Project overview and preliminary results

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Measurements

Particle Analysis Methods
LII
AFM
TERS

Measurement Single Cylinder Engine

Measurement Multi Cylinder Engine

Validation of full vehicle

Technology, procedures and understanding at task level

Optimized CPC

Optimized Catalytic Stripper

Optimized Calibration

Particle Characterization

Population Balance Model

Computational surrogates

Optimized Calibration

Implementation of calibration

Evaluation of robustness

Focus areas

Measurement Technology

Model Guided Application

Measurement Procedure & Application

Objectives

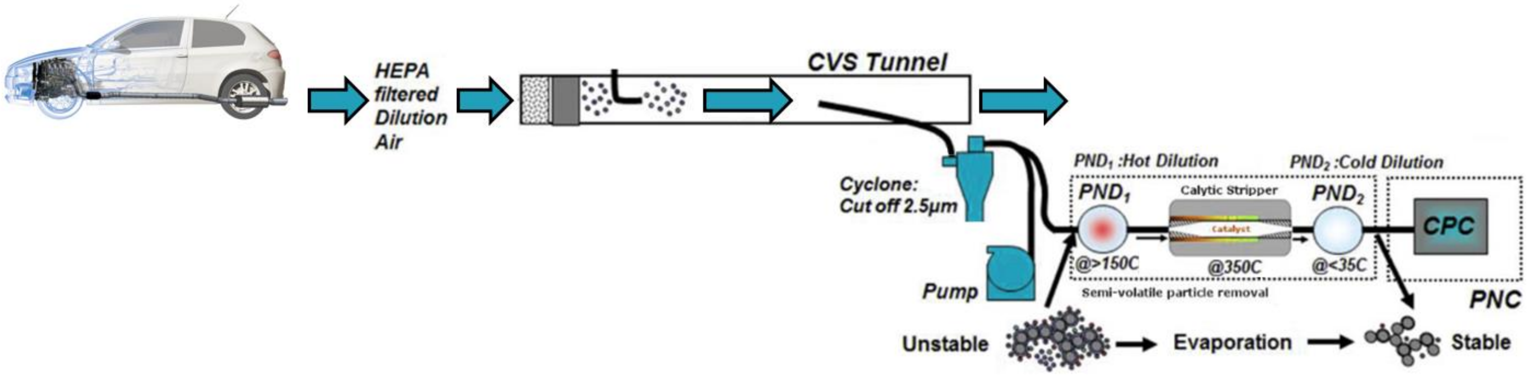
PEMs 4Nano

Technology
Demonstrate and evaluate the application and measurement technology in the development process

Understanding
Fundamental understanding of the particle formation, composition, size distribution and transport and the impact on the measurement procedure + demonstrate usability of model

Procedures
Robust and reliable measurement procedures for particles down to 10 nm and verified under real driving conditions

Technology: objectives



- Redesign/modify existing and established solid particle counting systems for laboratory and on-road measurements to lower the minimum particle size measurement limit to 10 nm
- Adapt semi-volatile particle removal system to remove non-solid particles while allowing penetration of solid particles in 10-23 nm range
- Demonstrate and evaluate the application and measurement
- Integrate a modified CPC and a CS into the solid particle counting systems

Technology: highlights

- Starting point: Two proven CPC models for laboratory and PEMS applications ($D_{50} = 23$ nm)
  - Goal: achieve $D_{50} \leq 10$ nm
- The CPCs were calibrated and validated
  - For validation thermally conditioned flame soot particles were used
  - Result: showed 50 % detection efficiency at 10 nm according to ISO 27891 requirements
- A catalytic stripper was calibrated with solid particle aggregates.
  - Goal: maximize system-measured solid particle penetration for 10 nm and below
  - Penetration efficiency needed to increase
  - > 60% was achieved (initial target was set to > 50%)
- Particle counting system calibration procedure was performed
  - Including Particle Count Reduction Factor (PCRF) calibration for both systems
- MGA validated against measurements for PSD and chemical characterization
  - Offers guidance on the role of dilution ratios, dilution pipe lengths, in-cylinder inhomogeneities, and surface vs bulk compositions

Technology: preliminary results

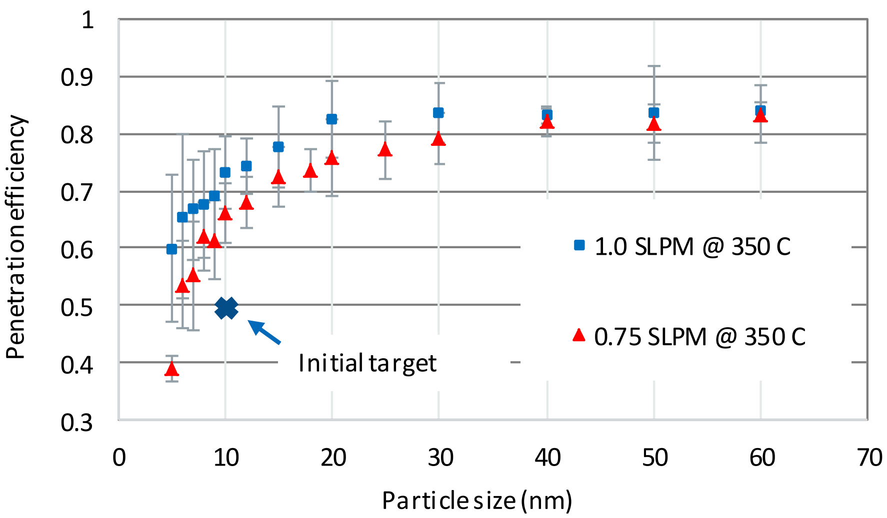
Catalytic stripper (CS) for SPN-PEMS

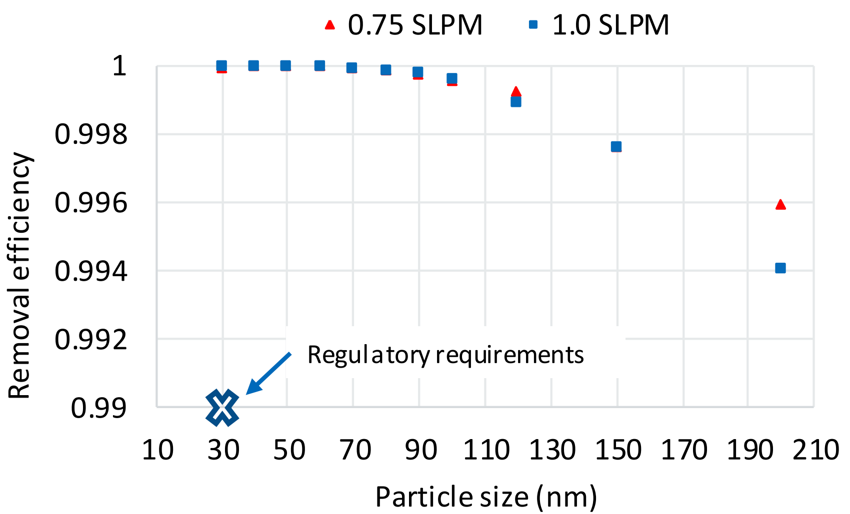
Solid particle penetration:

- 10-15% improvement in solid particle penetration
- 65-75% solid particle (silver) penetration at 10 nm size
- Meet the ambiguous target of 60% penetration even at 8 nm.

Semi-volatile particle removal:

Satisfy well beyond the regulatory requirements of >99% semi-volatile particle (tetracontane) removal ($> 10^4 \quad \#/cm^3$) at 30 nm size.





PEMs4Nano – H2020 Grant Agreement #724145

Understanding: particle characterization

- Thorough **physico-chemical characterization** of the smallest particles … needed for better understanding their influence on the particle measurement through the model guided application … optimization of the newly developed PEMS
- Use of a **single cylinder engine** @ Bosch as particle generator … generate a wide variety of particles by **testing various engine regimes**
- Build an **extensive database** on size-dependent particle structure, morphology, chemical composition … possible further use in engine optimization through the MGA … interest for other GV projects

- Laboratory single cylinder test engine
- *In-situ* measurement of particle size and volume fraction - LII
- Tailpipe and engine sampling of particulate matter
- *Ex-situ* physicochemical characterisation
- Particle growth and transport model

Understanding: measuring real-time and in-situ

Objectives of LII measurements:

- Measuring in real time and in situ the evolution of the LII signal in the exhaust line: variation of the soot volume fraction.

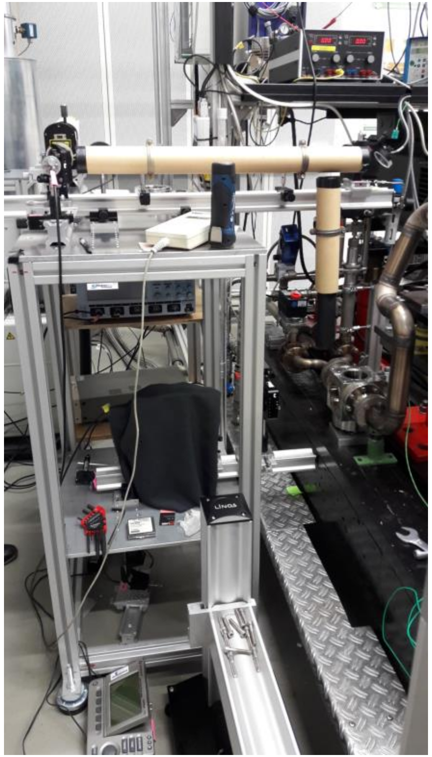
- **Realtime control of engine soot emissions for different engine setpoints**

- Comparison with other techniques: SMPS-EEPS

- limit of detection

- smallest size

- Remark: LII signal is assigned to carbon (metallic particles, oil, condensable species etc. do not contribute to the signal)



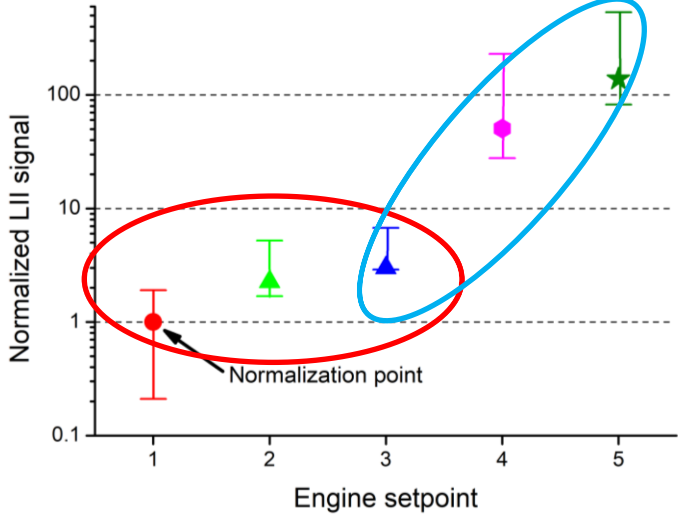
Understanding: measuring real-time and in-situ

