High Time-resolved SOA-formation Potential of Emissions from GDI engines

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Why we want to age the emissions (and how)

Aging forms secondary organic aerosol (SOA) through photo-oxidation in the atmosphere.

Important because: Filter samples taken by means of the reference method do not fit with atmospheric observations. Wood Burning example:
- At the test bench: OC/EC < 1
- In the atmosphere: OC/EC ~ 5 (Switzerland)
- Estimations: 50% of ambient OC comes from SOA (Lanz, ACP **7**, p. 1503, 2007).

By irradiating the sample with high intensity UVC and UVA light we create a high concentration of oxidative species (O_3, OH, NO_3), achieving the equivalent of days of atmospheric aging within 10 seconds.

OC = (particle-bounded) Organic Carbon
EC = Elemental Carbon (i.e. soot)

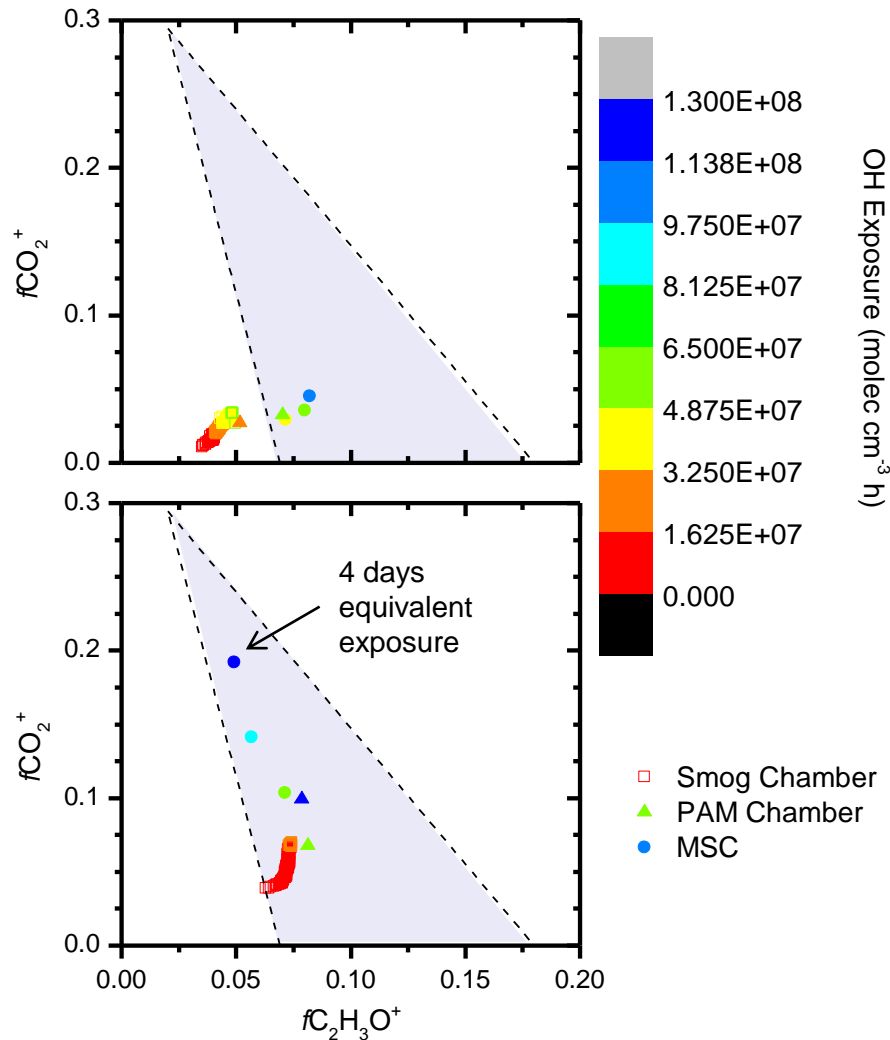## Micro Smog Chamber

Volume: 150ml
Flow: 1 lpm
Residence time: ~10 Seconds
O_3: up to 100ppm (atmosphere < 60ppb)
Light: UVC (20W) and UVA (30W)

- Dimensioned for slightly diluted emissions (e.g. 1:10) from wood burning appliances.
- No time resolved chemistry
- Oxidation degree can be adjusted through flow, length, or light intensity.

