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_x 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_x branch for isoprene-oxidized SOA formation ($ISOPO_2$+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 μg m^{-3}, respectively, fit using a density of 1.3 g cm^{-3} 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_2 pathway increases and NO pathway decrease. While the effect of shifting to high-yield HO_2 pathway is masked due to the reduced OH concentration (about -15%, Fig. S2). The total SOA concentration decreases from 3.4 ± 0.5 to 3.0 ± 0.4 μg m^{-3}. This 0.4 μg m^{-3}, 10% reduction is smaller than the change in VBS_agHigh scheme (0.5 μg 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 μg 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^{-1}.

Parent HC	**Oxidants**	**Surrogate product**	**α and C* (C* in μg m^{-3})**		**Yield at 10 (and 1) μg m^{-3}**
Monoterpenes $C_{10}H_{16}$	OH; HO_2	SOAM $C_{10}H_{16}O_4$	C*=5.435 α=0.067	C*=232.6 α=0.354	0.06 (0.01)
	O_3; HO_2		C*=5.435 α=0.067	C*=232.6 α=0.354	0.06 (0.01)
	NO_3		C*=61.35 α=1.000	0	0.14 (0.02)
Isoprene C_5H_8	OH; HO_2	SOAI $C_5H_{12}O_4$	C*=0.617 α=0.029	C*=116.0 α=0.232	0.05 (0.02)
Benzene C_6H_6	OH; HO_2	SOAB $C_6H_7O_3$	C*=0.001 α=0.227	0	0.23 (0.23)
	OH; NO		C*=0.302 α=0.044	C*=111.1 α=0.545	0.09 (0.04)
Toluene C_7H_8	OH; HO_2	SOAT $C_7H_9O_3$	C*=0.001 α=0.235	0	0.23 (0.23)
	OH; NO		C*=2.326 α=0.038	C*=21.28 α=0.074	0.05 (0.01)
Xylenes C_8H_{10}	OH; HO_2	SOAX $C_8H_{11}O_3$	C*=0.001 α=0.205	0	0.20 (0.20)
	OH; NO		C*=1.314 α=0.021	C*=34.48 α=0.061	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^{-1} for C* of 0.1, 1, 10, 100 µg m^{-3}, respectively.

Parent HC	Oxidants	Surrogate product	α for C* (C* in µg m^{-3})				Yield at 10 (and 1) µg m^{-3}
			C*=0.1	C*=1	C*=10	C*=100	
Monoterpenes $C_{10}H_{16}$	OH; HO_2	SOAM $C_{10}H_{16}O_4$	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_3; HO_2		0.08	0.019	0.18	0.03	0.19 (0.10)
	O_3; NO		0.04	0.0095	0.09	0.015	0.09 (0.05)
	NO_3		0	0	0.321	1.083	0.26 (0.04)
Isoprene C_5H_8	OH; HO_2	SOAI $C_5H_{12}O_4$	0	0.031	0	0.095	0.04 (0.02)
	NO_3		0	0	0.217	0.092	0.12 (0.02)
Benzene C_6H_6	OH; HO_2	SOAB $C_6H_7O_3$	0.37	0	0	0	0.37 (0.34)
	OH; NO		0	0.078	0	0.793	0.14 (0.05)
Toluene C_7H_8	OH; HO_2	SOAT $C_7H_9O_3$	0.36	0	0	0	0.36 (0.33)
	OH; NO		0	0.032	0.094	0.080	0.08 (0.03)
Xylene C_8H_{10}	OH; HO_2	SOAX $C_8H_{11}O_3$	0.30	0	0	0	0.30 (0.27)
	OH; NO		0	0.025	0.036	0.090	0.05 (0.02)

