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

Examples from FLAME-IV

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
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
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\textsubscript{t}/kg fuel)

Total NMOC EF: 41 g/kg

Individual NMOC \textit{i} based on speciation profile (mols NMOC\textsubscript{i} /kg fuel)
- benzene
- isoprene
- alpha-pinene
- C15 alkane
- ......

\textit{i} = 99 default
\textit{i} = 344 updated

34 surrogates based on modified MOZART-4 (mols NMOC\textsubscript{i} /kg fuel)
### Step 3: BOXMOX Simulations
(Figure from Knote et al., 2014)

<table>
<thead>
<tr>
<th>Simulation #</th>
<th>NO/NO$_2$ (ppb)</th>
<th>Speciation Profile</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1/1</td>
<td>default</td>
</tr>
<tr>
<td>2</td>
<td>0.1/1</td>
<td>intermed. NOx</td>
</tr>
<tr>
<td>3</td>
<td>0.01/0.1</td>
<td>default</td>
</tr>
<tr>
<td>4</td>
<td>0.01/0.1</td>
<td>low NOx</td>
</tr>
<tr>
<td>5</td>
<td>1/10</td>
<td>default</td>
</tr>
<tr>
<td>6</td>
<td>1/10</td>
<td>high NOx</td>
</tr>
</tbody>
</table>

**Graphical Representation:**
- Temperature ($T$) in Kelvin ($K$) ranging from 260 to 310
- Vertical axis for PBLH (m) showing values up to 1500
- Hour of the day ranging from 0 to 24
- Three seasonal times: summer, spring/autumn, winter
Results: Visualizing Speciation Profiles (MOZART-4 Surrogates)

Offset fractions are surrogates with carbon number > 3
Top 5 (% molar yield) surrogates are labeled

Distribution of total NMOCs (mole fraction)
>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

- Default
- Updated

- >C3 alkanes
- >C3 alkenes
- benzene
- toluene
- xylene
- monoterpenes
- isoprene
NOx levels drive changes in modeled OH and O₃; speciation profile update has small, but non-negligible effect on O₃ (up to 9 ppb/10% increase). Even with “high-NOx”, based on CH₂O/NO₂ 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

<table>
<thead>
<tr>
<th>SOA Yield Rank (high to low)</th>
<th>MOZART Surrogate</th>
</tr>
</thead>
<tbody>
<tr>
<td>limonene</td>
<td>limon</td>
</tr>
<tr>
<td>myrcene</td>
<td>myrc</td>
</tr>
<tr>
<td>3-carene</td>
<td>α-pin</td>
</tr>
<tr>
<td>α-pinene</td>
<td>α-pin</td>
</tr>
<tr>
<td>terpinolene</td>
<td>limon</td>
</tr>
<tr>
<td>β-pinene</td>
<td>b-pin</td>
</tr>
<tr>
<td><em>camphene (SOA yield unknown)</em></td>
<td>bigene</td>
</tr>
<tr>
<td>sabinene</td>
<td>b-pin</td>
</tr>
<tr>
<td>z-ocimene</td>
<td>myrc</td>
</tr>
<tr>
<td>β-phellandrene</td>
<td>limon</td>
</tr>
<tr>
<td>α-phellandrene</td>
<td>limon</td>
</tr>
<tr>
<td><em>tricyclene (SOA yield unknown)</em></td>
<td>bigalk</td>
</tr>
</tbody>
</table>
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