### SUPPORTING INFORMATION

### **SECTION S-1**

### -SOA Partitioning Model

The SOA treatment in CMAQv4.3 through v4.6 has been previously described in detail [1-3]. Briefly, the aerosol concentration of each of the *n* partitioning compounds,  $c_{aer,i}$ , formed from the SOA precursors shown in Table 1, is calculated for given values of  $c_{t,i}$  and  $c_{poc}$  at temperature T using the relationships

$$c_{aer,i} = c_{t,i} - c_i^* \frac{\frac{C_{aer,i}}{MW_i}}{\sum_{j=1}^n \frac{C_{aer,j}}{MW_j} + \frac{C_{POC}}{MW_{POC}} + \sum_{j=1}^k \frac{C_{aer,j}}{MW_j} \quad \text{for } i = 1, n \quad (S.1)$$

$$\frac{1}{c_i^*} = K_{om,i}(T) = K_{om,i}(T_{exp}) \frac{T}{T_0} \exp\left[\frac{\Delta H_{vap,i}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$
(S.2)

where  $c_{t,i}$  is the sum of the  $c_{aer,i}$  and  $c_{gas,i}$ , latter of which is the gas concentration. The concentration and molecular weight of the primary organic carbon aerosol are  $c_{poc}$  and  $MW_{poc}$ , respectively. The saturation concentration,  $c_i^*(T)$ , is defined by the Clausius-Clapeyron equation S.2. R is the ideal gas constant and  $T_0$  is the reference temperature. The molecular weights of the SOA compounds,  $MW_i$ , formed from each of the precursors, were estimated by multiplying the carbon mass of each of the precursor hydrocarbons by the OM/OC ratio (Table 1) measured in the laboratory by Kleindienst et al. [4]. The temperature-dependent partitioning between the gas and aerosol phases is controlled by the enthalpies of vaporization,  $\Delta H_{vap,i}$ , shown in Table 1. In these calculations, it is assumed the partitioning is not affected by the liquid water contents of the aerosol and surface adsorption can be neglected. In addition, all activity coefficients are assumed to be unity.

### -SOA Parameters

The  $\alpha$  and C\* values for monoterpene and sesquiterpene derived SOA, as reported by Griffin et al., (1999) [5] have been re-derived in this work to account for recent laboratory measurements that indicate the density of this SOA is 1.3 g cm<sup>-3</sup> [6-10] not 1.0 g cm<sup>-3</sup> as assumed in the calculation of the original parameters. In the original CMAQv4.7 release  $\alpha_{TRP}$  and  $\alpha_{SESQ}$  values from Griffin et al. were scaled up by 30%. We now realize that it is more accurate to derive new stoichiometric yields ( $\alpha$ ) and partitioning parameters (K<sub>om</sub> or C\*) from data in which *both* Y and M<sub>o</sub> are corrected using current information on SOA density.

The original SMPS-measured data from Griffin et al. [5] and Hoffmann et al. [11] has been corrected for density ( $\rho$ ) and new  $\alpha$  and C\* were derived from that  $\rho$ -corrected data. In the new fit, the ratio of  $C_1^*/C_2^*$  was fixed to be the same  $C_1^*/C_2^*$  value obtained in the original by Griffin et al., in order to maintain a similar distribution in the high and low volatility products. Otherwise, best fit methods derived products with similar volatility instead of providing high and

low volatility products. This fitting method was tested was by re-creating fits for the original data [5] for individual monoterpenes (see Table S-1). The following corrections to that data were required before fitting methods converged:

- 1.) For limonene, the yield value from the data point where  $M_o = 192.3 \ \mu g \ m^{-3}$  (present in Figure 3 of Reference [5] )was added from Hoffmann et al. [11]
- 2.) We excluded the  $\beta$ -carophylene data from Hoffmann, as it was not included in the original fit, though it is starred in Table 3 of Reference [5].
- 3.) There is a discrepancy in the  $\alpha$ -humulene data between Figure 4 and Table 2a of Reference [5]. The yield values at 2 points (Mo = 59.2 µg m<sup>-3</sup> and 54.2 µg m<sup>-3</sup>) were taken from the Table and not the Figure, as this was the case in the original fit.

The tabulated  $K_{OM}(1/C^*)$  values of  $\alpha$ -humulene and  $\beta$ -carophylyllene are averaged using 50:50 weighting factors and the methodology of Bian and Bowman [12], assuming  $M_0 = 10 \ \mu g \ m^{-3}$ , to obtain single C\* value for SOA derived from all sesquiterpenes  $K_{OM}(1/C^*)$  values for monterpenes were determined using the same method. The monoterpene weighting factors, listed in Table S2, are emission-based.

