NATURAL ENVIRONMENT RESEARCH COUNCIL

A consortium project within the APPRAISE programme

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

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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 O_3 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.

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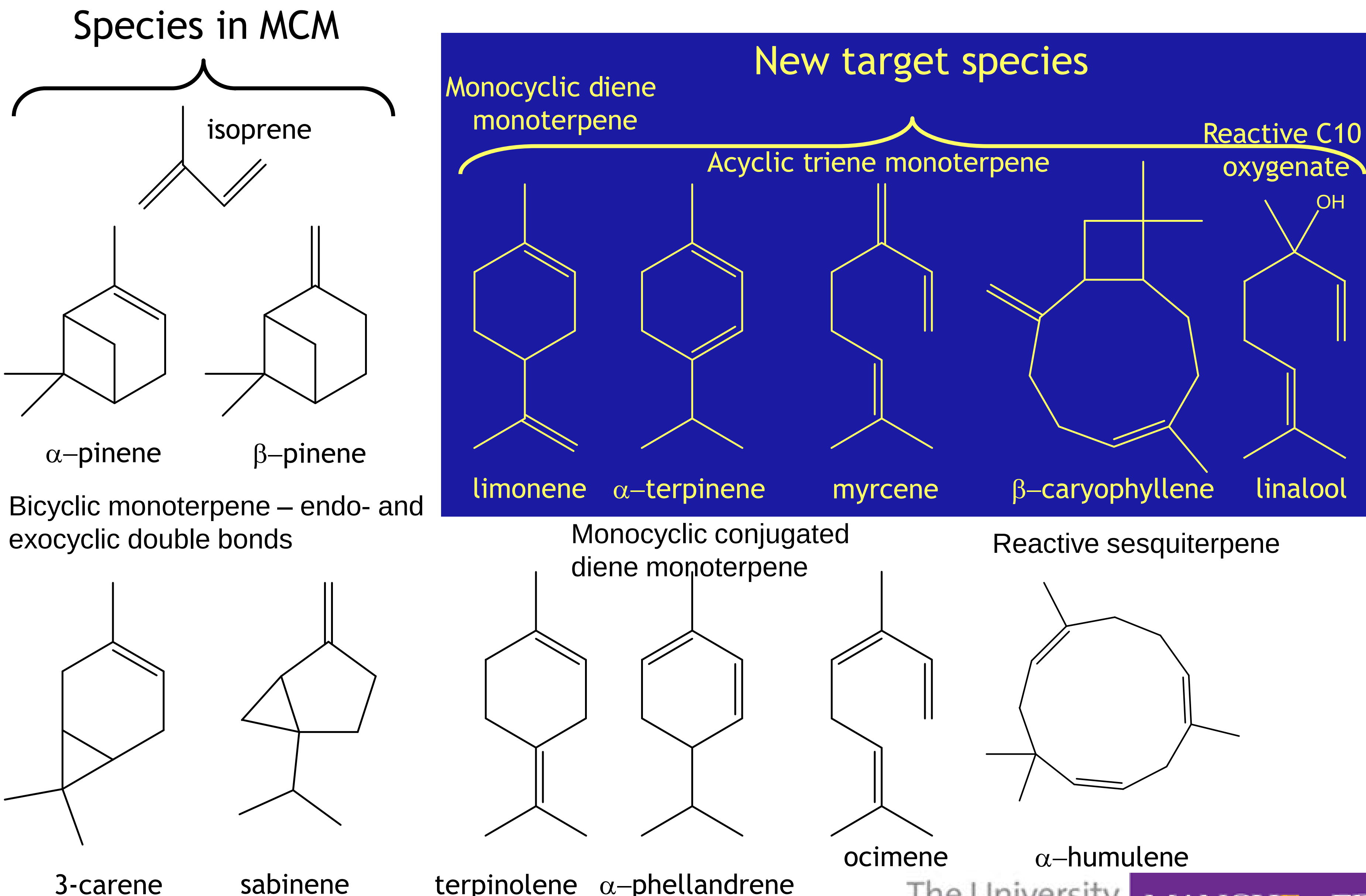
Chamber and mechanism development compounds chosen from emissions from tropical plant species based on Danum Valley tower footprint botanical survey



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Target compound reactivity and representative lifetimes

	k(OH)	k(O_3)	k(NO_3)	τ(OH)		τ(O_3)	
	10^{-12}	10^{-16}	10^{-12}	[OH] = 10^6 cm^{-3}	[OH] = 10^7 cm^{-3}	[O_3] = 10 ppb	[O_3] = 100 ppb
	cm^3 $molecule^{-1}$ s^{-1}						
limonene	171	2.0	12.2	1.6 hr	10 min	5.6 hr	33 min
α–terpinene	363	210	97	46 min	5 min	3.2 min	19 sec
myrcene	215	4.7	11.0	1.3 hr	8 min	2.4 hr	14 min
β–caryophyllene	197	116	19.0	1.4 hr	8 min	5.7 min	34 sec
linalool	159	4.3	11.2	1.7 hr	10 min	2.6 hr	16 min

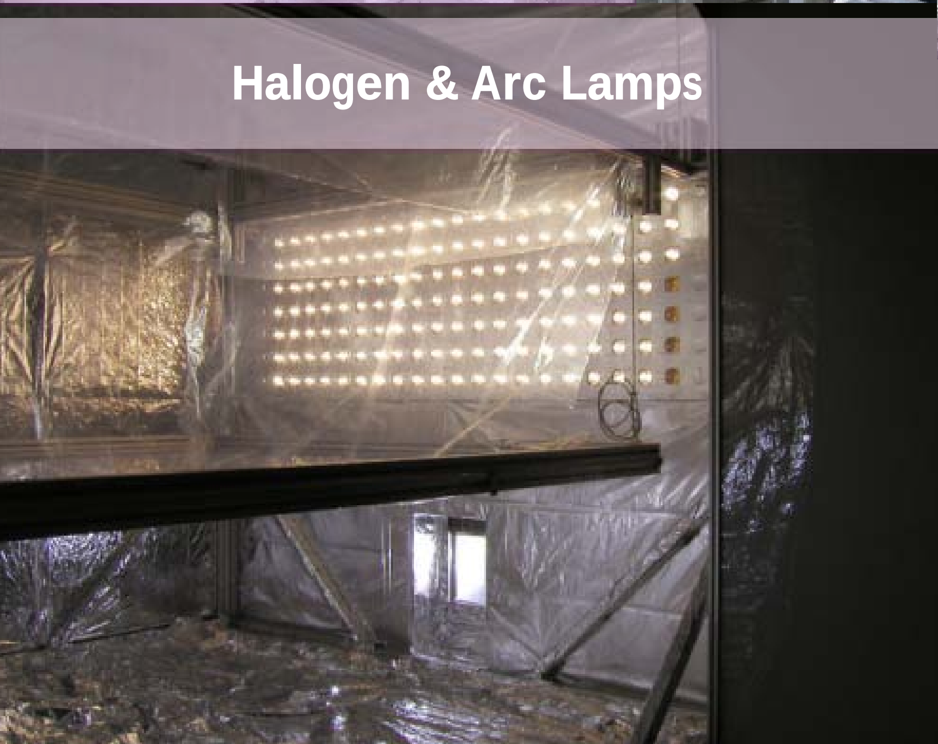
Ozonolysis OH yields:

limonene: 0.67
α–terpinene: 0.38
myrcene: 0.63
β–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)

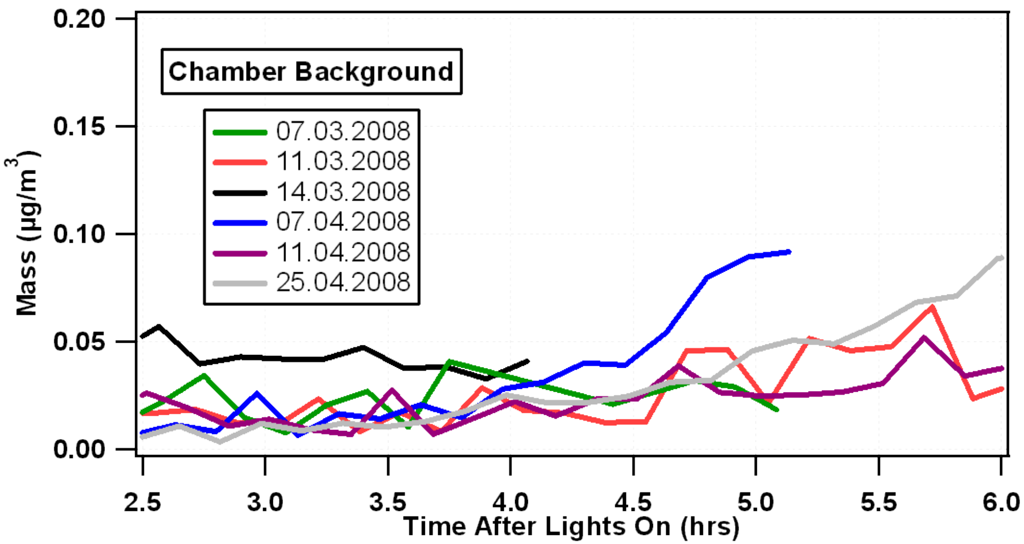

Inlet and sample ports

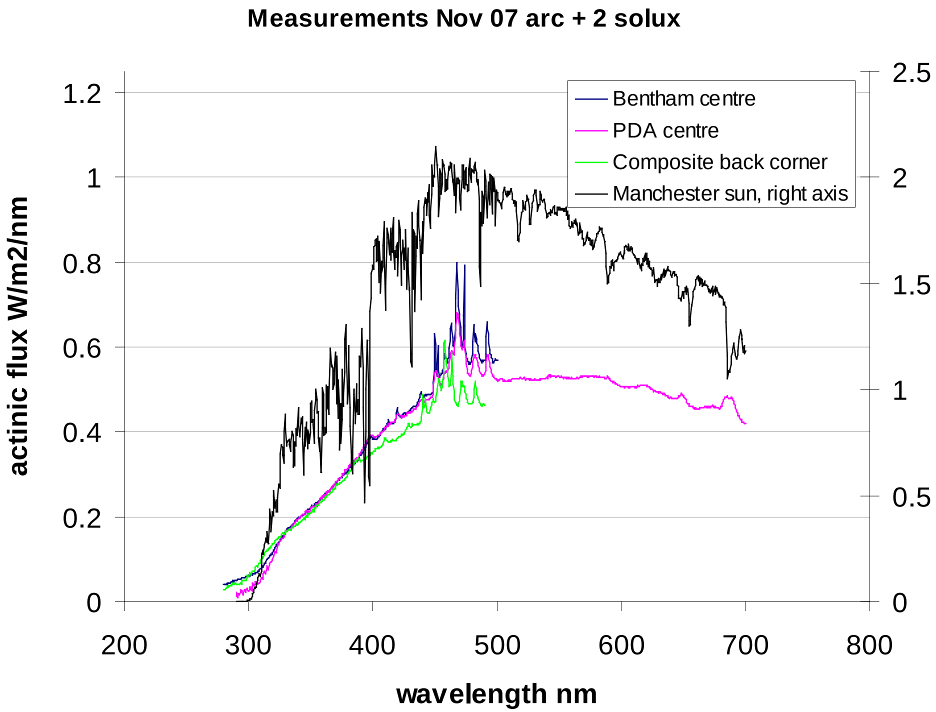

Halogen & Arc Lamps


Inlet System

Clean bag with realistic illumination

total aerosol background generally <0.05 µg m^{-3} under full illumination





Lamps good across the spectrum

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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).

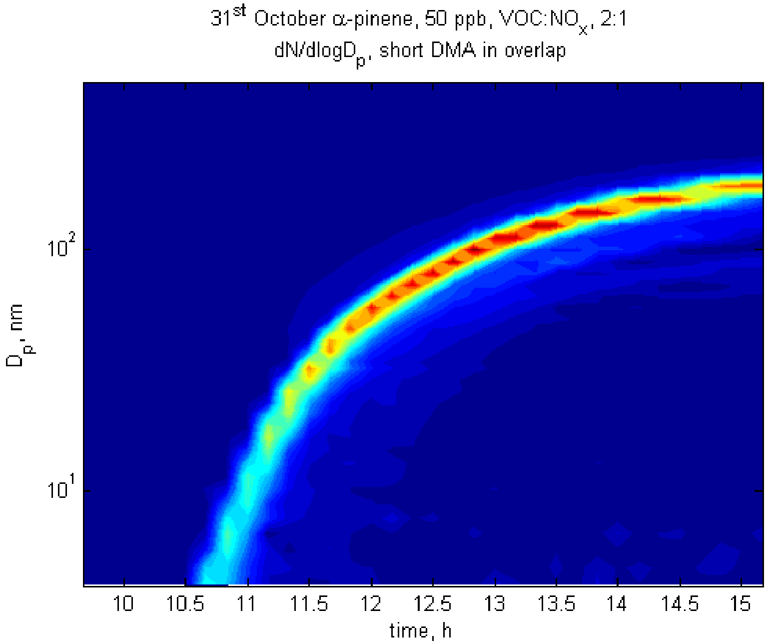
3 x isoprene + stable oxygenated organic seed
1 x limonene + stable oxygenated organic seed
1 x isoprene + $(NH_4)_2SO_4$ seed
1 x limonene + $(NH_4)_2SO_4$ seed

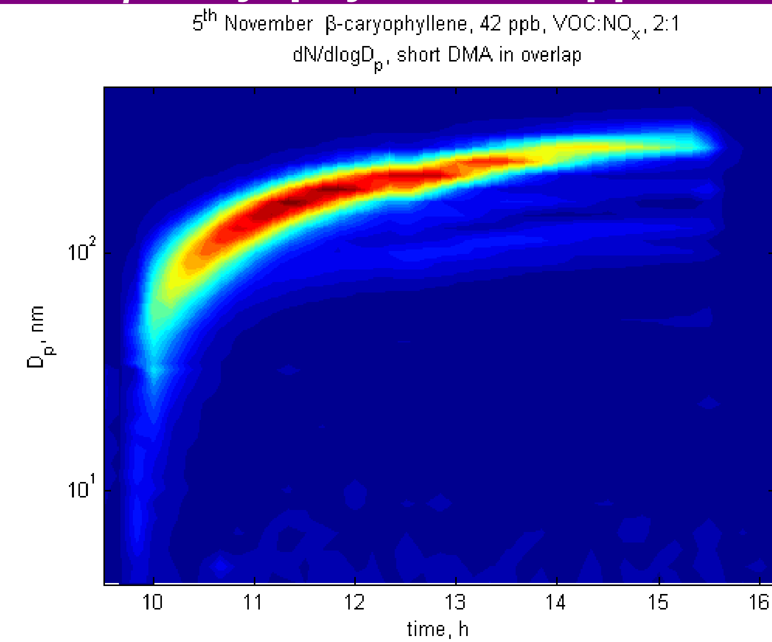
Online measurements included aerosol composition (AMS), size (DMPS), hygroscopicity (HTDMA), cloud activation (CCN), and gaseous VOCs / OVOCs by PTR-MS, O_3, NO_2, NO. Offline filter analyses by GCxGC/MS and LC/MS^n.

