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Decadal changes in summertime reactive oxidized nitrogen and surface ozone over the Southeast United States

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Supplementary Material

Table S1. Isoprene oxidation chemistry in AM3. T represents temperature (K).

Reactions	Reaction Rate	Note
Isoprene Daytime Chemistry		
ISOP + OH → ISOPO2	3.10×10^{-11}exp(350./T)	
ISOPO2→ 2.0*HO2 + CH2O + .333*MGLY + .5*GLYALD + 0.25*GLYX	4.07×10^{8}exp(-7694./T)	
ISOPO2 + NO → .90*NO2 + .90*HO2 + .9*CH2O + .55*MVK + 0.35*MACR + 0.1*ISOPNB	2.70×10^{-12}exp(350./T)	
ISOPO2 + HO2 → .937*ISOPOOH + .063*OH + .025*MACR + .038*MVK + .063*HO2 + .063*CH2O	2.06×10^{-13}exp(1300./T)	
ISOPO2 + ISOPO2 → 1.28*HO2 + .92*CH2O + .56*MVK + .36*MACR + .48*ROH + .5*HC5	1.54×10^{-13}	
ISOPO2 + CH3O2 → 1.1*HO2 + 1.22*CH2O + .28*MVK + .18*MACR + .3*HC5 + .24*CH3OH + .24*ROH	8.37×10^{-14}	
ISOPO2 + CH3CO3 → .887*HO2 + .747*CH2O + .453*MVK + .294*MACR + .14*HC5 + .113*DIBOO + {CO2} + CH3O2	1.68×10^{-12}exp(500./T)	
ISOPO2 + CH3CO3 → MEK + CH3COOH	1.87×10^{-13}exp(500./T)	
ISOPNB + OH → ISOPNBO2	2.40×10^{-12}exp(745./T)	
ISOPNBO2 + NO → .09*GLYALD + .09*HYAC + .69*CH2O + 0.88*NO2 + .44*MACRN + .69*HO2 + .26*MVKN + 0.21*DHDN	2.40×10^{-12}exp(360./T)	
ISOPNBO2 + HO2 → .06*GLYALD + .06*HYAC + .44*CH2O + .28*MACRN + .16*MVKN + .06*NO2 + .44*HO2 + .5*OH + .5*ISNP + 0.5*ROOH	8.70×10^{-14}exp(1650./T)	
ISOPNB + O3 → 0.05*HO2 + 0.05*OH + 0.11*MVKN + 0.32*MACRN + 0.16*HCOOH + 0.62*CH2O + 0.36*{CO2} + 0.21*CO + 0.06*C4NACID + 0.36*HPROPN + 0.1*MVKNOOH	3.70×10^{-19}	
ISNP + OH → .612*OH + .612*R4N1 + .386*ISOPNBO2	4.75×10^{-12}exp(200./T)	
ISOPOOH + OH → .387*ISOPO2 + .613*OH + .613*HC5	4.75×10^{-12}exp(200./T)	
ISOPOOH + OH → OH + IEPOX	1.90×10^{-11}exp(390./T)	
IEPOX + OH → IEPOXOO	5.78×10^{-11}exp(-400./T)	
IEPOXOO + HO2 → .725*HYAC + .275*GLYALD + .275*GLYX + .375*CH2O + .251*CO + .275*MGLY + 1.125*OH + .825*HO2	2.06×10^{-13}exp(1300./T)	
IEPOXOO + NO → .725*HYAC + .275*GLYALD + .275*GLYX + .375*CH2O + .074*HCOOH	2.70×10^{-12}exp(350./T)	

+ .251*CO + NO2 + .275*MGLY + .125*OH+ .825*HO2		
HC5 + OH → HC5OO	3.35×10^{-11}exp(380./T)	
HC5 + O3 → .6*MGLY + .1*OH + .12*CH2O + .28*GLYALD + .3*O3 + .4*CO + .2*H2 + .2*HYAC + .2*HCOOH	6.16×10^{-15}exp(-1814./T)	
HC5OO + NO → NO2 + .216*GLYX + .234*MGLY + .234*GLYALD + .09*RCHO + HO2 + .09*CO + .216*HYAC + .29*DHMOB + .17*MOBA	2.35×10^{-12}exp(350./T)	
HC5OO + NO → HNO3	3.50×10^{-13}exp(350./T)	
HC5OO + HO2 → .1*IAP + .9*OH + .9*MGLY + .9*GLYALD + .9*HO2	2.06×10^{-13}exp(1300./T)	
HC5OO + CH3O2 → .5*HO2 + .33*CO + .09*H2 + .18*HYAC + .25*C2H5OH + .5*HO2 + .13*GLYALD + .29*MGLY + .25*MEK+ .95*CH2O + .25*CH3OH	8.37×10^{-14}	
HC5OO + CH3CO3 → .216*GLYX + .234*MGLY + .234*GLYALD + .216*HYAC + .29*DHMOB + .17*MOBA + .09*RCHO + HO2 + .09*CO + CH3O2	1.68×10^{-12}exp(500./T)	
HC5OO + CH3CO3 → MEK + CH3COOH	1.87×10^{-13}exp(500./T)	
IAP + OH → .654*OH + .654*DHMOB + .346*HC5OO	5.31×10^{-12}exp(200./T)	
MOBA + OH → MOBAOO	2.79×10^{-11}exp(380./T)	
MOBA + O3 → OH + HO2 + MEK	2.00×10^{-17}	
MOBAOO + NO → RCHO + HO2 + NO2	2.35×10^{-12}exp(350./T)	
MOBAOO + NO → HNO3	3.50×10^{-13}exp(350./T)	
MOBAOO + HO2 → .5*OH + .5*HO2 + .5*RCHO + .5*C3H7OOH	2.06×10^{-13}exp(1300./T)	
MVK + OH → MVKO2	2.60×10^{-12}exp(610./T)	
MVK + O3 → .202*OH + .202*HO2 + .352*HCOOH + .535*CO + .05*CH3CHO + .95*MGLY + .05*CH2O	8.50×10^{-16}exp(-1520./T)	
MVKO2 + NO → .965*NO2 + .249*HO2 + .249*CH2O + .716*CH3CO3 + .716*GLYALD + .249*MGLY + .035*MVKN	2.70×10^{-12}exp(350./T)	
MVKO2 + HO2 → .38*MVKOOH + .62*OH + .37*GLYALD + .37*CH3CO3+ .13*MEK + .25*HO2 + .12*CH2O + .12*MGLY	1.82×10^{-13}exp(1300./T)	
MVKO2 + CH3O2 → .14*HO2 + .14*CH2O + .36*CH3CO3 + .36*GLYALD + .25*ROH + .5*HO2 + .14*MGLY + .25*MEK + .75*CH2O + .25*CH3OH	8.37×10^{-14}	
MVKO2 + CH3CO3 → .4*HO2 + .4*CH2O + .6*CH3CO3 + .6*GLYALD + .4*MGLY + CH3O2	1.68×10^{-12}exp(500./T)	
MVKO2 + CH3CO3 → MEK + CH3COOH	1.87×10^{-13}exp(500./T)	

