Application of aerosol mass spectroscopy for eddy-covariance measurements of speciated particle fluxes

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Why Measure Aerosol Fluxes?

- Measure deposition velocity ($V_d$) as a function of particle size, surface roughness and meteorology
- $V_d$ is important parameter in models of atmospheric transport (e.g. S, N, metals), air quality, climate change
- Quantify aerosol emissions from area sources (vehicles, heating, re-suspension)
- Until recently, most studies have focussed on measurement of aerosol number fluxes using CPCs (total) or optical particle spectrometer (size-segregated) - no fast sensors for aerosol chemistry
Why Measure Compound Specific Aerosol Fluxes?

- Deposition rate \( (V_d) \) depends on aerosol composition (e.g. growth of hygroscopic aerosol near vegetation)
- Aerosol exchange is often bi-directional \( \rightarrow \) particle number flux is the average of up- and downward moving components
  - e.g. emission of combustion derived organic particles and simultaneous deposition of seasalt at coastal city.
  - Other examples later on
- Derive information of formation of secondary particulate matter (gas-to-particle conversion): chemical processes; production rates.
- Distinguish e.g. between HOA and OOA

Operation Modes for Concentration Measurements

- **Mass-Spec Mode (MS)**
  - Scan from m/z 10 to 300 within 1/3 second
  - Alternate chopper between blocked (background) and open (all particles) position
  - Full composition data, but no size information
  - Typically average for 5 to 15 minutes, duty-cycle = 0.06% per m/z
- **Time-of-flight Mode (ToF)**
  - Chop particle beam
  - Cycle through some 10 m/z
  - Size-information of selected m/z
  - Typically average for 5 to 15 minutes, duty-cycle = 0.06% per m/z
- **Jump MS Mode (JMS)**
  - Similar to MS Mode (i.e. alternate open /closed)
  - Step through selected m/z (typically 10)
  - For each m/z: scan over peak, move to peak position
  - Typically average for 5 to 15 minutes (or shorter on aircraft) duty cycle; duty-cycle = 6% per m/z
- **Modes are alternated**
Good S/N for fast Measurements (alternating chopper position)

Eddy-covariance mode

- Like JMS, but:
  - beam 1 minute closed followed by 29 minutes open
  - Cycle through masses at 5 to 10 Hz
  - Synchronised recording of anemometer

\[ i_{\text{meas}} \{\text{ms}\} \quad d_c \{\%\} \]

Dwell time per m/z per cycle

Duty cycle per m/z
Applications to date

1. Urban fluxes
   a) Tests in Boulder, Colorado, June 2003
   b) Fluxes above Gothenburg, Sweden, February 2005

2. Exchange with vegetation
   a) Pine plantation at Duke Forest, North Carolina, July 2003
   b) Easter Bush grassland, Scotland, periodically since 2004
   c) Easter Bush slurry application, Scotland, April 2005
   d) Oak forest at Alice Holt SSSI, England, July 2005
Masses Monitored at Duke

<table>
<thead>
<tr>
<th>m/z</th>
<th>Target compound</th>
</tr>
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<tbody>
<tr>
<td>9</td>
<td>DC baseline</td>
</tr>
<tr>
<td>16</td>
<td>$\text{NH}_4^+$ ($\text{NH}_2^+$)</td>
</tr>
<tr>
<td>27</td>
<td>biogenic secondary organic?</td>
</tr>
<tr>
<td>28</td>
<td>air beam ($\text{N}_2^+$)</td>
</tr>
<tr>
<td>30</td>
<td>$\text{NO}_3^-$ (NO$^+$)</td>
</tr>
<tr>
<td>43</td>
<td>anthropogenic primary org.</td>
</tr>
<tr>
<td>44</td>
<td>oxidised secondary organics ($\text{CO}_2^+$)</td>
</tr>
<tr>
<td>48</td>
<td>$\text{SO}_4^{2-}$ ($\text{SO}^+$)</td>
</tr>
<tr>
<td>55</td>
<td>$\alpha$-pinene oxidation prod.?</td>
</tr>
<tr>
<td>57</td>
<td>anthropogenic primary organic</td>
</tr>
<tr>
<td>58</td>
<td>$\alpha$-pinene oxidation prod. with $\text{O}_3$</td>
</tr>
<tr>
<td>64</td>
<td>$\text{SO}_4^{2-}$ ($\text{SO}_2^+$)</td>
</tr>
<tr>
<td>93</td>
<td>$\alpha$-pinene oxidation prod. with NO$_x$</td>
</tr>
</tbody>
</table>


