO2 = APINP	2.66E-13*exp(1300.0/T)	Modified from MCMV3.3.1
APINO2 + NO = 0.25APINN + 0.75PINAL + 0.75NO2 + 0.75HO2	2.7E-12*exp(360.0/T)	Modified from MCMV3.3.1
APINO2 + NO3 = PINAL + NO2 + HO2	2.3E-12	Modified from MCMV3.3.1
APINP + OH = 0.4PINO3 + 0.6APINO2	1.83E-11	Modified from MCMV3.3.1
APINN + OH = 0.5PINAL + 0.5NO2 + 0.5HO2 + 0.5C96N + 0.5CH2O + 0.5AROMRO2	5.50E-12	Modified from MCMV3.3.1
PINAL + NO3 = HNO3 + PINO3	2.0E-14	Modified from MCMV3.3.1
PINAL + OH = PINO3	5.2E-12*exp(600.0/T)	Modified from MCMV3.3.1
PINO3 + HO2 = 0.44OH + 0.15O3 + 0.44C96O2 + 0.41PINO3H + 0.15PINONIC	2.66E-13*exp(1300.0/T)	Modified from MCMV3.3.1
PINO3 + NO3 = NO2 + CO2 + C96O2	2.3E-12	Modified from MCMV3.3.1
PINO3H + OH = PINO3	9.73E-12	Modified from MCMV3.3.1
PINONIC + OH = CO2 + C96O2	6.65E-12	Modified from MCMV3.3.1
C96O2 + HO2 = C96O2H	2.66E-13*exp(1300.0/T)	Modified from MCMV3.3.1
C96O2 + NO = 0.16C96N + 0.84NO2 + 0.84AROMRO2 + 0.84ACET + 0.84CH2O + 0.84RCO3 + 0.42MEK	2.7E-12*exp(360.0/T)	Modified from MCMV3.3.1
C96O2 + NO3 = NO2 + AROMRO2 + ACET + CH2O + RCO3 + 0.5MEK	2.3E-12	Modified from MCMV3.3.1
C96O2 + MO2 = HO2 + 0.75CH2O + 0.25MOH + 0.25C96O2H + 0.75AROMRO2 + 0.75ACET + 0.75CH2O + 0.75RCO3 + 0.375MEK	3.75E-13*exp(500.0/T)	Modified from MCMV3.3.1
C96O2H + OH = 0.5C96O2 + 0.5AROMRO2 + 0.5ACET + 0.5CH2O + 0.5RCO3 + 0.25MEK	2.6E-11	Modified from MCMV3.3.1
C96N + OH = 0.5NO2 + 0.5MONITS + 0.55AROMRO2 + 0.4ACET + 0.4CH2O + 0.4RCO3 + 0.3MEK	2.88E-12	Modified from MCMV3.3.1

