Discussions on the Potential Contribution of Secondary Organic Aerosol (including organonitrates) to $PM_{2.5}$ in Klamath Falls

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Outline

- Goal: To use thermodynamic modeling to assess the potential of secondary organic aerosol formation, relative to primary PM2.5 emissions, in Klamath Falls, OR
- Introduction to SOA modules in chemical transport models
- Approach
- Results

Overview of Relevant Gas-Phase Chemistry

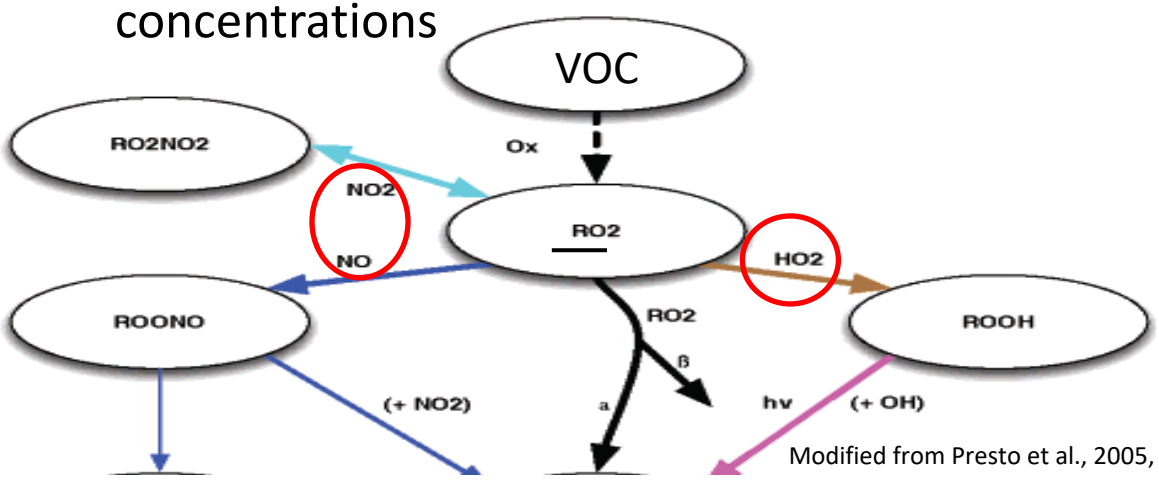
"Ox"

Day: OH, O_3 (HO_2, NO_x)

- Anthropogenic precursors: react w/OH
- Biogenic precursors
  - Isoprene reacts w/OH
  - Monoterpenes and sesquiterpenes react w/OH+O_3
- Then…branching based on NOx concentrations

Night: O_3, NO_3

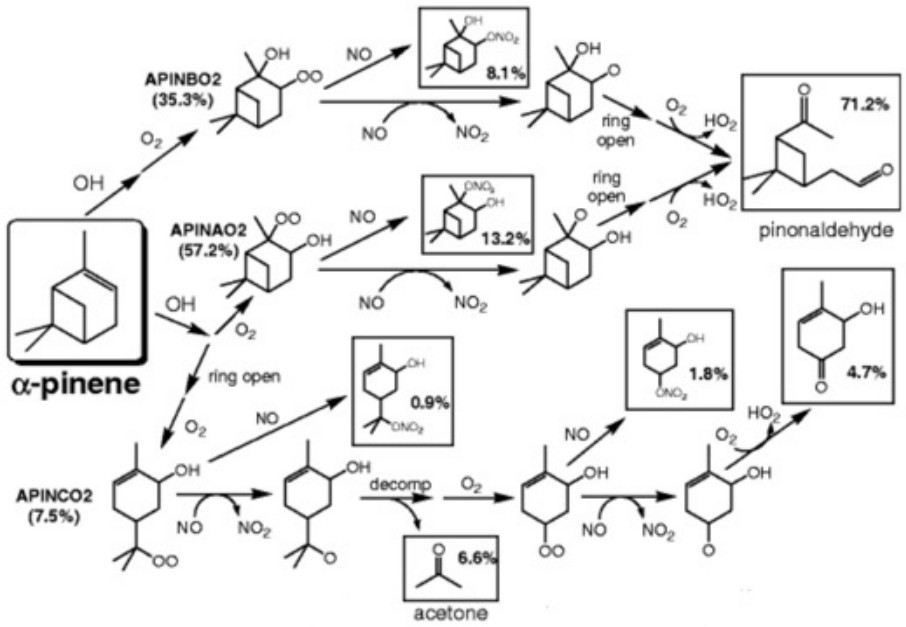
- Typically anthropogenic SOA precursors (benzene, xylene, toluene) react slowly with NO_3
- Biogenic precursors react w/NO_3
  - Isoprene, on order of reaction w/OH
  - Reactions w/α-,β-pinene particularly fast



