



## Supplement of

## Limited effect of anthropogenic nitrogen oxides on secondary organic aerosol formation

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## Simulation using "VBS\_agHigh\_isop" scheme.

The VBS schemes (VBS, VBS\_agHigh, etc.) that we implement into CAM4-chem as described in the main text are based on the published VBS parameterizations from Pye et al. (2010), which does not consider the high-NO<sub>x</sub> pathway for isoprene oxidation. Here we performed an additional simulation "VBS\_agHigh\_isop" to evaluate the effect of this omitted pathway.

In the VBS\_agHigh\_isop scheme, we add the high-NO<sub>x</sub> branch for isoprene-oxidized SOA formation (ISOPO<sub>2</sub>+NO) using the parameters from Lane et al. (2008). The SOA mass yields are 0, 0.00026, 0.0195, 0.013 for C\* of 0.1, 1, 10, 100  $\mu$ g m<sup>-3</sup>, respectively, fit using a density of 1.3 g cm<sup>-3</sup> to be consistent with Pye et al. (2010). Adding this pathway, the VBS\_agHigh\_isop scheme gives an annual mean SOA burden of 0.86 ± 0.05 Tg[C] and a net SOA production of 46.8 ± 1.9 Tg[C] per year, both of which are about 20% smaller than the VBS\_agHigh scheme, and larger than the two no-aging schemes (2-product and VBS). The VBS\_agHigh\_isop scheme shows no significant advantage over the VBS\_agHigh scheme in model-observation comparisons.

We then performed a sensitivity run using the VBS\_agHigh\_isop scheme, in which anthropogenic NO emissions are reduced by 50%. Results in the southeast US and the Amazon are shown in Fig. S5. SOAM and anthropogenic SOAs through each branch behave similar to the VBS\_agHigh. For isoprene oxidation in the southeast US, the HO<sub>2</sub> pathway increases and NO pathway decrease. While the effect of shifting to high-yield HO<sub>2</sub> pathway is masked due to the reduced OH concentration (about -15%, Fig. S2). The total SOA concentration decreases from  $3.4 \pm 0.5$  to  $3.0 \pm 0.4 \ \mu g \ m^{-3}$ . This 0.4  $\ \mu g \ m^{-3}$ , 10% reduction is smaller than the change in VBS\_agHigh scheme (0.5  $\ \mu g \ m^{-3}$ , 12%), and is smaller than one standard deviation of multi-year variation, suggesting the SOA response to the NO perturbation is not significant. In the Amazon, all branches show a decrease with reduced NO. The total SOA reduction (0.1  $\ \mu g \ m^{-3}$ , 2%) is non-significant. These conclusions are consistent with the VBS\_agHigh results.

**Table S1. SOA mass yields using default 2-product scheme (Heald et al., 2008 and references therein).** The reference temperature is 310K for monoterpenes and isoprene, and is 295K for benzene, toluene and xylenes. The enthalpy of evaporation is 42 kJ mol<sup>-1</sup>.

	Oxidants	Surrogate	α an	Yield at 10	
Parent HC		product	(C* in	(and 1) µg m <sup>-3</sup>	
Monoterpenes C <sub>10</sub> H <sub>16</sub>	OH; HO <sub>2</sub>		C*=5.435	C*=232.6	0.06 (0.01)
			α=0.067	α=0.354	
	O <sub>3</sub> ; HO <sub>2</sub>	SOAM	C*=5.435	C*=232.6	0.06 (0.01)
		$C_{10}H_{16}O_4$	α=0.067	α=0.354	0.06 (0.01)
	NO <sub>3</sub>		C*=61.35	0	0.14 (0.02)
			α=1.000	0	
Isoprene		SOAI	C*=0.617	C*=116.0	0.05 (0.02)
$C_5H_8$	$OH; HO_2$	$C_5H_{12}O_4$	α=0.029	α=0.232	
Benzene C <sub>6</sub> H <sub>6</sub>	OH; HO <sub>2</sub>		C*=0.001	0	0.23 (0.23)
		SOAB	α=0.227	0	
	OH; NO	$C_6H_7O_3$	C*=0.302	C*=111.1	0.09 (0.04)
			α=0.044	α=0.545	
Toluene C7H8	OH; HO <sub>2</sub>		C*=0.001	0	0.23 (0.23)
		SOAT	α=0.235	0	
	OH; NO	$C_7H_9O_3$	C*=2.326	C*=21.28	0.05 (0.01)
			α=0.038	α=0.074	
Xylenes C <sub>8</sub> H <sub>10</sub>	OH; HO <sub>2</sub>		C*=0.001	0	0.20 (0.20)
		SOAX	α=0.205	U	
	OH; NO	$C_8H_{11}O_3$	C*=1.314	C*=34.48	0.02 (0.01)
			α=0.021 α=0.0		0.03 (0.01)

## Table S2. SOA mass yields using updated 4-product VBS scheme (Pye et al., 2010 and references therein). The reference temperature is 295K and the enthalpy of evaporation is 73, 62, 51, 40 kJ mol<sup>-1</sup> for C\* of 0.1, 1, 10, 100 $\mu$ g m<sup>-3</sup>, respectively.

