

# Modeling the Formation of Secondary Organic Aerosol (SOA) in 0-D Box model framework

Special topic presentation

Samiha Binte Shahid

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# Outline

- Motivation
- Creating a Secondary Organic Aerosol (SOA) Model in 0-D box model framework
- Parameters of SOA model
- Verification of the SOA model
- Future work and SOA model set-up

## Motivation

- SAPRC box model doesn't have aerosol model.
- Framework of 0-D Atmospheric modeling (F0AM) doesn't have a thermodynamic equilibrium gas-particle partitioning model.
- In the Thornton et al. 2018 paper, "A Near-Explicit Mechanism Evaluation of Isoprene Photochemical Secondary Organic Aerosol Formation and Evolution: Simulation of Multiple Chamber Experiments with and without Added NO<sub>x</sub>" they developed a kinetic SOA model that is incorporated with F0AM box model. This is more suitable for explicit mechanisms such as- The Master Chemical Mechanism (MCM), Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO).
- My future research work needs a thermodynamic equilibrium partitioning SOA model to use with condensed mechanism- SAPRC-07, SAPRC-18.

# Kinetic SOA model

## Gas-phase reaction file

Species\_0 + OH → Species\_1, k1  
Species\_1 + OH → Species\_2, k2  
Species\_2 + OH → Species\_3, k3  
Species\_3 + OH → Species\_4, k4

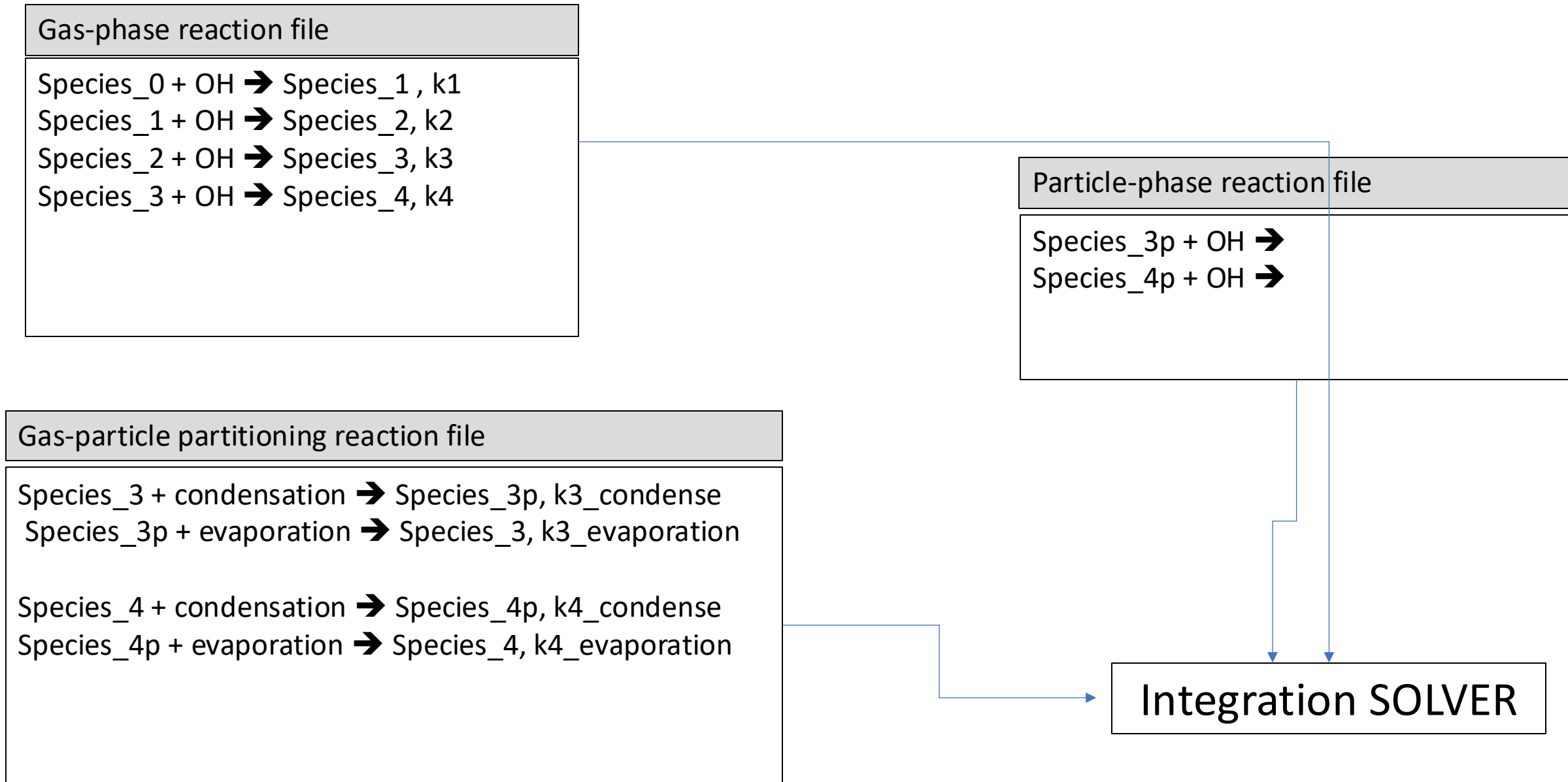
## Particle-phase reaction file

Species\_3p + OH →  
Species\_4p + OH →

## Gas-particle partitioning reaction file

Species\_3 + condensation → Species\_3p, k3\_condense  
Species\_3p + evaporation → Species\_3, k3\_evaporation  
  
Species\_4 + condensation → Species\_4p, k4\_condense  
Species\_4p + evaporation → Species\_4, k4\_evaporation

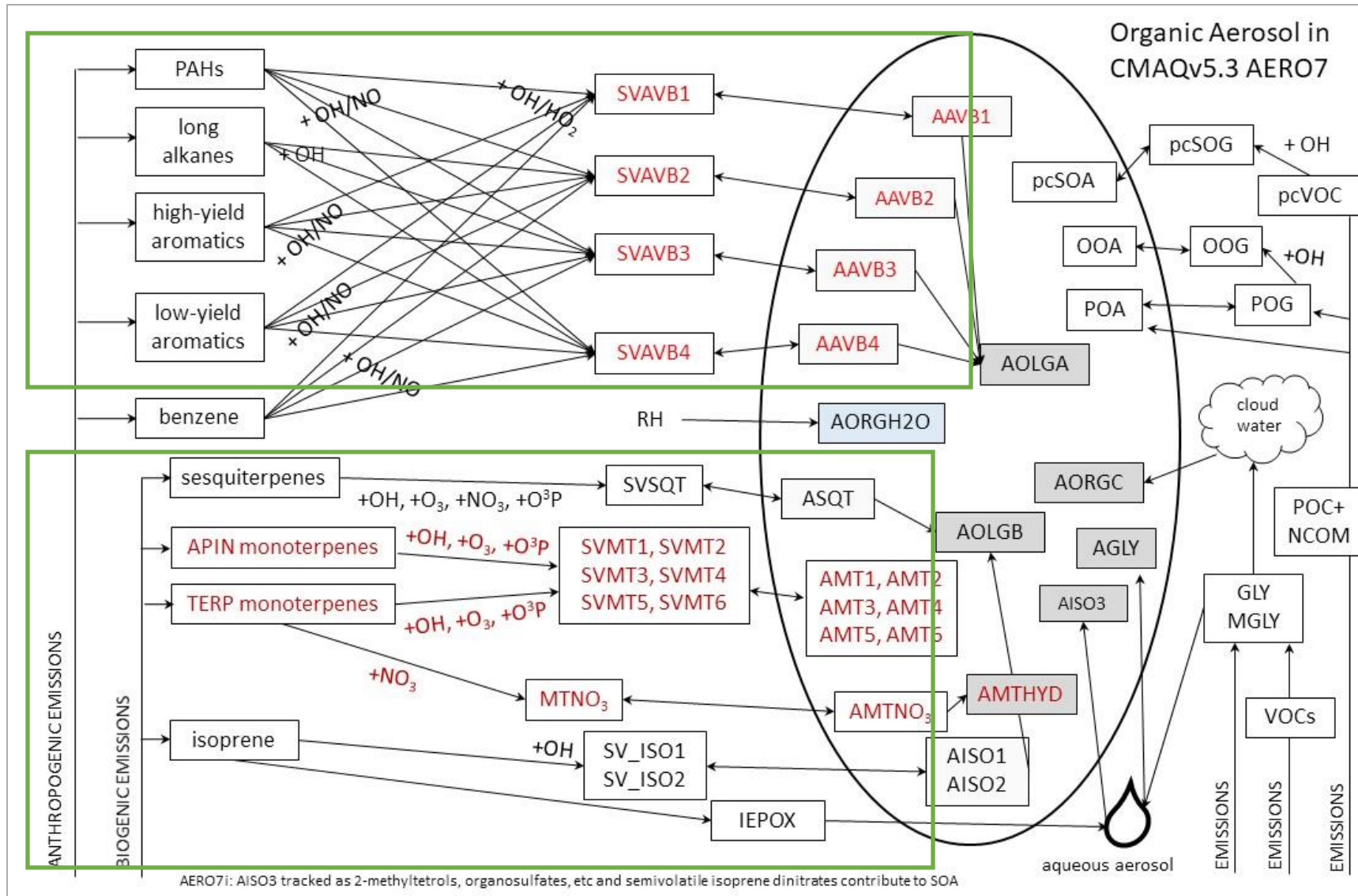
Integration SOLVER



## Creating a Secondary Organic Aerosol (SOA) Model in 0-D box model framework

- Thermodynamic equilibrium SOA model.
- Incorporated the CMAQ-AERO-07 SOA scheme and parameters.
- The concentration of reaction products resulting from VOC oxidation in the gas phase mechanism is time-dependent, and this information is fed into the Secondary Organic Aerosol (SOA) model. The SOA model then calculates the gas-particle partitioning of the reaction products and updates the gas-phase concentration accordingly. This updated information is then passed back to the gas-phase integration solver for further processing.
- The SOA model has been written in a way allows for easy updates to the SOA parameters. This ensures that the model can be adapted to new scheme and parameters.

# The F0AM-CMAQ Aerosol model Scheme



# The F0AM-CMAQ Aerosol model Scheme: Linking Gas-Phase mechanism to SOA model

- Reaction encounters are added to volatile organic compound (VOC) oxidation reaction which is passed on to the SOA model-

```
BENZ + OH = 0.116*OH + 0.29*R02C + 0.29*xH02 + 0.024*R02XC + 0.024*zRN03 + 0.57*H02 + 0.57*CRES + 0.116*AFG3 +  
0.29*xGLY + 0.029*xAFG1 + 0.261*xAFG2 + 0.314*yRA00H + -0.976*XC + BENZR02  
  
TOLUENE + OH = .181*H02 + .454*xH02 + .312*OH + .454*R02C + .054*R02XC + .054*zRN03 + .238*xGLY + .151*xMGLY +  
.181*CRES + .065*xBALD + .195*xAFG1 + .195*xAFG2 + .312*AFG3 + .073*yR600H + .435*yRA00H - .109*XC + TOLR02  
  
AR01 + OH = 0.166*H02 + 0.482*xH02 + 0.284*OH + 0.482*R02C + 0.068*R02XC + 0.068*zRN03 + 0.218*xGLY + 0.138*xMGLY  
+ 0.166*CRES + 0.049*xBALD + 0.164*xAFG1 + 0.193*xAFG2 + 0.284*AFG3 + 0.077*xPROD2 + 0.403*yRA00H + 0.147*yR600H +  
0.002*XC + TOLR02
```

- The concentration of product is directly passed on to the SOA model-

```
<AALK> SOAALK + OH = OH + 0.006*SVAVB2 + 0.052*SVAVB3 +  
0.081*SVAVB4 # 2.70e-12@-374;  
  
<AE51> BENZR02 + NO = NO + 0.034*SVAVB2 + 0.392*SVAVB4 # 1.0*K<BR07>;  
<AE52> BENZR02 + H02 = H02 + 0.146*SVAVB1 # 1.0*K<BR08>;
```

# The F0AM-CMAQ Aerosol model Scheme: SOA partitioning model parameters

```

107      Type( oa_type ), Save :: oa_list( n_oa_list ) = (/
108      !
109      !
110      !      PM      Vapor      Rxn Cntr      Alpha      CStar^      Enth-      O:C      OM:OC      ANTHROPOGENIC
111      !      Name      Name      Name*      alpy      POA      |      |      Nonvol-
112      !      -----      -----      -----      -----      -----      -----      -----      -----
167      & oa_type( 'AAVB1 ', 'SVAVB1 ', ' ', ' ', 0.0000, 0.010, 18.0E3, 1.227, 2.70, F, T, F, F ),
168      & oa_type( 'AAVB2 ', 'SVAVB2 ', ' ', ' ', 0.0000, 1.000, 18.0E3, .947, 2.35, F, T, F, F ),
169      & oa_type( 'AAVB3 ', 'SVAVB3 ', ' ', ' ', 0.0000, 10.000, 18.0E3, .803, 2.17, F, T, F, F ),
170      & oa_type( 'AAVB4 ', 'SVAVB4 ', ' ', ' ', 0.0000, 100.000, 18.0E3, .659, 1.99, F, T, F, F ),

147      & oa_type( 'ASQT ', 'SVSQT ', 'SESQRXN ', 1.5370, 24.9840, 40.0E3, .283, 1.52, F, F, T, F ),

125      & oa_type( 'AMT1 ', 'SVMT1 ', 'TRPRXN ', 0.040, 0.010, 102.0E3, .400, 1.67, F, F, T, F ),
126      & oa_type( 'AMT2 ', 'SVMT2 ', 'TRPRXN ', 0.032, 0.100, 91.0E3, .400, 1.67, F, F, T, F ),
127      & oa_type( 'AMT3 ', 'SVMT3 ', 'TRPRXN ', 0.032, 1.000, 80.0E3, .444, 1.72, F, F, T, F ),
128      & oa_type( 'AMT4 ', 'SVMT4 ', 'TRPRXN ', 0.103, 10.000, 69.0E3, .300, 1.53, F, F, T, F ),
129      & oa_type( 'AMT5 ', 'SVMT5 ', 'TRPRXN ', 0.143, 100.000, 58.0E3, .333, 1.57, F, F, T, F ),
130      & oa_type( 'AMT6 ', 'SVMT6 ', 'TRPRXN ', 0.285, 1000.000, 47.0E3, .200, 1.40, F, F, T, F ),
131      & oa_type( 'AMT7 ', 'SVMT7 ', 'TRPRXN ', 0.160, 10000.000, 36.0E3, .222, 1.43, F, F, T, F ),

```

- The parameters in SOA-partitioning model requires-  
alpha, cstar, enthalpy,  
molecular weight of the model  
species.



# SOA-Partitioning Model

$$VOC + OH = \alpha_1 P_1 + \alpha_2 P_2 + \dots + \alpha_n P_n$$

$$C_{tot,i} = \alpha_1 \frac{MW_i}{MW_{VOC}} \Delta VOC$$

$$C_{tot,i} = C_{aer,i} + C_{gas,i}$$

$$C_{aer,i} = C_{tot,i} - C_{gas,i}$$

$$C_{gas,i} = C_{sat,i} = C_{sat,i}^* \times X_{i,om}$$

$$C_{aer,i} = C_{tot,i} - C_{sat,i}^* \frac{C_{aer,i} / MW_i}{\sum_{j=1}^j (C_{aer,j} / MW_j) + C_{init} / MW_{init}}$$

$$C_{aer,i} = C_{tot,i} - C_{sat,i}^* \frac{C_{aer,i} / MW_i}{N}$$

$$C_{tot,i} = C_{aer,i} + C_{sat,i}^* \frac{C_{aer,i} / MW_i}{N}$$

$$C_{tot,i} = C_{aer,i} \left( 1 + \frac{C_{sat,i}^* / MW_i}{N} \right)$$

$$C_{aer,i} = C_{tot,i} \left( \frac{N \times MW_i}{N \times MW_i + C_{sat,i}^*} \right)$$

$$\frac{C_{aer,i}}{MW_i} = C_{tot,i} \left( \frac{N}{N \times MW_i + C_{sat,i}^*} \right)$$

# SOA-Partitioning Model

$$N = N_{other} + \sum_{i=1}^{i=i} C_{aer,i}/MW_i$$

$$f(N) = N_{other} - N + \sum_{i=1}^{i=i} C_{aer,i}/MW_i = 0$$

$$\frac{N_{other}}{N} - 1 + \sum_{i=1}^{i=1} \frac{C_{tot,i}}{C_{sat,i}^* + MW_i \times N} = 0$$

$$upb = \sum_{i=1}^{i=i} C_{tot,i}/MW_i$$

*lwb = Nonvolatile moles*

$$threshold = \sum_{i=1}^{i=1} \frac{C_{tot,i}}{C_{sat,i}^*}$$

# SOA-Partitioning Model

$$\frac{N_{other}}{N} - 1 + \sum_{i=1}^{i=1} \frac{C_{tot,i}}{C_{sat,i}^* + MW_i \times N} = 0$$

$$upb = \sum_{i=1}^{i=i} C_{tot,i} / MW_i$$

$lwb = \text{Nonvolatile moles}$

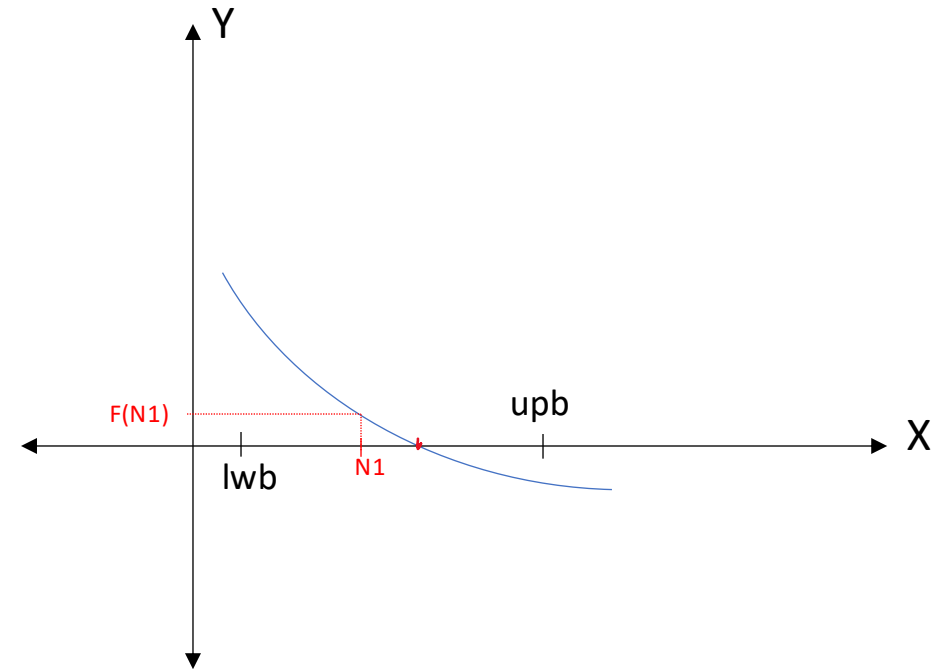
$$N1 = (lwb + upb) / 2$$

if  $f(N1)$  +ve:

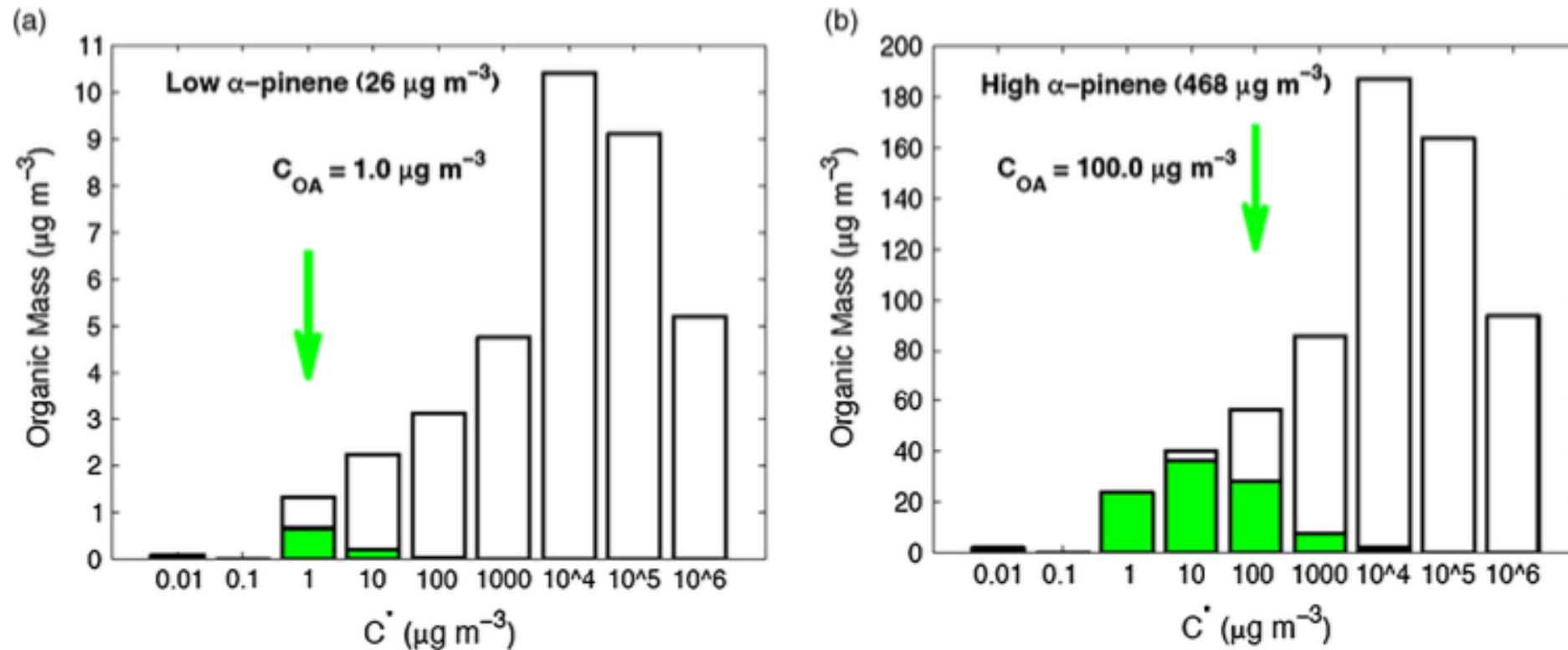
$$N2 = (N1 + upb) / 2$$

If  $f(N1)$  -ve:

$$N2 = (N1 + lwb) / 2$$



# SOA Model verification



**FIGURE 14.15** Increased condensation with increasing quantities of  $\alpha$ -pinene + ozone products, with the shaded portion of each bar showing the condensed-phase material and the remainder showing the material in the vapor phase: (a) partitioning when a relatively low concentration of  $\alpha$ -pinene is oxidized, resulting in  $1 \mu\text{g m}^{-3}$  of SOA mass or a fraction of SOA produced to  $\alpha$ -pinene consumed (the SOA yield) of 0.04; (b) partitioning with 18 times as much precursor, resulting in 100 times as much SOA and a SOA yield of 0.21. Note that the bin with 50:50 partitioning shifts to  $100 \mu\text{g m}^{-3}$ . (Source: Donahue, N. M., et al., *Atmos. Environ.* **43**, 94–106 (2009), Figure 1.)

# SOA Model verification

## Example: Partitioning in the VBS

To illustrate the process, let us consider SOA formation in the  $\alpha$ -pinene +  $O_3$  system. Let us assume that  $25 \mu\text{g m}^{-3}$  of  $\alpha$ -pinene is reacted and that for each  $1 \mu\text{g m}^{-3}$  reacted,  $1.47 \mu\text{g m}^{-3}$  of products result; this accounts for the mass increase owing to addition of oxygen. (The value is slightly different than the 1.4 used in Figures 14.13 and 14.14.) It is necessary to specify the fraction of the mass of reaction products in each volatility class to the total mass of 1.47. Say that this distribution is as follows:

$C^*$	0.01	0.1	1.0	10	100	$10^3$	$10^4$	$10^5$	$10^6$
Mass fraction	0.004	0.002	0.05	0.09	0.12	0.18	0.4	0.35	0.27

The mass fractions add up to 1.47. Now, begin at the  $0.01 \mu\text{g m}^{-3}$  bin. The mass of products in this bin is  $0.004 \times 25 = 0.1 \mu\text{g m}^{-3}$ . The fraction of that product in the particle phase is computed using (14.43). With  $C^* = 0.01$  and  $C_{OA} = 0.1$ ,  $X_p = 1/1.1 = 0.91$ , which we say is  $\sim 1.0$ . Now move to the 0.1 bin. The mass in the 0.1 bin is  $0.002 \times 25 = 0.05 \mu\text{g m}^{-3}$ . In calculating the fraction of OA in that bin, we have to consider the OA from both the 0.01 and 0.1 bins. This total is taken as  $0.1 + 0.05 = 0.15$ , where, for the moment, we put all the mass from the 0.1 bin into OA. Then, for the 0.1 bin,  $C^*/C_{OA} = 0.1/0.15$ , and  $X_p = 0.6$ . Let's call that 1.0. Now go to the 1.0 bin. The mass of products is  $0.05 \times 25 = 1.25 \mu\text{g m}^{-3}$ . Since we know that we are getting close to the 50/50 point in the  $X_p$  curve, let us arbitrarily put half of this product,  $0.625 \mu\text{g m}^{-3}$ , into this bin. Doing so, the  $C^*/C_{OA} = 1.0/0.775$  and  $X_p = 0.44$ , which is close enough to 0.5, so our assumption of putting half the mass into the OA phase was a good one. If we proceed to the  $10 \mu\text{g m}^{-3}$  bin, the mass of products =  $2.25 \mu\text{g m}^{-3}$ . It would seem reasonable to assume that one-tenth of this will partition into the particle phase, so

## SOA Model verification

we add  $0.225 \mu\text{g m}^{-3}$  to the accumulated  $C_{\text{OA}}$ , giving a total of  $1.0 \mu\text{g m}^{-3}$ . This results in  $X_p = 1/11$  for this bin, which is sufficiently close to 0.1. For the  $100 \mu\text{g m}^{-3}$  bin, the product is  $0.12 \times 25 = 3.0 \mu\text{g m}^{-3}$ . If we place 0.01 of this into the OA, then the total OA up to this bin = 1.03, and  $X_p \sim 0.01$ . From this bin on, we assume that the products remain entirely in the gas phase. With  $25 \mu\text{g m}^{-3}$  of  $\alpha$ -pinene reacted and a total of  $1.03 \mu\text{g m}^{-3}$  OA formed, the SOA yield =  $1.03/25 = 0.04$ .