Modified from Presto et al., 2005, *ES&T*

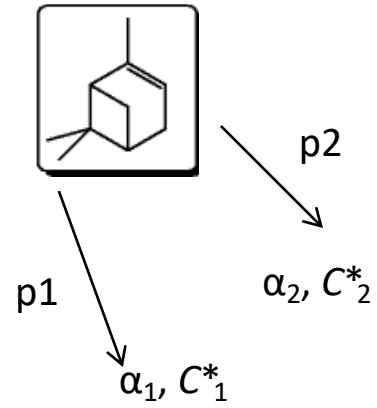
Overview of SOA Model Approaches: Two-Product (2p) and Volatility Basis Set (VBS)

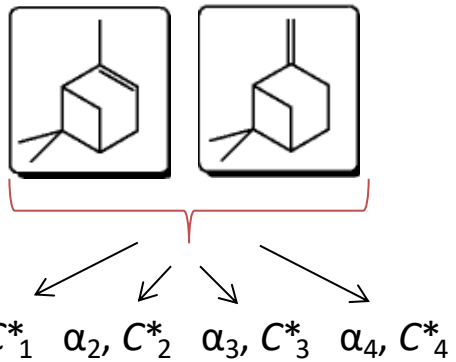
α-Pinene + OH (first generation)



α-Pinene + OH (lumped compounds)

2 products (2p)





N hydrocarbons (HC)

Products tracked
= 2 x *N*

Fit chamber data to obtain $\alpha_{1,2}$ and $C^*_{1,2}$ values

volatility basis set (VBS)

Products tracked
= *j* or *j* x *N*

bins 1 to *j* (usually 4)

Fix C^*_i, fit chamber data to obtain α_i values

Sources: Pinho et al., *J. Atmos. Chem.*; Odum et al., *ES&T; Donahue et al., ES&T*

SOA in CMAQv4.7 (2p)

No NO_x dependence; No independent NO_3 pathway

NO_x dependence

TABLE 1. Parameters in CMAQv4.7 SOA Module

gaseous precursor (model species)	oxidants	semivolatile products	α_i^f	$c^{*\,g}$ ($\mu g\ m^{-3}$)	ΔH_{vap} (kJ mol^{-1})	SOA species	M (g mol^{-1})	OM/OC ratio
Semivolatile SOA								
isoprene (ISOP[a] or ISOPRENE[b])	·OH	SV_ISO1	0.232	116.01	40	AISO1	96	1.6
		SV_ISO2	0.0288	0.617	40	AISO2	96	1.6
monoterpenes (TERP[a] or TRP1[b])	·OH, $O(^3P)$[e], O_3, ·NO_3	SV_TRP1	0.1393	14.792	40	ATRP1	168	1.4
		SV_TRP2	0.4542	133.7297	40	ATRP2	168	1.4
sesquiterpenes (SESQ[a,b])	O_3, ·OH, ·NO_3	SV_SQT	1.537	24.984	40	ASQT	378	2.1
long alkanes (ALK5[b])	·OH	SV_ALK	0.0718	0.020	40	AALK	150	1.56
high-yield aromatics (TOL[a] or ARO1[b])	·OH/NO	SV_TOL1	0.0758	2.326	18	ATOL1	168	2.0
		SV_TOL2	0.1477	21.277	18	ATOL2	168	2.0
low-yield aromatics (XYL[a] or ARO2[b])	·OH/NO	SV_XYL1	0.0386	1.314	32	AXYL1	192	2.0
		SV_XYL2	0.1119	34.483	32	AXYL2	192	2.0
benzene (BENZENE[a,b])	·OH/NO	SV_BNZ1	0.0942	0.302	18	ABNZ1	144	2.0
		SV_BNZ2	1.162	111.11	18	ABNZ2	144	2.0
Nonvolatile SOA								
high-yield aromatics[c]	·OH/·HO_2		0.471	[h]	[h]	ATOL3	168	2.0
low-yield aromatics[c]	·OH/·HO_2		0.373	[h]	[h]	AXYL3	192	2.0
benzene[c]	·OH/·HO_2		0.484	[h]	[h]	ABNZ3	144	2.0
isoprene	H^+			[h]	[h]	AISO3	162	2.7
aged aerosol	time			[h]	[h]	AOLGA	176.4	2.1
						AOLGB	252	2.1
glyoxal, methylglyoxal (GLY[a], MGLY[a,b,d])	·OH		0.04	[h]	[h]	AORGC	177	2.0

Carlton et al., *ES&T*, 2010

SOA in GEOS-Chem (VBS)

Table 1. SOA Yield Parameterizations at 298 K.

