Method development for PILS-IC for large volume environmental chamber experiments on amine-based aerosol

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Overview

1. Project Aims
2. Previous work
3. What is a PILS
4. 3rd Generation Environmental Chamber
5. Expectations & Challenges
Project Aims

- To understand nucleation process of aerosol generated by the amines
  - Monoethanolamine (MEA)
  - Piperazine (PZ or PIPA)
  - 2-amino-2-methyl-1-propanol (AMP)

- To investigate aerosol production from species as a function of amine and NO\textsubscript{x} loading
- To determine the composition of generated aerosol in terms of organic and inorganic fractions
Previous Work

Loy Yang PCC Plant:

- Hydrocarbon + NOx
- Hydrocarbon + NOx + MEA

- Comparative study
  - Hydrocarbons + NOx
  - Hydrocarbons + NOx + MEA

- Results used in ambient modelling (CMAR)

3D dispersion modelling (Latrobe)

Azzi M. et al. (2014). CSIRO, Australia
PILS

- Particle-into-Liquid Sampler

- Developed by Rodney J. Weber *et al.* late 90’s
- Based on particle growth devices
- Designed for rapid measurement
PILS

- Improvements published by Douglas A. Orsini et al. in 2003
- Commercially obtained from Metrohm AG

Orsini et al (2003) Atmos. Env. 37, 1243-1259
Selected Field Studies:

<table>
<thead>
<tr>
<th>Author</th>
<th>Detection</th>
<th>Time-resolution</th>
<th>Time/season</th>
<th>Campaign, Place</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weber et al. (2007)</td>
<td>WSOC</td>
<td>3 s</td>
<td>Many flights + ground based measurement campaign during summer 2004</td>
<td>Atlanta, GA + flights above over a large area of northern Georgia</td>
</tr>
<tr>
<td>De Gouw et al. (2008)</td>
<td>WSOC</td>
<td>1 min</td>
<td>1 month cruise + 18 flights during a month in summer</td>
<td>NEAQS-ITCT 2004, 18 research aircraft (WP-3D) flights above eastern US and the NOAA research ship cruising at Massachusetts and New Hampshire coast</td>
</tr>
<tr>
<td>Hennigan et al. (2008a, b)</td>
<td>WSOC</td>
<td>6 min</td>
<td>4 months</td>
<td>Atlanta</td>
</tr>
<tr>
<td>Hennigan et al. (2008c)</td>
<td>WSOC, IC</td>
<td></td>
<td>24 days</td>
<td>MILAGRO field campaign in Mexico City</td>
</tr>
<tr>
<td>Saarikoski et al. (2008)</td>
<td>IC</td>
<td>15 min</td>
<td>1 year (2006–2007)</td>
<td>SMEAR III station Helsinki, Finland</td>
</tr>
<tr>
<td>Miyazaki et al. (2009)</td>
<td>WSOC</td>
<td>6 min</td>
<td>26 days</td>
<td>Guangzhou, China</td>
</tr>
<tr>
<td>Miyazaki et al. (2009)</td>
<td>WSOC</td>
<td>6 min</td>
<td></td>
<td>PRIDE-PRD campaign, rural site Pearl River Delta region, China</td>
</tr>
<tr>
<td>Partshitshev et al. (2009)</td>
<td>GC-MS</td>
<td>2 h</td>
<td>6 days</td>
<td>SMEAR II station at Hyytiälä, Finland</td>
</tr>
</tbody>
</table>

Table adapted from Timonen et al. (2010). Atmos. Meas. Tech. 3, 1063-1074

Chamber Studies:

- Murphy et al. 2007 (offline IC; TMA, MA, TEA, DEA, EA, MEA)
- Clark et al. 2013 (online ToF; α-pinene, isoprene)
- Tang et al. 2013/2014 (online IC; TMA, DEA, BA / TMA, BA)
3rd gen. Environmental Chamber

- 24.7 m$^3$ (1.98m x 5.07m x 2.46 m)
  Chamber lined with FEP Teflon
- Flushed with clean air
- UV lights mounted at each end
  (40 BLB, 40 unfiltered blacklights)
- Monitoring devices: $O_3$, NO, NO$_2$, NO$_y$
  FTIR, SMPS, PILS-IC
Currently undergoing characterisation:
- Propene/NO\textsubscript{x} experiments
- NO\textsubscript{2} photolysis & UV spectra

### Particle Formation

<table>
<thead>
<tr>
<th>Time / min</th>
<th>Exp2</th>
<th>Exp3</th>
<th>Exp4</th>
<th>Exp5</th>
<th>Exp6</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.00</td>
<td>100.00</td>
<td>200.00</td>
<td>300.00</td>
<td>400.00</td>
</tr>
<tr>
<td>100.00</td>
<td>400.00</td>
<td>500.00</td>
<td>600.00</td>
<td>700.00</td>
<td>800.00</td>
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<tr>
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<td>1000.00</td>
<td>2000.00</td>
<td>3000.00</td>
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<tr>
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<td>6000.00</td>
<td>7000.00</td>
<td>8000.00</td>
<td>9000.00</td>
<td>10000.00</td>
</tr>
</tbody>
</table>

### Statistical Analysis

<table>
<thead>
<tr>
<th>Rate / min\textsuperscript{-1}</th>
<th>NEC</th>
<th>BLB</th>
<th>Both</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 STDEV</td>
<td>0.248</td>
<td>0.361</td>
<td>0.540</td>
</tr>
<tr>
<td></td>
<td>0.018</td>
<td>0.025</td>
<td>0.036</td>
</tr>
</tbody>
</table>
Online PILS: Expectations

- Characterisation of organic & inorganic fractions
- Shed light on observed bimodal behaviour of amines in SMPS (indirect)

![Particle Distribution Exp 723](image1)

![Particle distribution amine experiments](image2)
Online PILS: Work to date

- First calibrations with inorganic ions
Online PILS: Challenges

- First to be used with amines in Australia
- Development of methodology that maximises sensitivity
- Major challenge: large sample volume (16.7 lpm)
  - Possible approaches:
    - Top up chamber
    - Split sampling
    - Aliquot sampling
Summary

- PILS is not “brand new”, but new to CSIRO Environmental Chamber
- New 3rd generation chamber under commission
- Anticipated outcomes of current research:
  - PILS data will allow us to identify and quantify the inorganic and organic fractions of generated aerosol.
  - Information elucidates on the importance of these fractions in particle formation
  - Better understand amine-aerosol nucleation process(es)
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References:


