# Evaluating Complexity in Fire Emissions Modeling: Is More Better?

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# Outline

- Motivation
- Objectives
- Approach
  - Emission factors from FLAME-IV (fourth Fire Lab at Missoula Experiment)
    - Two-dimensional gas chromatography with time-of-flight mass spectrometry, GC×GC-TOFMS (Hatch et al., 2015)
    - Open path Fourier transform infrared spectroscopy, OP-FTIR (Stockwell et al., 2014)
    - High-resolution proton-transfer-reaction time-of-flight mass spectrometry, PTR-TOFMS (Stockwell et al., 2015)
  - Speciation profiles using FINN (Fire Inventory from NCAR, Wiedinmyer et al., 2011)
  - Box modeling using BOXMOX with a modified version of the MOZART-4 gas-phase chemical mechanism (Knote et al. , 2014)
- Results
- Conclusions and Next Steps

# Motivation: Advanced Analytical Approaches for Studying Biomass Burning Smoke → Improving Model Predictions

Significant increase in the mass of organic carbon/number of compounds identified and quantified in biomass burning studies

<u>Examples from FLAME-IV</u>

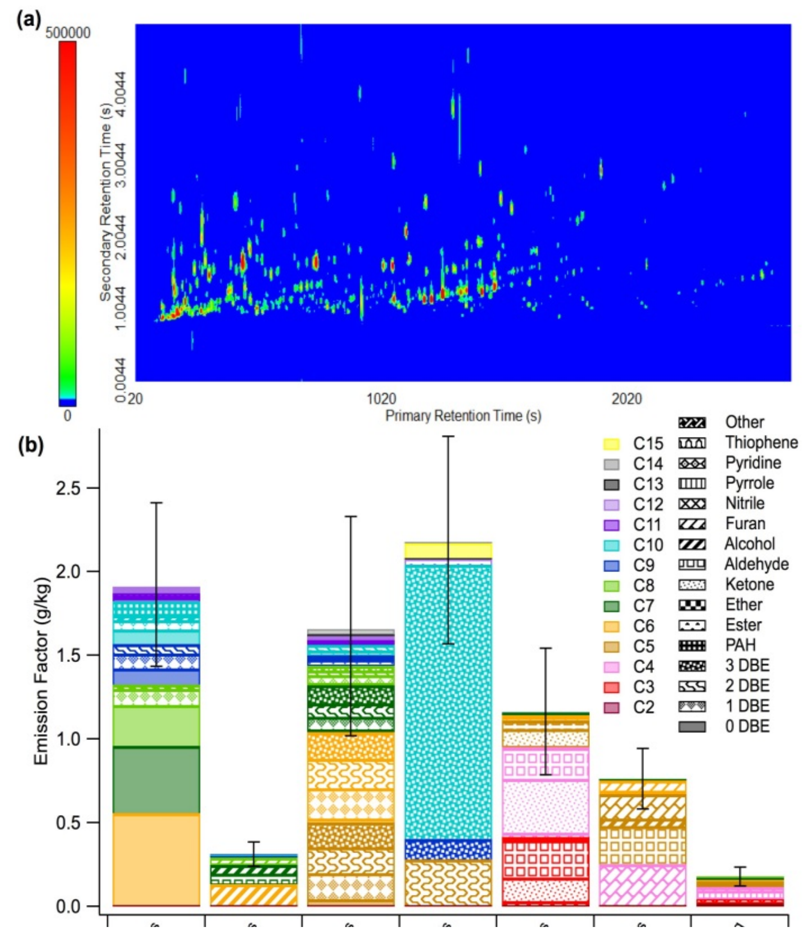
By PTR-TOFMS:

80-96% of detected non-methane organic carbon (NMOC) mass identified in comparison to 18-69% in Yokelson et al. (2013)

By GC×GC-TOFMS:

708 positively/tentatively identified NMOC compounds; 129-474 compounds per burn (6 fuel types)

Figure: Black Spruce
Total NMOC EF (g/kg): 8.2 ± 2.5
# Compounds Identified: 402




Categories: aromatics, oxygenated aromatics, hydrocarbons, terpenoids, oxygenated hydrocarbons, furans, contain N & S

# Objectives

1. Develop an updated speciation profile based on FLAME-IV measurements
2. Evaluate changes in targeted gas-phase pollutants and their precursors attributed to changes in the speciation profile
3. Assess effects of lumping on modeled pollutants and their precursors
4. Consider the potential of increased model complexity to improve air quality and climate predictions

# Approach

STEP 1: Develop an updated speciation profile (FLAME-IV EFs)

STEP 2: Map total NMOCs/kg of fuel to moles of surrogate compound/kg of fuel (FINN/MOZART-4)

STEP 3: Simulate changes in concentrations of pollutants and their precursors (BOXMOX)

# Step 1: Speciation Profiles Based on FLAME-IV EFs

- Default FINN speciation profile based on Akagi et al. (2011): 99 organic compounds
- Updated speciation profiles based on Hatch et al. (2015)/Stockwell et al. (2015): 344 organic species including 51 long chain (>C12) alkanes/alkenes and 39 monoterpenes

# Visualization of Step 2: Mapping from Total NMOC (kg/kg) to Individual Surrogates (moles/kg)

Emitted NMOCs based on FINN (kg $NMOC_t$/kg fuel)

Total NMOC EF: 41 g/kg

↓

Individual NMOC $i$ based on speciation profile (mols $NMOC_i$ /kg fuel)

$i$ = 99 default
$i$ = 344 updated

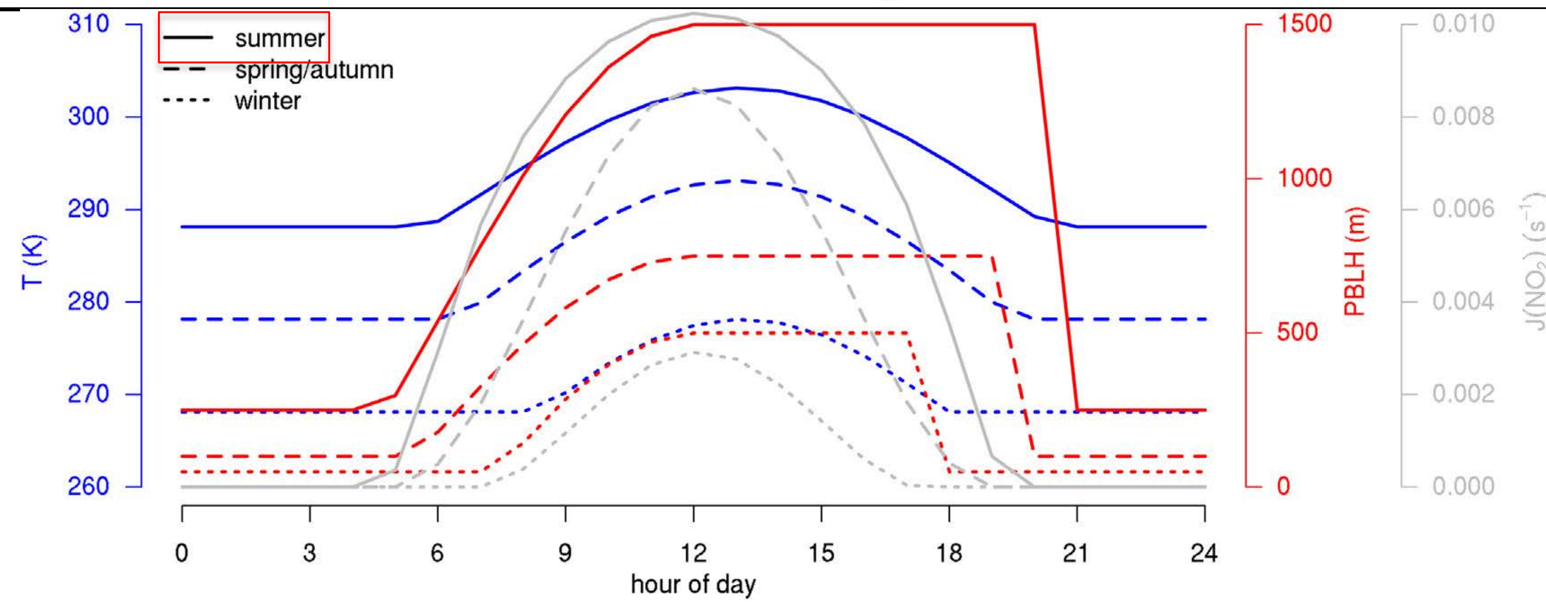
benzene
isoprene
alpha-pinene
C15 alkane
.......

↓

34 surrogates based on modified MOZART-4 (mols $NMOC_i$ /kg fuel)

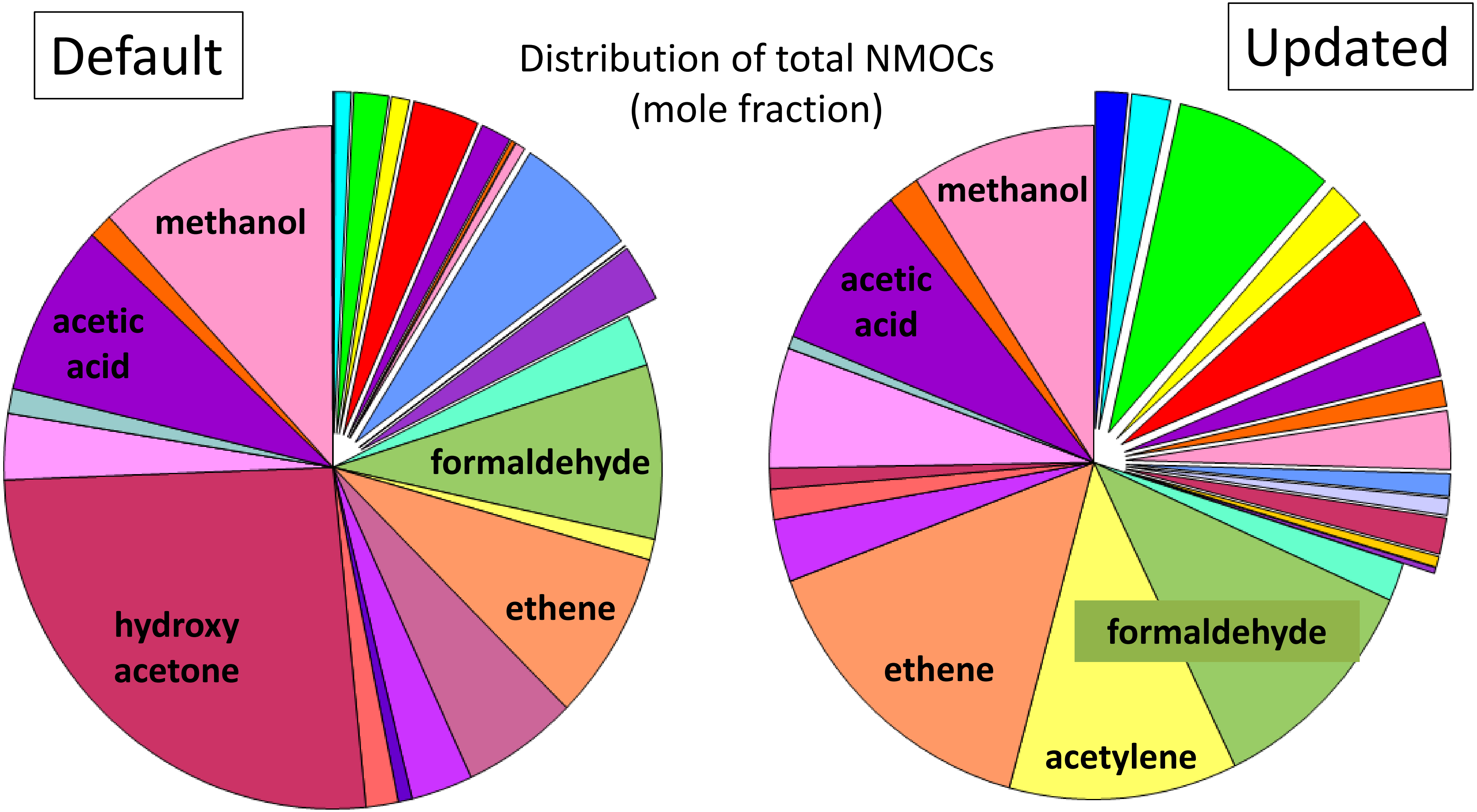
# Step 3: BOXMOX Simulations (Figure from Knote et al., 2014)

| Simulation # | $NO/NO_2$ (ppb) | | Speciation Profile |
|---|---|---|---|
| 1 | 0.1/1 | intermed. NOx | default |
| 2 | 0.1/1 | | updated |
| 3 | 0.01/0.1 | low NOx | default |
| 4 | 0.01/0.1 | | updated |
| 5 | 1/10 | high NOx | default |
| 6 | 1/10 | | updated |