Keller & Burtscher, 2012, Aerosol Sci. 49 pp. 9-20

Wood burning example (SOA)

- Micro smog chamber (MSC) SOA compares well to the chemical signature of ambient observations.

- For overlapping OH-exposures (i.e. similar amount of aging), the chemical signature after the flow-tube reactors is similar to smog chamber results.

- The extremely fast oxidation in flow reactors (3 orders of magnitude faster than in the atmosphere) does not seem to alter yield or composition.

Bruns *et al.*, AMT 8, 2315-2332, 2015

The Micro Smog Chamber (MSC) in a nutshell

- The MSC is a conditioning system that can oxidize precursor substances and form secondary aerosol within a few seconds.

- Goal: Better understanding of the processes that contribute to secondary aerosol formation.

- The MSC produces SOA with an oxidation degree at the upper level of atmospheric observations. The chemistry of SOA is similar to what is produced at the end of smog-chamber experiments.

- In the MSC, <u>secondary aerosol formation is driven by nucleation</u> over condensation. The resulting particle size depends upon the concentration of the precursor substances.

- As a consequence, the nucleation mode of secondary aerosol may be difficult to distinguish in systems that produce low concentrations of precursor substances (also in systems that produce other nucleation particles). In this cases, we recommend using the MSC on filtered emissions.

Setup for On-line Secondary Emission Measurements (Micro Smog Chamber)

**Framework: GasOMeP** (Gasoline Organic & Metal Particulates) project
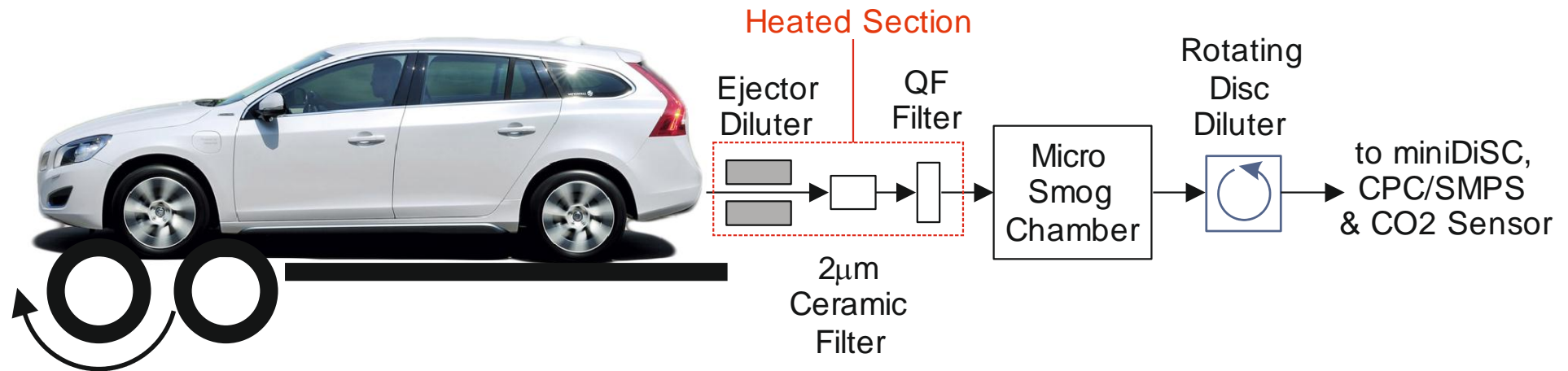

- The CPC was used during transient measurements (world-wide light duty test cycle, WLTC). The nanoSMPS was used during idling or on steady state cycles.
- CVS sampling is not possible due to secondary aerosol precursors in the CVS dilution air.

