Chamber studies of biogenic VOC emissions and SOA formation in the Aerosol Coupling in the Earth System (ACES) project

Gordon McFiggans\textsuperscript{1}, M. Rami Alfarra\textsuperscript{1}, Timo Carr\textsuperscript{2}, Nicholas Good\textsuperscript{1}, Jacqui Hamilton\textsuperscript{3}, Martin Irwin\textsuperscript{1}, Mike Jenkin\textsuperscript{4}, Alistair Lewis\textsuperscript{3}, Paul Monks\textsuperscript{2}, S. Fiona Turner\textsuperscript{1} and Kevin Wyche\textsuperscript{2}

\textsuperscript{1}Centre for Atmospheric Sciences, University of Manchester, Manchester, UK
\textsuperscript{2}Department of Chemistry, University of Leicester, Leicester, UK
\textsuperscript{3}Department of Chemistry, University of York, York, UK
\textsuperscript{4}Atmospheric Chemistry Services, UK
WP1: Chamber studies of biogenic VOC emissions and SOA formation,

This work package is focussed on studying the formation of organic aerosol from biogenic organic precursors within the controlled environment of a “smog” chamber. The specific objectives are:

i) To quantify BVOC emissions, in terms of physiological and environmental factors, from native and commercial tropical forest plant species.

ii) To characterise low vapour pressure gas phase organic compounds formed during the photo-oxidation and O₃ reaction with key BVOC species (selected as describe in Section 4) and to compare observations with species predicted by detailed mechanisms developed in WP3.

iii) To characterise the properties (number, size, hygroscopicity, small and large organic compound speciation, size-segregated broad speciation and CCN activation) and evolution of multicomponent aerosol particles formed in chamber experiments from a series of single precursor biogenic species under a range of photochemical and seed aerosol conditions.

iv) To compare organic aerosol formation processes elucidated from single precursor compound experiments with aerosols formed via an ensemble of precursor chemicals derived from a mesocosm atmosphere containing single plant species using the mesocosm as a feed chamber for the aerosol reaction chamber.

v) To use synthetic mixtures of precursor compounds to mimic selected mesocosm emissions to validate model predictions and mesocosm chamber experiments.
Chamber and mechanism development compounds chosen from emissions from tropical plant species based on Danum Valley tower footprint botanical survey.

**Species in MCM**
- Isoprene
- α-pinene
- β-pinene
- 3-carene
- Sabinene
- Terpinolene
- α-phellandrene
- Ocimene
- α-Humulene

**New target species**
- Monocyclic diene monoterpenes
  - Limonene
  - α-terpinene
  - Myrcene
  - β-Caryophyllene
  - Linalool
- Acyclic triene monoterpenes
- Reactive C10 oxygenates
- Monocyclic conjugated diene monoterpenes
- Reactive sesquiterpenes
## Target compound reactivity and representative lifetimes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k(\text{OH})$</th>
<th>$k(\text{O}_3)$</th>
<th>$k(\text{NO}_3)$</th>
<th>$\tau(\text{OH})$</th>
<th>$\tau(\text{O}_3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^{-12}$</td>
<td>$10^{-16}$</td>
<td>$10^{-12}$</td>
<td>$[\text{OH}] = 10^6 \text{ cm}^{-3}$</td>
<td>$[\text{OH}] = 10^7 \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>limonene</td>
<td>171</td>
<td>2.0</td>
<td>12.2</td>
<td>1.6 hr</td>
<td>10 min</td>
</tr>
<tr>
<td>$\alpha$-terpinene</td>
<td>363</td>
<td>210</td>
<td>97</td>
<td>46 min</td>
<td>5 min</td>
</tr>
<tr>
<td>myrcene</td>
<td>215</td>
<td>4.7</td>
<td>11.0</td>
<td>1.3 hr</td>
<td>8 min</td>
</tr>
<tr>
<td>$\beta$-caryophyllene</td>
<td>197</td>
<td>116</td>
<td>19.0</td>
<td>1.4 hr</td>
<td>8 min</td>
</tr>
<tr>
<td>linalool</td>
<td>159</td>
<td>4.3</td>
<td>11.2</td>
<td>1.7 hr</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

**Ozonolysis OH yields:**

- limonene: 0.67
- $\alpha$-terpinene: 0.38
- myrcene: 0.63
- $\beta$-caryophyllene: 0.06
- linalool: 0.68