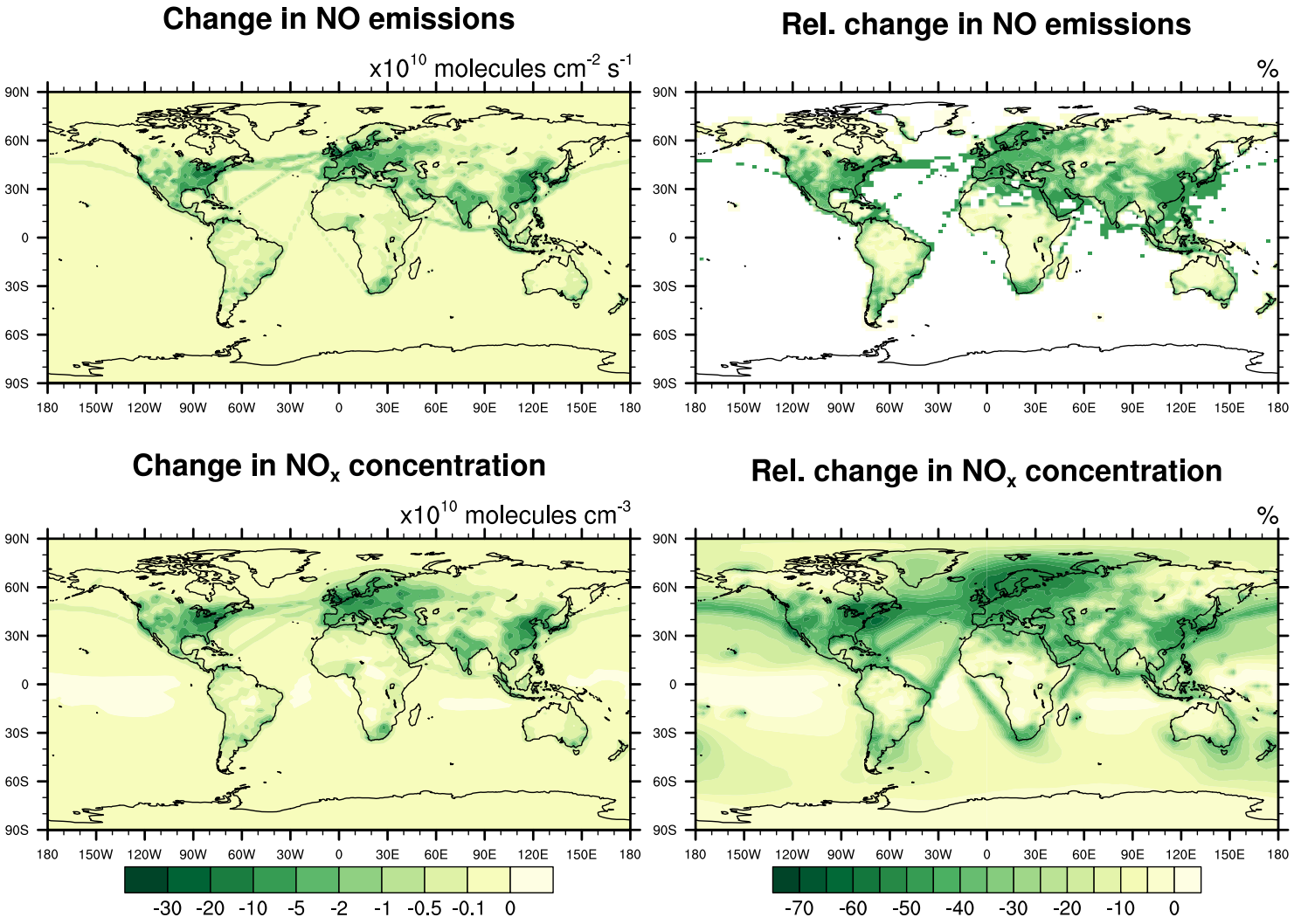

Figure S1. Absolute (left column) and relative (right column) changes of annual mean NO emissions (units: $\times 10^{10}$ molecules cm^{-2} s^{-1}) and simulated surface NO_x concentration (units: $\times 10^{10}$ molecules cm^{-3}) in the sensitivity run compared to the control run using VBS_agHigh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

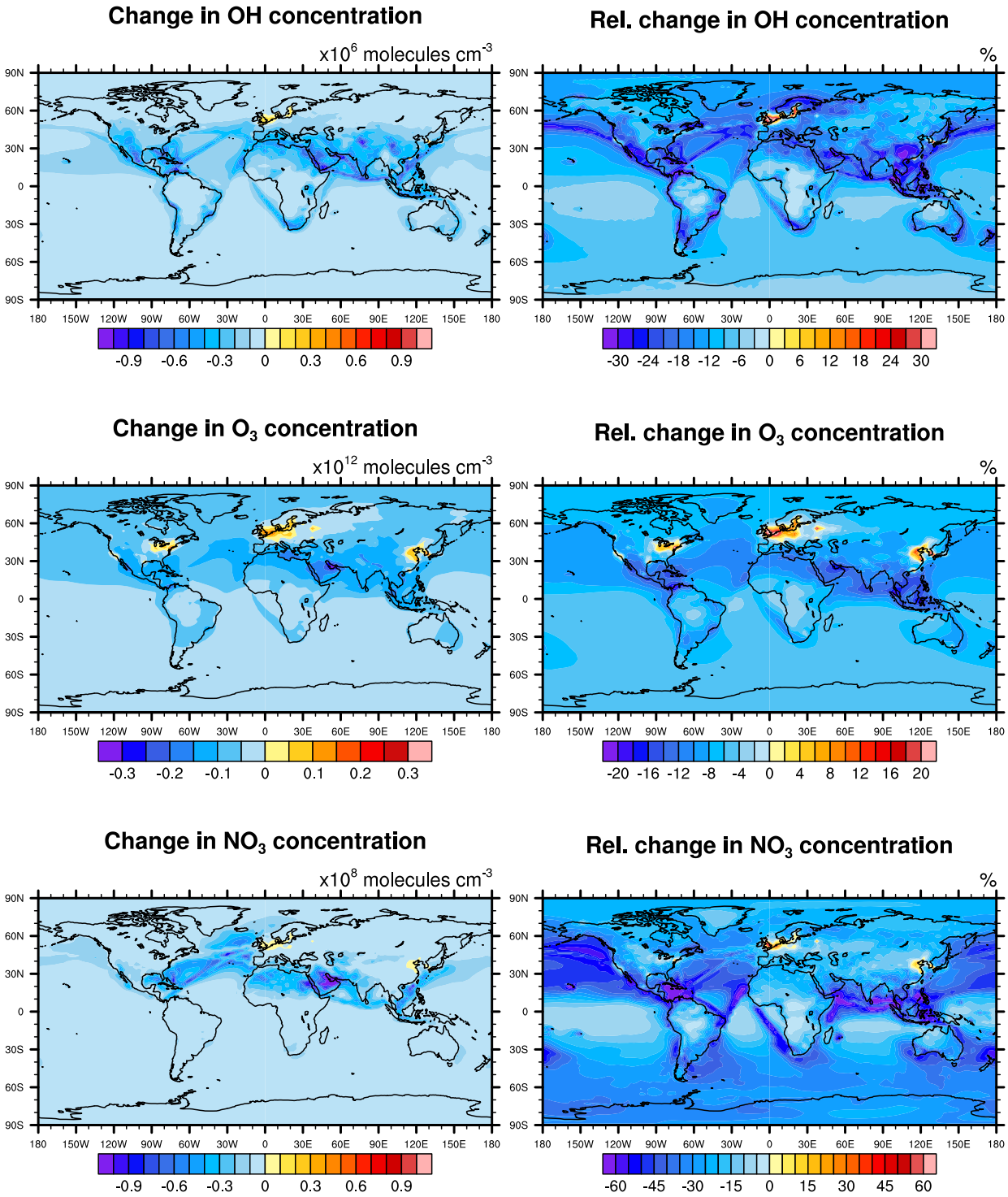

Figure S2. Absolute (left column) and relative (right column) changes of simulated annual mean surface OH ($\times 10^6$ molecules cm^{-3}), O_3 ($\times 10^{12}$ molecules cm^{-3}) and NO_3 concentrations ($\times 10^8$ molecules cm^{-3}) in the sensitivity run compared to the control run using VBS_agHigh scheme. Data are averaged from 2005 to 2009. Note that the range of color bars are different in each subplot.

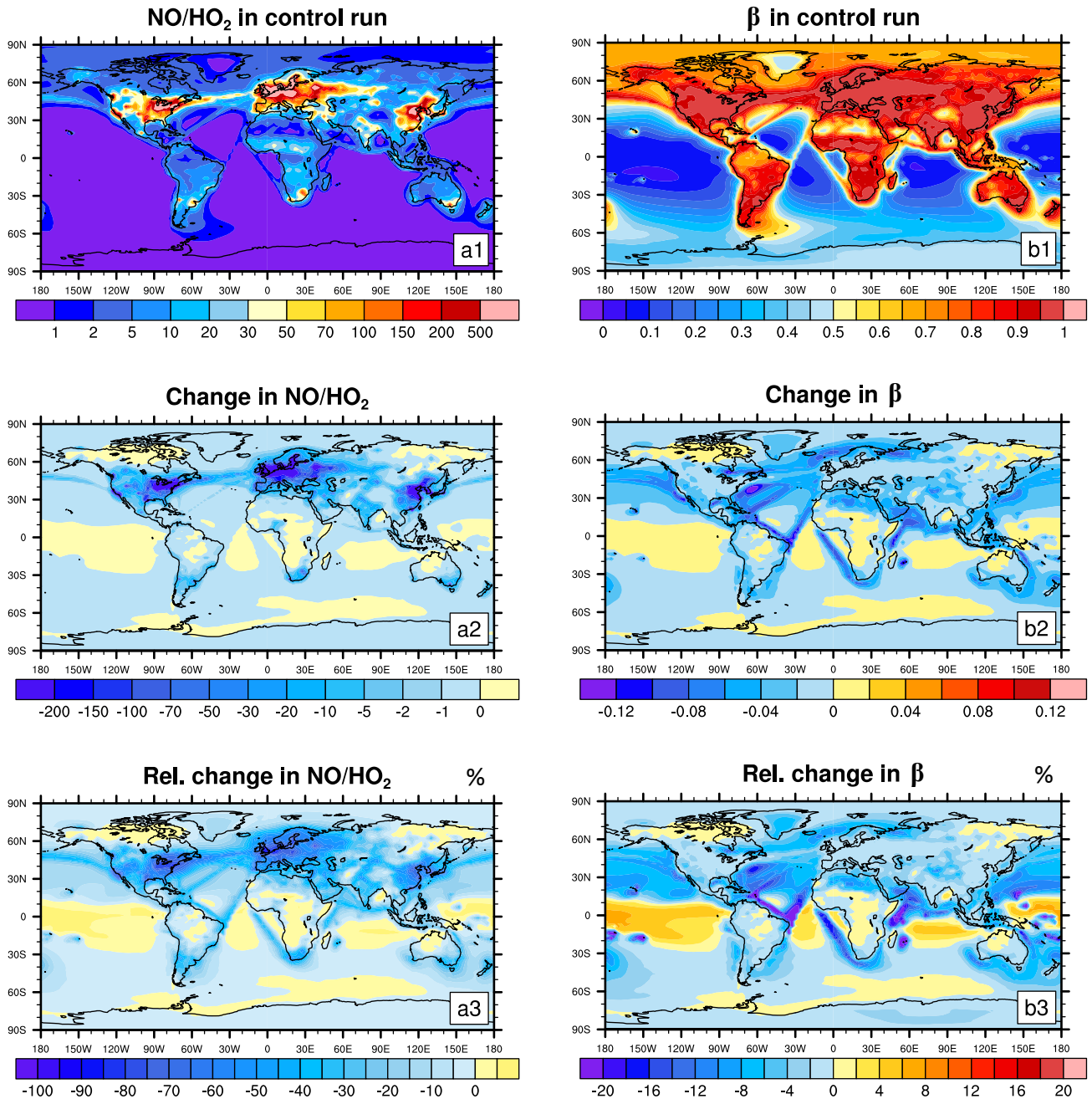

Figure S3. Left column: (a1) is the annual mean surface NO-to-HO_2 ratio (NO/HO_2) in the control run; (a2) and (a3) are the absolute and relative change of NO/HO_2 in the sensitivity run compared to the control run. Right column is similar to the left column but for annual mean surface branching ratio (β). Simulations use VBS_agHigh scheme. Data are averaged from 2005 to 2009. Note that the range of color bars are different in each subplot.