# **SECTION S-2**

# -Gas Phase Chemistry

The SAPRC-99 gas-phase chemical mechanism was revised to incorporate the new SOA module, with the new reactions and species listed in Table S2. The chemical mechanism of ARO1 (b1OH) was modified by adding a peroxy-radical operator (ARO1RO2), with a product yield equal to that of RO2\_R. To implement the dependency of SOA formation on the availability of NO<sub>x</sub>, two reactions of ARO1RO2 were added (AR1N and AR1H). ARO1RO2 can react with either NO to produce TOLNRXN or HO2 to produce TOLHRXN. The counter species TOLNRXN and TOLHRXN are used to track the contributions of the aromatic peroxy radical with NO and HO2, respectively.

A gas phase mechanism for BENZENE (BENZ) was explicitly added to the SAPRC-99 mechanism. In addition, a peroxy-radical operator (BENZRO2) was added which can react with either NO to produce BENZNRXN or HO2 to produce BENZHRXN (BNZN and BNZH). The mechanism of ARO2 (b2OH) was modified by adding a peroxy-radical operator (ARO2RO2) which can also react with either NO to produce XYLNRXN or HO2 to produce XYLHRXN. BNZNRXN, BNZHRXN, XYLNRXN, and XYLHRXN serve as counter species.

The reactions of monoterpene (TRP1) with OH, O3, NO3, and O3P were modified to add counter species TERPRXN (t1OH, t1O3, t1N3, t1OP). Sesquiterpene (SESQ) is not, at present, a chemical species in SAPRC99. To estimate SOA from SESQ, three chemical reactions were added (SSO3, SSOH, and SSN3); each reaction produces the SESQRXN counter species. To estimate SOA from isoprene, the reaction of ISOPRENE with OH was modified to add the counter species ISOPRXN (isOH), while the reaction of ALK5 with OH was modified to add the counter species ALK5RXN (a5OH). The addition of any counter species or any peroxy radical operator does not affect the ozone chemistry.

## **SECTION S-3**

### -Boundary Concentrations

The significant changes to the chemical mechanism required updates to the standard boundary concentrations used in CMAQ. Boundary concentrations for the following species categories are required: anthropogenic SOA; biogenic SOA; semivolatile species associated with each particulate; gas phase precursors; and inorganic particulates. Note that concentrations at the boundary for cloud-produced SOA were set to zero because average background values are poorly constrained.

The boundary concentrations for the non-oligomeric aromatic SOA were based on the global modeling results reported by Henze et al. (2008) [13]. The boundary concentrations for alkane SOA and anthropogenic oligomers were based on the ratios of the concentrations of alkane SOA and anthropogenic oligomer SOA to the concentrations of aromatic SOA in the domain interior under clean boundary conditions. Similarly, the boundary concentrations of non-oligomeric monoterpenes, non-acid catalyzed isoprene, and sesquiterpenes SOA were computed based on global modeling work of Chung and Seinfeld (2002) [14] and Liao et al. (2007) [15]. Acid-catalyzed SOA isoprene and biogenic oligomer concentrations were scaled in the same manner as done above.

The boundary semivolatile species associated with each SOA species were calculated, assuming equilibrium between the gas and aerosol phases, using the equation:

$$c_{gas,i} = \frac{c_{aero,i}}{c_{POA} + \sum_{j=1}^{N} c_{aero,i}} c_{i}^{*}(T)$$
(S.3)

where  $c_{poa}$  is the mass of primary organic aerosol, estimated to be 0.150 µg/m<sup>3</sup> from global modeling results (Chung and Seinfeld, 2002), [14].

The impacts of the gas phase precursor boundary concentrations on the monoterpene, isoprene, and benzene concentrations were investigated. It was determined that, due to their high reactivity, monoterpene and isoprene concentrations have no discernable impact, as their concentrations decreased by several orders of magnitude within 100 km from the border. On the other hand, benzene boundary concentrations did significantly impact their levels within the domain. To account for this influence, the benzene boundary concentration was set to 44.5 ppt based on field measurements of air toxics in remote locations [16].

Boundary concentrations for inorganic particulate species were the same as those used in previous CMAQ calculations. However, boundary concentrations for the particle number and surface area were recalculated based on the new SOA species.

For species without vertical profile information, the concentration profiles M(z) were estimated, using known surface concentration M(0), using

$$M(z) = M(0)e^{(-z/H_p)}$$
 (S.4)  
3

where the scale height,  $H_p$ , is 900 m and 730 m for the marine and remote continental environments, respectively.