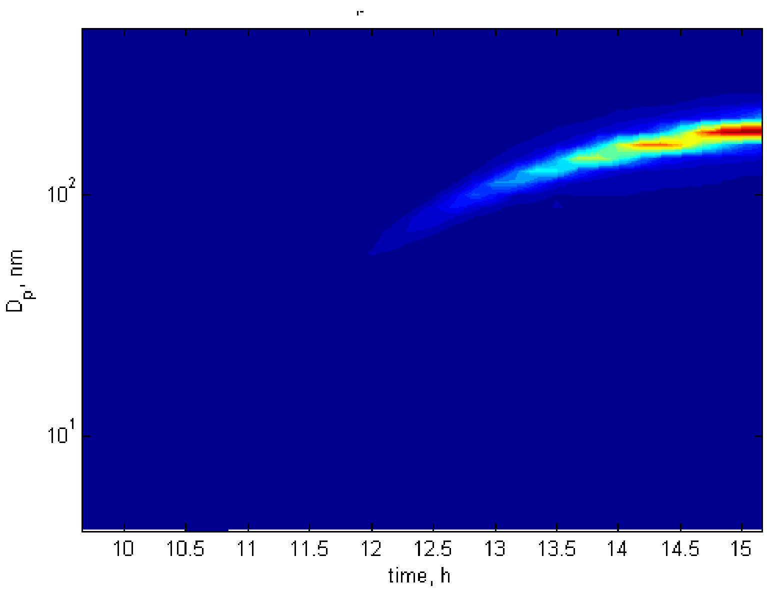
PART 1, Measurement Techniques - DMPS Aerosol Size Distributions

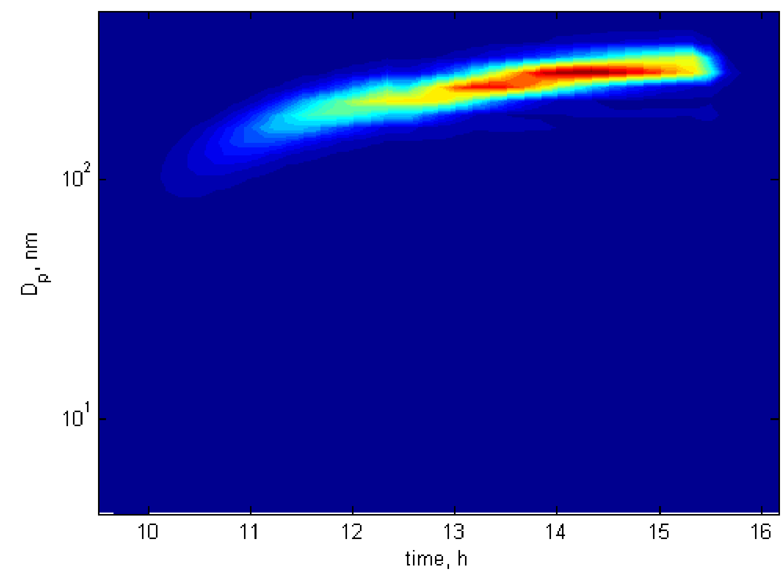
delayed onset nucleation — **α-pinene, 42 ppb, 31st Oct**

faster nucleation — **β-caryophyllene, 42 ppb, 5th Nov**

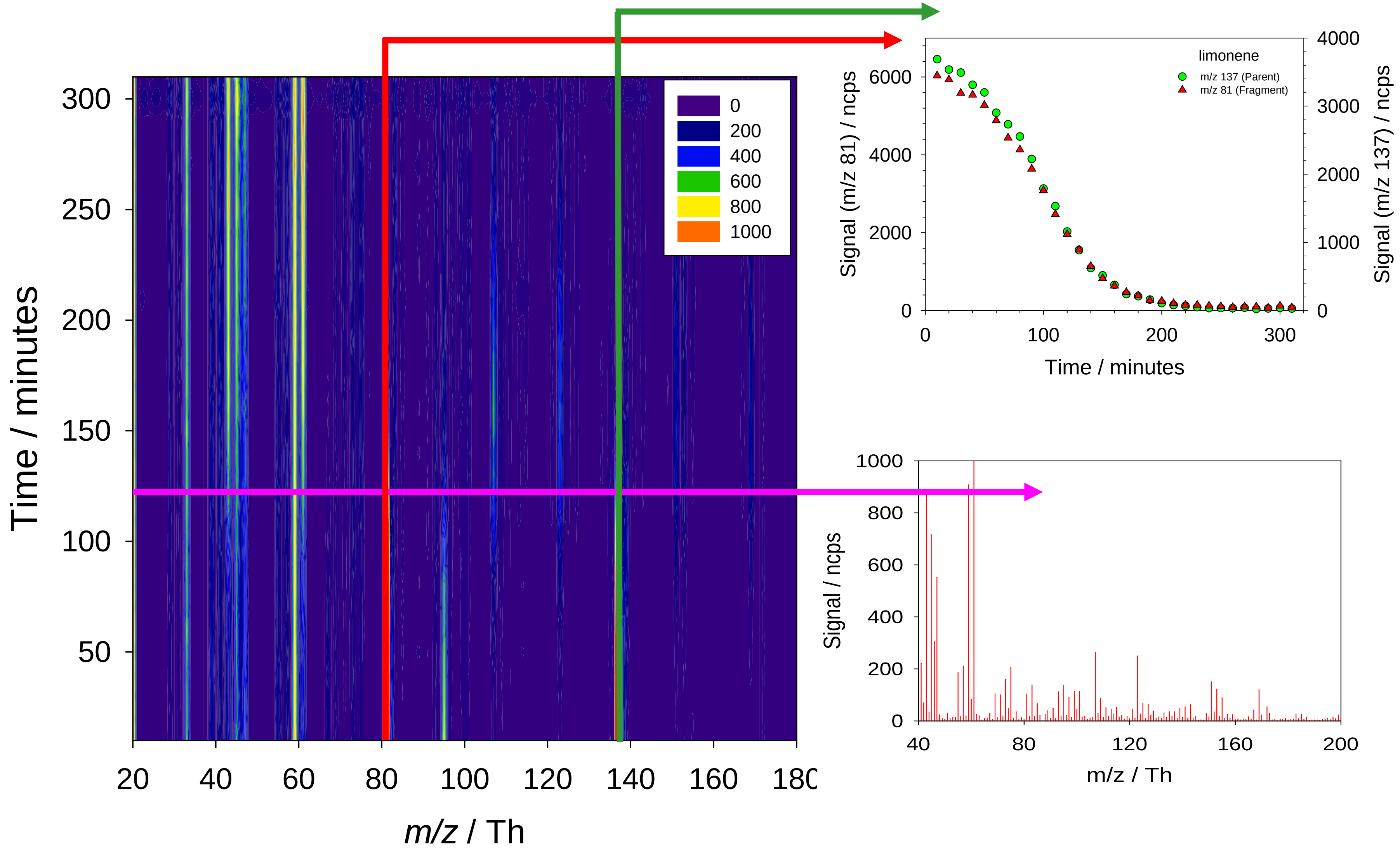




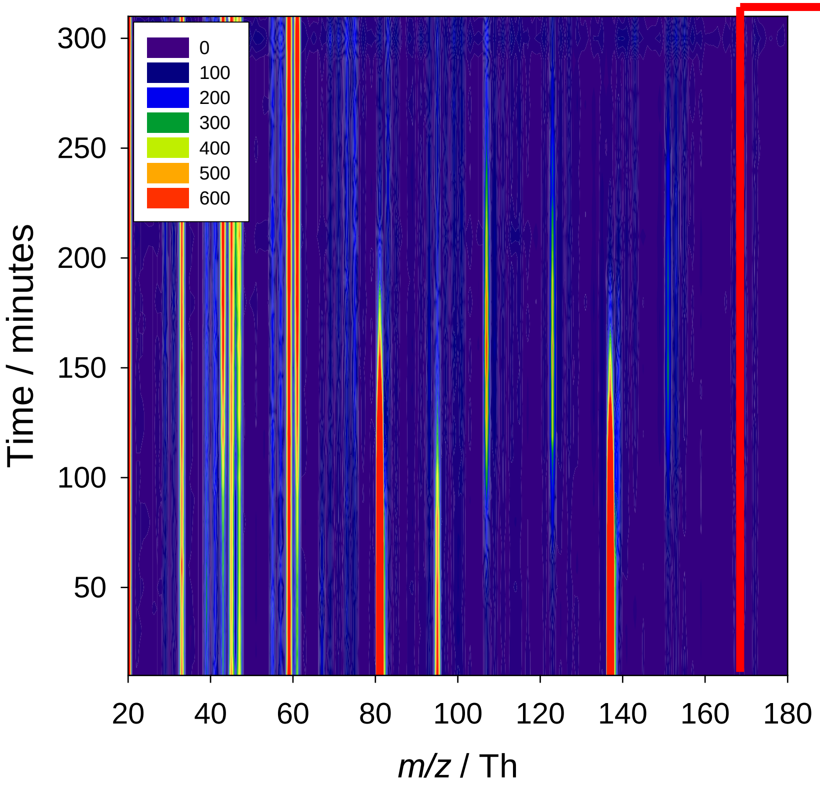


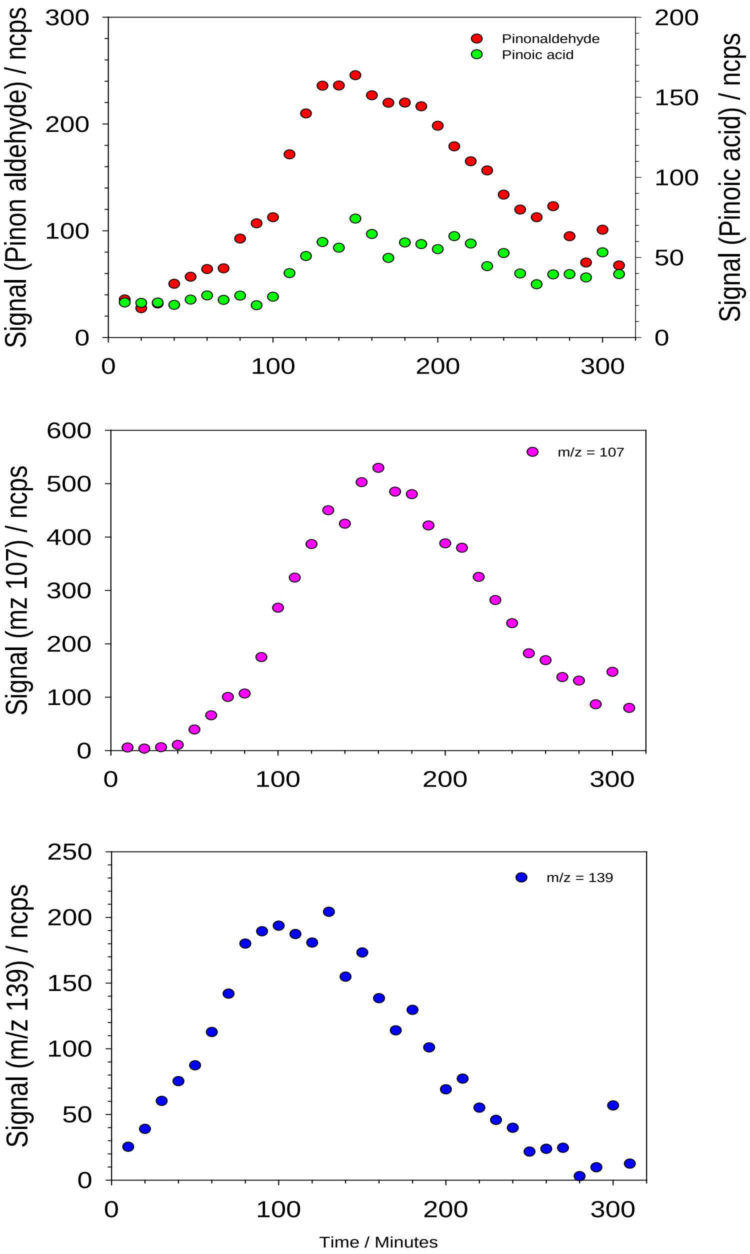


Online PTR-MS: Limonene



Limonene Oxid^n Products





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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 α-pinene <30 ppb
- 05/11/07 and 06/11/07 β-caryophyllene (42 ppb and 210 ppb)
- 08/11/07 and 09/11/07 α -terpinene (42 and 210 ppb)
- 29/11/07 and 30/11/07 limonene and ocimene
- low limonene

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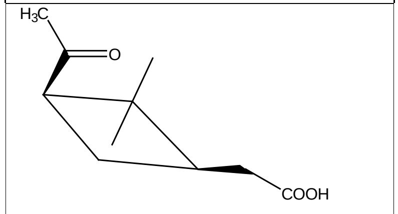
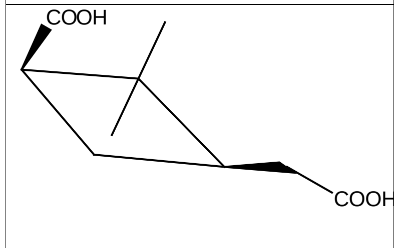
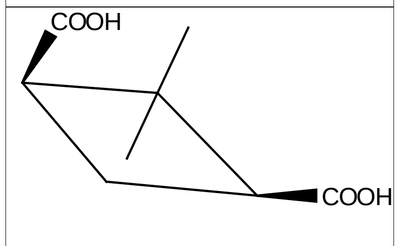
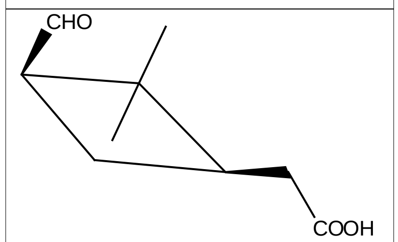
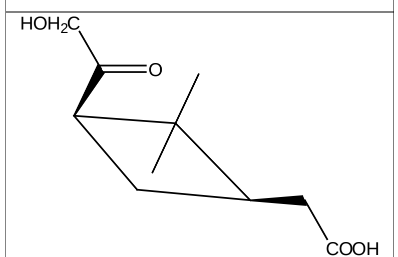
α-pinene SOA

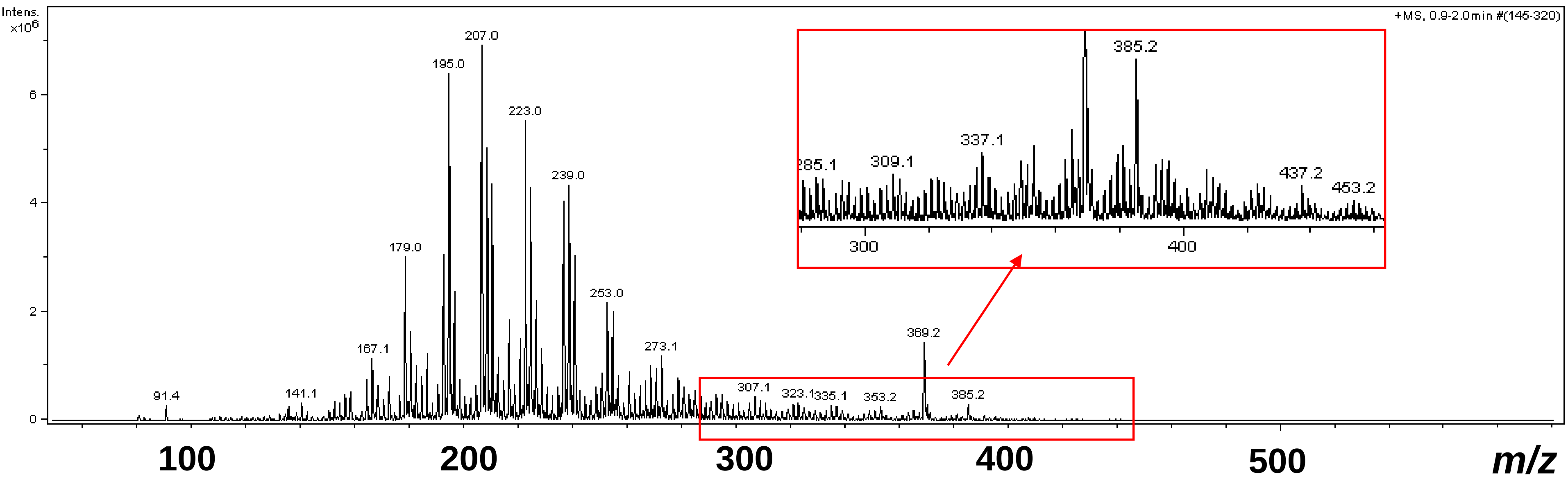
- 2 experiments 09/10/2007 and 10/10/2007
- Both $[VOC]_0$ < 30 ppb
- Ran as a test against historical samples at Euphore
- Run-to-run reproducibility ~ 10 %.
- Compounds identified by MS^2 and reference to previous work

