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Simulating secondary organic aerosol in a regional air quality model using the statistical oxidation model – Part 1: Assessing the influence of constrained multi-generational ageing

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Table S.1: Details of the chemical transport model and modeling system used in this work.

Domain	California	Eastern US
Resolution	24 km, nested 8 km	36 km
Grid cells	44 x 43; 63 x 30	65 x 65
Time Period	July 15 - Aug 2, 2005	Aug 15 - Sep 2, 2006
Meteorology	WRF v3.4 run with NAM reanalysis data	
Emissions	Anthropogenics: CARB (2000) Wildfires: NCAR Biogenics: MEGAN Gridded using UCD emissions processor	Anthropogenics+Wildfires: NEI (2005) Biogenics: MEGAN Gridded using SMOKE version 2.5
Gas-phase mechanism	SAPRC-11 (Carter and Heo, 2013)	
Inorganics	ISORROPIA (Nenes et al., 1998)	
Initial/Boundary conditions	MOZART-NCEP (Emmons et al., 2010)	
SOA model	2-product model, acid-catalyzed SOA from isoprene, oligomerization, (Carlton et al., 2010)	

Table S.2: SAPRC-11 model species, surrogate molecules and BaseM parameters for two-product model.

SAPRC-11 Species	Descriptor	Surrogate to determine BaseM fits	NO_x	*Kp*		α		Reference
ALK_C06	Long alkanes	*n*-dodecane	Low	0.200	0.010	0.001	0.016	Loza et al. (2014)
			High	0.200	0.010	0.000	0.018	
ALK_C07	Long alkanes	*n*-dodecane	Low	0.200	0.010	0.000	0.028	Loza et al. (2014)
			High	0.200	0.010	0.001	0.035	
ALK_C08	Long alkanes	*n*-dodecane	Low	0.200	0.010	0.000	0.088	Loza et al. (2014)
			High	0.200	0.010	0.005	0.084	
ALK_C09	Long alkanes	*n*-dodecane	Low	0.200	0.010	0.003	0.147	Loza et al. (2014)
			High	0.200	0.010	0.013	0.105	
ALK_C10	Long alkanes	*n*-dodecane	Low	0.200	0.010	0.009	0.232	Loza et al. (2014)
			High	0.200	0.010	0.029	0.217	
ALK_C11	Long alkanes	*n*-dodecane	Low	0.200	0.010	0.018	0.341	Loza et al. (2014)
			High	0.200	0.010	0.041	0.250	
ALK_C12	Long alkanes	*n*-dodecane	Low	0.200	0.010	0.035	0.447	Loza et al. (2014)
			High	0.200	0.010	0.048	0.279	
ALK_C13	Long alkanes	*n*-dodecane	Low	0.200	0.010	0.083	0.441	Loza et al. (2014)
			High	0.200	0.010	0.047	0.228	
Benzene	Benzene	Benzene	Low	0.283	0.026	0.281	0.127	Ng et al. (2007)
			High	100.000	0.013	0.074	0.642	
ARO1	High-yield aromatics	Toluene	Low	0.215	0.001	0.617	0.001	Zhang et al. (2014)
			High	18.502	0.023	0.021	0.537	
ARO2	Low-yield aromatics	*m*-xylene	Low	0.269	0.111	0.322	0.080	Ng et al. (2007)
			High	0.160	0.001	0.078	0.001	
Isoprene	Isoprene	Isoprene	Low	5.434	0.008	0.021	0.594	Chhabra et al. (2011)
			High	0.136	0.003	0.004	0.409	
TRP1/SESQ	Terpenes	α-pinene	Low	100.000	0.004	0.102	0.671	Chhabra et al. (2011), Griffin et al. (1999)
			High	0.549	0.009	0.046	0.489	

Cascading Oxidation Model (COM)

The Cascading Oxidation Model (COM) is based on the implementation of the multi-generational oxidation scheme in Baek et al. (2011). It is described in Table S.2 and can be demonstrated using the following example. In the Base model, benzene formed two semi-volatile products under high NO_x conditions (low-volatility product SV_BNZ1 and high-volatility product SV_BNZ2) and one non-volatile product under low NOx conditions (SV_BNZ3). Under the multi-generational oxidation scheme, the vapors of the high-volatility product, SV_BNZ2, were allowed to react with the OH radical using the same reaction rate constant as the parent (in this case, benzene) to form the low-volatility product, SV_BNZ1. In turn, the vapors of the low-volatility product, SV_BNZ1, were allowed to react with the OH radical using the same reaction rate constant as the parent to the non-volatile product SV_BNZ3. The scheme was extended for all the Base model species.

Table S.3: Reactions added to SAPRC-11 to model multi-generational oxidation of SOA. For consistency, the names of the SAPRC-11 model species and the Base model species are kept the same as those described in CMAQ v4.7[1]. The species SV_ALK2, SV_ISO4, SV_TRP3 and SV_SQT2, denoted with an asterisk, are new non-volatile species added to SAPRC-11.

VOC	SAPRC-11 model species	Semi-volatile Base model species	Multi-generational aging reactions added to SAPRC11
Alkanes	ALK5	SV_ALK	SV_ALK + OH = SV_ALK2*
Benzene	BENZENE	SV_BNZ1, SV_BNZ2	SV_BNZ2 + OH = SV_BNZ1 SV_BNZ1 + OH = SV_BNZ3
High-yield aromatics	ARO1	SV_TOL1, SV_TOL2	SV_TOL2 + OH = SV_TOL1 SV_TOL1 + OH = SV_TOL3
Low-yield aromatics	ARO2	SV_XYL1, SV_XYL2	SV_XYL2 + OH = SV_XYL1 SV_XYL1 + OH = SV_XYL3
Isoprene	ISOPRENE	SV_ISO1, SV_ISO2	SV_ISO1 + OH = SV_ISO2 SV_ISO2 + OH = SV_ISO4*
Terpenes	TRP1	SV_TRP1, SV_TRP2	SV_TRP2 + OH = SV_TRP1 SV_TRP1 + OH = SV_TRP3*
Sesquiterpenes	SESQ	SV_SQT	SV_SQT + OH = SV_SQT2*

For the South Coast Air Basin (SoCAB), the organic aerosol (OA) predictions from the COM simulation were modestly higher than the Base simulation (predicted mean at STN sites increased from 5.5 μg m^{-3} to 8.1 μg m^{-3} and that at IMPROVE sites increased from 2.4 μg m^{-3} to 4.6 μg m^{-3}), bringing the model-measurement comparison (aggregated across three STN and three IMPROVE sites) within the 'good model performance' criteria set by EPA (fractional bias $<\pm35\%$ and fractional error$<50\%$) [2]. In SoCAB, OA was dominated by POA and hence changes in OA concentrations were modest despite a factor of 4 to 8 increase in secondary organic aerosol (SOA) concentrations. In contrast, the OA predictions from the COM simulation for the eastern US changed substantially; predicted mean at STN sites increased from 2.8 μg m^{-3} to 7.6 μg m^{-3} and that at IMPROVE sites increased from 2.3 μg m^{-3} to 7.4 μg m^{-3}. However, that change did not lead to an improvement in the model-measurement comparison, i.e. the fractional bias changed from a large negative bias (-48%) to a large positive bias (36%) and had no effect on the fractional error.

Table S.4: Domain- and episode-averaged SOA concentrations in µg m^{-3} from different precursors for the BaseM and SOM simulations for SoCAB and the eastern US. The direction of the arrow shows increase (up arrow), no change (horizontal arrow) or decrease (down arrow) in averaged SOA concentrations for the SOM simulations relative to the BaseM simulations.

SOA precursor	SoCAB		Eastern US	
	BaseM	SOM	BaseM	SOM
Alkanes	0.001	0.003 ↑	0.009	0.021 ↑
Aromatics	0.037	0.047 ↑	.110	0.112 →
Isoprene	0.066	0.043 ↓	.166	0.150 ↓
Monoterpenes	0.227	0.149 ↓	.521	0.400 ↓
Sesquiterpenes	0.043	0.044 →	.297	0.342 ↑

Thermodenuder Model

The model of Cappa and Jimenez (2010)[3] was used to simulate evaporation of SOA particles in a thermodenuder (TD). The TD design considered here used a plug flow residence time of 30 seconds in the heated section and 15 seconds in the denuder section. In the heated section the temperature increased from 25 C to the target temperature in 6 seconds. Cooling in the heated section began 80% of the way through the heated section. Vapors were assumed to be lost to the walls of the denuder section only. Monodisperse particles were assumed with an initial diameter of 120 nm. The accommodation coefficient was assumed to be unity, and the diffusivity of the evaporating molecules was assumed to be 3.9 x 10^{-5} m^2 s^{-1}. Evaporation from the particles was treated dynamically. The SOA concentration at 25 C was assumed in all simulations to be 1 µg m^{-3}.

Acknowledgements

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