What is the result if  $500 \mu\text{g m}^{-3}$  of  $\alpha$ -pinene is reacted? We can follow the same procedure of apportioning the oxidation products bin-by-bin. We find that the  $C_{\text{OA produced}} = 118 \mu\text{g m}^{-3}$  and the  $\text{SOA yield} = 118/500 = 0.236$ . (This calculation is the subject of Problem 14.6 at the end of this chapter.) By increasing the initial VOC concentration 20-fold, we find that the SOA yield increases from 4% to 23.6%. This example highlights the fact that with a greater amount of VOC reacted, the ultimate SOA yield increases owing to the fact that the larger mass of SOA shifts the gas-particle partitioning of more volatile compounds toward the particle phase. In fact, most of the particle-phase SOA compounds at a mass loading of  $118 \mu\text{g m}^{-3}$  are not in the particle phase at a loading of  $1 \mu\text{g m}^{-3}$ .

In the calculations above, we started by assuming the distribution of volatilities of the oxidation products. Ordinarily, these will not be known a priori. It is necessary to make an initial guess, go through the bin-by-bin calculation, and then adjust the distribution by trial-and-error to fit the observed data. The curve in Figure 14.16 is a result of that process. Note that for the case in Figure 14.16 the SOA contained in the  $10^4$ ,  $10^5$ , and  $10^6$  bins, as indicated by the dark gray bars, had to be assumed to close the mass balance on SOA.

# SOA Model verification

The VBS in SOA model. The enthalpy value is assumed.

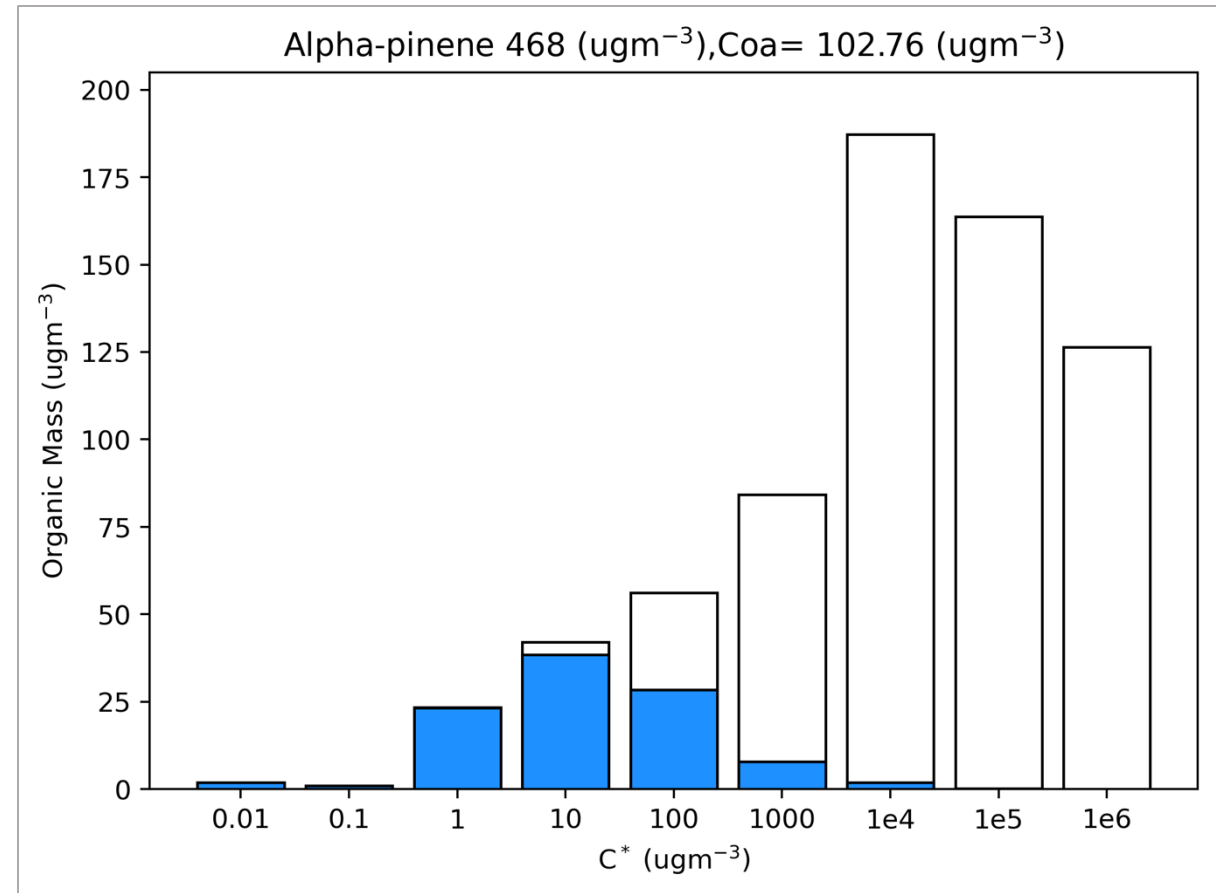
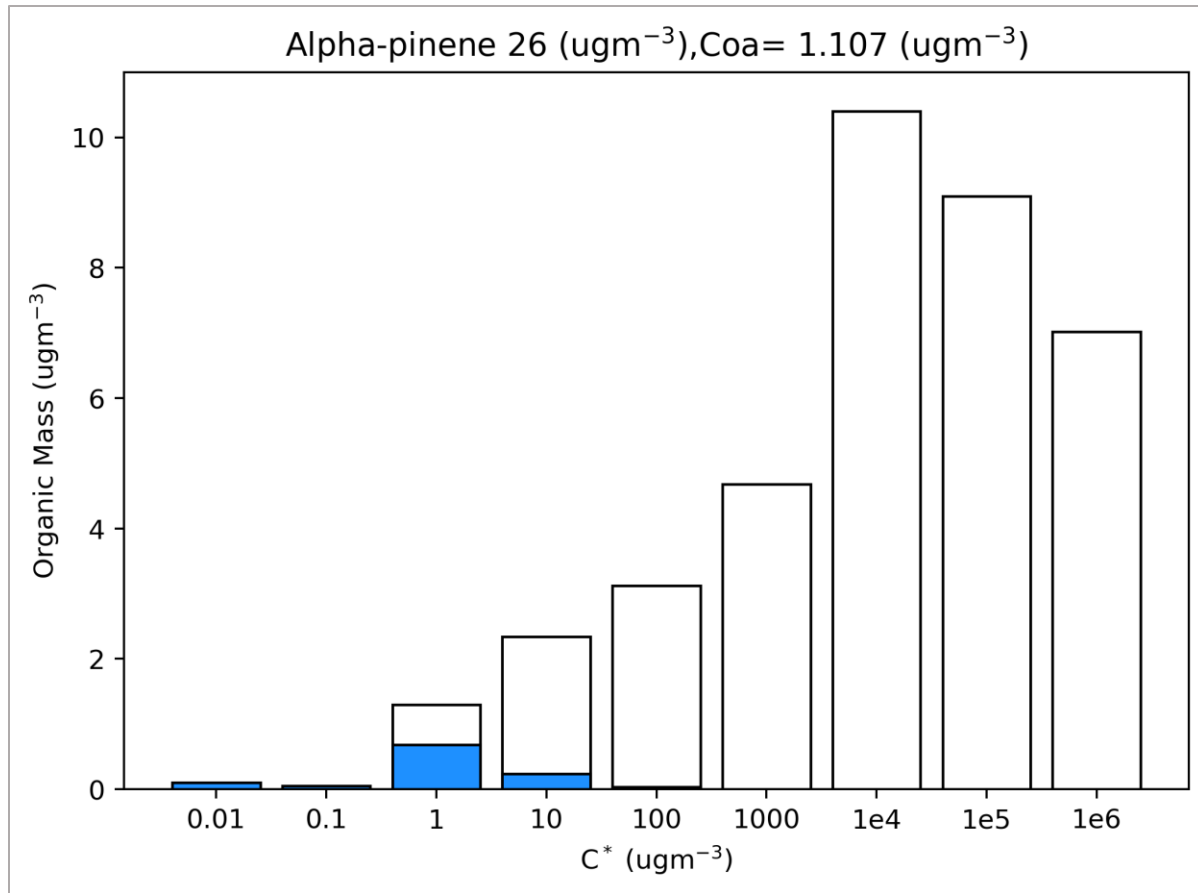
```
In [50]: test.oaspc[['name', 'gas_name', 'ctr_name', 'alpha', 'cstar', 'enth']]
```

```
Out[50]:
```

	name	gas_name	ctr_name	alpha	cstar	enth
0	AAPIN1	SVAPIN1	APINRXN	0.004	0.01	102000
1	AAPIN2	SVAPIN2	APINRXN	0.002	0.10	102000
2	AAPIN3	SVAPIN3	APINRXN	0.050	1.00	102000
3	AAPIN4	SVAPIN4	APINRXN	0.090	10.00	102000
4	AAPIN5	SVAPIN5	APINRXN	0.120	100.00	102000
5	AAPIN6	SVAPIN6	APINRXN	0.180	1000.00	102000
6	AAPIN7	SVAPIN7	APINRXN	0.400	10000.00	102000
7	AAPIN8	SVAPIN8	APINRXN	0.350	100000.00	102000
8	AAPIN9	SVAPIN9	APINRXN	0.270	1000000.00	102000