BPINO2 + HO2 = BPINP	2.66E-13*exp(1300.0/T)	Modified from MCMV3.3.1
BPINO2 + NO = 0.25BPINN + 0.75CH2O + 0.75NO2 + 0.75HO2 + 0.75BPINO	2.7E-12*exp(360.0/T)	Modified from MCMV3.3.1
BPINO2 + NO3 = CH2O + NO2 + HO2 + BPINO	2.3E-12	Modified from MCMV3.3.1
BPINN + OH = 0.5BPINON + 0.5AROMRO2 + CH2O + 0.5NO2 + 0.5HO2 + 0.5BPINO	4.7E-12	Modified from MCMV3.3.1
BPINP + OH = BPINO2	1.33E-11	Modified from MCMV3.3.1
BPINO + OH = BPINOO2	1.55E-11	Modified from MCMV3.3.1
BPINOO2 + HO2 = BPINOOH	2.66E-13*exp(1300.0/T)	Modified from MCMV3.3.1
BPINOO2 + NO = BPINON	4.32E-13*exp(360.0/T)	Modified from MCMV3.3.1
BPINOO2 + NO = NO2 + HO2 + 0.27LIMO3 + 0.6ACET + 0.6RCHO + 0.6R4O2	2.27E-12*exp(360.0/T)	Modified from MCMV3.3.1
BPINOO2 + MO2 = HO2 + 0.23LIMO3 + 0.4ACET + 0.4RCHO + 0.4R4O2 + 0.75CH2O + 0.25MOH + 0.25BPINOOH	3.75E-13*exp(500.0/T)	Modified from MCMV3.3.1
BPINOO2 + NO3 = NO2 + HO2 + 0.27LIMO3 + 0.6ACET + 0.6RCHO + 0.6R4O2	2.3E-12	Modified from MCMV3.3.1
BPINOOH + OH = BPINOO2	8.59E-11	Modified from MCMV3.3.1
BPINON + OH = 0.5MONITS + 0.5NO2 + 0.085LIMO3 + 0.3ACET + 0.3RCHO + 0.3R4O2	3.24E-12	Modified from MCMV3.3.1
LIMO2 + HO2 = 0.37LIMKET + 0.63LIMAL	2.66E-13*exp(1300.0/T)	Modified from MCMV3.3.1
LIMO2 + NO = 0.25LIMN + 0.75NO2 + 0.75HO2 + 0.28LIMKET + 0.47LIMAL	2.7E-12*exp(360.0/T)	Modified from MCMV3.3.1
LIMO2 + NO3 = NO2 + HO2 + 0.37LIMKET + 0.63LIMAL	2.3E-12	Modified from MCMV3.3.1
LIMAL + OH = LIMO3	1.1E-10	Modified from MCMV3.3.1
LIMAL + O3 = 0.3LIMKB + 0.33CH2OO + 0.67CH2O + 0.6LIMO3 + 0.6OH	8.3E-18	Modified from MCMV3.3.1
LIMAL + NO3 = AROMRO2 + LIMNB	2.6E-13	Modified from MCMV3.3.1
LIMKET + OH = LIMKO2	9.97E-11	Modified from MCMV3.3.1
LIMKET + O3 = 0.27LIMKO2 + 0.865OH + 0.73LIMO3	1.5E-16	Modified from MCMV3.3.1
LIMKET + NO3 = LIMNB + AROMRO2	9.4E-12	Modified from MCMV3.3.1
LIMN + OH = 0.5LIMNB + 0.32LIMO3 + 0.18LIMKO2 + 0.5NO2	1.1E-10	Modified from MCMV3.3.1
LIMN + O3 = CH2O + 0.5NO2 + 0.4LIMO3 + 0.5LIMNB	8.3E-18	Modified from MCMV3.3.1
LIMN + NO3 = NO2 + LIMNB + AROMRO2	2.6E-13	Modified from MCMV3.3.1
LIMKO2 + NO = 0.16LIMNB + 0.84NO2 + 0.84LIMKB + 0.84HO2	2.7E-12*exp(360.0/T)	Modified from MCMV3.3.1
LIMKO2 + HO2 = LIMO3H	2.66E-13*exp(1300.0/T)	Modified from MCMV3.3.1
LIMKO2 + NO3 = NO2 + LIMKB + HO2	2.3E-12	Modified from MCMV3.3.1
LIMKO2 + MO2 = 0.75LIMKB + 0.25LIMO3H + 0.75CH2O + 0.25MOH + HO2	3.75E-13*exp(500.0/T)	Modified from MCMV3.3.1
LIMKB + OH = LIMO3	3.6E-11	Modified from MCMV3.3.1
LIMKB + NO3 = NO2 + LIMO3	1.22E-11*exp(-1862.0/T)	Modified from MCMV3.3.1
LIMNB + OH = 0.5MONITS + 0.5NO2 + 0.5LIMO3	6.3E-12	Modified from MCMV3.3.1

