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Chamber Studies of Diesel Aerosol

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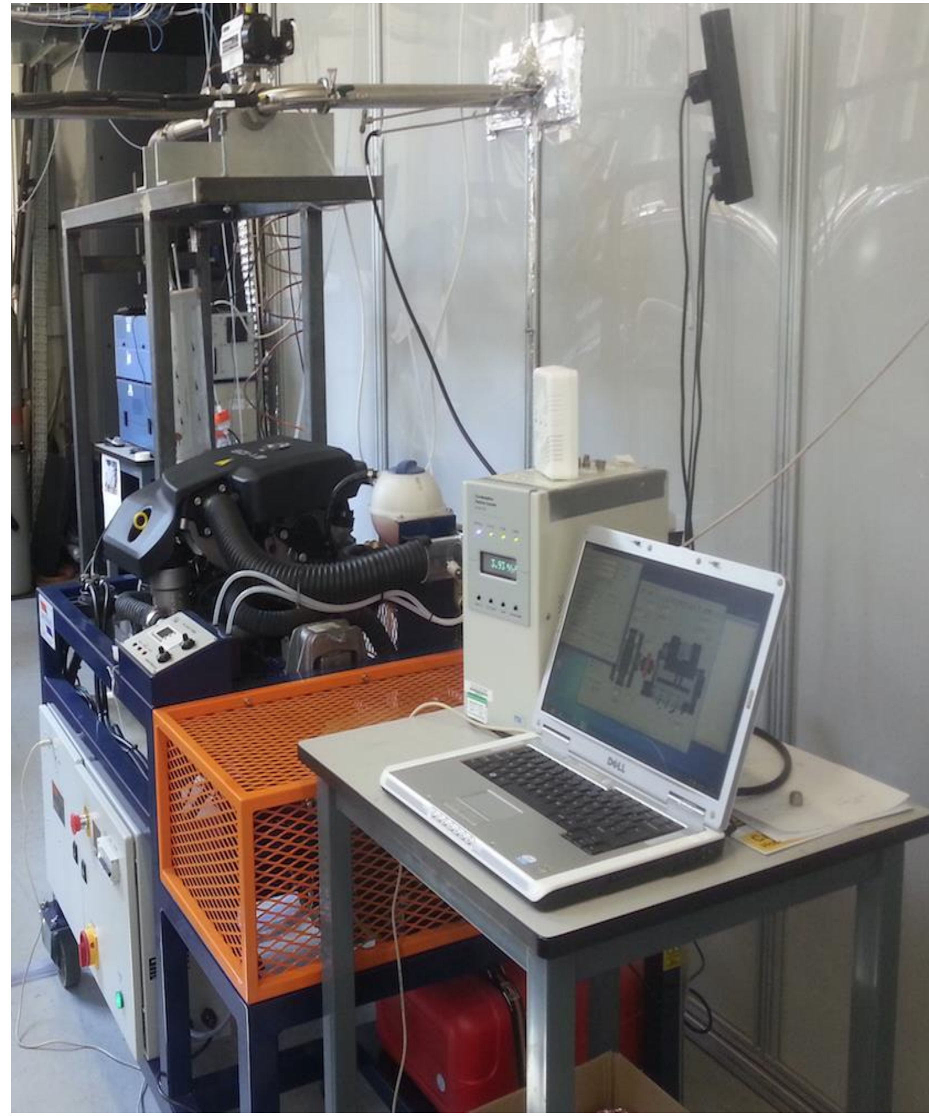
Motivation

- Diesel PM is a major issue in urban air quality, particularly at roadside
- Diesel VOCs are suggested to have a very high SOA yield, but not very well represented in air quality models
- Black carbon is known to have a significant radiative forcing effect, particularly on local scales, but is complicated by morphology and coatings
- Light-duty diesel, in spite of representing 33% of the UK light duty fleet, is not very well studied by the atmospheric community

Engine Rig

- Armfield dynamometer rig
- VW 1.9L SDI engine
  - Normally aspirated
  - Oxidising catalyst and silencer fitted
  - EURO 4 equivalent
- Controllable according to revs and load



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Manchester Aerosol Chamber (MAC)

- 18 m^3 teflon bag
- Collapsible, can be filled and emptied in minutes
- Can be illuminated by a combination of halogen bulbs and a filtered xenon arc lamp, designed to simulate the solar spectrum
- Sampling points for online instruments
- Entire contents can be collected on a filter during emptying

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Experimental Procedures

- Dilution: Bag initially filled with scrubbed and filtered air and a brief injection of exhaust fumes is performed (typically <1s)
  - Mixing occurs through convection
  - Concentrations are referenced to CO_2 concentrations
  - Further dilution can be performed by partially flushing the bag and refilling with clean air
- Photochemistry: Bag is illuminated with simulated solar light (UV and visible)
- Additional injections: Gasoline or biogenic VOCs added

Advantages

- Engine is a controllable and atmospherically relevant source of soot particles and VOCs
- Dilutions to atmospheric concentrations and measurements with atmospheric instrumentation, so relevant to atmospheric measurements
- Can capture transient engine running conditions
  - Not possible with a dilution tunnel
- Can perform atmospheric processing simulations over a period of hours
  - Semivolatile repartitioning
  - Photochemistry
- Can perform detailed characterisation work over extended time periods
  - Some instrument scans can take hours

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Instruments

- Gases
  - NO_x, CO_2, O_3
  - VOCs (2D GC)
- Online particle microphysics
  - CPC
  - DMPS/SMPS
  - CPMA
- Online particle composition
  - SP2
  - AMS
  - OCEC
  - Thermal denuder / catalytic stripper
- Online particle hygroscopicity
  - HTDMA
  - Monodisperse CCN
- Online Particle Optical Properties
  - PASS
  - CAPS PM_{SSA}
- Offline Particle Composition
  - 2D GC
  - OCEC
  - LC-ESI-MS

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Progress to Date

- Two major campaigns (COMPART 1 and 2) completed, focusing on chemistry
- Two minor campaigns (COMPART 1.5 and 2.5) completed, focusing on optical properties and comparisons with direct exhaust instruments
- One major campaign (COMPART 3) to come this summer