# SOA Model verification

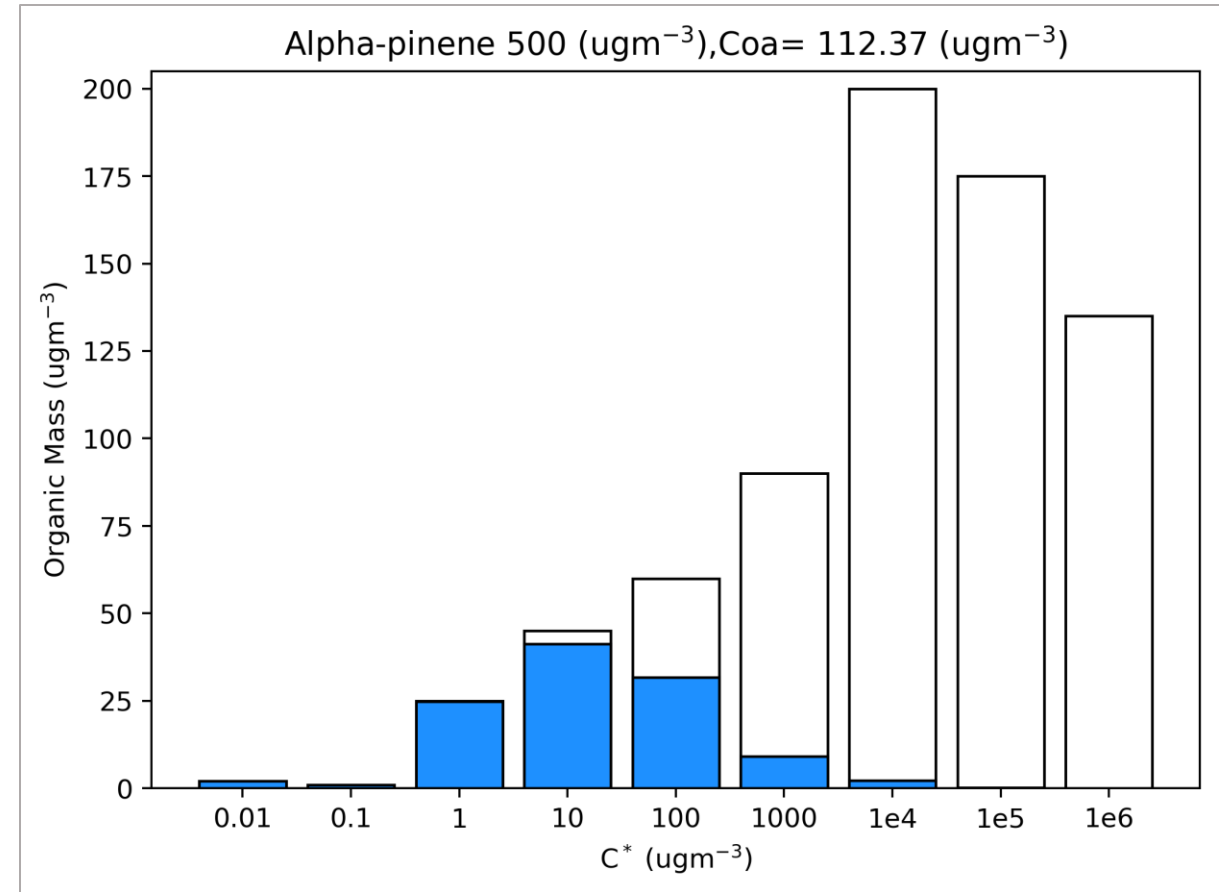
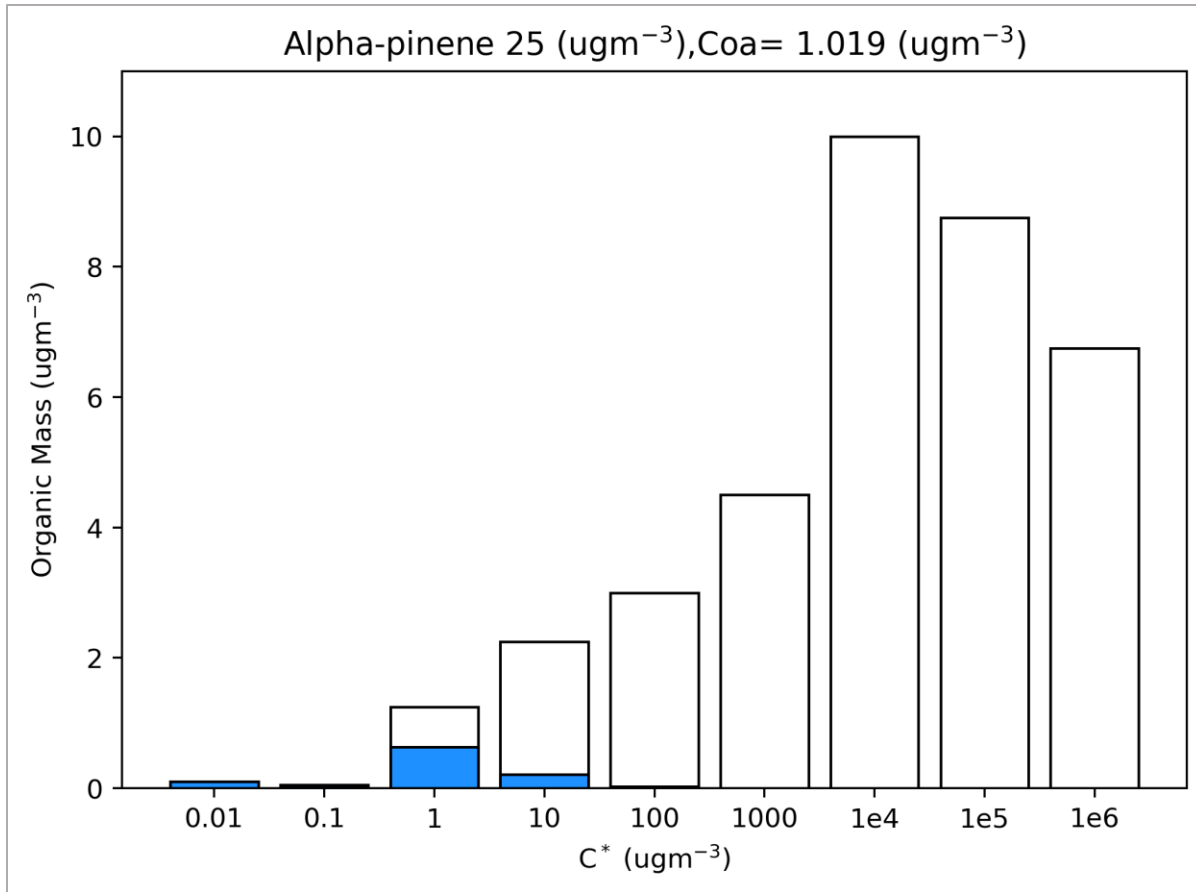
Output from SOA model