LIMO3 + HO2 = 0.44OH + 0.15O3 + 0.44CO2 + 0.44MCO3 + 0.44RCHO + 0.176CH2O + 0.352R4O2 + 0.41LIMO3H + 0.15LIMO2H	2.66E-13*exp(1300.0/T)	Modified from MCMV3.3.1
LIMO3 + NO = NO2 + CO2 + MCO3 + RCHO + 0.4CH2O + 0.8R4O2	2.7E-12*exp(360.0/T)	Modified from MCMV3.3.1
LIMO3 + NO3 = NO2 + CO2 + MCO3 + RCHO + 0.4CH2O + 0.8R4O2	2.3E-12	Modified from MCMV3.3.1
LIMO3H + OH = LIMO3	9.73E-12	Modified from MCMV3.3.1
LIMO2H + OH = CO2 + MCO3 + RCHO + 0.4CH2O + 0.8R4O2	6.65E-12	Modified from MCMV3.3.1
PIO2 + HO2 = PIP	2.66E-13*exp(1300.0/T)	Modified from MCMV3.3.1
PIO2 + NO = PIN	6.75E-13*exp(360.0/T)	Modified from MCMV3.3.1
PIO2 + NO = NO2 + HO2 + 0.45MVK + 0.45ACET + 0.1CH2O + 0.675MYRCO	2.03E-12*exp(360.0/T)	Modified from MCMV3.3.1
PIO2 + NO3 = NO2 + HO2 + 0.45MVK + 0.45ACET + 0.1CH2O + 0.675MYRCO	2.3E-12	Modified from MCMV3.3.1
PIP + OH = 0.3OH + 0.7AROMRO2 + 0.3MVK + 0.3ACET + 0.1CH2O + 0.78MYRCO	6.05E-12*exp(440.0/T)	Modified from MCMV3.3.1
PIP + O3 = 0.3OH + 0.7AROMRO2 + 0.3MVK + 0.3ACET + 0.1CH2O + 0.78MYRCO	1.35E-15*exp(-520.0/T)	Modified from MCMV3.3.1
PIP + NO3 = 0.5OLNN + 0.5NO2 + 0.15OH + 0.35AROMRO2 + 0.15MVK + 0.15ACET + 0.05CH2O + 0.39MYRCO	1.06E-12*exp(490.0/T)	Modified from MCMV3.3.1
PIN + OH = 0.7AROMRO2 + 0.7MONITU + 0.3NO2 + 0.3MYRCO	6.05E-12*exp(440.0/T)	Modified from MCMV3.3.1
PIN + O3 = 0.7AROMRO2 + 0.7MONITU + 0.3NO2 + 0.3MYRCO	1.35E-15*exp(-520.0/T)	Modified from MCMV3.3.1
PIN + NO3 = 0.5OLNN + 1.15NO2 + 0.35AROMRO2 + 0.35MONITU + 0.15MYRCO	1.06E-12*exp(490.0/T)	Modified from MCMV3.3.1
MYRCO + OH = HO2 + AROMRO2 + 1.5CH2O + MEK + 0.5ACET + 0.5MVK + 0.5GLYC	6.05E-12*exp(440.0/T)	Modified from MCMV3.3.1
MYRCO + O3 = OH + AROMRO2 + 1.5CH2O + MEK + 0.5ACET + 0.5MVK + 0.5GLYC	1.35E-15*exp(-520.0/T)	Modified from MCMV3.3.1
MYRCO + NO3 = 0.5OLNN + 0.5NO2 + 0.5HO2 + 0.5AROMRO2 + 0.75CH2O + 0.5MEK + 0.25ACET + 0.25MVK + 0.25GLYC	1.06E-12*exp(490.0/T)	Modified from MCMV3.3.1
APINO2 + MO2 = PINAL + 1.75HO2 + 0.25MOH + 0.75CH2O 3.75E-13, 500.0 APINO2 + MCO3 = PINAL + HO2 + 0.1ACTA + 0.9CO2 + 0.9MO2	1.87E-12*exp(500.0/T)	Modified from MCMV3.3.1
BPINO2 + MO2 = 1.75HO2 + 0.25MOH + 1.75CH2O + BPINO 3.75E-13, 500.0 BPINO2 + MCO3 = BPINO + CH2O + HO2 + 0.1ACTA + 0.9CO2 + 0.9MO2	1.87E-12*exp(500.0/T)	Modified from MCMV3.3.1
LIMO2 + MO2 = 0.37LIMKET + 0.63LIMAL + 1.75HO2 + 0.25MOH + 0.75CH2O	3.75E-13*exp(500.0/T)	Modified from MCMV3.3.1

LIMO2 + MCO3 = 0.37LIMKET + 0.63LIMAL + HO2 + 0.1ACTA + 0.9CO2 + 0.9MO2	1.87E-12*exp(500.0/T)	Modified from MCMV3.3.1
PIO2 + MO2 = 0.45MVK + 0.45ACET + 0.675MYRCO + 1.75HO2 + 0.25MOH + 0.85CH2O	3.75E-13*exp(500.0/T)	Modified from MCMV3.3.1
PIO2 + MCO3 = 0.45MVK + 0.45ACET + 0.1CH2O + 0.675MYRCO + HO2 + 0.1ACTA + 0.9CO2 + 0.9MO2	1.87E-12*exp(500.0/T)	Modified from MCMV3.3.1
PINO3 + MO2 = CH2O + 0.75HO2 + 0.25PINONIC + 0.75C96O2+ 0.75CO2	1.87E-12*exp(500.0/T)	Modified from MCMV3.3.1
PINO3 + MCO3 = C96O2 + 2CO2 + MO2	3.75E-14*exp(500.0/T)	Modified from MCMV3.3.1
LIMO3 + MO2 = 0.75HO2 + CH2O + 0.75CO2 + 0.75MCO3 + 0.75RCHO + 0.3CH2O + 0.6R4O2 + 0.25LIMO2H	1.87E-12*exp(500.0/T)	Modified from MCMV3.3.1
LIMO3 + MCO3 = CO2 + MO2 + MCO3 + RCHO + 0.4CH2O + 0.8R4O2	3.75E-14*exp(500.0/T)	Modified from MCMV3.3.1
APINP + hv = PINAL + OH + HO2	use the same as CH3OOH	Modified from MCMV3.3.1
PINAL + hv = CO + HO2 + C96O2	use the same as ActAld	Modified from MCMV3.3.1
PINO3H + hv = OH + CO2 + C96O2	use the same as CH3OOH	Modified from MCMV3.3.1
PINONIC + hv = OH + CO2 + C96O2	use the same as MGLYX	Modified from MCMV3.3.1
C96O2H + hv = OH + AROMRO2 + ACET + CH2O + RCO3 + 0.5MEK	use the same as CH3OOH	Modified from MCMV3.3.1
BPINP + hv = OH + CH2O + HO2 + BPINO	use the same as CH3OOH	Modified from MCMV3.3.1
BPINOOH + hv = OH + HO2 + 0.27LIMO3 + 0.6ACET + 0.6RCHO + 0.6R4O2 :	use the same as CH3OOH	Modified from MCMV3.3.1
LIMO3H + hv = OH + CO2 + MCO3 + RCHO + 0.4CH2O + 0.8R4O2	use the same as CH3OOH	Modified from MCMV3.3.1
LIMO2H + hv = OH + CO2 + MCO3 + RCHO + 0.4CH2O + 0.8R4O2	use the same as MGLYX	Modified from MCMV3.3.1
PIP + hv = OH + HO2 + 0.450MVK + 0.45ACET + 0.100CH2O + 0.675MYRCO	use the same as H2O2	Modified from MCMV3.3.1
LIMAL + hv = CO + HO2 + 0.900LIMO3	use the same as ActAld	Modified from MCMV3.3.1
Monoterpene PNs		
LIMO3 + NO2 = LIMPAN	Same as PAN	
LIMPAN = LIMO3 + NO2	Same as PAN	
PINO3 + NO2 = PINPAN	Same as PAN	
PINPAN = PINO3 + NO2	Same as PAN	

[1]*jv* is model j-value (photolysis frequency, s^{-1}).

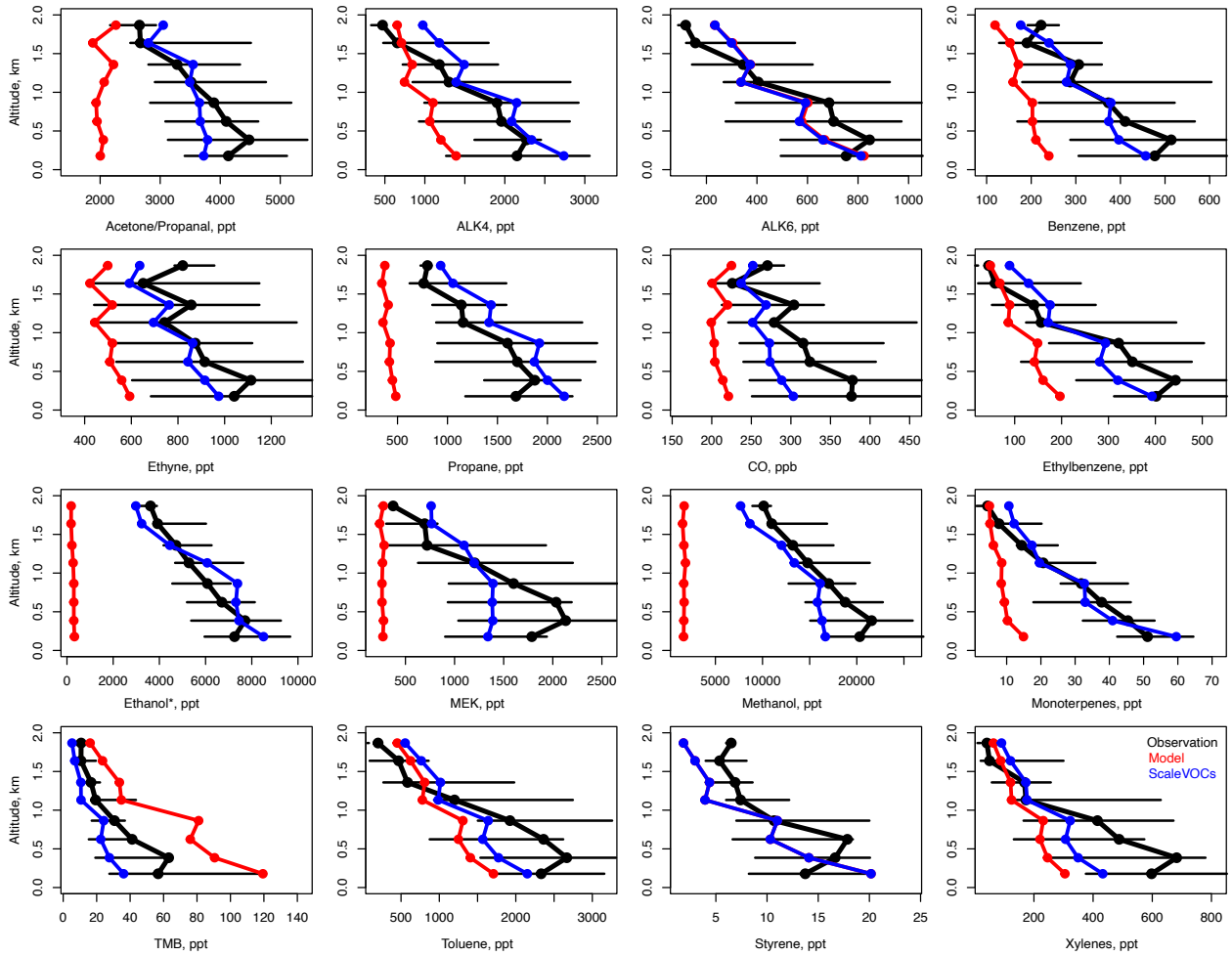

Figure S1 – Mean vertical profiles in the SMA (domain of Fig. 1) of the base model (red) and the model with scaled VOCs (blue) against observations (black) for all species individually increased to better match observations.

