Updating chemical mechanisms to include the OH oxidation of key reactive biomass burning non-methane organic gases

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Many Acknowledgements

**Fire Lab (2016) Team Photo**

**FIREX-AQ (2019) Team Photo**

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**Model Development during Fire Lab:**
Coggon et al. (2019) - ACP

**Model Application to ambient plume**
Muller et al. (2016) - ACP
Understudied VOCs can be major sources of ozone and SOA

E.g. Furans – understudied ozone precursors

Understudied VOCs can be major sources of ozone and SOA. For example, furans are understudied ozone precursors. Furans constitute a significant fraction of OH reactivity currently missing from models.

Aromatics
Terpenes
Misc. hydrocarbons
Oxygenates
N- contain.

Furans

Average VOC/CO ratio during Firelab 2016

Total emission of structure ppb : mol CO ppm

Koss et al. (2018). ACP. Non-methane organic gas emissions from biomass burning: identification, quantification, and emission factors from PTR-ToF during the FIREX 2016 laboratory experiment
Process-level Understanding Key to Evaluating Smoke Chemistry

E.g. Phenolics – understudied SOA precursors

**Catechol**

\[
\text{OH} \quad \text{OH} \quad \text{NO}_2
\]

\[k_{\text{OH}} \sim 1 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\]

**Nitrocatechol**

*OH oxidation of phenolic compounds can sequester NO\text{\textsubscript{x}}, which could have implications on downwind ozone formation.*

*Nitrophenolic compounds are absorbing chromophores that can contribute to SOA and brown carbon formation.

Yield > 30%

Finewax et al. 2018
Process-level Understanding Key to Evaluating Smoke Chemistry

**E.g. Phenolics – understudied SOA precursors**

Catechol → Nitrocatechol

\[ \text{k}_{\text{OH}} \sim 1 \times 10^{-10} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1} \]

Emission and SOA:

- Alkanes: 18.8%, 3.5%
- Aromatics: 16.9%, 5.1%
- Biogenic: 10.9%, 11.3%
- Furans: 32.6%, 21.0%
- Phenolics: 20.8%, 59.1%

- Aerosol Phase: Yield > 30%
- Finewax et al. 2018

Small Chamber

Smoke (VOCs, Particles, NO$_x$) + O$_3$

$hv = 254$ nm

- Barrel–sized Teflon chamber
- Short experiments (<45 min)
- Long Time Scales (~5 days OH exposure)

Investigating Smoke Chemistry in Firelab

The MIT “mini-chamber”
Investigating Smoke Chemistry in Firelab

Small Chamber

- Barrel–sized Teflon chamber
- Short experiments (<45 min)
- Long Time Scales (~5 days OH exposure)

Smoke (VOCs, Particles, NOₓ) + O₃
hv = 254 nm

Methods

Proton Transfer Reaction Time Of Flight Mass Spectrometer (PTR-ToF-MS)
- Sensitive to broad range of VOCs
- Over 150 compounds identified

Iodide Chemical Ionization Mass Spectrometer (I-CIMS)
- Sensitive to oxygenated VOCs and inorganic species

The MIT “mini-chamber”
Coggon et al. ACP (2019) – Updates to Master Chemical Mechanism using 2016 Fire Lab experiments

**Biomass Burning Mechanism Development**

**MCM Includes:**
- Oxygenates
- Alkenes
- Aromatics
- Phenolic
  - Catechol
  - Cresol
  - Phenol

**Coggon et al. Added:**
- Guaiacol
- Furans
  - Furan
  - 2-methylfuran
  - 2,5-dimethylfuran
  - furfural
  - methyl fufural

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\(^\alpha\)Wolfe et al. (2016). Geosci. Model Dev. The Framework for 0-D Atmospheric Modeling (F0AM) v3.1
General Chemistry of Furans Added to MCM

Updated MCM Chemistry

- Missing OH reactivity
- Added to MCM (furan + phenolic chemistry)
- MCM 3.3.1

Unsaturated Dicarbonyls

Hydroxyfuranones

Aschmann et al. (2014)
General Chemistry of Furans Added to MCM

Updated MCM Chemistry

- **Missing OH reactivity**
- **Added to MCM (furan + phenolic chemistry)**
- **MCM 3.3.1**

Fraction of Total OH Reactivity

R₁, R₂ = H or CH₃

Unsaturated Dicarbonyls

Maleic Anhydride

Hydroxyfuranones
Chemistry of Phenolics Added to MCM

**Updated MCM Chemistry**

- **Missing OH reactivity**
- **Added to MCM (furan + phenolic chemistry)**
- **MCM 3.3.1**

**Catechol**

- $\text{OH} + \text{OH} \rightarrow \text{OH} \quad [30\% \text{ yield}]$
- $\text{NO}_2 + \text{OH} \rightarrow \text{OH} \quad [20\% \text{ yield}]$

**Guaiacol**

- $\text{OH} + \text{OCH}_3 \rightarrow \text{OCH}_3 \quad [20\% \text{ yield}]$

Model Comparison for Key Primary Emissions

Measurements by PTR-ToF-MS

- Butanol-d9
- Benzene
- Toluene
- Styrene
- Monoterpenes
- Phenol
- Cresol
- Guaiacol
- Furan
- Methylfuran

Mixing Ratio (ppb) vs. Experimental Time (min)
Key Secondary Products – MCM v 3.3.1

- **Hydroxyfuranone** and **me-hydroxyfuranone** are major masses detected by I-CIMS.
- In the **absence** of furan chemistry, the profiles of these masses is not well-explained by the MCM.
When furan chemistry is included, the temporal profiles of these masses are better explained.
Recall the expected chemistry of furans

**Unsaturated Dicarbonyls**

**Maleic Anhydride**

**Hydroxyfuranones**

**No Furans Included**
Recall the expected chemistry of furans.
**Key Secondary Products – MCM v 3.3.1 + Phenolic Chemistry**

**Guaiacol**

\[ \text{Guaiacol} \xrightarrow{\text{OH, OCH}_3, \text{OH}} \text{Nitroguaiacol} \]

- Reaction with \( \text{NO}_2 \)
- 20% yield

**Nitroguaiacol**

- Model Output (ppb)
- Mixing ratio (ppb)

**Experimental Time (min)**

0 10 20 30 40

Model Output (ppb)

0.10

0.05

0.01

0

**Aerosol Phase**
• Furan chemistry can explain major secondary products observed by PTR-ToF-MS and I-CIMS.

• Inclusion of phenolic compounds explains observed behavior of nitroaromatics.

• How do these updates translate to chemistry observed in a real biomass burning plume?
Key Secondary Products – MCM v 3.3.1 + Phenolic Chemistry

Model results from an understory fire, described by Mueller et al. (2016)
Model results from an understory fire, described by Mueller et al. (2016)

- Furan chemistry needed to explain maleic anhydride formation.
- Inclusion of furans increases simulated ozone by ~10%.
- How do changes to other VOCs impact simulated ozone?

[Graphs showing changes in concentrations of various compounds over time.]
Test Ozone Sensitivity to Changes in VOCs

- Ozone increases in response to fast-reacting species (e.g. furans)
- Ozone decreases are observed for a doubling in phenolic compounds.
- How does this affect the reactive nitrogen budget?

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percent Change in Ozone after a Doubling in VOC Mixing Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural</td>
<td>*</td>
</tr>
<tr>
<td>HCHO</td>
<td>*</td>
</tr>
<tr>
<td>Propene</td>
<td>*</td>
</tr>
<tr>
<td>Ethylene</td>
<td>*</td>
</tr>
<tr>
<td>Furanone</td>
<td>*</td>
</tr>
<tr>
<td>Furan</td>
<td>*</td>
</tr>
<tr>
<td>Methyl Furan</td>
<td>*</td>
</tr>
<tr>
<td>Dimethylfuran</td>
<td>*</td>
</tr>
<tr>
<td>Methanol</td>
<td></td>
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<tr>
<td>Isoprene</td>
<td></td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td></td>
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<tr>
<td>Phenol</td>
<td></td>
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<tr>
<td>Cresol</td>
<td></td>
</tr>
<tr>
<td>Catechol</td>
<td></td>
</tr>
</tbody>
</table>

* Furan species
Test NO\textsubscript{y} Sensitivity to Changes in NO\textsubscript{x} and VOCs

\begin{itemize}
  \item $\sim 10\%$ of the NO\textsubscript{x} is converted to nitroaromatics
  \item $\sim 35\%$ of the NO\textsubscript{x} is converted to peroxycetyl nitrates
  \item $\sim 30\%$ of the NO\textsubscript{x} is converted to HNO\textsubscript{3}
\end{itemize}
Conclusions

• Furan chemistry plays a major role in the formation of secondary products observed by chemical ionization mass spectrometers.

• Ambient measurements of hydroxy furanones, maleic anhydride, and nitroaromatics can be used to constrain the chemistry of furans and phenolic compounds, and possibly infer other important parameters, such as OH exposure.

• Nitroaromatics may significantly participate in the NO\(_y\) budget, and better ambient constraints on these compounds are needed in both the gas and aerosol phases.

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