# SOA Model verification

Output from SOA model

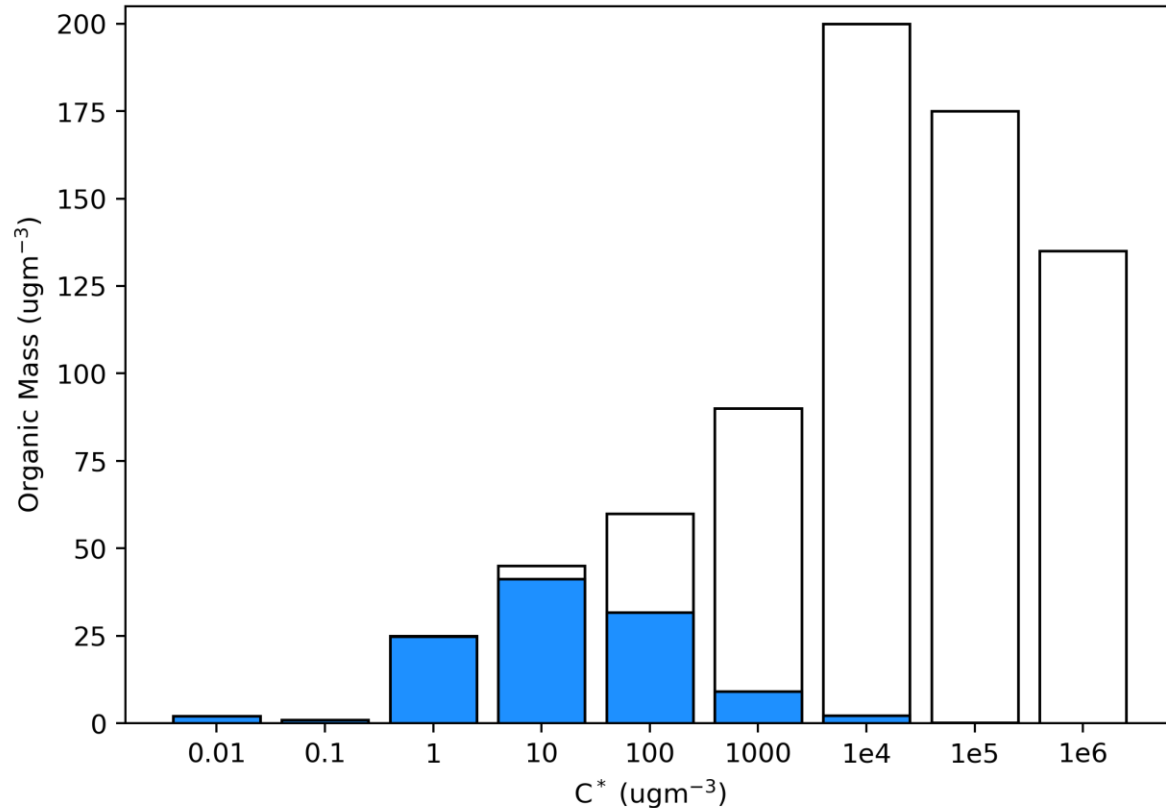


# SOA Model verification

Output from SOA model: Temperature sensitivity test

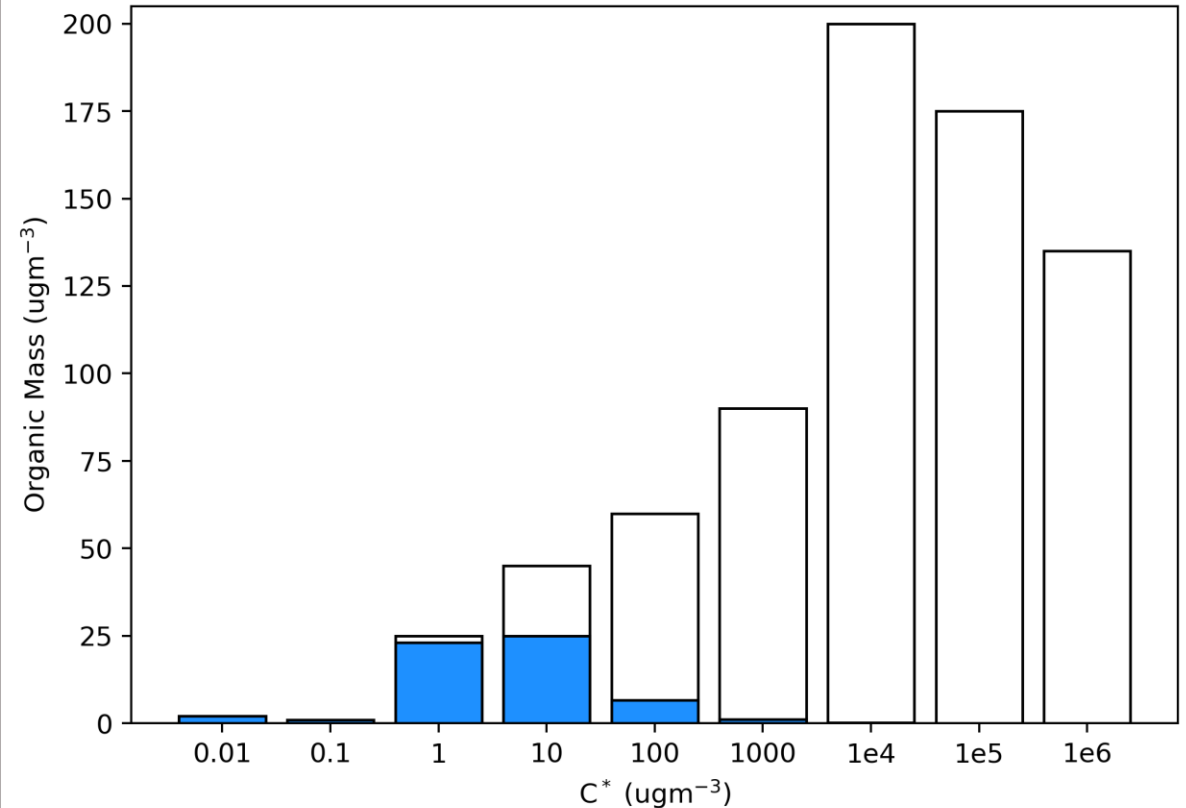
T= 298 K

Alpha-pinene 500 ( $\mu\text{g m}^{-3}$ ), Coa= 112.37 ( $\mu\text{g m}^{-3}$ )



T= 310 K

Alpha-pinene 500 ( $\mu\text{g m}^{-3}$ ), Coa= 59.21 ( $\mu\text{g m}^{-3}$ )



# SOA Model verification

**14.8B** The biogenic hydrocarbon limonene ( $\text{C}_{10}\text{H}_{16}$ ) is a precursor to SOA. A range of products result from the OH oxidation of limonene, but for the purpose here of modeling its SOA formation it will be assumed that there are three principal products given in the table below. It is desired to model the formation of limonene SOA using the Volatility Basis Set. Limonene at a mixing ratio

## PROBLEMS

**625**

of 10 ppb (concentration =  $2.55 \times 10^{11} \text{ molecules cm}^{-3}$ ) reacts with OH. The product of the limonene-OH rate constant and the OH concentration is  $3.4 \times 10^{-4} \text{ s}^{-1}$ . The values of the saturation mass concentration at 298 K for the three assumed oxidation products are given in the table. Assume that at  $t = 0$ , an initial amount of absorbing organic aerosol  $M_o = 0.1 \mu\text{g m}^{-3}$  exists. Compute the time evolution of the concentration of each product in each volatility bin and the total organic aerosol until all the limonene is reacted and the final SOA yield.

Oxidation product	Formula	Stoichiometric coefficient	$C^*$ ( $\mu\text{g m}^{-3}$ )
Maleic acid	$\text{C}_4\text{H}_4\text{O}_4$	0.24	1
4-Isoprenyl-1-methyl-1-hydroxy-2-oxocyclohexane	$\text{C}_{10}\text{H}_{16}\text{O}_2$	0.16	0.1
Ketalimonic acid	$\text{C}_8\text{H}_5\text{O}_2$	0.04	0.01

# SOA Model verification

## input in SOA model

### Gas-phase module

$LIM + OH \rightarrow 0.24 \cdot SVLIM1 + 0.16 \cdot SVLIM2 + 0.04 \cdot SVLIM3$  (gas-phase reaction)

The gas-phase module integrates following differential equations-

$$\begin{aligned} dLIM &= \int_0^t k[OH][LIM].dt \\ dSVLIM1 &= \int_0^t 0.24 * k[OH][LIM].dt \\ dSVLIM2 &= \int_0^t 0.16 * k[OH][LIM].dt \\ dSVLIM3 &= \int_0^t 0.04 * k[OH][LIM].dt \end{aligned}$$

#### Input of gas-phase module:

Initial concentration: [2.5e11, 0, 0, 0]

This gets updated from aerosol module.

Rate of reaction K : 3.4e-4 s-1

time-step (dt) = 0.3s

Total time = 60s

#### Output of gas-phase module:

Time dependent concentration of SVLIM1, SVLIM2, SVLIM3.

### Aerosol module

$SVLIM1 \rightarrow ALIM1$

$SVLIM2 \rightarrow ALIM2$

$SVLIM3 \rightarrow ALIM3$

#### Initial concentration:

Output from gas-phase module SVLIM1, SVLIM2, SVLIM3

Initial aerosol concentration: 1e-23 ug/m3

#### Parameter dataset:

```
In [66]: oaspc[['name', 'gas_name', 'cstar', 'op_mw', 'og_mw']]
Out[66]:
```

	name	gas_name	cstar	op_mw	og_mw
0	ALIM1	SVLIM1	1.00	116.0	116.0
1	ALIM2	SVLIM2	0.10	168.0	168.0
2	ALIM3	SVLIM3	0.01	133.0	133.0

og\_mw is molecular weight of gas-phase species (SVLIM1, SVLIM2, SVLIM3)

op\_mw is molecular weight of aerosol-phase species (ALIM1, ALIM2, ALIM3)

#### Meteorology:

T=298 K

P = 101325 pa

#### Output:

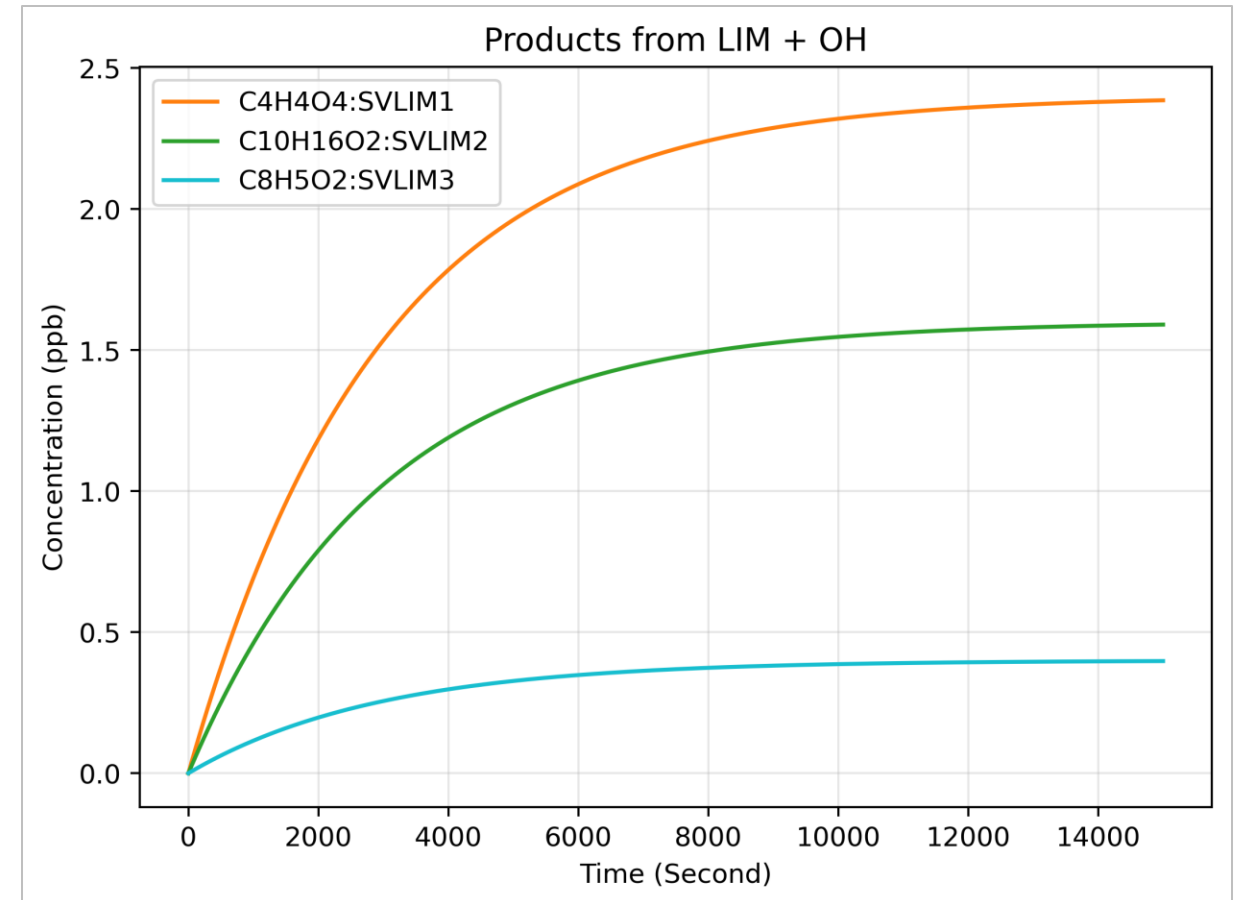
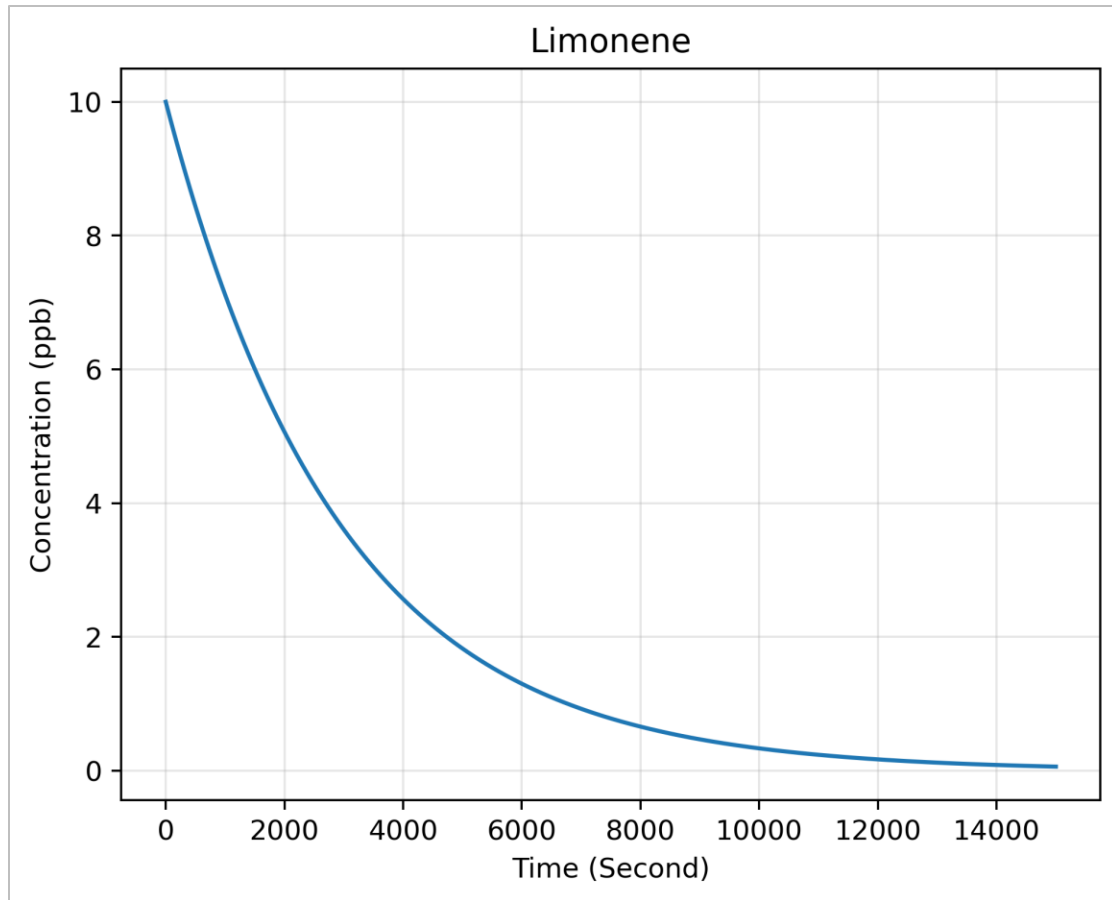
Concentration of ALIM1, ALIM2, ALIM3 in ug/m3

Updates SVLIM1, SVLIM2 and SVLIM3 concentration which is passed on to gas-phase module.

