Understanding the Biogenic Species Responsible for Atmospheric New Particle Growth

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Motivation: explain and predict growth rates of freshly nucleated particles

- Observed growth rate can be up to 50 times higher than that calculated from sulfuric acid condensation.
- We can express observed growth rate ($GR_{obs}$) according to:

$$GR_{obs} = GR/GR_{H2SO4}$$
Tool for direct determination of compounds in nanoparticles

High-resolution time-of-flight Thermal Desorption Chemical Ionization Mass Spectrometer (HTOF-TDCIMS)

Instrument characteristics:

Resolution: 3000 Th/δTh (V-mode)
Maximum m/z: 50,000
Acquisition rate: 5 Hz
Operation principle

Select narrow size range of particles

Deposit particles on Pt wire

Heat wire and desorb material in ion source
Desorption and ionization

H$_3$O$^+$
Field campaign BEACHON-RoMBAS 2011

Site elevation ~2400m a.s.l.
Ponderosa pine dominated forest
Major monoterpenes: $\alpha$-/ß-pinene, $\Delta$-carene
Particle formation event during BEACHON-RoMBAS 2011

NCAR/ACD/UA: PSD Combined particle size distribution (BEACHON-ROMBAS-2011)

SO2 (ppbv)
Negative ion signal from 20 nm particles

Normalized signal vs. m/z ratio showing various compounds such as NO2, NO3, SO2, SO3, C2H5O4, HSO4, and SO5. The graph indicates a peak at m/z 40 for NO2 on August 10, 2011, at 17:06:48.
Major ions identified in 20 nm particles

<table>
<thead>
<tr>
<th>Inorganic:</th>
<th>Organic:</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$</td>
<td>CHO$_2$</td>
</tr>
<tr>
<td>NO$_3$</td>
<td>C$_2$H$_3$O$_2$</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>C$_2$HO$_3$</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>C$_2$H$_3$O$_3$</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>C$_3$H$_3$O$_3$</td>
</tr>
<tr>
<td>HSO$_4$</td>
<td>C$_2$HO$_4$</td>
</tr>
<tr>
<td>SO$_5$</td>
<td>C$_3$H$_3$O$_4$</td>
</tr>
</tbody>
</table>

34 ions related to organic signal identified
Comparison bulk aerosol vs. 20 nm particle composition

- Nitrates
- Sulfates
- Organics

Relative abundance

August 8 | August 9 | August 10 | August 11

0.0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5

20 nm
Biogenic particle formation in a flow tube

Continuous flow
Residence time ~ 15 – 60 s

α-pinene concentration ~ 200 ppb
Ozone concentration ~ 500 ppb
Stable particle concentration

Exhaust
Ozone generator
Zero air generator
α-Pinene cylinder
SMPS
TDCIMS
Hepa filter
Ozone monitor

(C) Thomas Karl - www.tomkarl.com
Gas-phase measurements with PTR-TOF-MS

C<sub>8</sub>H<sub>13</sub>O<sub>4</sub> (m/z = 173.078)

C<sub>9</sub>H<sub>13</sub>O<sub>4</sub> (m/z = 187.088)

C<sub>10</sub>H<sub>17</sub> (m/z = 137.132)
HTOF-TDCIMS signal from α-pinene ozonolysis

20 nm particles negative ions

2011-12-22 18:17:56
Conclusions

• Ambient newly formed 20nm particles exhibit significant amounts of inorganic material, predominantly sulfur compounds.

• Organic fraction still increasing at particle sizes > 20nm

• Mono-/dicarboxylic acids dominate (negative) organic signal

• α-pinene SOA from flow tube shows same compounds as found in the organic signals from ambient data
Thank you

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