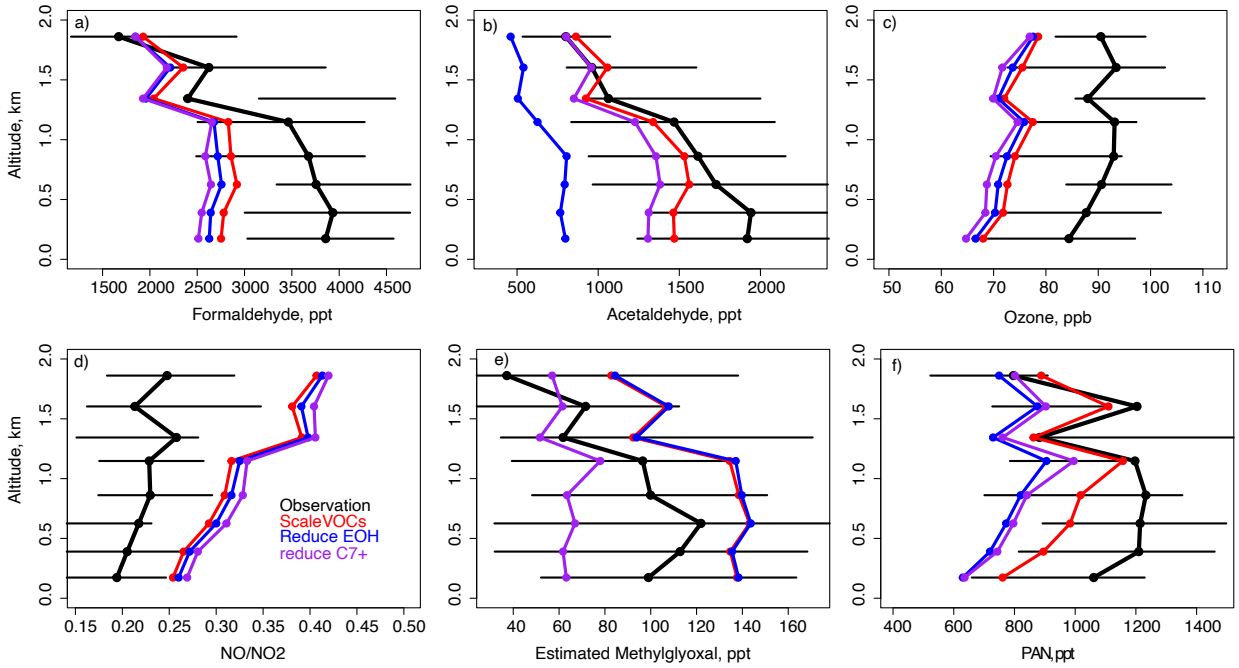

Figure S2 – Mean vertical profiles in the SMA for a) formaldehyde, b) acetaldehyde, c) ozone, d) NO/NO_2, e) estimated methylglyoxal, and f) PAN. Methylglyoxal is estimated as 67% of glyoxal observations based on the similar yield from toluene in GEOS-Chem but the 67% shorter lifetime. Model sensitivities are described in Sections 3 and 4 where "Reduce EOH" and "Reduce C7+" refer to the removal of scaled ethanol and C7+ aromatic emissions over South Korea, respectively.

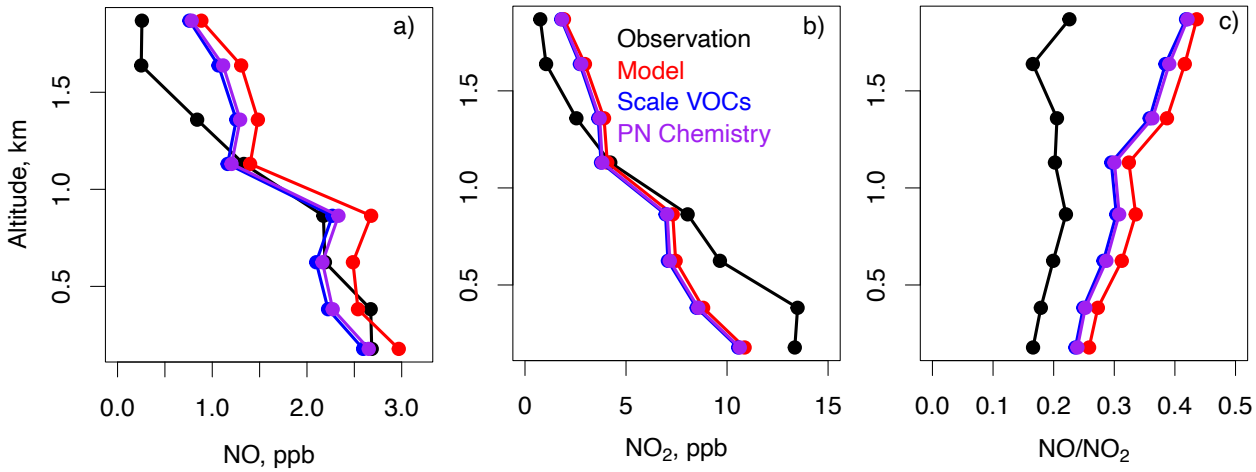

Figure S3 – Mean vertical profiles in the SMA for a) NO, b) NO_2, and c) NO/NO_2. Model sensitivities are described in Section 4.

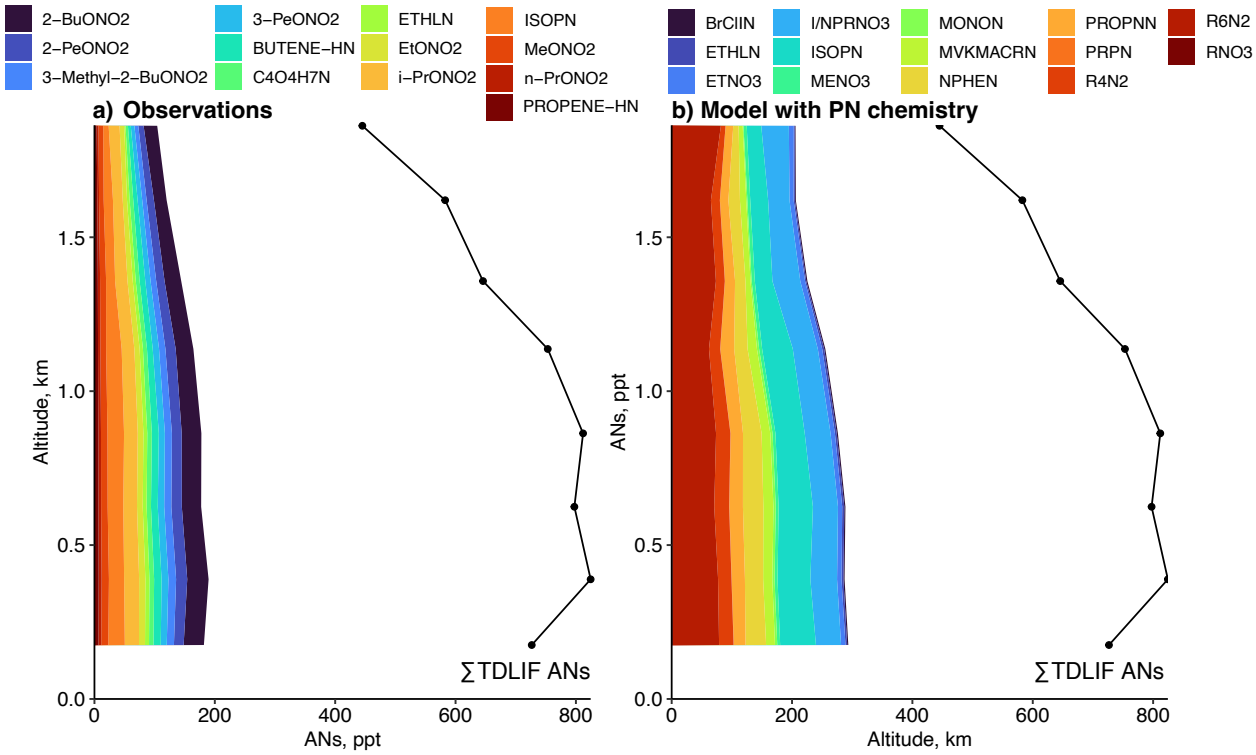

Figure S4 – Speciated mean vertical profiles of modeled ANs for the domain of Fig. 1 compared against observed ANs (solid black line) for a) observations and b) model with added PN chemistry.