- In practice, OH and O$_3$ initiated chemistry will occur in both photo-oxidation and dark experiments
- NO$_3$ initiated chemistry will also be represented in mechanisms (O($^3P$) and NO$_2$ initiated chemistry will also not be overlooked)
University of Manchester Chamber
(18 m³, collapsable, T & RH controlled)

Halogen & Arc Lamps

Inlet and sample ports

Inlet System
Clean bag with realistic illumination

total aerosol background generally <0.05 μg m⁻³ under full illumination

Lamps good across the spectrum
Experiments Oct-Nov ’07 and Feb-May ’08

During the first intensive chamber programme, from 5th October - 30th November 2007, 20 photo-oxidation experiments were conducted at a single VOC / NOx ratio of 2 / 1, at nominal 25°C and dewpoint of 15°C (RH 60%):

- 10 x chamber background
- 10 x α-pinene
- 4 x β-caryophyllene
- 2 x α-terpinene
- 2 x limonene
- 2 x ocimene / limonene mixture

for “low” and “high” concentrations (42 and 210ppbv, c. 50 and 250ppbv).

Online measurements included aerosol composition (AMS), size (DMPS), hygroscopicity (HTDMA), cloud activation (CCN), and gaseous VOCs / OVOCs by PTR-MS from 29th October. Full suite available: 29th October to 9th November. 29th February - 28th April 2008. 19 more photo-oxidation experiments conducted at VOC / NOx of 2 / 1 and same nominal conditions:

- 7 x chamber background
- 6 x β-caryophyllene
- 6 x limonene

again for “low” and “high” concentrations (42 and 210ppbv, nominally 50 and 250ppbv). Objective: provide snapshot filters of entire chamber contents at different times to investigate ageing using the York analysis.
June ’08 series of experiments...

The ongoing intensive chamber programme, from 16th June - 11th July 2008, 14 photo-oxidation experiments being conducted at a single VOC / NOx ratio of 2 / 1, at nominal 25°C and dewpoint of 21°C (RH 80%), plus additional “experiments of opportunity” in final week:

4 x chamber background  
2 x myrcene  
2 x linalool  

for “low” and “high” concentrations (42 and 210ppbv, c. 50 and 250ppbv).

3 x isoprene + stable oxygenated organic seed  
1 x limonene + stable oxygenated organic seed  
1 x isoprene + (NH₄)₂SO₄ seed  
1 x limonene + (NH₄)₂SO₄ seed  

Online measurements included aerosol composition (AMS), size (DMPS), hygroscopicity (HTDMA), cloud activation (CCN), and gaseous VOCs / OVOCs by PTR-MS, O₃, NO₂, NO. Offline filter analyses by GCxGC/MS and LC/MSⁿ.
PART 1, Measurement Techniques - DMPS Aerosol Size Distributions

delayed onset nucleation

α-pinene, 42 ppb, 31st Oct

31st October α-pinene, 50 ppb, VOC NOx, 2:1
dN/dlogDp, short DMA in overlap

faster nucleation

β-caryophyllene, 42 ppb, 5th Nov

5th November β-caryophyllene, 42 ppb, VOC NOx, 2:1
dN/dlogDp, short DMA in overlap
Online PTR-MS: Limonene

Time / minutes

$m/z$ / Th

Signal (/ ncps)

limonene

$m/z$ 137 (Parent)
$m/z$ 81 (Fragment)
Limonene Oxidation Products

- **m/z**
  - 20 40 60 80 100 120 140 160 180

- **Time (minutes)**
  - 0 100 200 300
  - 0 50 100 150 200 250
  - 100 150 200 250

- **Signal**
  - (m/z 139) / ncps
  - (m/z 107) / ncps
  - (Pinaldehyde) / ncps
  - (Pinoic acid) / ncps

- **m/z = 139**
  - Time / Minutes
  - 0 100 200 300
  - 0 50 100 150 200 250
  - 100 150 200 250

- **m/z = 107**
  - Time / Minutes
  - 0 100 200 300
  - 0 50 100 150 200 250
  - 100 150 200 250

- **m/z = 139**
  - Time / Minutes
  - 0 100 200 300
  - 0 50 100 150 200 250
  - 100 150 200 250
Offline Separation & Mass Spectrometric Analysis

Ultra Hi-Vol Filter Sampling
- Empty the entire chamber contents through a pre-fired quartz 47 mm filter
- Use blower at 3 m$^3$ min$^{-1}$ for 5 to 6 minutes