Variation of LII signal with engine setpoints

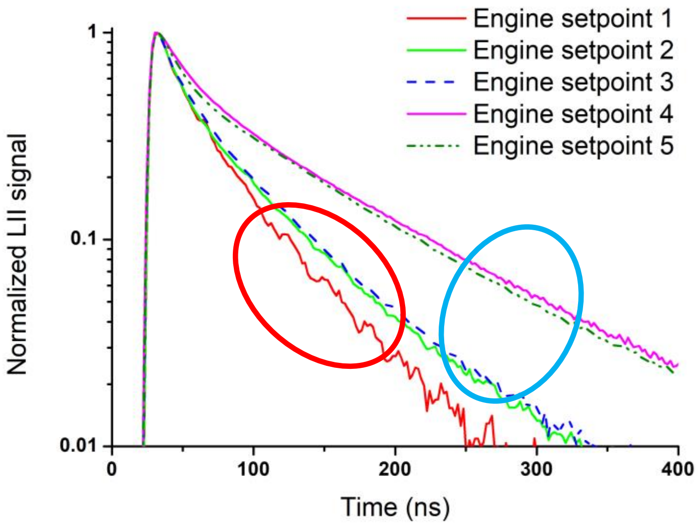
Pmi = 5, 8, 10 bars; SOI=-270

SOI=-270, -305, -311; Pmi=10 bars

Variation of LII intensity: soot volume fraction



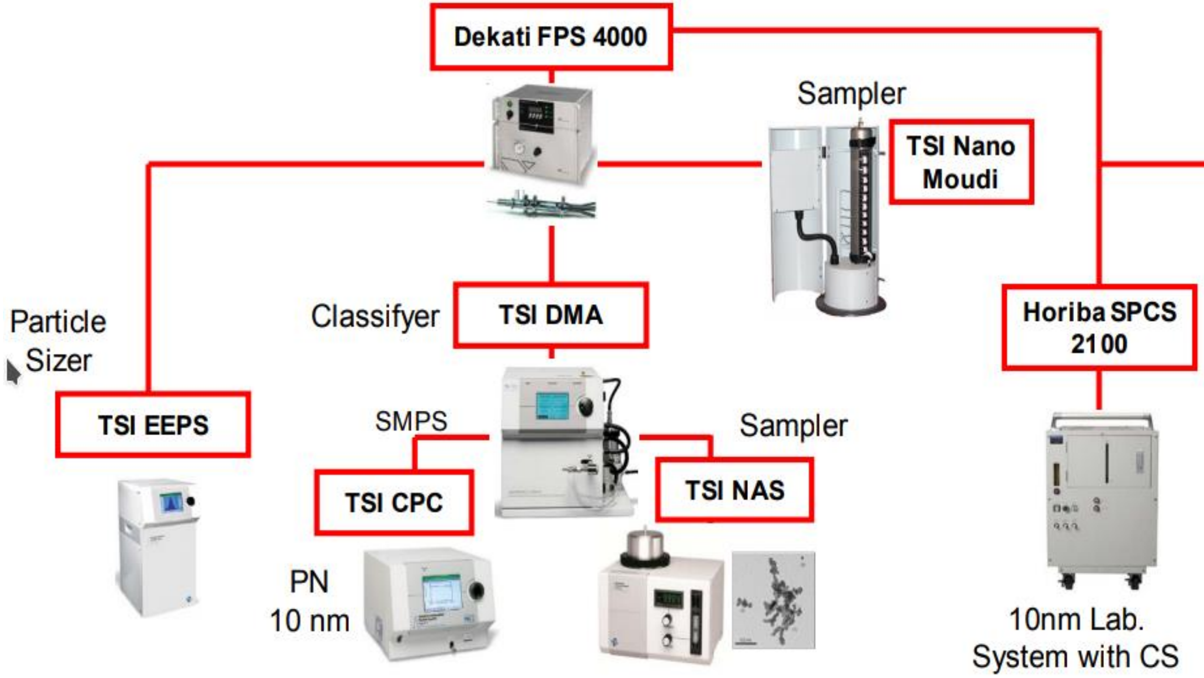
Variation of LII decay-time: « mean soot diameter » indicator

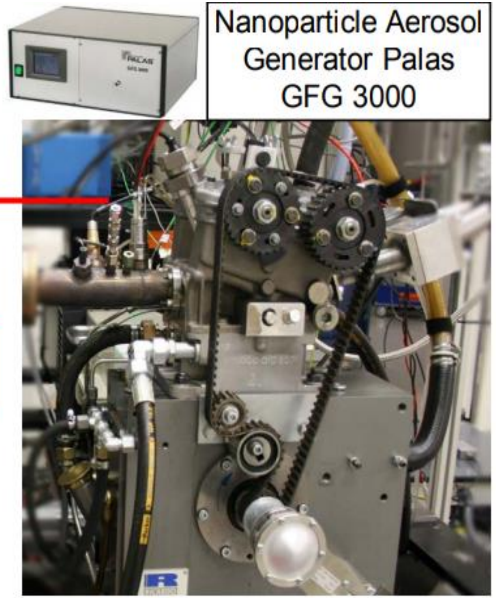


SOI: start of injection before firing

Pmi: indicated mean pressure

Sampling line





- Single cylinder engine
- Displacement: 449 cm³, ε=12.5
- GDI and PFI mode possible

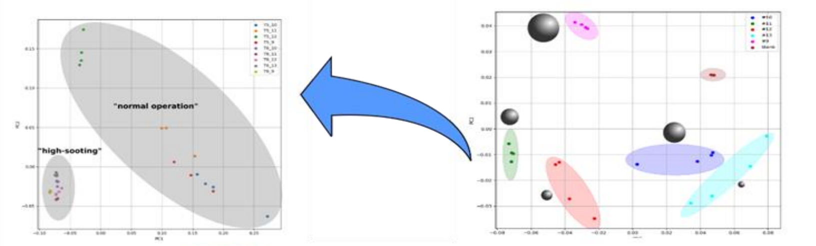
EEPS =Engine Exhaust Particle Sizer
FPS =Fine Particle Sampler

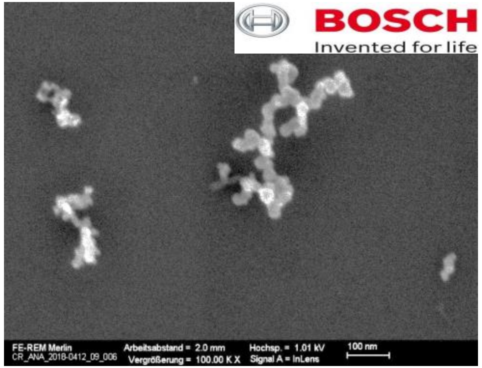
PFI = Port Fuel Injection
GDI = Gasoline Direct Injection

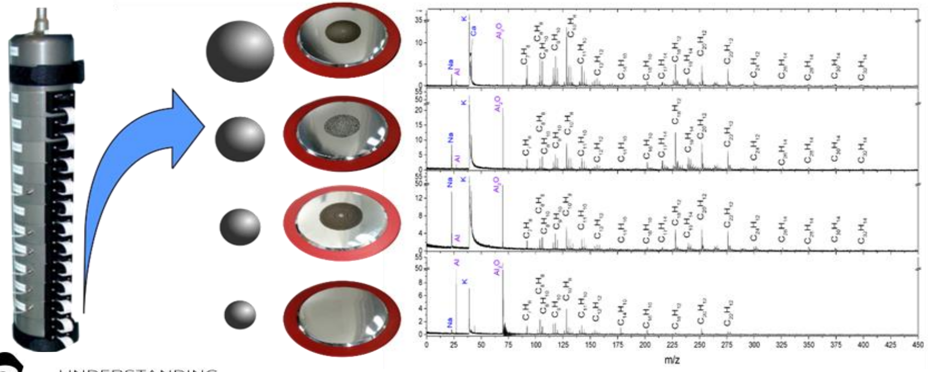
DMA = Differential Mobility Analyzer
SMPS = Scanning Mobility Particle Sizer

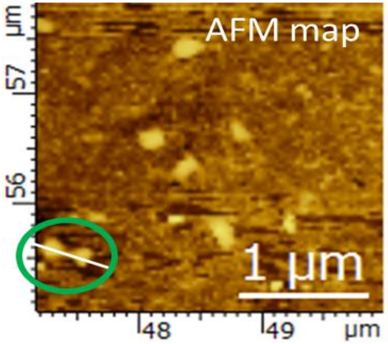
Understanding: ex-situ particle characterization

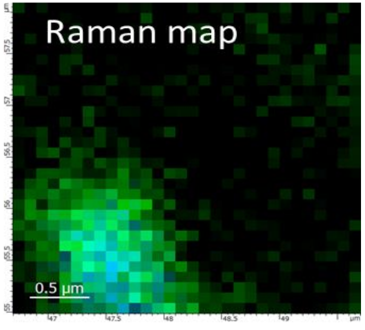
Size-selective sampling and off-line analyses
by mass spectrometry, electron and atomic force microscopy, Raman spectroscopy
+ advanced statistical analysis
Chemical composition, structure, morphology







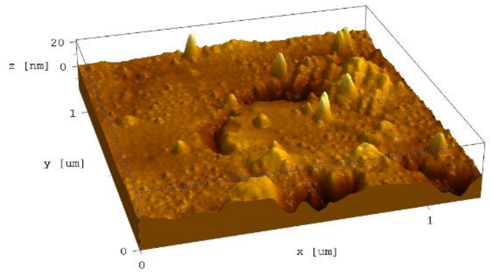


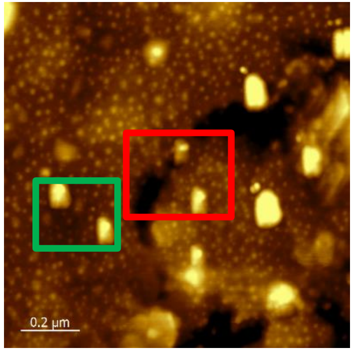


UNDERSTANDING, ACCELERATED

AFM and TERS structural analyses

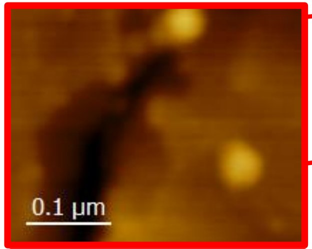
AFM 3D/2D topography of collected PM (18-10 nm)