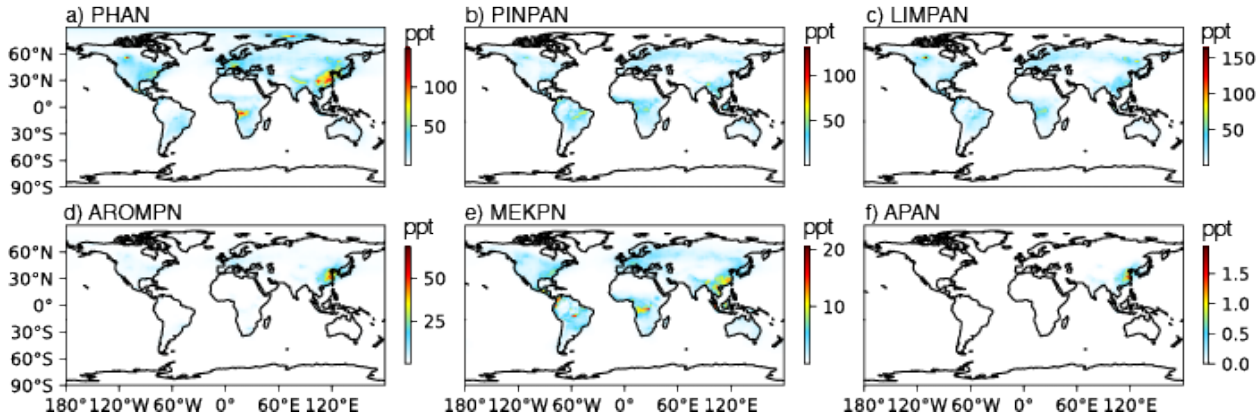

Figure S4 – Global average surface concentrations at 2×2.5° from 5/1/16 to 6/10/16 for a) PHAN, b) PINPAN, c) LIMPAN, d) AROMPN, e) MEKPN, and f) APAN.

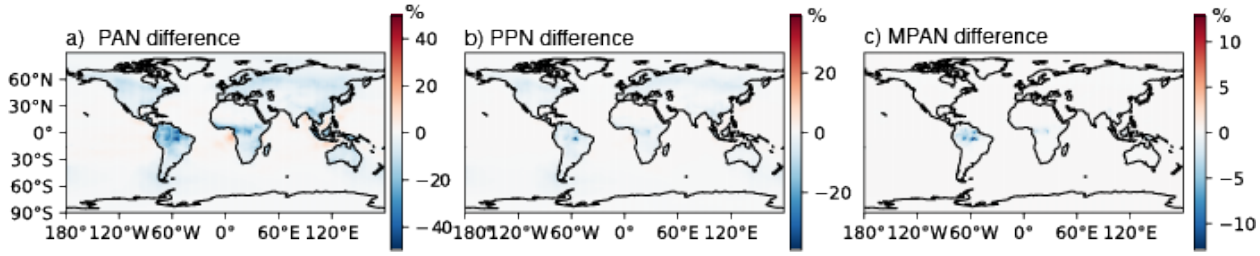

Figure S5 – Global average difference at 2×2.5° from 5/1/16 to 6/10/16 between the model with scaled VOCs and new PN chemistry and the base model for a) PAN, b) PPN, and c) MPAN.

Section S1. Exploring model biases with F0AM

We perform a box-modeling experiment to see whether the good agreement with observed HCHO (found by Nault et al. (2024) in their work simulating airborne observations with F0AM) would be degraded in a similar manner as GEOS-Chem which underestimated HCHO by approximately 50% in the base model (Section 4) when applying the model bias to the F0AM setup described in Nault et al. (2024). We first reduce the concentrations of the VOCs and CO input into F0AM by the model bias given in Table S3 for the lowest model layer (~0.2 km). As shown in Fig. S6, reduced VOCs and CO result in F0AM underestimating HCHO by 24%. Mean model OH increased by 11% from 4.6E6 to 5.1E6 molec cm^{-3}, which we attribute to the reduced sink from CO and VOCs. Average F0AM-calculated OH reactivity went down 2 s^{-1} from 9 s^{-1} to 7 s^{-1}, and pO_3 went down 2 ppb hr^{-1}, from an average of 5 ppb hr^{-1} to 3 ppb hr^{-1}. However, as shown in Fig. S6, NO_2 was in good agreement with observations, as ozone is the main driver of conversion of NO to NO_2. Constraining ozone in our F0AM model to observations was inconsistent in our attempts to understand the impact of the VOC and CO bias on model chemistry, as this bias reduced pO_3 by 20%. When we also considered the GEOS-Chem ozone bias of -25% as part of our model inputs, we found that the good agreement with observed NO_2 was degraded to a bias of -22% and the formaldehyde bias partially improved from -24% to -19% (Fig. S7). Mean model OH increased by only 5% as the reduced sink from VOCs was balanced by reduced loss of OH by NO_2 + OH to produce HNO_3. Therefore, we summarize the impacts of insufficient VOCs and CO in GEOS-Chem as 1) missing production of ozone from VOCs and CO through HO_2/RO_2 + NO, 2) underestimated loss of OH by reaction with VOCs and CO, 3) underestimated conversion of NO to NO_2 by ozone which results in underestimated loss of OH by reaction with NO_2.

In GEOS-Chem, when we scaled up the species in Table S3 (except for ozone), we reduced the model HCHO bias from -47% to -32% (1 ppb). This is in contrast to F0AM where the constrained VOCs, CO, and methane were able to reproduce HCHO observations (Nault et al., 2024). We explain the remaining low bias in GEOS-Chem by the fact that 1) the model underestimates reactivity of intermediate species which provide additional HCHO production, and conversion of NO to NO_2 by HO_2 and RO_2; 2) we are not able to achieve perfect agreement with VOC observations, which is possible with F0AM; and 3) model ozone remains underestimated leading to insufficient NO_2 and thus insufficient loss of OH resulting in a HCHO lifetime against OH that is too short. This NO_2 underestimate is made worse by insufficient model resolution in addition to underestimated VOCs. As discussed in Section 4, underestimated model ozone could have additional factors such as insufficient production upwind where constraints on model VOCs and CO are minimal, or production from mechanisms such as photolysis of particulate nitrate.