MVKOOH + OH → .791*OH + .791*MEK + .209*MVKO2	8.78×10^{-12}exp(200./T)	
MVKN + OH → .65*HCOOH + NO3 + .65*MGLY + .35*CH2O	1.60×10^{-12}	
MACR + OH → .45*MAO3 + .55*MACRO2	8.00×10^{-12}exp(380./T)	
MACR + O3 → .261*OH + .202*HO2 + .326*HCOOH + .569*CO + .88*MGLY + 0.12*CH2O	1.40×10^{-15}exp(-2100./T)	
MACR + NO3 → MAO3 + HNO3	3.40×10^{-15}	
MACRO2 + HO2 → 0.42*MACROOH + 0.58*OH + 0.58*HYAC + 0.58*CO+ 0.58*HO2	1.82×10^{-13}exp(1300./T)	
MACRO2 + NO3 → NO2 + HYAC + CO + HO2	2.30×10^{-12}	
MACRO2 + NO → .97*NO2 + 0.97*HO2 + 0.97*CO + 0.97*HYAC + .03*MACRN	2.70×10^{-12}exp(360./T)	
MACRO2 → CO + HYAC + OH	0.5	
MACRO2 + CH3O2 → .595*HYAC + .255*MGLY + .595*CO + 1.255*CH2O + 1.7*HO2 + .15*ROH	8.37×10^{-14}	
MACRO2 + CH3CO3 → .85*HO2 + .143*MGLY + .857*HYAC + .857*CO + .143*CH2O + CH3O2	1.68×10^{-12}exp(500./T)	
MACRO2 + CH3CO3 → MEK + CH3COOH	1.87×10^{-13}exp(500./T)	
MACROOH + OH → MACRO2	1.84×10^{-12}exp(200./T)	
MACROOH + OH → HYAC + OH	4.40×10^{-12}exp(380./T)	
MACRN + OH → MACRNO2	3.20×10^{-12}	
MACRNO2 + NO → .08*CH3COOH + .08*CH2O + .07*MGLY + .85*HYAC+ 1.85*NO2 + 0.15*NO3 + .07*HCOOH	2.70×10^{-12}exp(350./T)	
MACRNO2 + HO2 → .08*CH3COOH + .08*CH2O + .15*NO3 + .07*HCOOH + .07*MGLY + .85*HYAC + .85*NO2 + OH	1.82×10^{-13}exp(1300./T)	
MAO3 + NO → NO2 + CH2O + .65*CH3O2 + 0.65*CO + .35*CH3CO3	8.70×10^{-12}exp(290./T)	
MAO3 + HO2 → .44*OH + .15*O3 + .44*CH2O + .29*CH3O2 + .41*MAOP + 0.15*CH3CO3 + 0.15*MACO2H + 0.29*CO	5.20×10^{-13}exp(980./T)	
MAO3 + NO3 → NO2 + 0.35*CH3CO3 + CH2O + 0.65*CH3O2 + 0.65*CO	4.00×10^{-12}	
MAO3 + CH3O2 → CH2O + HO2 + CH2O + CH3CO3	1.68×10^{-12}exp(500./T)	
MAO3 + CH3O2 → RCOOH + CH2O	1.87×10^{-13}exp(500./T)	
MAO3 + CH3CO3 → CH3O2 + CH2O + CH3CO3	2.50×10^{-12}exp(500./T)	
MAO3 + NO2 + M → MPAN + M	ko=9.00E-28*$(300/T)^{8.90}$; ki=7.70E-12*$(300/T)^{0.20}$; f=0.60; usr53	
MPAN → MAO3 + NO2	1.111×10^{28}exp(-14000./T)*usr53	
MPAN + OH → HYAC + CO + NO2	2.90×10^{-11}	

MPAN + O3 → NO2 + .6*CH2O + HO2	8.20×10^{-18}	
MACO2H + OH → 0.35*CH3CO3 + 0.65*CH3O2 + CH2O + 0.65*CO	1.51×10^{-11}	
MAOP + OH → MAO3	6.13×10^{-13}exp(200./T)	
MAOP + OH → MAOPO2	3.60×10^{-12}exp(380./T)	
MAOPO2 + HO2 → HYAC + 2*OH	1.82×10^{-13}exp(1300./T)	
MAOPO2 + NO → HYAC + OH + NO2	2.35×10^{-12}exp(350./T)	
MAOPO2 + MAOPO2 → 2*HYAC + 2*OH	8.37×10^{-14}	
MAOPO2 + CH3O2 → .7*HYAC + .7*OH + CH2O + .7*HO2 + .3*C2H5OH	8.37×10^{-14}	
MAOPO2 + CH3CO3 → HYAC + OH + CH3O2	1.68×10^{-12}exp(500./T)	
MAOPO2 + CH3CO3 → CH3COOH + MEK	1.87×10^{-13}exp(500./T)	
GLYALD + OH → 0.2*GLYX + HO2 + 0.8*CH2O + 0.8*CO	1.00×10^{-11}	MCM v3.3.1
GLYX + OH → HO2 + 2*CO	3.10×10^{-12}exp(340./T)	
GLYX + NO3 → HNO3 + HO2 + 2*CO	$k_1=1.4\times10^{-12}$exp(-1860./T); k_1*(M*0.21+3.5×10^{18}) /(M*0.42+3.5×10^{18})	
MGLY + OH → CH3CO3 + CO	1.50×10^{-11}	
MGLY + NO3 → HNO3 + CO + CH3CO3	1.40×10^{-12}exp(-1860./T)	
HYAC + OH → MGLY + HO2	frac=1.-23.7exp(-T/70.); 2.15×10^{-12}exp(305./T)*frac	
HYAC + OH → .5*HCOOH + OH + .5*CH3COOH + .5*CO + .5*CH3O2	2.15×10^{-12}exp(305./T)*(1-frac)	
Isoprene Nighttime Chemistry		
ISOP + NO3 → INO2	3.15×10^{-12}exp(-450./T)	
INO2 + NO → ISN1 + NO2 + HO2	2.70×10^{-12}exp(360./T)	MCM v3.2
INO2 + NO3 → ISN1 + NO2 + HO2	2.30×10^{-12}	MCM v3.2
INO2 + HO2 → 0.22*MVK + 0.015*MACR + 0.235*OH + 0.235*NO2 + 0.235*CH2O + 0.77*INPN	2.05×10^{-13}exp(1300./T)	Schwantes et al.(2015)
INO2 + INO2 → 2.0*ISN1 + 1.2*HO2	1.30×10^{-12}	
INPN + OH → ISN1 + OH	1.03×10^{-10}	
ISN1 + OH → 0.52*C510O2 + 0.48*ISNOO	4.16×10^{-11}	
ISN1 + NO3 → ISNOO + HNO3	5.95×10^{-12}exp(-1860./T)	
ISN1 + O3 → 0.555*NOA + 0.52*GLYX + 0.445*MGLY + 0.075*H2O2 + 0.445*HO2 + 0.89*CO + 0.89*OH + 0.445*NO2	2.40×10^{-17}	
ISNOO + HO2 → 0.15*NC4CO2H + 0.15*O3 + 0.41*NC4CO3H + 0.44*NOA + 0.44*CO + 0.44*HO2 + 0.44*OH	5.20×10^{-13}exp(980./T)	
ISNOO + NO → NOA + CO + HO2 + NO2	7.50×10^{-12}exp(290./T)	
ISNOO + NO2 → C5PAN1	$k_o=2.7\times10^{-28}$*M*$(300./T)^{7.1}$; $k_1=1.2\times10^{-11}$*$(300./T)^{0.9}$; fc=k_o/k_1; fcc=0.75-1.27*$\log_{10}$ 0.3;	

	$nfc=10^{\frac{\log_{10} 0.3}{(1+(\log_{10} fc/fcc)^2)}}$; $k_o k_1/(k_o+k_1)$*nfc	
ISNOO + NO3 → NOA + CO + HO2 + NO2	4.00×10^{-12}	
ISNOO + ISNOO → 0.6*NC4CO2H + 1.4*NOA + 1.4*CO + 1.4*HO2	1.00×10^{-11}	
C510O2 + HO2 → C510OOH	2.05×10^{-13}exp(1300./T)	
C510O2 + NO → NO2 + NOA + GLYX + HO2	2.70×10^{-12}exp(360./T)	
C510O2 + NO3 → NO2 + NOA + GLYX + HO2	2.30×10^{-12}	
C510O2 + C510O2 → 0.6*C510OH + 1.4*NOA + 1.4*GLYX + 1.4*HO2	9.20×10^{-14}	
C510OH + OH → NOA + GLYX + HO2	2.69×10^{-11}	
C510OOH + OH → C510O2	2.81×10^{-11}	
NC4CO2H + OH → NOA + HO2 + CO	2.16×10^{-11}	
NC4CO3H + OH → ISNOO	2.52×10^{-11}	
NOA + OH → MGLY + NO2	1.00×10^{-12}	
C5PAN1 → ISNOO + NO2	$k_o=4.9\times10^{-3}$*M*exp(-12100./T); $k_1=5.4\times10^{16}$exp(-13830./T); $fc=k_o/k_1$; fcc=0.75-1.27*$\log_{10}$ 0.3; $nfc=10^{\frac{\log_{10} 0.3}{(1+(\log_{10} fc/fcc)^2)}}$; $k_o k_1/(k_o+k_1)$*nfc	
C5PAN1 + OH → NOA + CO + CO + NO2	2.16×10^{-11}	
Isoprene Ozonolysis		
ISOP + O3 → .325*MACR + .244*MVK + .845*CH2O + .11*H2O2 + .27*OH + .128*C3H6 + .051*CH3O2 + .522*CO + .204*HCOOH + .199*CH3CO3 + .026*HO2	1.00×10^{-14}exp(-1970./T)	
Photolysis of major organic nitrates		
ISOPNB + hν → HC5 + NO2 + HO2	1.21×10^{-6} s^{-1}	Calculated based on 24-hr average of modeled results
MACRN + hν → NO2 + HYAC + HO2 + CO	8.48×10^{-5} s^{-1}	
MVKN + hν → GLYALD + NO2 + CH3CO3	1.36×10^{-5} s^{-1}	
NOA + hν → CH3CO3 + CH2O + NO2	8.48×10^{-6} s^{-1}	
ISN1 + hν → NOA + 2.0*CO + 2.0*HO2	1.36×10^{-4} s^{-1}	
TERPN1 + hν → NO2	1.21×10^{-6} s^{-1}	
TERPN2 + hν → NO2	1.21×10^{-6} s^{-1}	

Table S2. Monoterpene oxidation chemistry in AM3. T represents temperature (K).

Reactions	Reaction Rates (molecule^{-1}cm^{3}s^{-1})	Note
$C10H16 + OH \rightarrow TERPO2$	$1.2\times10^{-11}\exp(440/T)$	Atkinson and Arey (2003)
$TERPO2 + NO \rightarrow 0.74{*}NO2 + 0.26{*}TERPN1$	$2.7\times10^{-12}\exp(360/T)$	Saunders et al. (2003)
$TERPO2 + HO2 \rightarrow$ products	$2.9\times10^{-13}\exp(1300/T)$	Saunders et al. (2003)
$TERPO2 + TERPO2 \rightarrow$ products	$1.68\times10^{-12}\exp(500/T)$	Tyndall et al. (2001)
$C10H16 + O3 \rightarrow$ products	$5.30\times10^{-16}\exp(-530/T)$	RCAM2
$C10H16 + NO3 \rightarrow 0.1{*}TERPN2 + 0.9{*}NO2$	$1.2\times10^{-12}\exp(490/T)$	Atkinson and Arey (2003)

Table S3. Heterogeneous loss of related species in the model.

Reactions	Reaction Rate or Uptake Coefficient	Note
GLYX → AGLYX	$\gamma_{glyx} = 1.0\times10^{-3}$	
MGLY → AMGLY	$\gamma_{mgly} = 1.0\times10^{-7}$	
IEPOX → AIEPOX	$\gamma_{iepox} = 1.0\times10^{-3}$	
ISOPNB → AONJ	$\gamma_{IN} = 5.0\times10^{-3}$	Fisher et al.(2016)
TERPN1 → AONJ	$\gamma_{MN} = 1.0\times10^{-2}$	Fisher et al.(2016)
AONJ → HNO3 + ROH	$k = 9.26\times10^{-5}\ s^{-1}$	Pye et al.(2015)

Table S4. Statistical analysis of ozone and major RON species from the base case and no_hydro case[a].

Tracers[b]	2004								2013							
	base				no_hydro				base				no_hydro			
	FB	FE	NMB	NME	FB	FE	NMB	NME	FB	FE	NMB	NME	FB	FE	NMB	NME
Ozone	9.4×10^{-2}	0.16	9.4×10^{-2}	0.16	0.11	0.16	0.11	0.16	0.17	0.19	0.16	0.19	0.17	0.20	0.16	0.20
NO_x	0.19	0.55	8.2×10^{-2}	0.59	0.25	0.56	0.14	0.61	-3.6×10^{-2}	0.42	-5.3×10^{-2}	0.44	-1.3×10^{-2}	0.43	-3.2×10^{-2}	0.45
HNO_3[c]	-1.4×10^{-2} (7.4×10^{-2})	0.32 (0.41)	5.1×10^{-3} (2.6×10^{-2})	0.32 (0.41)	-4.8×10^{-2} (3.5×10^{-2})	0.33 (0.39)	-2.2×10^{-2} (6.0×10^{-3})	0.32 (0.38)	0.15	0.45	5.4×10^{-4}	0.41	0.015	0.50	-0.11	0.44
PAN	0.25	0.49	0.17	0.42	0.31	0.49	0.23	0.43	5.4×10^{-2}	0.36	5.6×10^{-2}	0.35	5.2×10^{-2}	0.38	6.2×10^{-2}	0.37
∑ANs[d]	-0.19	0.37	8.9×10^{-2}	0.65	0.16	0.58	0.29	0.75	-5.9×10^{-2}	0.57	-0.16	0.45	0.29	0.79	-7.3×10^{-3}	0.46
NO_y[c]	6.4×10^{-2} (6.5×10^{-2})	0.33 (0.40)	6.3×10^{-2} (3.8×10^{-2})	0.32 (0.36)	0.11 (0.12)	0.34 (0.39)	0.11 (0.10)	0.34 (0.38)	-5.7×10^{-3}	0.27	-4.2×10^{-2}	0.27	-2.9×10^{-2}	0.29	-6.0×10^{-2}	0.28
Wet deposition of NO_3^-	-0.40	0.50	-0.39	0.46	—	—	—	—	-0.51	0.56	-0.43	0.45	—	—	—	—
MDA8 ozone	0.30	0.32	0.33	0.35	—	—	—	—	0.39	0.40	0.45	0.46	—	—	—	—

[a]Descriptions of the two cases can be found in Table 2. FB=$\frac{2}{N}\sum_{i=1}^{N}(P_i - O_i)/(P_i + O_i)$, FE=$\frac{2}{N}\sum_{i=1}^{N}|P_i - O_i|/(P_i + O_i)$,

NMB=$\sum_{i=1}^{N}(P_i - O_i)/\sum_{i=1}^{N}O_i$, MNE=$\frac{1}{N}\sum_{i=1}^{N}|P_i - O_i|/\sum_{i=1}^{N}O_i$, where P_i and O_i are modeled and observed data, and N is number of valid data.

[b]For ozone, NO_x, HNO_3, PAN, ∑ANs and NO_y, observations are from ICARTT, SENEX and SEAC[4]RS within the boundary layer (< 1.5 km); for wet deposition of NO_3^-, observations are from NADP; for MDA8 ozone, observations are from EPA AQS data during July–August of 2004 and 2013 at monitoring stations in Fig. S2.

[c]Statistical results of HNO_3 and NO_y in 2004 (ICARTT) outside of and within the brackets used observed HNO_3 measured by mist chamber/IC by University of New Hampshire and Chemical Ionization Mass Spectrometer (CIMS) by California Institute of Technology, respectively.

[d]Statistical results of ∑ANs in 2013 used observations during SEAC[4]RS.

Table S5. Lifetimes of major organic nitrates from isoprene and monoterpenes in AM3.

Species in AM3	Formation Pathways	Lifetime[a]
ISOPNB[b]	C_5 β-hydroxy nitrate from isoprene oxidation by OH	1.2 (1.4)
ISN1	C_5 carbonyl nitrate from isoprene oxidation by NO_3	3.6 (3.5)
INPN	C_5 nitrooxy hydroperoxide from isoprene oxidation by NO_3	8.5 (7.8)
MVKN	Methyl vinyl ketone nitrate from ISOPNB oxidation by OH	9.6 (9.3)
MACRN	Methacrolein nitrate from ISOPNB oxidation by OH	1.5 (1.4)
ISNP	C_5 nitrooxy hydroperoxide from isoprene oxidation by OH	12 (12)
PROPNN	Propanone nitrate from oxidation of INPN and ISN1	17.6 (16.2)
DHDN[c]	C_5 dihydroxy dinitrate from ISOPNB oxidation by OH	11.4 (10.3)
TERPN1	Nitrate from monoterpene oxidation by OH	19.6 (18.8)
TERPN2	Nitrate from monoterpene oxidation by NO_3	14.1 (14.4)
PAN		0.72 (0.66)
HNO_3		16(16)

[a]Lifetimes (h) are calculated based on the total chemical loss rate, dry and wet deposition flux of each. compound during July–August of 2004; values in brackets are from July–August of 2013. It should be noted that the lifetimes listed here are 24-h average, different from estimates by Müller et al. (2014).
[b]The lifetime of ISOPNB includes impacts of aerosol hydrolysis.
[c]The lifetime of DHDN is based on dry and wet deposition since it is not removed by chemical oxidation.