Parent HC	Oxidants	Surrogate	α for C* (C* in μg m <sup>-3</sup> )				Yield at 10
		product	C*=0.1	C*=1	C*=10	C*=100	(and 1) µg m <sup>-3</sup>
Monoterpenes C <sub>10</sub> H <sub>16</sub>	OH; HO <sub>2</sub>	SOAM C <sub>10</sub> H <sub>16</sub> O4	0.08	0.019	0.18	0.03	0.19 (0.10)
	OH; NO		0.04	0.0095	0.09	0.015	0.09 (0.05)
	O <sub>3</sub> ; HO <sub>2</sub>		0.08	0.019	0.18	0.03	0.19 (0.10)
	O <sub>3</sub> ; NO		0.04	0.0095	0.09	0.015	0.09 (0.05)
	NO <sub>3</sub>		0	0	0.321	1.083	0.26 (0.04)
Isoprene	OH; HO <sub>2</sub>	SOAI	0	0.031	0	0.095	0.04 (0.02)
$C_5H_8$	NO <sub>3</sub>	$C_5H_{12}O_4$	0	0	0.217	0.092	0.12 (0.02)
Benzene	OH; HO <sub>2</sub>	SOAB	0.37	0	0	0	0.37 (0.34)
$C_6H_6$	OH; NO	$C_6H_7O_3$	0	0.078	0	0.793	0.14 (0.05)
Toluene	OH; HO <sub>2</sub>	SOAT	0.36	0	0	0	0.36 (0.33)
$C_7H_8$	OH; NO	$C_7H_9O_3$	0	0.032	0.094	0.080	0.08 (0.03)
Xylene	OH; HO <sub>2</sub>	SOAX	0.30	0	0	0	0.30 (0.27)
$C_{8}H_{10}$	OH; NO	$C_8H_{11}O_3$	0	0.025	0.036	0.090	0.05 (0.02)



Figure S1. Absolute (left column) and relative (right column) changes of annual mean NO emissions (units:  $\times 10^{10}$  molecules cm<sup>-2</sup> s<sup>-1</sup>) and simulated surface NO<sub>x</sub> concentration (units:  $\times 10^{10}$  molecules cm<sup>-3</sup>) in the sensitivity run compared to the control run using VBS\_agHigh scheme. Data are averaged from 2005 to 2009.



Figure S2. Absolute (left column) and relative (right column) changes of simulated annual mean surface OH (×10<sup>6</sup> molecules cm<sup>-3</sup>), O<sub>3</sub> (×10<sup>12</sup> molecules cm<sup>-3</sup>) and NO<sub>3</sub> concentrations (×10<sup>8</sup> molecules cm<sup>-3</sup>) in the sensitivity run compared to the control run using VBS\_agHigh scheme. Data are averaged from 2005 to 2009. Note that the range of color bars are different in each subplot.



Figure S3. Left column: (a1) is the annual mean surface NO-to-HO<sub>2</sub> ratio (NO/HO<sub>2</sub>) in the control run; (a2) and (a3) are the absolute and relative change of NO/HO<sub>2</sub> in the sensitivity run compared to the control run. Right column is similar to the left column but for annual mean surface branching ratio ( $\beta$ ). Simulations use VBS\_agHigh scheme. Data are averaged from 2005 to 2009. Note that the range of color bars are different in each subplot.



Figure S4. Probability density function of annual mean surface branching ratio ( $\beta$ ) at global scale, in the southeast US and in the Amazon.



Figure S5. Annual mean surface SOA concentration ( $\mu g m^{-3}$ ) in the control run and the sensitivity run (with 50% anthropogenic NO emission off) from different pathways using the VBS\_agHigh\_isop scheme, averaged over the southeast U.S. [32°-40°N, 95°-77°W] and the Amazon [17°S-5°N, 77°-55°W]. The numbers above each bar denote the relative contributions (%) of each SOA formation pathway to the total SOA concentration change. The sum of all numbers equals -100% due to the overall decrease in total SOA.