# Results: Visualizing Speciation Profiles (MOZART-4 Surrogates)

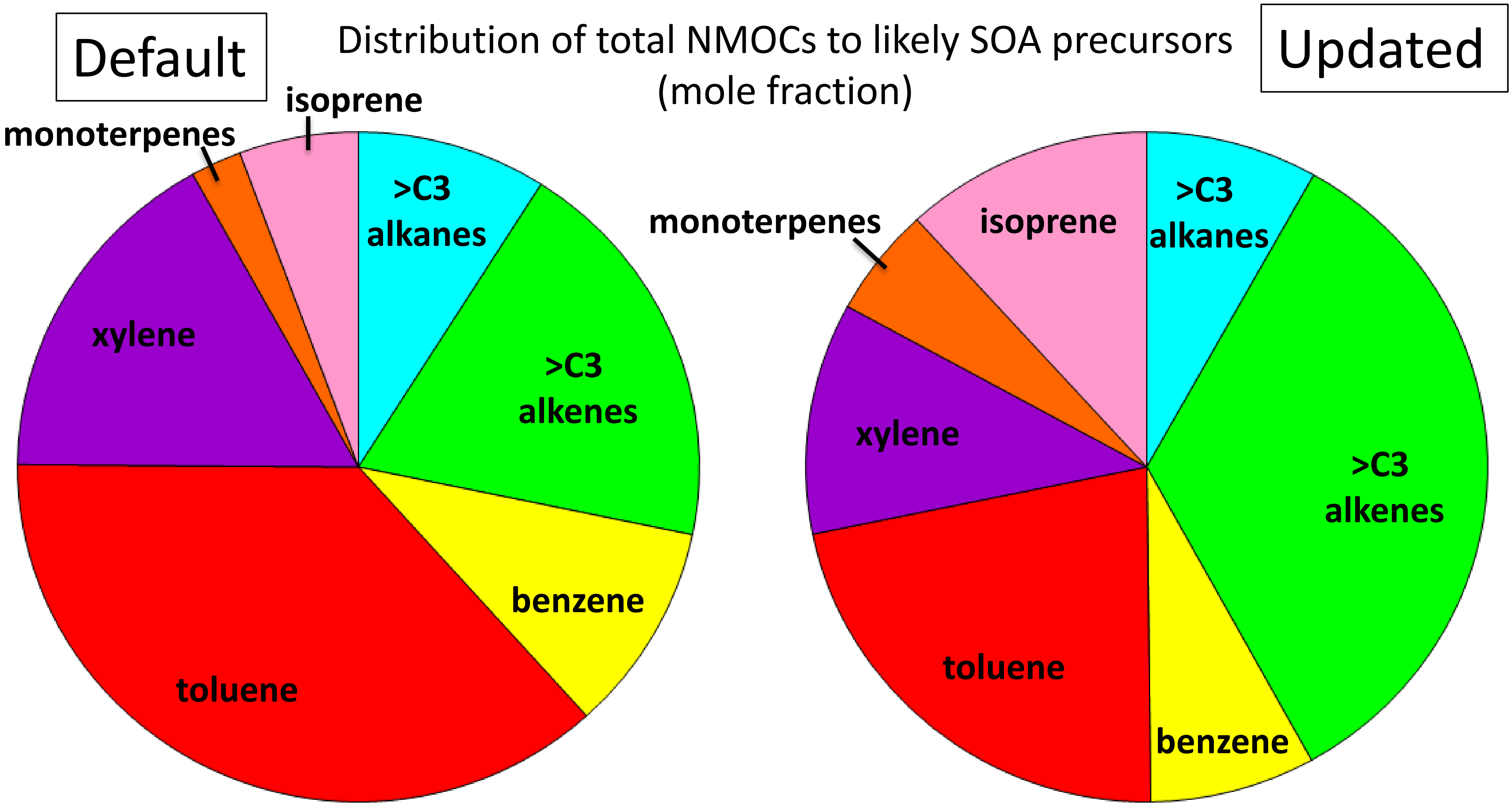
Distribution of total NMOCs (mole fraction)




Offset fractions are surrogates with carbon number > 3

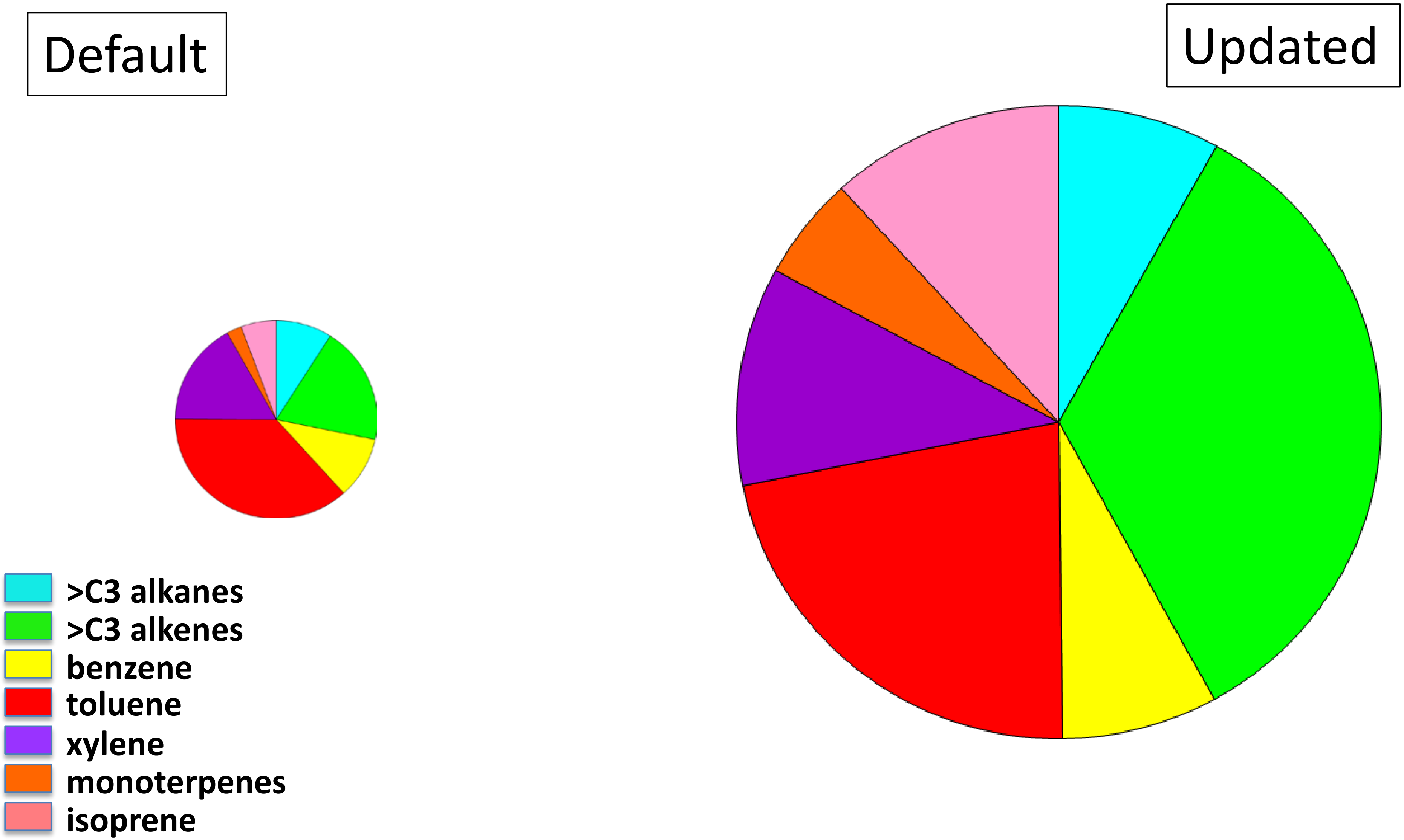
Top 5 (% molar yield) surrogates are labeled

# Results: Visualizing Speciation Profiles, Focus on Likely Secondary Organic Aerosol (SOA) Precursors

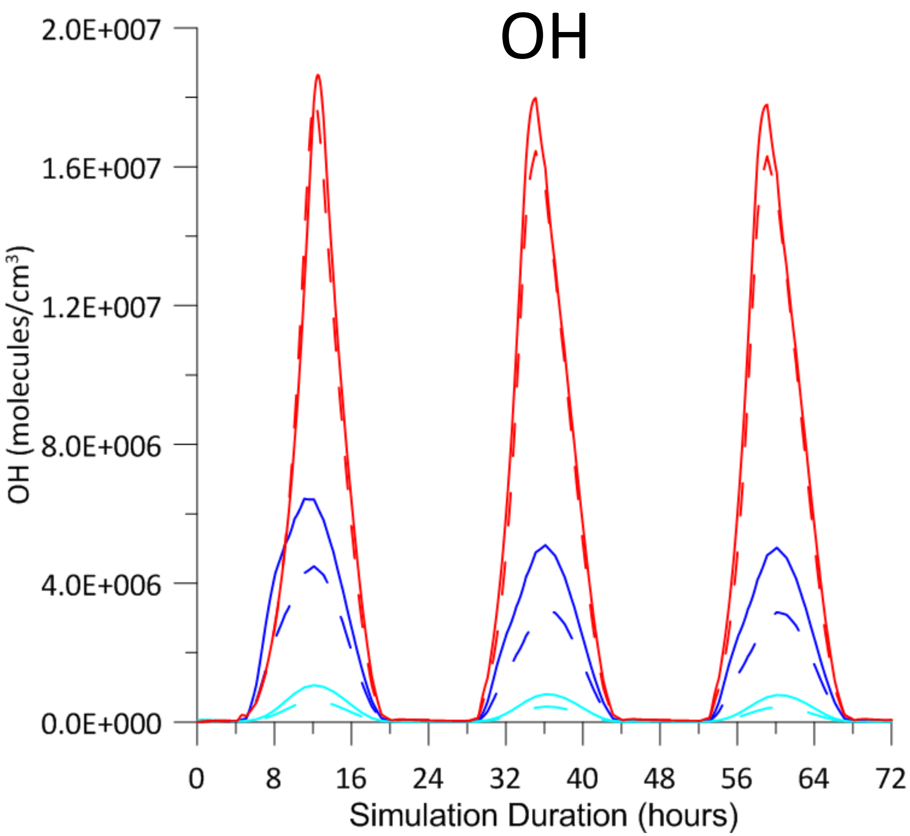


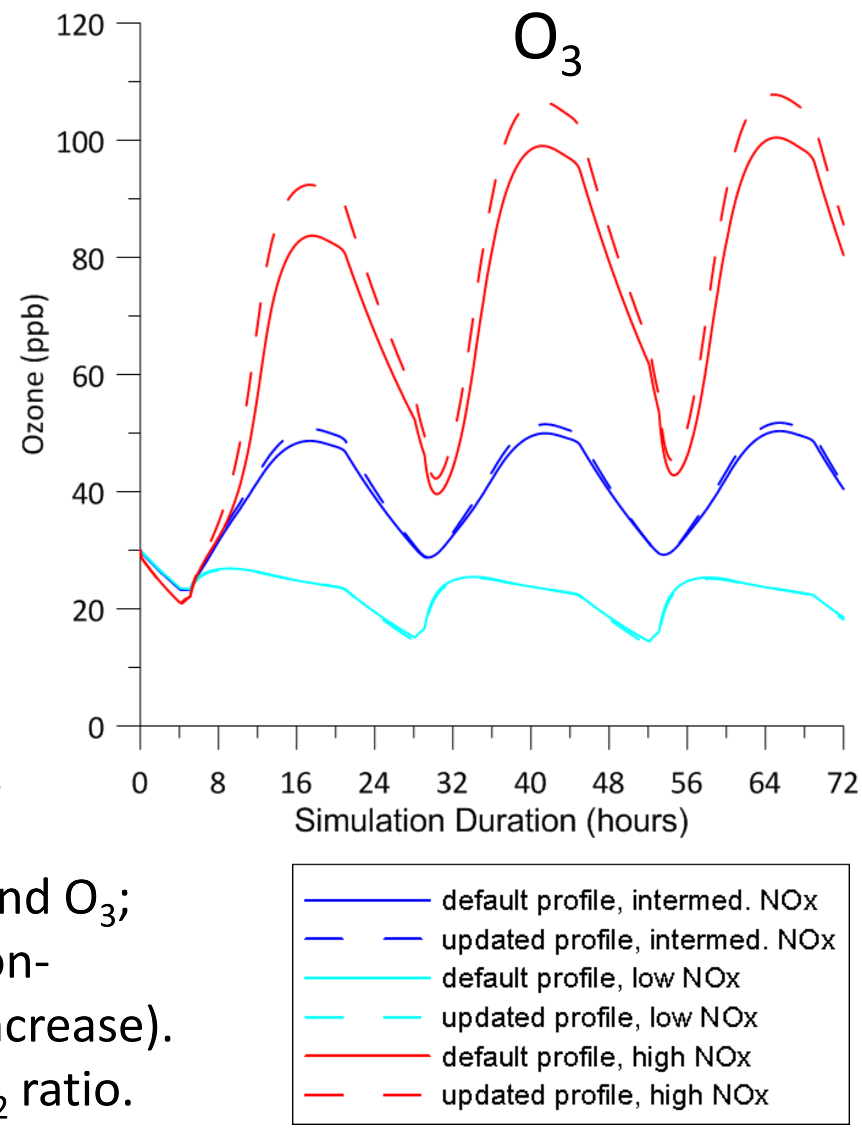

>C3 alkanes (BIGALK) and >C3 alkenes (BIGENE) do not serve as SOA