Reference GDI - 85% Ethanol
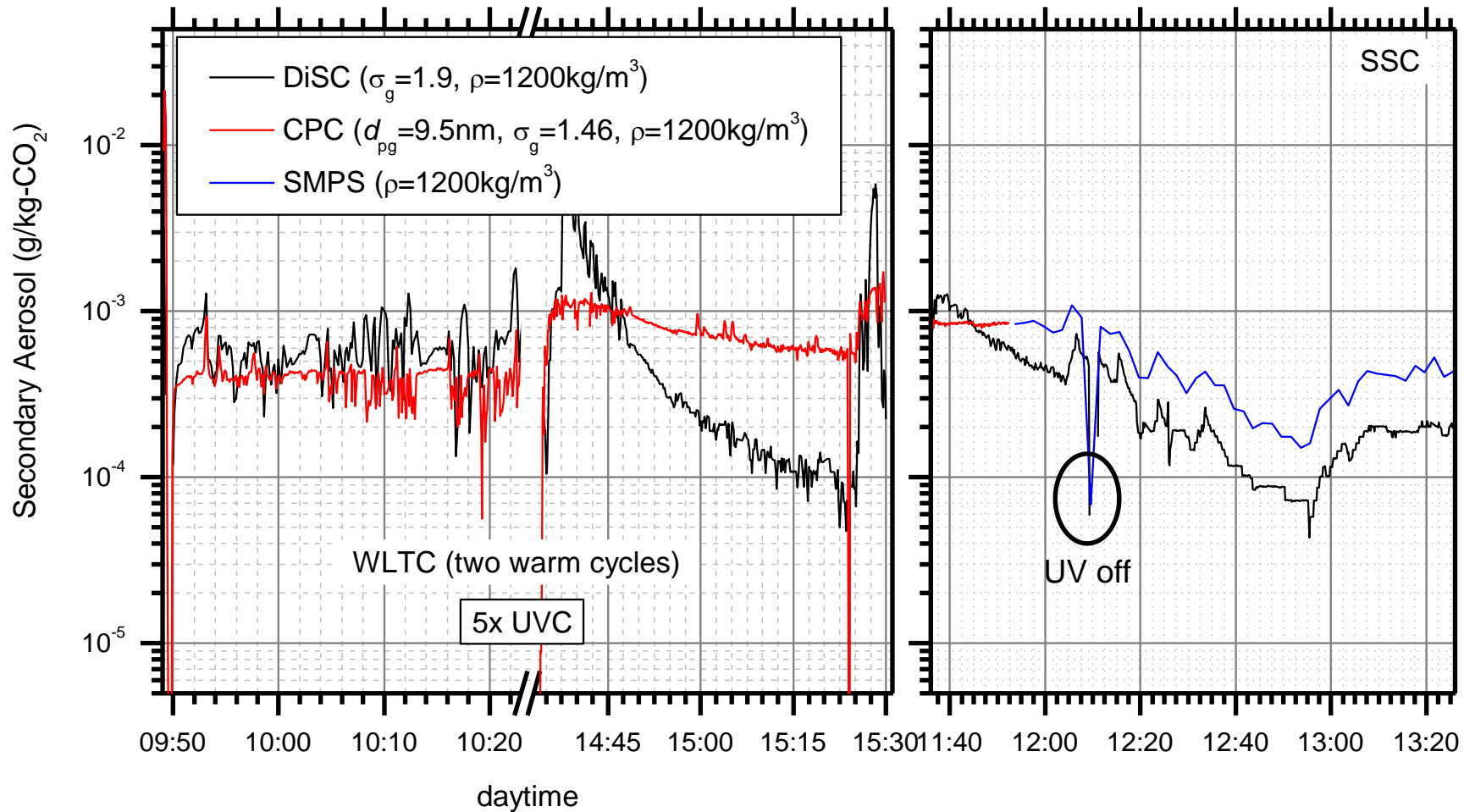
First approach, using default instrument parameters:

- Good agreement between nanoSMPS and CPC (dpg and sg obtained from SMPS data during Steady State Cycle).
- Particles too small for miniDiSC.
- Good separation between background (i.e. UV light off) and cycle data.
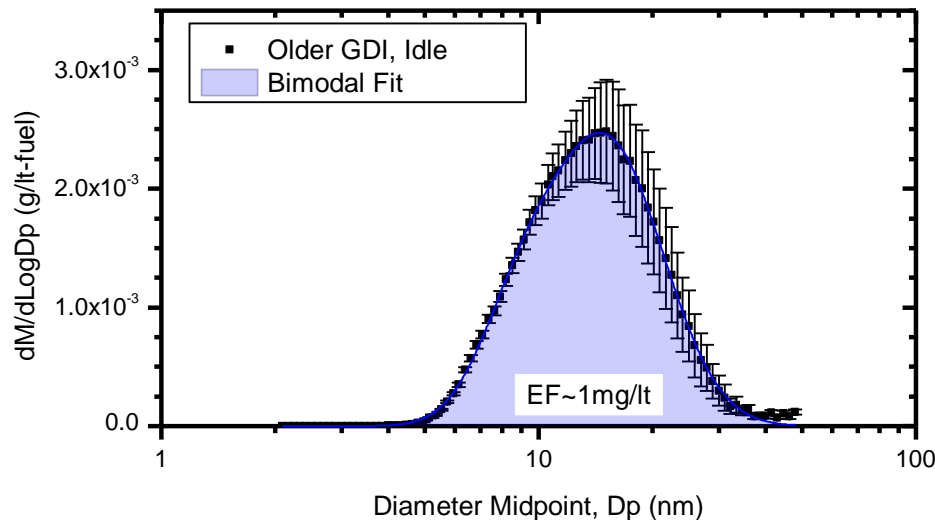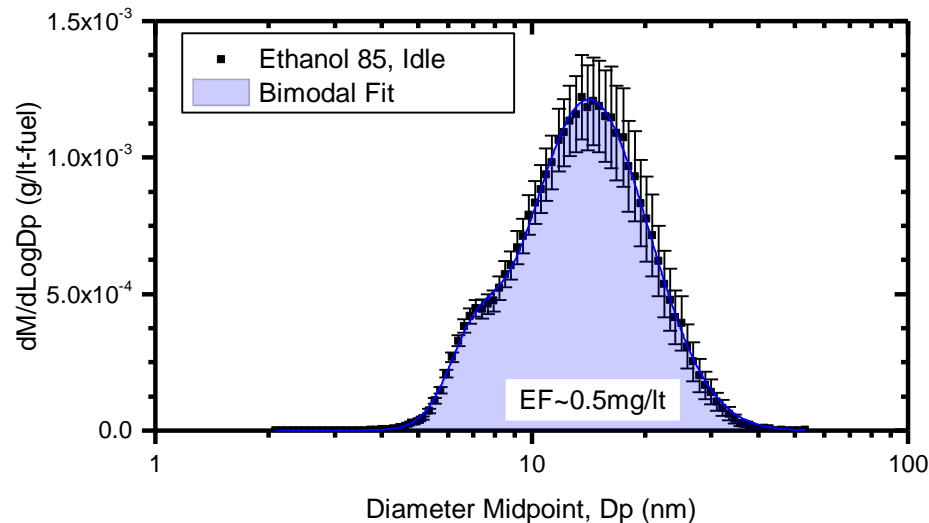
Emission Factor Determination

- The mass emission factor is calculated from the average size distributions (during idling or steady state).

- An average mass per particle is then estimated and used to compute the emission factor during transient cycles.

- Assumptions required are particle density (ρ=2000kg/m^3 from previous wood burning studies) and CO_2 production per liter fuel (e.g. 1.64 Kg-CO2/lt-E85 and 2.35 Kg-CO2/lt-Gasoline*).

- Size distributions always appear to be bimodal. This is more pronounced for number size distribution, specialy for the ethanol mix.

