Organic Chemical Composition of Gases & Particles Measured During the October 2017 Northern California Wildfire Plumes

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Atmospheric Chemical Mechanisms Conference, Nov 13, 2020
Large wildfires have become more common in the western US

- Since 2015, annual average PM$_{2.5}$ is clearly increased by wildfires
Oct 2017 Northern California Wildfires

- Fires triggered by power line/electrical failures, developed under the Diablo wind.
- On the “deadliest & most destructive California wildfires” list

<table>
<thead>
<tr>
<th>Fire</th>
<th>Size (hectares)</th>
<th>Structures destructed</th>
<th>Deaths</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tubbs</td>
<td>14,895</td>
<td>5,643</td>
<td>22</td>
</tr>
<tr>
<td>Redwood Valley</td>
<td>14,780</td>
<td>544</td>
<td>9</td>
</tr>
<tr>
<td>Atlas</td>
<td>20,891</td>
<td>781</td>
<td>6</td>
</tr>
<tr>
<td>Nuns</td>
<td>22,008</td>
<td>1,355</td>
<td>3</td>
</tr>
</tbody>
</table>
Impacts on SF Bay Area Air Quality

PUBLIC HEALTH

News // California Wildfires

San Francisco AQI jumps to 271 on Friday, worst air quality ever recorded in the city

Amy Graff, SFGATE
Nov. 16, 2018 | Updated: Nov. 16, 2018 4:35 p.m.
Gas and particles in wildfire smoke

• Organic gases and particles are the main pollutants emitted from wildfires.

Unknowns:
• What is the **molecular composition** of wildfire smoke organic aerosol (BBOA) we inhaled?
• Can **primary BBOA marker compounds** indicate the type of fuel burned?
• What are the **secondary BBOA markers**?
Measurements

- UC Berkeley campus: ~ 60 km from the fires
- Collected 74 filter samples (3-4 h) using a 6-channel sequential sampler, analyzed with GC×GC-ToFMS
- Measured volatile organic compounds (VOCs) by PTR-ToFMS

From thermal desorption and derivatization

1st column: volatility separation

2nd column: polarity separation

Modulator

To ToF-MS
Sugars are dominant components of BBOA particles

- Quantified 570+ organic compounds in the particle phase. Up to 20% of OC can be explained by the GC × GC measurements.
- Sugar & sugar derivatives are the dominant compounds in smoke particles
- Level of PAHs are below 0.3% of total quantified OA (up to 5% in fresh smoke)
Biomass burning markers indicate fuels & SOA

Cluster 1: smoke from Atlas fire (hardwood)
Cluster 2: aged smoke from Sonoma County fires
Cluster 3: fresh smoke from Sonoma County fires (hardwood & softwood)

Primary BBOA markers

Secondary BBOA markers

- 4-nitrocatechol
- Methylnitrocatechols

Clusters shown:
- Cluster A
- Cluster B
- Cluster C
- Cluster D
- Cluster E

Concentration [µg m⁻³]

Solar radiation [W m⁻²]

Mass ratios

Concentration [µg m⁻³]
A unique daytime secondary BBOA factor

### Multifunctional aliphatic acids

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>11-Oct</th>
<th>12-Oct</th>
<th>13-Oct</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,4-dihydroxybutanoic acid</td>
<td>C₅H₈O₄</td>
<td>13.3</td>
<td>13.9</td>
<td>20.3</td>
</tr>
<tr>
<td>citramalic acid</td>
<td>C₅H₆O₃</td>
<td>0.0</td>
<td>8.4</td>
<td>11.5</td>
</tr>
<tr>
<td>pimelic acid</td>
<td>C₇H₁₀O₄</td>
<td>26.8</td>
<td>26.0</td>
<td>26.0</td>
</tr>
<tr>
<td>2,2-bis(hydroxymethyl)propionic acid</td>
<td>C₅H₉O₄</td>
<td>17.5</td>
<td>32.8</td>
<td>16.9</td>
</tr>
<tr>
<td>malic acid</td>
<td>C₆H₈O₄</td>
<td>32.3</td>
<td>32.8</td>
<td>50.5</td>
</tr>
<tr>
<td>suberic acid</td>
<td>C₇H₁₀O₄</td>
<td>0.0</td>
<td>11.4</td>
<td>11.9</td>
</tr>
<tr>
<td>threonic acid</td>
<td>C₅H₈O₄</td>
<td>14.9</td>
<td>10.3</td>
<td>9.9</td>
</tr>
<tr>
<td>2,3,4-trihydroxybutyric acid</td>
<td>C₅H₈O₃</td>
<td>7.3</td>
<td>4.9</td>
<td>4.5</td>
</tr>
<tr>
<td>2,3-dimethylsuccinic acid</td>
<td>C₅H₈O₃</td>
<td>5.2</td>
<td>5.3</td>
<td>5.8</td>
</tr>
<tr>
<td>α-ketoglutaric acid</td>
<td>C₅H₈O₃</td>
<td>0.0</td>
<td>7.4</td>
<td>3.7</td>
</tr>
<tr>
<td>2-pentenedioic acid</td>
<td>C₅H₈O₃</td>
<td>5.7</td>
<td>2.8</td>
<td>3.1</td>
</tr>
<tr>
<td>maleic acid</td>
<td>C₅H₆O₄</td>
<td>0.0</td>
<td>6.5</td>
<td>6.3</td>
</tr>
<tr>
<td>pinic acid</td>
<td>C₅H₈O₄</td>
<td>12.7</td>
<td>8.2</td>
<td>10.3</td>
</tr>
<tr>
<td>2,3-dihydroxy-4-oxo pentanoic acid</td>
<td>C₅H₈O₃</td>
<td>2.2</td>
<td>5.9</td>
<td>9.3</td>
</tr>
<tr>
<td>3-methyl-1,2,3-butaneetricarboxylic acid (MBTCA)</td>
<td>C₁₀H₁₆O₄</td>
<td>2.6</td>
<td>0.0</td>
<td>2.4</td>
</tr>
</tbody>
</table>