precursors in the full MOZART-4 chemical transport model

# Results: Visualizing Speciation Profiles, Focus on Likely SOA Precursors-*SCALED* based on relative mass



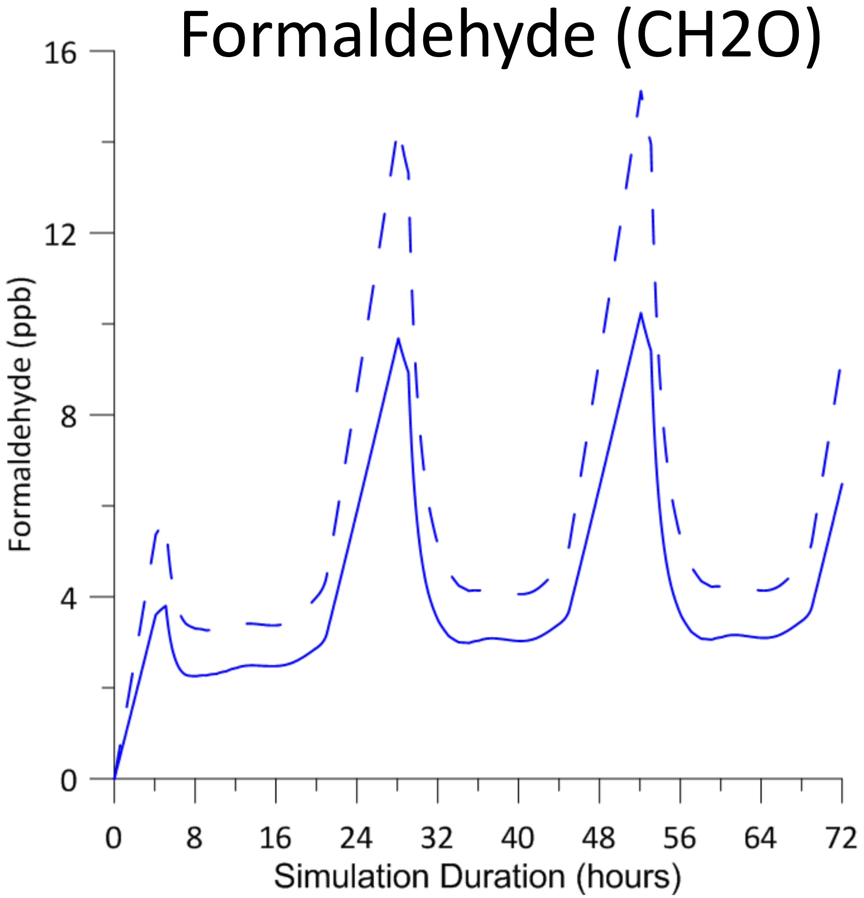
# Results: Species Unchanged by Speciation Profiles