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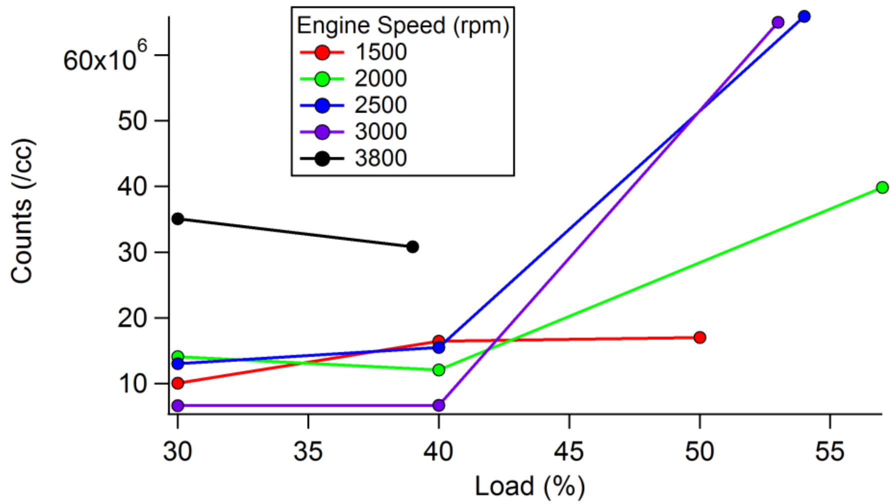
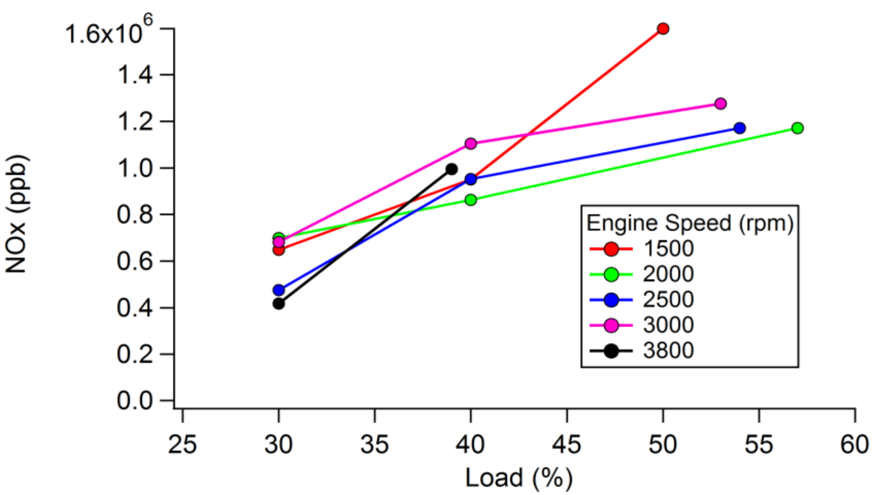
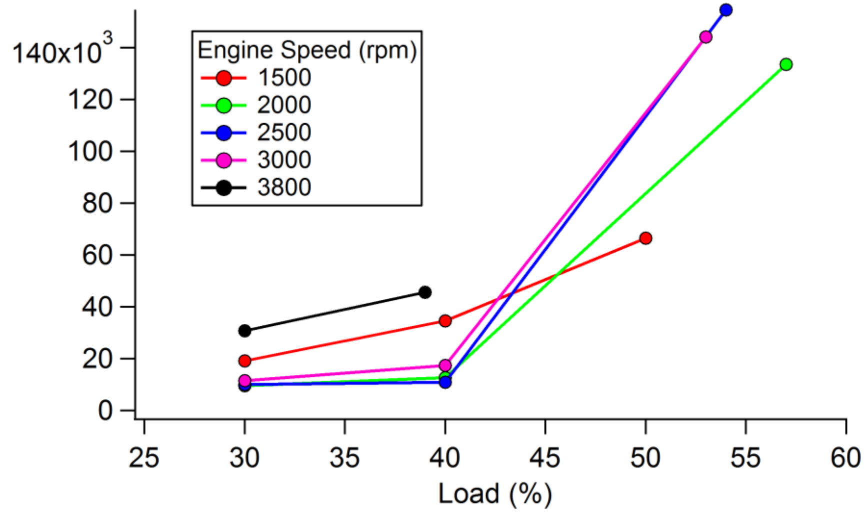
Engine Mapping

- Data converted to tailpipe equivalent using CO_2 concentrations
- Play with multiple variables, e.g. speed, load, exhaust treatment



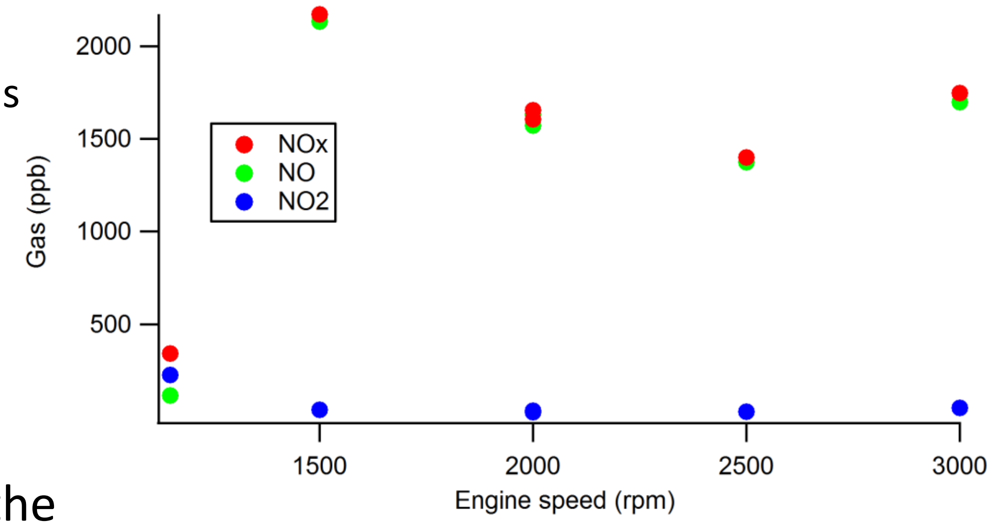




Too much NO_x!

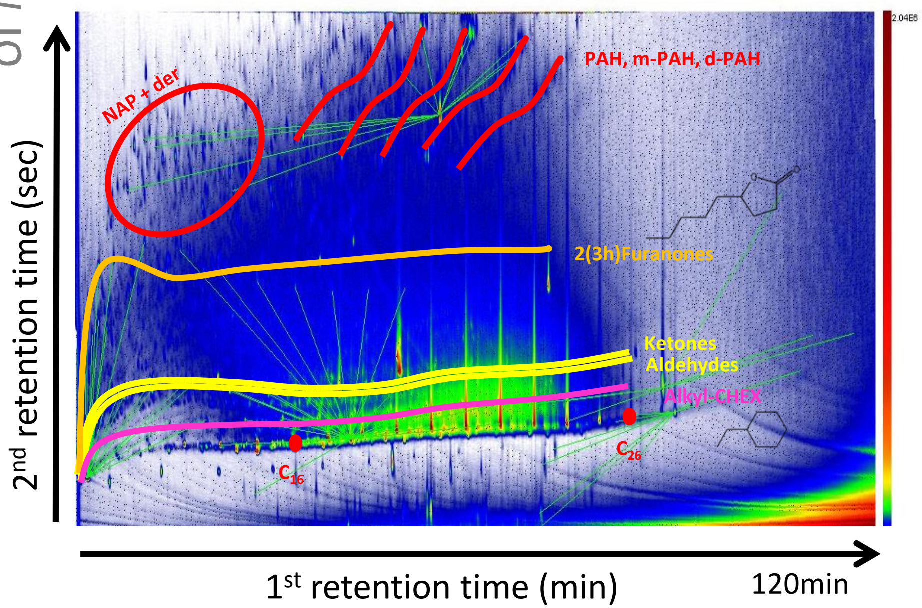
- Discovered the NO concentrations were too high to allow photochemistry to proceed as it suppressed ozone and peroxy concentrations

- Possible solutions:
  - Add an excess of ozone
    - Would need silly concentrations
  - Add a source of additional radicals (e.g. HONO)
    - Possibly creates an unrealistic chemical regime
    - Been done before in other chambers
  - Add more VOCs to rebalance the VOC:NO_x ratio
    - Could also contribute to SOA, so the diesel SOA would not be measurable

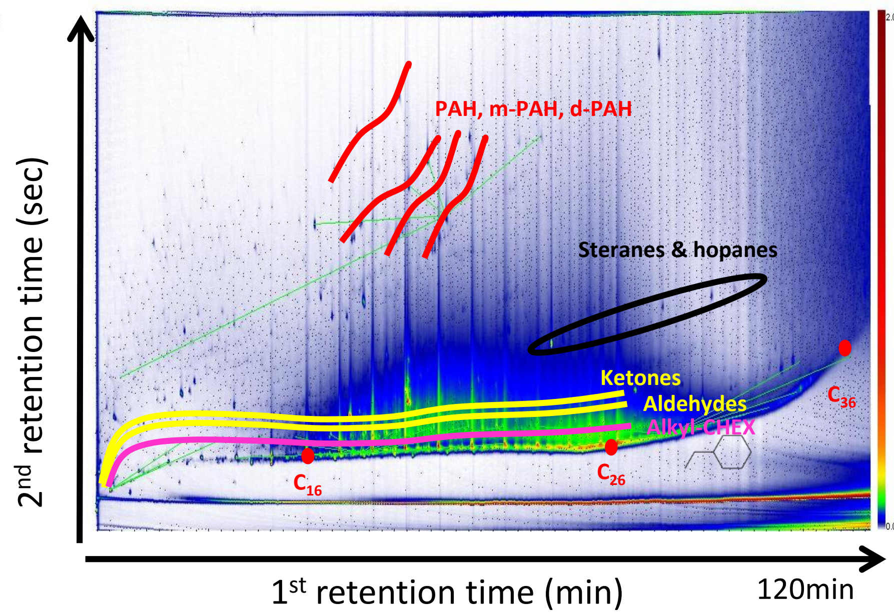


‘Cold Idle’

Filter 18: **14/08/14** - Cold idle engine, dilution 15:1



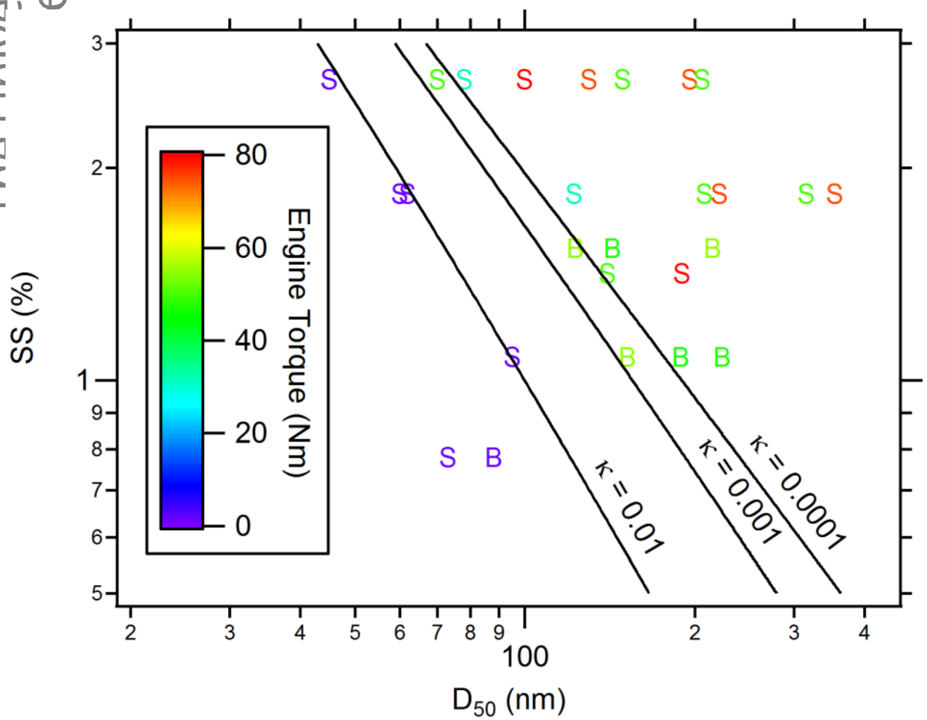
Filter 21: **15/08/14** – 2000 RPM, 40% Load, warm, 10:1

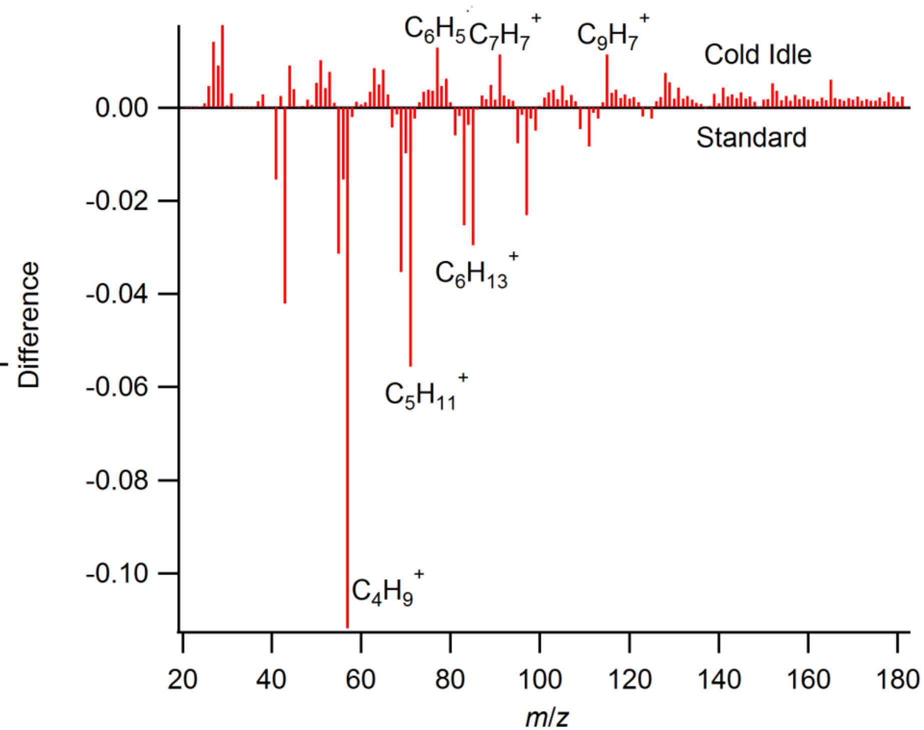


- Abundance of aromatic compounds
- Abundance of polar compounds
- Very little constituents larger than C_{23}

- Abundance of aliphatic compounds
- Other aromatic compounds are still present, but with lower abundance
- Two UCMs: 1) $C_{16} – C_{23}$
  2) $C_{23} – C_{30}$

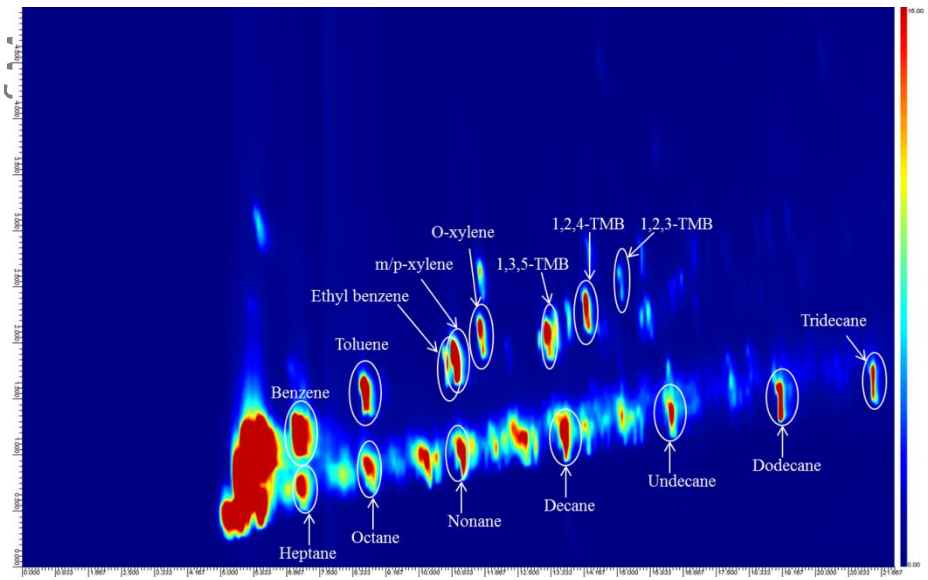
CCN and AMS view

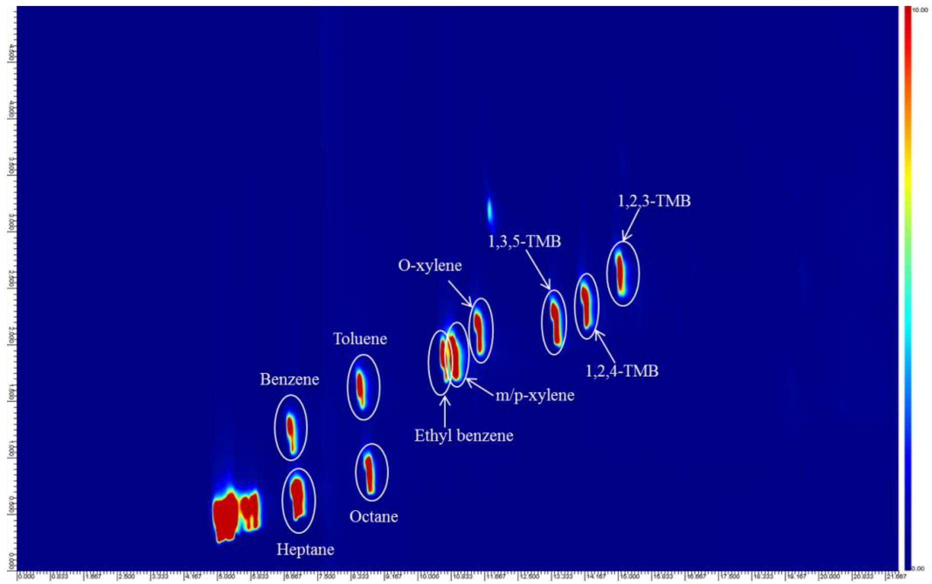




- Detectable trends in cloud condensation nuclei (CCN) behaviour, but atmospherically insignificant
- Differences in chemical composition of particles seen by Aerosol Mass Spectrometer (AMS)

Gas phase view





- Online VOCs quantified using a dual trap 2D GC
- As well as quantifying SOA precursors, the decay of well-characterised VOCs can be used to infer OH concentrations

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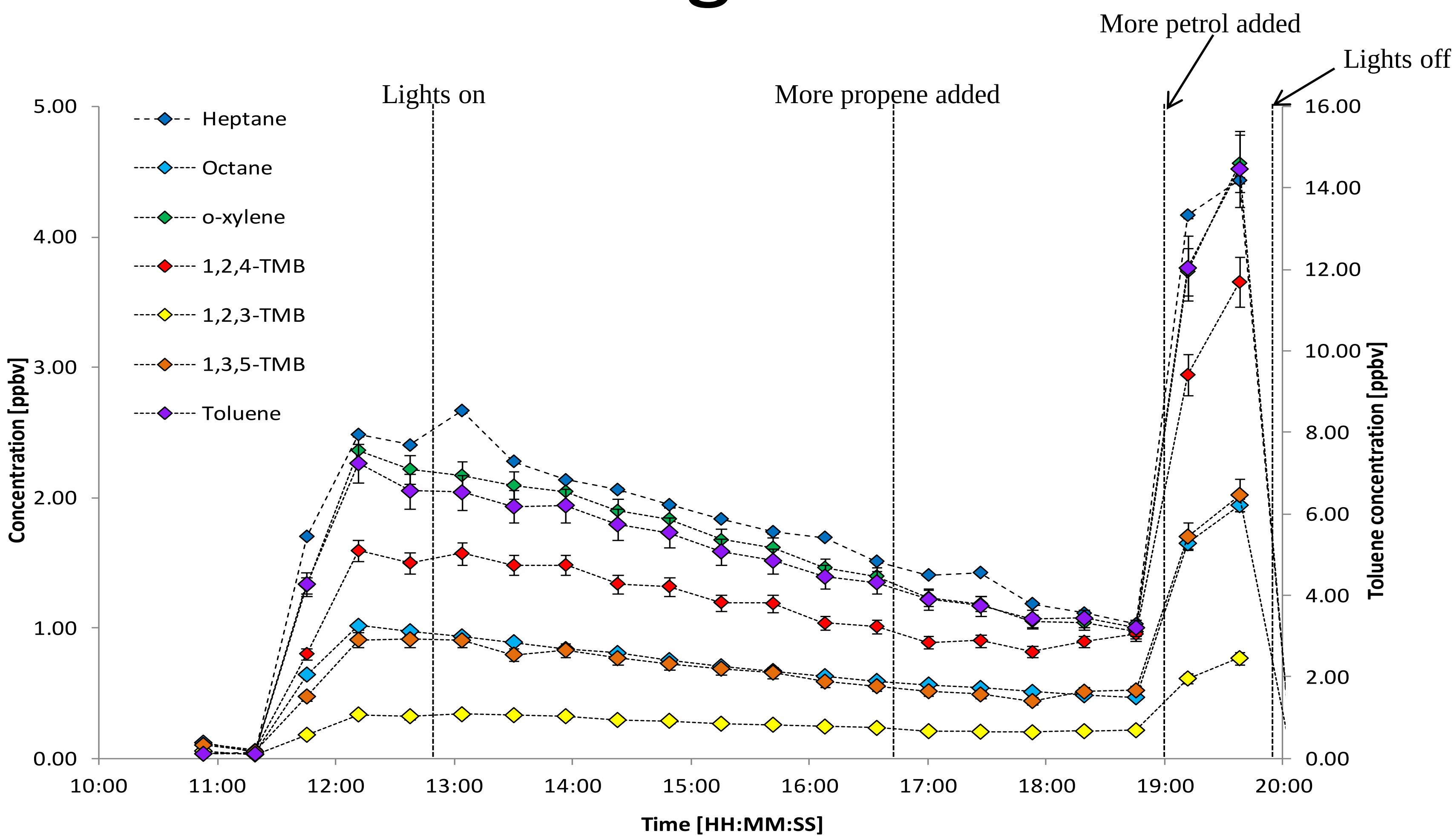
Adding VOCs



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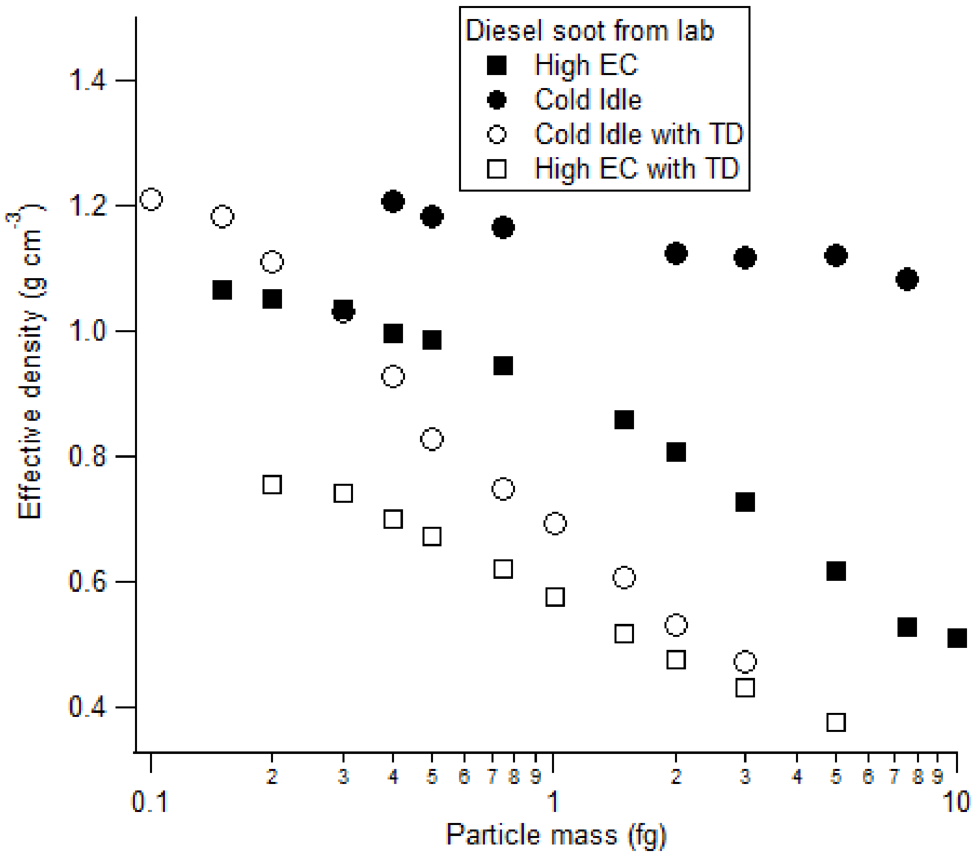
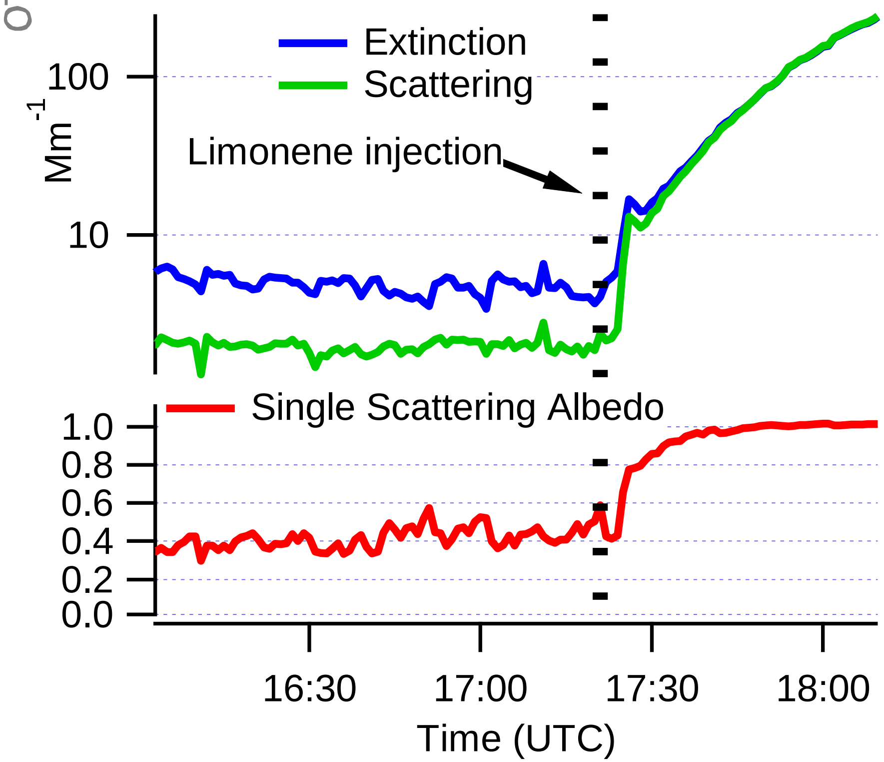
Particle Shape

- Effective density measured using CPMA-SMPS combination
- ‘High EC’ is 2000 rpm with 10 minute warm-up
- Cold idle particles spherical, ‘high EC’ particles and denuded cold idle particles fractal



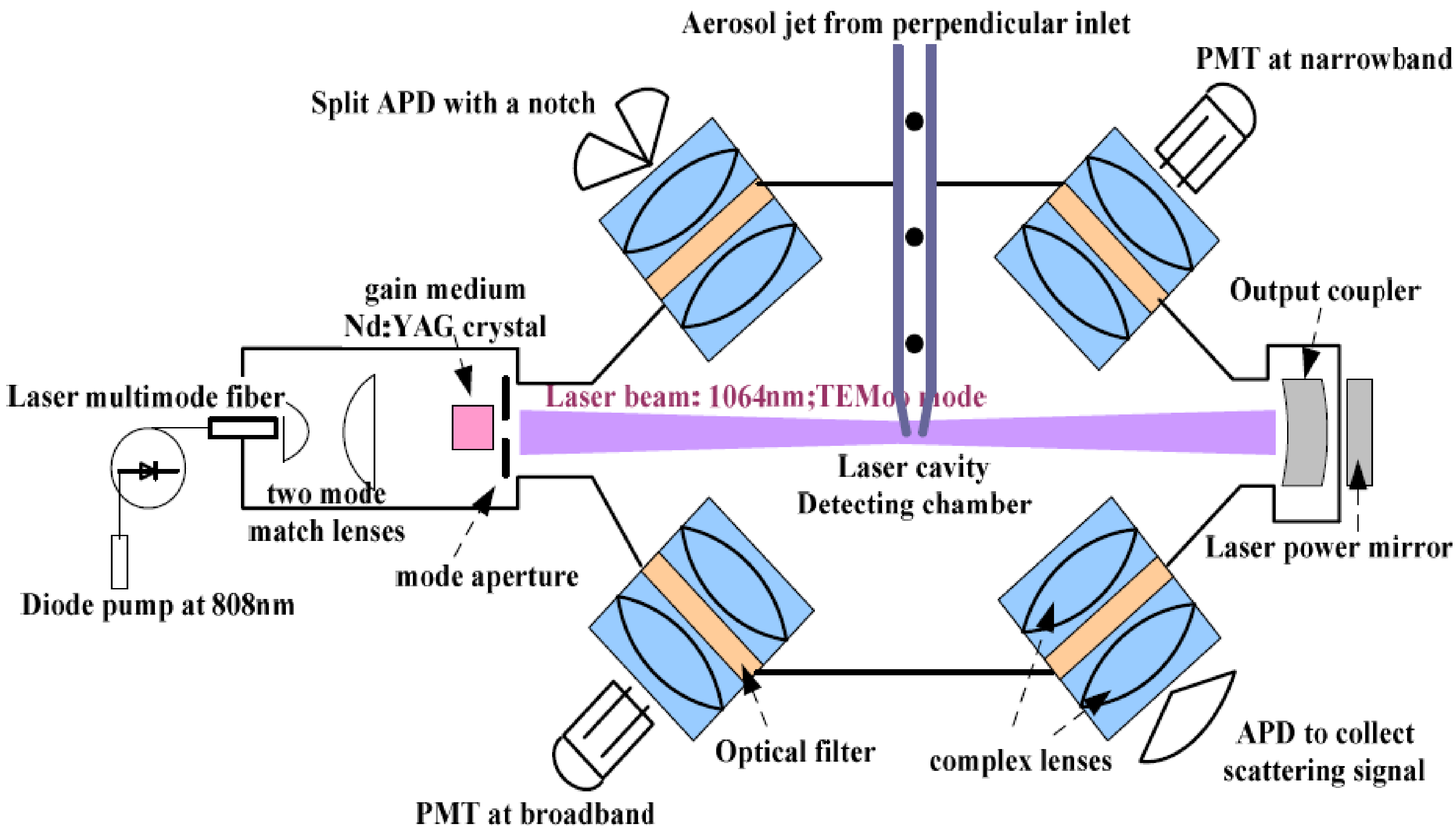
Optical Properties



Data from Aerodyne CAPS PM_{SSA}

- Effect of adding SOA coatings:
  - Increase in size
  - Increase in absorption
  - Bigger increase in scattering
  - Increase in single scattering albedo
- Qualitatively, this is all expected
- Quantitatively modelling these is a subject of debate and a source of uncertainty in atmospheric radiative transfer models

DMT Single Particle Soot Photometer (SP2)

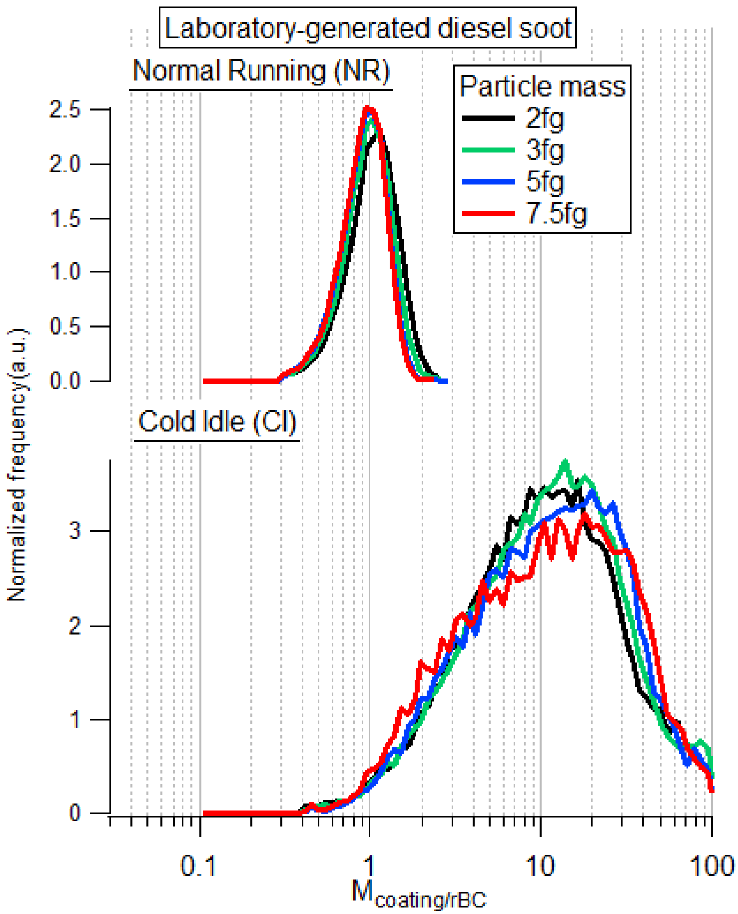


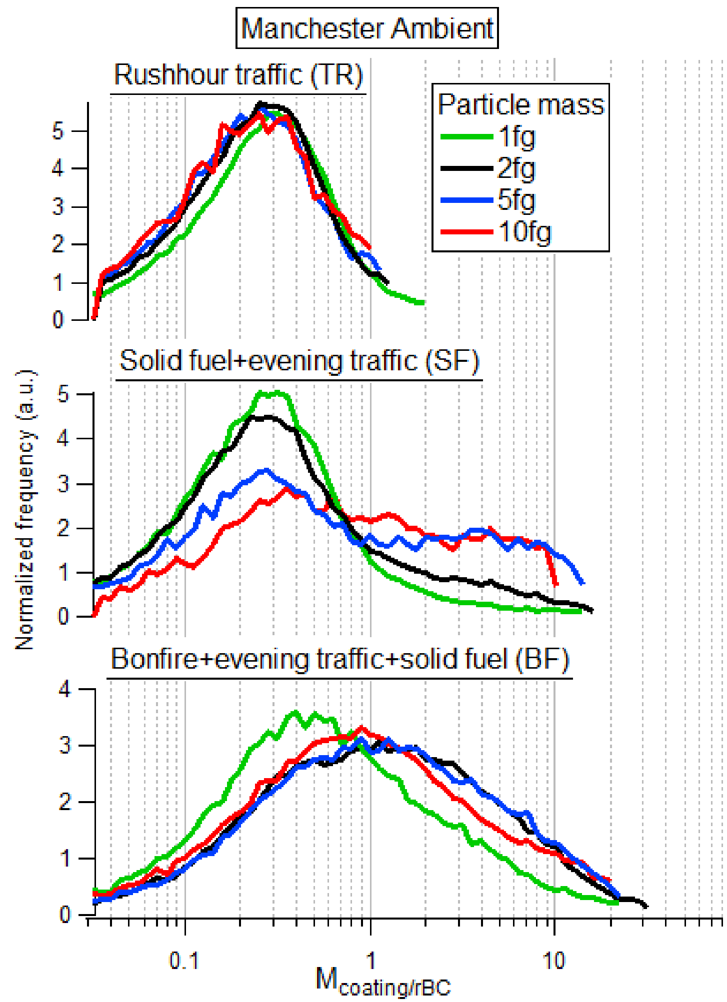
CPMA – SP2 data products

- Measures single-particle refractory black carbon (rBC) mass through laser induced incandescence (LII)
- Single particle scattering cross section at 1064 nm through leading edge only (LEO) fitting
- Coupled with a CPMA, gives scattering cross section as a function of rBC mass fraction, which can be compared with model outputs

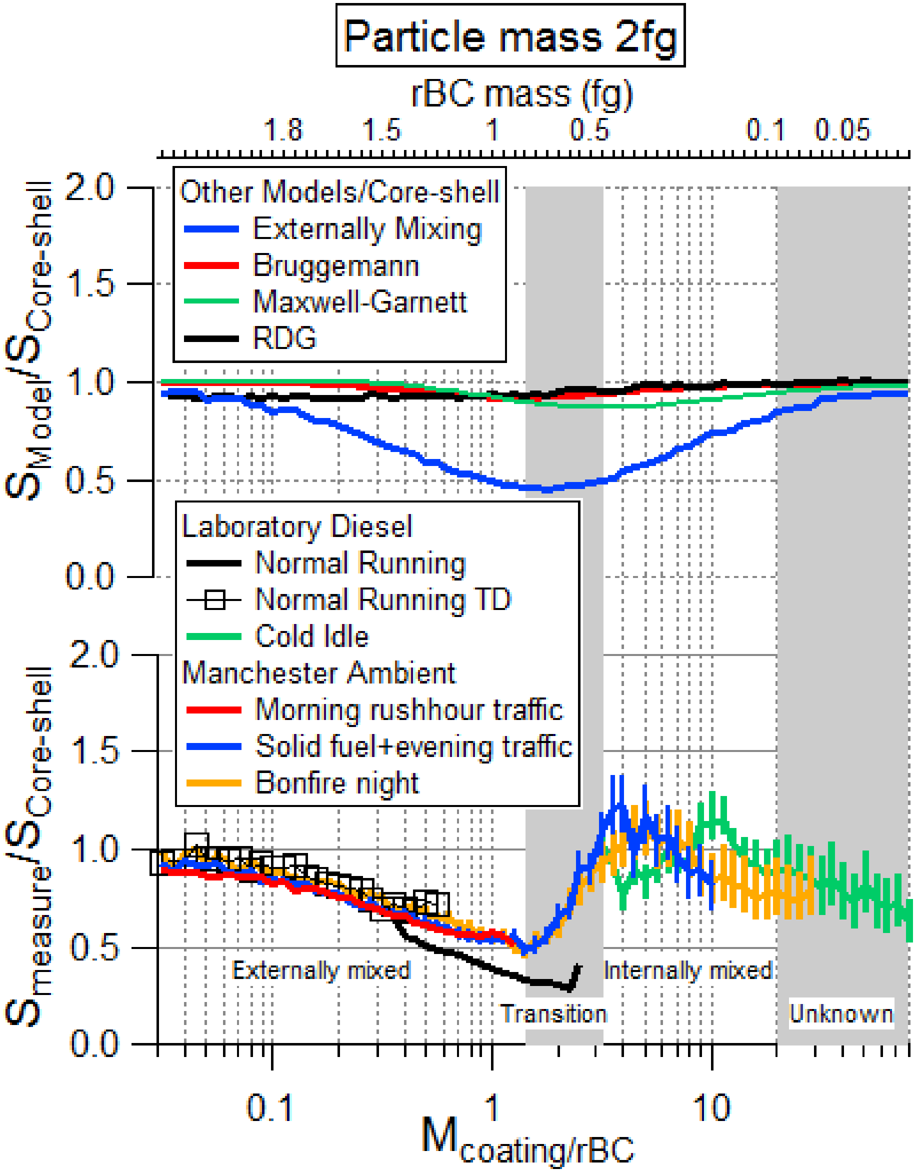
Measurements

- Normal running = ‘high EC’
- Ambient measurements taken in Manchester around bonfire night 2014





Single Particle Optical Properties



- Thickly-coated particles ($M_{coating/rBC}$ >2) consistent with core-shell Mie
  - Also consistent with other internally mixed models
- Thinly-coated particles consistent with external mixing, i.e. independent scattering of core and coating
  - Probably due to coating material filling in voids or small gaps in agglomerates

Implications

- Because of the large real refractive index of BC in the NIR, the coating enhancement in NIR scattering is analogous to the coating enhancement in optical absorption
  - Absorption not measured in this experiment because the DMT PASS did not have sufficient signal-to-noise and CAPS PM_{SSA} does not measure absorption directly
- This implies a hybrid microphysical model of optical properties is appropriate, with negligible absorption enhancement for thinly-coated particles
- May help to reconcile some of the seemingly contradictory measurements of atmospheric absorption enhancement

Conclusions

- The COMPART experiments are currently ongoing in Manchester
- Emissions from a light duty diesel engine coupled to a dynamometer are fed into an 18 m^3 teflon bag
- Atmospheric processing is simulated and the aerosol studied using a wide variety of instrumentation
- Interesting contrasts in the aerosol composition, shape and optical properties have been noted with engine running conditions
- Optical measurements suggest that a hybrid model may be most appropriate to describe properties
- Watch this space!

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Acknowledgements

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