* from the molecular formula of ethanol and the recommendations under: http://www.eia.gov/oiaf/1605/coefficients.html#tbl2

Reference GDI - Euro 5 (Gasoline)
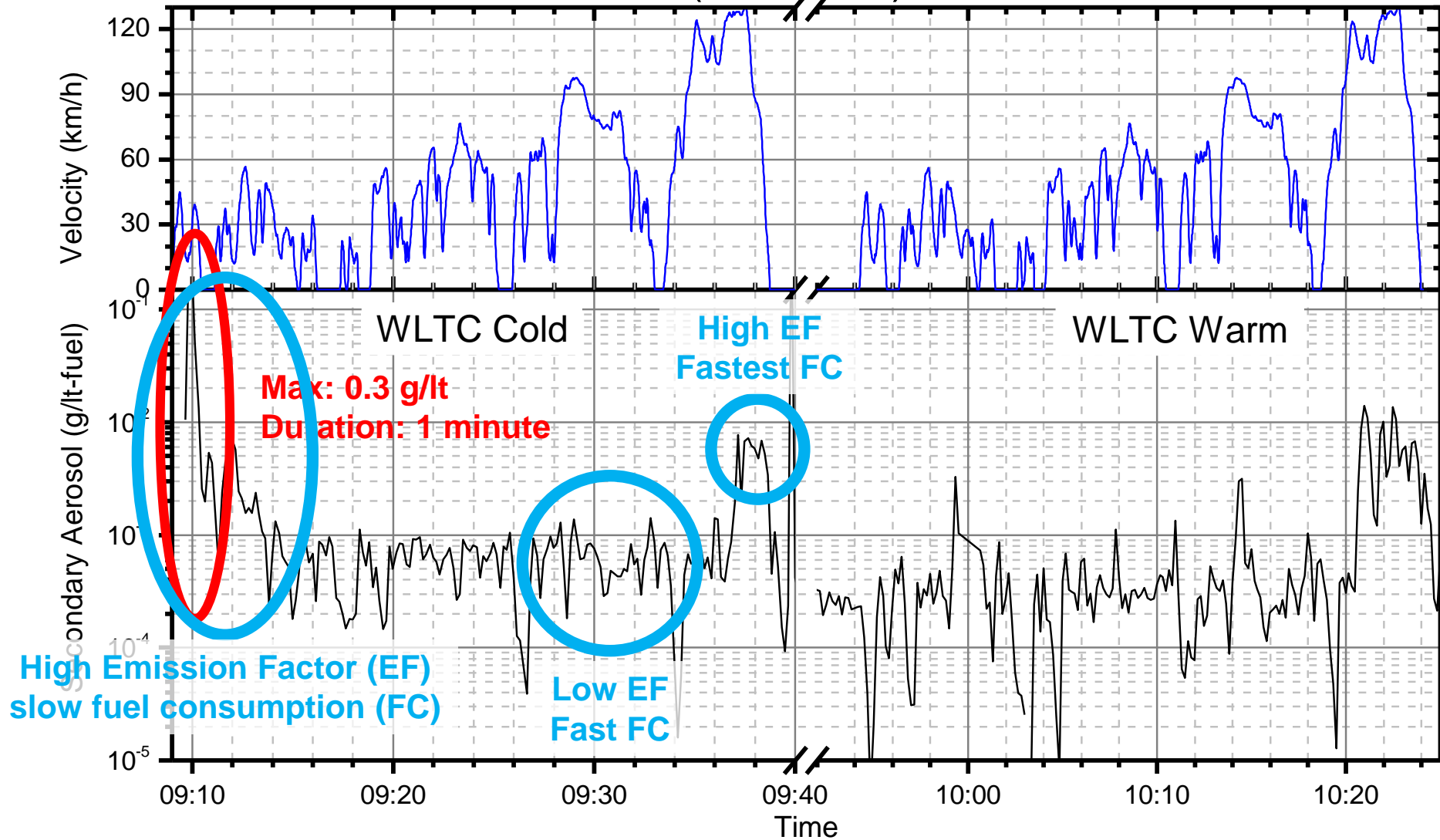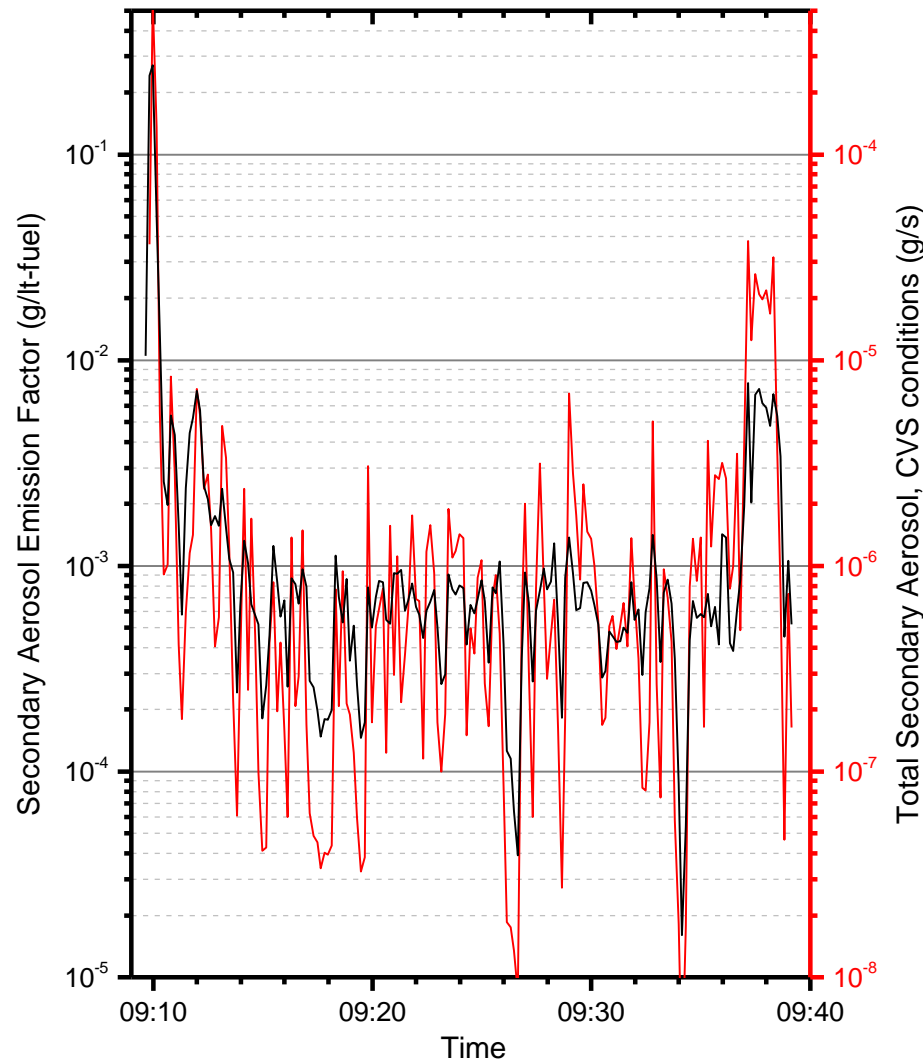
Calculating a cycle-average value