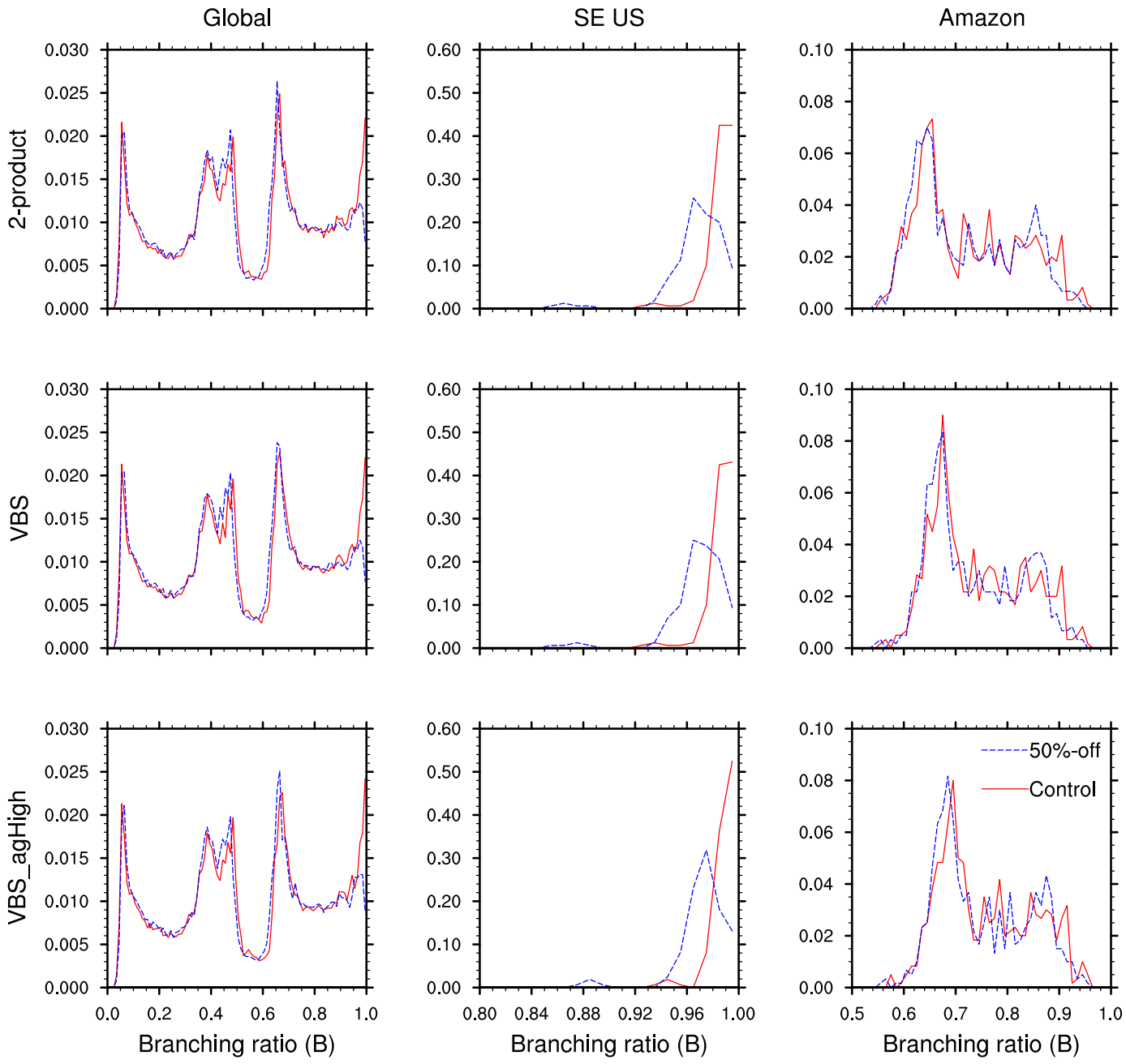

Figure S4. Probability density function of annual mean surface branching ratio (β) at global scale, in the southeast US and in the Amazon.