SOA Component Analysis Using
- GCxGC-MS to look at small semi-volatiles
- LC-MS to study oligomeric compounds

Samples analysed so far (NB LC-MS$^n$ only)

- 09/10/07 and 10/10/07 $\alpha$-pinene $<30$ ppb
- 05/11/07 and 06/11/07 $\beta$-caryophyllene (42 ppb and 210 ppb)
- 08/11/07 and 09/11/07 $\alpha$-terpinene (42 and 210 ppb)
- 29/11/07 and 30/11/07 limonene and ocimene
- low limonene
α-pinene SOA

- 2 experiments 09/10/2007 and 10/10/2007
- Both [VOC]₀ < 30 ppb
- Ran as a test against historical samples at Euphore
- Run-to-run reproducibility ~ 10 %.
- Compounds identified by MS² and reference to previous work

• + pinonaldehyde
Molecular weight distribution

- Inject water extract of filters directly into MS to get a molecular weight distribution
- Maximum abundance at around 190-230 Da
- Small amount of higher molecular weight species but minor component
But, due to the sizing technique and measurement uncertainties, data analysis is not trivial.

- Measurement is run through the forward model.
- Then back through to validate.
- An error estimate is obtained by adding noise to the signal and repeatedly inverting.
GF_{D,90%} evolution, limonene SOA compounds on \((\text{NH}_4)\text{SO}_4\) injected seed, 1\textsuperscript{st} July

![Graphs showing GF_{D,90%} evolution over time for different dry sizes.](image-url)
DMT Continuous flow Cloud Condensation Nucleus (CCN) Counter

\[ A_F = \frac{N_{CCN}}{N_{CPC}} \]
Broad and narrow range of $S$ scanned

$A_F$ plotted against $S$

$S_{crit}$ calculated by fitting a sigmoid to data
Combining $G_{D}$ and CCN behaviour: $\alpha$-Terpinene, 210ppb, NOx 105ppb

**HTDMA, sub-saturated growth**

**CCN counter, supersaturated growth**
Aerodyne Aerosol Mass Spectrometer (AMS) - Quadropole version now replaced with CToF version
PART 2 SOA formed from β-caryophyllene photo-oxidation

Graphs showing the changes in concentrations of different pollutants over time after lights on, including O₃, NOₓ, NO, NO₂, Limonene 250ppb, and B-Caryophyllene 250ppb.
• ~45 ions detected with high [VOC]
• Inc. 9 with m/z > precursor
• 99% oxidation of precursor (independent of initial conc^n.)
SOA formed in β-caryophyllene photo-oxidation

- 2 samples
  - 05/11/07 $[\text{VOC}]_0 = 42$ ppb
  - 06/11/07 $[\text{VOC}]_0 = 210$ ppb

- Unlike mono-terpene studies there is NO evidence of oligomer formation in these samples
- Need to compare to those aged longer
LC-MS$^n$ β-caryophyllene SOA

- Using MS$^2$, 10 out of 12 major peaks identified in chromatogram
- 4 seen in previous studies
- 6 tentatively identified by fragmentation patterns

50 ppb  
250 ppb

+ve  
-ve
NEGATIVE

<table>
<thead>
<tr>
<th>Compound</th>
<th>MW</th>
<th>m/z</th>
<th>rt</th>
</tr>
</thead>
<tbody>
<tr>
<td>nor-caryophyllenic acid</td>
<td>172</td>
<td>171</td>
<td>20.7</td>
</tr>
<tr>
<td>2-(2-carboxyethyl)-3,3-dimethylcyclobutanecarboxylic acid</td>
<td>200</td>
<td>199</td>
<td>30.8</td>
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<tr>
<td>3-(3,3-dimethyl-2-(3-oxobutyl)cyclobutyl)-3-hydroxypropanoic acid</td>
<td>242</td>
<td>241</td>
<td>43.7</td>
</tr>
<tr>
<td>2-(2-(2-carboxyethyl)-3,3-dimethylcyclobutyl)acrylic acid</td>
<td>226</td>
<td>225</td>
<td>43.8</td>
</tr>
<tr>
<td>b-caryophyllonic acid</td>
<td>252</td>
<td>251</td>
<td>45.9</td>
</tr>
</tbody>
</table>
Effect of $[\text{VOC}]_0$ on SOA composition

- Peak SOA concentration in chamber $155_{210\text{ppb}}$ vs $67_{42\text{ppb}} \mu g \ m^{-3}$.
  - Ratio high to low ~ 3:1 at end of experiment
  - (collected mass ~ 1200mg vs 500 mg, ratio 2.4)

Ratio 210 ppb / 42 ppb

<table>
<thead>
<tr>
<th>Less than 2.0</th>
<th>2.0 - 3.5</th>
<th>Greater than 3.5</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Molecule 1" /> 1.1</td>
<td><img src="image2" alt="Molecule 2" /> 2.5</td>
<td><img src="image3" alt="Molecule 3" /> 11.0</td>
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<tr>
<td><img src="image4" alt="Molecule 4" /> 0.8</td>
<td><img src="image5" alt="Molecule 5" /> 3.2</td>
<td><img src="image6" alt="Molecule 6" /> &lt;LOD in 50ppb</td>
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<tr>
<td><img src="image7" alt="Molecule 7" /> 0.4</td>
<td><img src="image8" alt="Molecule 8" /> 2.9</td>
<td><img src="image9" alt="Molecule 9" /> 17.0</td>
</tr>
</tbody>
</table>

More in 42 ppb | Around equal | More in 210 ppb
Comparison of estimated properties

More in 42 ppb sample

- Boiling point = 675 K
- VP = 3 x 10^{-5} torr
- Log (p) = 0.58 - 1.01
- (octanol:water)

More polar and water soluble

More in 210 ppb sample

- Boiling point = 740 K
- VP = 1 x 10^{-6} torr
- Log (p) = 2.7-3.01
- (octanol:water)

Less polar but also less volatile
AMS fragments in SOA generated in β-caryophyllene photo-oxidation

![Graphs showing SOA mass and m43/SOA, m44/SOA over time.](image-url)
CCN properties of β-caryophyllene SOA

- Graph: β-Caryophyllene - 50ppb
- X-axis: Time of Day (13:00 to 17:00)
- Y-axis: Critical Supersaturation (%S)
- Color gradient: 
  - 0.0
  - 0.2
  - 0.4
  - 0.6
  - 0.8
  - 1.0

- Scatter plot: (m/z 44: SOA) %
- Y-axis: Degree of oxygenation
- X-axis: Time after lights on (hr)
  - 0.0
  - 0.5
  - 1.0
  - 1.5
  - 2.0
  - 2.5
  - 3.0
  - 3.5
  - 4.0

Graphs show the changes in critical supersaturation and degree of oxygenation over time.
Hygroscopic properties of $\beta$-caryophyllene SOA

BUT $GF_{D,90\%}$ is low and stays the same with time:

Sub-saturated and super-saturated results do not match!
PART 3 Physical & Chemical properties of BSOA from various precursors: Can the picture be really simplified?

Collated HTDMA data: Initial SOA GF$_{D,90\%}$ and change with aging differs greatly with changing precursor
- SOA from different precursors like water to different degrees
Can the picture be simplified? SOA $GF_{D,90\%}$ differs more with changing precursor than changing concentration.
Can the picture be simplified? Linalool, Note initial rate of change of $G_{D,90\%}$
Can the picture be simplified? Linalool, $GF_{D.90\%}$ change is reflected in rate of change of fraction activated to CCN.
Can the picture be simplified? Myrcene, Note initial rate of change of $GF_{D,90\%}$. 

- Growth Factor at 90%, $GF_{D,90\%}$
- Dry diameter, nm
- Time after lights on, h
- 50 ppb Myrcene
- 250 ppb Myrcene
Can the picture be simplified? Myrcene, more rapid $G_{D.90\%}$ change is also seen in earlier change of fraction activated.

![Graph showing time after lights on (hrs) versus FA (%) with dry diameter (nm) on the x-axis and FA (%) on the y-axis. The graph includes a legend indicating 0.5% supersaturation and a purple bar with 210 ppb Myrcene.]
Molecular composition of SOA from biogenic precursors

Same m/z but different rt and MS² fragmentation depending on precursor
PART 4 Future work: full analysis of the seeded work ... inorganics and stable organic seeds

Limonene 50ppb on stable oxygenated organic SOA
Taking emissions from tropical plant species (ULanc)

Future work: the mesocosm experiments - using the plant chamber to fill the bag... & building up synthetic VOC mixtures

Identifying gaseous and aerosol components for linkage to MCM by CIR-ToF-MS (ULEic)
GCxGC/MS (UYork)
LC/MS^n (UYork)