



# Nanoparticle and secondary aerosol emissions of EURO6d-level passenger cars fueled with gasoline, diesel and natural gas: The role of exhaust after-treatment byproducts

O. Sippula<sup>1,2</sup> Pauli Simonen<sup>1,3</sup>, G. Mustafa<sup>1\*</sup> A. Hartikainen<sup>1</sup>, T. Kokkola<sup>1</sup>, M. Somero<sup>1</sup>, M. Ihalainen<sup>1</sup>, P. Yli-Pirilä<sup>1</sup>, H. Oikarinen<sup>1,3</sup>, L. Ala-Hakuni<sup>2</sup>, A. Mukherjee<sup>1</sup>, M. Shahzaib<sup>1</sup>, R. Zimmermann<sup>4,5</sup>, P. Karjalainen<sup>3</sup>

<sup>1</sup>Department of Environmental and Biological Sciences, **University of Eastern Finland**, Finland

<sup>2</sup>Department of Chemistry and Sustainable Technology, **University of Eastern Finland**, Finland

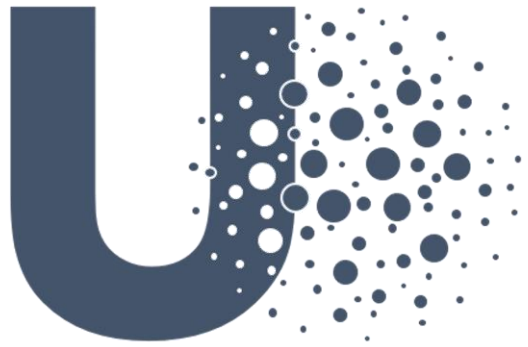
<sup>2</sup>Aerosol Physics Laboratory, Physics Unit, **Tampere University**, Finland

<sup>3</sup>Department of Technical Physics, **University of Eastern Finland**, Finland

<sup>4</sup>Joint Mass Spectrometry Center, Analytical Chemistry, **University of Rostock**, Germany

<sup>5</sup>Joint Mass Spectrometry Center, **Helmholtz Zentrum München**, Germany

\*Institute of Climate and Energy Systems, ICE-3: Troposphere, Forschungszentrum Jülich, Germany

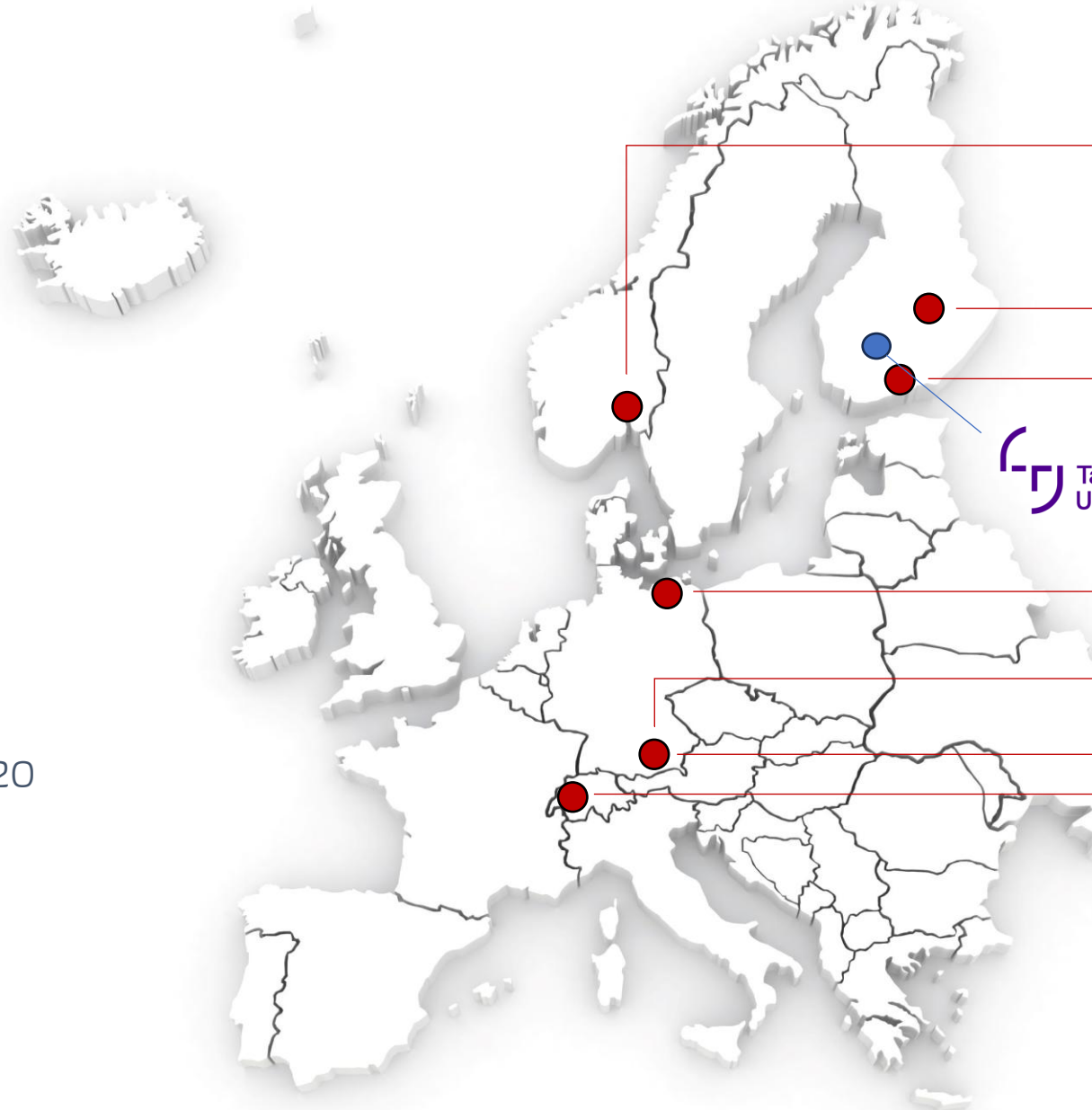


# ULTRHAS

Ultrafine particles from  
Transportation -  
Health  
Assessment of  
Sources

Duration: Sept. 2021 – Nov. 2025

Call: H2020 LC-MG-1-14-2020



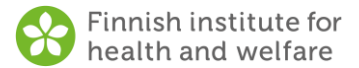
Coordinator:  
Johan Øvrevik



Norwegian Institute of Public Health



UNIVERSITY OF  
EASTERN FINLAND



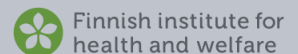
HelmholtzZentrum münchen  
German Research Center for Environmental Health



Funded by  
the European Union



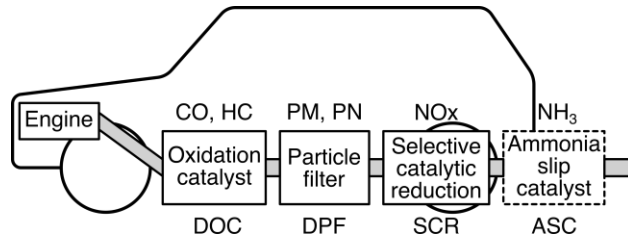
HelmholtzZentrum münchen  
German Research Center for Environmental Health



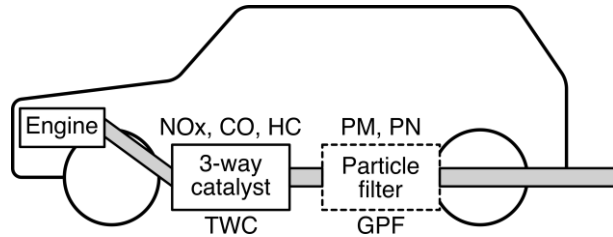
# Introduction

- Euro 6d compliant vehicles:

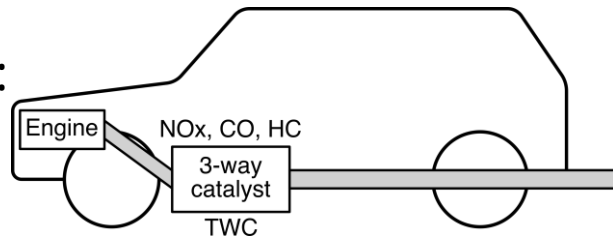
Diesel:



Gasoline:



Biogas & CNG:  
(compressed natural gas)



## Background:

- Diesel vehicles require extensive exhaust after-treatment to fulfill emission regulations.
- Latest EURO6d emission standard has led to the use of particle filters (GPF) also in gasoline vehicles.
- Low particle emissions (solid,  $D_p > 23$  nm) reported for CNG and biogas vehicles even when not equipped with particle filters.

## Research questions:

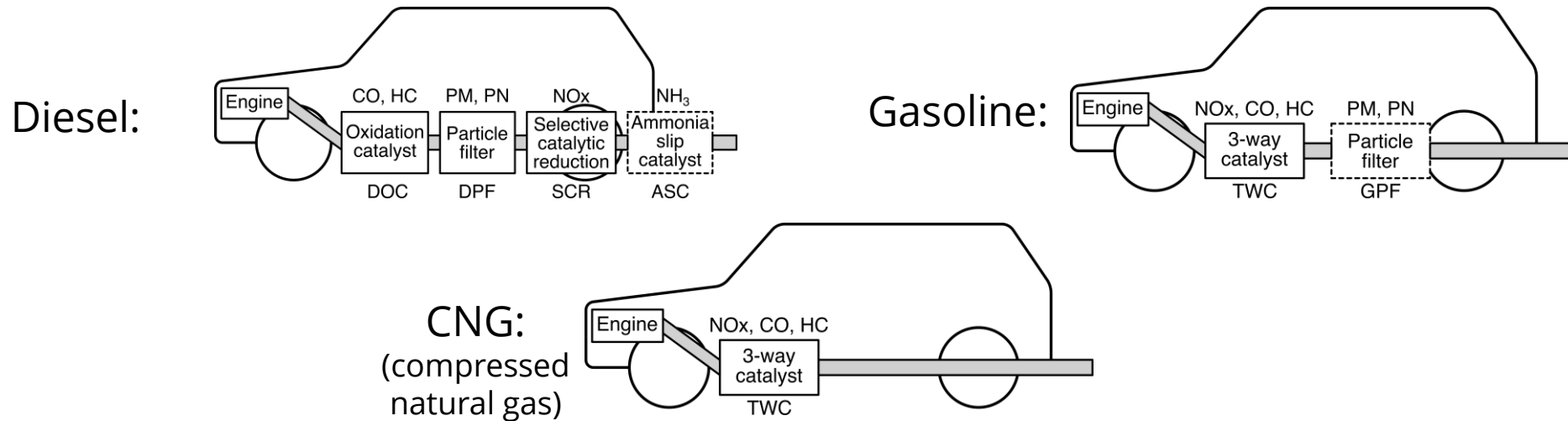
- How ultrafine particle emissions differ between different powertrains, including also particles beyond the regulation range? (down to 1 nm particles)
- What are the secondary aerosol formation potentials of the emissions?
- How gaseous emissions differ between powertrains and how they explain the measured secondary aerosol potential?



# Methods

Vehicle name	Fuel	Engine displacement (L)	Model year	Mileage (km)	Emission class	After-treatment	Total number of 1-hour cycles
Gasoline	95E10 gasoline	1.0 (GDI)	2023	20 000	Euro 6d-ISC-FCM	3-way catalyst, GPF	41
CNG	Compressed natural gas	1.0	2019	50 000	Euro 6d-TEMP-EVAP-ISC	3-way catalyst	30
Diesel	Winter diesel	1.6	2019	40 000	Euro 6d-TEMP	DOC, DPF, SCR	30

- Euro 6d compliant vehicles:



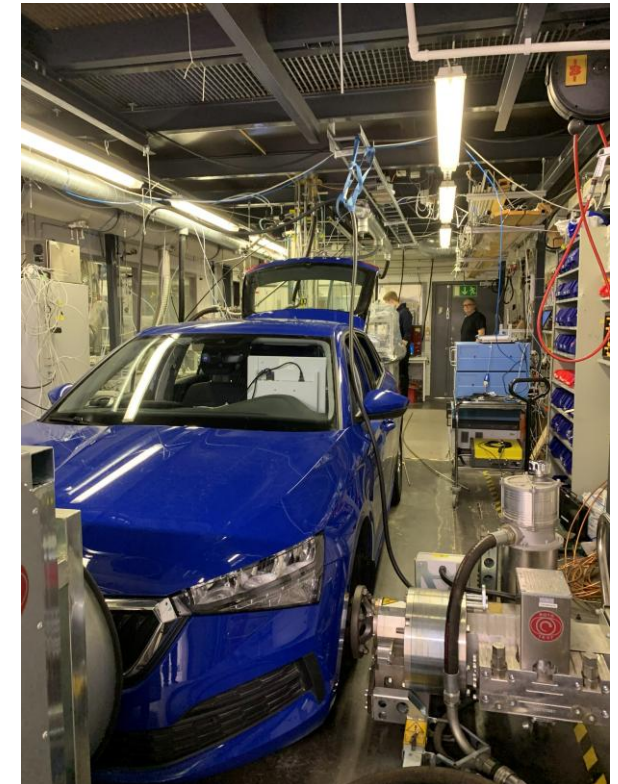
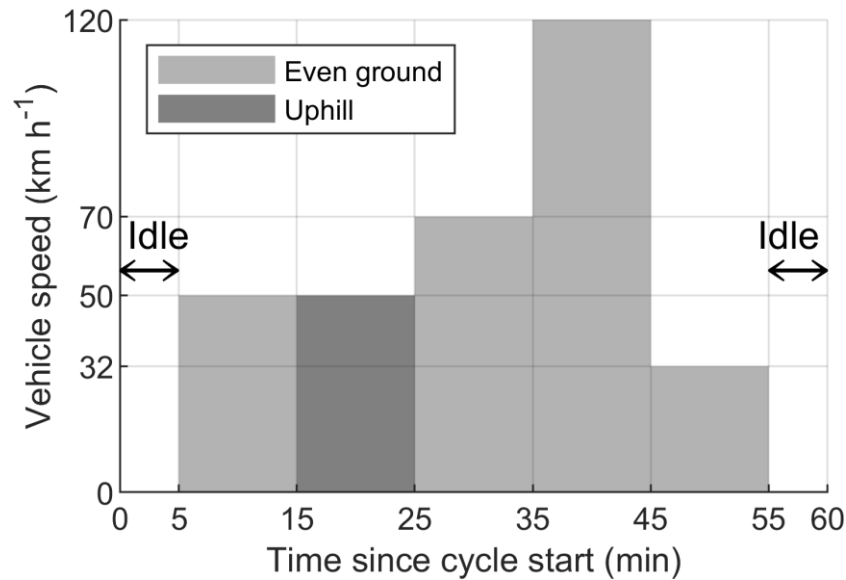


# Methods

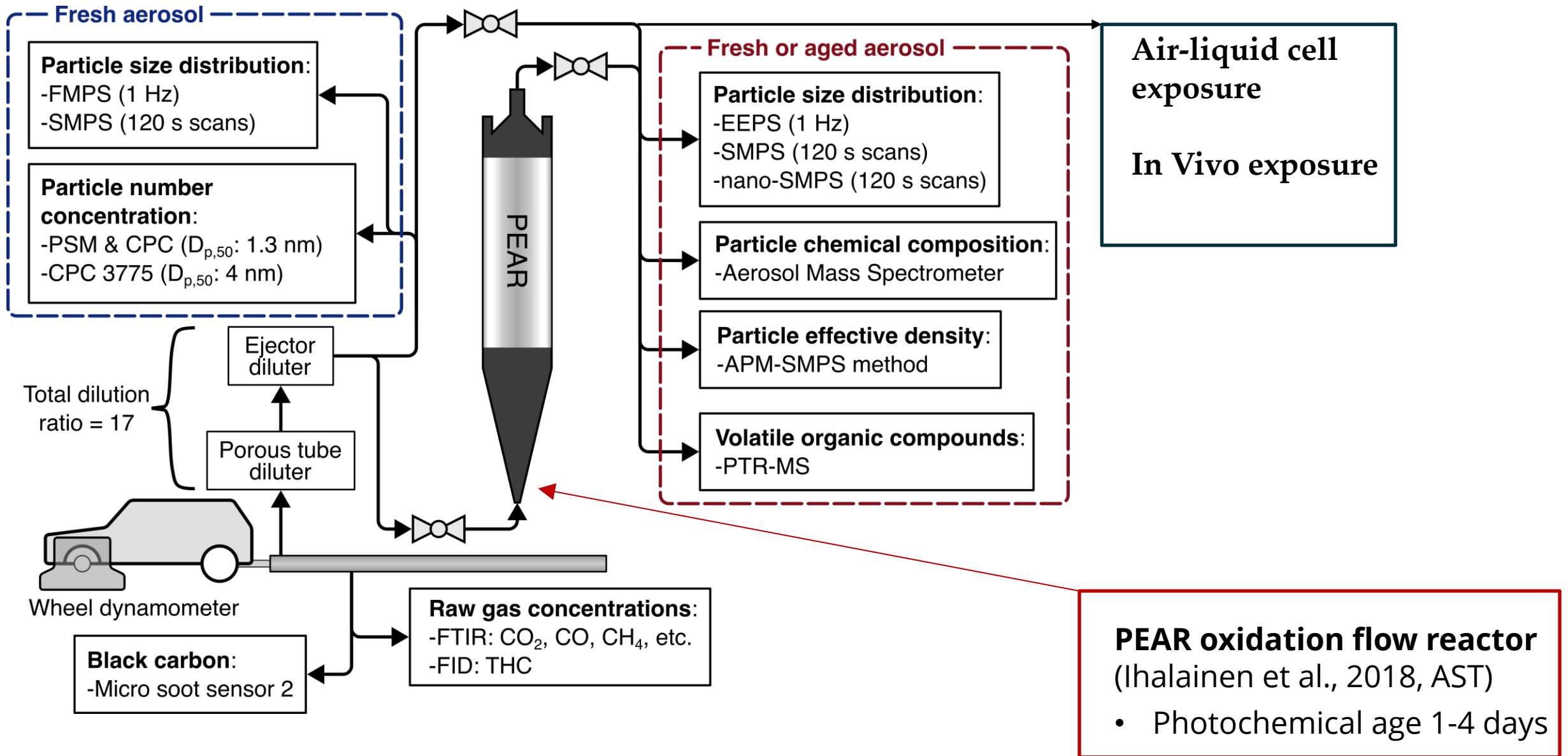
Vehicle name	Fuel	Engine displacement (L)	Model year	Mileage (km)	Emission class	After-treatment	Total number of 1-hour cycles
Gasoline	95E10 gasoline	1.0 (GDI)	2023	20 000	Euro 6d-ISC-FCM	3-way catalyst, GPF	41
CNG	Compressed natural gas	1.0	2019	50 000	Euro 6d-TEMP-EVAP-ISC	3-way catalyst	30
Diesel	Winter diesel	1.6	2019	40 000	Euro 6d-TEMP	DOC, DPF, SCR	30

- 1 experiment consists of 4 consecutive 60 min driving cycles
- >1500 km of driving with each vehicle
- 3 DPF regenerations observed

Driving cycle:



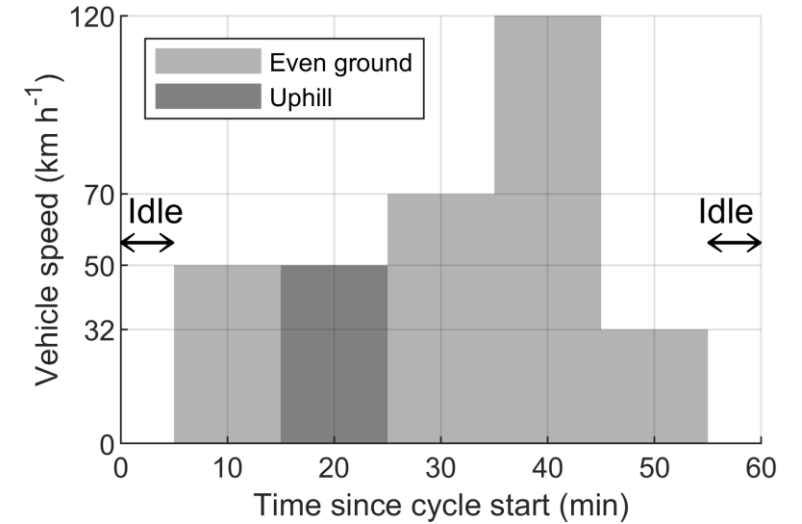
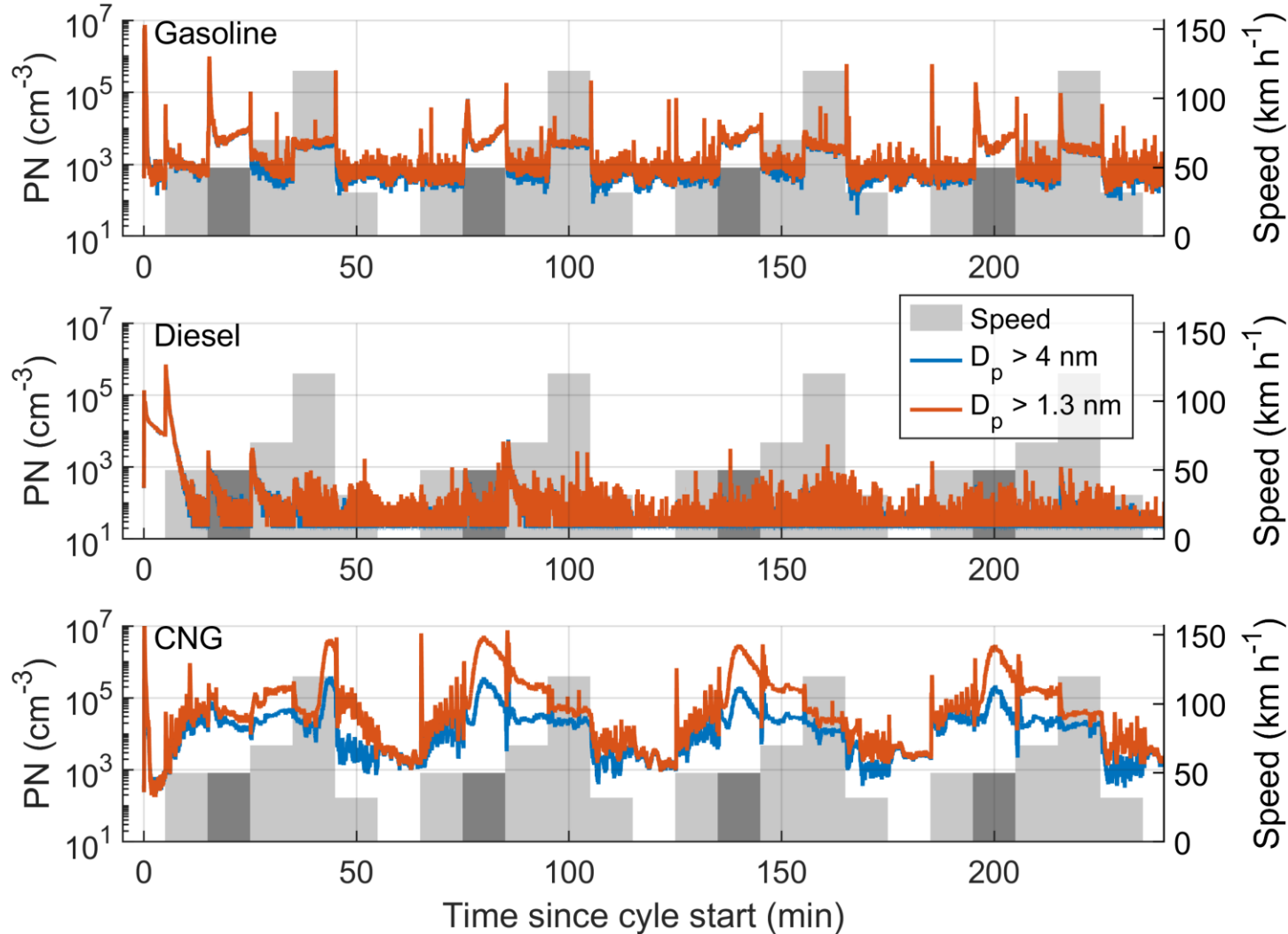
# Methods





# Results - fresh particulate emissions

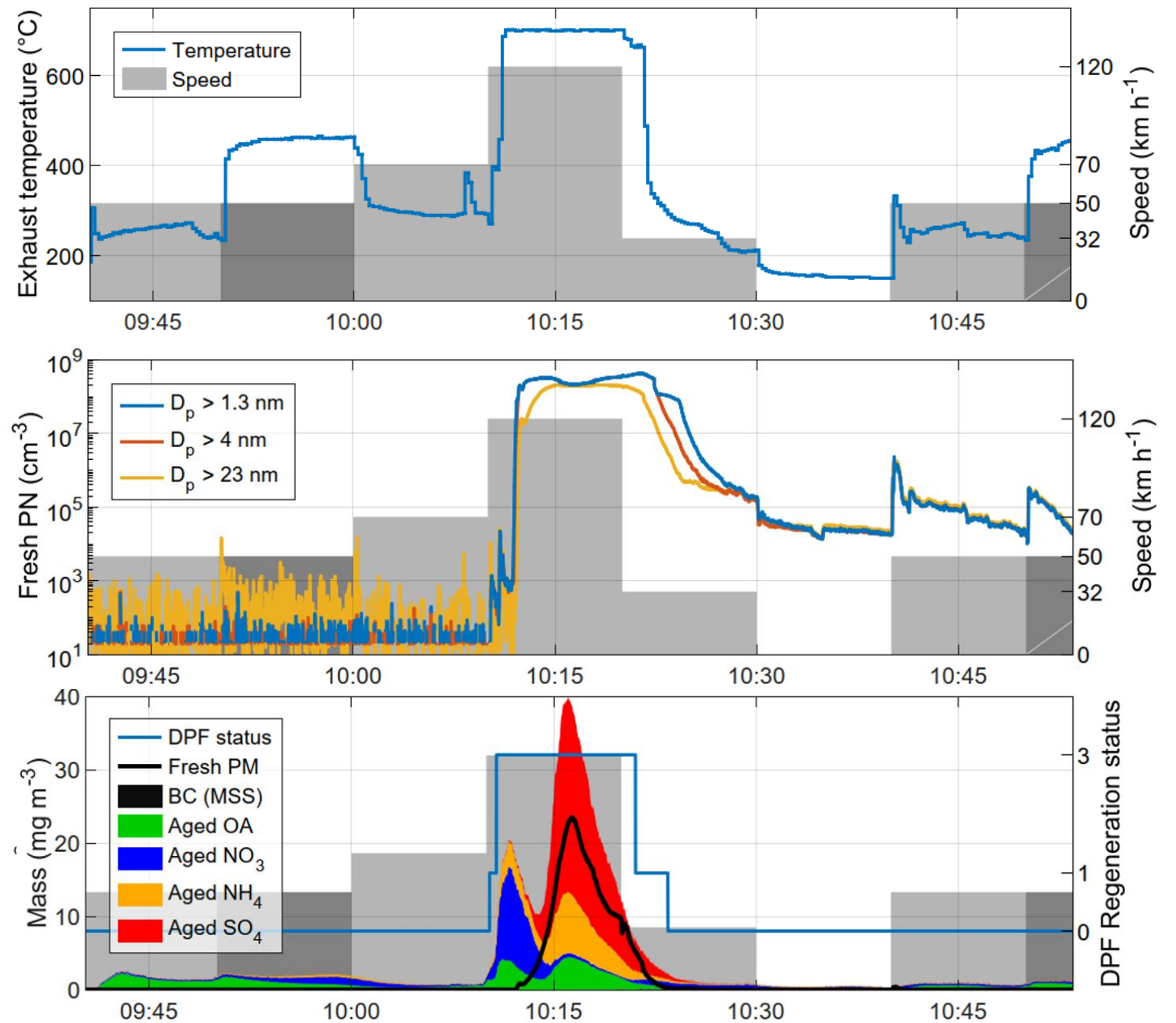
Tailpipe particle number concentrations:





# Results - Diesel particulate emissions during regeneration

- DPF regeneration occurred roughly with the interval of 500 km
- Primary particle mass emitted during DPF regeneration: 4-152 mg

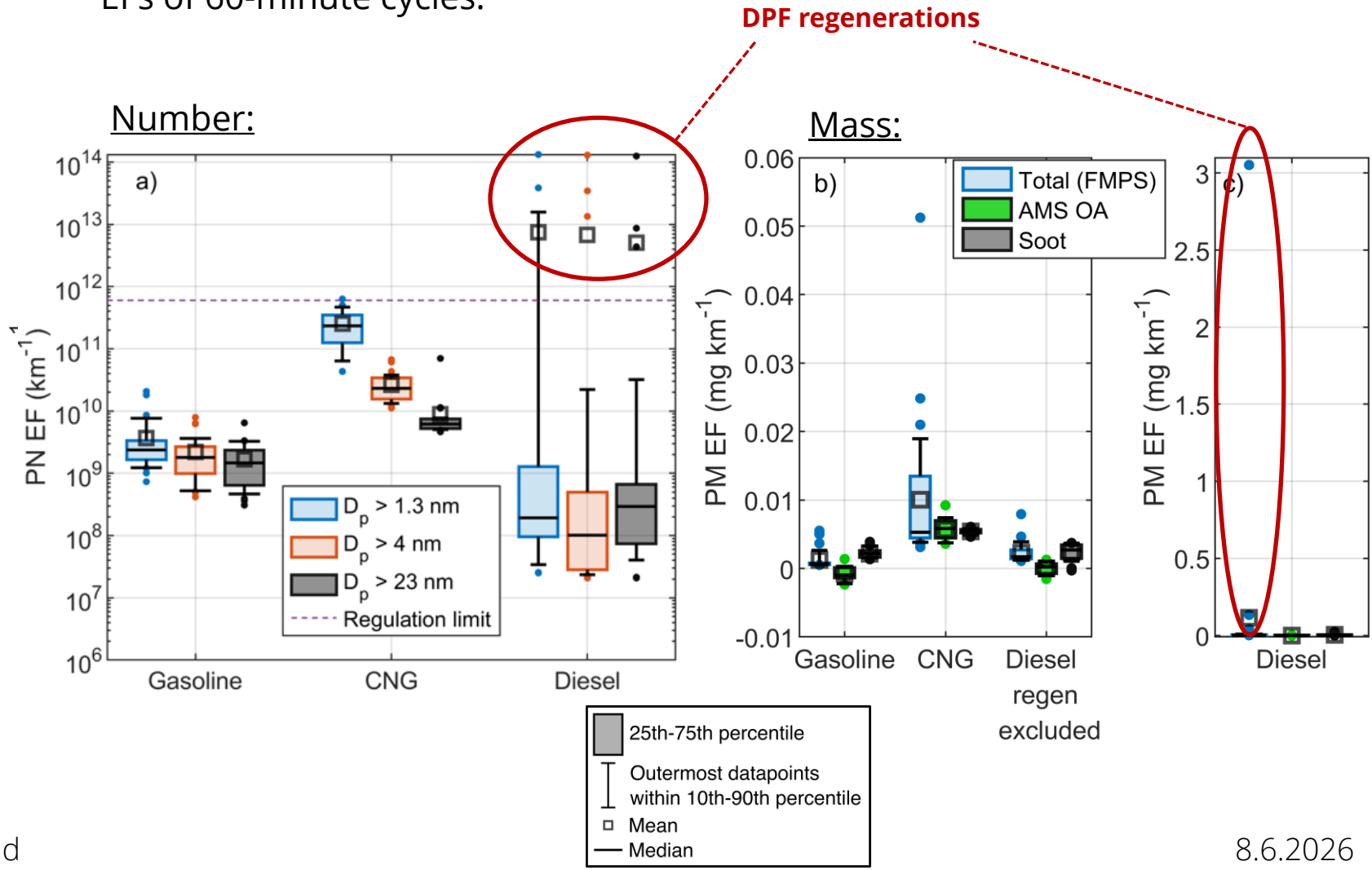




# Results - fresh particulate emissions

EFs of 60-minute cycles:

- Regulation limits:
  - $6 \times 10^{11}$  #/km (PN; solid,  $D_p > 23$  nm)
  - 4.5 mg/km (PM)
- CNG fresh emissions typically highest
- Diesel regenerations have a drastic effect on particle number emission

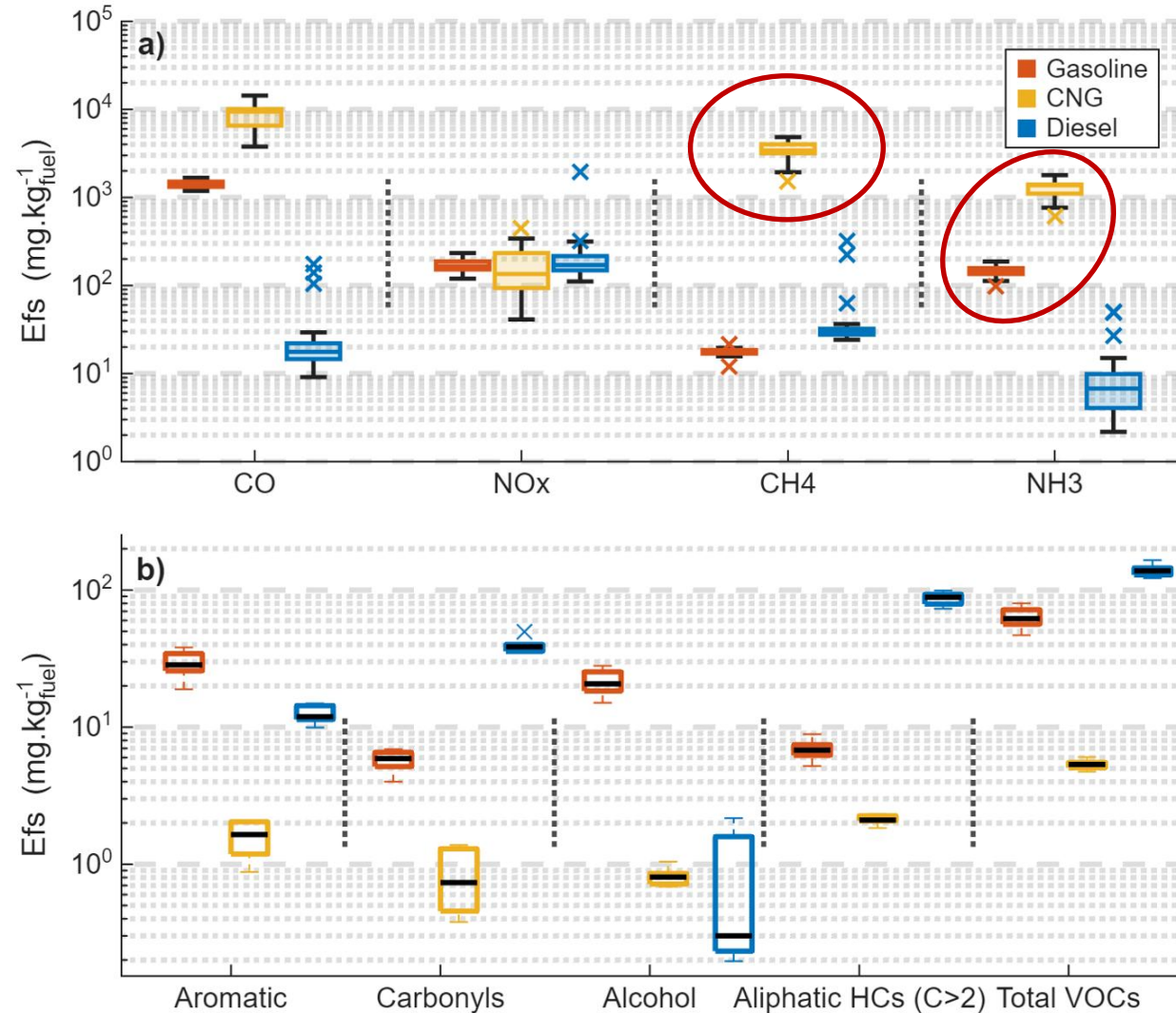




# Results – fresh gas emissions

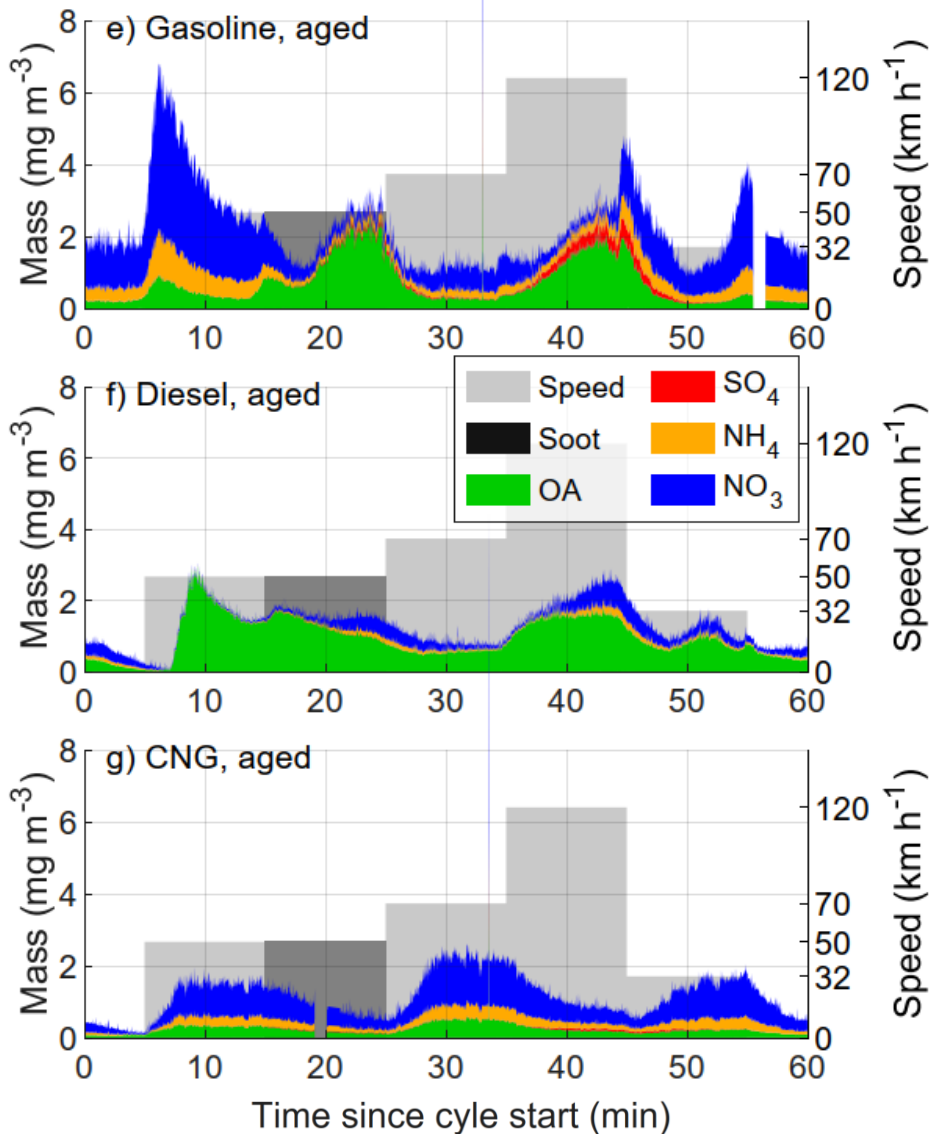
- High CH<sub>4</sub>-slip from CNG car
- High NH<sub>3</sub> emissions from CNG and gasoline cars (formed as a byproduct in the TWC catalysts)
- Large differences in VOC compositions

Emission factors of 60-minute cycles:

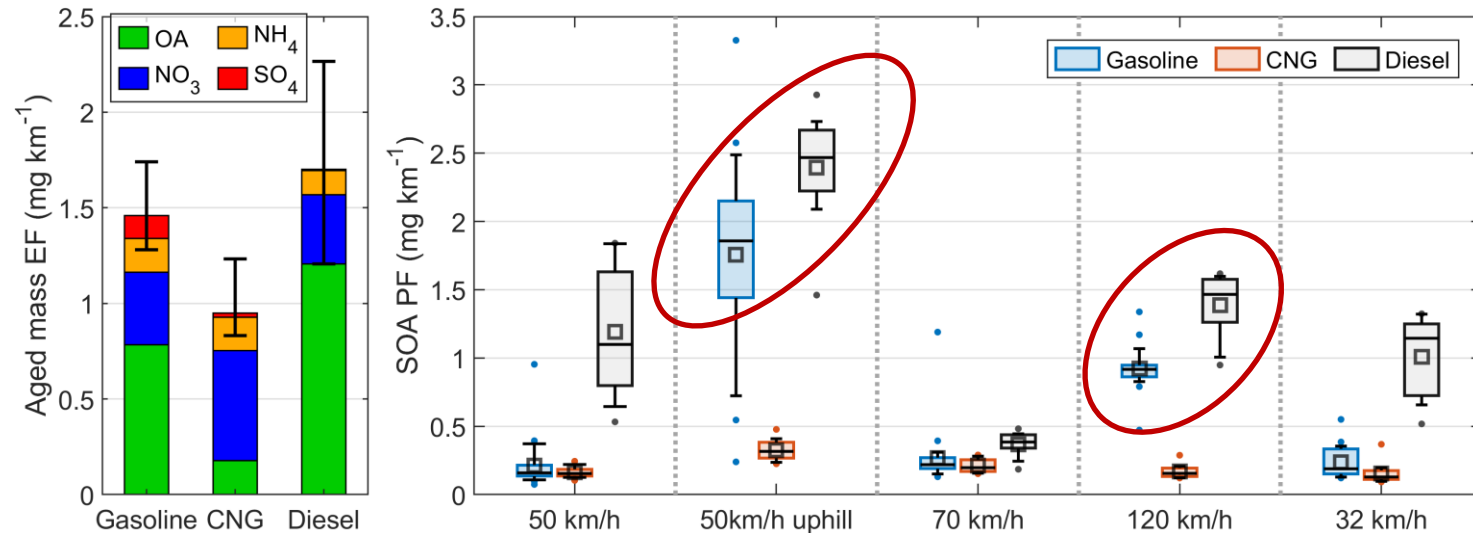


# Results - secondary aerosol formation

Aged aerosol time series



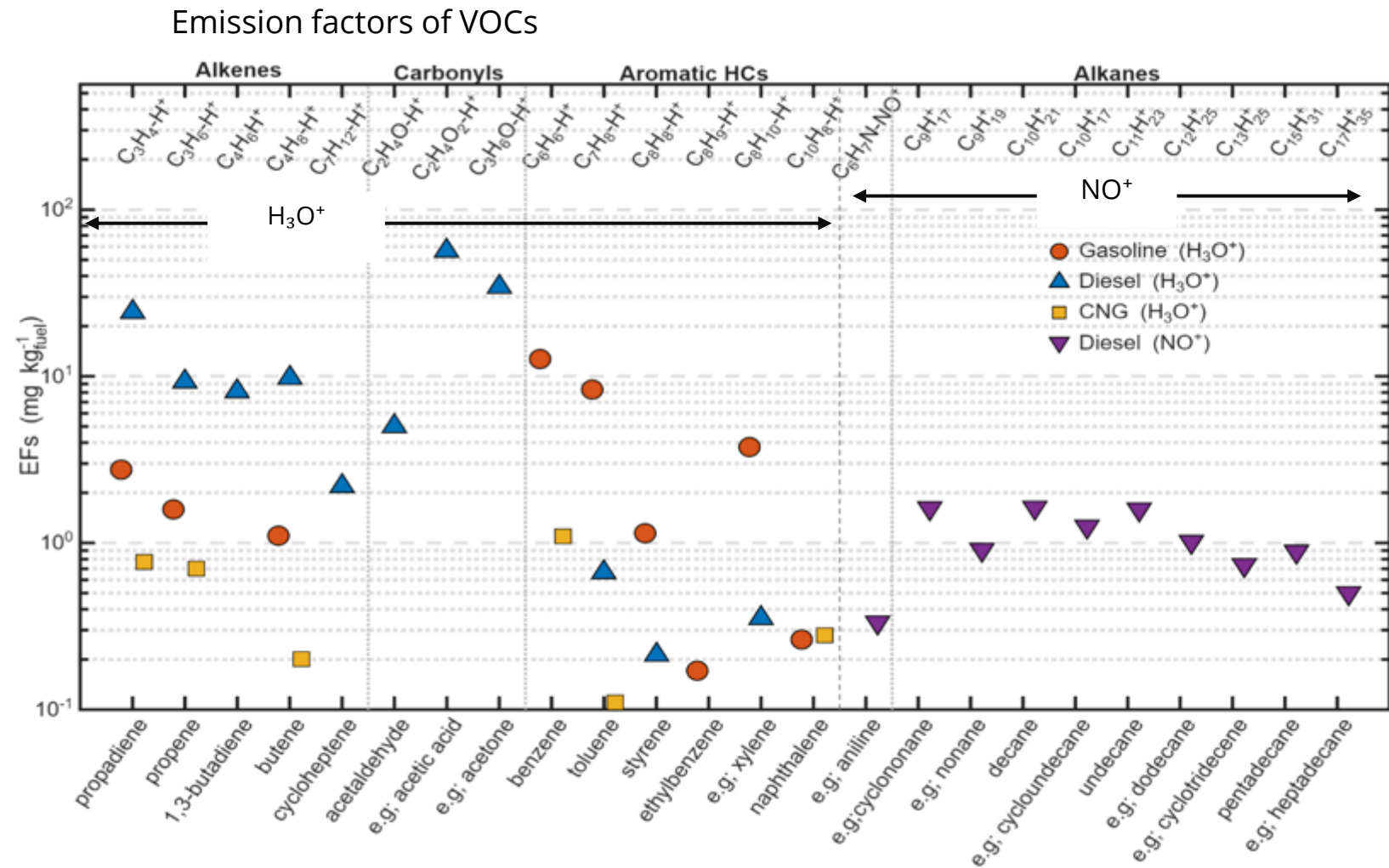
Secondary aerosol and SOA emission factors



- Up to ~1000-times increase in particle mass due to aging
- Ammonium nitrate important secondary aerosol constituent with cars equipped with a 3-way catalyst (gasoline and CNG)
- Low SOA with CNG
- High SOA with gasoline and diesel at high engine loads

# Results - volatile organic emissions

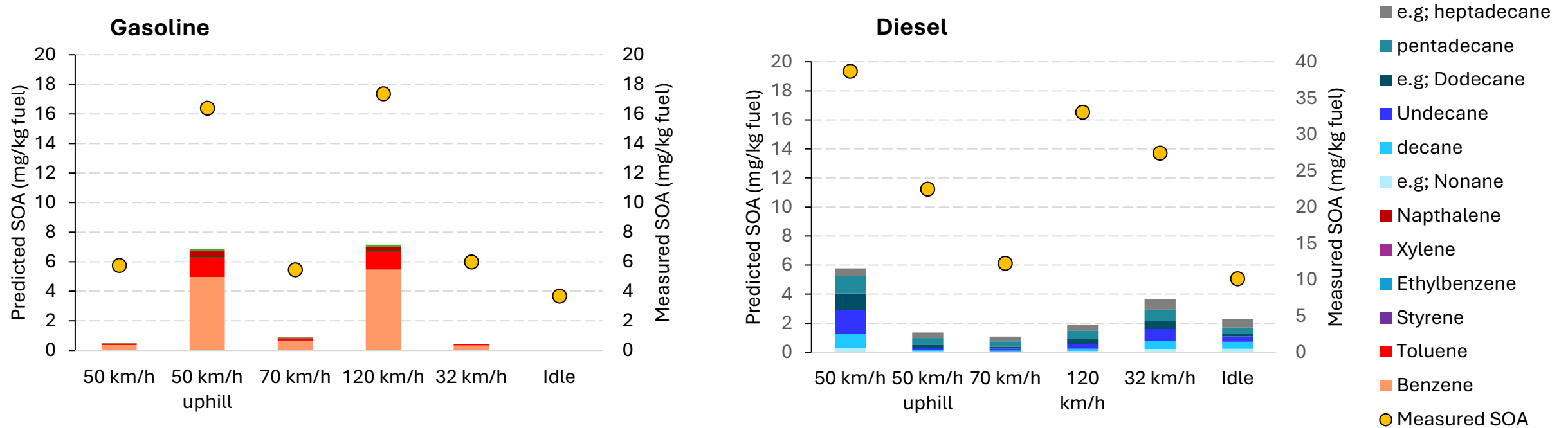
- $\text{H}_3\text{O}^+$  and  $\text{NO}^+$  reagent ion modes were used in PTR to measure VOC with varying proton affinities
  - ~ 100 molecular formula assigned and quantified
- Gasoline:
  - Highest aromatic hydrocarbon emissions
- Diesel:
  - Alkenes & carbonyls
  - alkanes identified at  $\text{NO}^+$  mode
- CNG: cleanest in terms of NMVOCs





# Results - secondary aerosol formation

## SOA predicted vs SOA measured

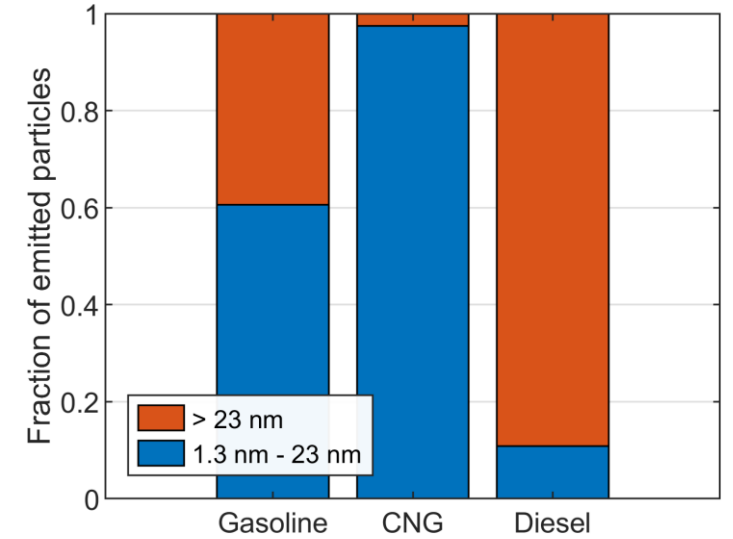


- Aromatic VOC:s identified as the main precursor group for SOA in gasoline and CNG
- Long-chain aliphatics the main identified SOA precursor for diesel



# Conclusions

- Low primary particle emission factors on all metrics (when compared to other transportation sources)
- Large fraction of particle number emissions outside of the regulation range (<23 nm) for CNG and gasoline cars
- Byproducts from the exhaust gas after-treatment systems strongly influence emissions of EURO6 cars
  - Diesel: Considerable particle number emissions from DPF regeneration
  - CNG & gasoline: Ammonia emissions
- Secondary aerosol formation increases particle mass 2-3 orders of magnitudes for passenger cars





# Thank you / Acknowledgements:

P. Simonen, A. Hartikainen, M. Ihalainen, T. Kokkola, M. Somero, P. Yli-Pirilä, G. Mustafa, H. Oikarinen, L. Ala-Hakuni, A. Mukherjee, M. Shahzaib, T. Streibel, D. Shukla, M. Rohkamp, Q. He, S. Piel, S. Jeong, U. Etzien, A. Das, L. Schwalb, T. Gröger, A. Barth, M. Sklorz, B. Gündling, M. Kalberer, B. Buchholz, A. Hupfer, T. Adam, H. Czech, T. Hohaus, M. Saraji-Bozorgzad, P. Jalava, B. Rothen-Rutishauser, O. Hänninen, S. Di Bucchianico, P. Karjalainen, J. Øvrevik, R. Zimmermann



UEF// University of Eastern Finland



UNIVERSITY OF EASTERN FINLAND



Funded by the European Union

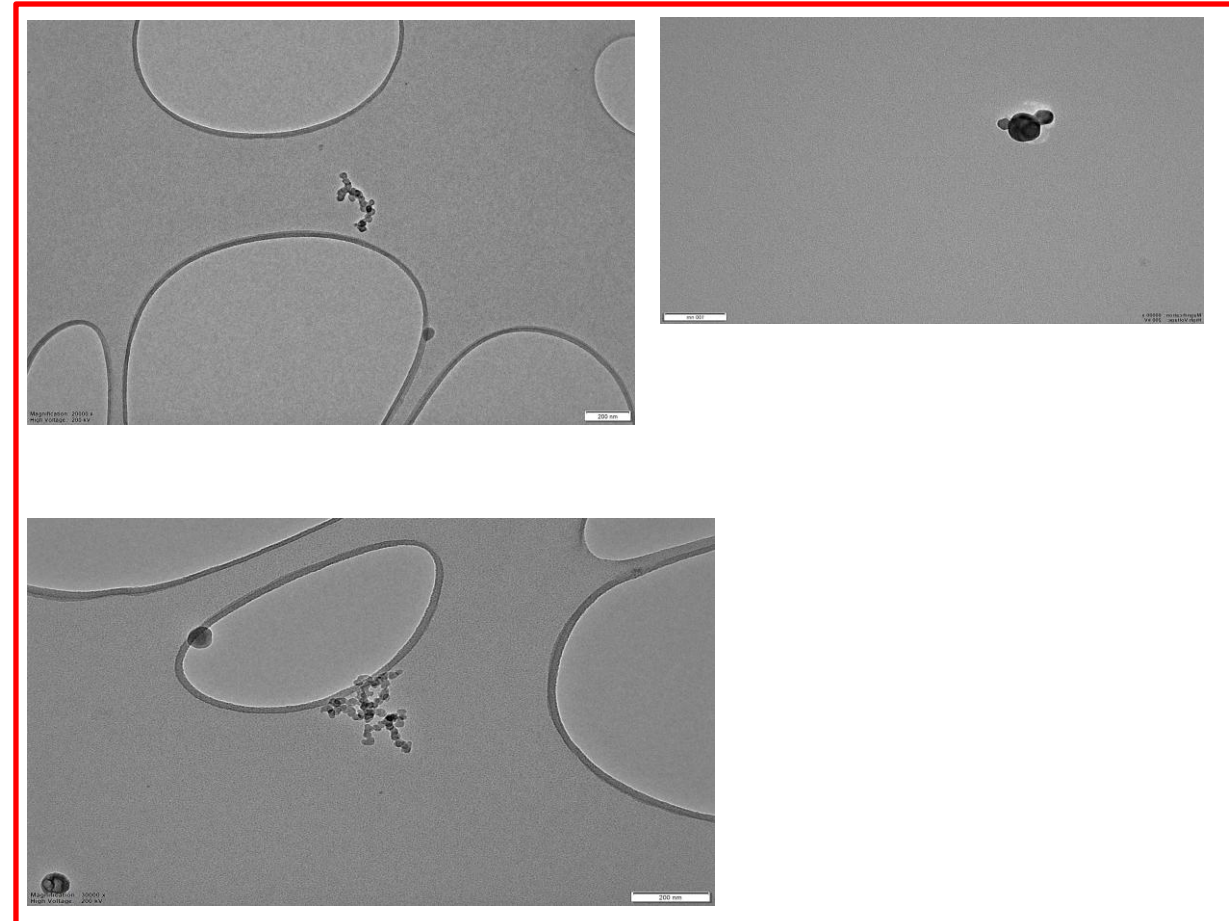
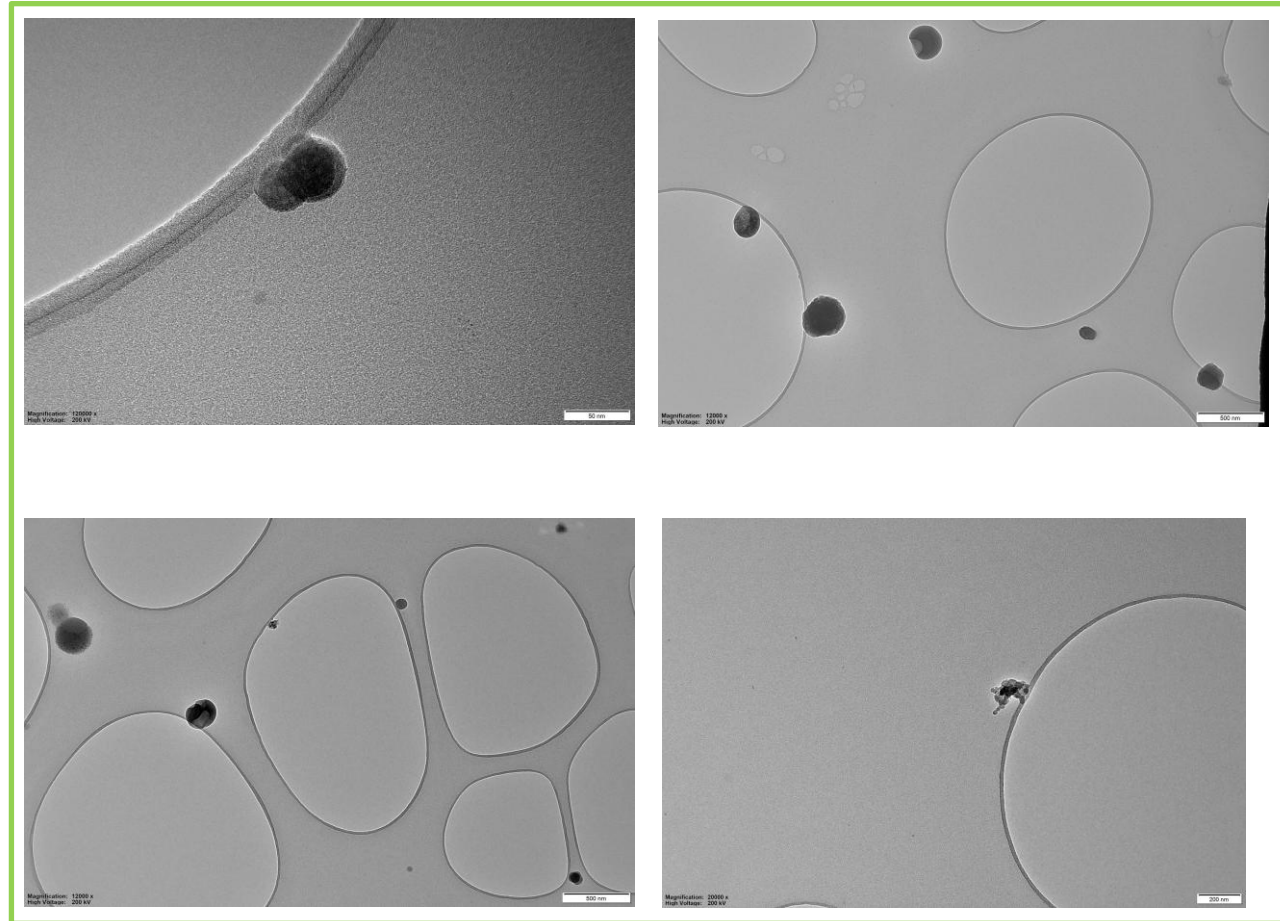
This work was supported by EU Horizon2020 project ULTRHAS (agreement 955390).



# Primary particle morphologies

CNG **Primary** (full cycle)

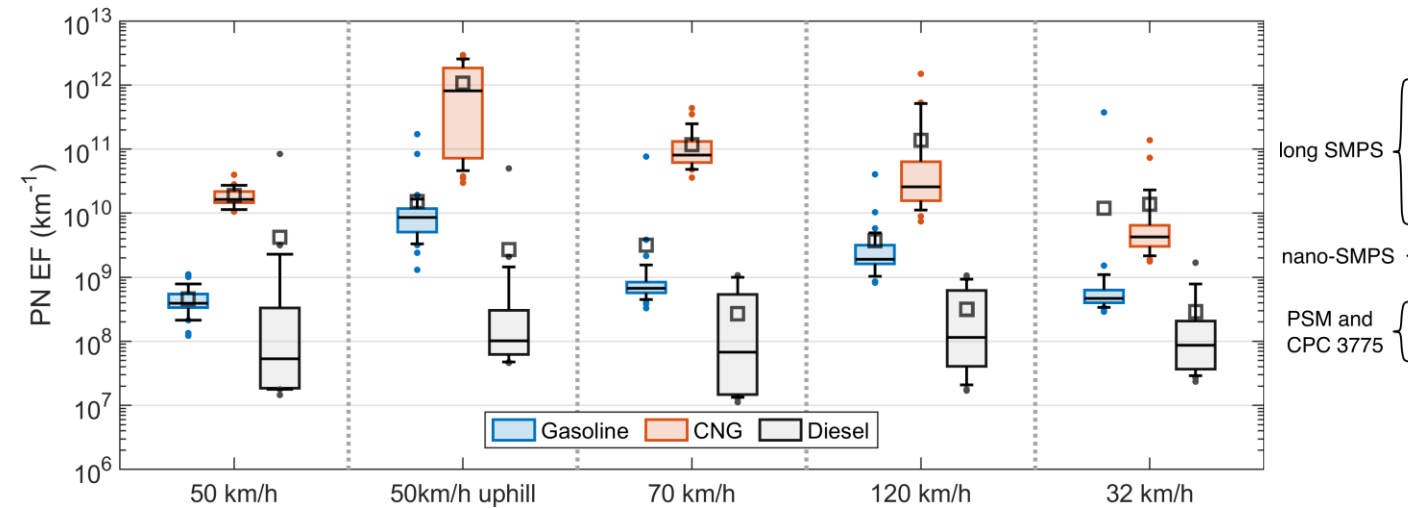
Gasoline **Primary** (full cycle)





# Results – fresh particulate emissions

Particle number EFs for each driving phase:



CNG particle size distributions:

