Emissions and chemistry of biomass burning: I⁻ ToF-CIMS during the FireLab 2016 campaign

Bin Yuan
NOAA Earth System Research Laboratory
CIRES, University of Colorado
Paul Scherrer Institute (PSI)
bin.yuan@psi.ch

Aerodyne User Meeting in Beijing
May, 2017
Outline

- FireLab 2016 campaign
- Iodide CIMS results
- Inter-comparison with other instruments
FireLab 2016

Wind Tunnel:
- Mini Chamber:
  - HR-AMS
  - SP-HR-AMS
  - CAPS, PASS
  - CRD-PAS, SP2
  - CO, CO2, O3
  - SP2, CLAP, POPS
  - PAX, SMPS
  - WSOC-PILS
- Mixing Drum for BC and BrC:

Control Room:
- H3O+CIMS
- I-CIMS
- PAM

Viewing Room:
- PILS-ESI
- Ny, NO, sampler

Samplers:
- Gas: GCxGC-ToF-MS (EI)
- Particle: GCxGC-ToF-MS (VUV)
- DI-MS, PILS

Room Burns:
- BrC-PILS
- BBCEAS
- CRDPAS
- NEPH

Aerodyne Lab:
- LToF-AMS
- PTR-MS
- ECHAMP
- PAM
- CO, CO2, NOx, HCHO, CH4, C2H6, C3H8, ..
Iodide ToF-CIMS

\[ \text{I}^- + X \rightarrow \text{IX}^- \]

**Inorganic acids:** HONO, HNCO, HNO$_3$, HCl

**Organic species:**
- Oxygenated VOCs (≥2 O)
- Organic nitrates (and nitro compounds)
20 m ½” Teflon Permeation Tube

DCOOH

Capillary

430 mbar

100-400 cc/min

~100 L/min

Zero Air

MFC ~ 4 L/min

Bubbler

FM

PC

Pump

Pump

CIMS

MIT-mini chamber

Flow legend

Common

Smoke

BG

~ 1 L/min
Engelmann Spruce

Fire25: Canopy
Mainly Flaming
MCE=0.953
med-N fuel

Fire26: Duff
Smoldering
MCE=0.818
high-N fuel
<table>
<thead>
<tr>
<th>No.</th>
<th>Fire25: Canopy</th>
<th>Fire26: Duff</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M173  ICH2O2</td>
<td>Formic acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M237 ICH6H6O2</td>
</tr>
<tr>
<td>2</td>
<td>M237 IC6H6O2</td>
<td>Catechol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M173 ICH2O2</td>
</tr>
<tr>
<td>3</td>
<td>M174 IHNO2</td>
<td>HONO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M251 IC7H8O2</td>
</tr>
<tr>
<td>4</td>
<td>M217 IC3H6O3</td>
<td>Lactic acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M253 IC6H6O3</td>
</tr>
<tr>
<td>5</td>
<td>M251 IC7H8O2</td>
<td>Guaiacol/Methylcatechol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M265 IC8H10O2</td>
</tr>
<tr>
<td>6</td>
<td>M253 IC6H6O3</td>
<td>Trihydroxylbenzene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M259 IC5H8O4</td>
</tr>
<tr>
<td>7</td>
<td>M259 IC5H8O4</td>
<td>Glutaric acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M252 C6H7INO2</td>
</tr>
<tr>
<td>8</td>
<td>M243 IC5H8O3</td>
<td>Levulinic acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M187 IC2H4O2</td>
</tr>
<tr>
<td>9</td>
<td>M203 IC2H4O3</td>
<td>Glycolic acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M271 IC6H8O4</td>
</tr>
<tr>
<td>10</td>
<td>M263 IC8H8O2</td>
<td>Phenylacetic acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M219 C3H8O3</td>
</tr>
<tr>
<td>11</td>
<td>M229 IC4H6O3</td>
<td>Ketobutyric acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M222 C5H5INO</td>
</tr>
<tr>
<td>12</td>
<td>M187 IC2H4O2</td>
<td>Acetic acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M229 IC4H6O3</td>
</tr>
<tr>
<td>13</td>
<td>M241 IC5H6O3</td>
<td>Dihydro-furancarboxylic acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M243 IC5H8O3</td>
</tr>
<tr>
<td>14</td>
<td>M271 IC6H8O4</td>
<td>Dimethyl maleate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M203 IC2H4O3</td>
</tr>
<tr>
<td>15</td>
<td>M265 IC8H10O2</td>
<td>Dimethoxybenzene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M273 IC6H10O4</td>
</tr>
<tr>
<td>16</td>
<td>M249 IC7H6O2</td>
<td>Benzoic acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M279 IC8H8O3</td>
</tr>
<tr>
<td>17</td>
<td>M219 IC3H8O3</td>
<td>Glycerol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M241 IC5H6O3</td>
</tr>
<tr>
<td>18</td>
<td>M227 IC4H4O3</td>
<td>Hydroxy-furanone</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M251 IC8H12O</td>
</tr>
<tr>
<td>19</td>
<td>M215 IC3H4O3</td>
<td>Pyruvic acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M92 C2H4O4</td>
</tr>
<tr>
<td>20</td>
<td>M239 IC5H4O3</td>
<td>Furoic acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M154 IHCN</td>
</tr>
</tbody>
</table>

**Aromatics**  **Furans**  **Simple organic acids**  **N-Containing**  **Inorganic**
Fire26: Engelmann Spruce - Duff

MIT Mini-Chamber

- **Light on**
  - Catechol
  - Trihydroxylbenzene
  - Tetrahydroxylbenzene

- **Light off**
  - Glycolic acid
  - Succinic acid
  - NO$_3^-$ fragment
  - Nitrobenzene

Graph showing signal changes over time with peaks indicating the release of various compounds during light on and light off periods.
Fire26: Engelmann Spruce - Duff
MIT Mini-Chamber

Loss

Formation

Large flux of secondary formation for oxidized species!

----->Strong SOA formation??

log(signal)

mass defect

m/z

Odd Mass, Loss

Odd Mass, Formation

Even Mass, Loss

Even Mass, Formation
Oxidation Flow Reactor (OFR)

- Ages smoke in real-time
- OH exposure is fixed
- Investigation of smoke chemistry as a function of burn stage (e.g., flaming vs. smoldering)

**OFR OH Generation**

\[
\begin{align*}
H_2O + h\nu_{185} & \rightarrow OH + H \\
O_2 & \rightarrow O_3 \\
H + O_2 & \rightarrow HO_2 \\
O_3 + h\nu_{254} & \rightarrow O(1D) + O_2 \\
O_2 + h\nu_{185} & \rightarrow 2O(3P) \\
O(1D) + H_2O & \rightarrow 2OH
\end{align*}
\]

*Leaded by Matt Coggon*
Inter-comparison between H$_3$O$^+$ CIMS (i.e. PTR-TOF) and I$^-$ CIMS

- High variability burn
- Good agreement
Inter-comparison for Fire 25
I-CIMS vs $\text{H}_3\text{O}^+\text{CIMS}$

- multiple compounds per mass
- low sensitivity of either instrument
• Three instruments measure different compounds/classes with some overlap
Summary

- VOC emissions from biomass burning depend on the types of fuels, combustion efficiency and fuel compositions;

- I- CIMS indicates a large flux of oxygenated VOCs from the aging of biomass burning plumes;

- Different VOC instruments may be measuring different classes of compounds;
Acknowledgement

**NOAA ESRL CSD**
Carsten Warneke, Jim Roberts, Matt Coggon, Abby Koss, Joost de Gouw

**University of Colorado Boulder**
Jordan Krechmer, Hyungu Kang, Harald Stark, Jose Jimenez

**Massachusetts Institute of Technology**
Christopher Lim, Jesse Kroll

**University of Montana**
Vanessa Salimovic, Robert Yokelson