1. Using CVS-corrected data (i.e. taking into account exhaust flow)

2. Using an average emission factor (EF, e.g. ratio of secondary aerosol to CO_2 or to fuel consumption)

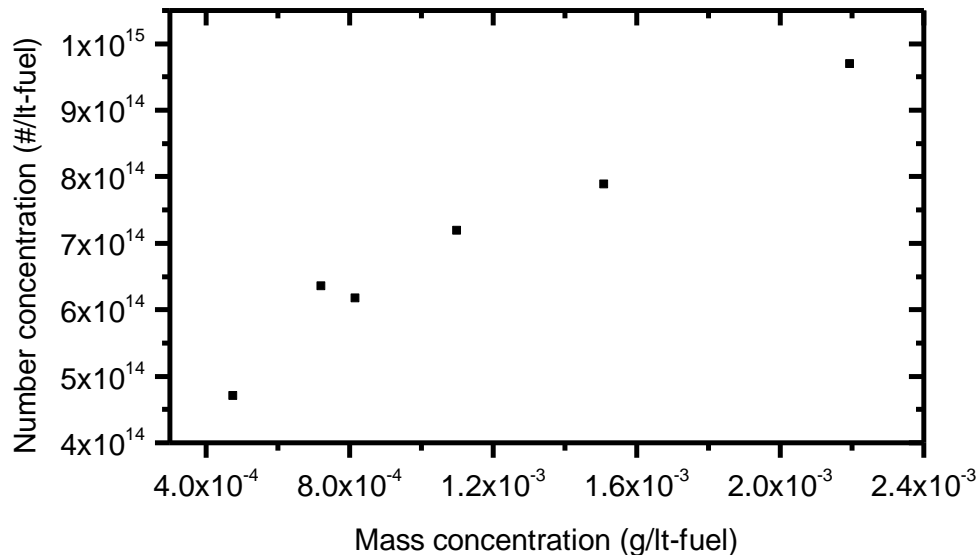3. "Bag sampling method" on partial flow (i.e. non-CVS).

