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Supplement of

Why do models overestimate surface ozone in the Southeast United States?

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Supplementary Material

Table S1 – Species Added to GEOS-Chem

Species	Note
HPALD	Hydroperoxyaldehydes ($C_5H_8O_3$)
HC187	Epoxide oxidation product m/z 187-189
DHDN	C_5 dihydroxydinitrate

Table S2 – Reaction Rates and Productions Updated in GEOS-Chem

Reaction	Reference	Rate Constant	Reference
RIO_2 + HO_2 → 0.937RIP + 0.063OH + 0.025MACR + 0.038MVK + 0.063HO_2 + 0.063CH_2O	(Liu et al., 2013)	2.06E-13*exp(1300/T)	(Saunders et al., 2003)
RIO_2 + NO → 0.91NO_2 + 0.82HO_2 + 0.82CH_2O + 0.476MVK + 0.344MACR + 0.058HC_5 + 0.03DIBOO + 0.009ISOPND + 0.081ISOPNB	(Liu et al., 2013;Fisher et al., 2016)	2.7E-12*exp(350/T)	(Paulot et al., 2009a)
RIO_2 → HO_2 + HPALD	(Peeters et al., 2009;Peeters and Muller, 2010;Crounse et al., 2011)	4.07E8*exp(-7694/T)	Rate adjusted by Crounse et al. (2011)
RIO_2 + RIO_2 → 0.91HO_2 + 0.75CH_2O + 0.45MVK + 0.29MACR + 0.09DIBOO + 1.11HC5 + 0.29CO	(Xie et al., 2013)	2.3E-12	(Xie et al., 2013)
HPALD + OH → MGLY + CO + CH_2O + OH	(Squire et al., 2015)	5.1E-11	(Wolfe et al., 2012)
HPALD + $h\upsilon$ → OH + HO_2 + 0.5GLYC + 0.25 GLYX + 0.25MGLY + CH_2O + 0.5 HAC	(Stavrakou et al., 2010)	Rate is equivalent to MACR photolysis	(Peeters and Muller, 2010)
ISOPND + OH → 0.1IEPOX + 0.9 ISOPNDO_2 + 0.1NO_2	(Jacobs et al., 2014)	1.2E-11*exp(652/T)	(Lee et al., 2014)
ISOPNB + OH → 0.1IEPOX + 0.90ISOPNBO_2 + 0.1NO_2	(Jacobs et al., 2014)	2.4E-12*exp(745/T)	(Lee et al., 2014)
ISOPNDO_2 + NO → 0.019MACRN + 0.057HCOOH + 0.27HAC + 0.210ETHLN + 0.15CH_2O + 0.790NO_2 + 0.3GLYC + 0.3PROPNN + 0.61HO_2 + 0.27DHDN + 0.075MVKN + 0.057ISOPNDO_2 $^{(a)}$	(Lee et al., 2014)	2.4E-12*exp(360/T)	(Lee et al., 2014)
ISOPNBO_2 + NO → 0.09GLYC + 0.09HAC + 0.69CH2O + 0.44MACRN + 0.69HO_2 + 0.26MVKN + 0.88NO_2 + 0.21DHDN	(Lee et al., 2014)	2.4E-12*exp(360/T)	(Lee et al., 2014)
ISOPNDO_2 + HO_2 →0.01MACRN + 0.2HAC + 0.2ETHLN + 0.07CH_2O + 0.23GLYC + 0.23PROPNN + 0.5HO_2 + 0.5OH + 0.06MVKN + 0.5ISNP $^{(b)}$	(Lee et al., 2014)	8.7E-14*exp(1650/T)	(Lee et al., 2014)
ISOPNBO_2 + HO_2 → 0.06GLYC + 0.06HAC + 0.44CH_2O + 0.28MACRN + 0.16MVKN + 0.06NO_2 + 0.44HO_2 + 0.5OH + 0.5ISNP $^{(b)}$	(Lee et al., 2014)	8.7E-14*exp(1650/T)	(Lee et al., 2014)
ISOPND + O_3 → 0.06NO_2 + 0.37OH + 0.24PROPNN + 0.26ETHLN + 0.26HAC + 0.24GLYC + 0.63CO_2 + 0.24MOH + 0.09EOH + 0.2CH_2O + 0.1MCO3 + 0.06GLYX + 0.16HAC + 0.14PROPNN + 0.3$HNO_3$$^{(d)}$	(Lee et al., 2014)	2.9E-17	(Lee et al., 2014)
ISOPNB + O_3 → 0.05HO2 + 0.05OH + 0.11MVKN + 0.32MACRN + 0.16HCOOH + 0.62CH2O + 0.36CO2 + 0.21CO + 0.06PROPNN + 0.36PROPNN$^{(c)}$ +	(Lee et al., 2014)	3.7E-19	(Lee et al., 2014)