Table S6. Non-radical species used in AM3.

Species Name	Description
ISOP	isoprene
CH2O	formaldehyde
MGLY	methyl-glyoxal
GLYALD	glycolaldehyde
GLYX	glyoxal
MVK	methylvinyl ketone
MACR	methacrolein
ISOPNB	see Table S5
ISOPOOH	hydroxy hydroperoxide from isoprene oxidation by OH
HC5	$C_5H_8O_2$, see Paulot et al. (2009)
ROH	alcohol with the carbon number ≥ 3
CH3OH	methanol
MEK	ketones with the carbon number > 3
CH3COOH	methyl hydroperoxide
HYAC	hydroxyacetone
MACRN	see Table S5
MVKN	see Table S5
DHDN	see Table S5
ISNP	see Table S5
ROOH	hydroperoxides with the carbon number ≥ 3
HCOOH	formic acid
C4NACID	C_4 hydroxy nitrooxy carboxylic acid, see Lee et al. (2014)
HPROPN	hydroxy propyl nitrate, see Lee et al. (2014)
MVKNOOH	MVKN with one additional hydroperoxide group, see Lee et al. (2014)
IEPOX	isoprene epoxydiol
RCHO	propyl aldehyde
DHMOB	$C_5H_8O_4$, see Paulot et al. (2009)
MOBA	C_5 acid from isoprene
IAP	peroxides from HC5 oxidation by OH
C3H7OOH	propyl hydroperoxide
CH3CHO	acetaldehyde
MACROOH	hydroperoxide from MACR oxidation by OH
MAOP	peroxide from MAO3
MACO2H	organic peroxide
MPAN	peroxymethacryloyl nitrate
C2H5OH	alcohol
ISN1	see Table S5
INPN	see Table S5
NOA	propanone nitrate
NC4CO2H	C_5 nitrate with a carboxylic acid group from isoprene oxidation by NO_3, see MCM v3.2

NC4CO3H	C_5 nitrate with a peroxy acid group from isoprene oxidation by NO_3, see MCM v3.2
C5PAN1	C_5 peroxy nitrate from isoprene oxidation by NO_3, see MCM v3.2
C510OOH	C_5 nitrate with a hydroperoxide group from isoprene oxidation by NO_3, see MCM v3.2
C510OH	C_5 nitrate from isoprene oxidation by NO_3, see MCM v3.2
C3H6	propylene
C10H16	monoterpenes
TERPN1	see Table S5
TERPN2	see Table S5

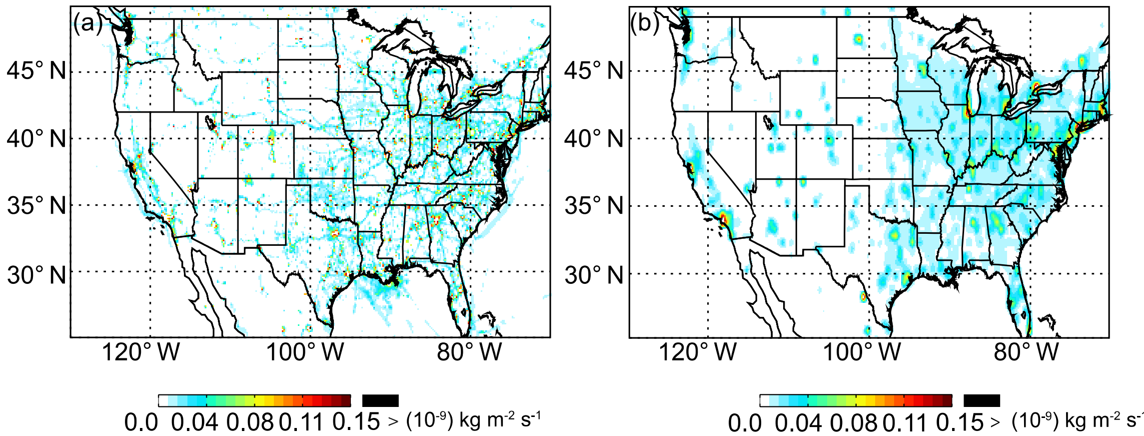

Figure S1. Anthropogenic NO_x emission rate during July–August 2013 of (a) NEI11v1 inventory and (b) RCP8.5.

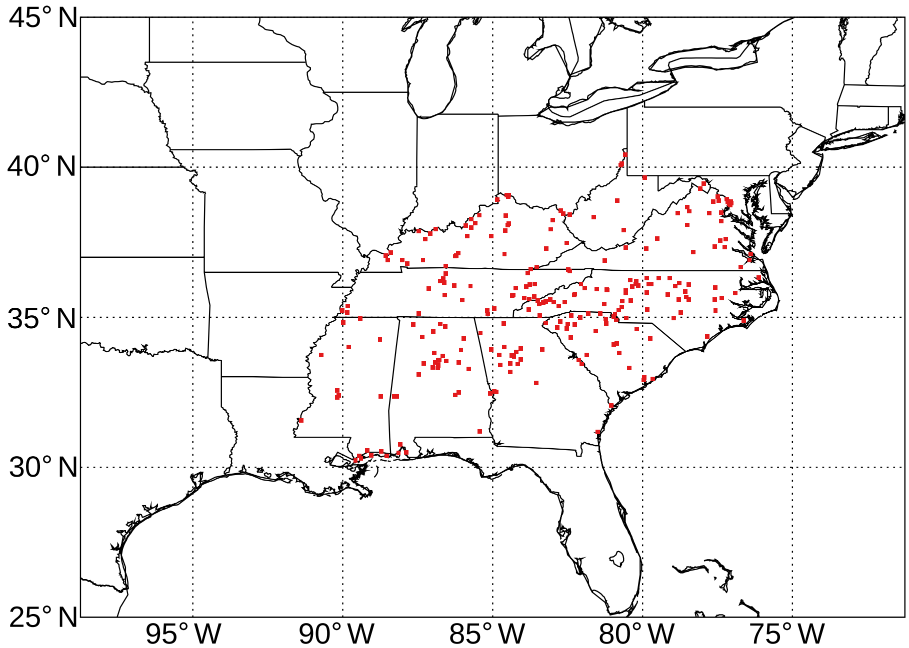

Figure S2. EPA AQS ozone monitoring sites in the Southeast U.S., from which EPA provides the MDA8 metric used in our study.