Identified Product	Structure	M_r (g mol^{-1})
Pinonic acid		
		
		
		
	Structure	
		

•+ pinonaldehyde

Molecular weight distribution

- Inject water extract of filters directly into MS to get a molecular weight distribution

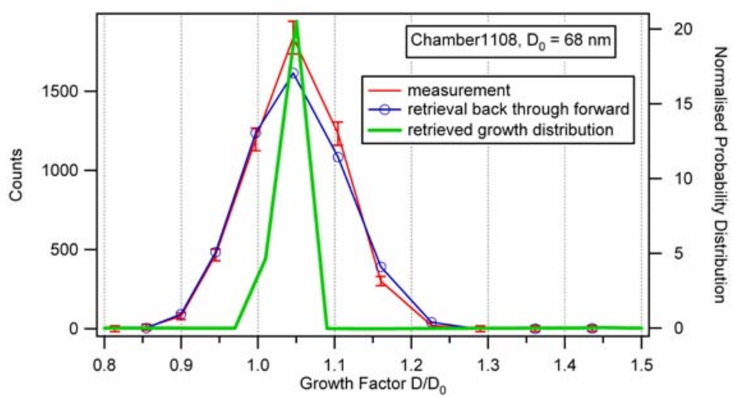


- Maximum abundance at around 190-230 Da
- Small amount of higher molecular weight species but minor component

Hygroscopic Growth Factor measurements by HTDMA

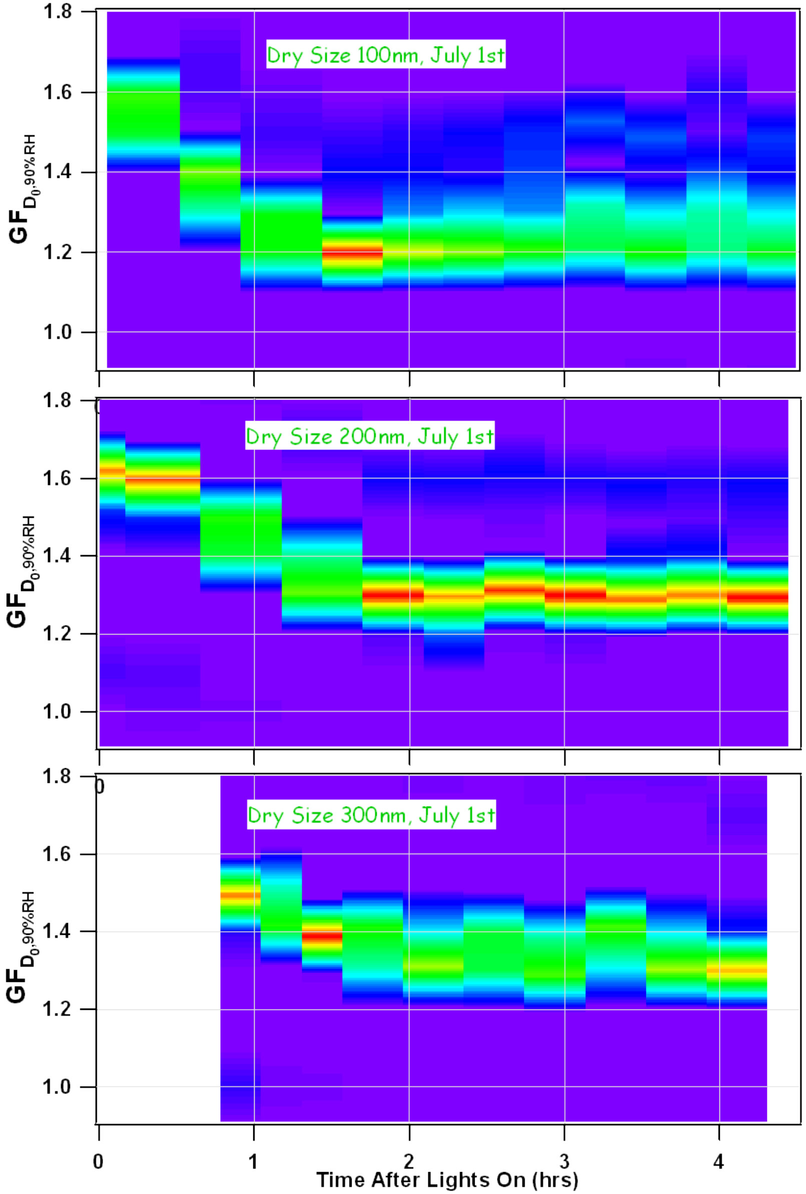
Sample → Dry Size Cut → Humidified 90%RH → Measure Size Distribution → $GF_{D,90\%}$ Dist

But, due the sizing technique and measurement uncertainties data analysis is not trivial



- Measurement is run through the forward model
- Then back thorough to validate
- An error estimate is obtained by adding noise to the signal and repeatedly inverting

$GF_{D,90\%}$ evolution, limonene SOA compounds on $(NH_4)_2SO_4$ injected seed, 1st July



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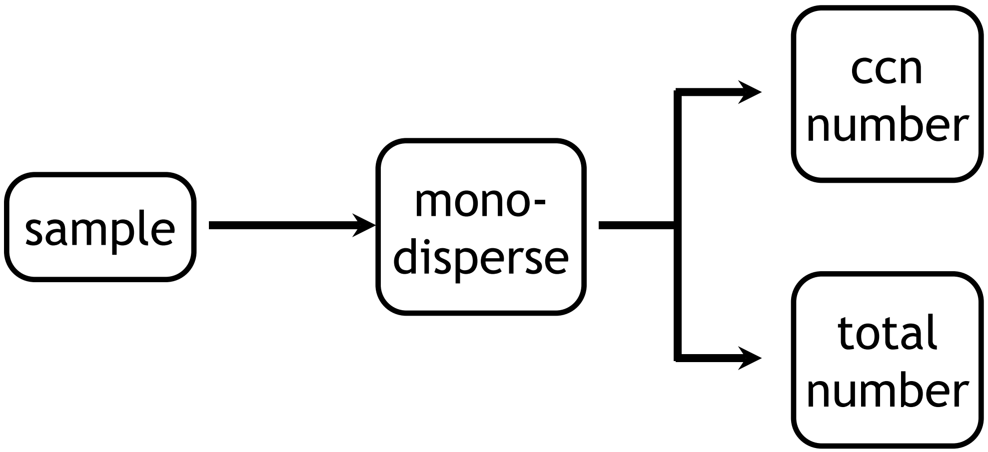
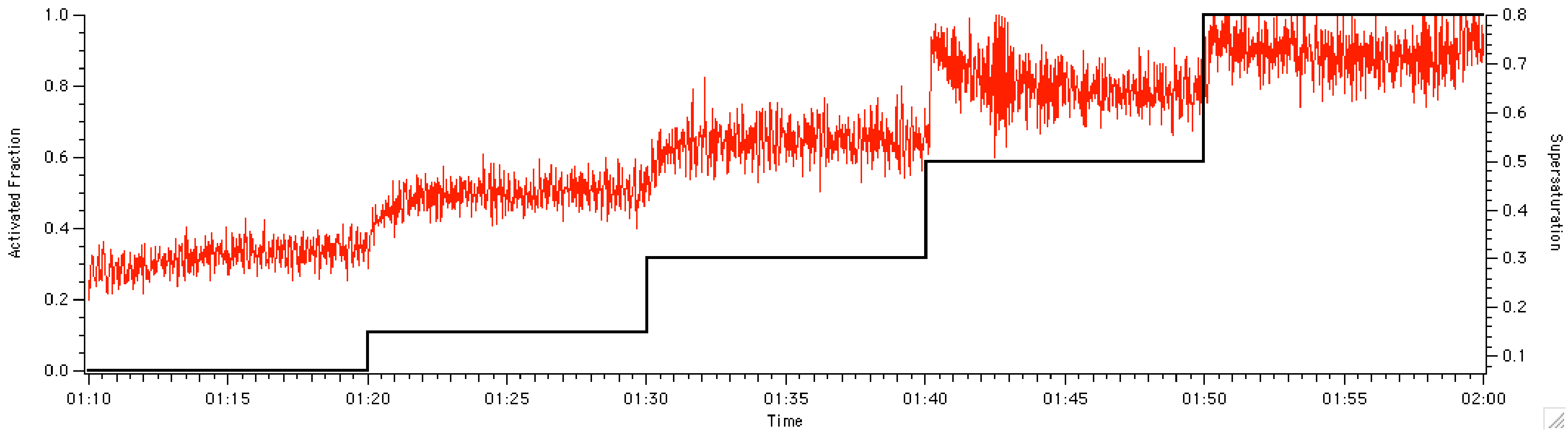
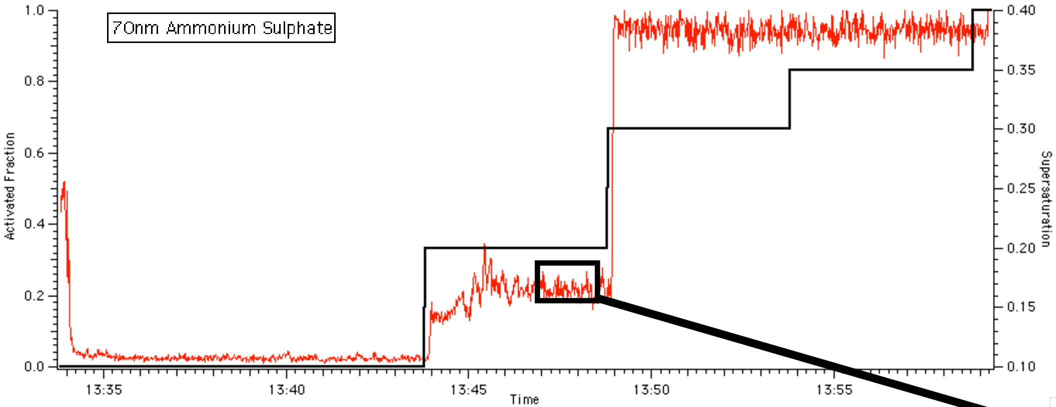
DMT Continuous flow Cloud Condensation Nucleus (CCN) Counter

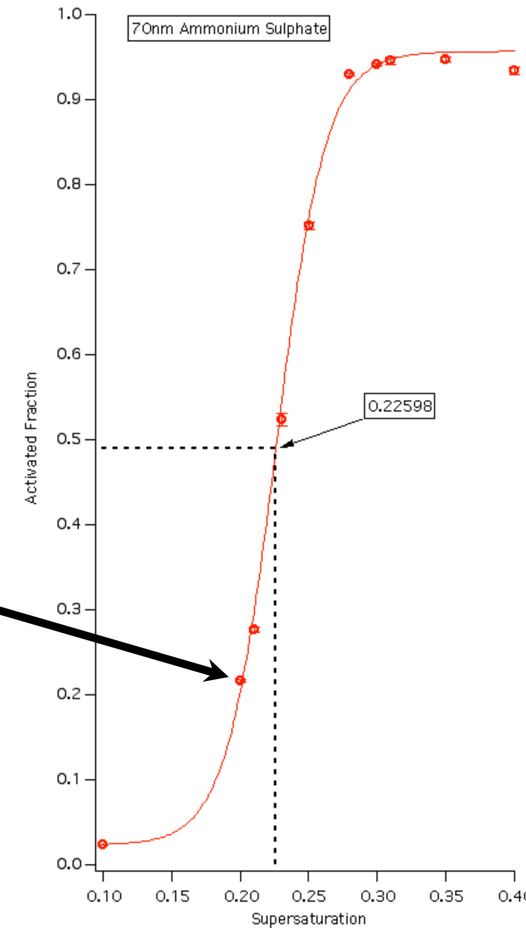


$$A_F = \frac{N_{CCN}}{N_{CPC}}$$



CCN Data Analysis





Broad and narrow range of S scanned

A_F plotted against S

S_{crit} calculated by fitting a sigmoid to data

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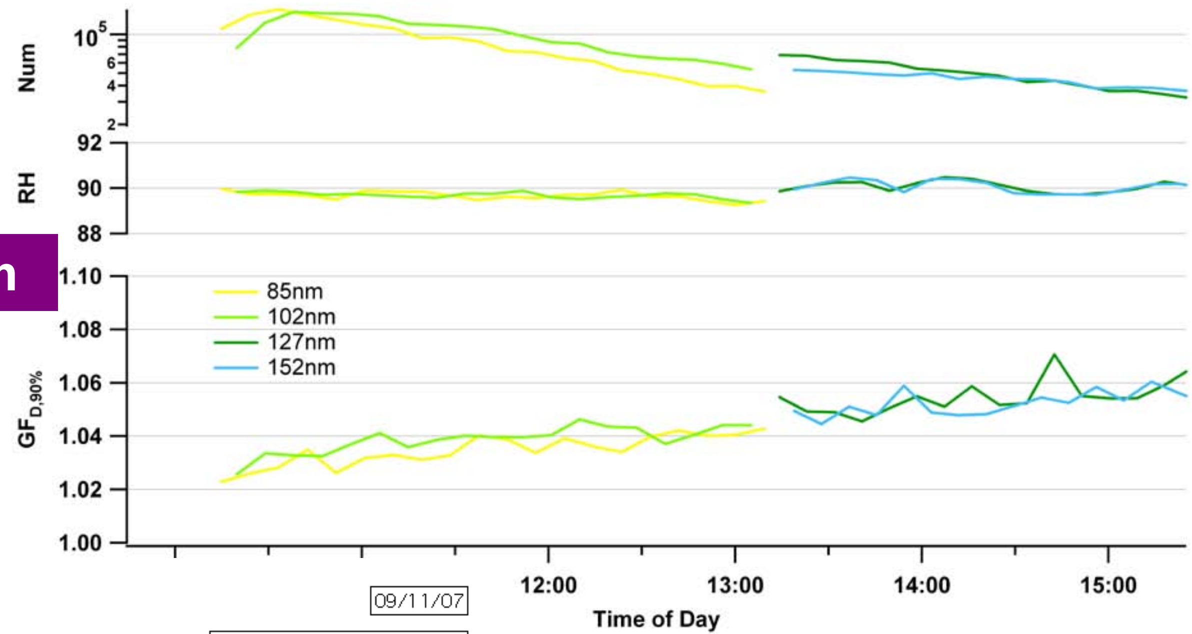
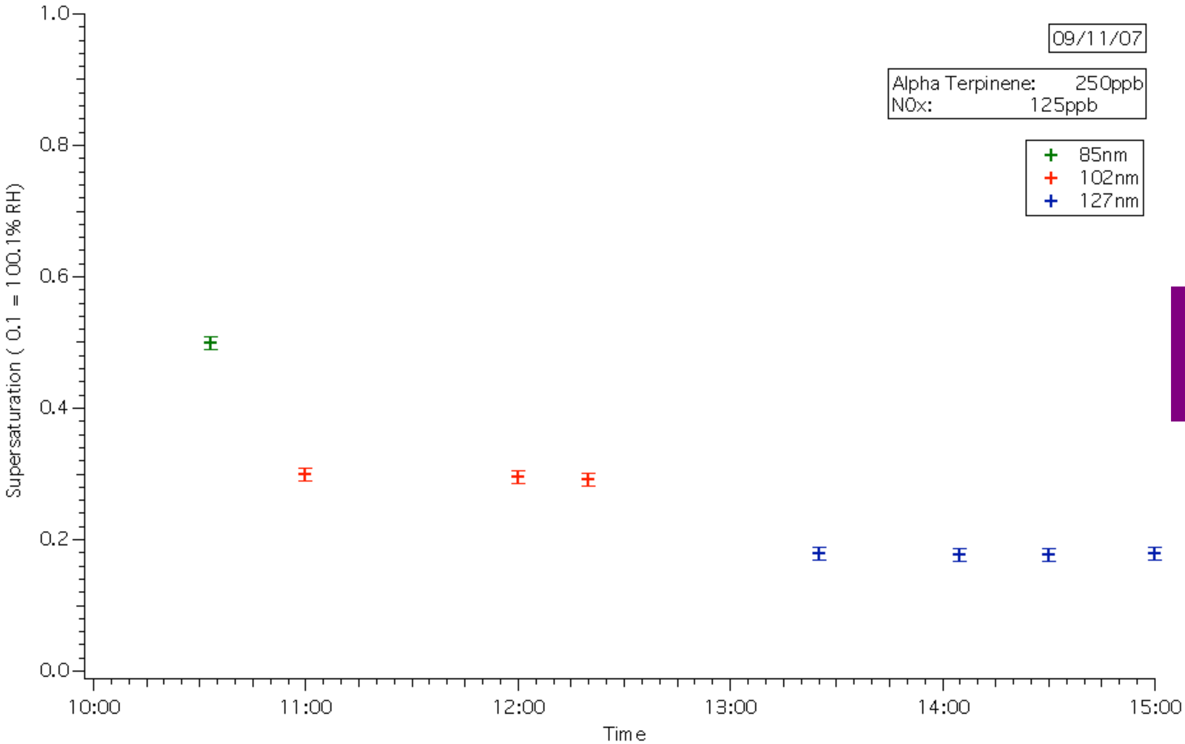
Combining GF_D and CCN behaviour: α-Terpinene, 210ppb, NOx 105ppb

HTDMA, sub-saturated growth



CCN counter, supersaturated growth



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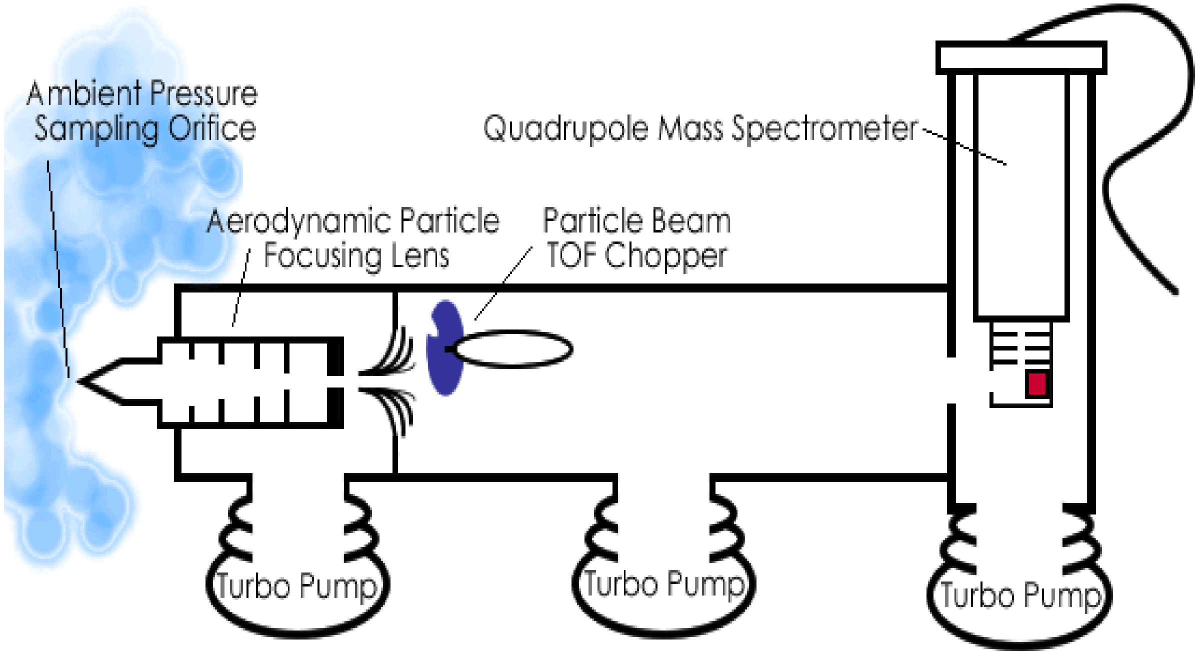
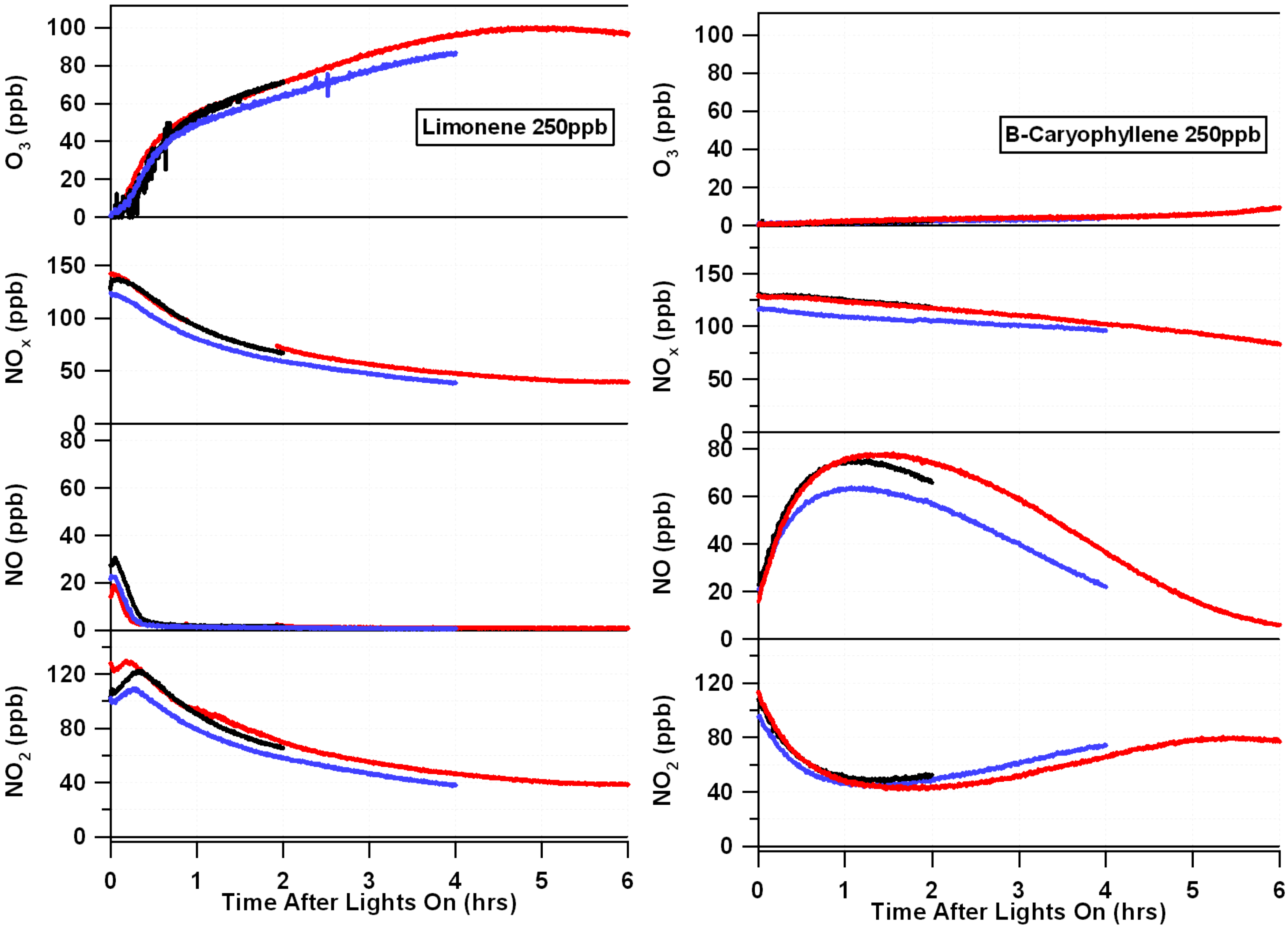
Aerodyne Aerosol Mass Spectrometer (AMS) – Quadropole version now replaced with CToF version



PART 2 SOA formed from β-caryophyllene photo-oxidation



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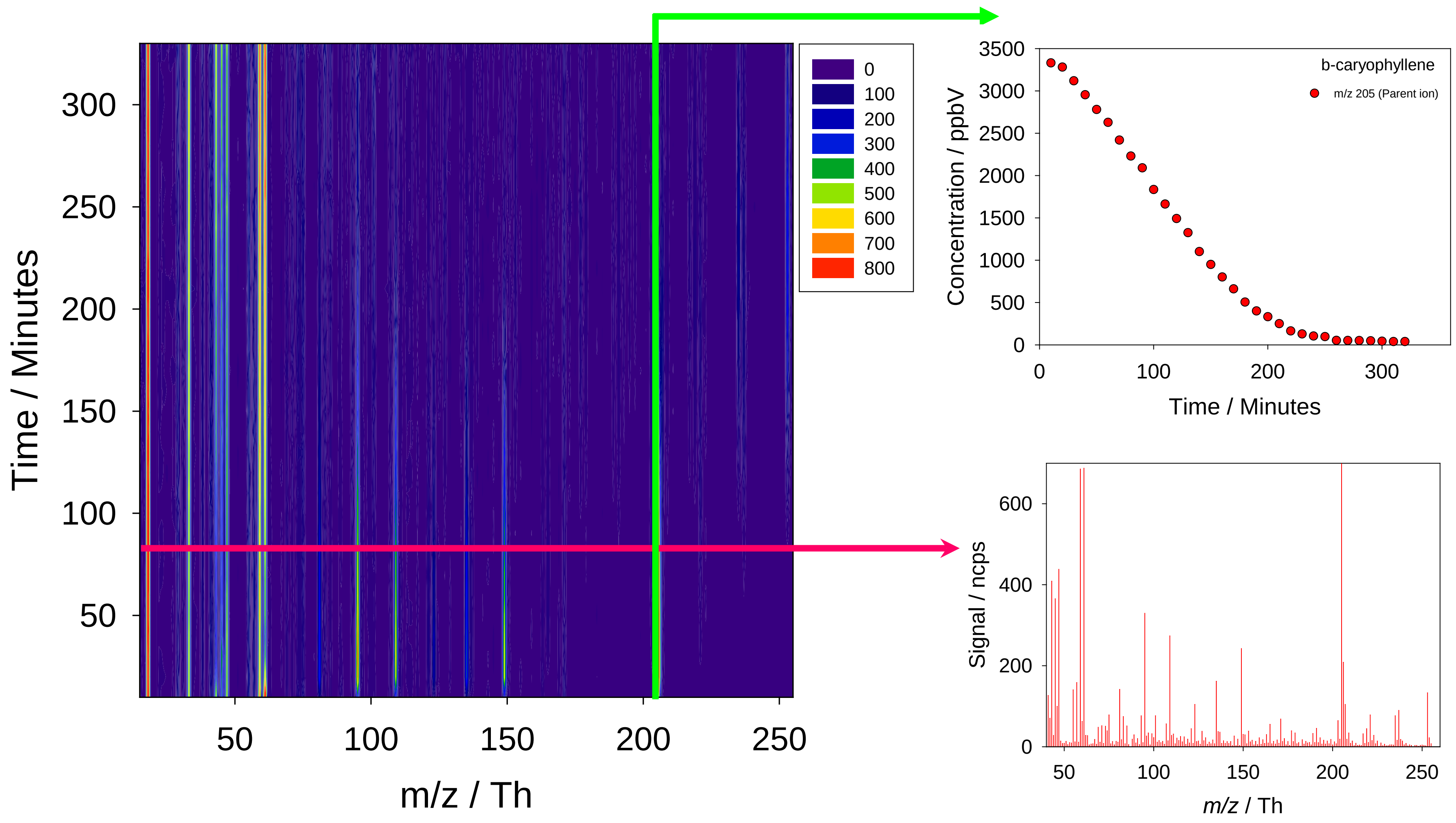
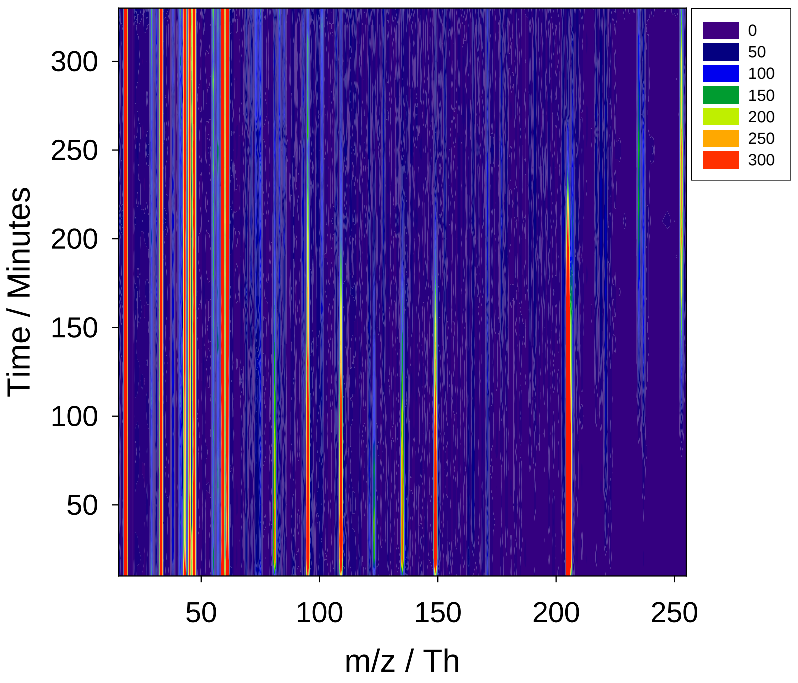
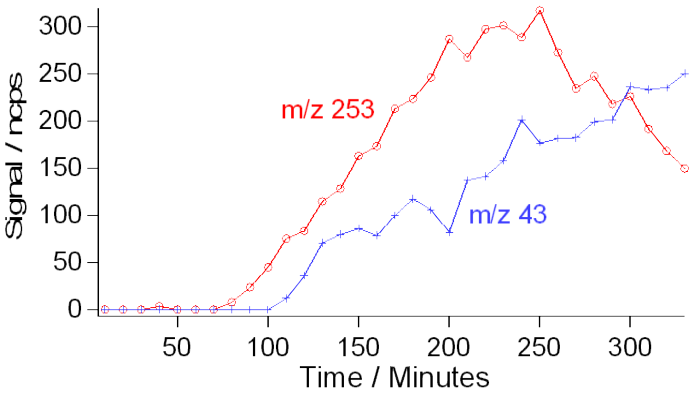
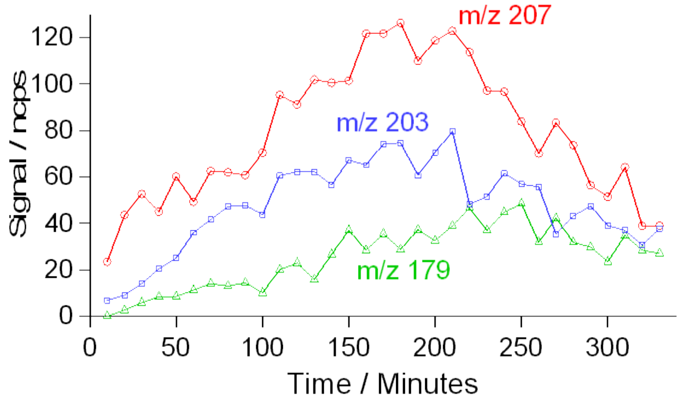
β-caryophyllene



β-caryophyllene



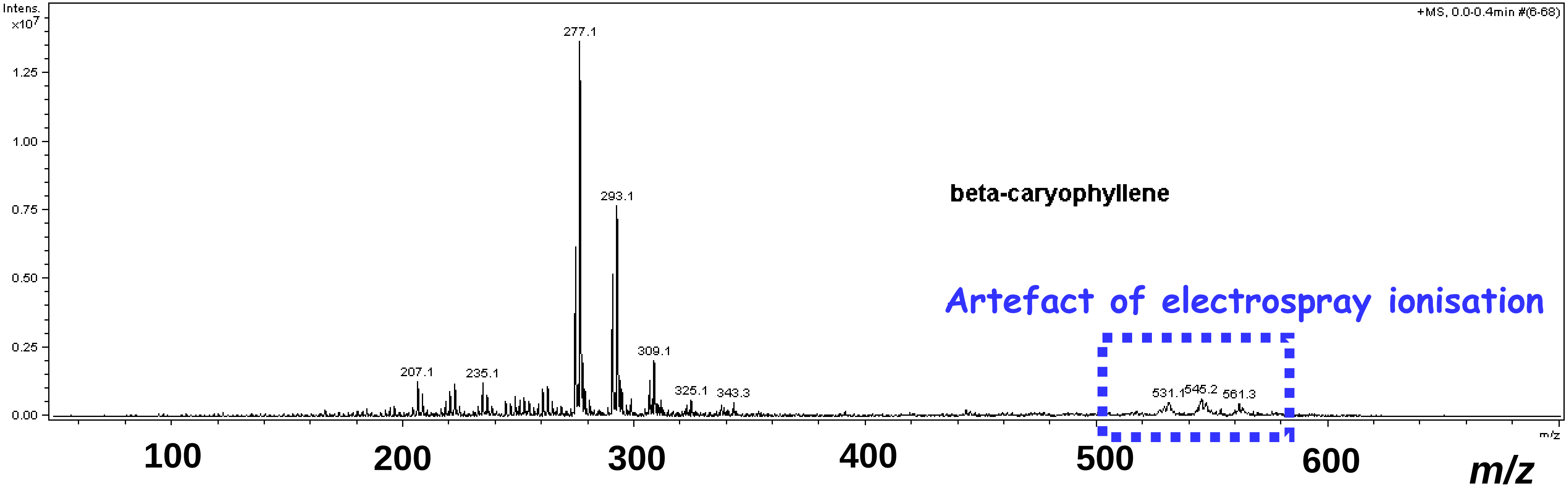




- ~45 ions detected with high [VOC]
- Inc. 9 with *m/z* > precursor
- 99% oxidation of precursor (independent of initial conc^{n}.)

SOA formed in β-caryophyllene photo-oxidation

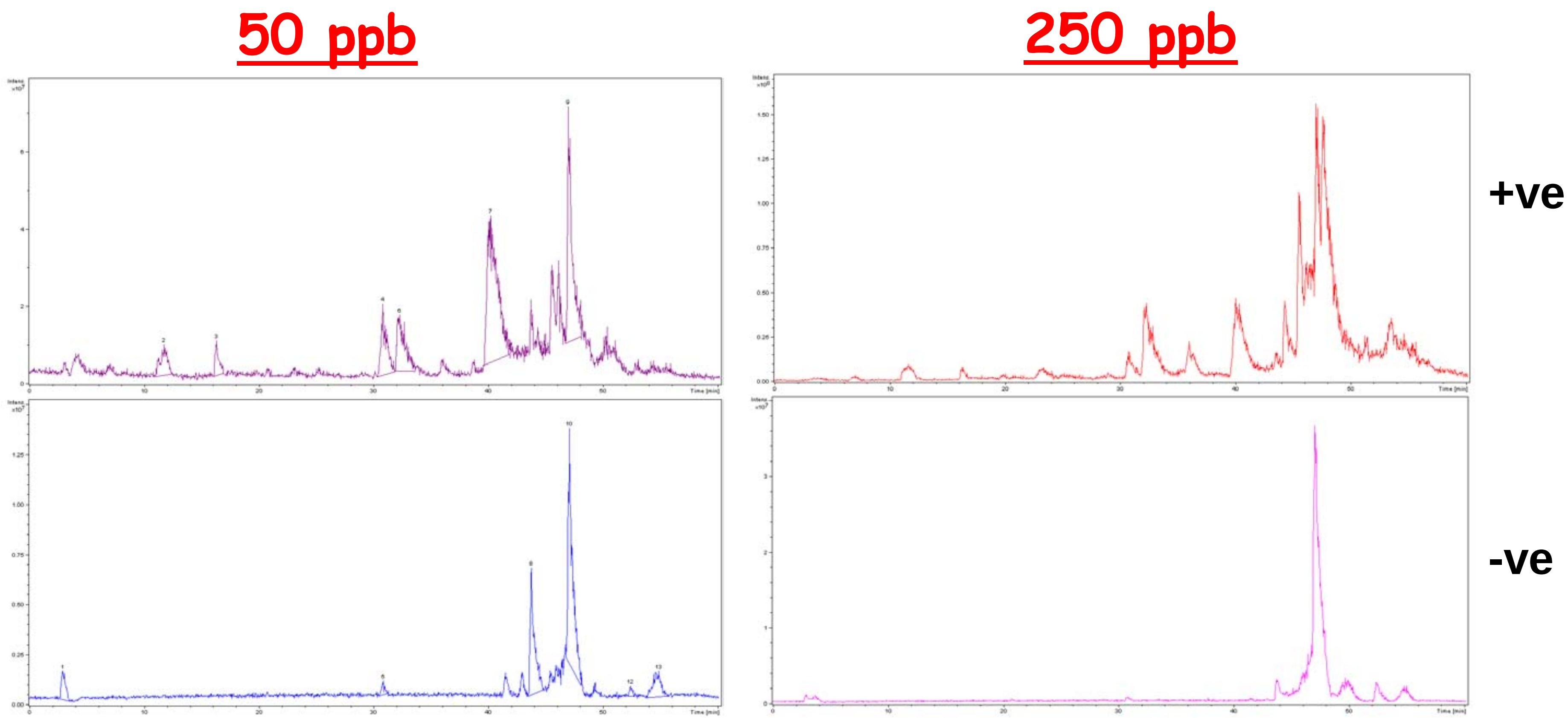
- 2 samples
  - 05/11/07 $[VOC]_0$ = 42 ppb
  - 06/11/07 $[VOC]_0$ = 210 ppb

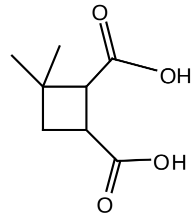
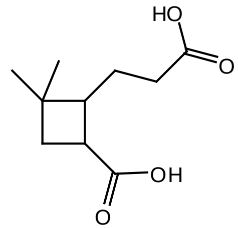
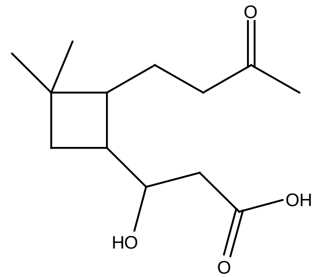
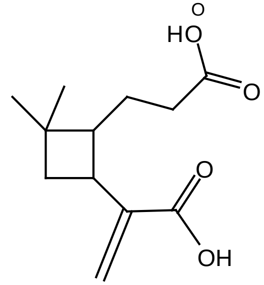
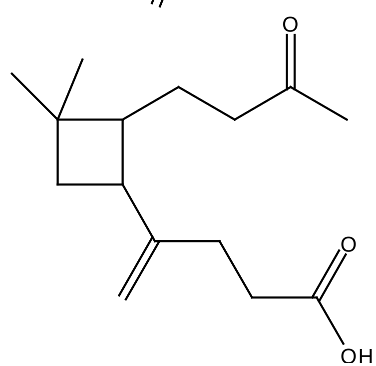


  - Unlike mono-terpene studies there is NO evidence of oligomer formation in these samples
  - Need to compare to those aged longer

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



NEGATIVE Compound		MW	m/z	rt
nor-caryophyllenic acid		**172**	**171**	**20.7**
2-(2-carboxyethyl)-3,3-dimethylcyclobutanecarboxylic acid		**200**	**199**	**30.8**
3-(3,3-dimethyl-2-(3-oxobutyl)cyclobutyl)-3-hydroxypropanoic acid		**242**	**241**	**43.7**
2-(2-(2-carboxyethyl)-3,3-dimethylcyclobutyl)acrylic acid		**226**	**225**	**43.8**
b-caryophyllonic acid		**252**	**251**	**45.9**

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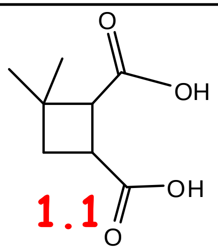
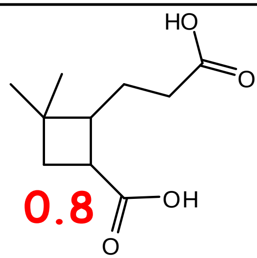
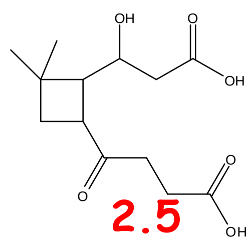
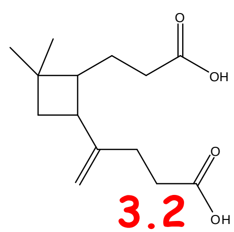
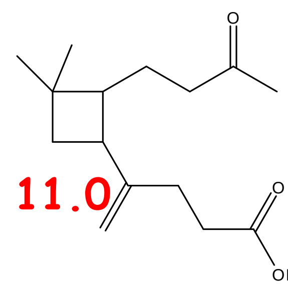
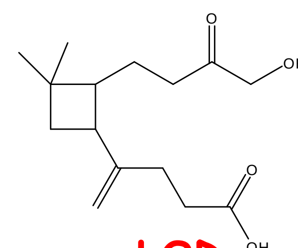
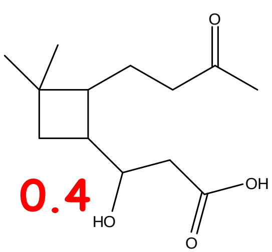
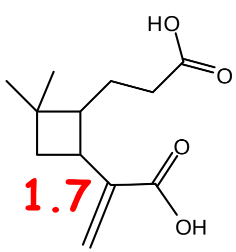
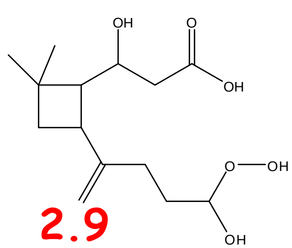
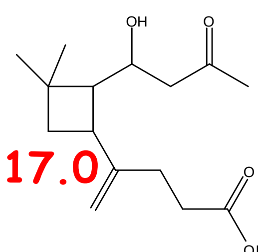
Effect of $[VOC]_0$ on SOA composition

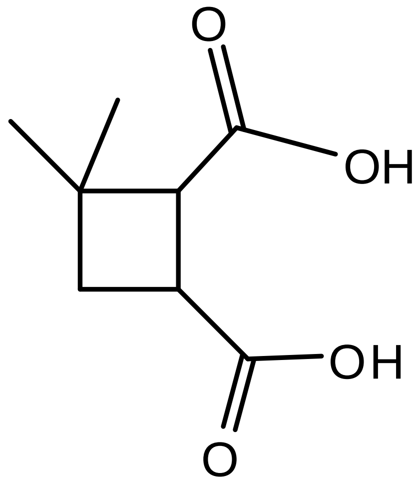
- Peak SOA concentration in chamber 155_{210ppb} vs 67_{42ppb} µg m^{-3}.
  - Ratio high to low ~ 3:1 at end of experiment
    - (collected mass ~ 1200mg vs 500 mg, ratio 2.4)

Ratio 210 ppb / 42 ppb

Less than 2.0	2.0 - 3.5	Greater than 3.5
 1.1  0.8	 2.5  3.2	 11.0  <LOD in 50ppb
 0.4  1.7	 2.9	 17.0
More in 42 ppb	**Around equal**	**More in 210 ppb**