### Oxygenated aromatic compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>11-Oct</th>
<th>12-Oct</th>
<th>13-Oct</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,7-dimethyl-1,3-isobenzofuranone</td>
<td>C₁₀H₁₃O₂</td>
<td>0.8</td>
<td>1.3</td>
<td>2.0</td>
</tr>
<tr>
<td>1-phenyl-1-penten-3-one</td>
<td>C₁₀H₁₂O</td>
<td>2.4</td>
<td>6.4</td>
<td>9.1</td>
</tr>
<tr>
<td>1,3-dihydroxyanthracene</td>
<td>C₁₄H₁₀O₂</td>
<td>6.3</td>
<td>3.3</td>
<td>3.3</td>
</tr>
<tr>
<td>protocatechic acid</td>
<td>C₇H₆O₄</td>
<td>43.5</td>
<td>25.3</td>
<td>35.2</td>
</tr>
<tr>
<td>phthnic acid</td>
<td>C₄H₆O₄</td>
<td>27.7</td>
<td>45.9</td>
<td>68.5</td>
</tr>
<tr>
<td>gallic acid</td>
<td>C₇H₆O₃</td>
<td>2.2</td>
<td>2.6</td>
<td>2.6</td>
</tr>
</tbody>
</table>
VOCs in wildfire smoke

- Over 70% of non-methane organic carbon in smoke was in VOCs
- VOCs in smoke may undergo photooxidation, producing harmful OVOCs, O$_3$ and SOA
Daytime oxidation produced oxygenated VOCs

\[ \Delta NMOG = \left( \frac{\Delta X}{\Delta CH_3CN} \right)_{\text{day}} - \left( \frac{\Delta X}{\Delta CH_3CN} \right)_{\text{night}} \]

\[ \Delta NMOG_{\text{fraction}} = \frac{\left( \frac{\Delta X}{\Delta CH_3CN} \right)_{\text{day}} - \left( \frac{\Delta X}{\Delta CH_3CN} \right)_{\text{night}}}{\left( \frac{\Delta X}{\Delta CH_3CN} \right)_{\text{night}}} \]

The daytime plume traveled ~ 7-8 hours to Berkeley.

The nighttime plume traveled ~ 2-3 hours to Berkeley.
Correlation with furan (primary) and maleic anhydride (secondary) reveals the source of VOCs

\[ R^2 \text{ with maleic anhydride} \]

Aromatic nitrogen-containing
Benzenoid
Furanoid
Hydrocarbon
Aliphatic nitrogen-containing
Others
Aliphatic oxygenated
Sulfur-containing
Terpenoid

\[ \text{furan/furfural + OH} \rightarrow \text{maleic anhydride} \]

lifetime of furan = 4.4 hours if [OH] = 1.5×10^6 molec cm\(^{-3}\)
Summary

• Sugars & sugar derivatives, mono-acids, aromatic compounds and terpenoids are the main components of BBOA particles.

• A group of multifunctional acids and oxygenated aromatic compounds were identified as potential daytime BB SOA tracers.

• There was substantial change of BBOA composition during transport under sunlight.

• Thanks for watching! We look forward to your questions, comments & suggestions!

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