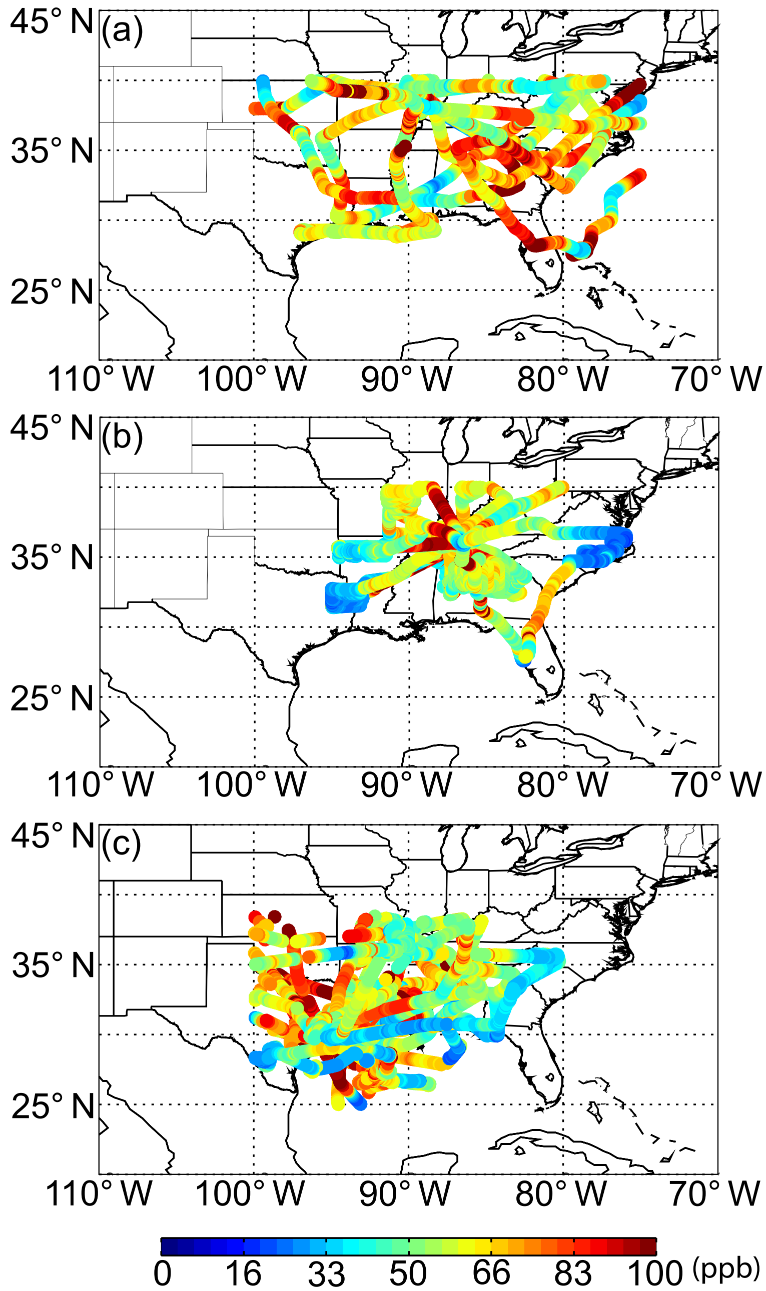

Figure S3. Ozone (ppb) along daytime flight tracks during (a) ICARTT (up to 12 km) (b) SENEX (up to 6 km) and (c) SEAC^{4}RS (up to 12.5 km). Data from biomass burning, urban plumes, stratospheric air and outside of the 25–40° N latitude and 100–75° W longitude region are excluded.

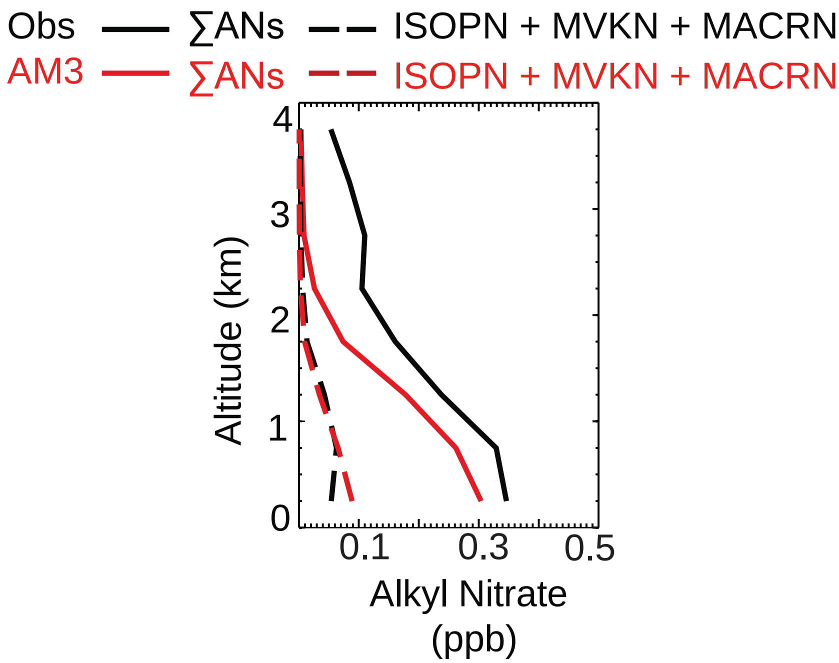

Figure S4. Mean vertical profiles of ∑ANs (solid lines) and sum of ISOPN, MVKN and MACRN (dashed lines) during SEAC[4]RS from observations (black) and AM3 with hydrolysis of ISOPNB (red). The discrepancy between ∑ANs and sum of ISOPN, MVKN and MACRN is attributed to monoterpene nitrates and a C5 dihydroxy dinitrate (DHDN) and nighttime NO_3 oxidation products from isoprene.