Parent HC	Oxidant	α for C* (C* in $\mu g/m^3$)					RMSE[a]	Yield at	Data
		nonvolatile	0.1	1	10	100	[$\mu g/\mu g$]	10 $\mu g/m^3$	
Monoterpenes and sesquiterpenes									
LIMO	OH, O_3; NO	0	0	0.474	0.117	1.419	0.145	0.62	dark high-NO_x limonene ozonolysis (Zhang et al., 2006), refit using a density of 1.3 g/cm^3
MTPA/O	OH, O_3; NO	0	0.04	0.0095	0.09	0.015	NA	0.09	based on low-NO_x fit, adjusted for NO_x based on Ng et al. (2007a) and Pathak et al. (2007)
SESQ	OH, O_3; NO	0	0	0.000	1.146	2.981	NA	0.84	based on low-NO_x fit, adjusted for NO_x based on Ng et al. (2007a)
LIMO	OH, O_3; HO_2	0	0	0.366	0.321	0.817	0.068	0.57	dark low-NO_x limonene ozonolysis (Zhang et al., 2006), refit using a density of 1.3 g/cm^3
MTPA/O	OH, O_3; HO_2	0	0.08	0.019	0.18	0.03	0.016	0.19	dark α-pinene ozonolysis (Shilling et al., 2008), not wall loss corrected
SESQ	OH, O_3; HO_2	0	0	0.000	0.574	1.489	0.037	0.42	β-caryophyllene and α-humulene [VOC/NO_x]>3ppbC/ppb (Griffin et al., 1999a), fit using a density of 1.3 g/cm^3
all terpenes	NO_3	0	0	0.000	0.321	1.083	0.057	0.26	β-pinene+NO_3 (Griffin et al., 1999a), fit using a density of 1.3 g/cm^3
Isoprene									
ISOP	NO_3	0	0	0.000	0.217	0.092	0.023	0.12	Ng et al. (2008)
ISOP	OH	0	0	0.031	0.000	0.095	0.003	0.04	low-NO_x photooxidation (Kroll et al., 2006)
Aromatics									
BENZ	OH; NO	0	0	0.078	0.000	0.793	0.005	0.14	benzene high-NO_x photooxidation (Ng et al., 2007b)
TOLU	OH; NO	0	0	0.032	0.094	0.080	0.001	0.08	toluene high-NO_x photooxidation (Ng et al., 2007b)
XYLE	OH; NO	0	0	0.025	0.036	0.090	0.002	0.05	xylene high-NO_x photooxidation (Ng et al., 2007b)
BENZ	OH; HO_2	0.37	0	0	0	0	NA	0.37	benzene low-NO_x photooxidation (Ng et al., 2007b)
TOLU	OH; HO_2	0.36	0	0	0	0	NA	0.36	toluene low-NO_x photooxidation (Ng et al., 2007b)
XYLE	OH; HO_2	0.30	0	0	0	0	NA	0.30	xylene low-NO_x photooxidation (Ng et al., 2007b)
IVOCs									
NAP	OH; NO	0	0	0.039	0.296	0.235	0.036	0.20	naphthalene high-NO_x photooxidation (Chan et al., 2009)
NAP	OH; HO_2	0.73	0	0	0	0	NA	0.73	naphthalene low-NO_x photooxidation (Chan et al., 2009)

NO_x dependence mono- and sesquiterpenes

Independent NO_3 pathway for all terpenes

Pye et al., 2010

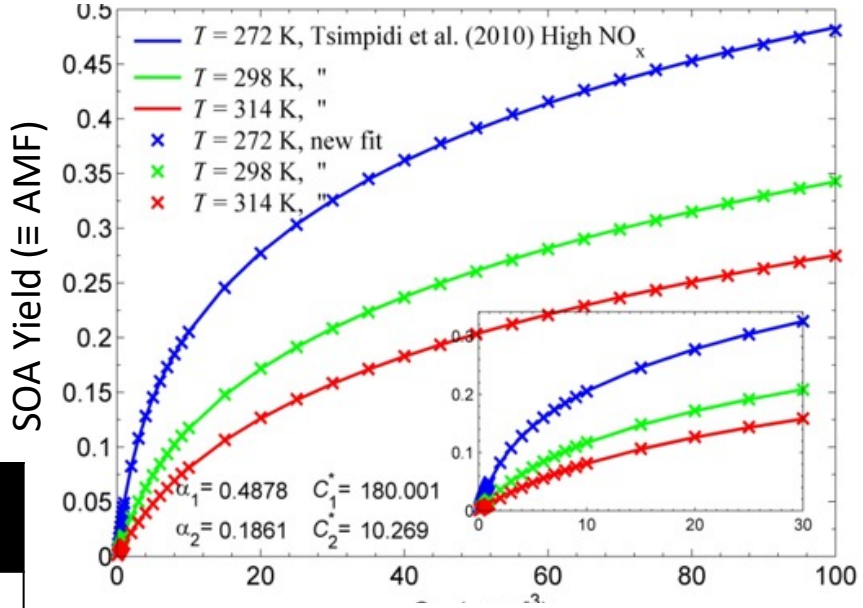
“2p-VBS”

2p-VBS parameters: take advantage of the VBS fitting approach and collation of new and old chamber data

- Used VBS (Tsimpidi et al., 2010) to generate “data” points at each of 3 temperatures; fit “data” points
- Generated two-product parameters for all precursors in CMAQ, added parameters for NOx dependent pathway for biogenic precursors

Precursor (w/OH, high NOx)	Yield @ ΔHC = 10 ug m^{-3} , 2p-VBS	Yield @ ΔHC = 10 ug m^{-3} , VBS
BENZ	0.12	0.14
TOL	0.07	0.08
XYL	0.04	0.05
ISO	0.01	n/a
MTRP	0.09	0.09
SQT	0.84	0.84

VBS and 2p-VBS Parameterizations of Aromatic 1/Toluene



Example fit above. To left, comparison of predicted yields using 2p-VBS parameterization with yield using a VBS parameterization (Pye et al., 2010).

Barsanti, Carlton, Chung in preparation

Assumptions and Approach

Cases:

1. Klamath County: 1.6 x 10^4 km^2
2. Area approximating area of influence around monitoring site: 225 km^2

Winter Conditions:

Mixed-Layer Height: 200 m
Average Daytime Temp.: 40°F
Average Nighttime Temp.: 20°F

Duration of Simulation: 12 hours

Daytime chemistry:

12-hr average OH: 2 x 10^6 molecules/cm^3
24-hr average O_3: 7 x 10^{11} molecules/cm^3

No NO/HO_2 assumptions, consider one pathway at a time

Nighttime chemistry:

12-hr average NO_3: 2.5 x 10^8 molecules/cm^3

Breakdown of biogenic terpene emissions:

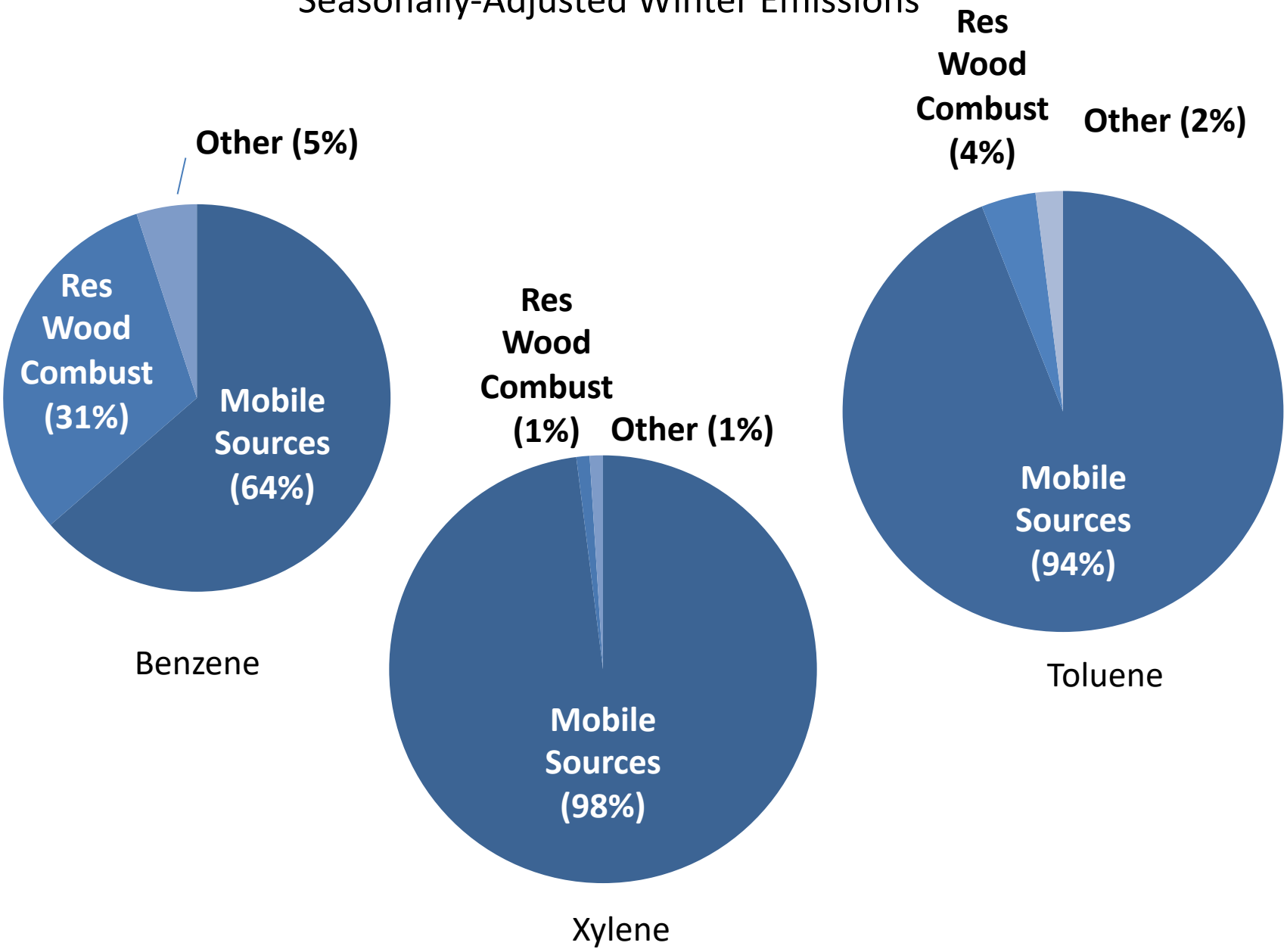
31% sesquiterpenes (sqt)
69% monoterpenes (mtrp)

Seasonally-averaged emissions from C. Swab, ODEQ.

SOA parameters based on Carlton et al. (2010), Pye et al. (2010), Barsanti et al. (in prep.)

Goal: To evaluate the potential importance of SOA formation in Klamath Falls non-attainment area by comparing predicted SOA with primary $PM_{2.5}$ emissions in a fully-closed box model.

Seasonally-Adjusted Winter Emissions



Summary of Estimated SOA Formation

Case 1 and variations used to demonstrate sensitivity to inputs (assumed PM2.5 50% organic)

Precursor contribution to SOA (high to low) :

toluene, benzene, xylene (low NOx) →

benzene, toluene, xylene (high NOx) →

Precursor (w/OH, high NOx)	Anthropogenic SOA(µg/m³), % of total PM2.5	Biogenic SOA (µg/m³), % of total PM2.5	Total PM2.5 (primary + SOA)
Case 1: low-NOx	0.08, 2.5%	1.6, 52%	3.1
Case 1: low-NOx, *T* correction on biogenic emissions	0.08, 3.3%	0.9, 38%	2.4
Case 1: high-NOx	0.02, <0.5%	3.5, 71%	4.9
Case 1: NO_3 (nighttime chemistry)	n/a	4.3, 75%	5.7
Case 2: low-NOx, 20% organic	6.9, 9%	2.3, 4%	52
Case 2: low-NOx, 50% organic	7.6, 9%	3.0, 6%	53
Case 2: high-NOx, 20% organic	5.4, 4%	3.2, 6%	50
Case 2: high-NOx, 50% organic	7.1, 6%	4.3, 8%	52

Notes: Predicted SOA depends on background organic $PM_{2.5}$ loading; assumed primary $PM_{2.5}$ was 20-50% organic as noted. For case 2, anthropogenic field burning emissions omitted and biogenic emissions reduced by half.

Take Home Points

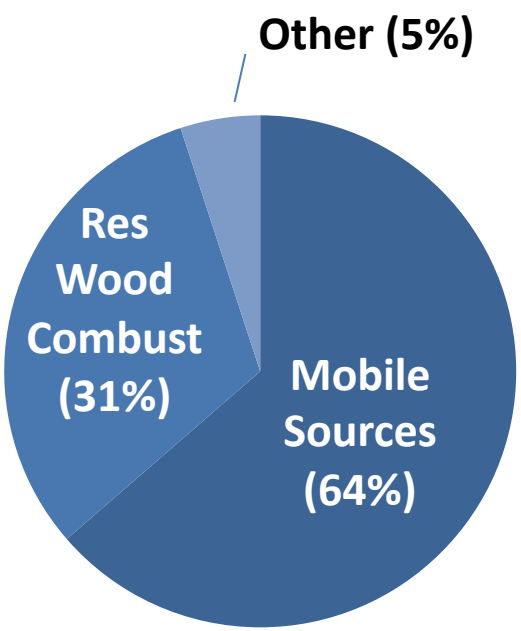
- An attempt to understand SOA contributions to total PM2.5

- Anthropogenic SOA contributes ~4-9%, and biogenic contributes ~4%-8% to the total PM2.5 during wintertime in Klamath Falls

- Need 3-D Airshed modeling to estimate SOA source contributions more accurately

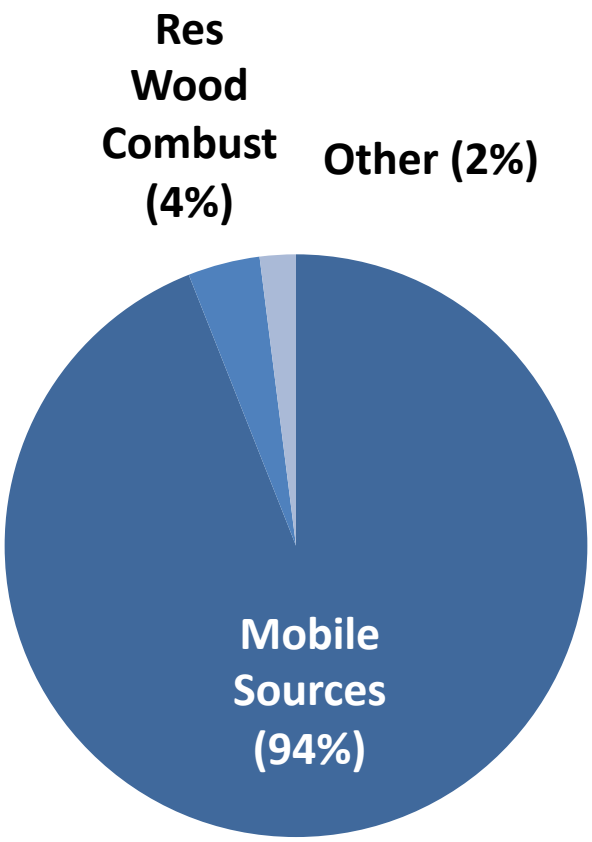
Additional Slides

Seasonally-Adjusted Benzene Emissions (≥ 1 % of Total)



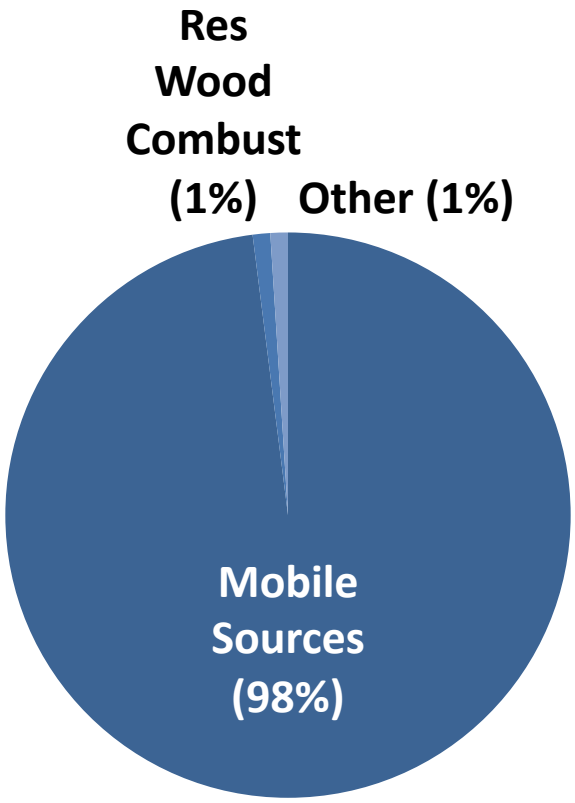
Data Category	Group	% Contribution to Total Benzene Emissions
Onroad	Mobile Sources/Highway Vehicles - Gasoline/Light Duty Gasoline Vehicles (LDGV)	0.267
Onroad	Mobile Sources/Highway Vehicles - Gasoline/Light Duty Gasoline Trucks 1 & 2 (M6) = LDGT1 (M5)	0.170
Nonpoint	Residential Wood Combustion: Woodstove_NotCertified	0.098
Onroad	Mobile Sources/Highway Vehicles - Gasoline/Light Duty Gasoline Trucks 3 & 4 (M6) = LDGT2 (M5)	0.070
Nonroad	Mobile Sources/Pleasure Craft/Gasoline 2-Stroke	0.063
Nonpoint	Residential Wood Combusiont: Insert_NonCertified	0.051
Nonpoint	Residential Wood Combustion: Woodstove_Certified_Catalytic	0.039
Nonpoint	Residential Wood Combustion: Woodstove_Certified_NonCatalytic	0.036
Nonpoint	Residential Wood Combustion: Central_Furnace	0.032
Nonpoint	Residential Wood Combusiont: Insert_Certified_NonCatalytic	0.025
Nonpoint	Residential Open Burning: Municipal Waste (check SCC)	0.025
Nonpoint	Storage and Transport/Petroleum and Petroleum Product Storage/Gasoline Service Stations	0.023
Nonroad	Mobile Sources/Off-highway Vehicle Gasoline, 2-Stroke/Recreational Equipment	0.017
Nonpoint	Residential Wood Combustion: Insert_Certified_Catalytic	0.016
Onroad	Mobile Sources/Highway Vehicles - Gasoline/Heavy Duty Gasoline Vehicles 2B thru 8B & Buses (HDGV)	0.015

Seasonally-Adjusted Toluene Emissions (≥ 1 % of Total)



Data Category	Group	% Contribution to Total Toluene Emissions
Onroad	Mobile Sources/Highway Vehicles - Gasoline/Light Duty Gasoline Vehicles (LDGV)	0.315
Onroad	Mobile Sources/Highway Vehicles - Gasoline/Light Duty Gasoline Trucks 1 & 2 (M6) = LDGT1 (M5)	0.202
Nonroad	Mobile Sources/Pleasure Craft/Gasoline 2-Stroke	0.164
Nonroad	Mobile Sources/Off-highway Vehicle Gasoline, 2-Stroke/Recreational Equipment	0.089
Onroad	Mobile Sources/Highway Vehicles - Gasoline/Light Duty Gasoline Trucks 3 & 4 (M6) = LDGT2 (M5)	0.083
Nonpoint	Residential Wood Combustion: Woodstove_NotCertified	0.024
Onroad	Mobile Sources/Highway Vehicles - Gasoline/Heavy Duty Gasoline Vehicles 2B thru 8B & Buses (HDGV)	0.022
Nonpoint	Storage and Transport/Petroleum and Petroleum Product Storage/Gasoline Service Stations	0.018
Nonpoint	Residential Wood Combusiont: Insert_NonCertified	0.012

Seasonally-Adjusted Xylene Emissions (≥ 1 % of Total)



Data Category	Group	% Contribution to Total Xylene Emissions
Nonroad	Mobile Sources/Pleasure Craft/Gasoline 2-Stroke	0.282
Onroad	Mobile Sources/Highway Vehicles - Gasoline/Light Duty Gasoline Vehicles (LDGV)	0.266
Onroad	Mobile Sources/Highway Vehicles - Gasoline/Light Duty Gasoline Trucks 1 & 2 (M6) = LDGT1 (M5)	0.170
Nonroad	Mobile Sources/Off-highway Vehicle Gasoline, 2-Stroke/Recreational Equipment	0.096
Onroad	Mobile Sources/Highway Vehicles - Gasoline/Light Duty Gasoline Trucks 3 & 4 (M6) = LDGT2 (M5)	0.070
Onroad	Mobile Sources/Highway Vehicles - Gasoline/Heavy Duty Gasoline Vehicles 2B thru 8B & Buses (HDGV)	0.019
Nonpoint	Storage and Transport/Petroleum and Petroleum Product Storage/Gasoline Service Stations	0.011
Nonpoint	Residential Wood Combustion: Woodstove_NotCertified	0.010

Seasonally-Adjusted Emissions Summary

Seasonally-Adjusted Primary $PM_{2.5}$ Emissions (≥ 1 % of Total)

Data Category	Group	% Contribution to Total Primary $PM_{2.5}$
Nonpoint	Prescribed Burning: ANTHROPOGENIC	0.547
Nonpoint	Mobile Sources/Unpaved Roads/unknown (fugitive dust: vehicle related)	0.071
Nonpoint	Residential Wood Combustion: Woodstove_NotCertified	0.066
Nonpoint	Residential Wood Combusiont: Insert_NonCertified	0.034
Nonpoint	Residential Wood Combustion: Woodstove_Certified_NonCatalytic	0.031
Nonpoint	Residential Open Burning: Brush	0.023
Nonpoint	Residential Wood Combustion: Woodstove_Certified_Catalytic	0.023
Nonpoint	Residential Wood Combusiont: Insert_Certified_NonCatalytic	0.022
Nonpoint	Mobile Sources/Paved Roads/All Paved Roads (fugitive dust: vehicle related)	0.021
Nonpoint	CAFO: Beef Cattle: Total (non-permitted sources)	0.017
Nonpoint	Residential Wood Combustion: Central_Furnace	0.014
Point	Industrial Processes/Pulp and Paper and Wood Products/Plywood Operations	0.013
Nonpoint	Residential Wood Combusiont: Fireplace	0.012
Point	External Combustion Boilers/Industrial/Wood/Bark Waste	0.012
Nonpoint	Residential Wood Combustion: Insert_Certified_Catalytic	0.010

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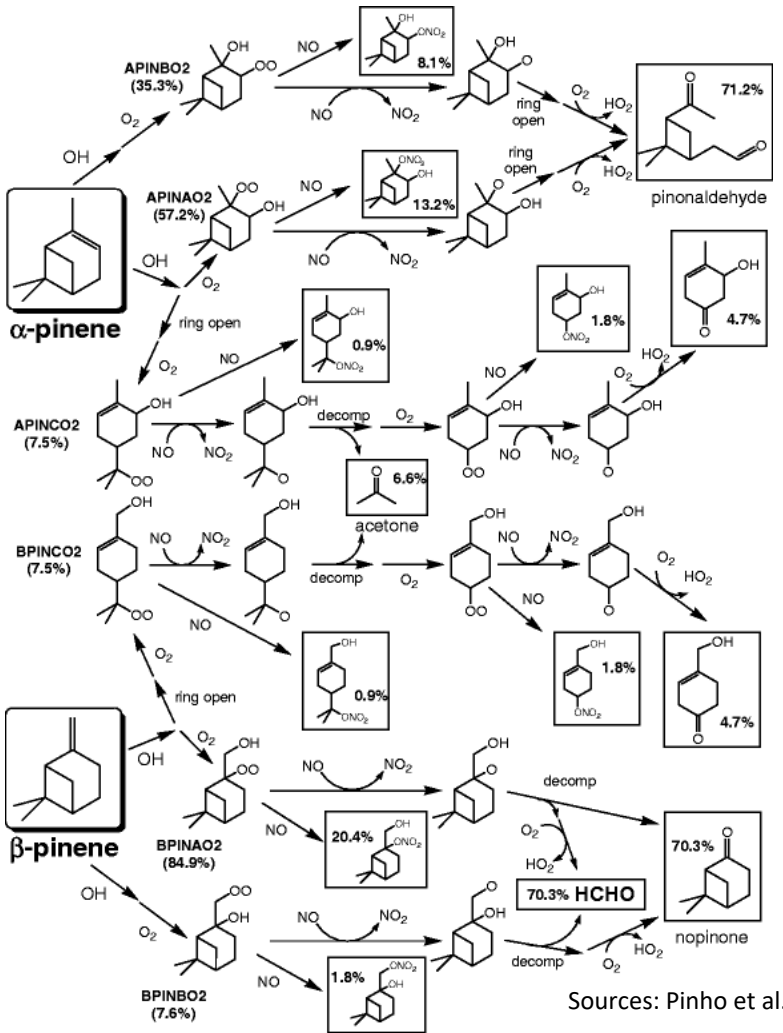
α,β-Pinene + OH (first generation)



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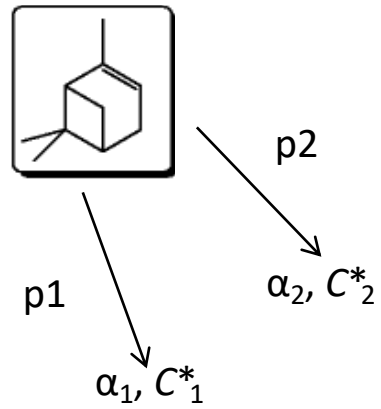
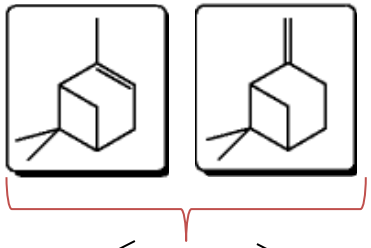
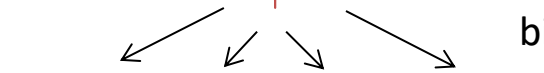
2 products (2p)







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Fix C^*_i, fit chamber data to obtain α_i values

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Assumptions and Approach

Case 1: Klamath County: 1.6 x 10^4 km^2

Case 2: Area approximating area of influence around monitoring site: 225 km^2

Height of Mixing Layer (winter): 200 m

Average Winter Daytime Temp.: 40°F (278K); Average Winter Nighttime Temp.: 20°F (267K)

Duration of Simulation: 12 hours

Daytime chemistry: 12-hr average OH: 2.0 x 10^6 molecules/cm^3; 24-hr average O_3: 7.0 x 10^{11} molecules/cm^3

No NO/HO2 assumptions, consider one pathway at a time

Nighttime chemistry: 12-hr average NO_3: 2.5 x 10^8 molecules/cm^3

Breakdown of biogenic terpene emissions: 31% sesquiterpenes (sqt); 69% monoterpenes (mtrp)

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