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SQT		$\alpha_1$	$\alpha_2$	<b>K</b> 1	K2	Residual
β-caryophyllene	Griffin/Hoffman	1.00		0.0416		0.0053
	initial best fit:1	1.18		0.0266		0.0013
	product model	1.52.62.6		0.00045		0.000105
	final values	1.53696		0.02047		0.002185
$\alpha$ -humulene	Griffin/Hoffman	1.00		0.0501		0.01875
	initial best fit:1 product model	1.25394		0.0313		0.0095
	final values	1.63012		0.02409		0.016094
TERP						
$\alpha$ -pinene	Griffin/Hoffman	0.0380	0.3260	0.1710	0.0040	0.000105
	initial best fit: 2 product model	0.0127	0.2274	1.9891	0.0102	0.000101
	fixed <sup>K1</sup> / <sub>K2</sub> best fit	0.02068	0.23755	0.35389	0.00827	0.00009
	final values	0.02689	0.30882	0.27222	0.00636	0.000153
β-pinene	Griffin/Hoffman	0.1300	0.4060	0.0440	0.0049	0.00169
	initial best fit: 2 product model	0.37694	0.0400	0.0219	0.0050	0.000164
	fixed <sup>K1</sup> / <sub>K2</sub> best fit	0.13701	0.41211	0.04112	0.00457	0.001688
	final values	0.17812	0.53575	0.03163	0.0051	0.002852
$\Delta^3$ -carene	Griffin/Hoffman	0.0540	0.5170	0.0430	0.0042	0.000948
	initial best fit: 2 product model	0.2296	0.2296	0.0077	0.0077	0.00100
	fixed <sup>K1</sup> / <sub>K2</sub> best fit	0.15756	0.58504	0.01924	0.00189	0.000897
	final values	0.20482	0.76055	0.01480	0.00145	0.001516
limonene	Griffin/Hoffman	0.2390	0.3630	0.0550	0.0053	0.00043
	initial best fit: 2 product model	0.22379	0.22379	0.02719	0.02719	0.00016
	fixed <sup>K1</sup> / <sub>K2</sub> best fit	0.44759		0.02719		0.000163
	final values	0.58186		0.02092		0.000275
sabinene	Griffin/Hoffman	0.0670	0.3990	0.2580	0.0038	0.000051
	initial best fit: 2 product model	0.09466	0.09466	0.04163	0.04163	0.000296
	fixed <sup>K1</sup> / <sub>K2</sub> best fit	0.06010	0.38332	0.30249	0.004455	0.000045
	final values	0.07813	0.49831	0.23269	0.00343	0.000077

Table S-1. Parameter ( $\alpha$  and K) values for individual sesquiterpenes and monoterpenes.

Table S-2. Final parameters for lumped CMAQ species

	<b>≜</b>				
		$\alpha_1$	<b>A</b> 2	C*1	C*2
SQT	revised CMAQ values	1.537		24.984	
	original CMAQv4.7	1.300		12.193	
TERP	revised CMAQ values	0.1393	0.4542	14.7922	133.7297
	original CMAQv4.7	0.1123	0.5013	7.466	110.77

Note: The original CMAQv4.7 values are currently employed in the public version of CMAQv4.7's orgaer5.f subroutine. Revised values will be implemented in the next public release of CMAQ scheduled for 2011.

 Table S-3. Biogenic SOA weighting factors

Compound	Weighting	$\alpha_1$	K <sub>om,1</sub>	$\alpha_2$	K <sub>om,2</sub>
	factor				
α-pinene	0.40	0.38	0.171	0.326	0.0040
β-pinene	0.25	0.13	0.44	0.406	0.0049
$\Delta^3$ -carene	0.15	0.054	0.043	0.517	0.0042
sabinene	0.10	0.067	0.258	0.399	0.0038
limonene	0.10	0.239	0.055	0.363	0.0053

A value of  $M_0 = 10 \ \mu g \ m^{-3}$  was used in the lumping equation of Bian and Bowman [12].

Reaction	Reaction	Rate constant
number		
b1OH	ARO1 + OH = Products + <b>0.765*ARO1RO2</b>	$1.81*10^{-12}e^{355/T}$
AR1N	ARO1RO2 + NO = NO + TOLNRXN	$2.70*10^{-12}e^{360/T}$
AR1H	ARO1RO2 + HO2 = HO2 + TOLHRXN	$1.90*10^{-13}e^{1300/T}$
BENZ	<b>BENZENE + OH = Products + 0.764*BENZRO2</b>	$2.47 * 10^{-12} e^{-206/T}$
BNZN	BENZRO2 + NO = NO + BNZNRXN	$2.70*10^{-12}e^{360/T}$
BNZH	BENZRO2 + HO2 = HO2 + BNZHRXN	$1.90 * 10^{-13} e^{1300/T}$
b2OH	ARO2 + OH = Products + <b>0.804*ARO2RO2</b>	$2.64 * 10^{-11}$
AR2N	ARO2RO2 + NO = NO + XYLNRXN	$2.70 * 10^{-12} e^{360/T}$
AR2H	ARO2RO2 + HO2 = HO2 + XYLHRXN	$1.90*10^{-13}e^{1300/T}$
t1OH	TRP1 + OH = Products + TRPRXN	$1.83 * 10^{-11} e^{449/T}$
t1O3	TRP1 + O3 = Products + TRPRXN	$1.08 * 10^{-15} e^{-821/T}$
t1N3	TRP1 + NO3 = Products + TRPRXN	$3.66 * 10^{-12} e^{175/T}$
t1OP	TRP1 + O3P = Products + TRPRXN	$3.27 * 10^{-11}$
SSO3	SESQ + O3 = O3 + SESQRXN	$1.16*10^{-14}$
SSOH	SESQ + OH = OH + SESQRXN	$1.97 * 10^{-10}$
SSN3	SESQ + NO3 = NO3 + SESQRXN	$1.90 * 10^{-11}$
isOH	ISOPRENE + OH = Products + <b>ISOPRXN</b>	$2.50*10^{-11}e^{408/T}$
a5OH	ALK5 + OH = Products + ALK5RXN	$1.11*10^{-11}e^{-52/T}$