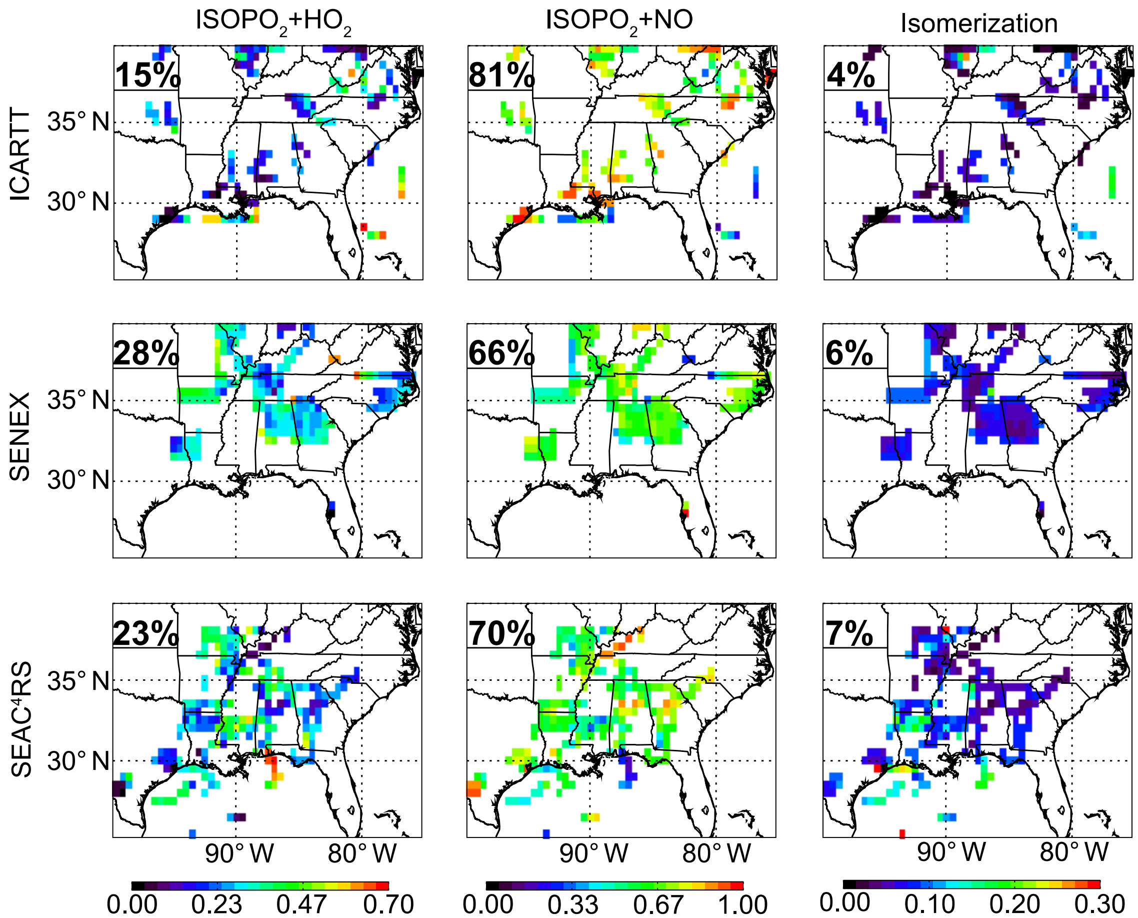

Figure S5. Ratio of major $ISOPO_2$ loss pathways to the total $ISOPO_2$ loss (sum of the three individual pathways) during ICARTT (July–August of 2004, top), SENEX (June–July of 2013, middle) and SEAC^{4}RS (July–September of 2013, bottom) in the boundary layer (below 1.5 km). Bold number in each panel is the mean percentage of each pathway to the total $ISOPO_2$ loss.

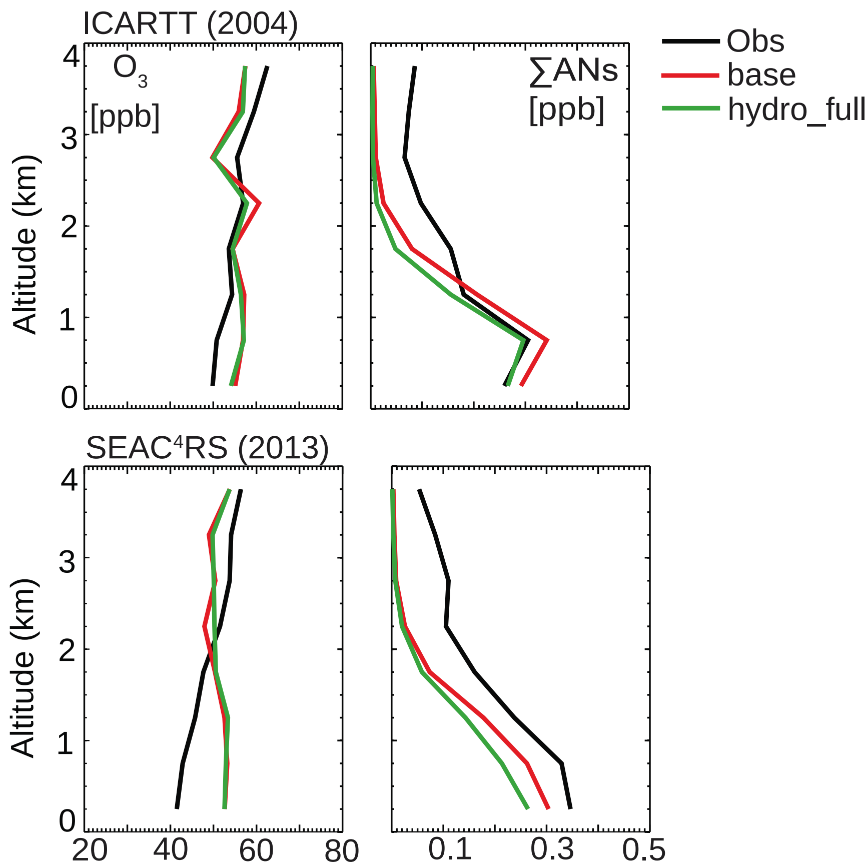

Figure S6. Mean vertical profiles of ozone and ∑ANs during ICARTT (top) and SEAC^{4}RS (bottom). Red lines are results of AM3 with ISOPNB hydrolysis only; green lines are from AM3 with hydrolysis of ISOPNB, DHDN and TERPN1.