Table S3. Scale factors for modeled VOCs

Species	Base Model Bias[1]	Scale VOCs Bias[1]
ACET	-44%	-4%
ALK4	-40%	+15%
BENZ	-38%	+8%
C2H2	-40%	-4%
C3H8	-71%	+16%
CO	-28%	-7%
EBZ	-50%	-2%
EOH	-95%	+13
MEK	-78%	-4%
MOH	-88%	-14%
MTPA	-57%	+5
TMB	+93	-43%
TOLU	-30%	-12%
STYR	-84%	-29%
XYLE	-39%	-14%
O3	-23%	-16%

[1]Average below 2km from Figure S1.

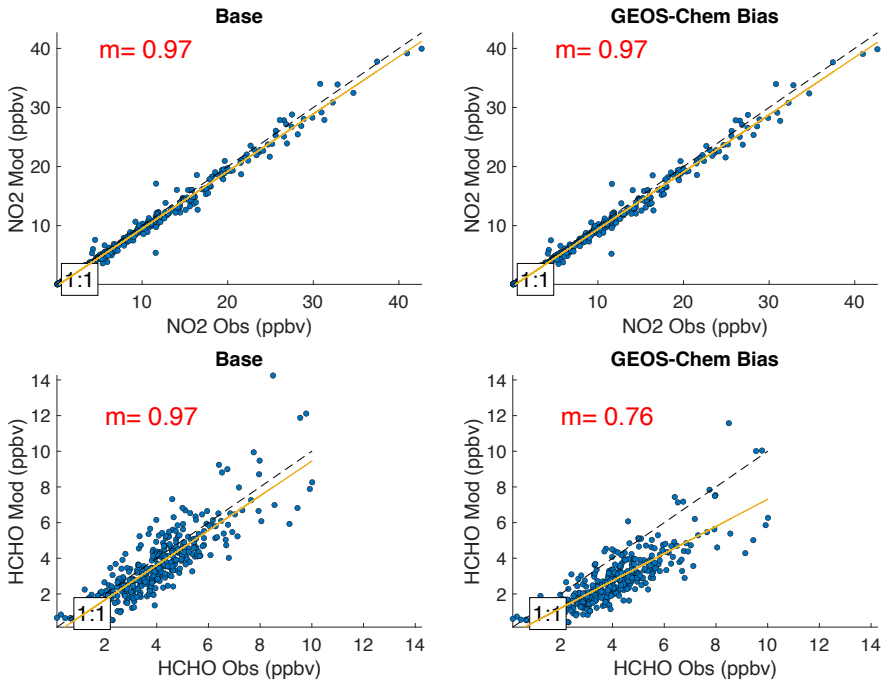

Figure S6 – F0AM results from the base model described in Nault et al. (2024) and after applying the model bias in Table S3 ("GEOS-Chem Bias"). The slope of the regression line is given inset and the dashed line shows the 1-1 line.

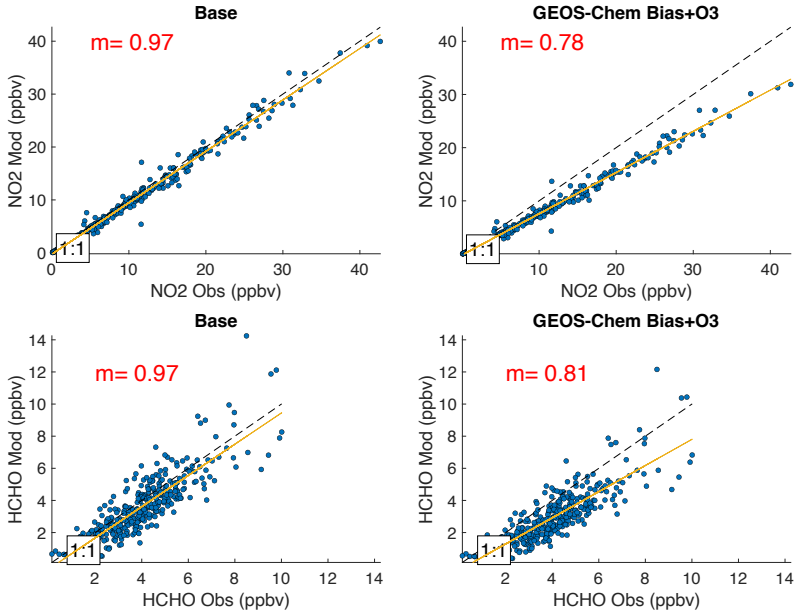

Figure S7 – Same as Fig. S6 but now showing the F0AM simulation including the model ozone bias ("GEOS-Chem Bias+O3").