 Table S-2. Reactions and Operators added to SAPRC to accommodate new SOA mechanism.

Bolded species are new to the condensed SAPRC-99 treatment implemented inCMAQv4.7.

<b>Reaction</b>	Reaction	Rate constant
R128	TOL + OH = Products + <b>0.765*TOLRO2</b>	$1.80x10^{-12}e^{355/T}$
SA01	TOLRO2 + NO = NO + TOLNRXN	$2.70*10^{-12}e^{360/T}$
SA02	TOLRO2 + HO2 = HO2 + TOLHRXN	$1.90 * 10^{-13} e^{1300/T}$
SA05	<b>BENZENE + OH = Products + 0.764*BENZRO2</b>	$2.47 * 10^{-12} e^{-206/T}$
SA06	BENZRO2 + NO = NO + BNZNRXN	$2.70*10^{-12}e^{360/T}$
SA07	BENZRO2 + HO2 = HO2 + BNZHRXN	$1.90 * 10^{-13} e^{1300/T}$
R138	XYL + OH = Products + <b>0.804*XYLRO2</b>	$1.70x10^{-11}e^{116/T}$
SA03	XYLRO2 + NO = NO + XYLNRXN	$2.70 * 10^{-12} e^{360/T}$
SA04	XYLRO2 + HO2 = HO2 + XYLHRXN	$1.90 * 10^{-13} e^{1300/T}$
R150	TERP + OH = Products + TRPRXN	$1.50x10^{-11}e^{449/T}$
R151	TERP + O3 = Products + TRPRXN	$1.25 x 10^{-15} e^{-821/T}$
R152	TERP + NO3 = Products + <b>TRPRXN</b>	$3.70x10^{-12}e^{175/T}$
R149	TERP + O = Products + TRPRXN	$3.60x10^{-11}$
SA08	SESQ + O3 = O3 + SESQRXN	$1.16*10^{-14}$
<b>SA09</b>	$\mathbf{SESQ} + \mathbf{OH} = \mathbf{OH} + \mathbf{SESQRXN}$	$1.97 * 10^{-10}$
SA10	SESQ + NO3 = NO3 + SESQRXN	$1.90 * 10^{-11}$
R142	ISOP + OH = Products + ISOPRXN	$2.54 x 10^{-11} e^{407.6/T}$

Table S-3. Reactions and Operators added to CB05 to accommodate new SOA mechanism.

Bolded species are new to the condensed CB-05 treatment implemented inCMAQv4.7.



**Figure S-1. Schematic of CMAQv4.6 SOA model.** There is no volatility distribution and all SOA species are treated as semi-volatile. Double headed arrows across the gas/particle interface represent the equilibrium partitioning of semi-volatile SOA species.



Figure S-2. Locations of monitoring sites used in this evaluation. Note that these are sites that passed all screening criteria [2] and were used in the evaluation of  $OC_{sec}$  predictions



Figure S-3. Monthly-Averaged Anthropogenic SOA Predictions with CMAQv4.6 (top) and CMAQv4.6s (bottom row).



Figure S-4. Seasonally-averaged biogenic SOA Predictions with CMAQv4.6 (top row) and CMAQv4.6s (bottom).



**Figure S-5.** Comparison of mechanistic CMAQv4.6 and semi-empirical OC<sub>sec</sub> estimates (•). In all regions, but the west and west pacific, CMAQv4.6 OCsec predictions decrease in the summer, while observational-estimates attain maximum values during the same period.



**Figure S-6**. Comparison of mechanistic CMAQv4.6s and semi-empirical  $OC_{sec}$  estimates (•). There is a persistent negative bias in the CMAQ predictions, but seasonal trends are similar in all regions.