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Developing Reactivity- and Source-Based Monoterpene Parameterizations for SOA Modeling

## **Overview of SOA Formation**

2. Oxidized products with low vapor pressure condense to new or existing particles (partitioning constant:  $K_p/C^*$ ; autooxidation yield)

 $H_{3}C$   $H_{3}C$   $H_{3}C$   $CH_{3}$   $CH_{3}$  C

3. Products undergo multiphase reactions  $(K_{eq}/k_{rxn}$  for accretion product formation, aqueous chemistry, organic salt formation)

 $\int_{CH_3}^{CH_2} 1$ . Emission and oxidation of gas-phase organic compounds (net flux; gas-phase reactivity:  $k_{OH}$ ,  $k_{O3}$ ,  $k_{NO3}$ ; RO<sub>2</sub> fate/lifetime)



### Model Components Involved in Prediction of SOA Formation

<u>Amount of precursor emitted</u> (non-methane organic compound, NMOC, or volatile organic compound, VOC): Emission factor (EF) from emissions model

#### Amount of precursor reacted:

Reaction rate constants ( $k_{OH}$ ,  $k_{O3}$ ,  $k_{NO3}$ ) and reacted hydrocarbon ( $\Delta$ HC) from gas phase chemical mechanism model

Extent of gas/particle partitioning:

Gas/particle partitioning constants ( $K_p$  or  $C^*$ : function of vapor pressure, activity, and PM properties) and PM mass from aerosol model

Amounts ( $\alpha$ ) and volatilities ( $K_p$  or  $C^*$ ) of oxidation products have historically been derived from chamber studies.

# Schematic of SOA Processes in CMAQ



CMAQv5.1 (5.2), aer6i (Pye et al., 2015)

Total amount of SV\_TRP1, SV\_TRP2 calculated by  $\Delta MNTRP^*\alpha_{TRP1}$ ,  $\Delta MNTRP^*\alpha_{TRP2}$ .

Partitioning based on  $C^*_{\text{TRP1}}$ ,  $C^*_{\text{TRP2}}$ .

Parameters weighted by emissions (αpinene).

# One Monoterpene Surrogate Is Not Enough

- Gas phase reactivity/lifetime varies by orders of magnitude
- 2. Autooxidation yields vary with terpene precursor (e.g., Jökinen et al., 2015, *PNAS*)
- SOA formation yields also vary with terpene precursor (e.g., Lee et al., 2006, *JGR*; Fry et al., 2014, *ES&T*)



Based on Atkinson and Arey, 2003

## **Research Questions and Tools**

- What is the diversity of terpene emissions from biogenic and biomass burning sources (including as represented in models)?
- Can that diversity be represented by a single monoterpene with varying parameters (source-specific)? (one monoterpene surrogate, with static parameters, is not enough)
- Can we represent SOA formation from monoterpenes with an optimized number of monoterpene surrogates (reactivitybased)?

#### Primary Tools

Two-dimensional gas chromatography with time-of-flight mass spectrometry for measuring gaseous organic compounds

GEKCO-A for modeling gas-phase chemistry and SOA formation

### USFS Fuel Characteristics Classification System Vegetation Map



https://www.fs.fed.us/pnw/fera/fft/fccsmodule.shtml

### Speciation of Terpenoids from Laboratory Burns of Individual Fuel Types

- Measurements from Missoula Fire Lab (FIREX)
- Average of 4-7 canopy and composite burns
- Other fuels: juniper and sagebrush
- Boxes represent smoke measurements
- Red markers are needle essential oils, blue are wood/twig essential oils (literature)
- Reflects influence of speciation on emissions



### Fractional α-Pinene Emissions Based on MEGAN



### GECKO-A to Explore (Parameterize) SOA Formation from Diverse Monoterpenes

GECKO-A Box Model (Aumont et al., 2005, ACP) Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere: Gas/particle partitioning calculated for individual compounds, assumes thermodynamic equilibrium; vapor pressures calculated using group contribution methods

Metrics of Interest:

- Rates and extents of SOA formation
- Reaction pathways (RO<sub>2</sub>-NO, RO<sub>2</sub>-HO<sub>2</sub>, etc.)
- Structure and property distributions of intermediate products
- Structure and property distributions of major products in gas and particle phases

Model Configuration:

• 6 generations oxidation • oxidation time = 48 hours • T = 298K • RH =

5% ■ zenith angle fixed at 50%

# Monoterpene Simulations: Controlled Reactivity Model, Max SOA (µg/m<sup>3</sup>)

Precursor	[HC] <sub>o</sub> = 10 ppb, OA = 1 μg/m <sup>3</sup>	[HC] <sub>o</sub> = 50 ppb, OA = 1 μg/m <sup>3</sup>	[HC] <sub>o</sub> = 0.5 ppb, OA = 10 μg/m <sup>3</sup>
Sabinene	7.11		
z-Ocimene	8.99	49.93	
3-Carene	9.77	61.07	
Terpinolene	13.75	89.64	
β-Myrcene	16.68	97.46	
α-Terpinene	14.86	95.44	
α-Pinene	12.83	96.34 (34%)	0.51 (18%)
β-Pinene	16.12	113.22	
γ-Terpinene	19.20	101.19	
α-Phellandrene	17.96	109.58	
Camphene	22.39	163.56 (58%)	0.86 (30%)
Limonene	35.49	201.38 (71%)	0.90 (32%)

# 2p and VBS Parameterizations of SOA Formation



## **Developing SOA Parameterizations**



- 1. Individual compounds under varying conditions (shown above)
- 2. Reactivity-based: run clustering algorithm, fit grouped compounds
- 3. Source-based: weight parameters based on emissions

# Predicted Yield, Parameters Based on GECKO-A Simulations

	k <sub>OH</sub>	k <sub>O3</sub>	k <sub>NO3</sub>	Yield @ 10 µg/m <sup>3</sup> OA
z-Ocimene (*cluster 1)	2.52E-10	5.40E-16	2.20E-11	14%
$\alpha$ -Pinene (*cluster 2)	5.23E-11	8.44E-17	6.16E-12	20%
α-Phellandrene (*cluster 3)	3.13E-10	3.00E-15	7.30E-11	24%
Camphene (cluster 4)	5.33E-11	9.00E-19	6.54E-13	34%
Limonene (cluster 5)	1.60E-10	2.13E-16	1.22E-11	40%
Lodgepole Pine	1.63E-10	9.18E-16	2.56E-11	24%
Douglas Fir	8.84E-11	1.09E-16	5.92E-12	30%
Northern CA	1.17E-10	1.90E-16	9.74E-12	20%
Central US	1.00E-10	1.47E-16	8.34E-12	21%
CMAQ default (Carlton et al., 2010)	gas-phase chemical mechanism dependent			9%
CMAQ 2pVBS (Barsanti et al., 2013)				9%

### **Predicted SOA Mass: Biogenic SOA**



### **Predicted SOA Mass: Biomass Burning**



## Summary



2. While mechanistic models are imperfect, consider use to develop updated SOA parameterizations. We are working on two: reactivity-based (harder) and source-based (easier). Next step, to evaluate SOA predictions (to the extent possible).

1. Great diversity in monoterpene emissions and subsequently their atmospheric reactivity. <u>Not well</u> <u>represented in models.</u>



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