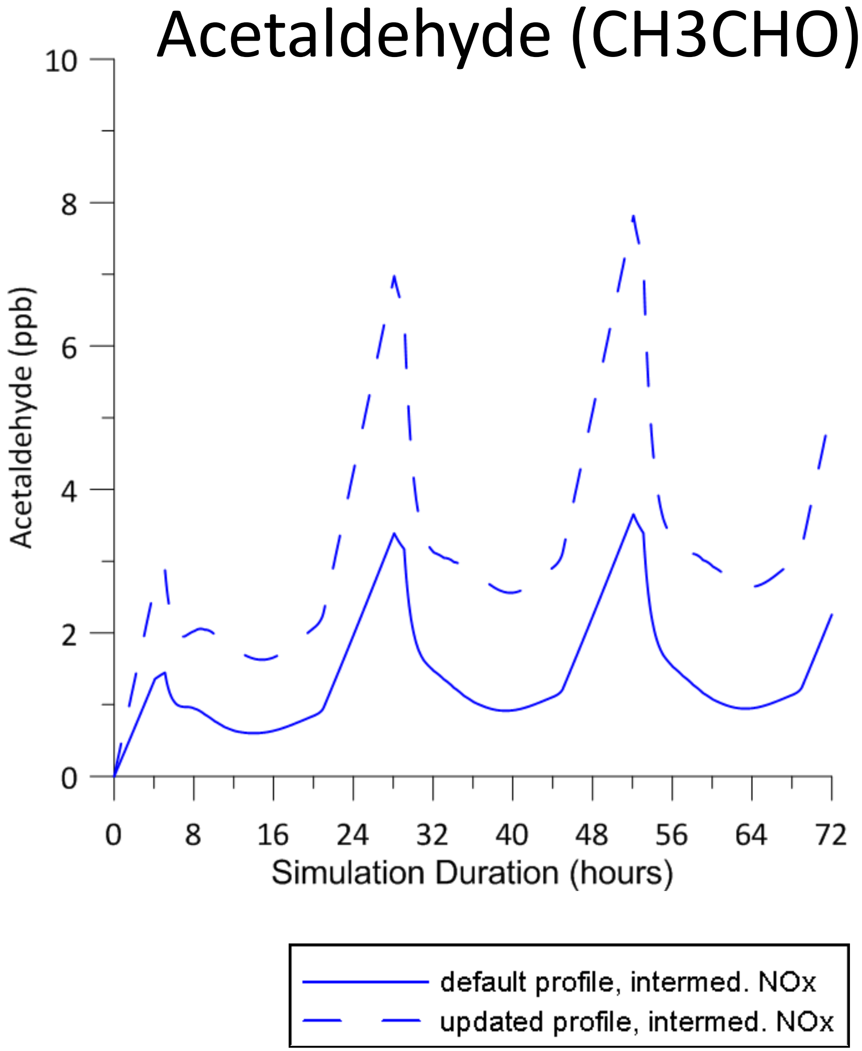



NOx levels drive changes in modeled OH and $O_3$; speciation profile update has small, but non-negligible effect on $O_3$ (up to 9 ppb/10% increase). Even with “high-NOx”, based on $CH_2O/NO_2$ ratio.

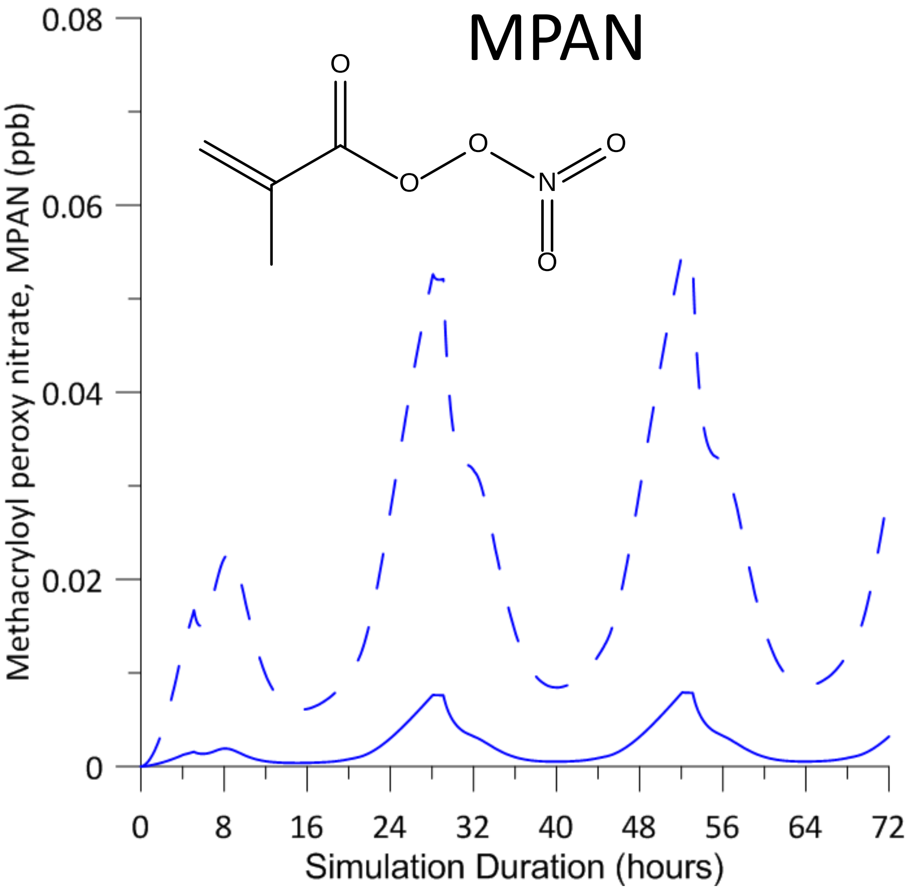
# Results: Species Changed by Speciation Profiles

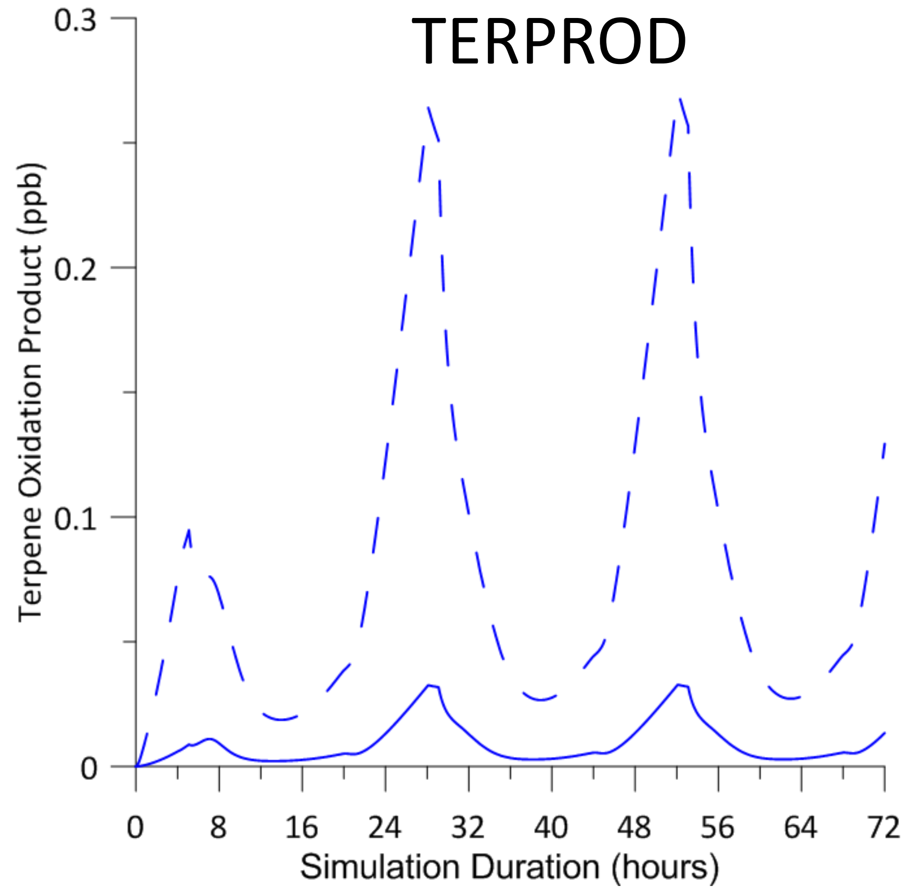



Significant increases in formaldehyde (up to 50%) and acetaldehyde (up to 180%)

# Results: Species Changed by Speciation Profiles- Terpene Oxidation Products




Factor of 15 increase in oxidation product of isoprene (MPAN) and factor of 10 increase in lumped monoterpenes (TERPROD)

# Results: Comparison of Lumping Based on Reactivity vs. SOA Formation Potential

| SOA Yield Rank (high to low) | MOZART Surrogate |
|---|---|
| limonene | limon |
| myrcene | myrc |
| 3-carene | α-pin |
| α-pinene | α-pin |
| terpinolene | limon |
| β-pinene | b-pin |
| *camphene (SOA yield unknown)* | **bigene** |
| sabinene | b-pin |
| z-ocimene | myrc |
| β-phellandrene | limon |
| α-phellandrene | limon |
| *tricyclene (SOA yield unknown)* | **bigalk** |

# Conclusions

- Revised speciation profile fundamentally changes composition of emitted NMOC as represented in model
- Changes in $O_3$ are modest (up to 9%), while changes in gas-phase species such as acetaldehyde and formaldehyde are significant ("caveat": as lumped in MOZART-4 and represented in BOXMOX simulations)
- Increases in terpene emissions leads to increases in terpene oxidation products
- SOA precursors, terpenes, not necessarily lumped with regard for potential SOA yield
- Some likely SOA precursors are lumped with surrogates that do not form SOA in models; 5% of bigalk and 15% of bigene (by EF) have carbon numbers > 10

# Next Steps

- Evaluate effects of updated speciation profile in full three-dimensional chemical transport model
  - gas-phase pollutants
  - SOA precursors and PM mass loadings
- Assess alternative alkane/alkene/terpene lumping schemes
- Modify gas-phase chemical mechanism to treat SOA formation by larger alkanes and alkenes
- Evaluate model skill as a function of updated speciation profile and modified lumping schemes