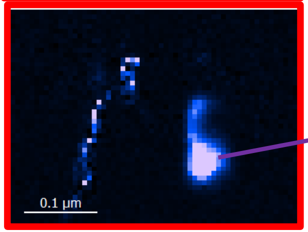




Zone 1

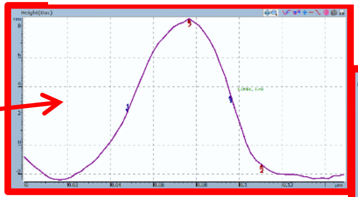
High resolution AFM topography



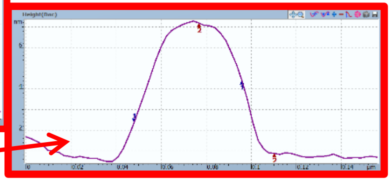


TERS map (G band)

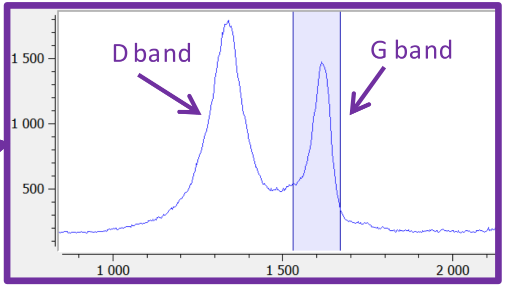
Particle 1: height 10 nm width < 48 nm



Particle 2: height 6 nm width < 43 nm

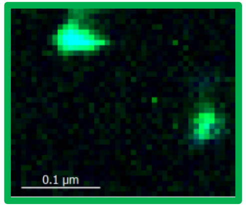


Average spectrum of Particle 2

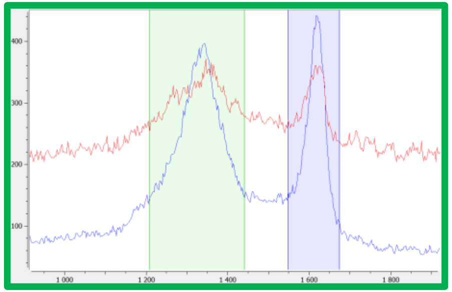


Zone 2

TERS map (G&D bands)

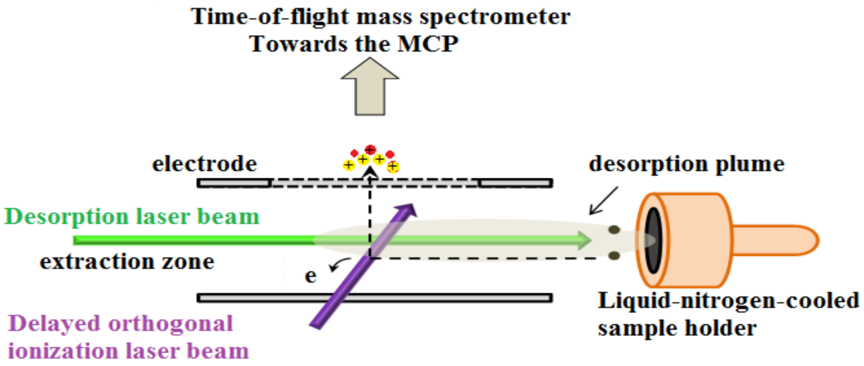


Average spectra of Particles 3&4



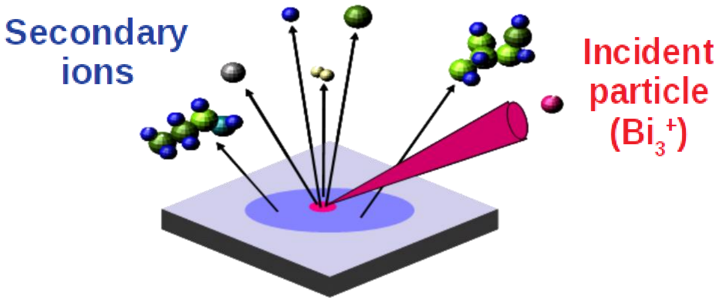
Mass spectrometry techniques

Two step Laser Mass Spectrometry (L2MS)



- Controlled fragmentation
- Ultra-sensitive to PAHs (attomol)
- Selective (laser ionization at 3 wavelengths)

Secondary Ion Mass Spectrometry (ToF-SIMS)



- High fragmentation
- High mass resolution
- Mapping, depth profiling

Chemical composition … selective ionization

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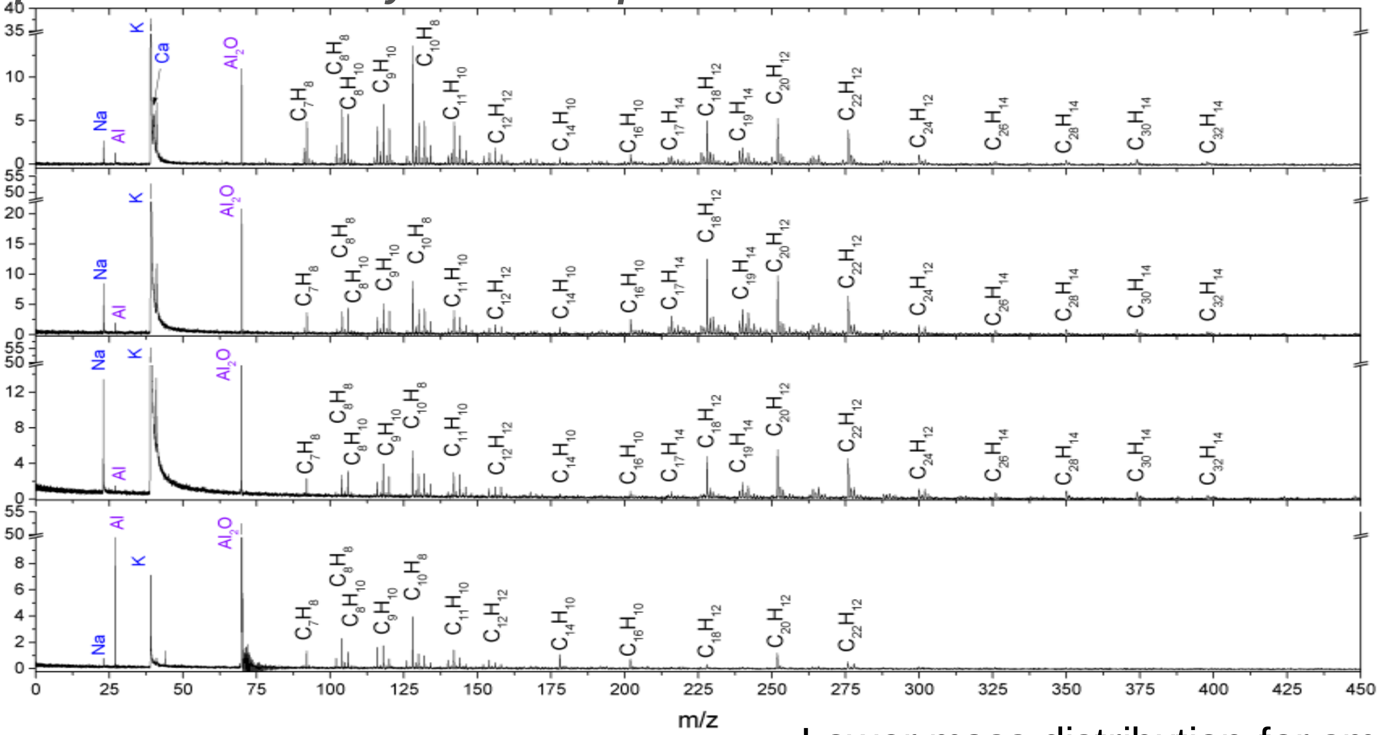
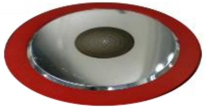
Spectra dominated by aromatic species