# SOA Model verification

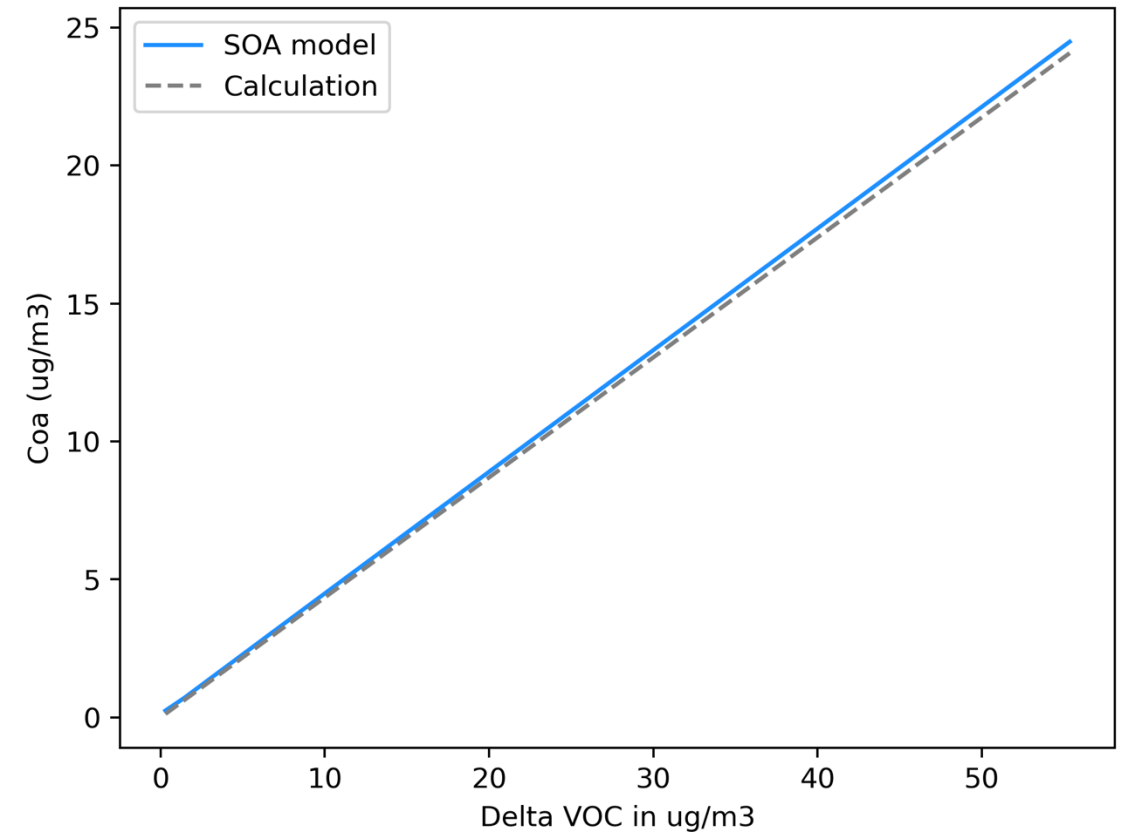
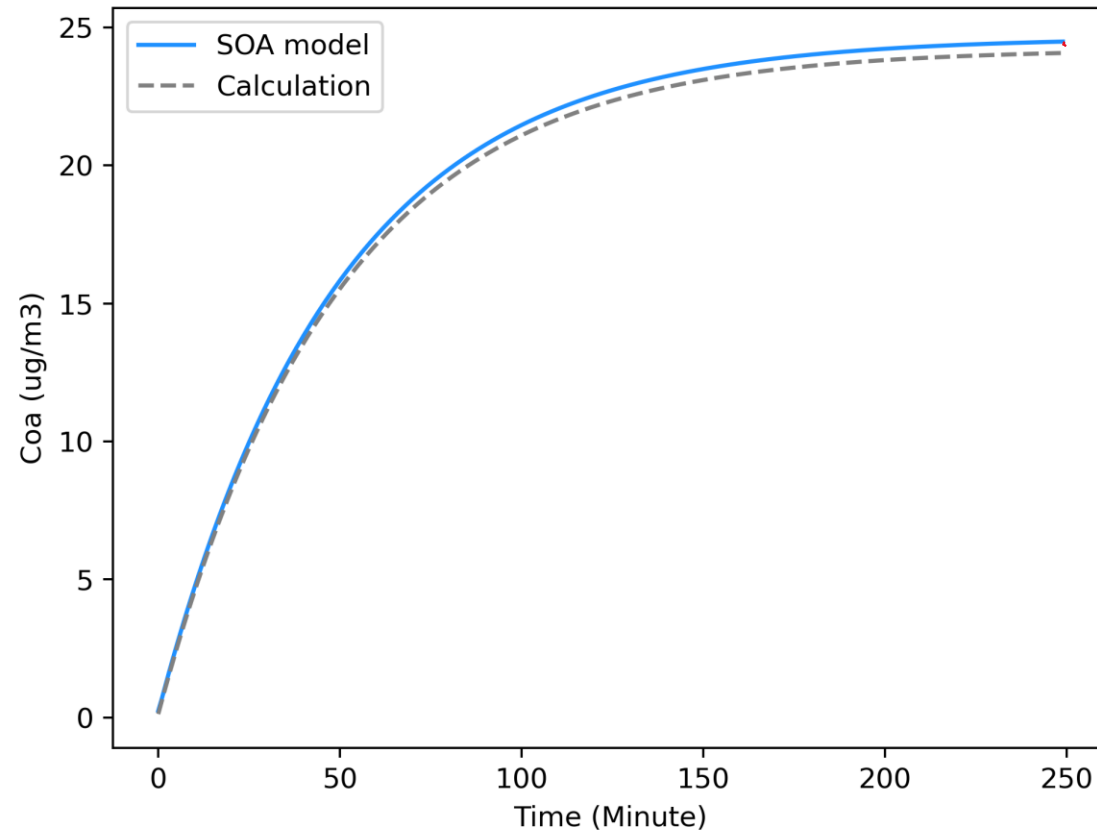
## Output from SOA model

Output from the gas-phase reaction solver. These figures show as limonene decays the products are forming. This figure doesn't show the updated concentration of the gas-phase products from the aerosol module.



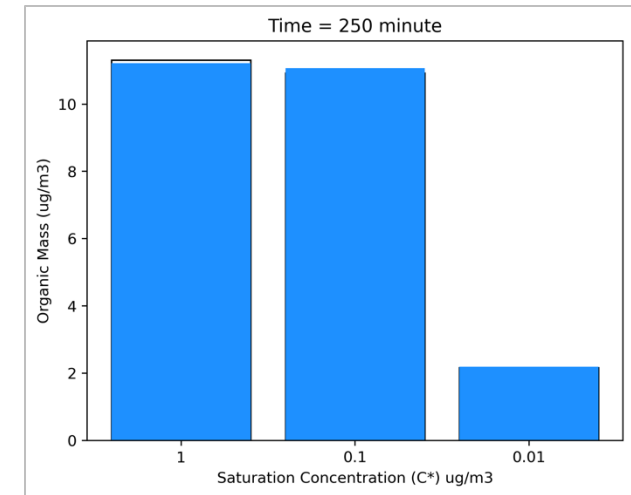
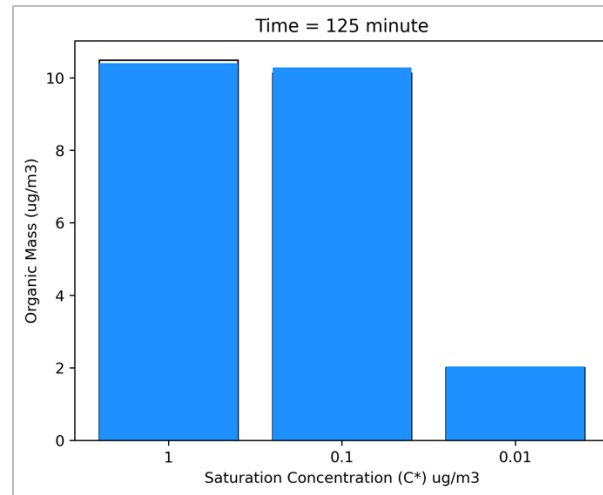
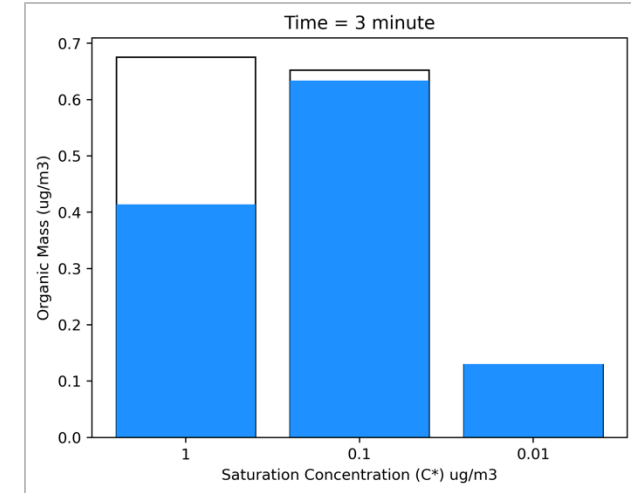
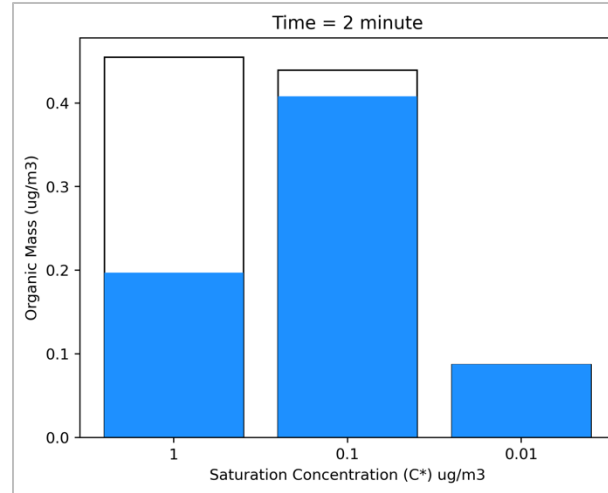
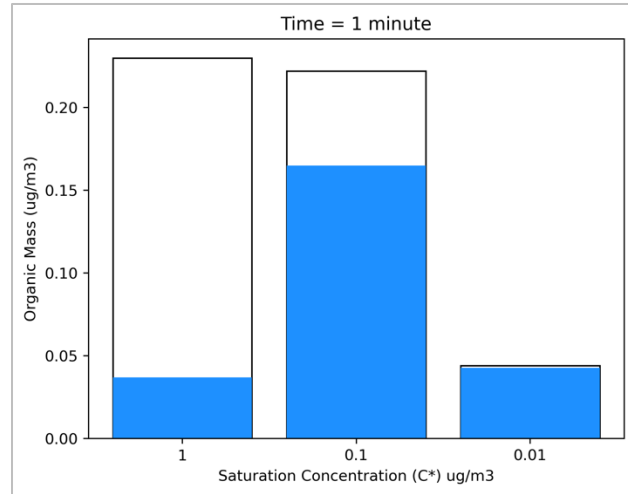
# SOA Model verification

## Output from SOA model



# SOA Model verification

## Output from SOA model



Thank you