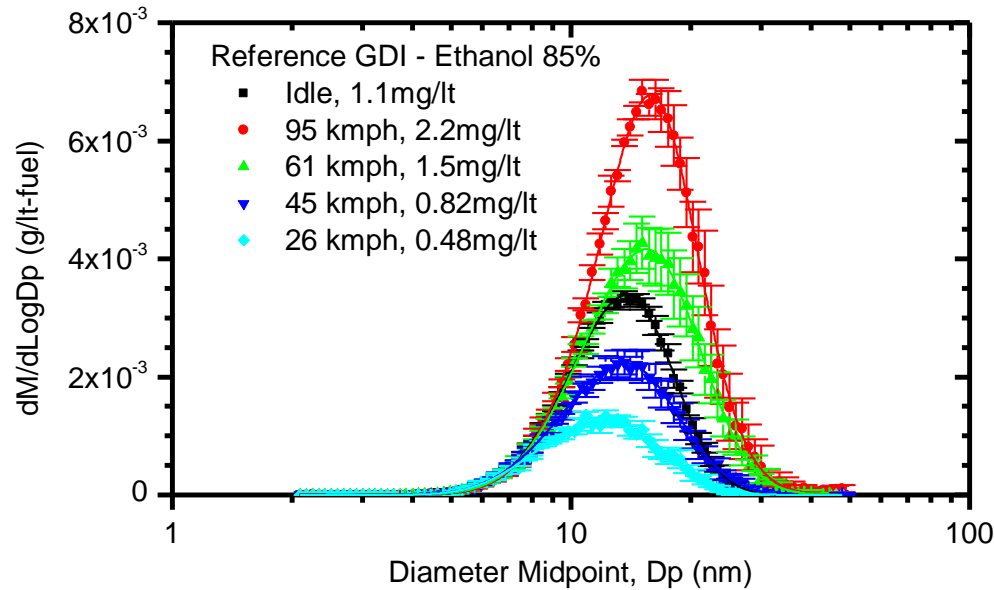| Method	Cold Cycle [mg/km]	Warm Cycle [mg/km]	Cold / Warm
CVS	0.68	0.33	2.1x
EF	0.58	0.12	4.8x
Bag	0.26	0.13	2.0x

Older GDI - Euro 3 (Gasoline)
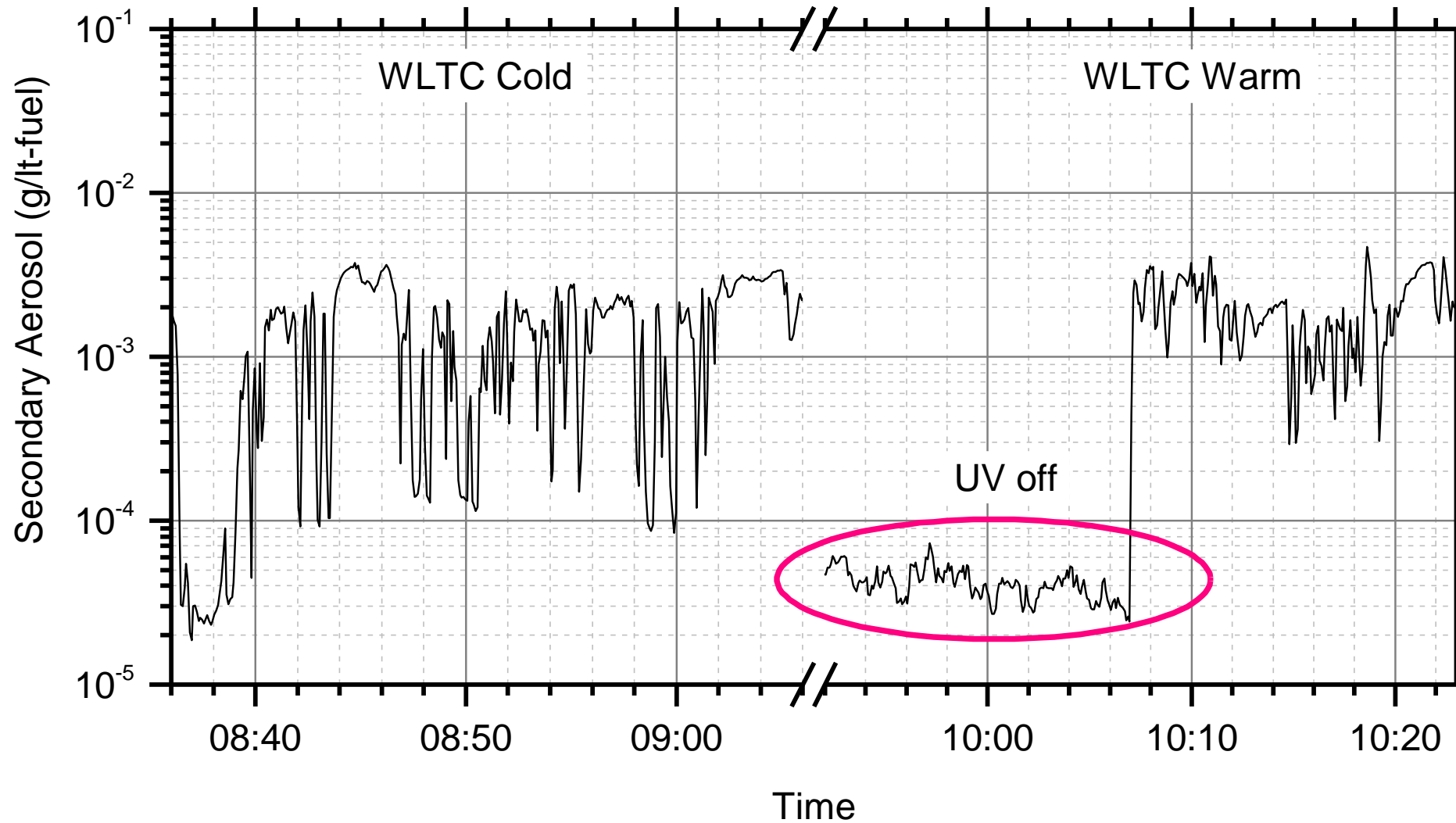
How about Diesel?

- Only one diesel vehicle tested so far (Euro 5)

- Secondary aerosol production under the detection limit of our system.

Questions that are still open

How does MSC results compare against smog-chamber and PAM chamber measurements?

Can transient cycles be predicted based on results from steady state? (comparison against PAM chamber may help answer this)

Is linearity a good approximation?

What causes the bimodal size distribution? Maybe a mixture of SOA and other secondary aerosol?

What about loses in the system?

Summary

- GASOMEP is the first project that uses the Micro Smog Chamber to investigate Secondary Aerosol production from vehicle emissions.

- Low precursor concentrations require working with filtered emissions.

- The typical particle size for the secondary aerosol is very small (mode $d_p \sim 10nm$) due to fast oxidation and the absence of seed aerosol. As a result, only few instruments (e.g. nanoSMPS, UCPC, etc) can be considered as detectors.

- Emission factors calculated so far are of the order of 10^{-4} g/km (for a WLTC test).

- In general, we observe high cold start emissions for GDI vehicles. The emissions are typically a factor two higher during a cold WLTC test than during a subsequent warm WLTC.

- The secondary aerosol from the tested Diesel vehicle (Euro 5) was below our detection limit throughout the whole cycle.