R2PI at 266 nm



180-100 nm



100-56 nm

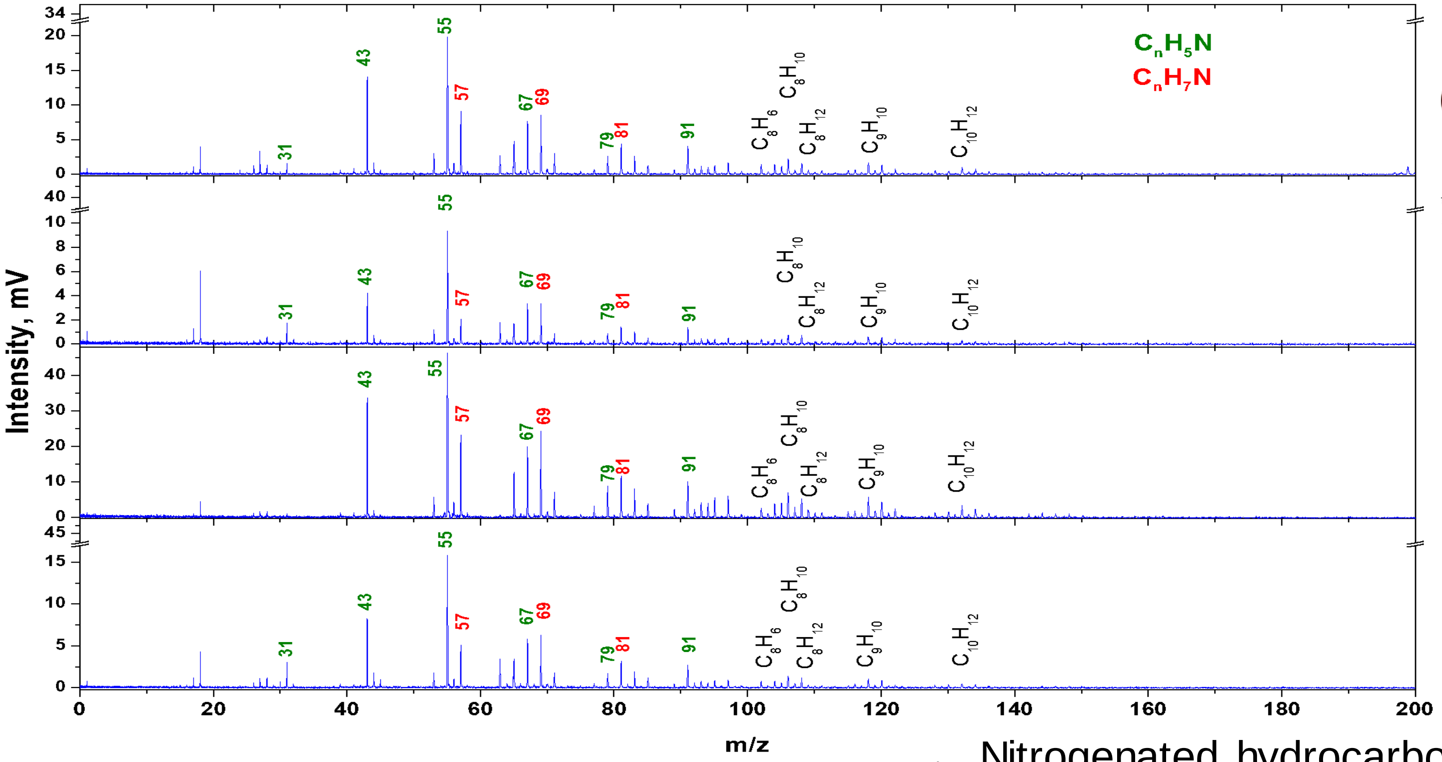
56-32 nm

32-18 nm

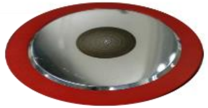
- Lower mass distribution for smallest particles

Chemical composition … selective ionization

SPI at 157 nm (7.9 eV)



180-100 nm



100-56 nm

56-32 nm

32-18 nm

- Nitrogenated hydrocarbons are present

Chemical composition … selective ionization

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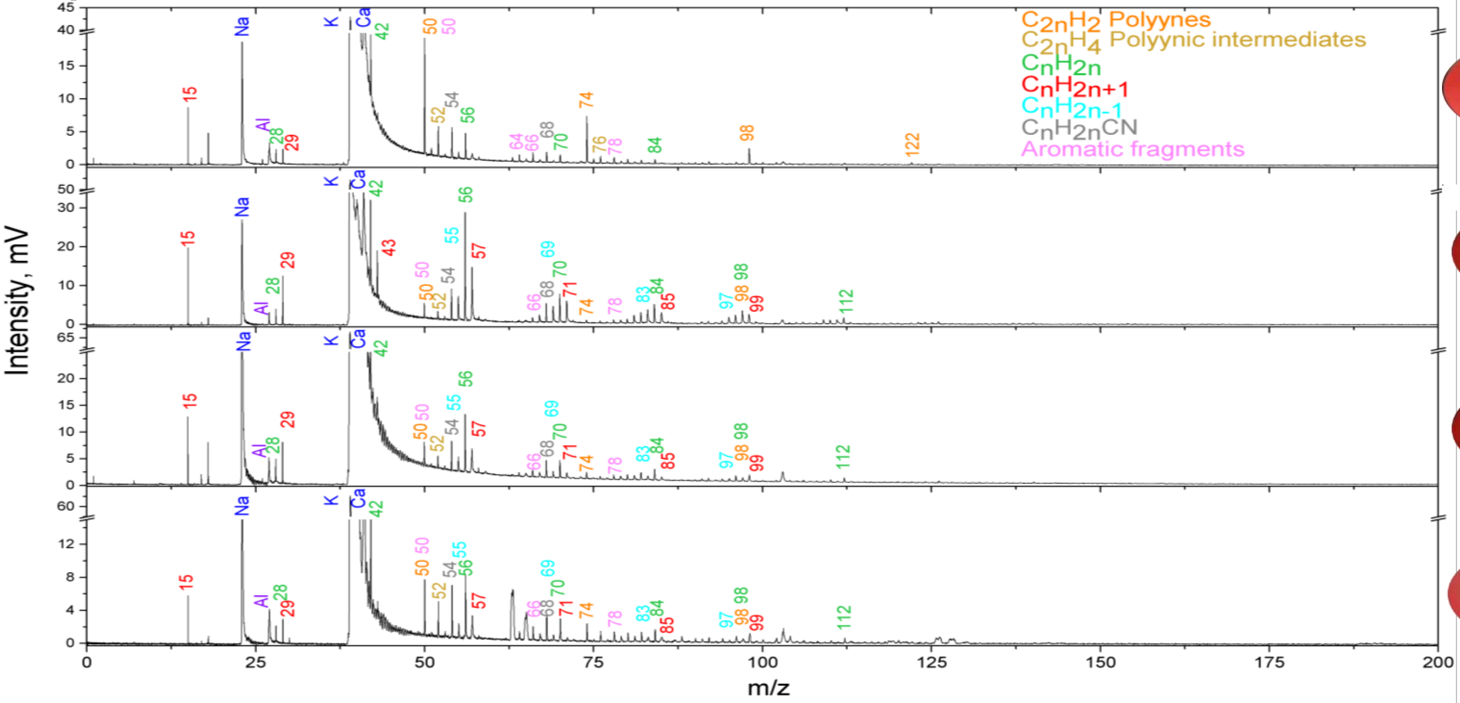
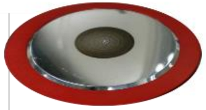
Spectra contain other chemical families

SPI at 118 nm (10.5 eV)



180-100 nm



100-56 nm

56-32 nm

32-18 nm

Less obvious difference for smallest particles … need to use statistical analyses to differentiate

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Understanding: conclusions

- The combination of **L2MS**, **SIMS** and **PCA** allows determination of detailed molecular level surface chemical composition of soot particles.

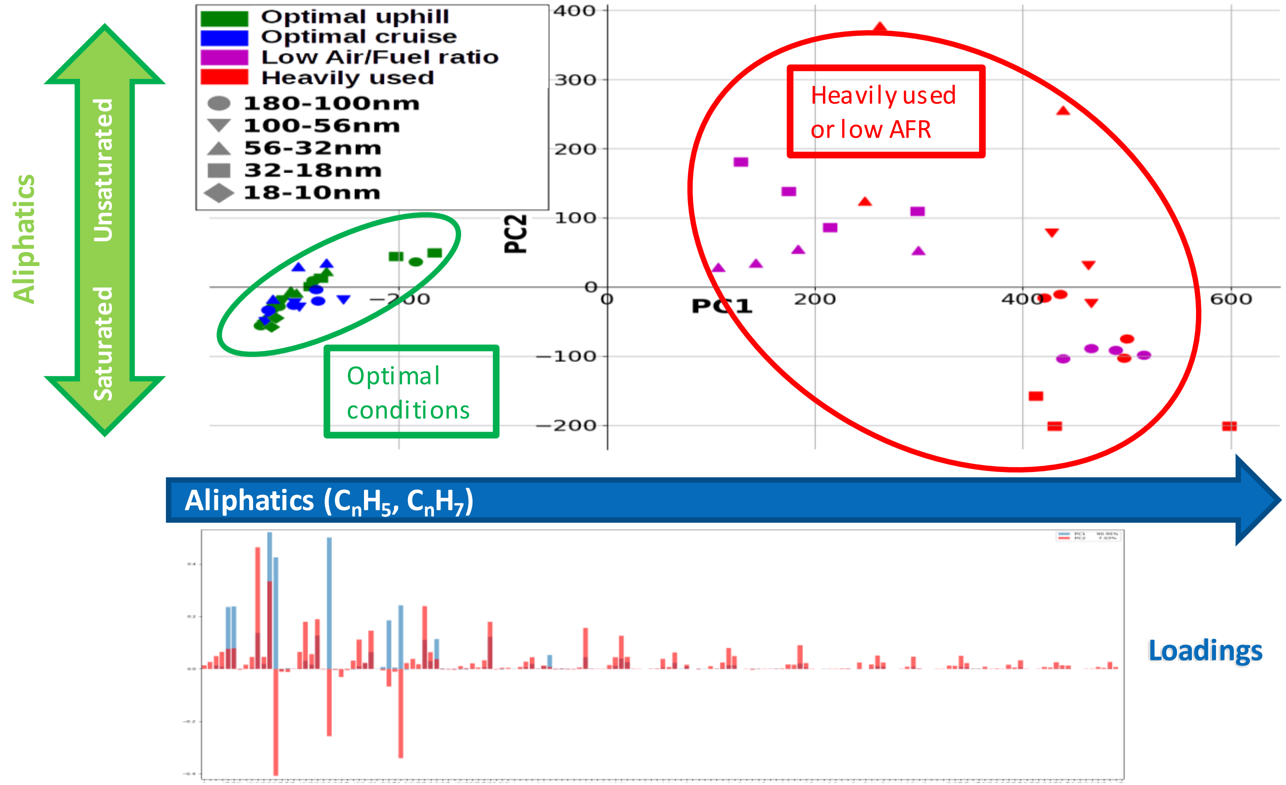
- The use of **size-selective** sampling allowed us to chemically characterize surface chemistry of particles down to 10 nm.

- Identification of key chemical markers, coupled with powerful PCA statistics, allowed discrimination of:

  - ▲ **Gasoline-specific** (PAHs, phenol, nitro-phenol)
  - ▲ **Lubricant-specific** (Hopanoids, steranes and cycloalkanes)
  - ▲ **Engine-specific** (metals and metal oxides)

- By identifying marker species, we have clearly discriminated particles by **source**, **particle size** and **engine regime**

Regime discrimination … SIMS+PCA



Loadings

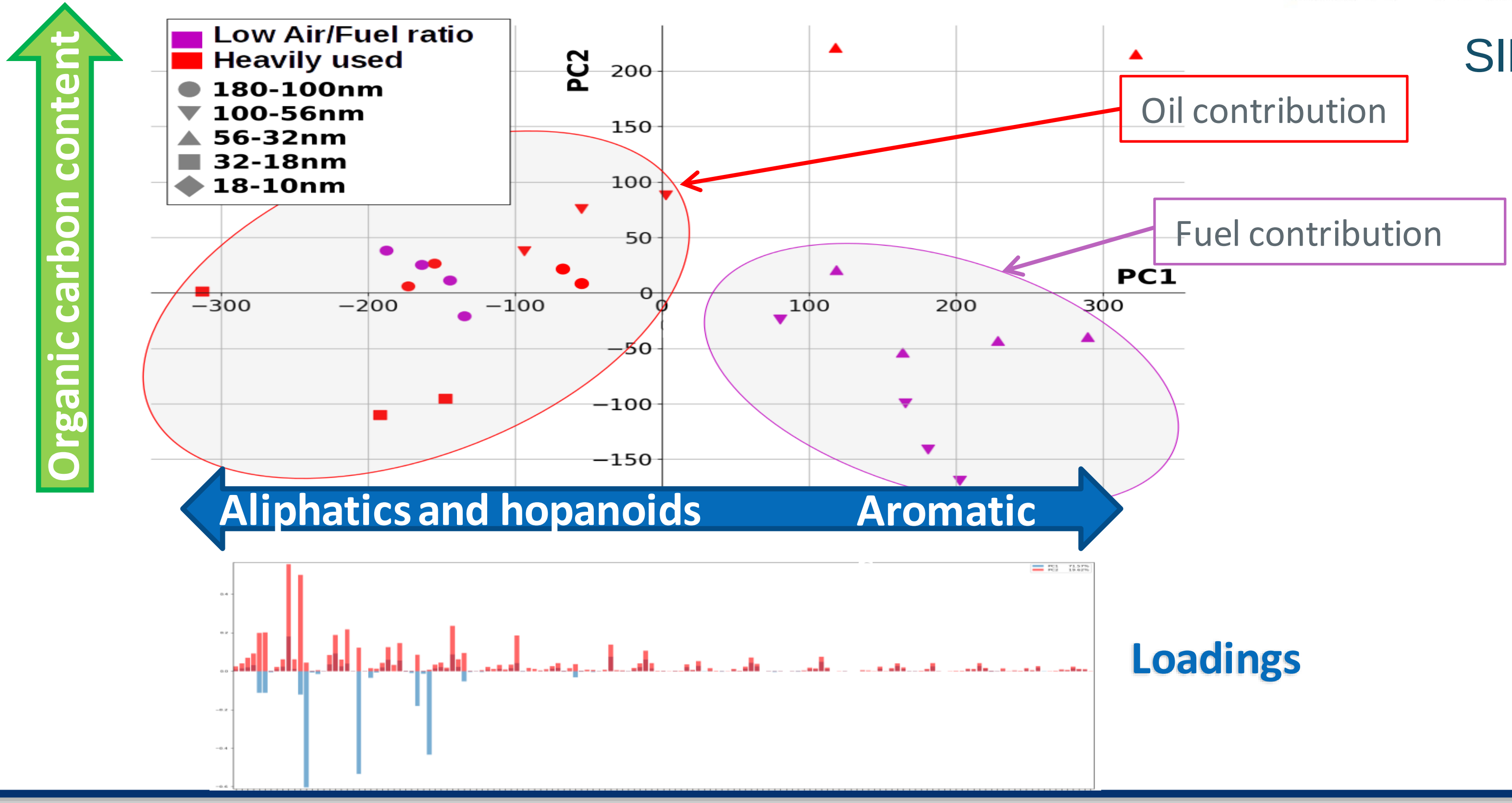
SIMS

Identification of chemical markers to discriminate particles produced in different engine conditions as benchmark for MGA

e.g.: aliphatics discriminate optimal from non-optimal regimes

Source discrimination … SIMS + PCA

SIMS



Loadings

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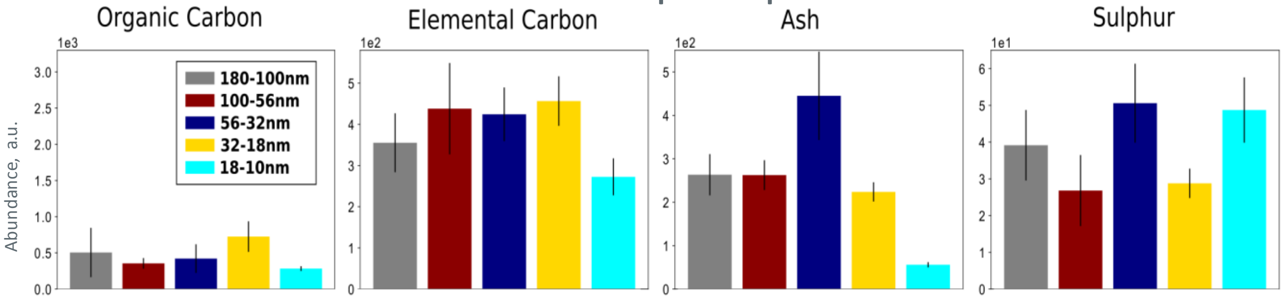
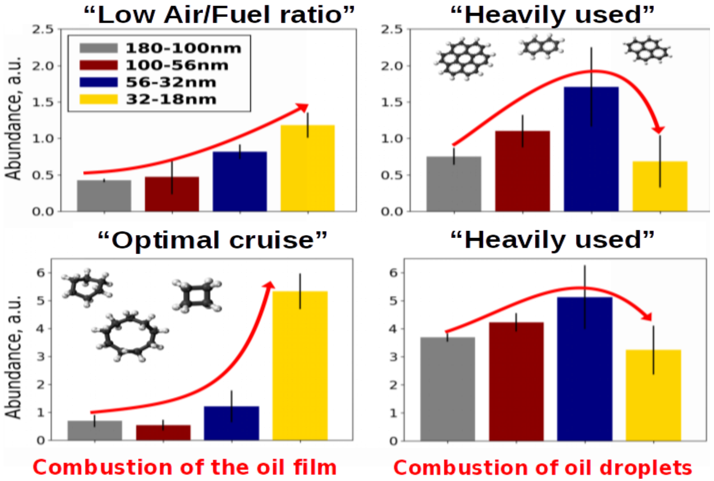
Size-dependent chemical analysis

Particle benchmark -"Optimal uphill"



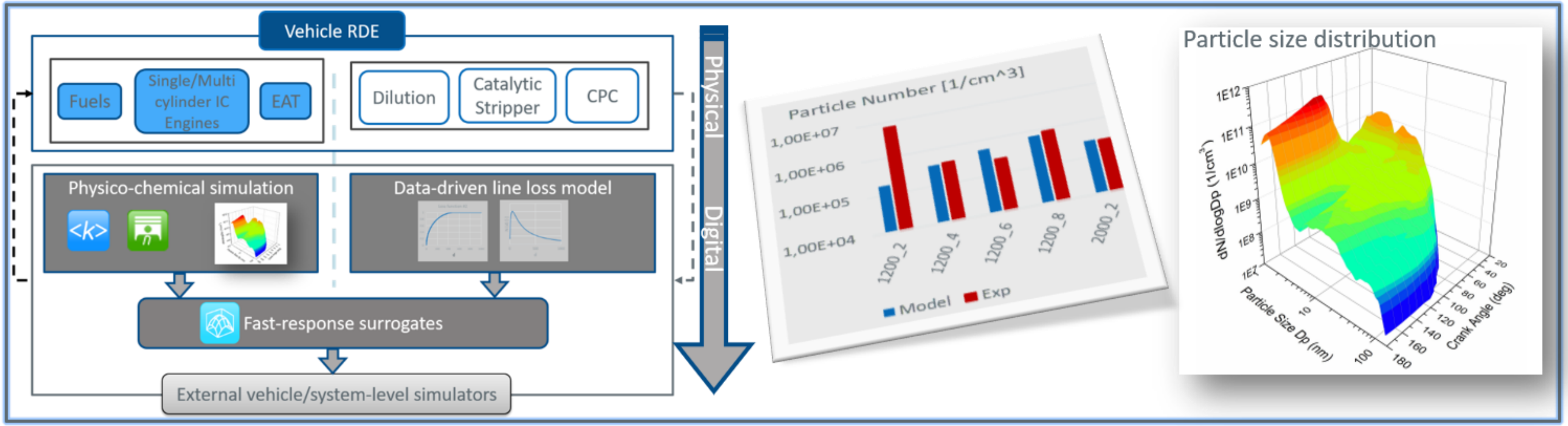
Clear trends in **size** and **source** have been identified for:



- **Cycloalkane and bicycloalkane fragments** (C_nH_{2n-3}) - markers of lubricating oil
- **Polycyclic aromatic hydrocarbons (PAH)** - building blocks of soot particles

Size variation by chemical category delivered as key input to the Model Guided Application (U.Cam + CMCL)

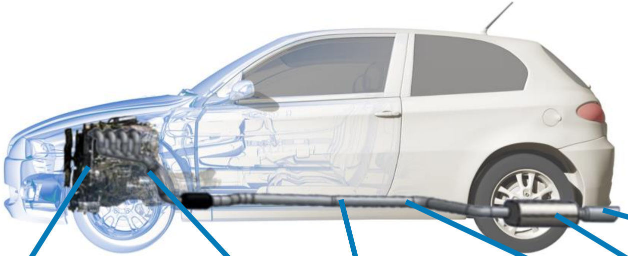
Model guided application (MGA)

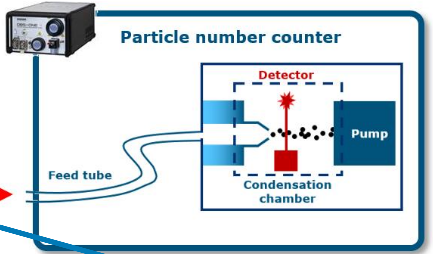


- MGA combines physico-chemical and statistical algorithms to simulate the particulate emissions in IC engine driven vehicles, to offer:
  - ✓ Sensitivity of PM and PN to operating conditions in IC engines and vehicles
  - ✓ Particle size distribution, PM, PN, aggregate composition and morphology as a function of fuel characteristics, engine operating modes, after-treatment and RDE attributes
  - ✓ Thermodynamic boundary conditions at various sampling points to reduce the need for measuring "everything"

Physico-chemical simulation: fuel to tailpipe

PEMs 4Nano



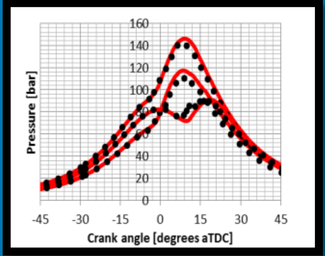


Fuel

$$HO_2+HO_2 \Rightarrow H_2O_2+O_2$$
$$H_2O_2+M \Rightarrow OH+OH+M$$
$$H_2O_2+HO_2+H_2$$
$$H_2O_2+H=OH+H_2O$$
$$H_2O_2+O=OH+HO_2$$
$$H_2O_2+OH=H_2O+HO_2$$

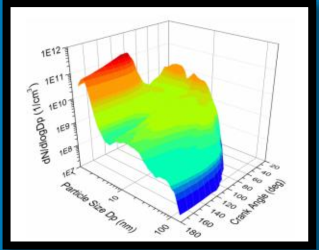
RON, MON, pathways

In-cylinder



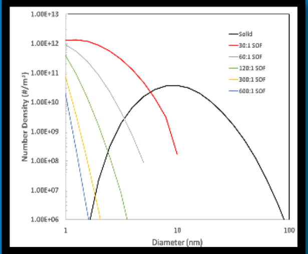
Combustion, emissions

Exhaust



Particulates: PM, PN

Tailpipe



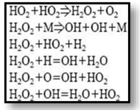
Particulates: PM, PN

MGA components and relationship with measurements

Physico-chemical Simulation

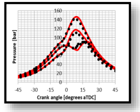
Fuel

RON, MON, pathways



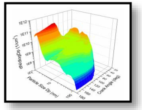
In-cylinder

Combustion, emissions



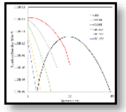
Exhaust

Particulates: PM, PN



Tailpipe

Particulates: PM, PN



Statistical algorithms

- Parameter estimation
- Computational Surrogates
- Validation

Experimental data (engine test bench & vehicle)

Fuel

Fuel analysis:
- composition
- evaporation curve
- amount of aromatics

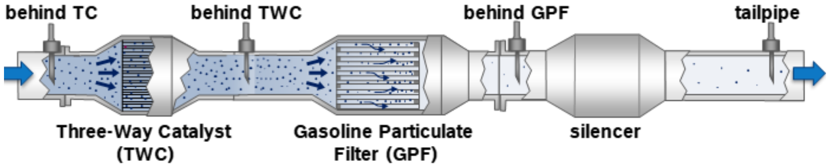
In-cylinder

Combustion & emissions:
- pressure trace analysis
- engine out raw emissions

Exhaust & Tailpipe

behind TC | behind TWC | behind GPF | Tailpipe

PN10 and PN23 analysis at various sampling positions along the exhaust

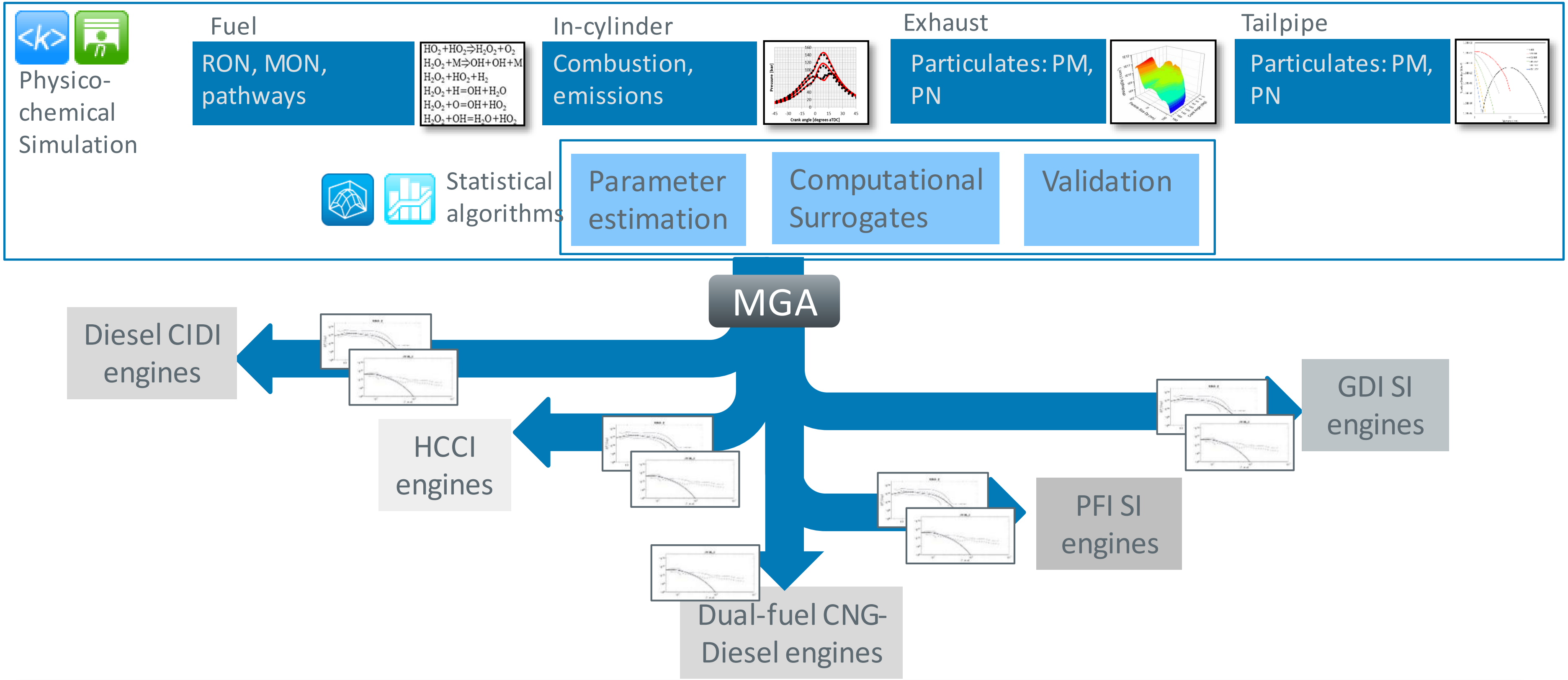


CVS tunnel

PN10 & PN23 in CVS tunnel (vehicle roller test bench)

Example for GDI engine

Understanding: MGA to provide the range



Understanding: modelling fuel to tailpipe

Inputs

Fuel specifications

SCRE & MCRE ICEs
Vehicles & drive cycles:
Operating conditions

Loss transfer functions for measurement components

MGA

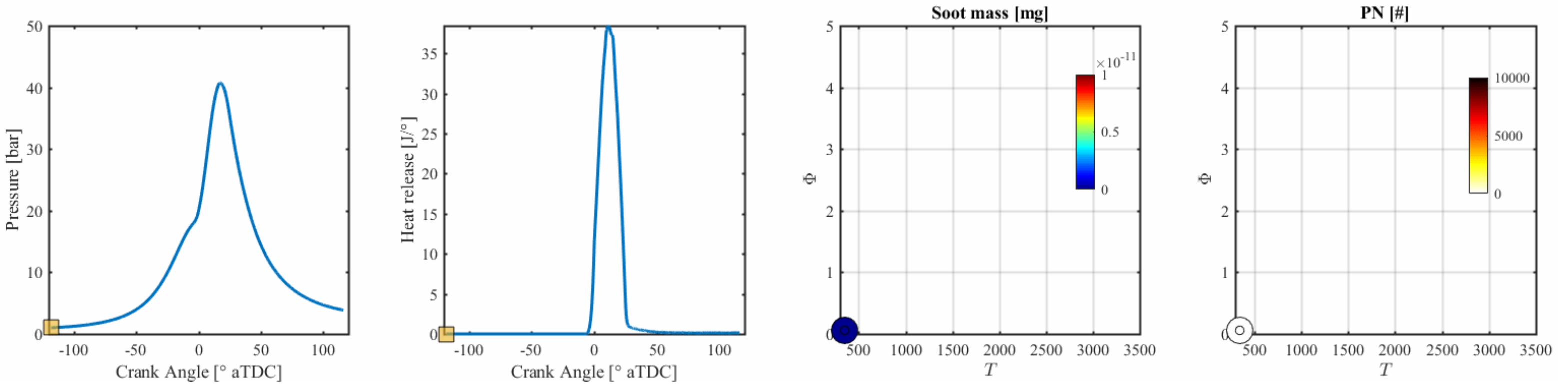
- SRM Engine Suite™: Particle population balance includes soot, ash, sulphates and volatiles
- *k*inetics™ reactor network to account for dilution and sampling
- Validation of engine-out PSDs at multiple loads-speeds
- Dilution and temperature thresholds based on the number density of solids and SOF

Outputs

PM
PN
PSD
composition
Sensitivities
Surrogates

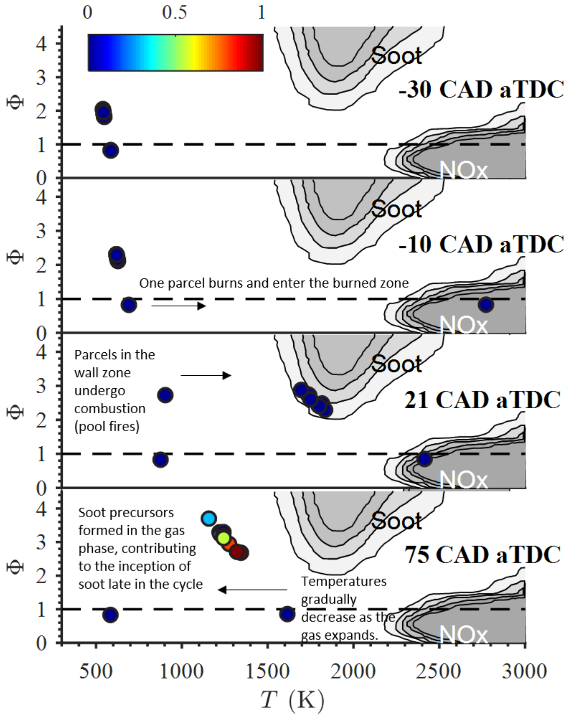
Understanding: guidance on inhomogeneities

CMCL Innovations



MGA offers Φ-T plots as a function of the engine operating conditions at various load-speed points

Understanding: guidance on inhomogeneities



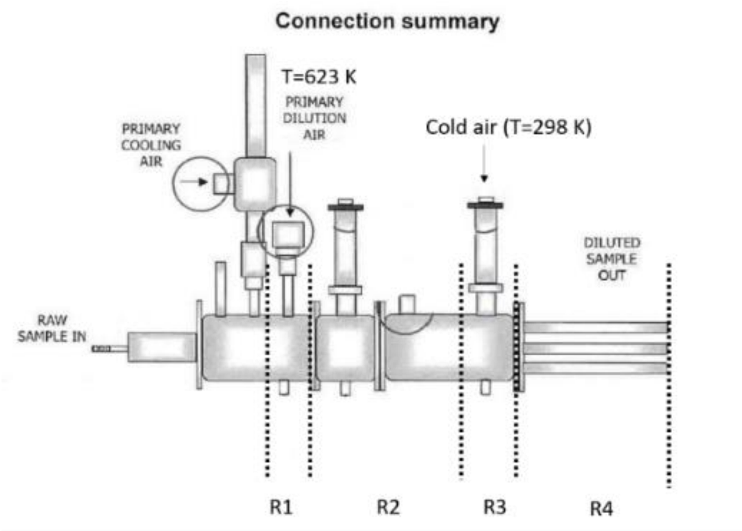
The parcels are coloured according to the soot mass within them and the values are normalised to 1×10^{-7} kg.

- MGA maps the in-cylinder inhomogeneities in Φ-T space with the soot and NO_x emissions
- Φ-T plots of stochastic parcels at 4 stages in the engine cycle. There are 2 bulk parcels (stoichiometric) and 10 wall parcels (rich).
- One parcel burns at spark and enters the NO_x zone. Mass is transferred from the unburned parcel into the burned parcel as the simulation proceeds
- Later in the simulation, the wall parcels burn and enter the soot zone
- Soot precursors (coronene) formed in the wall parcels contribute to the inception of solid soot particles.

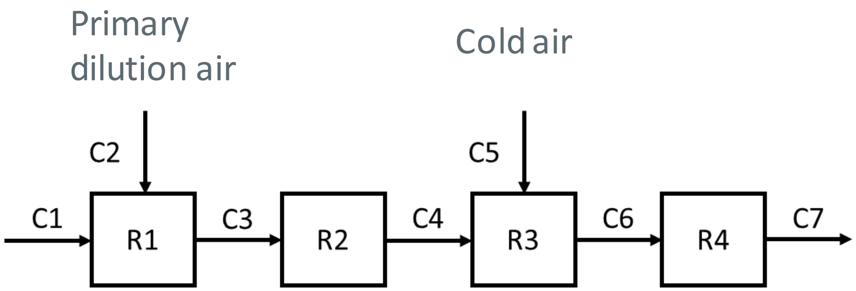
MGA offers Φ-T plots as a function of the engine operating conditions at various load-speed points

Understanding: sensitivity to dilution

Example: Dekati sampling system

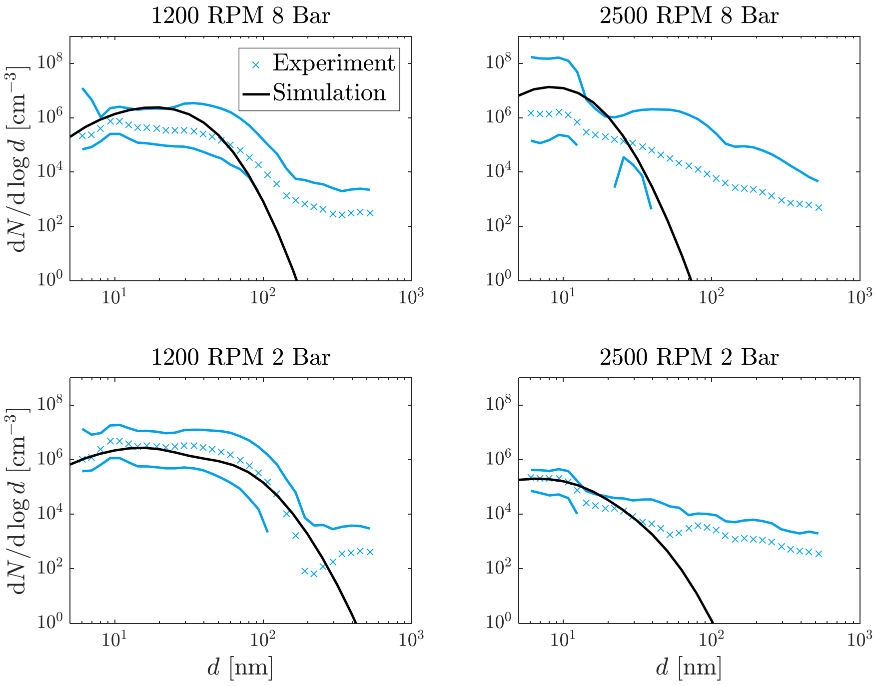


*k*inetics: reactor network

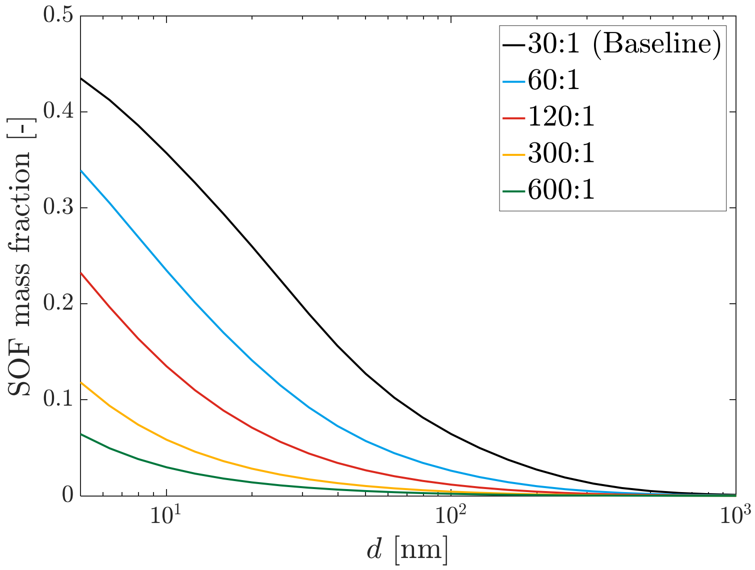


Understanding: sensitivity to dilution

Aggregate size distribution over load-speed operation



Solids and SOF sensitivity to dilution



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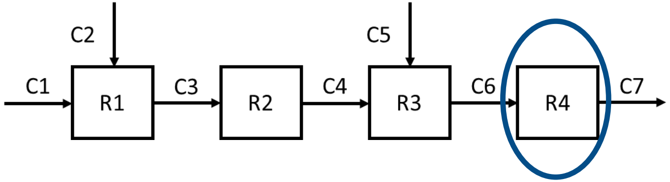
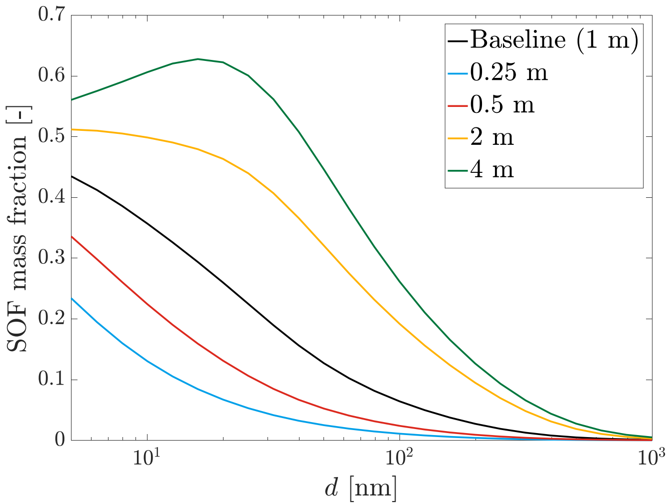
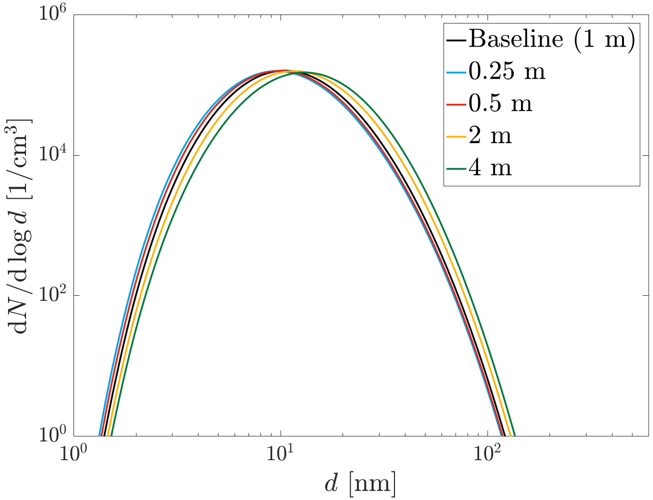
Understanding: sensitivity to pipe length



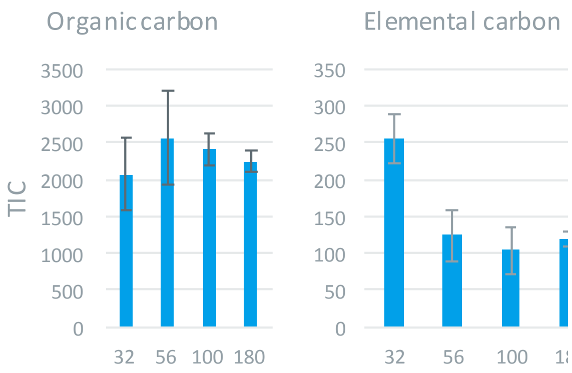
Size of R4 (pipe) can be varied easily.
Effects on measured PN can be assessed.



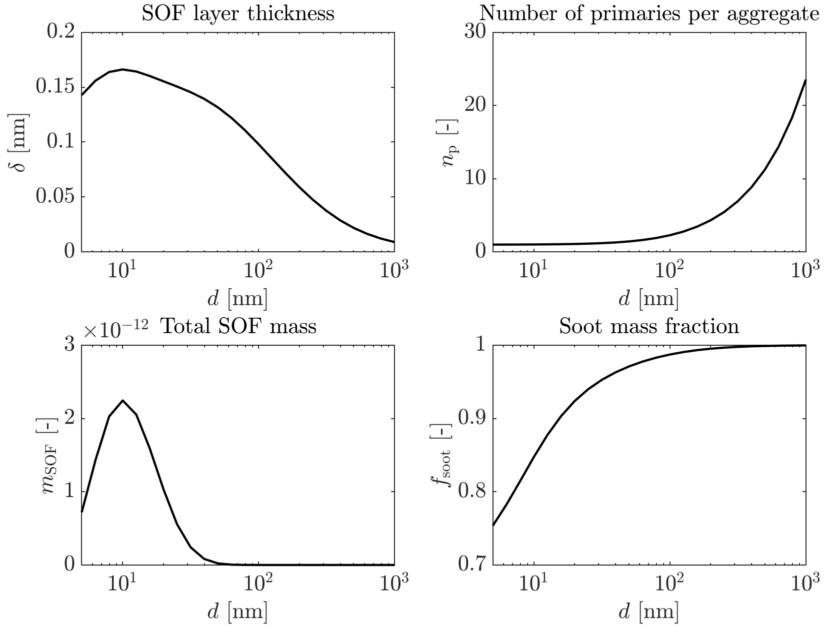


Understanding: guidance – bulk vs. surface

Measurements



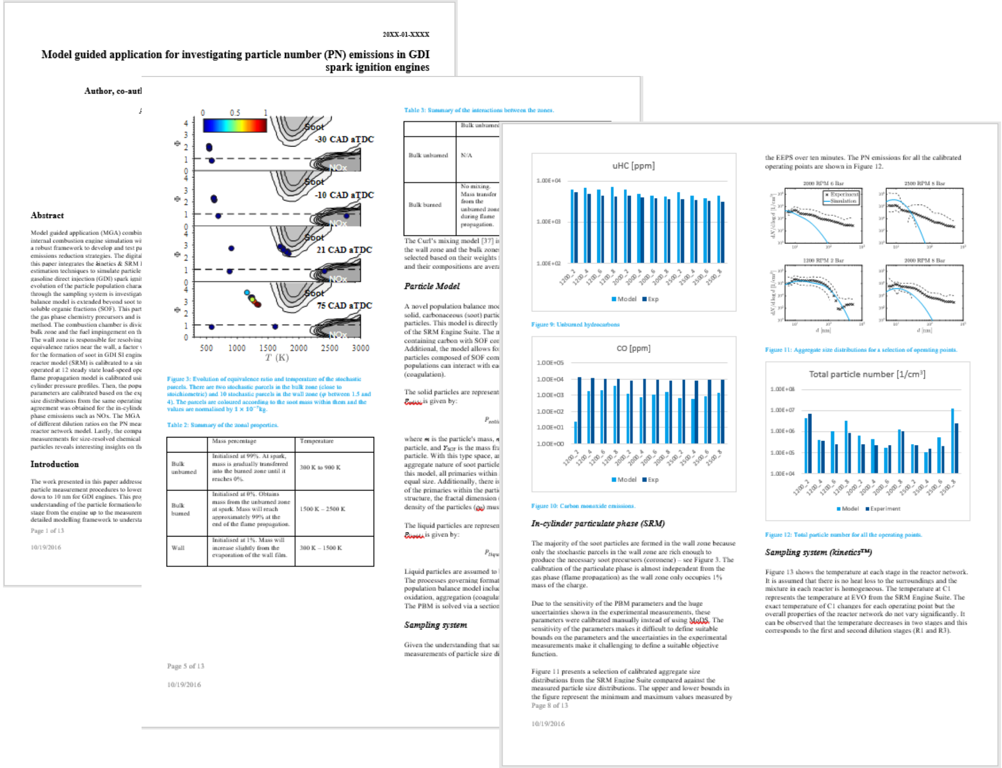
MGA



- Elemental carbon in opposite trend with soot mass fraction
- SOF layer thickness matches organic carbon
- Validated a surface characterisation technique using SOF layer thickness

Understanding: MGA - dissemination

PEMs 4Nano

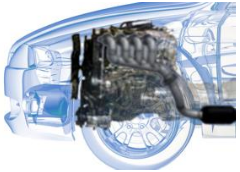


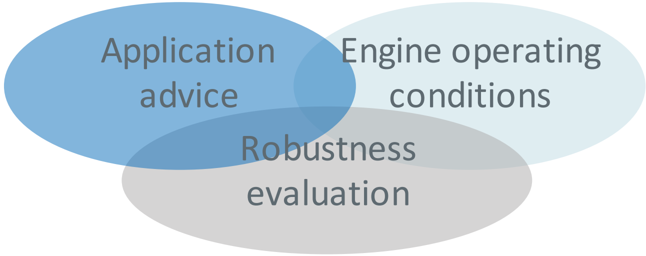
- MGA on a GDI SI single cylinder engine
- MGA maps in-cylinder inhomogeneities in Φ-T w.r.t. soot and NO_x emissions
- Sensitivity to dilution and temperature during sampling
- Size-resolved chemical characterisation: bulk vs surface
- Draft manuscript prepared
- MGA on a GDI SI multi-cylinder engine started

Procedures: objectives

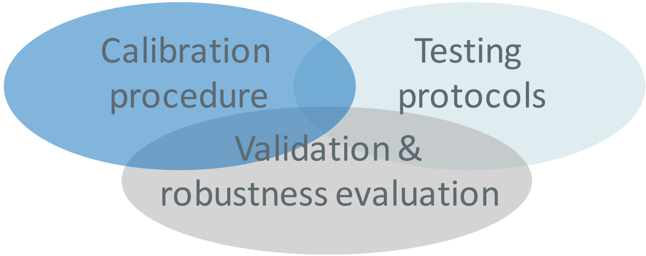
Recommendation for PN > 10 nm assessment…

… during **engine development process**



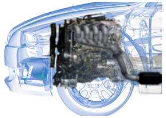


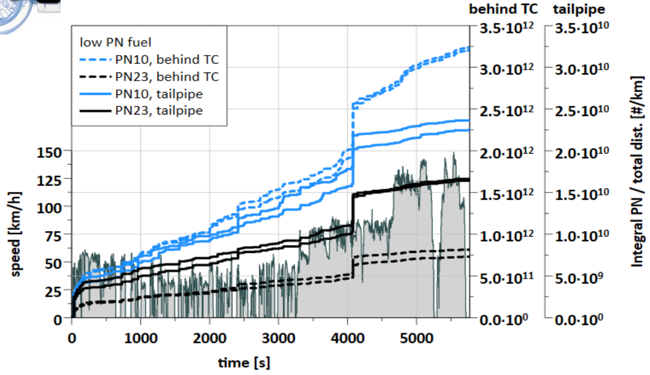
… during **vehicle RDE testing**



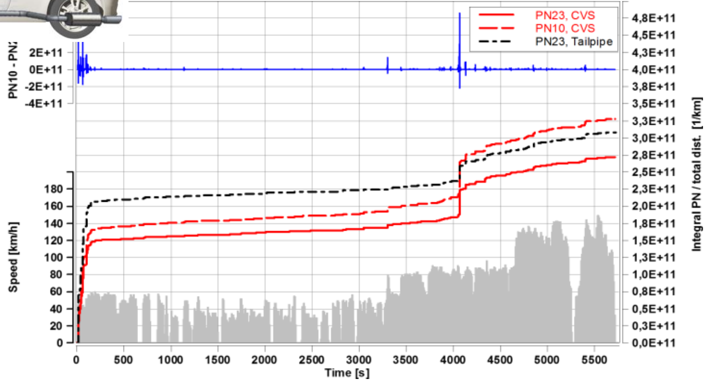
Procedures: preliminary results

Engine test bench





Roller test bench



Differences between…

… **engine and roller test bench**, but <u>relative</u> **trends are similar**

… **individual test points** (e.g. tailpipe and CVS), but "**emission events" are similar**

PN10 and PN23 show a **comparable temporal behaviour, PN10 emission is simply higher**

→ **Relative trends observed from engine test bench measurement are transferable to roller test bench**

→ **New measurement system can be applied and handled like an established PN23 measurement system**

Procedures: test schedule

2 vehicles on real road

4 vehicles on chassis dyno

multi- cylinder engine (I4, 2.0l, T/C, GDI)

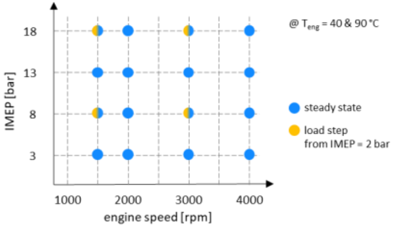
single cylinder engine

Fundamentals/
PN characterisation with:

- SEM. TEM
- AFM-Raman, TERS
- ToF-SIMS, L2MS
- LII
- CPMA
- AAC

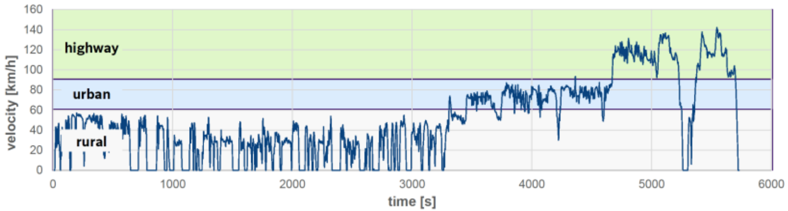
single operating points

Procedure for **engine developement process**



Mini map, load steps, WLTC & RDE cycle

Procedure for **vehicle RDE testing**



NEDC, WLTC & RDE cycle

vehicle 1: C-segment[2]: GDI engine: I4, 2.0l, T/C with GPF
vehicle 2: D-segment[2]: GDI engine: I4, 2.0l, T/C without GPF
vehicle 3: SUV-segment (Basis Euro5-6c): GDI engine: I4, 2.0l, T/C without GPF
vehicle 4: B/C-segment (Basis Euro6d-Temp): GDI engine: I3/I4, 1.0-1.5l, with GPF

[1] production engine as basis, modifications on engine hardware & ECU calibration

[2] demonstrator vehicle (Basis EU6) with modified vehicle & engine hardware as well as modified engine calibration

Conclusions

Technology

- Two systems (laboratory + PEMS) including subcomponents (e.g. CPC, CS) have been modified for >10 nm measurements
- Laboratory system validated and in use since April 2018
- PEMS currently under validation

Understanding

- On-line/off-line multi-technique characterization of a wide variety of size-selected particles :
  - for powerful discrimination protocols
  - for extensive database of particle physical and chemical properties as input for MGA
- MGA aligned with measurements on the size-resolved surface (organic carbon) versus bulk (elemental carbon) compositions.

Procedures

- PEMs4Nano lab system can be applied and handled according to PMP-recommendation
- MGA combining physico-chemical simulation and statistical algorithms to offer sensitivities in particle characterisation as a function of RDE attributes

End of presentation

www.PEMs4Nano.eu

Industry

Research partners

Service partner

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