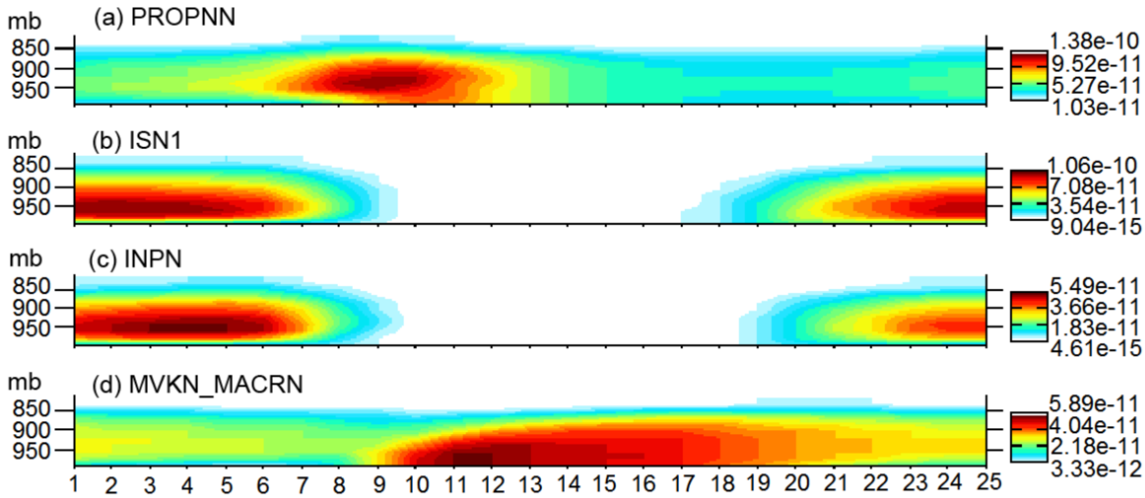

Figure S7. Modeled diurnal variation of PROPNN, ISN1, INPN and MVKN + MACRN (MVKN_MACRN) in the boundary layer of the Southeast U.S. The x-axis is the local time, and y-axis is the pressure. Color bar indicates the concentration in volume mixing ratio.

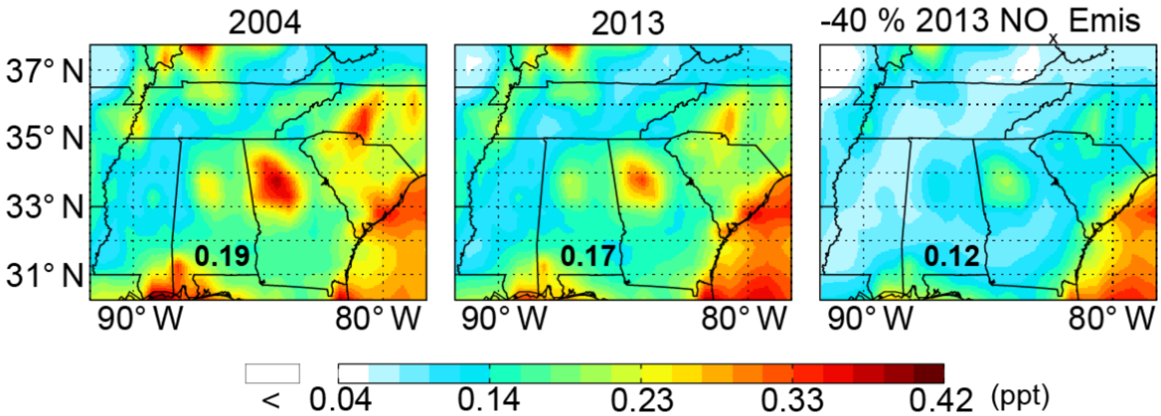

Figure S8. Averaged OH concentration from 10:00 to 14:00 LT during July–August of 2004, 2013, and a scenario with 40 % reduction of anthropogenic NO_x emissions of 2013 from AM3. Bold number in each panel is the regionally-averaged OH concentration.

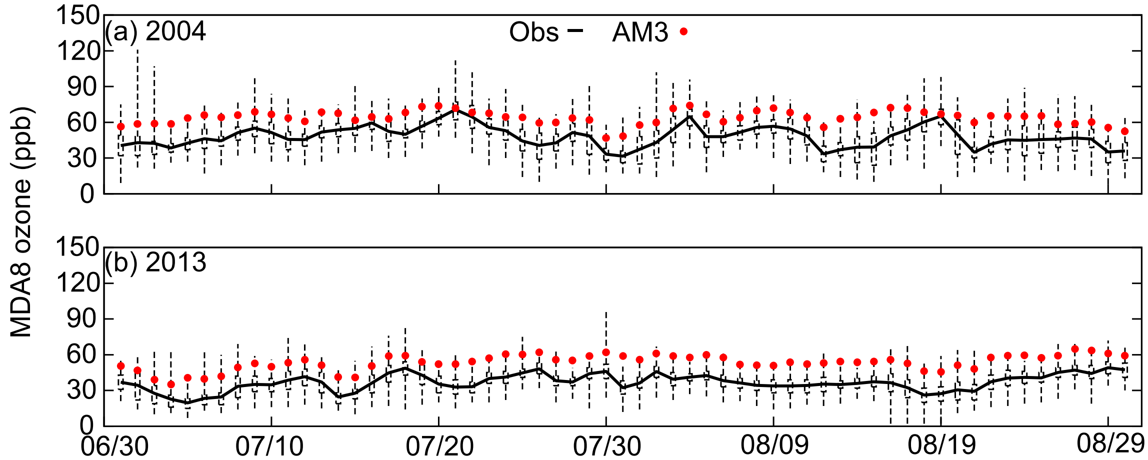

Figure S9. Daily MDA8 ozone during July–August of 2004 (a) and July–August of 2013 (b) averaged over 157 EPA AQS monitoring sites shown in Fig. S2. Horizontal axis is month and day of the year. Black lines, dash boxes and whiskers are the mean, interquartile range and lowest and highest observations; red dots are the mean of AM3.

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