0.1MVKN + 0.41HNO3(d)			
IEPOX + OH → IEPOXOO	(Paulot et al., 2009b)	4.82E-11*exp(-400/T)(e)	(Bates et al., 2014)
IEPOXOO + HO_2 → 0.085HAC + 0.025GLYC + 0.085GLYX + 0.085MGLY + 1.125OH + 0.825HO_2 + 1.1CO_2 + 0.375CH2O + 0.278HCOOH + 0.6CO + 0.44HC187(f)	(Bates et al., 2014)	2.06E-13*exp(1300/T)	(Paulot et al., 2009b)
IEPOXOO + NO → 0.117HAC + 0.088GLYC + 0.088GLYX + 0.088MGLY + 0.125OH + 0.825HO_2 + 0.8CO_2 + 0.375CH_2O + 0.142HCOOH + 0.678CO + NO_2 + 0.473HC187(f)	(Bates et al., 2014)	2.7E-12exp*(350/T)	(Paulot et al., 2009b)
HC187 + OH → 0.5MCO_3 + 0.5MGLY + 0.5HO_2 + 0.5CO + CH_2O	(Bates et al., 2014)	1.4E-11	(Bates et al., 2014)

(a) The yields are not identical to the Lee et al. (2014) values and there is artificial recycling of $ISOPNDO_2$ to account for non-unity reactants (i.e. in Lee et al. (2014) one $ISOPNDO_2$ reacts with 1.06$ISOPNDO_2$).

(b) In Lee et al. (2014), a C5 hydroperoxide is formed (ROOH). In order to close the nitrogen budget this would have to be ISNP – a peroxide species with a nitrate group.

(c) Replace C4NACID in Lee et al. (2014) with PROPNN.

(d) HNO_3 added to this reaction to close the nitrogen budget, as we replace ethyl nitrate with its oxidation product, peroxyacetyl nitrate.

(e) Update pre-exponential factor of this reaction in globchem.dat from Bates et al. (2014).

(f) Other organic products were identified by Bates et al. (2014). These structural isomers are replaced with CO for the epoxide product (m/z 201) and a new species (also added as a tracer) is added to GEOS-Chem to account for the m/z 187 and 189 isomers.

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Evaluation of NEI11v1 NO_x Scaling

We consider the uncertainty in the scaling of NO_x emissions from NEI11v1 by 50% due to the presence of soil NO_x in the Southeast US. As shown in Figure 1, surface NO_x emissions in the Southeast US in GEOS-Chem for August and September 2013 include fuel combustion, soils, fertilizer use, and open fires, which total 153 Gg N. Emissions from soils and fertilizer use total 31 and 13 Gg N, respectively. Fuel combustion contributes 104 Gg N after scaling NEI11v1, and open fires the remaining 5 Gg N. Emissions of NO_x from soils vary greatly with precipitation patterns, fertilizer practices, and soil conditions, all of which are discussed further in Hudman et al, 2012. We show that after NO_x scaling of NEI11v1, GEOS-Chem is able to represent aircraft observations of NO_x (Figure 2) and wet deposition observations of nitrate (Figure 3) with good agreement.

We run the following model simulations to account for the 43 Gg of NO_x

1. GEOS-Chem run with un-scaled NEI11v1 NO_x emissions and un-scaled fertilizer use.
2. GEOS-Chem run with un-scaled NEI11v1 NO_x emissions and zero fertilizer use and natural emission from soils.