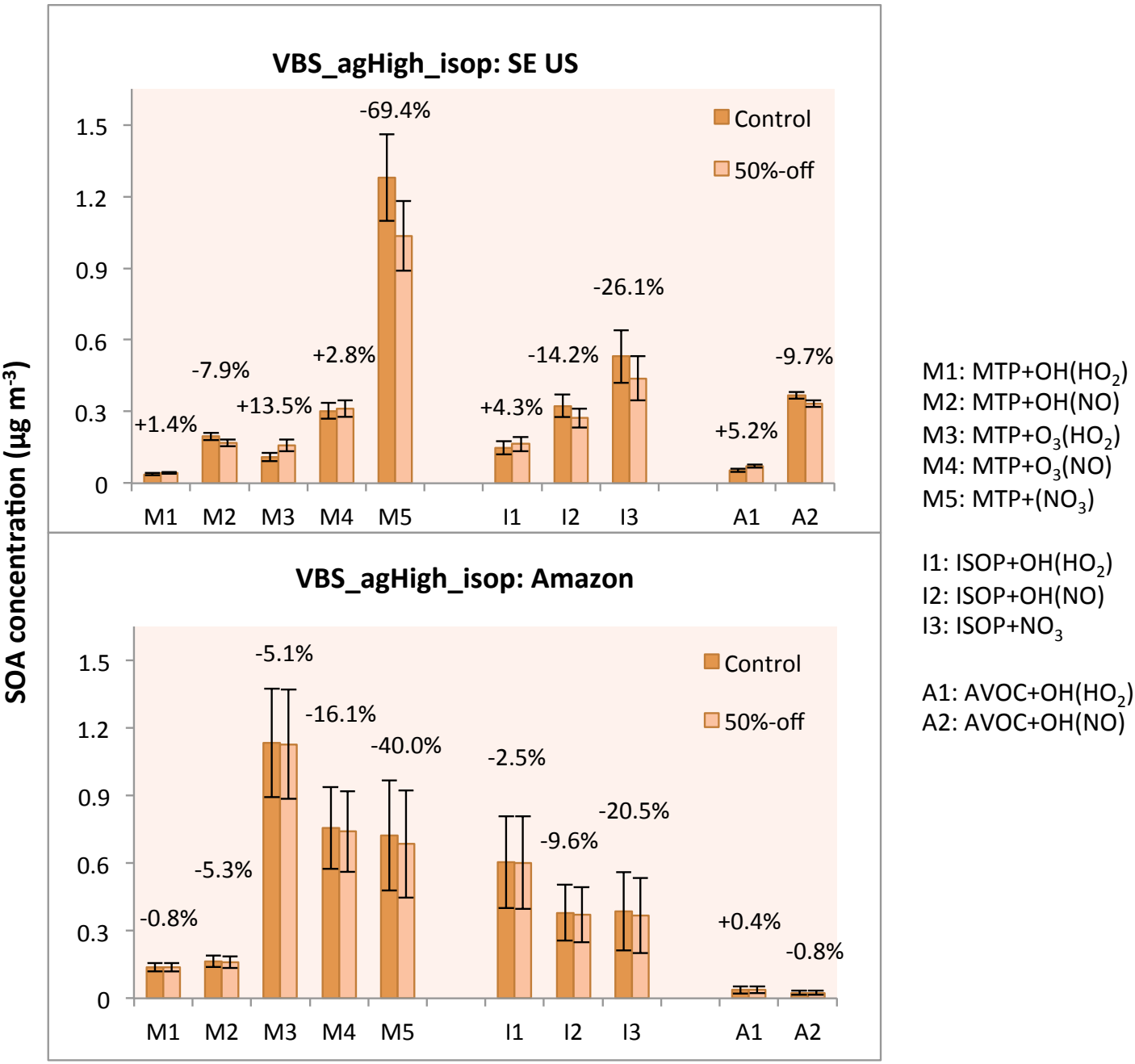

Figure S5. Annual mean surface SOA concentration (μg m^{-3}) in the control run and the sensitivity run (with 50% anthropogenic NO emission off) from different pathways using the VBS_agHigh_isop scheme, averaged over the southeast U.S. [32°-40°N, 95°-77°W] and the Amazon [17°S-5°N, 77°-55°W]. The numbers 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.