Comparison of estimated properties

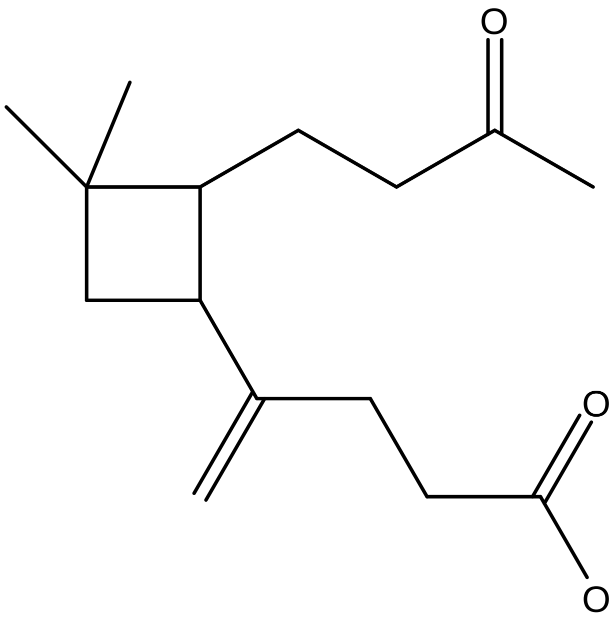
More in 42 ppb sample



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

More polar and water soluble

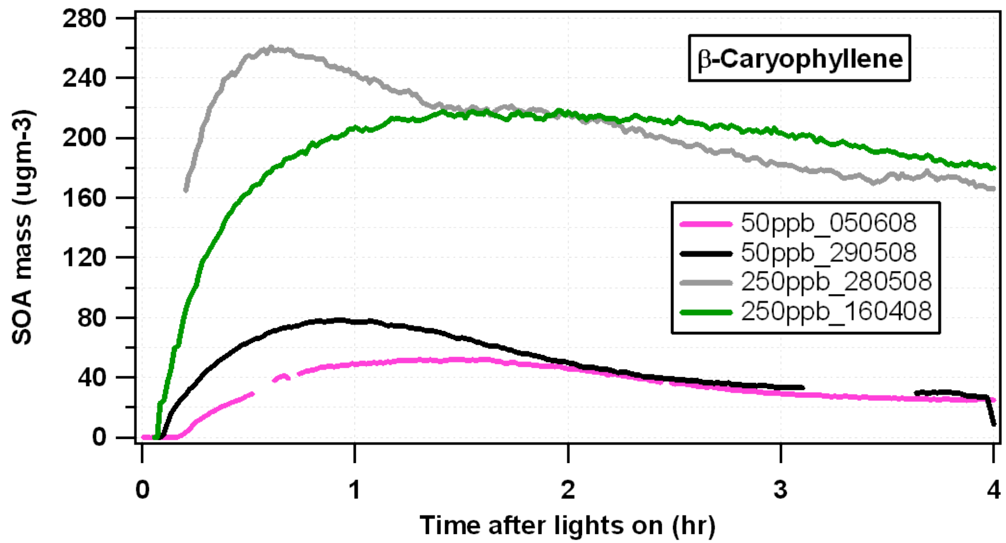
More in 210 ppb sample

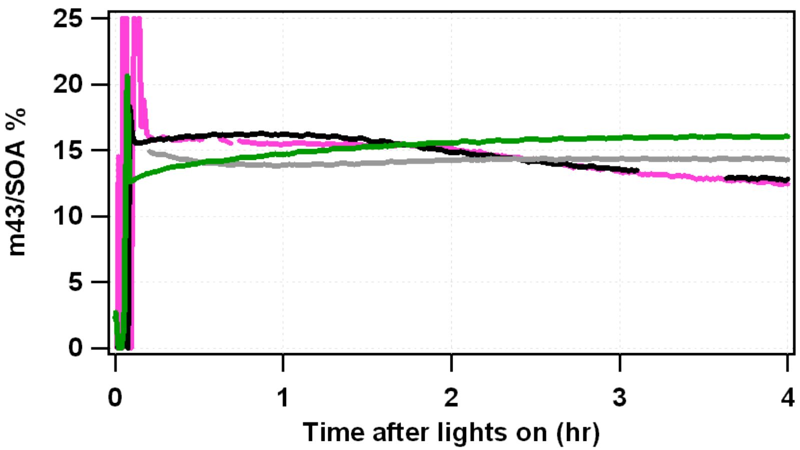


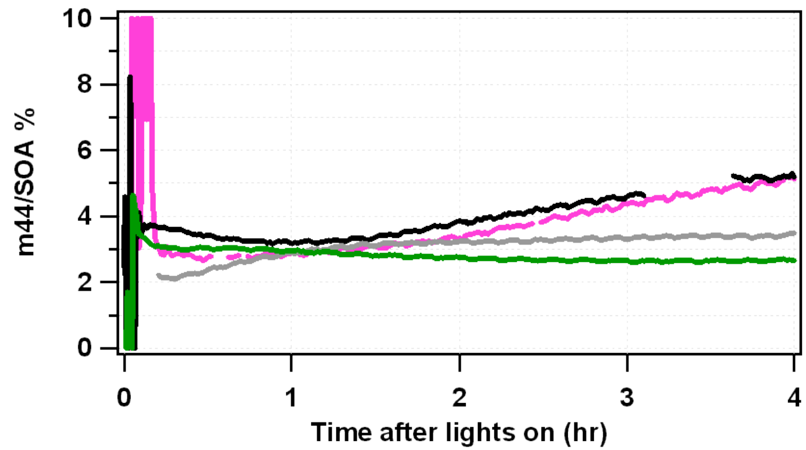
- Boiling point = 740 K
- VP = 1 x 10^{-6} torr
- Log (p) = 2.7-3.01
- (octanol:water)

Less polar but also less volatile

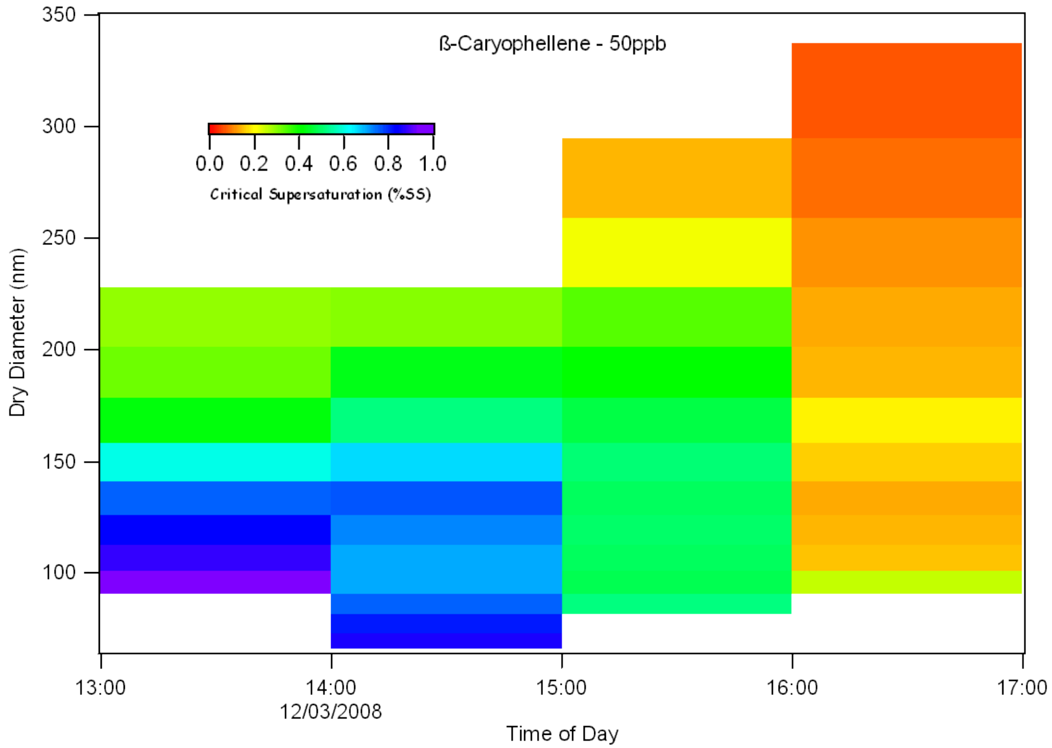
AMS fragments in SOA generated in β-caryophyllene photo-oxidation

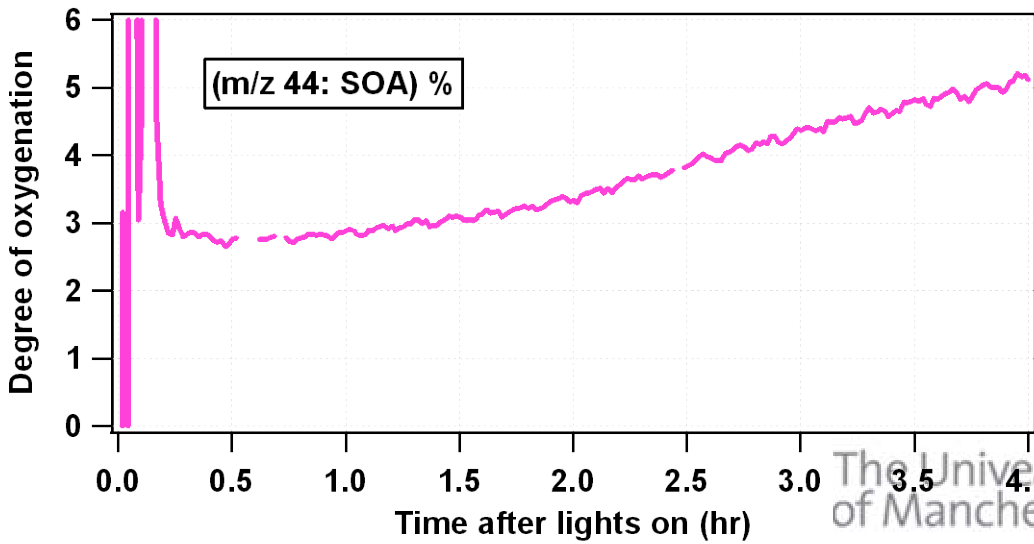




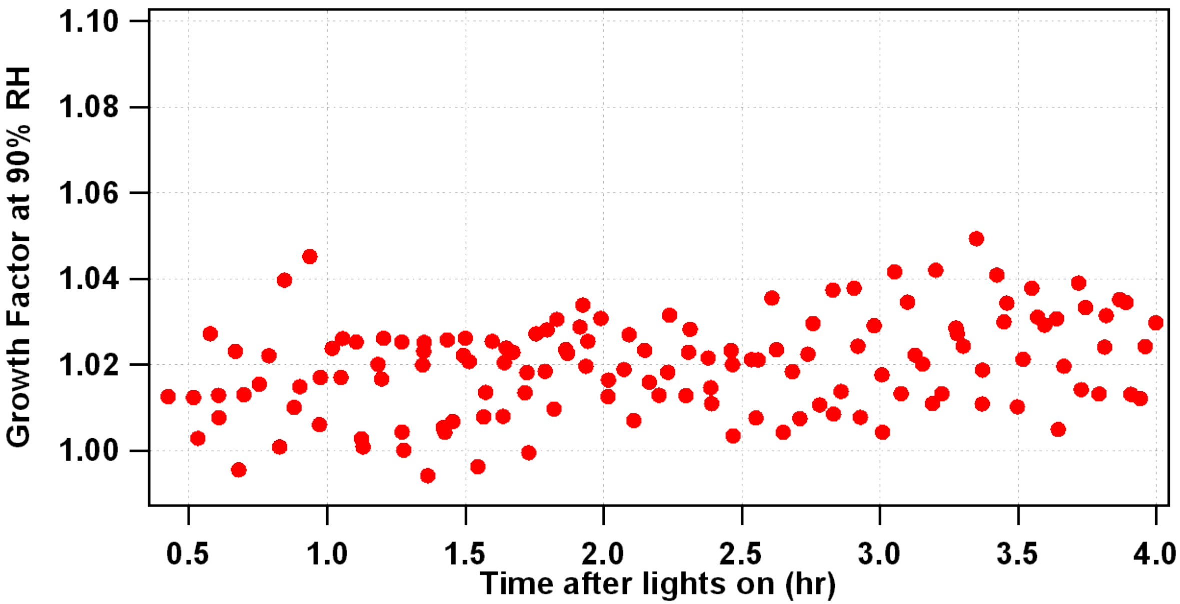


CCN properties of β-caryophyllene SOA





Hygroscopic properties of β-caryophyllene SOA



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

Sub-saturated and super-saturated results do not match!

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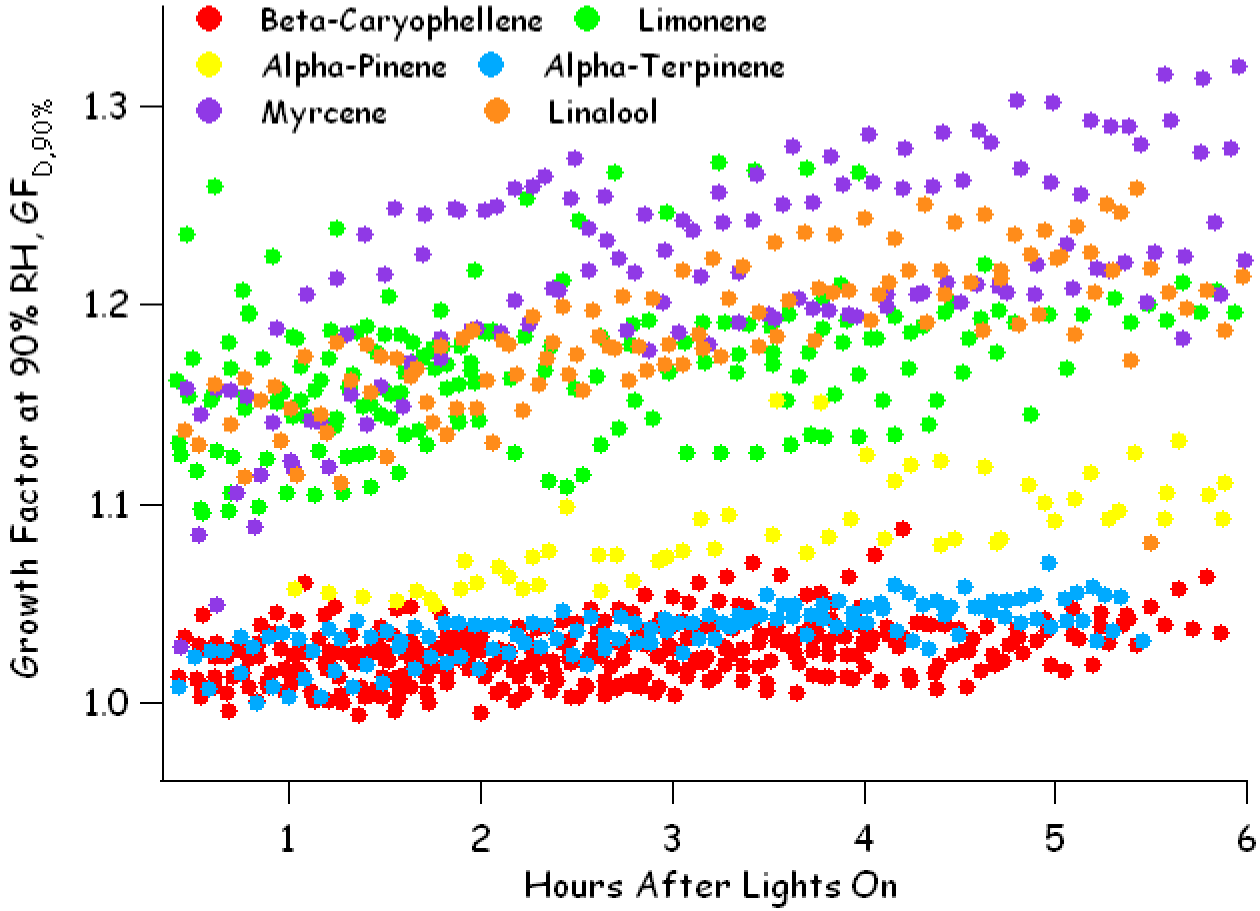
PART 3 Physical & Chemical properties of BSOA from various precursors: Can the picture be really simplified??

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



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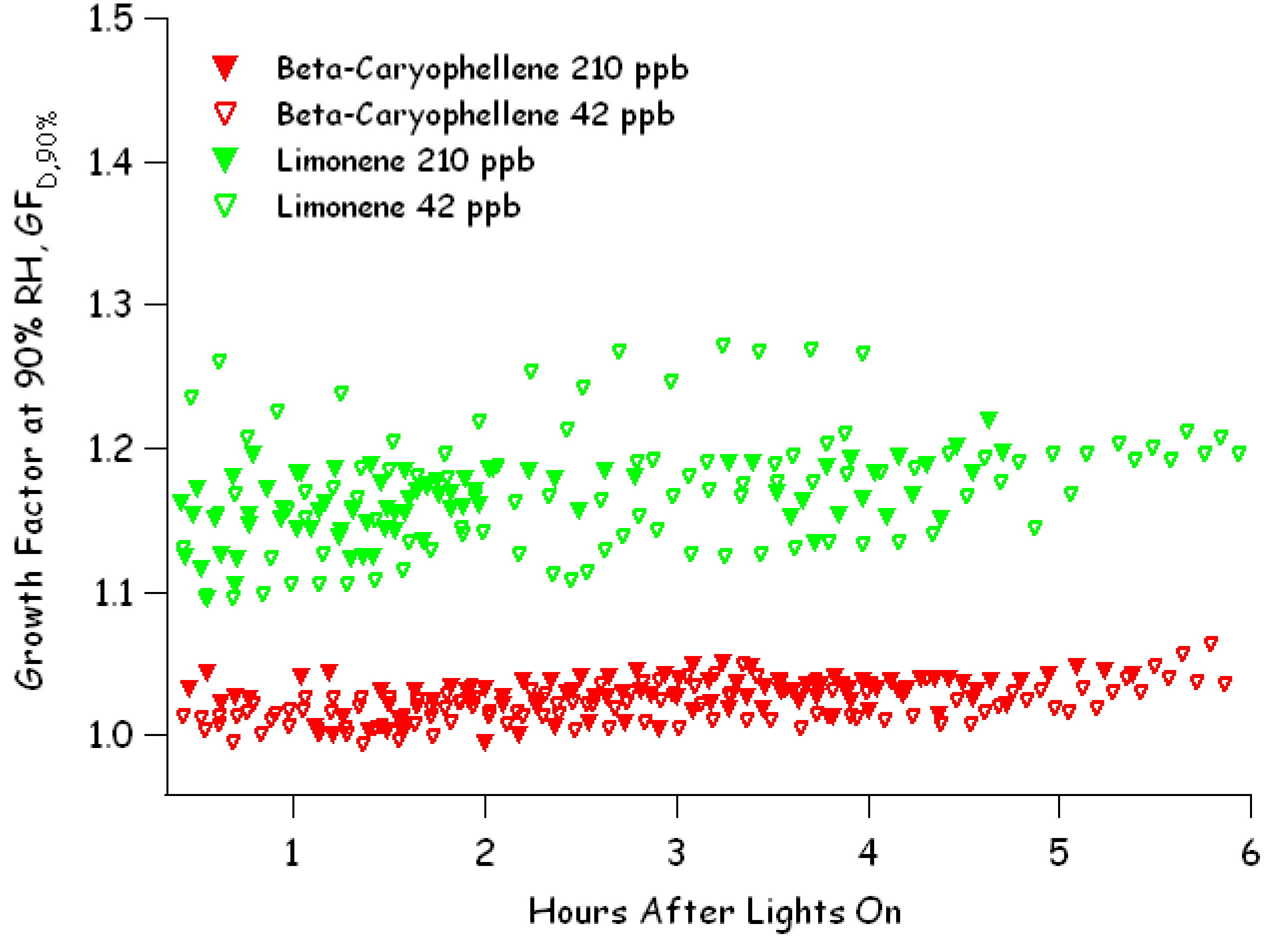
Can the picture be simplified? SOA $GF_{D,90\%}$ differs more with changing precursor than changing concentration



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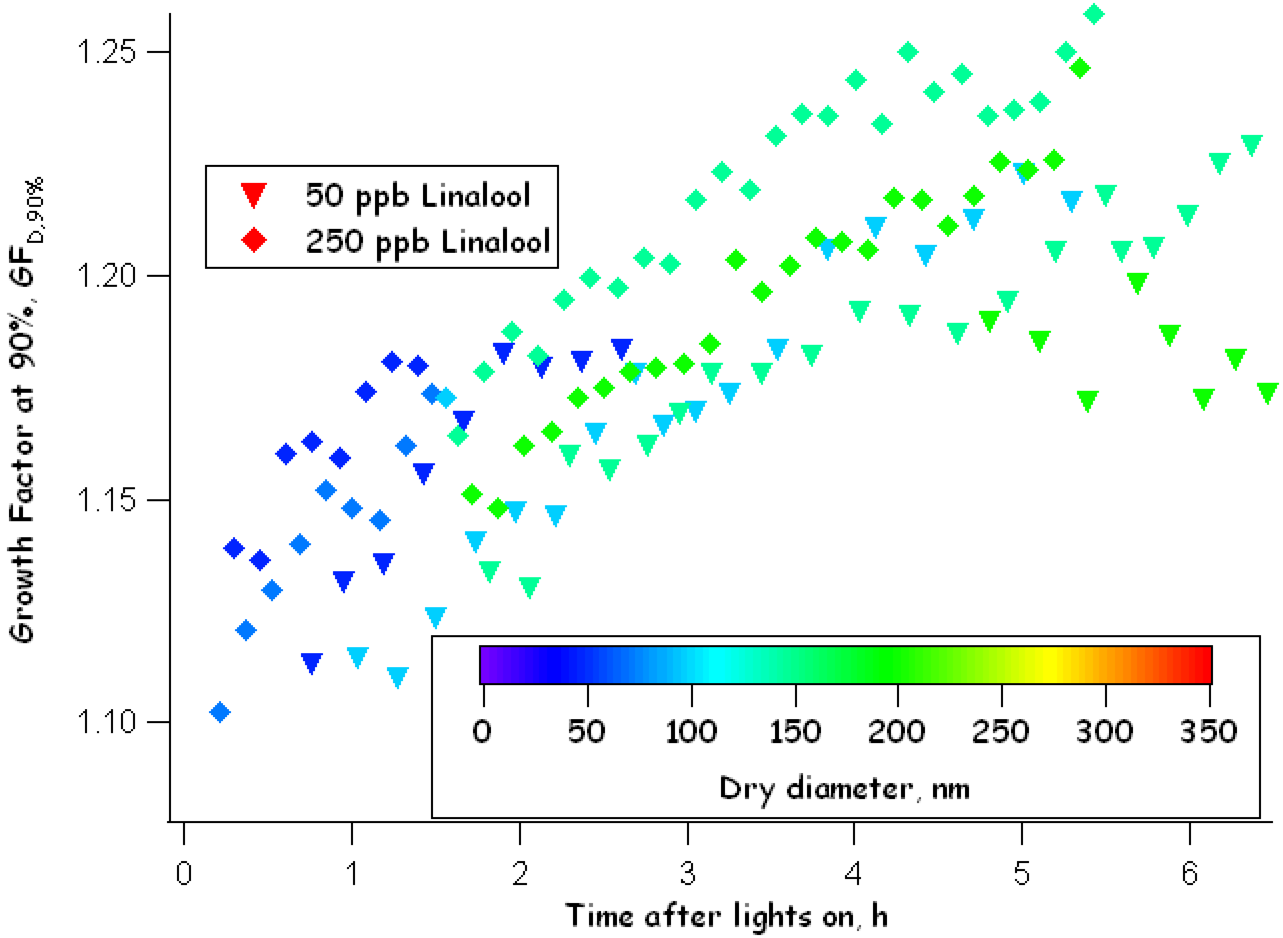
Can the picture be simplified? Linalool, Note initial rate of change of $GF_{D.90\%}$



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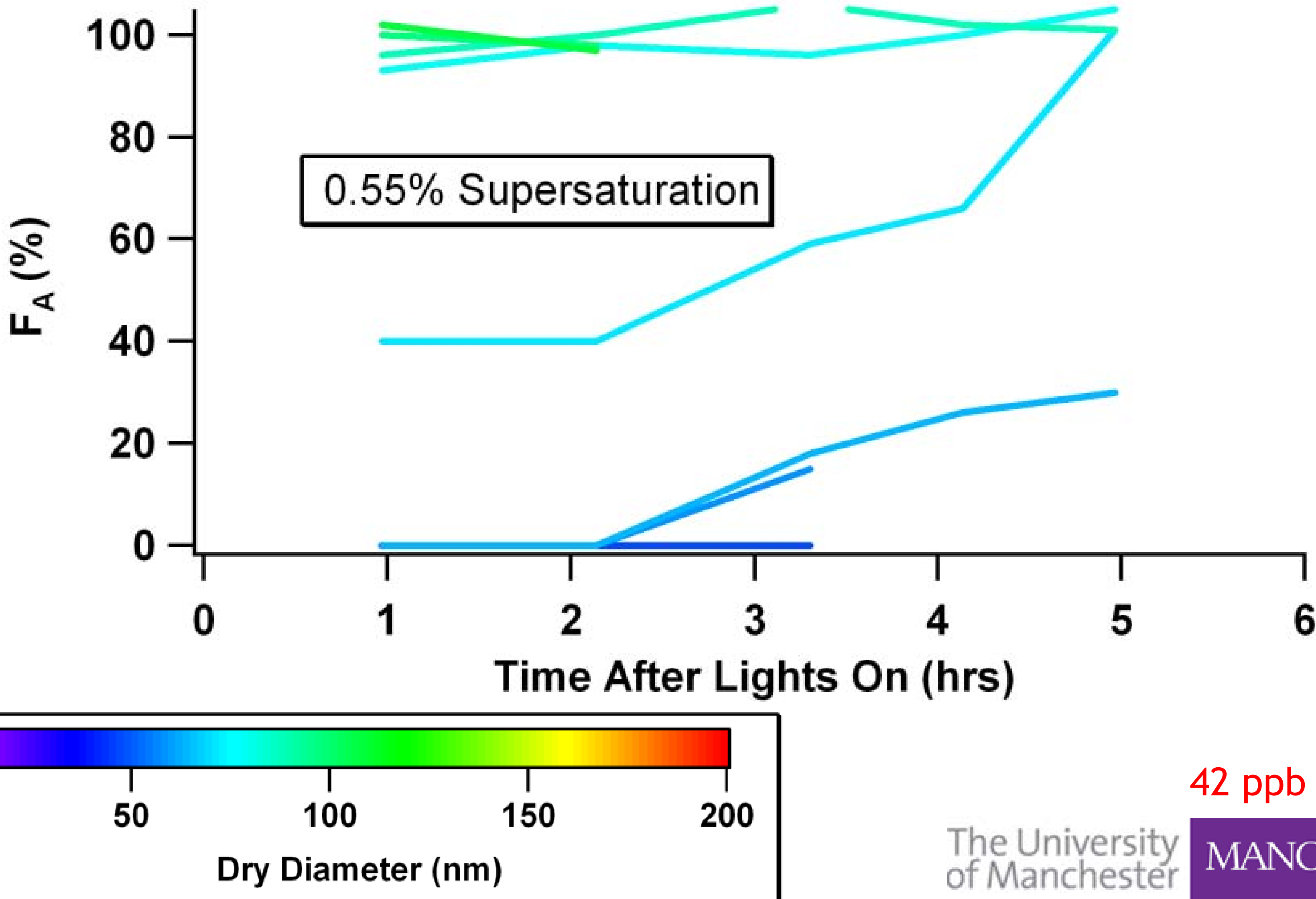
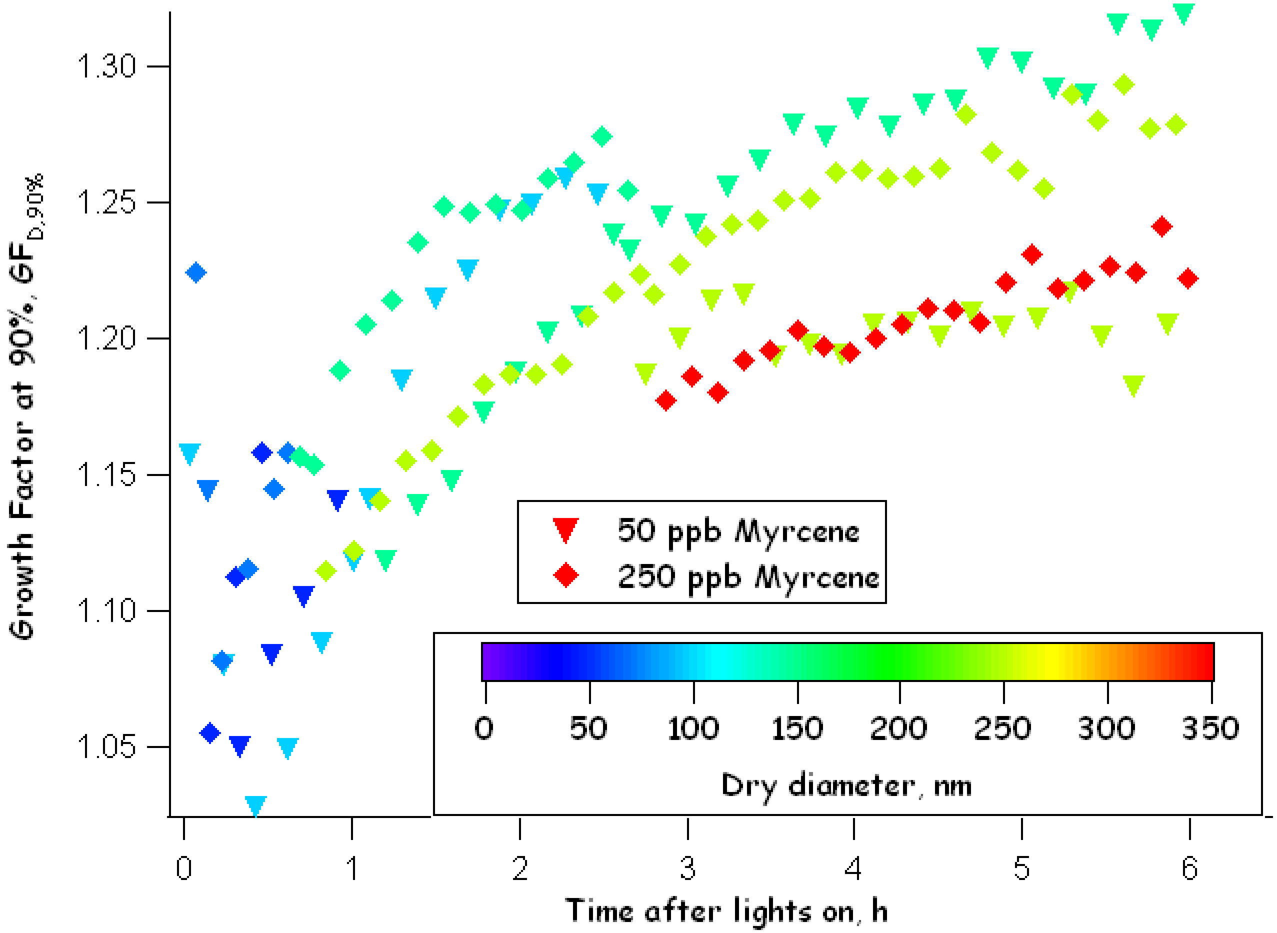
Can the picture be simplified? Linalool, $GF_{D.90\%}$ change is reflected in rate of change of fraction activated to CCN



42 ppb Linalool

Can the picture be simplified? Myrcene, Note initial rate of change of $GF_{D,90\%}$



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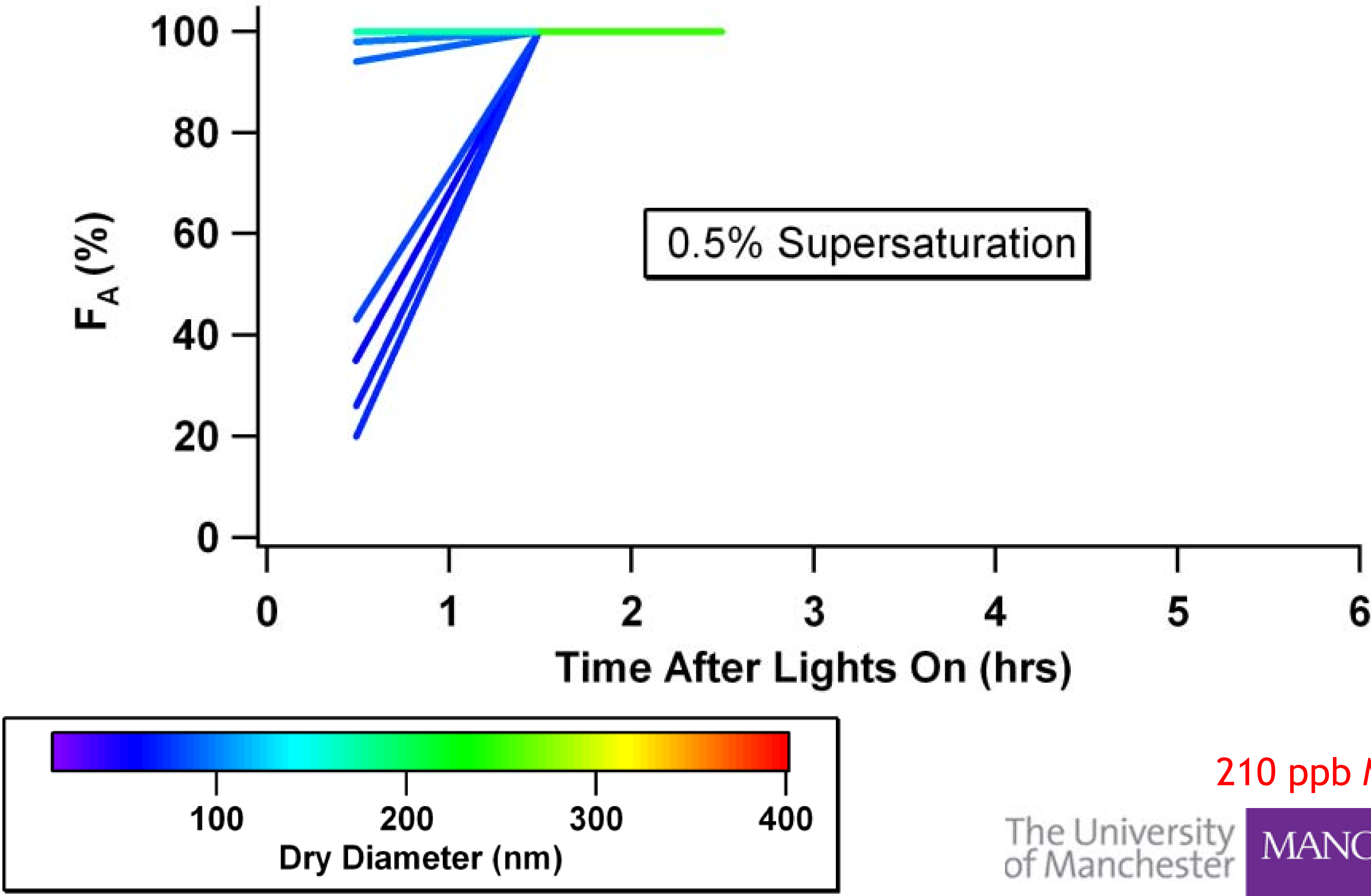
Can the picture be simplified? Myrcene, more rapid $GF_{D.90\%}$ change is also seen in earlier change of fraction activated



210 ppb Myrcene

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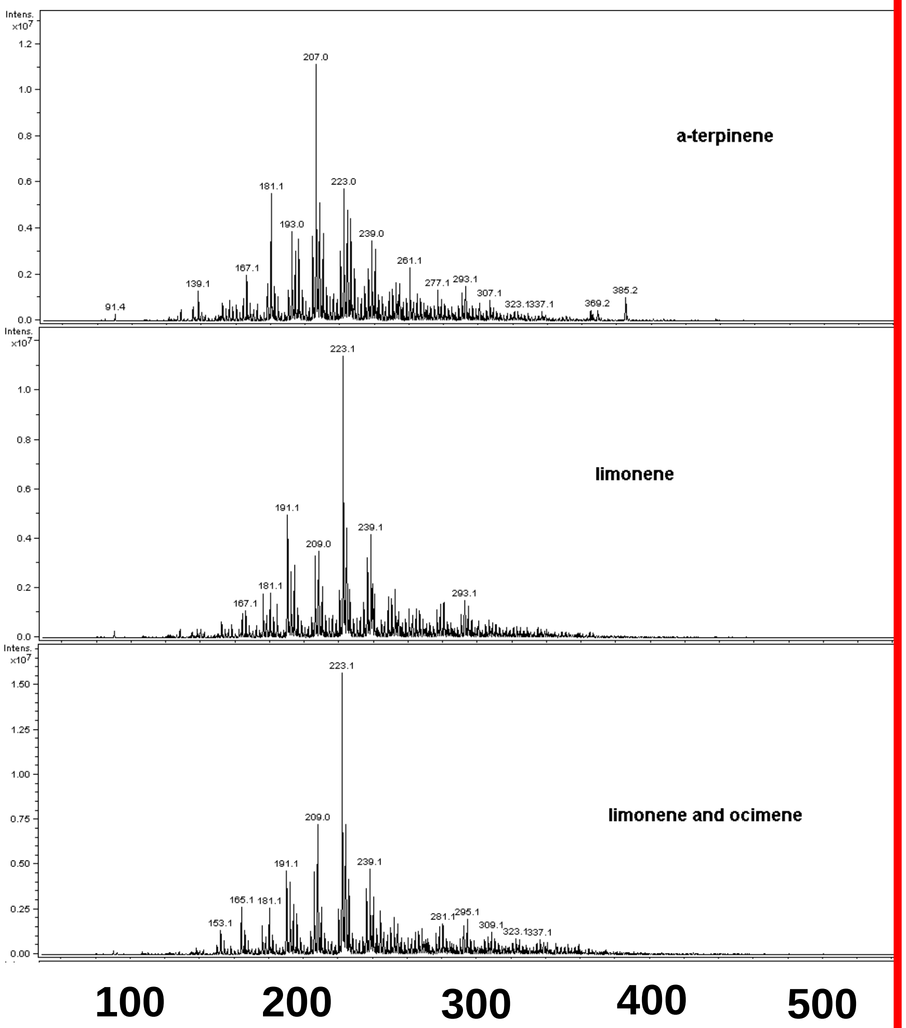
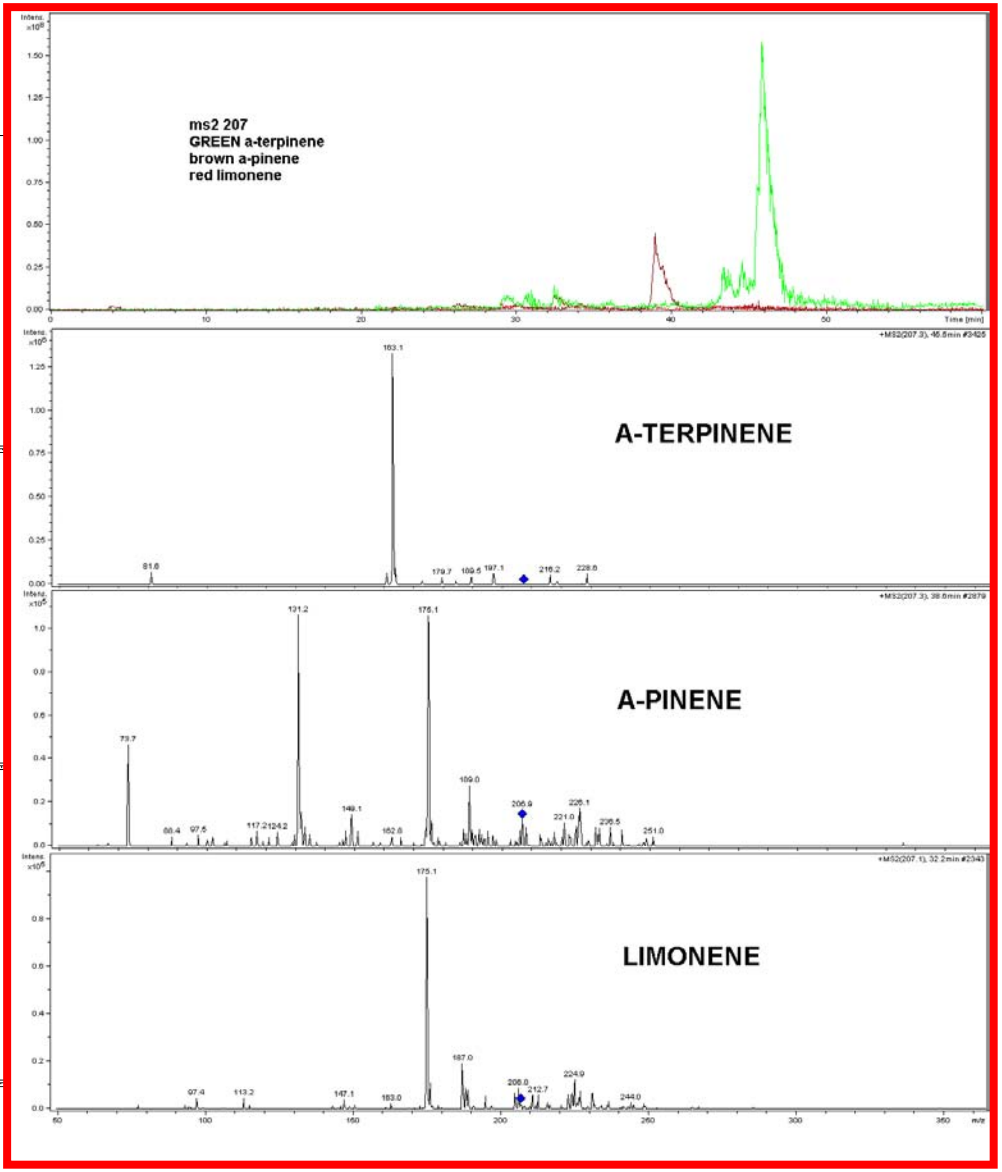
Molecular composition of SOA from biogenic precursors





Same *m/z* but different rt and MS^2 fragmentation depending on precursor

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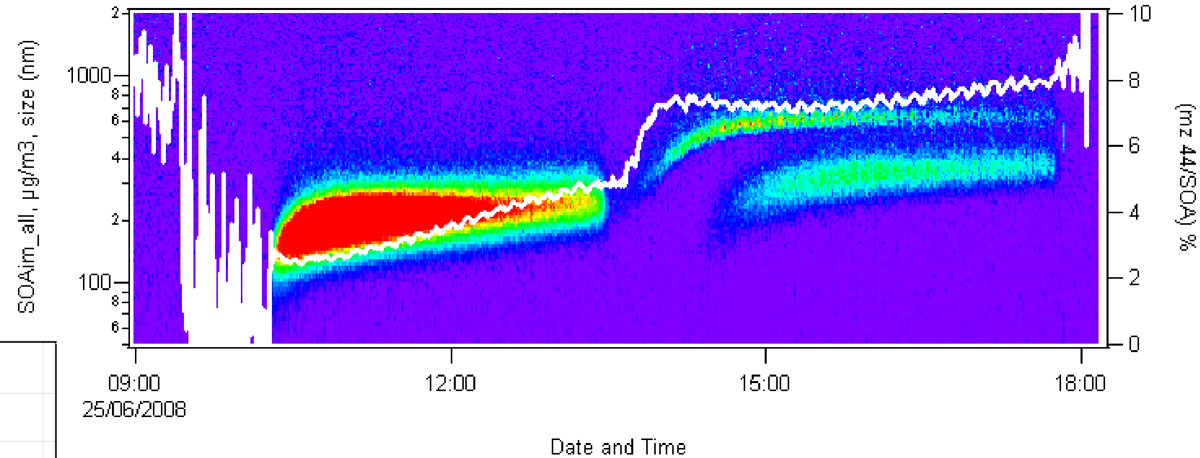
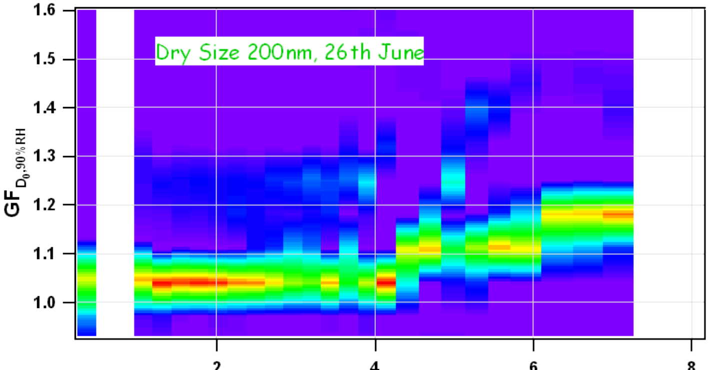
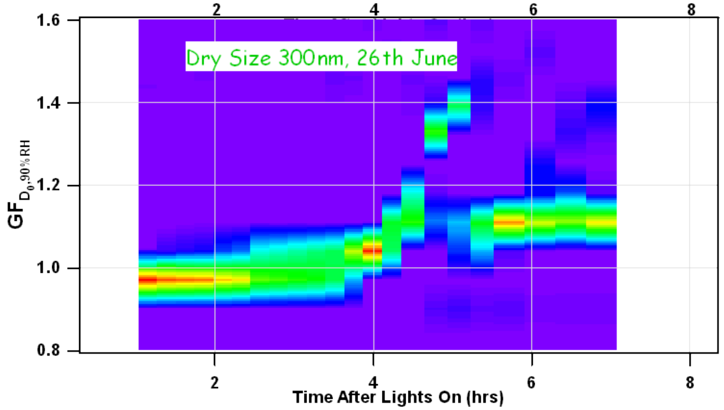
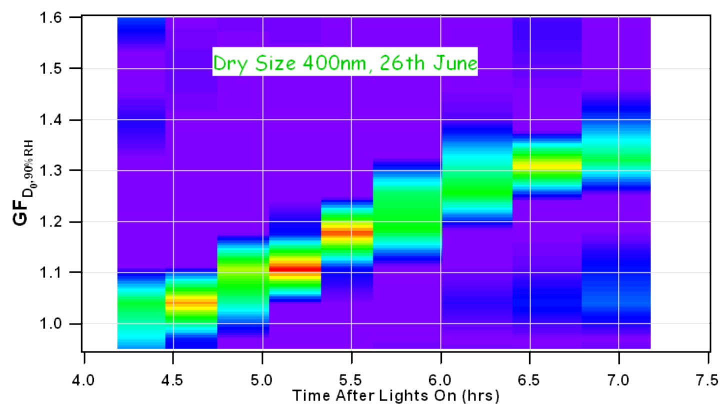
PART 4 Future work: full analysis of the seeded work … inorganics <u>and</u> stable organic seeds

Limonene 50ppb on stable oxygenated organic SOA









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

Taking emissions from tropical plant species (ULanc)

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

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