

Wir schaffen Wissen – heute für morgen

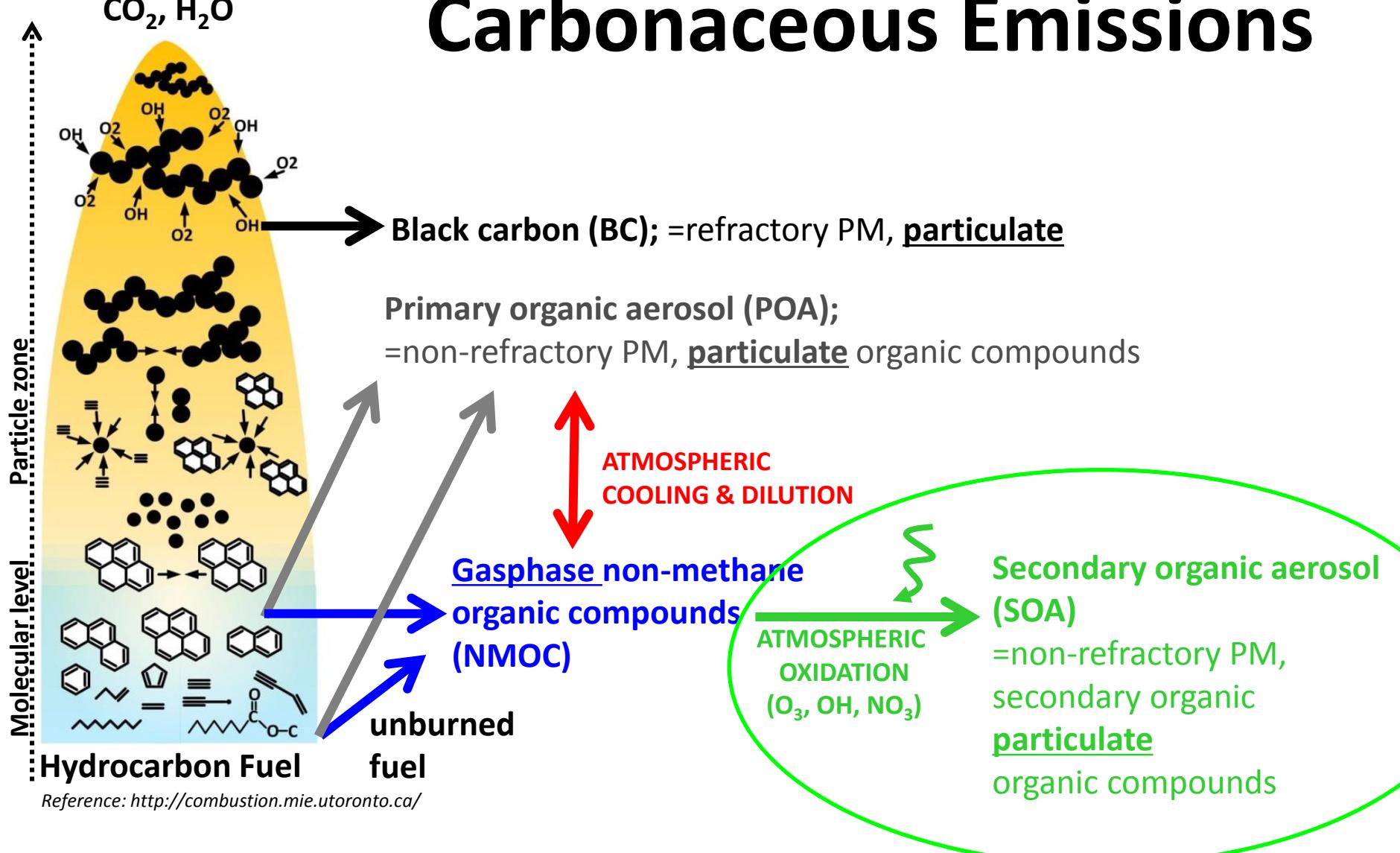
Gas Phase Composition and Secondary Organic Aerosol Formation from Gasoline Direct Injection Vehicles Investigated in Batch and Flow Reactors:

Do gasoline particle filters (GPFs) help us to clean
(secondary) carbonaceous particulate matter?

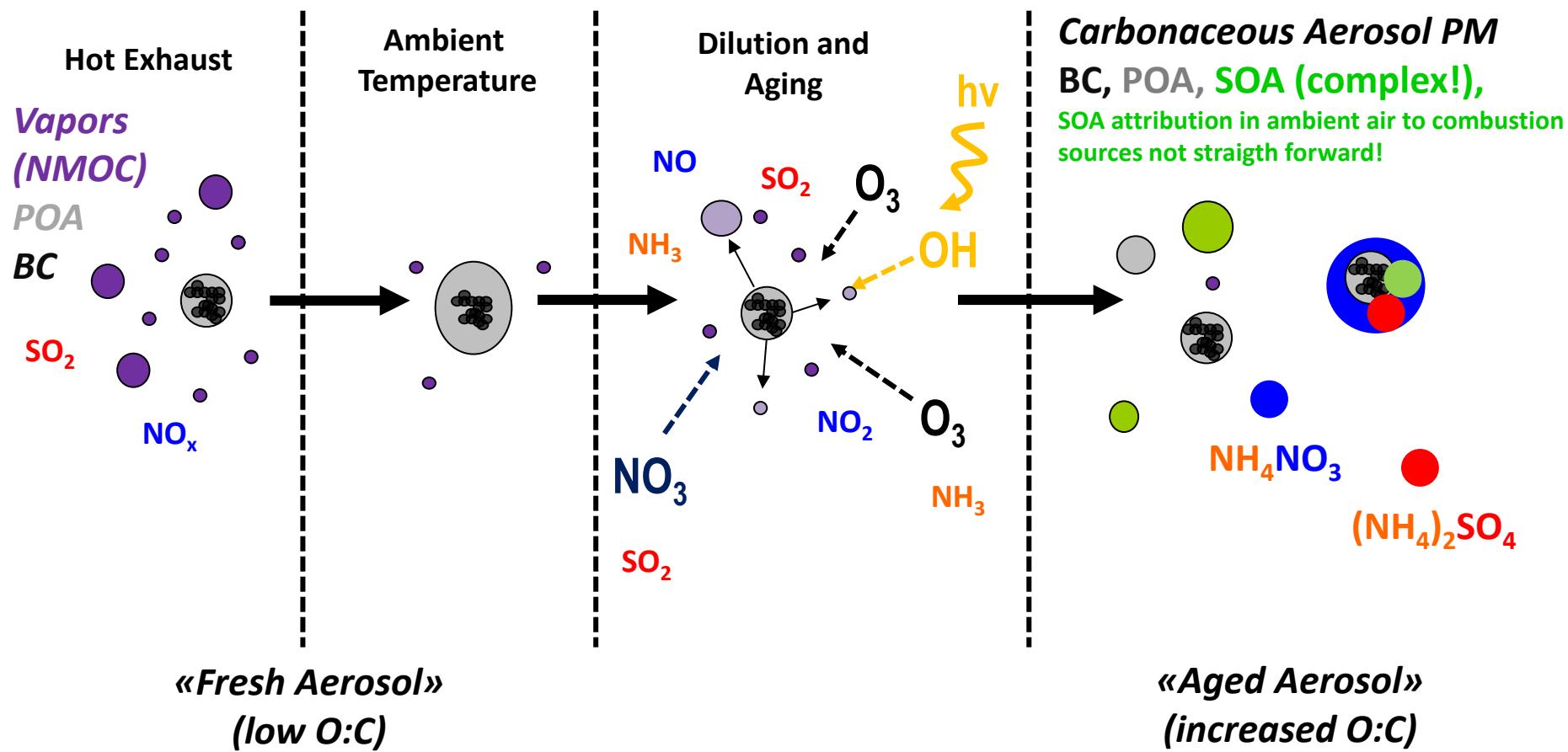
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and the “Gasomep” Project Collaborators from PSI, EMPA, FH Berne/Biel, and FHNW Windisch

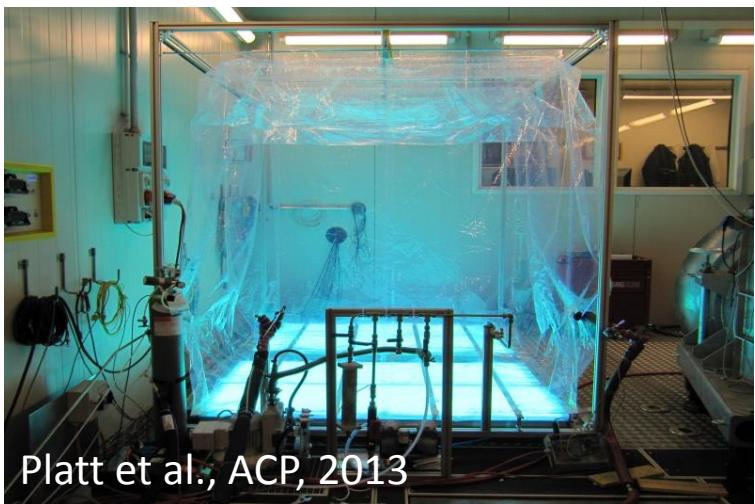
Paul Scherrer Institute, Laboratory of Atmospheric Chemistry, Switzerland

Carbonaceous Emissions



SOA formation





Platt et al., ACP, 2013

PSI Mobile Smog Chamber (SC), $V = 10 \text{ m}^3$

UVA lamps, I_{\max} at $\lambda = 350 - 400 \text{ nm}$
picture taken when installed at JRC Ispra, (2013)

Vehicle testing:

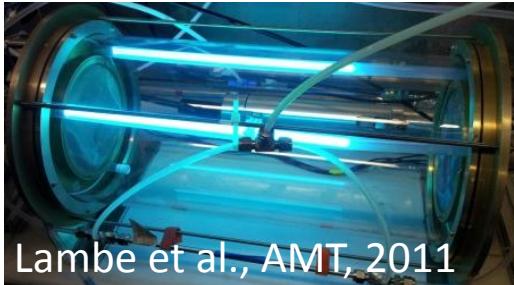
Gasoline Light Duty (Euro 4/5),
including GDI, with 2 prototype GPFs

GDI1: Opel Insignia (Euro 5b+), standard and w/GPF

GDI2: Opel Zafira Tourer (Euro 5b+), standard

GDI3: VW Golf Plus (Euro 4), standard

GDI4: Volvo V60 (Euro 5a, but «looks-like» Euro 6)
standard and w/GPF and w/catGPF

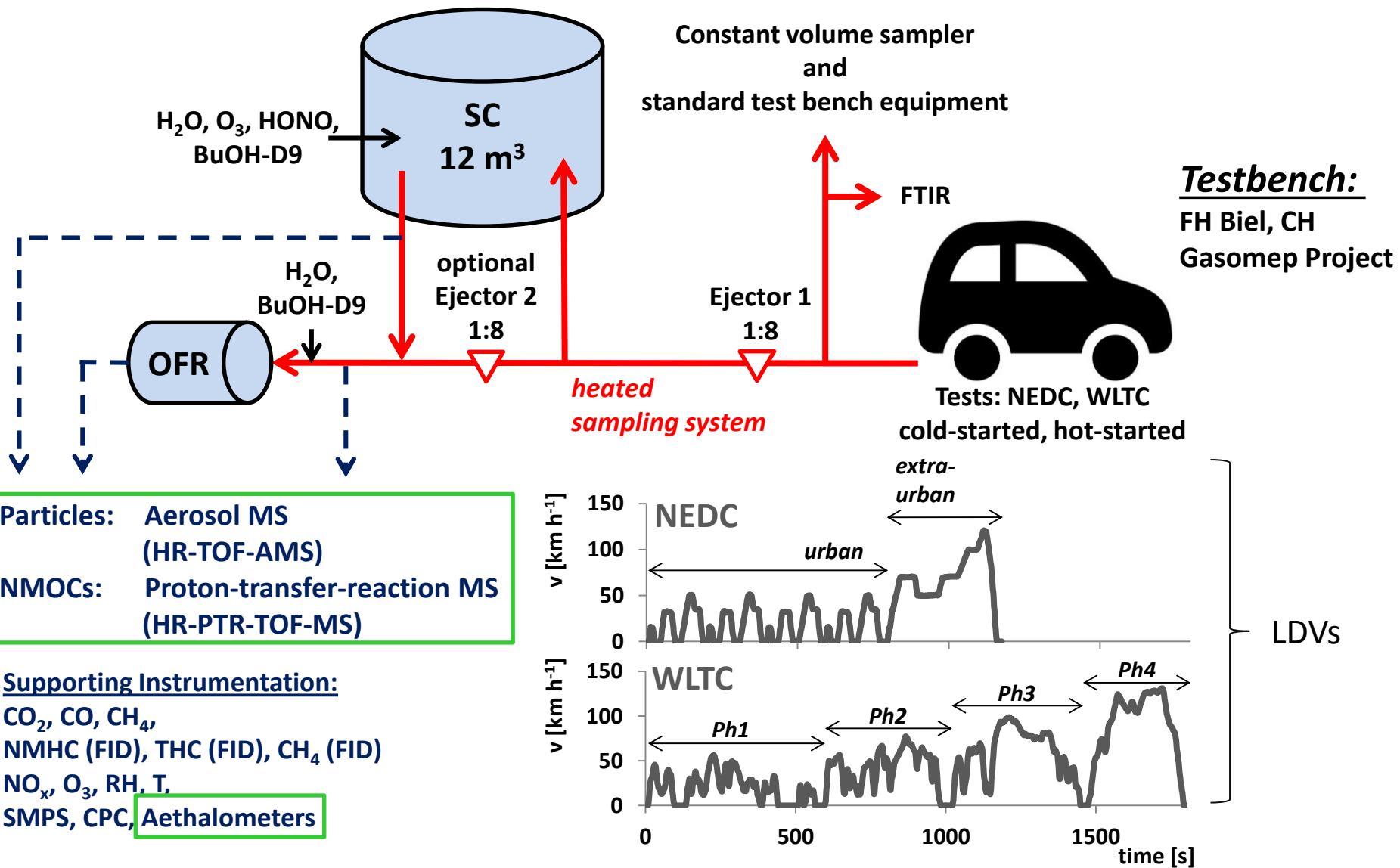


Oxidation Flow Reactor (OFR)
 $V = 0.015 \text{ m}^3$

UVC lamps,
 $\lambda = 185 \text{ nm}$ and 254 nm
«OFR185»

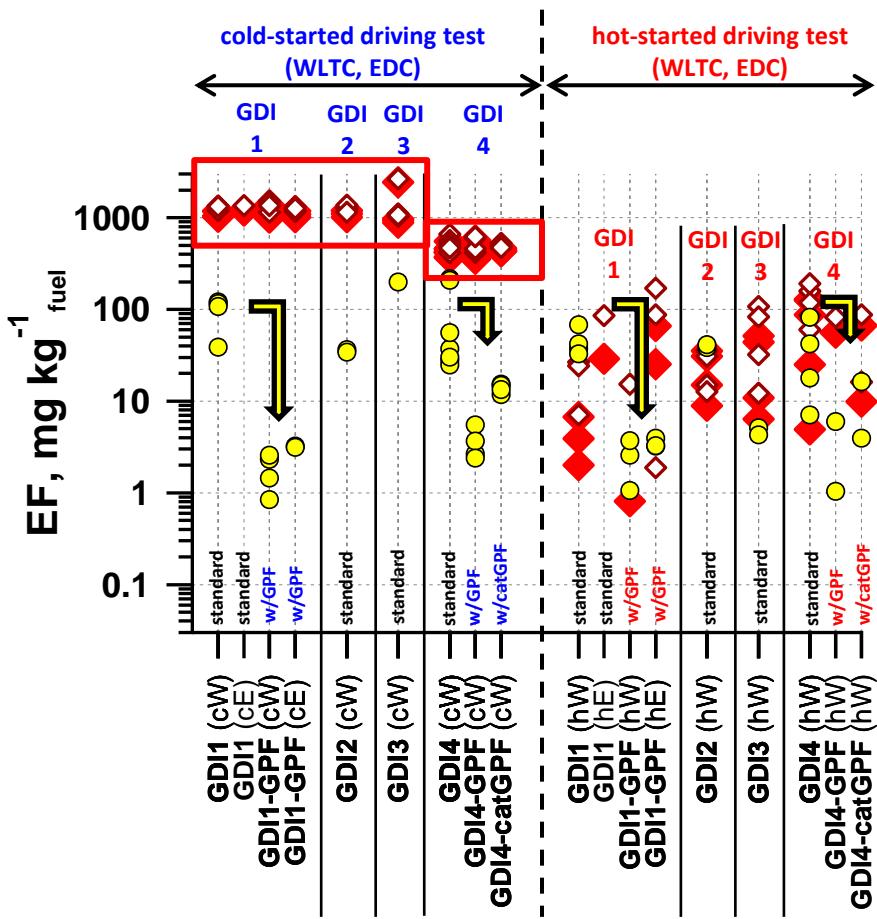


Vehicle installed in Biel, in 2014



RESULTS

GDI emissions: cold vs hot, standard vs GPF



Gaseous emissions:

- ◆ Total HC (CVS, FID)
- ◆ Non-methane HC (CVS, FID)

Particulate emissions:

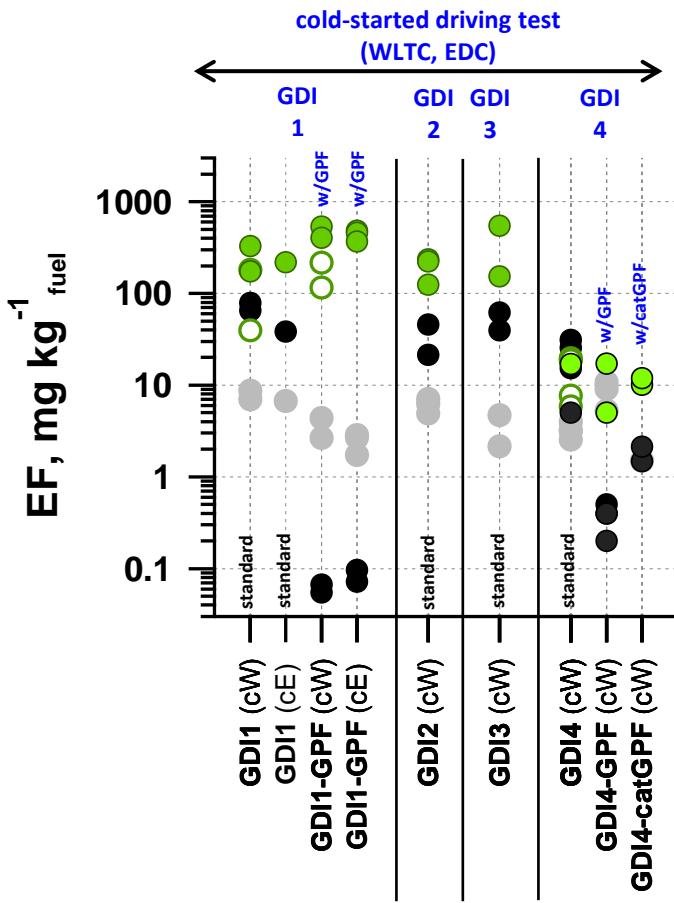
- ◆ Primary PM (CVS, gravimetric)

Conclusions:

- cold-started cycles NMHC and THC > hot-started
- cold-started cycles PM ~ hot-started
- cold-started WLTC similar to EDC (NMHC, PM)
- hot-started WLTC «seems» < EDC for 1 vehicle (NMHC)
- **GDI4 is a «Euro 6-alike»:**
similar HC emissions as recent Euro 6 results:
 - NMHC significantly reduced during cold-started cycles (factor 3), but no difference during hot-started cycles.
 - Gravimetric primary PM not reduced!
- **GPF and catGPF:**
 - No influence on NMHC and THC emission factors
 - Significant reduction in particulate matter!

=> How about secondary organic aerosol (SOA)?

GDI emissions: cold vs hot, standard vs GPF



Particulate emissions:

- Primary Black Carbon (BC, SC): refractory
- Primary Organic Aerosol (POA, SC): non-refractory

SOA {

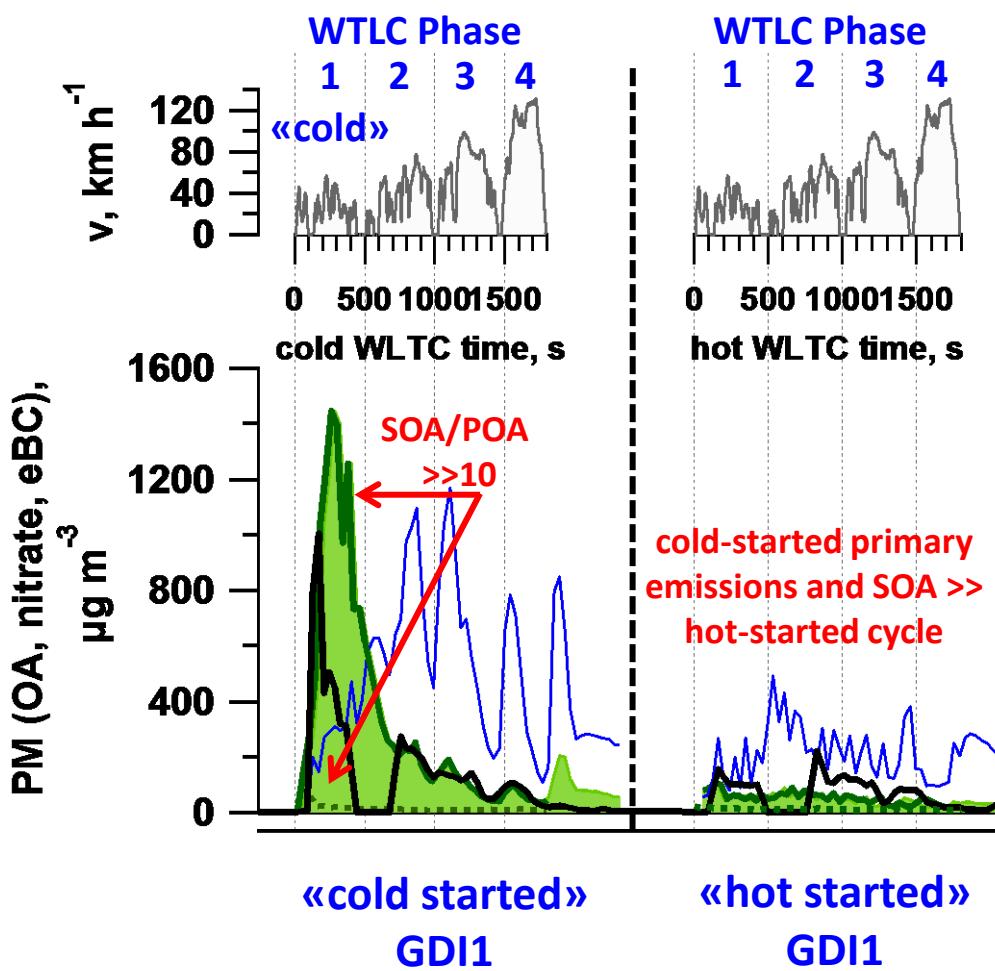
- Secondary Organic Aerosol (SOA)
- Secondary Organic Aerosol (SOA)

Conclusions:

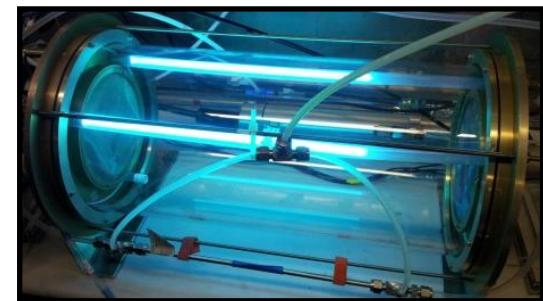
- **Refractory PM (Black Carbon) >> Non-refractory primary POA** (primary PM dominated by Black Carbon (also «Elemental Carbon»)).
- **GDI4 («Euro 6»-alike):**
 - no reduction in BC or POA compared to GDI1-3
 - SOA reduced in analogy to reduced NMHC emissions!
- **GPF and catGPF:**
 - Significant reduction in refractory PM (Black carbon)!
 - No reduction in POA (gaseous when passing GPF)
 - No influence on SOA (gaseous precursor pass by the GPF)

=> Which driving/engine condition is causing the SOA formation?

Time-resolved SOA as function of WLTC

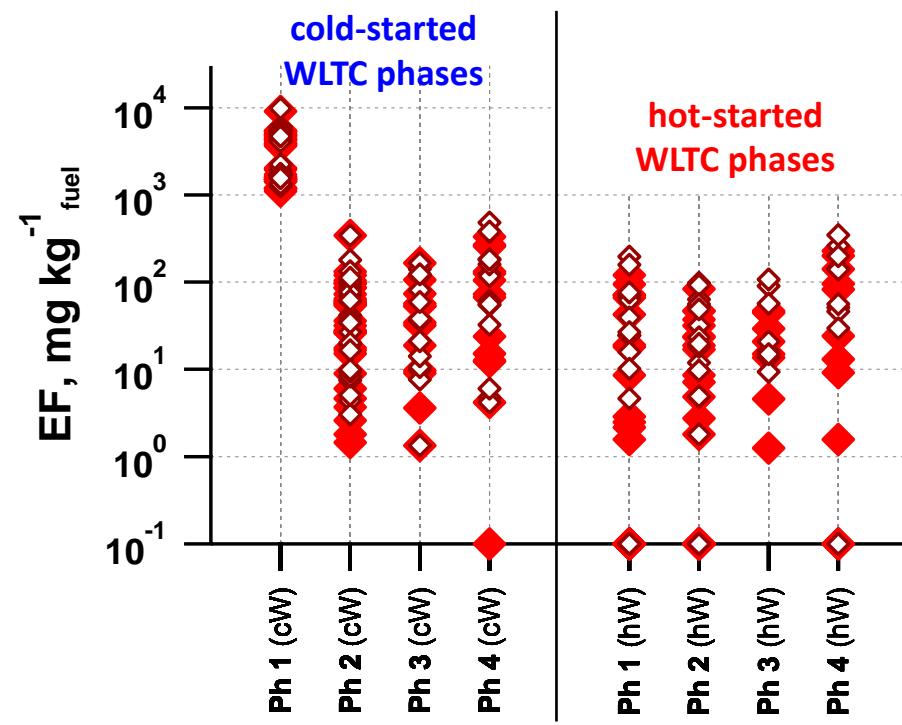


OFR

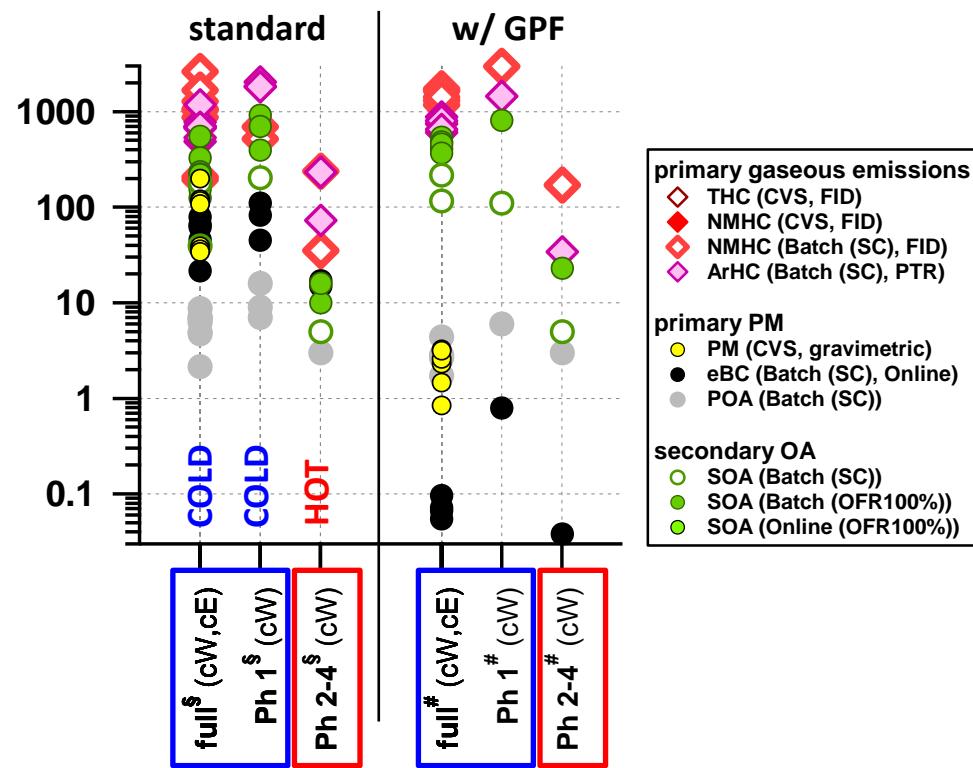


- WLTC speed profile
- OFR outlet (UV on, secondary)
 - OA profile during WLTC cycle
 - OA
 - NO₃
- OFR outlet (primary)
 - POA reference (UV off)
 - eBC

GDI emissions as function of test cycle phase (i.e. driving behavior and engine condition)



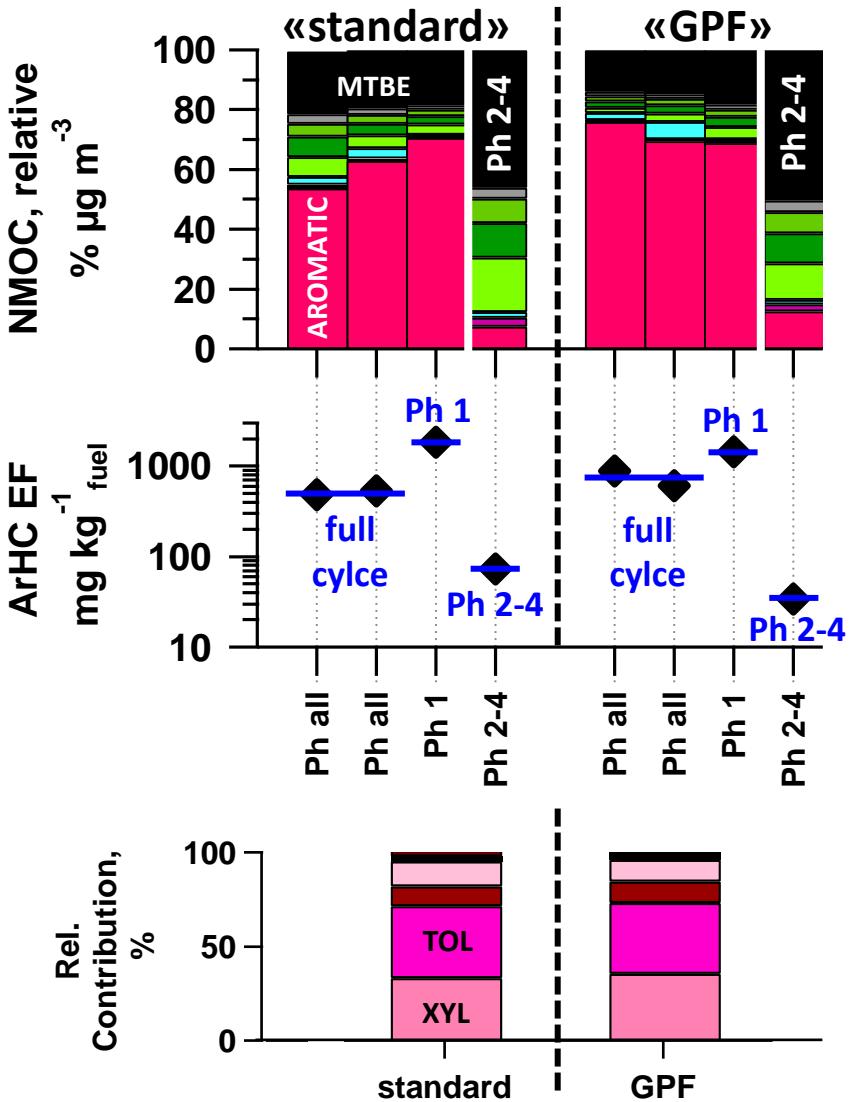
*cold-started (cW) vs hot-started (hW)
WLTC (GDI1-4)*



[§]*GDI1-3 standard vs [#]GDI1 w/GPF
cold-started WLTC (cW) and EDC (cE)*

Cold-started emissions (especially engine start-up) dominate the total emissions over the driving cycle!
=> Are aromatic hydrocarbons important precursors for SOA under those conditions?

Cold-start and GPF influence on NMOC

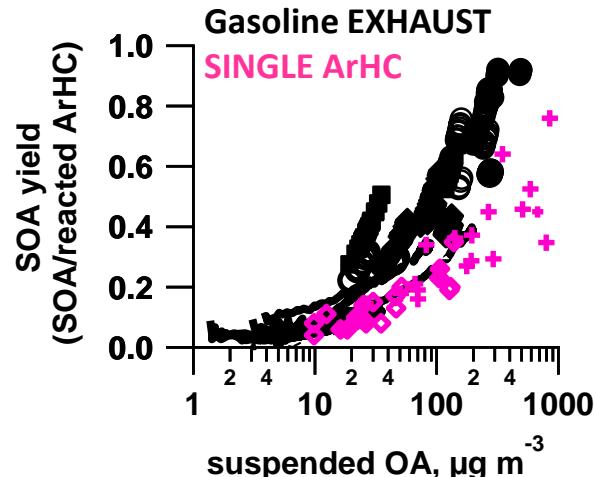


HYDROCARBONS
structurally not assigned
 ■ likely short-chain aliphatic/fragments (*m/z* 41, 43, 57), and unassigned compounds
 ■ likely aliphatic

AROMATIC HC
■ e.g. alkyl benzenes
■ O-containing, e.g. benzaldehyde

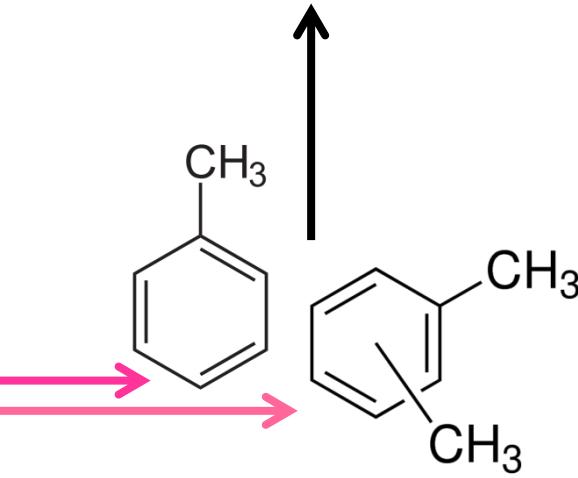
OXYGEN CONTAINING
■ Carbonyls, e.g. HCHO
■ Acids, e.g. CH₃COOH
■ Others

NITROGEN CONTAINING
■ e.g. CH₃CN

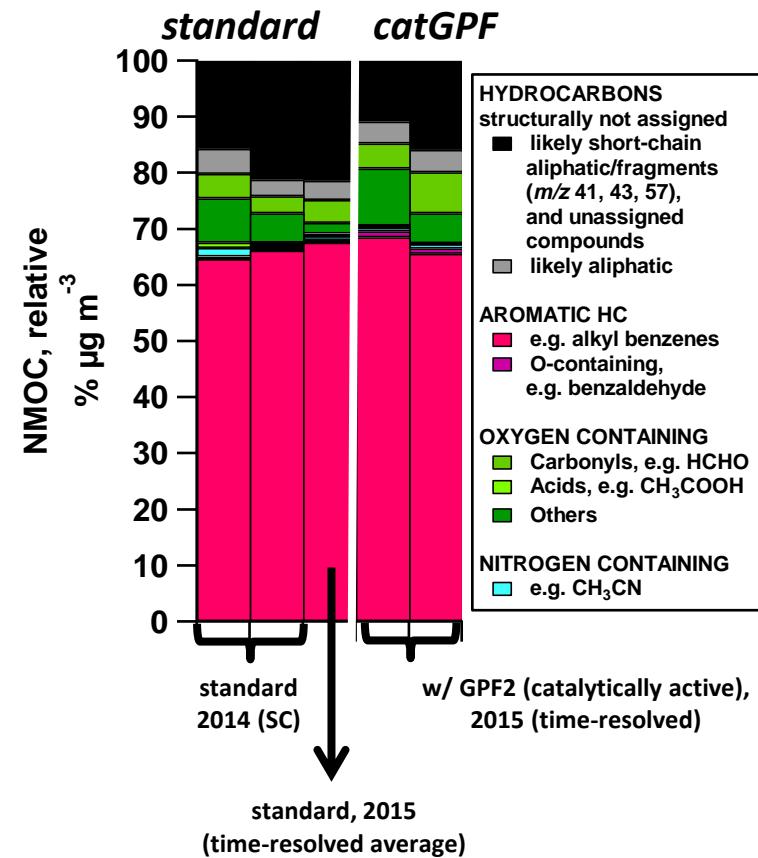
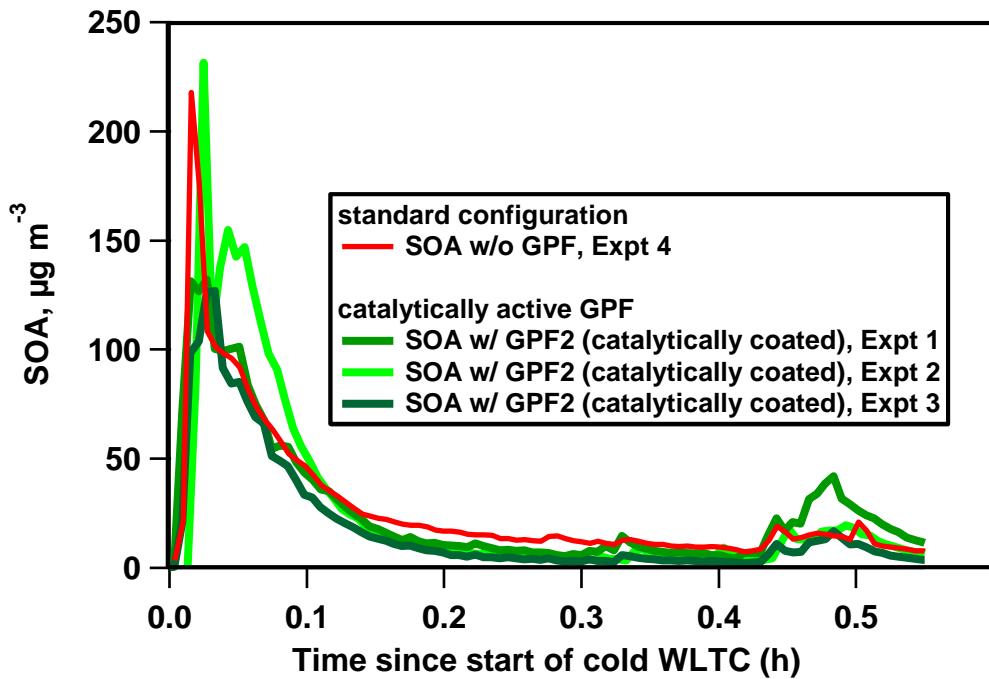


Alkylated Benzenes (> 95% of total AROMATIC HC)

- BENZENE
- TOLUENE
- XYLEMES, ETHYLBENZENE
- C₃-ALKYL-BENZENES



Catalytically coated GPF does not influence NMOCs and SOA either.



Conclusions

- **DOC/DPF: very effective for BC, POA**
- **Modern diesel SOA is low (precursors are removed by after-treatment system)**
- **GDI technology moves LDV exhaust towards higher BC emissions; SOA a big contributor too**
- **GPFs can significantly reduce BC and hence total PM emissions (high BC/POA)**
- **(Retrofitted) GPF (catalytically coated or uncoated) does not influence the NMOC fraction, SOA precursors and SOA**
 - most SOA precursors are emitted when after-treatment system is cold
 - only few aromatic compounds appear dominant
- **Cold-start effect remains an issue also with (cat)GPF!**
 - Lower light-off temperatures for catalytic converters, hydrocarbon traps for extremely volatile material (monocyclic aromatics), or aromatic-free fuel are needed in addition to GPFs.
 - Speciated NMOC fraction needs attention in regulatory testing!
 - Euro6 might already solve parts of the NMHC issue, but more work is needed!

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Thank you!



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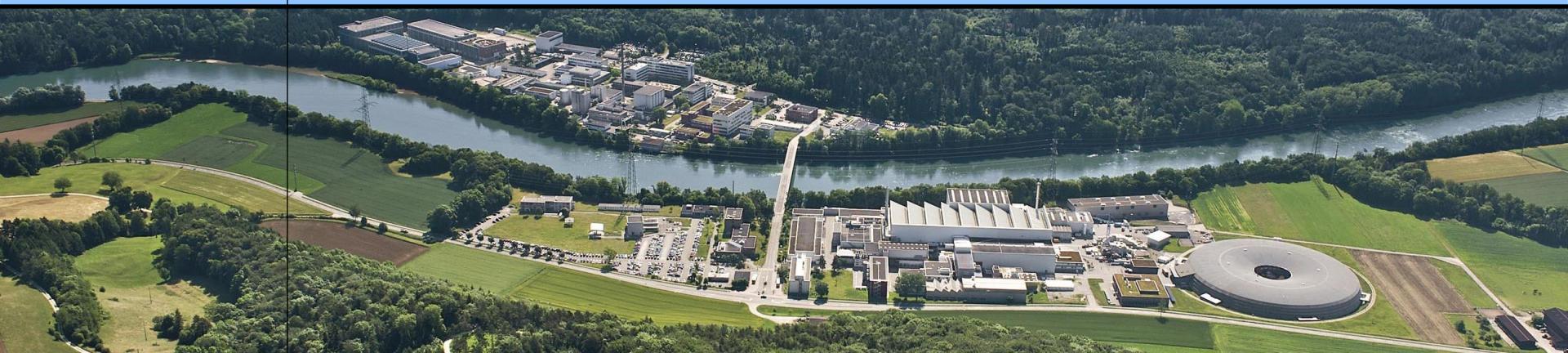


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References:

Pieber et al., (in preparation), 2017

Platt et al., (accepted), 2017



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QUESTIONS?

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