Sulphate Comparison above a City

Concentration [µg m$^{-3}$]  
Flux [ng m$^{-2}$ s$^{-1}$]  
Deposition velocity [mm s$^{-1}$]
Nitrate Comparison above a City

Concentration [µg m⁻³]

Flux [ng m⁻² s⁻¹]

Deposition velocity [mm s⁻¹]

Sulphate Comparison above Forest

Concentration [µg m⁻³]

Flux [ng m⁻² s⁻¹]

Deposition velocity [mm s⁻¹]

R²=0.90
y = 0.931 x + 0.321

R²=0.85
y = 0.958 x - 0.093

y = 0.980 x + 52.3
Integrated Co-spectral Density Functions (Ogives)

Averaged diurnal cycles of fluxes of NO$_3^-$ and m/z 55

VOC data courtesy of Thomas Karl & Brad Baker
Average emission: 4 ng SO$_4^{2-}$ S m$^{-2}$ s$^{-1}$ = 1.2 kg S ha$^{-1}$ yr$^{-1}$

Estimated S wet deposition at this site: 15 kg S ha$^{-1}$ yr$^{-1}$

→ Emission constitutes about 8% of the S input!

### Averaged Diurnal Cycles - Gothenburg

Averaged diurnal cycles for various fluxes at Gothenburg are shown. The graphs display CO$_2$, NO$_3^-$, and organics fluxes over a 24-hour period with peaks at different times for each.
Urban NO$_3^-$ Emission

Nitrate emission was also observed in Boulder:

Deposition Velocities to the Urban Environment derived from sulphate flux measurements
Conclusions I: System Performance

1. The AMS eddy-flux system provides a very sensitive tool to measure speciated aerosol fluxes.
2. 30-minute detection limits of the more sensitive AMS system are about 3 ng m⁻² s⁻¹ for sulphate fluxes and 2 mm s⁻¹ for sulphate deposition velocities.
3. Good statistics are achieved for accumulation mode aerosol for concentrations > 0.5 µg m⁻³.
4. Straight eddy-covariance allows standard eddy-covariance QA/QC criteria to be applied (→ ogives).
5. Aerosol flux measurements provide deposition rates to forest and urban areas. Emitted species can be omitted from the analysis.
6. Aerosol flux measurements provide both qualitative and quantitative information on SBA formation above within plant canopies and urban areas.
Conclusions II: Initial Findings

**Forest:**
- $\text{NO}_3^-$ was deposited throughout the day ($V_d: 1 \text{ - } 4 \text{ mm s}^{-1}$).
- Indication for SBOA formation during midday, possibly linked to $\alpha$-pinene oxidation.
- $\text{SO}_4^{2-}$ emission observed, probably representing oxidation of biogenic S precursors. This amounts to 8% of the S wet input.
  - Terrestrial surfaces may control their S burden and CCN.
- Aerosol exchange is complex and particle number fluxes do not always follow the 'expected' pattern. Trust your measurements!
- Aerosol formation processes need to be considered when particle deposition velocities are derived from particle number fluxes, which represent the net effect of competing emission and deposition processes.

**Urban:**
- $\text{NO}_3^-$ is emitted or (more likely) formed below measurement point; absence of $\text{NO}_3^-$ emission during snow consistent with HNO$_3$ intermediate
- Small emission or formation of oxygenated aerosol is observed
- Deposition rates of $\text{SO}_4^{2-}$ appear to be large
  - (nighttime: 6 mm s$^{-1}$; daytime: 20 mm s$^{-1}$) (Gothenburg only)

Limitations and Outlook

**Limitations:**
- Organic fragmentation different for concentrations and fluxes → hard to derive organics mass fluxes
- No information on size-dependence

**Future Developments:**
- Implement light-scatter probe to measure size simultaneously
- Change from quadrupole to time-of-flight MS → Near 100% duty cycle for all masses
  - Use chopper for size-segregated fluxes
  - Derive full organic spectrum in flux mode (not just concentrations)