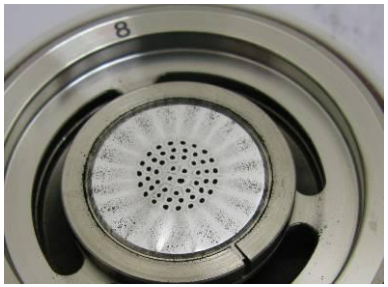
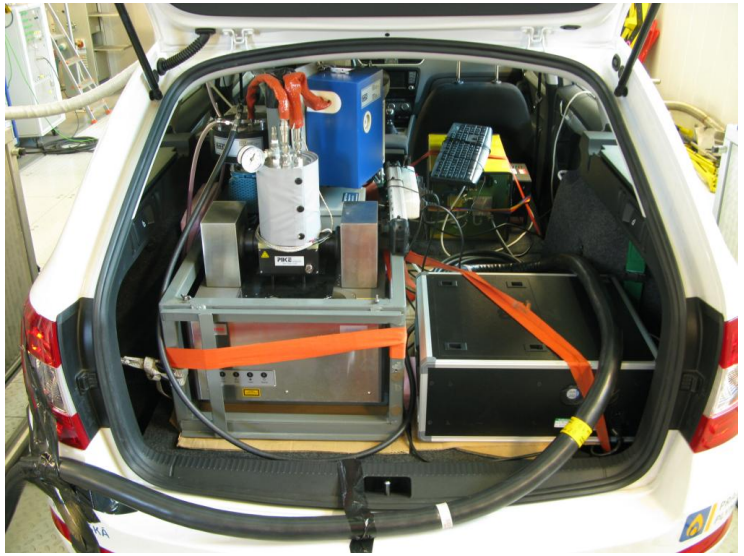
On-road measurement of emissions of reactive nitrogen compounds and greenhouse gases from Euro 6 diesel and natural gas vans using an on-board FTIR





Michal Vojtíšek, Vít Beránek, Vojtěch Klír

Center for Vehicles for Sustainable Mobility, Czech Technical University in Prague

Petr Jindra, Martin Pechout

Czech University of Life Sciences in Prague

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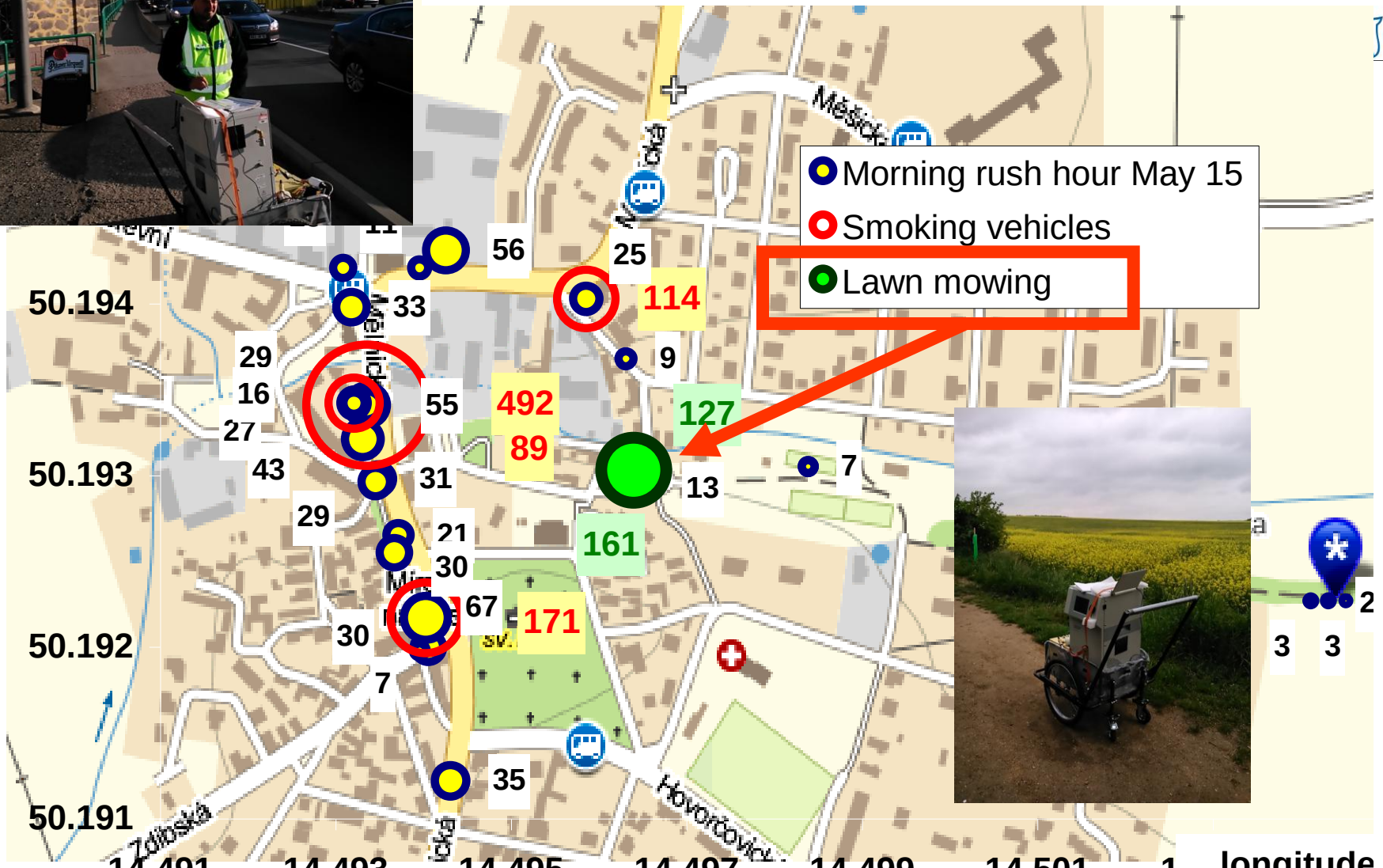
Particulate matter and tropospheric ozone are causing over 400 thousands of premature deaths annually in the EU

(vehicle accidents less than 40 thousands/year)

Internal combustion engines are among cleanest combustion devices. But they do not have chimneys, and they are not far outside of the cities. They are among us in the streets where we inhale.

Total particle counts, 10-500 nm
thousands of particles per cm3
Líbeznice, 15. 5. 2014, morning rush hour



Emission limits in broader perspective

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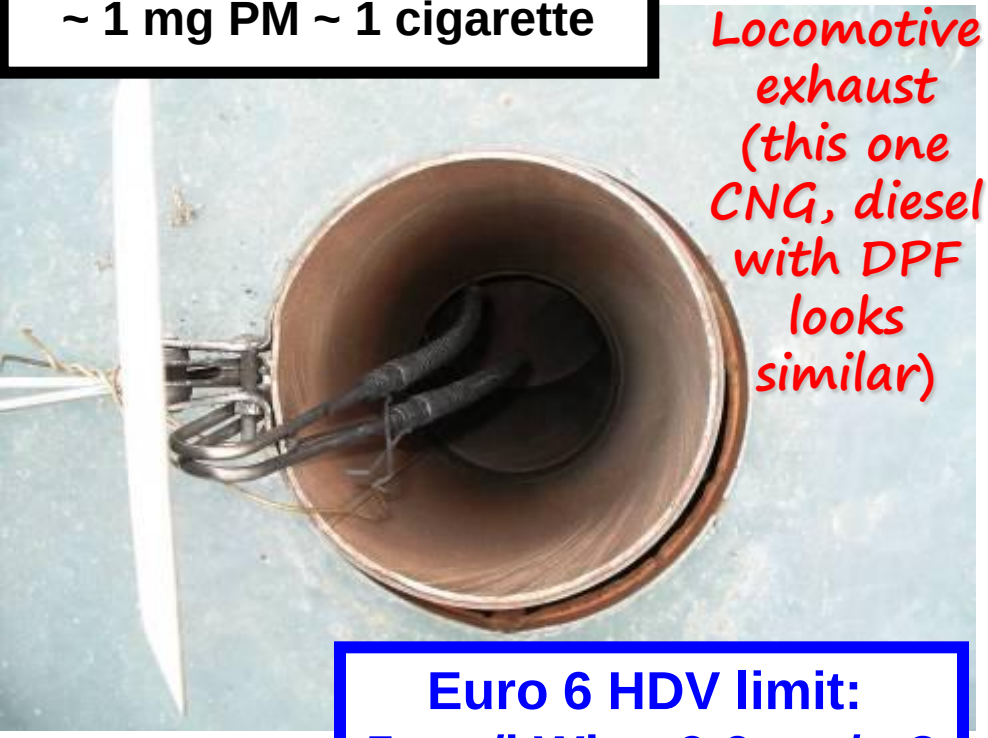
Particles are measured by mass or by count, just like we sell fruits and vegetables – it is difficult to measure by other parameters, even though they may be more relevant.

Euro 6 bus - 1 km of travel
~ 1 mg PM ~ 1 cigarette



Locomotive exhaust (this one CNG, diesel with DPF looks similar)

Euro 6 HDV limit:
5 mg/kWh ~ 0,6 mg/m3

Burning of trash ~ 500 mg/m3
Christian et al., Atmos. Chem. Phys., 10, 565–584, 2010

Home heating stove chimney

Czech limit for local heating up to 300 kW
(Reg. 201/2012, appendix 10)
125-150 mg/m3 from 1.1.2014
60-75 mg/m3 from 1.1.2018

Problematic pollutants in engine exhaust

- **Particles** + secondary aerosol
- **NO_x** + tropospheric ozone
- CO, benzene, lead – no longer a problem

New and emerging problems:

- NO_2 - formation in oxidation catalysts
- NH_3 - formation in reduction catalysts
- - formation in three-way catalysts when run rich
- Aldehydes – oxygenated fuels (ethanol)

Greenhouse gases

- N_2O - NO_x reduction catalysts (SCR, LNT)
- CH_4 - natural gas engines, LNT catalyst

Natural gas as the "clean fuel"

- Mostly methane (ethane, hydrogen, nitrogen, CO2)
- Can be produced from biomass (biomethane)
- Relatively safe fuel (stable, low health risks, high ignition energy)
- Stored compressed (CNG) or liquified (LNG)
- Combustion produres some nanoparticles, nitrogen oxides, aldehydes,…
- High-temperature processes in engines lead to formation of NOx
- Any engine produces nanoparticles from lubricating oil

Natural gas as the "clean fuel"

- Early CNG engines much cleaner (Holmén and Ayala, 2002) and lower toxicity (Turrio-Baldassarri et al., 2006) than diesel
- But diesel with DOC/DPF better than natural gas with no aftertreatment (Kado et al., 2005)
- „State of the art" CNG: optimized compression ratio, stoichiometric air-fuel ratio, three-way catalyst → no problem
- "State of the art" diesel: DOC/DPF/SCR/ammonia slip catalyst → no problem (Hesterberg 2011)
- When state of the art compared, not much difference CNG-diesel (Nylund et al., 2004), (Hesterberg et al., 2008)

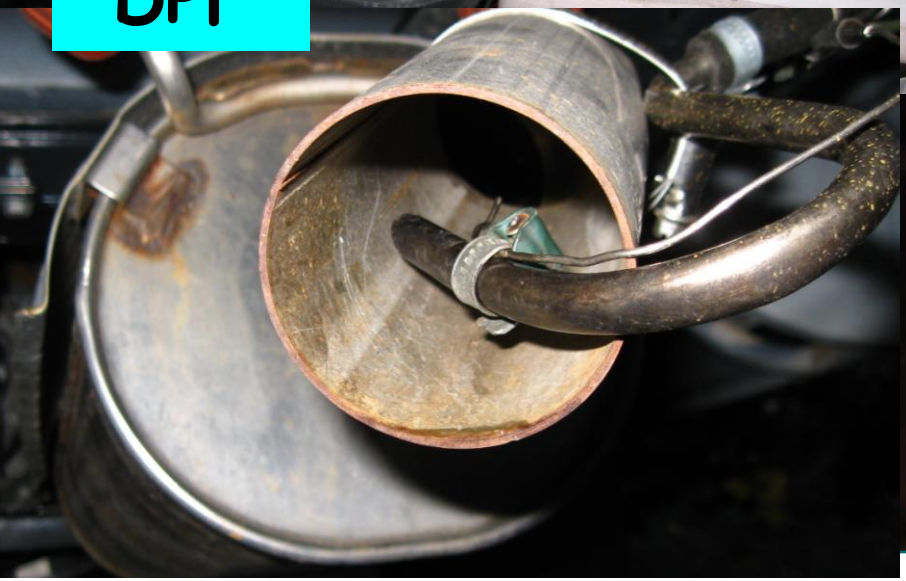
With advanced engine and aftertreatment technologies, are the differences attributable to fuel merely academic?

Is state of the art the reality?

- **In the EU, maybe not !!! (i.e., DieselGate)**

Is diesel PM becoming more of a question of public policy rather than technology?

With DPF



Euro 5 with no DPF
(Prague, CZ)

Real-world emissions could be higher than during „standardized tests“ (i.e., type approval)

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- **Optimization for type-approval conditions**
  - No EGR at full load
  - Catalyst sized for low flow and too small for high loads
- **Technology limits**
  - low SCR temperature – cold start, creep
- **Malfunction & deterioration**
- **„No one is watching“**
  - Switching off EGR, LNT fuel / SCR urea injection
  - „Cycle beating“ strategy
  - DPF removal, SCR deactivation, etc.

„DieselGate“: NEDC cold („test mode”, EGR, low Nox) vs. hot (non-test mode, less EGR, more NOx

(VW Passat, Euro 5, measured by the authors for a BBC documentary)

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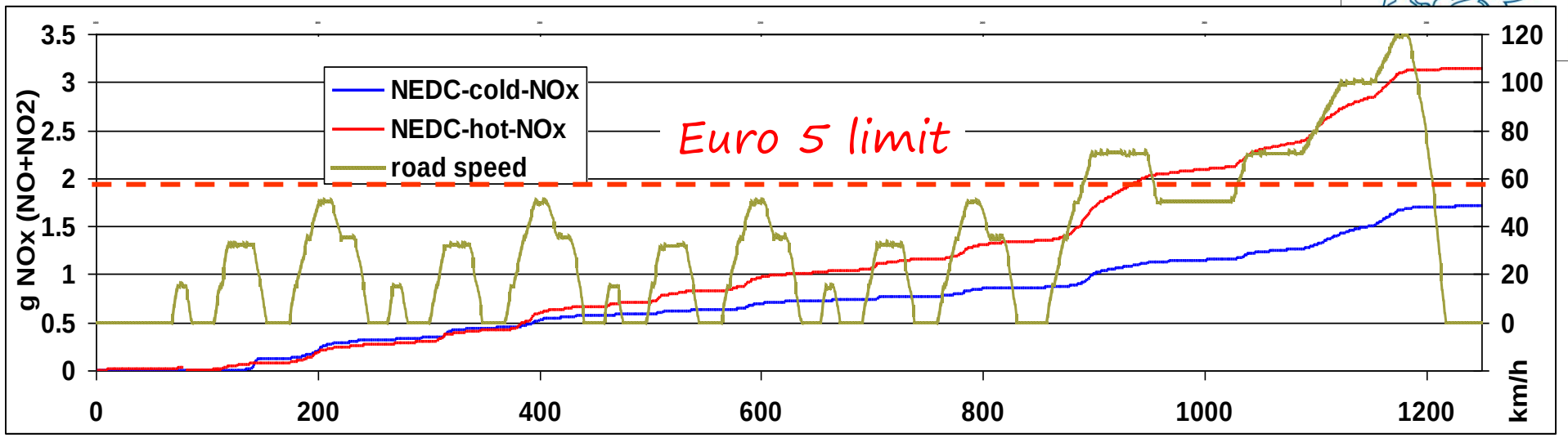
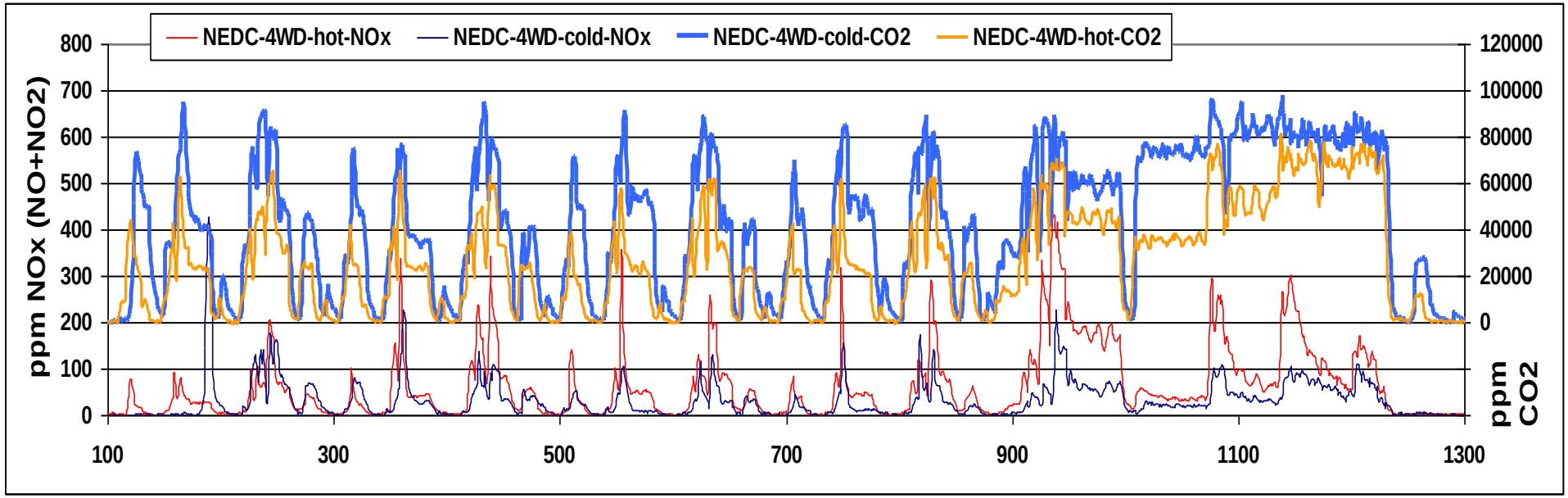
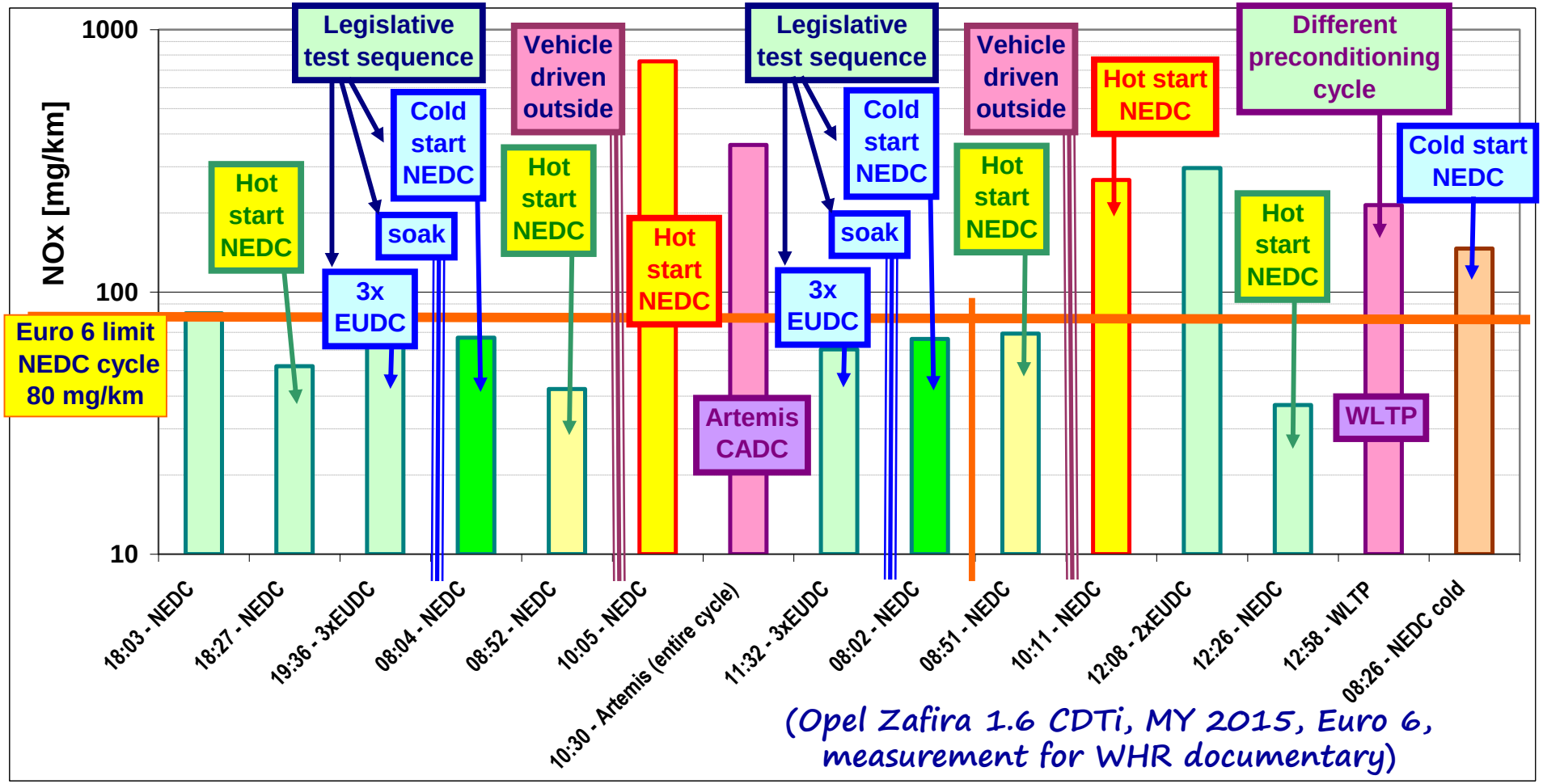
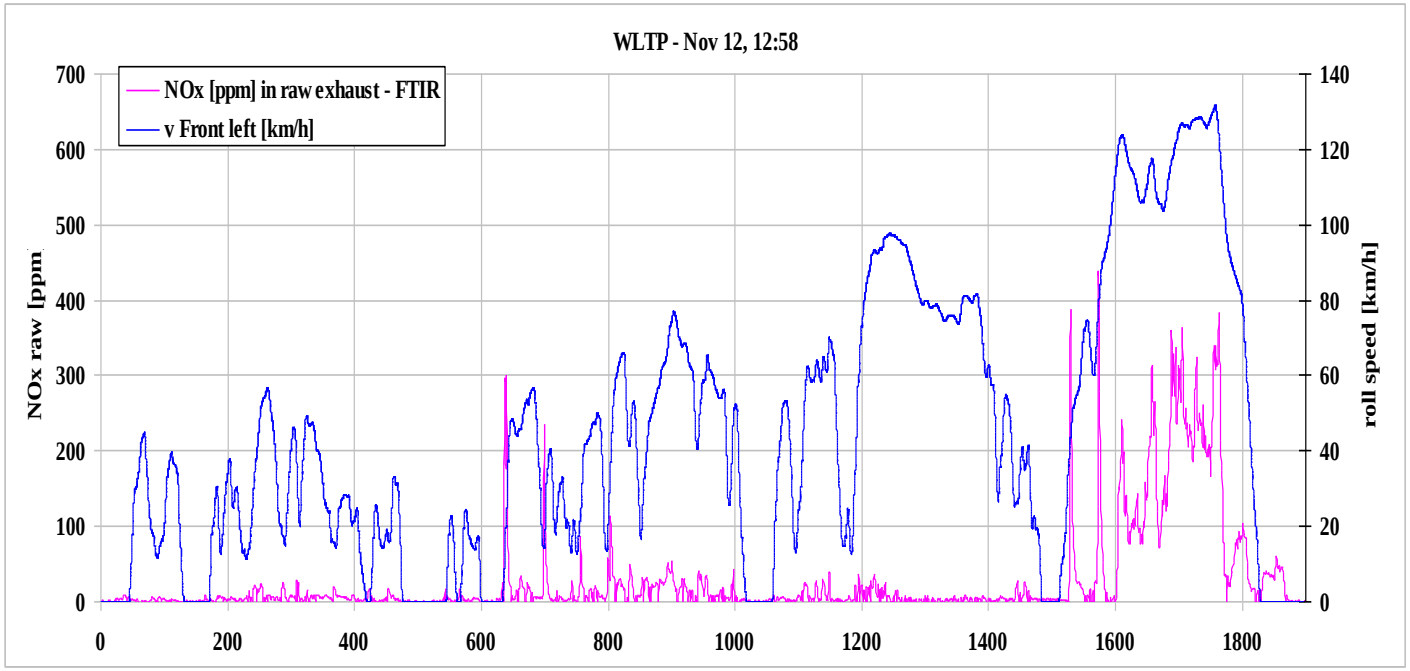


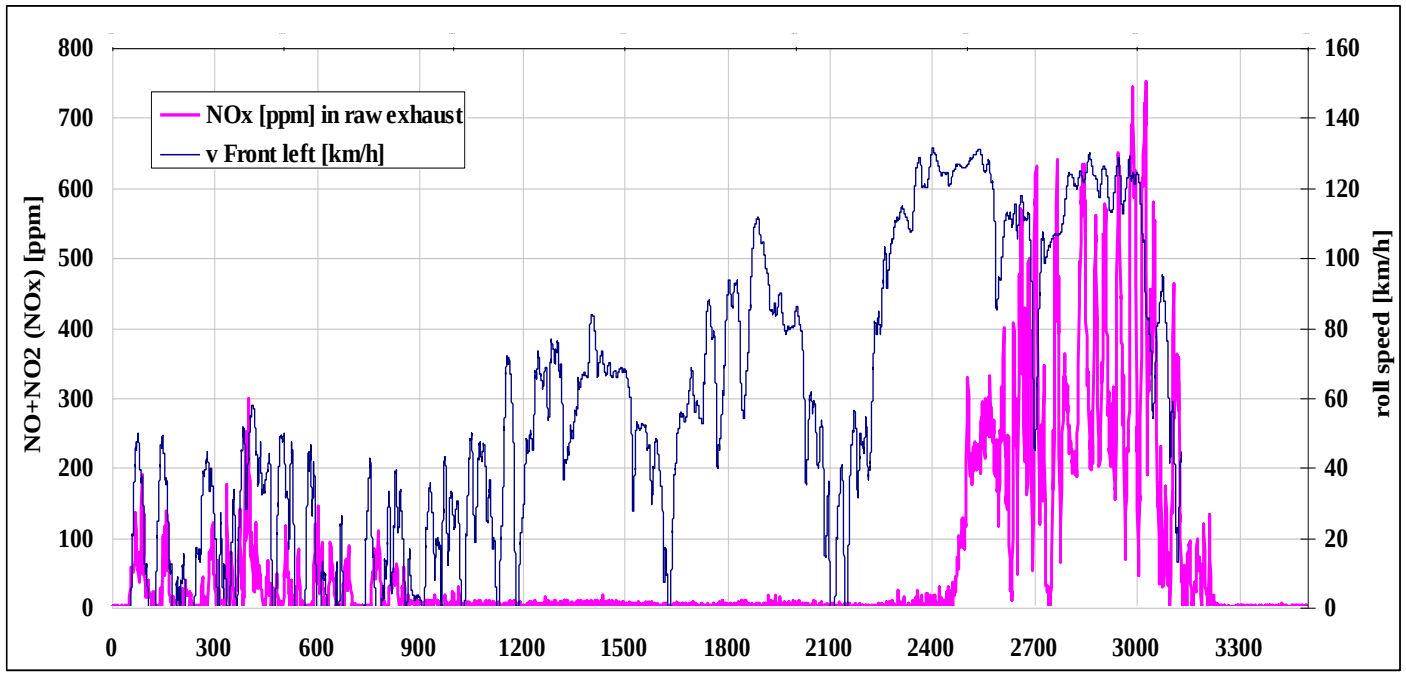


„DieselGate“: Cooling of the ambient air sensor during preconditioning triggers “high NOx” operation during subsequent test cycle …



(Opel Zafira 1.6 CDTi, MY 2015, Euro 6, measurement for WHR documentary)





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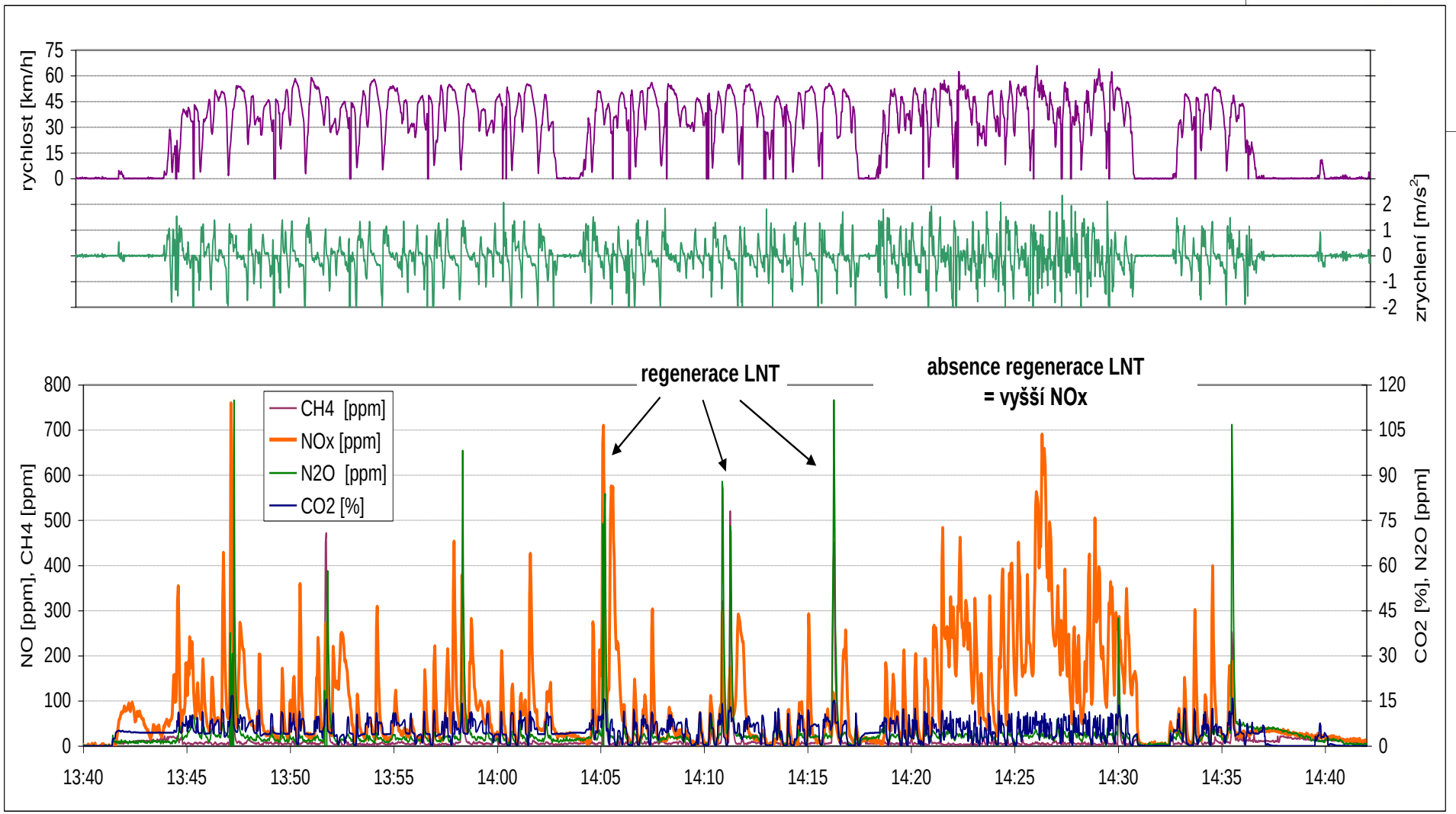
<- WLTC cycle

NOx concentrations in the exhaust increase at higher speeds and loads than those experienced in NEDC

Opel Zafira diesel, MY 2015, Euro 6

<- CADC cycle (Artemis)

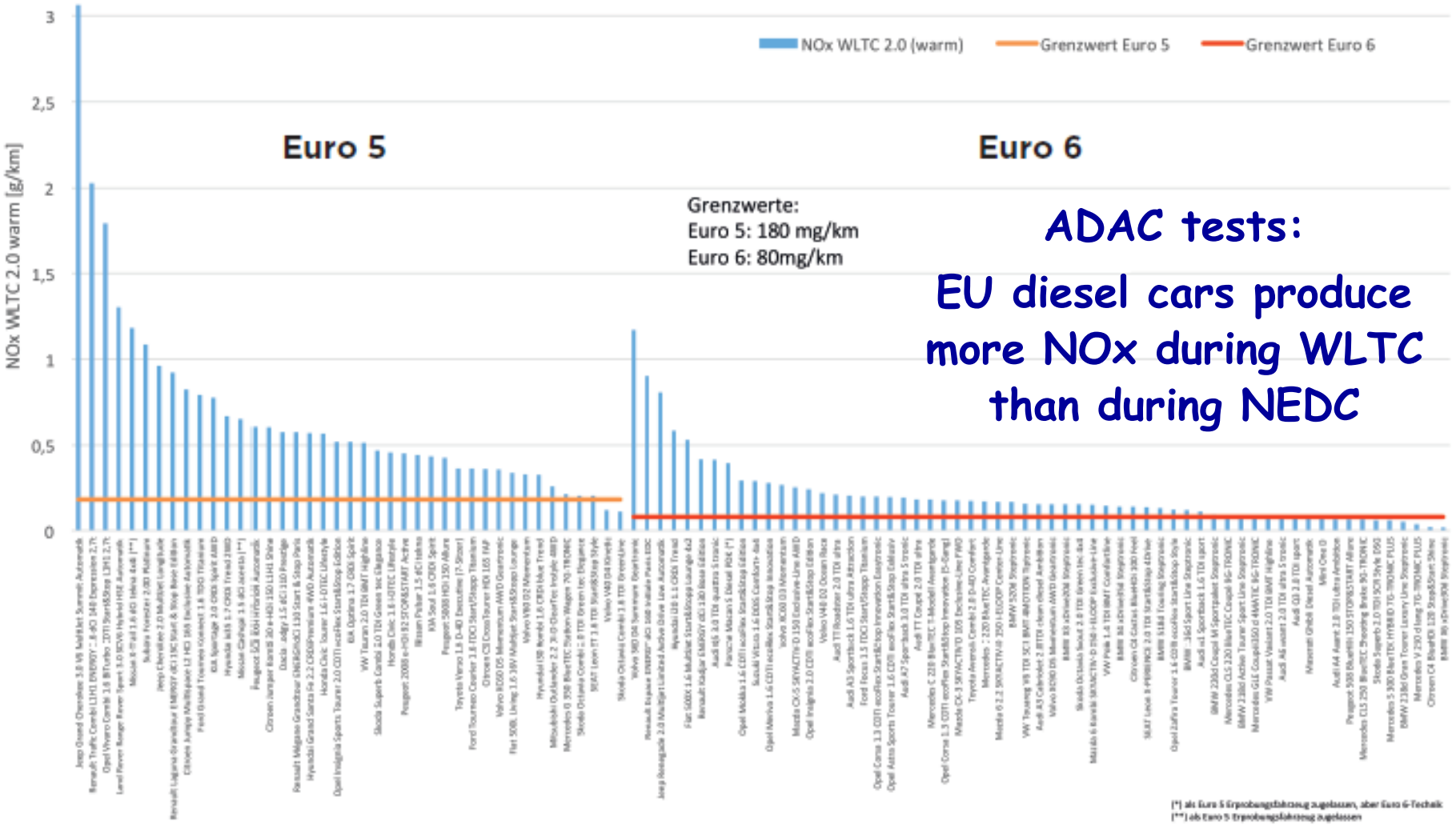
Automobil, r.v. 2015, Euro 5, naftový motor s LNT



Při dynamičtější jízdě nedocházelo k regeneraci zásobníkového katalyzátoru („úspora paliva“?) a emise NO_x byly výrazně vyšší.

ADAC EcoTest: Stickoxide im WLTC 2.0 (warm)

Euro 5 und Euro 6 Diesel Pkw - getestet ab 2014



SOR CN12 Euro 6 diesel bus – Hradčany military airport

Average emissions - Braunschweig cycle: 195 mg/km NO_x.

At 37 liters / 100 km, 220 g/kWh: 162 mg/kWh (Euro 6: 460 mg/kWh)

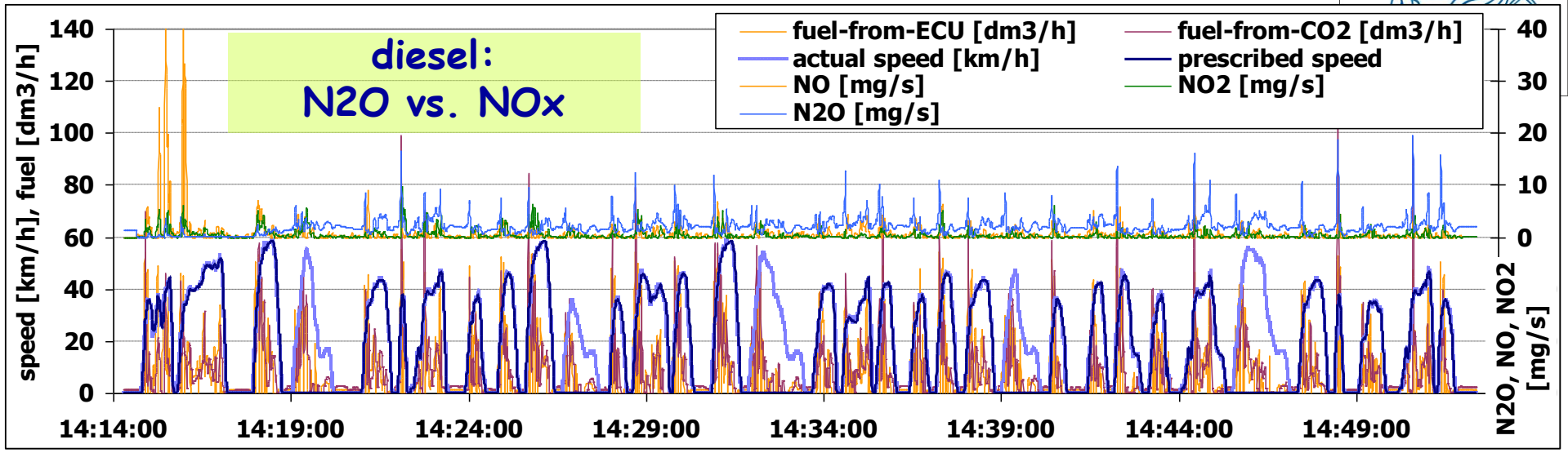
Diesel car NOx limit: 180 mg/km Euro 5, 80 mg/km Euro 6

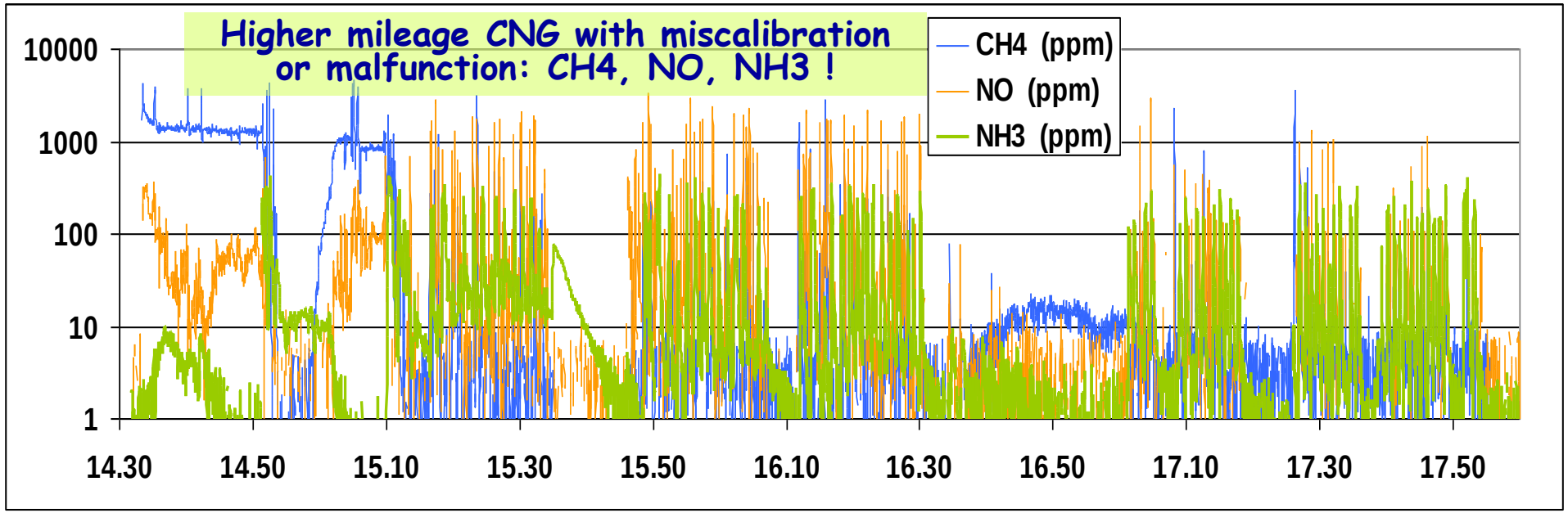
Diesel car real driving NOx: Euro 3-5: 1000 mg/km

One Euro 5 car = 1000 mg/km = 5 buses !!!
But 5 buses can transport 100x more people.

SOR CN12 Euro 6 diesel bus – Hradčany military airport

NO, NO2, N2O, NH3, ..., CO, CO2, PM



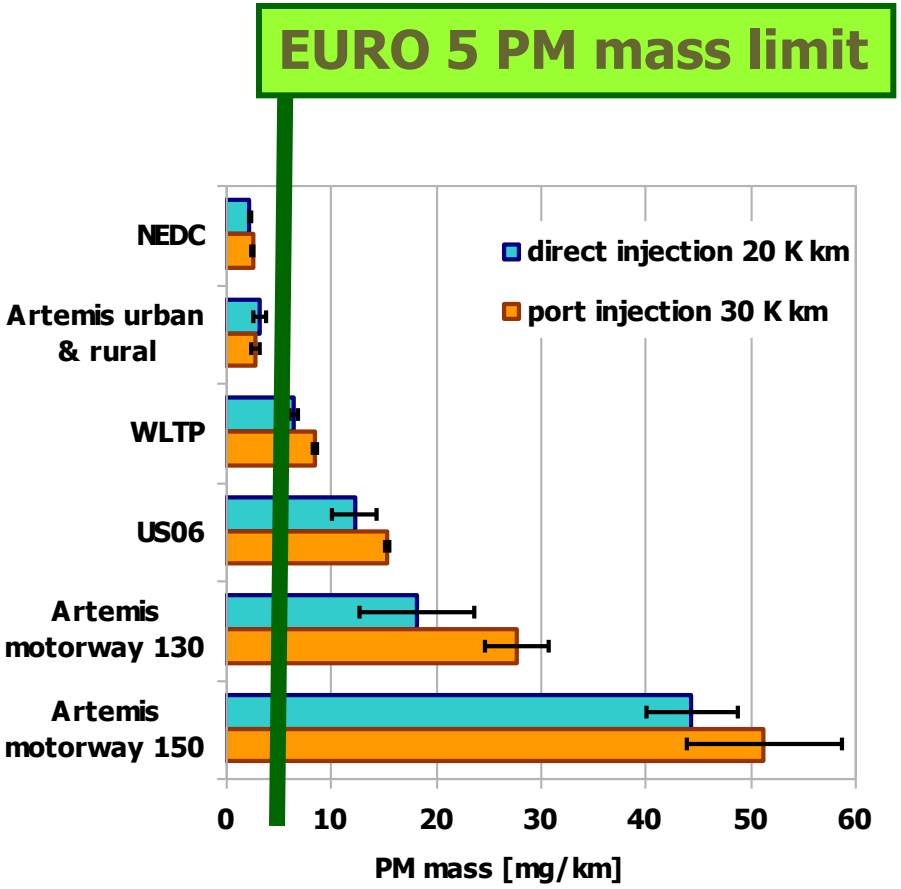


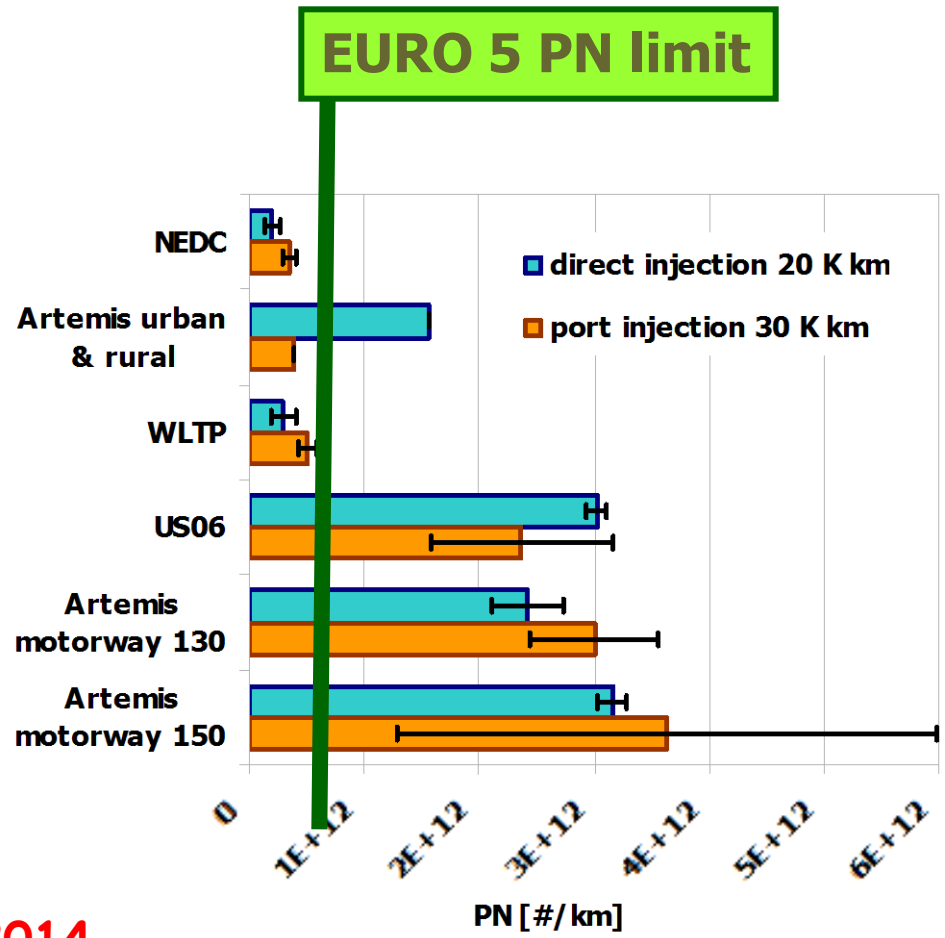
Answer to Imad Khalek's question on PN from PFI

Gasoline engine PM: Choice of cycles

WLTP is "not as lame as NEDC", but does it cover the problem – enrichment at high load (prohibited by EPA)**?**

US06 and Artemis motorway cycles as a supplement?





From Vojtisek-Lom, ETH 2014

Study goals

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What is the real emissions benefit of switch to natural gas on exhaust emissions?

- This study: light utility vehicles, Euro 6
  - Harder to replace by public and non-motorized transport
  - 4 x diesel, 4 x CNG (1 station wagon + 3 vans each fuel)
  - 1 van with non-functional DPF replaced
  - Comprehensive laboratory and on-road evaluation
- On the road:
  - Urban route in Prague (21 km)
  - Composite route outside of Prague (65 km)
  - Nanoparticles, reactive nitrogen NO, NO2, NH3, greenhouse gases N2O, CH4, CO2, aldehydy
- Laboratory:
  - NEDC, WLTP, Artemis (CADC), NYCC, US06 cycles
  - Particle size distributions, offline analysis of PAH

Vehicles

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Case for EU light-duty utility vehicles:

Similar type approval as cars

Cars can be replaced by electric, non-motorized, public transit

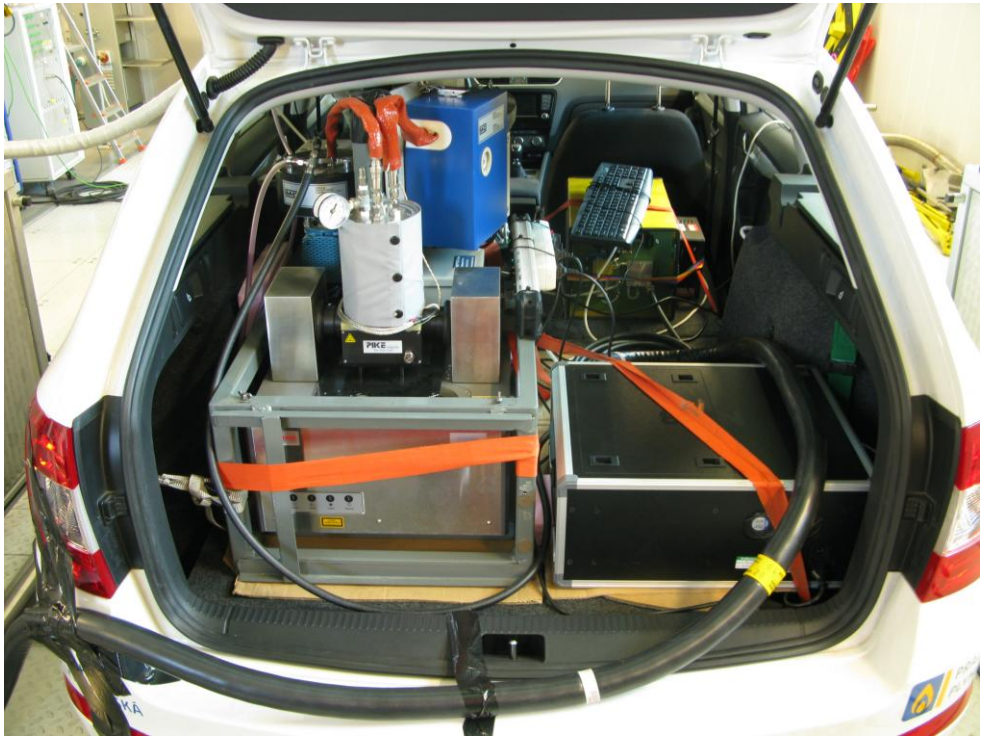
Heavy trucks can be routed to rail

Light utility vehicles are difficult to replace …

Model	Engine	Model year	Mileage [km]	Fuel All CNG factory & dual-fuel	Test weight [kg]
Škoda Octavia	1,6 TDI CR DPF/81 kW	2014	42 567	Diesel	1 594
Škoda Octavia	1,4 TSI G-TEC/81 kW	2015	21 293	CNG (Gasoline)	1 683
OPEL Zafira	2.0 CDTI ecoFLEX /96 kW	2014	27 201	Diesel	2 070
VW Touran	1,4 TSI EcoFuel/110 kW	2014	68 343	CNG (Gasoline)	2 039
VW Caddy	1,6 TDI/75 kW *Euro 5*	2014	39 434	Diesel	1 886
VW Caddy	2,0 MPI EcoFuel/80 kW	2014	60 102	CNG (Gasoline)	1 910
Fiat Doblo	1,6 MultiJet/77 kW	2016	489	Diesel	1 772
Fiat Doblo	1,4 T-Jet/88 kW	2016	10 417	CNG (Gasoline)	1 682

On-board instrumentation

- Gaseous compounds: FTIR & MiniPEMS
- Particles: NanoMet3
- Operating data: EOBD
- Poloha: GPS



FTIR spectrometer

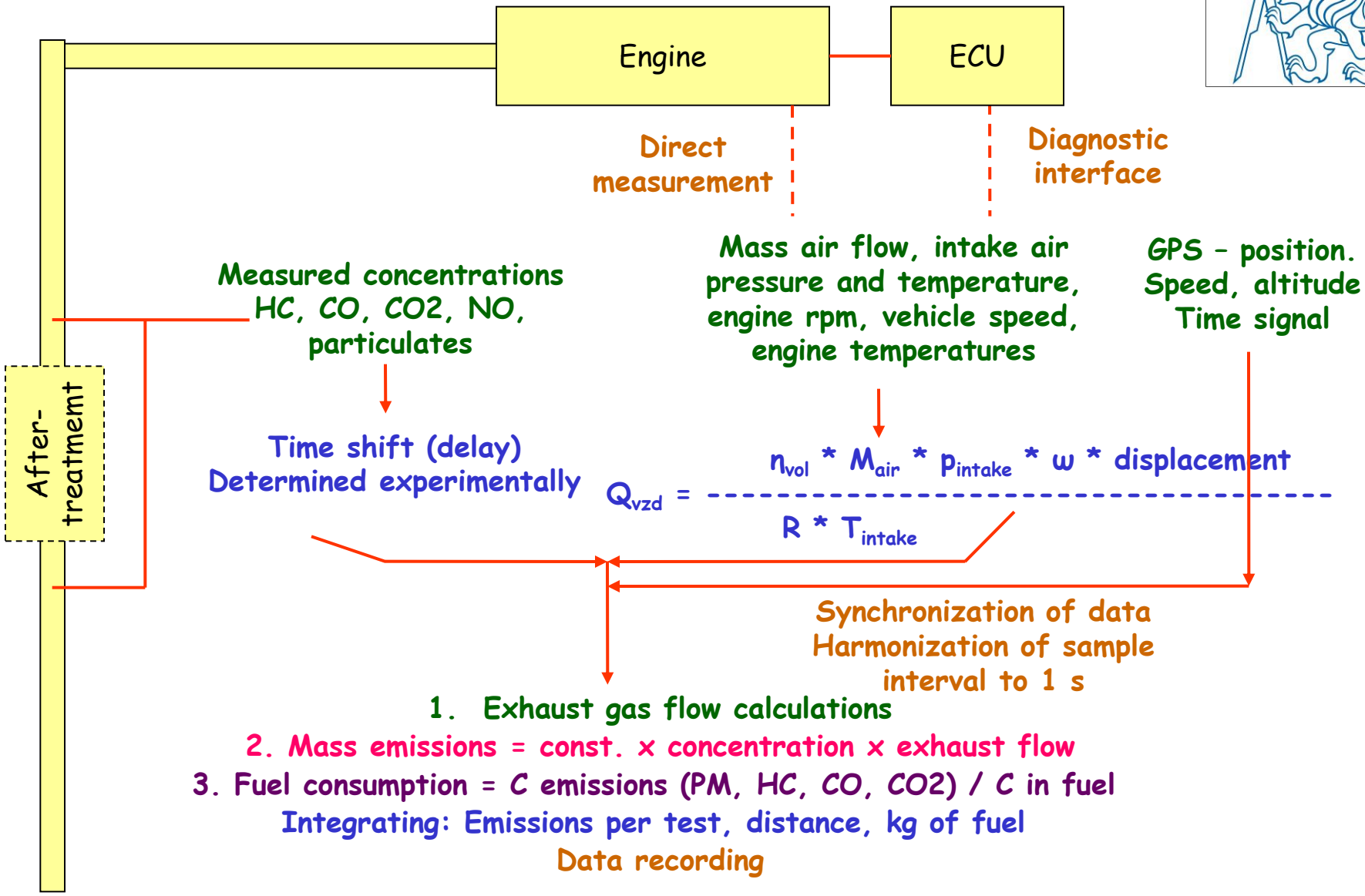
- Nicolet Antaris IGS
- 5 m path length, 130°C
- 0.5 cm^{-1}, 1 Hz resolution
- ZnSe optics, 4000-650 cm^{-1}

NanoMet3

- Diffusion classifier, detection by electrometer
- Output correlated with particle number (PN) per Euro 6 (PMP, non-volatile particles detected at 50% efficiency at 23 nm)

Low-cost on-board system overview

(Vojtisek-Lom and Cobb, CRC On-road vehicle emissions workshop, 1998)



FTIR (Fourier Transform Infra Red) Spectrometer

- measures large portion of infrared spectra
- quantification of compounds absorbing in IR through deconvolution of spectra

- greenhouse gases CO2, CH4, N2O
- reactive nitrogen compounds NO, NO2, NH3, HCN, HCNO
- various heterogeneous molecules present in concentrations that can be detected and discerned from other compounds
- this study: MCT detector, ZnSe optics, 0.5 cm-1 resolution, 6 m path length, 130° C

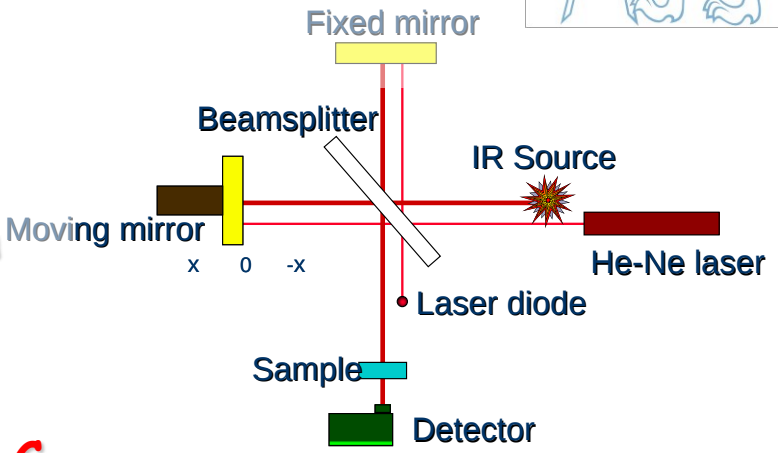
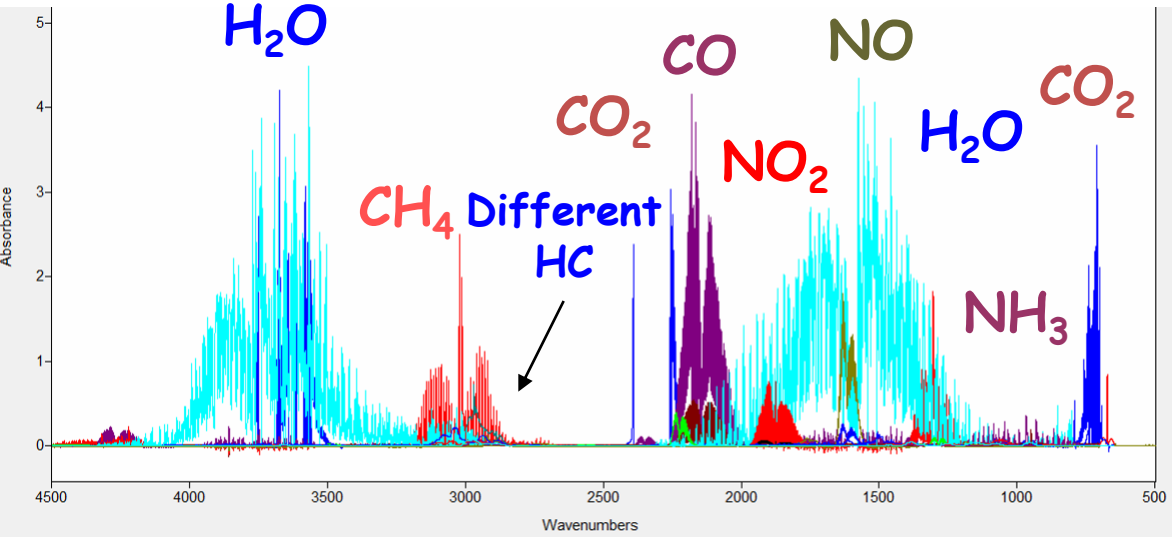
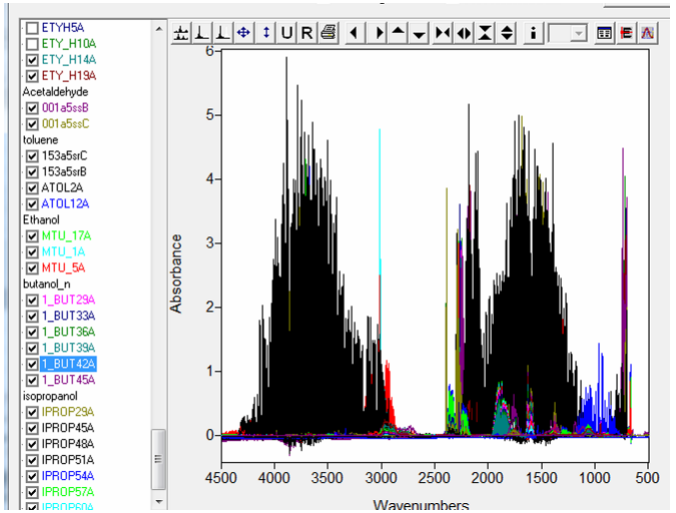


Diagram: Nicolet





On-board FTIR packages

Both liquid nitrogen cooled MCT detector, ZnSe optics,
130 C sampling train, 0.5 cm^{-1} optical resolution, 4000-650 cm^{-1}

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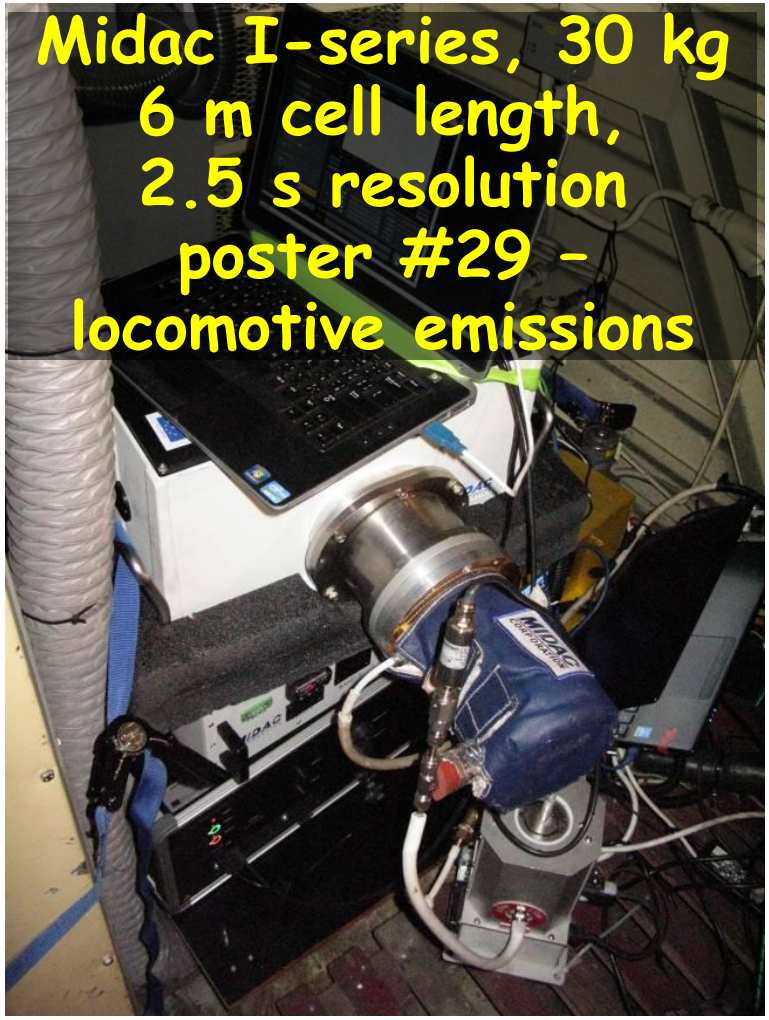
Nicolet Antaris IGS, 70 kg
5 m cell length, 1 s resolution

Midac I-series, 30 kg
6 m cell length,
2.5 s resolution
poster #29 –
locomotive emissions



The "MiniPEMS" (Poor man's PEMS) concept: Focus on making the test possible & practical.

Variances within and among vehicles are often greater than the uncertainty of simpler instruments

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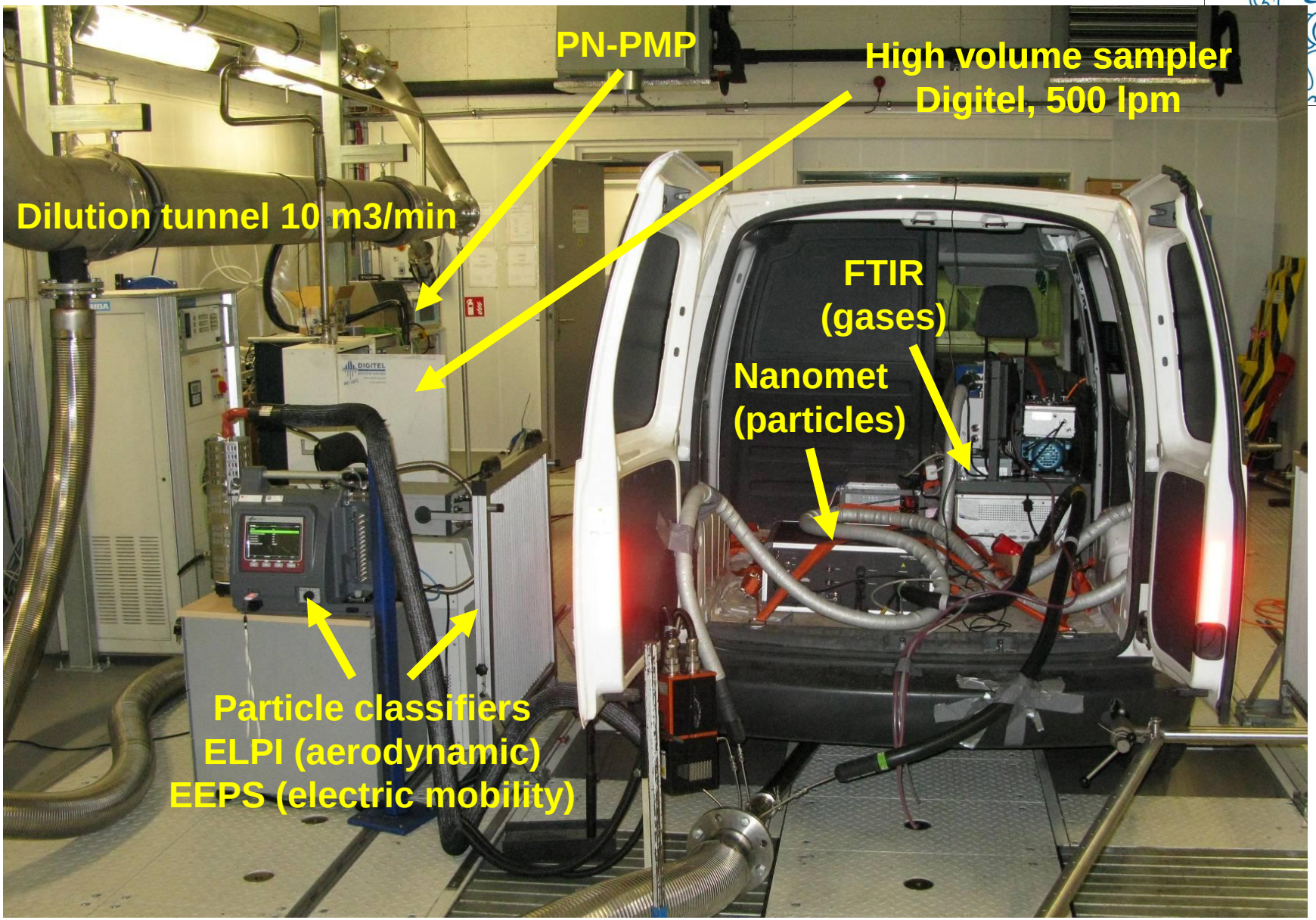
Home-made instrument

CO, CO2, indicative HC: NDIR
NO, NO2, O2: electrochemical
Indicative PN: Ionization chamber

Intake air flow:
calculated from engine rpm, intake air pressure and temperature
Position and speed: GPS
Exhaust gas temp: thermocouple

LiFeYPO battery, 3 hours runtime
9 kg, 40x22x22 cm

Laboratory tests



On-board system validation

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On-board system:

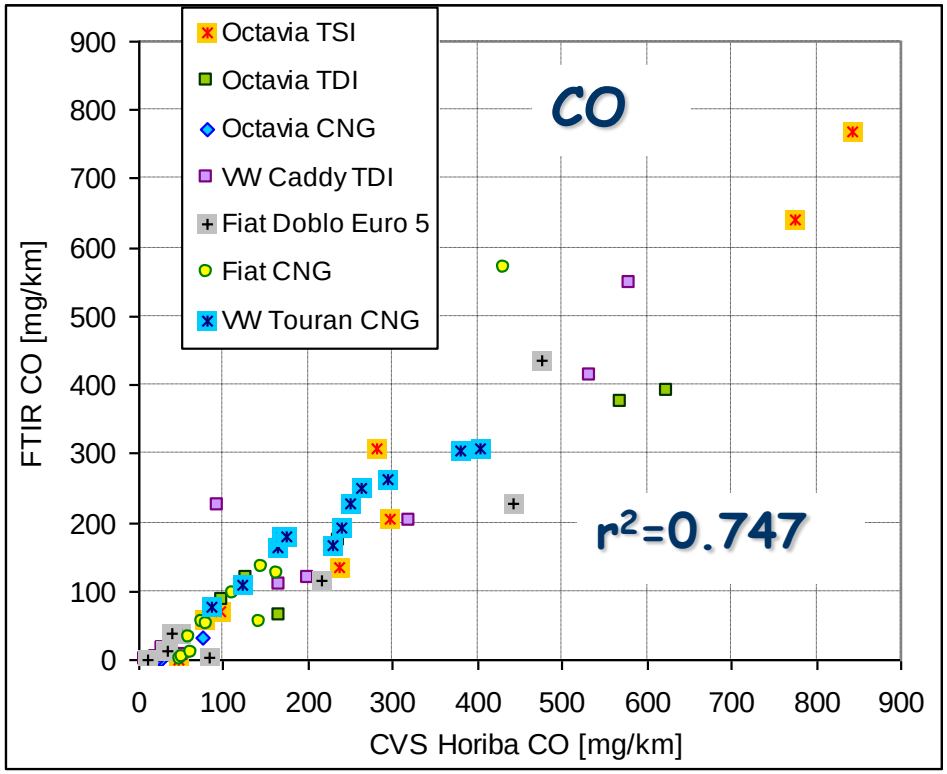
concentrations in raw exhaust measured by FTIR

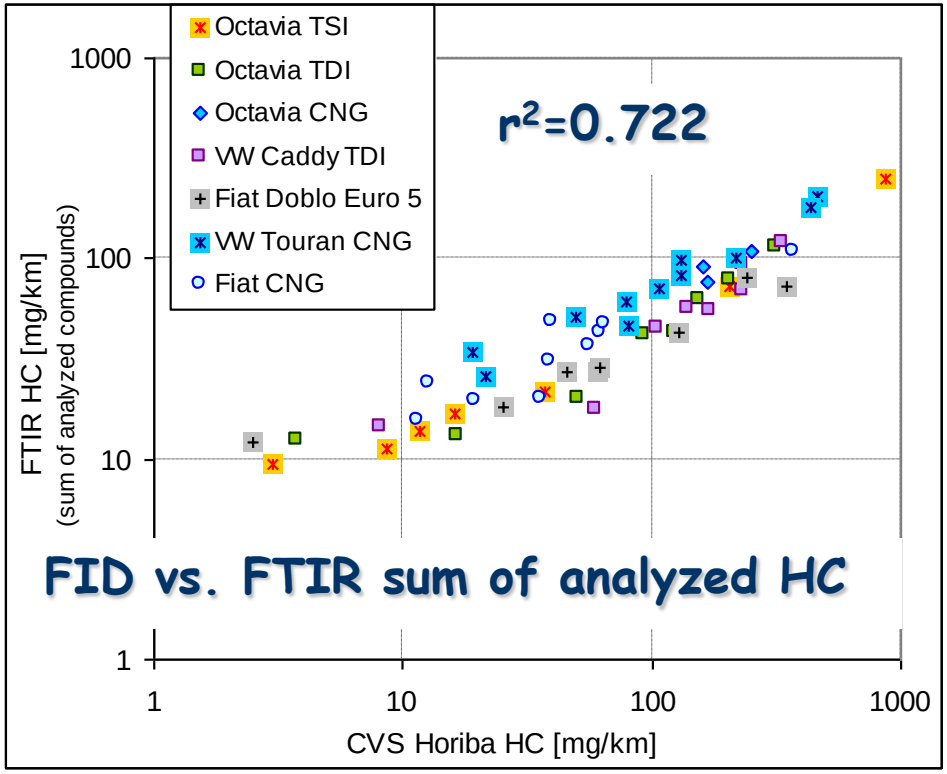
exhaust flow calculated (speed-density method)

Laboratory: Diluted exhaust (CVS), traditional on-line measurements

Each point plotted = emissions per cycle

Agreement requires correct a) concentration, b) flow, c) synchronization





Vojtisek-Lom et al., Sci. Tot. Env (in review)

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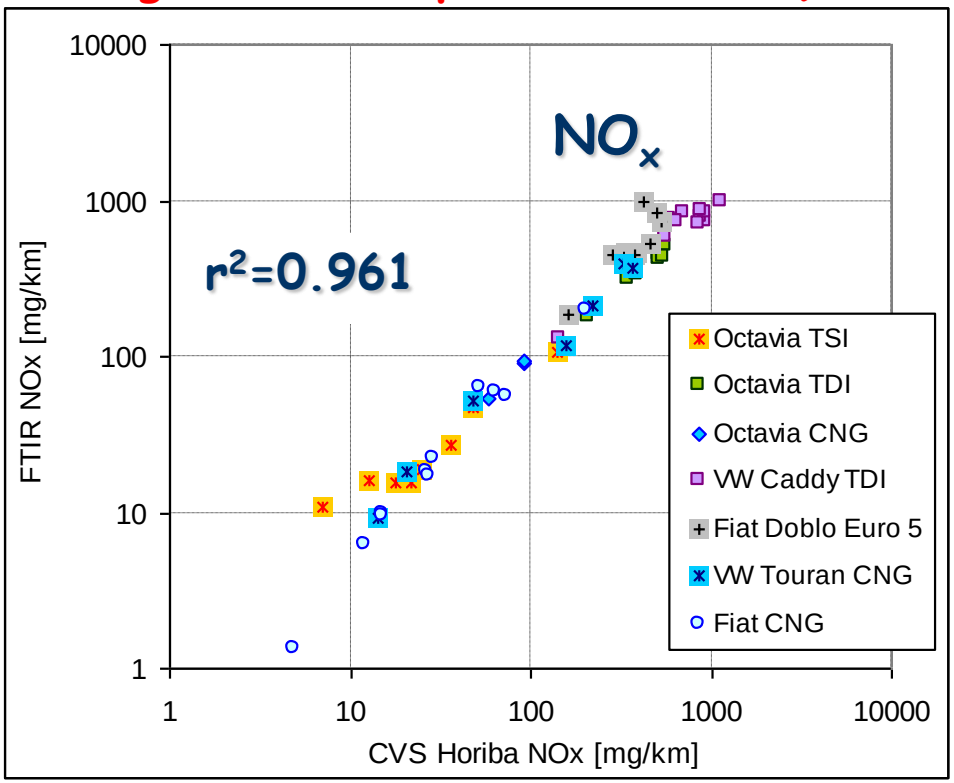

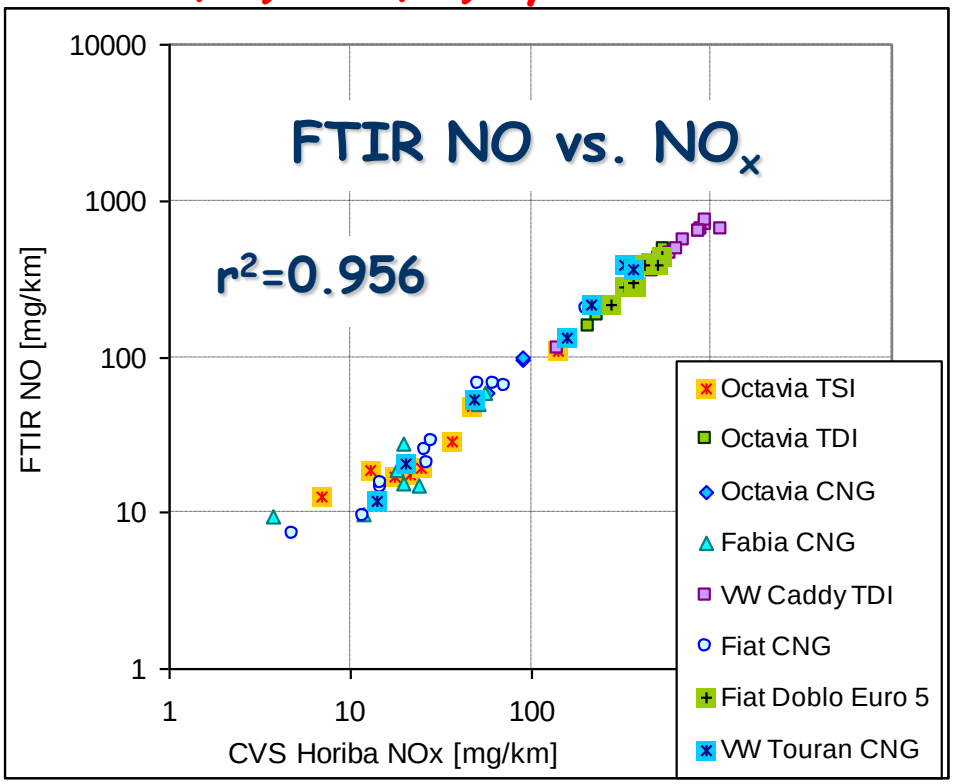

Vojtisek-Lom et al., Sci. Tot. Env (in review)

High NO_2 & high NO_2/NO_x

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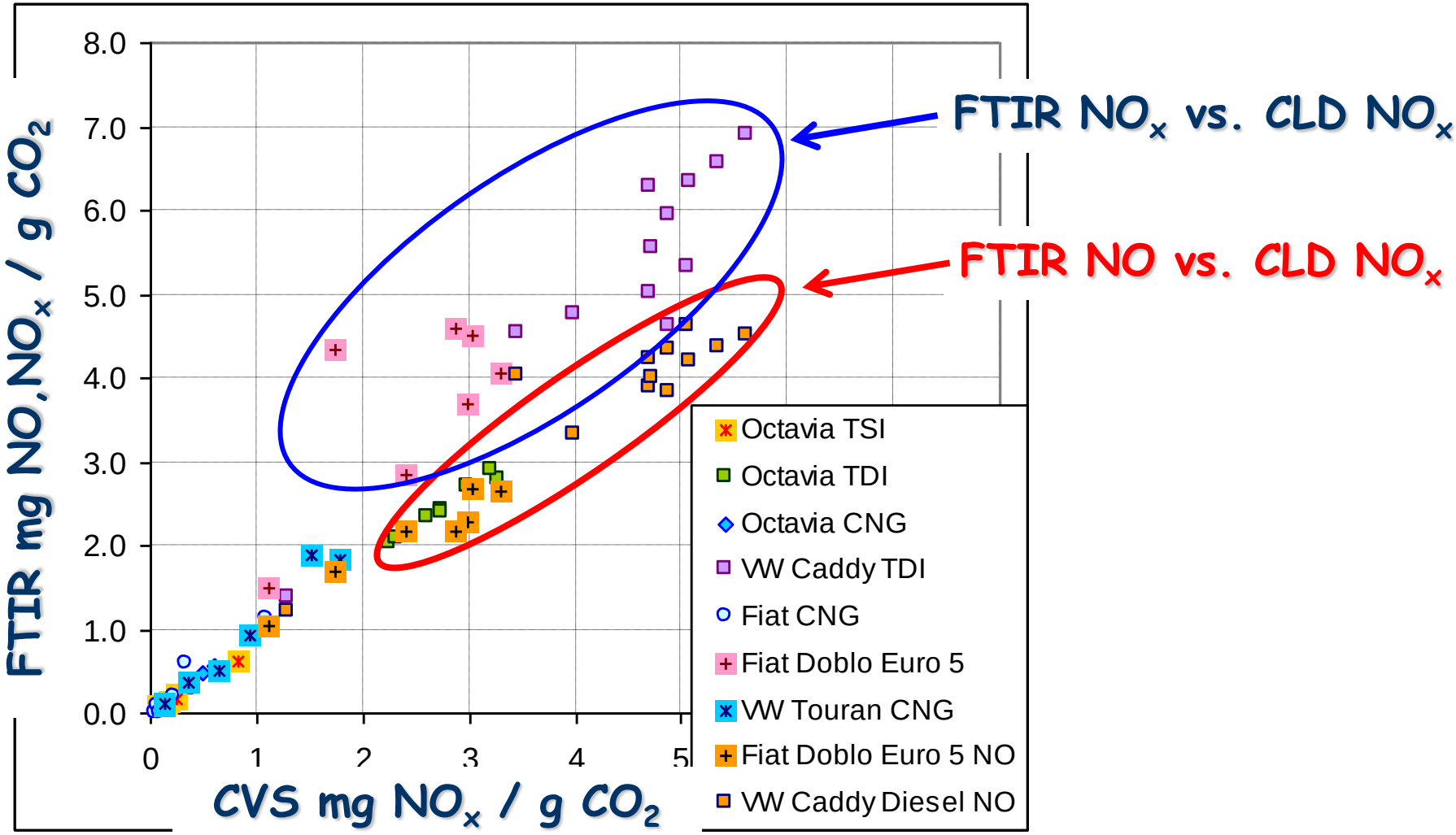
The reference method – chemiluminescence – may have limitations – NO_2 loss to condensate ? inefficient conversion NO_2 → NO ?



Vojtisek et al.: On-road measurement of emissions of reactive nitrogen compounds and greenhouse gases from Euro 6 diesel and natural gas vans using an on-board FTIR. ETH Conference on Combustion Generated Nanoparticles 2017

Total number of non-volatile particles (PN)

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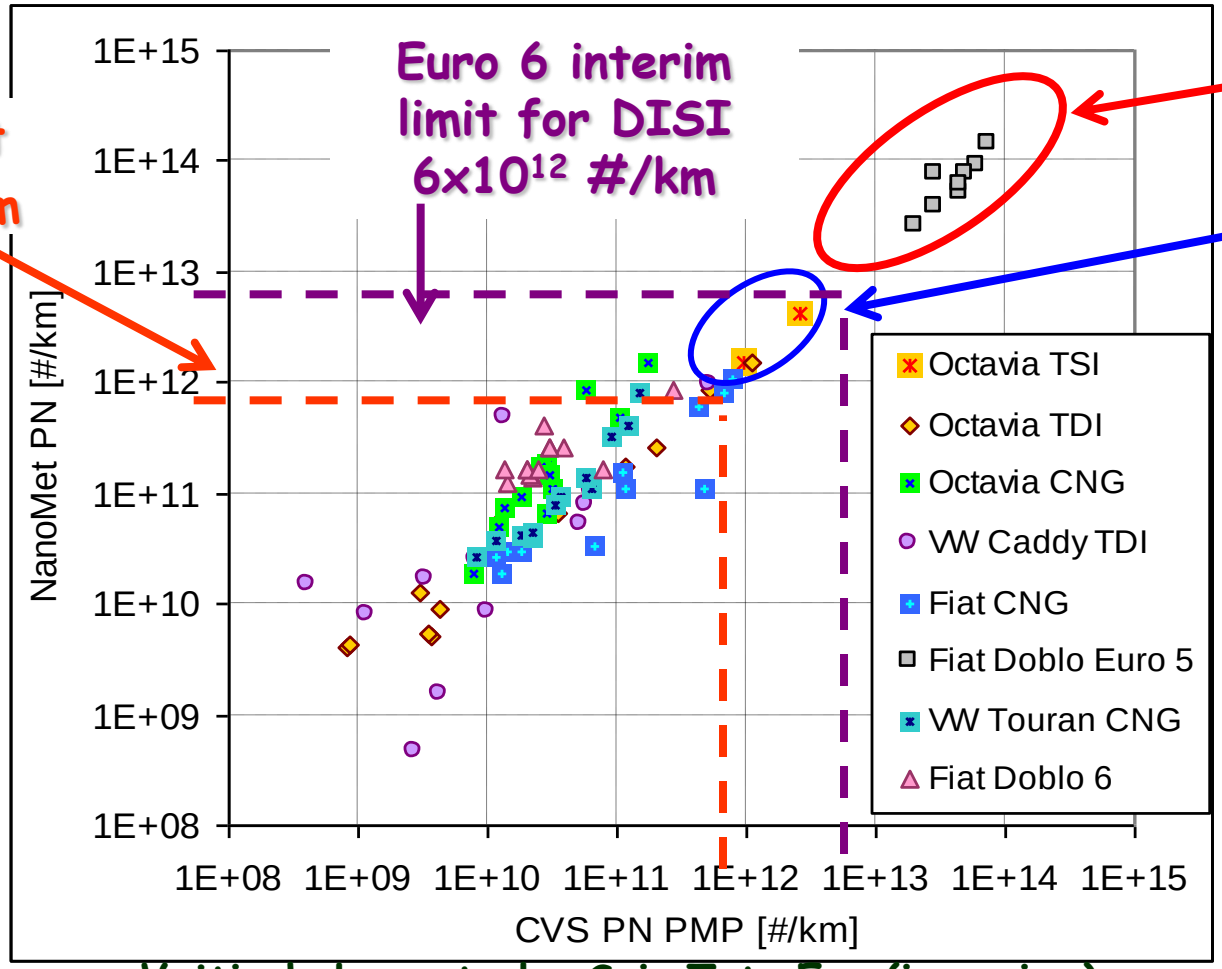
NanoMet3 – raw exhaust, relies on calculated exhaust flow and data synchronization; diffusion charger measures approximately total particle length (different principle); correlation with PN (PMP) established on diesel vehicles (EC Joint Research Center)



Vojtisek-Lom et al., Sci. Tot. Env (in review)

NOy - Artemis urban vs. urban on-road

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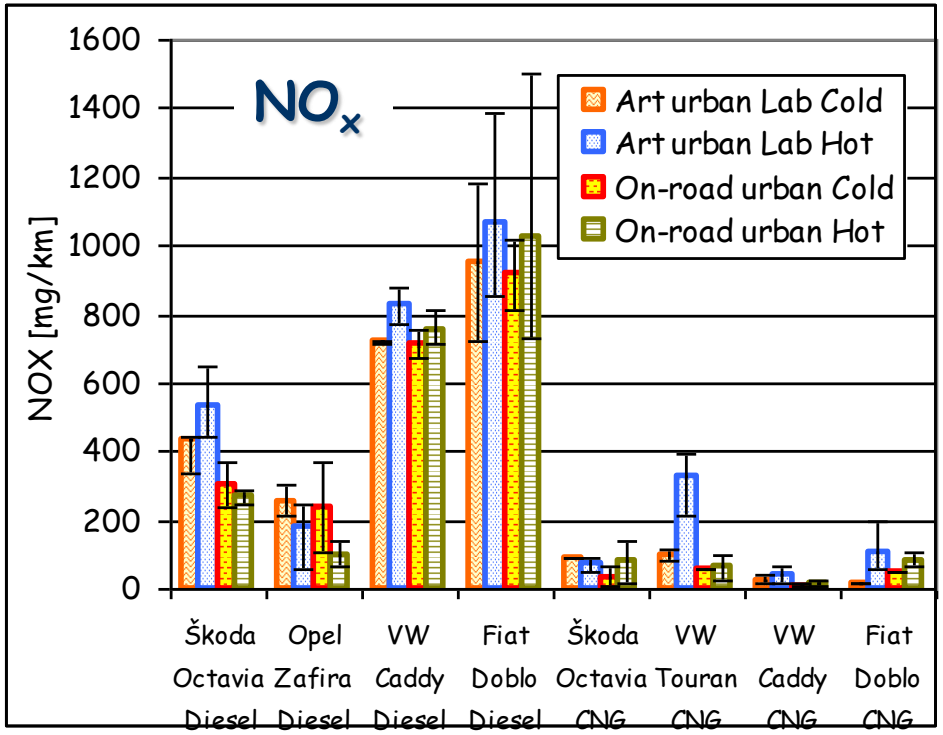
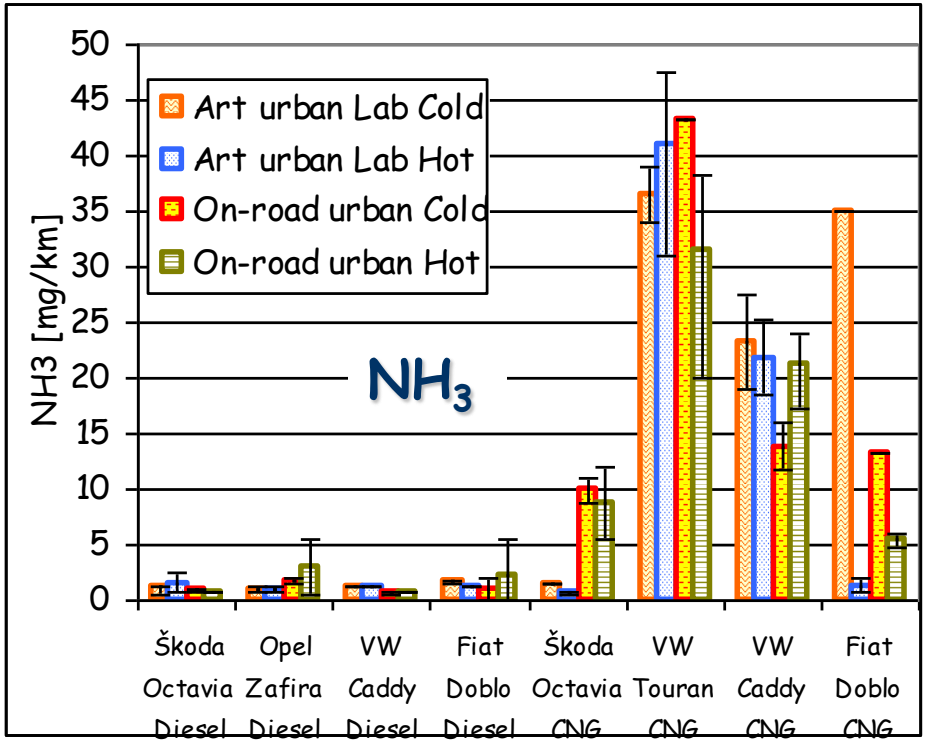
NOx: CNG – NOx in tens of mg/km

Diesel – consistently in hundreds of mg/km

NH3: Diesel – negligible, CNG – several tens of mg/km

Ammonia contributes to secondary PM formation (but how severe are the health effects?)





NOx – What about NEDC?

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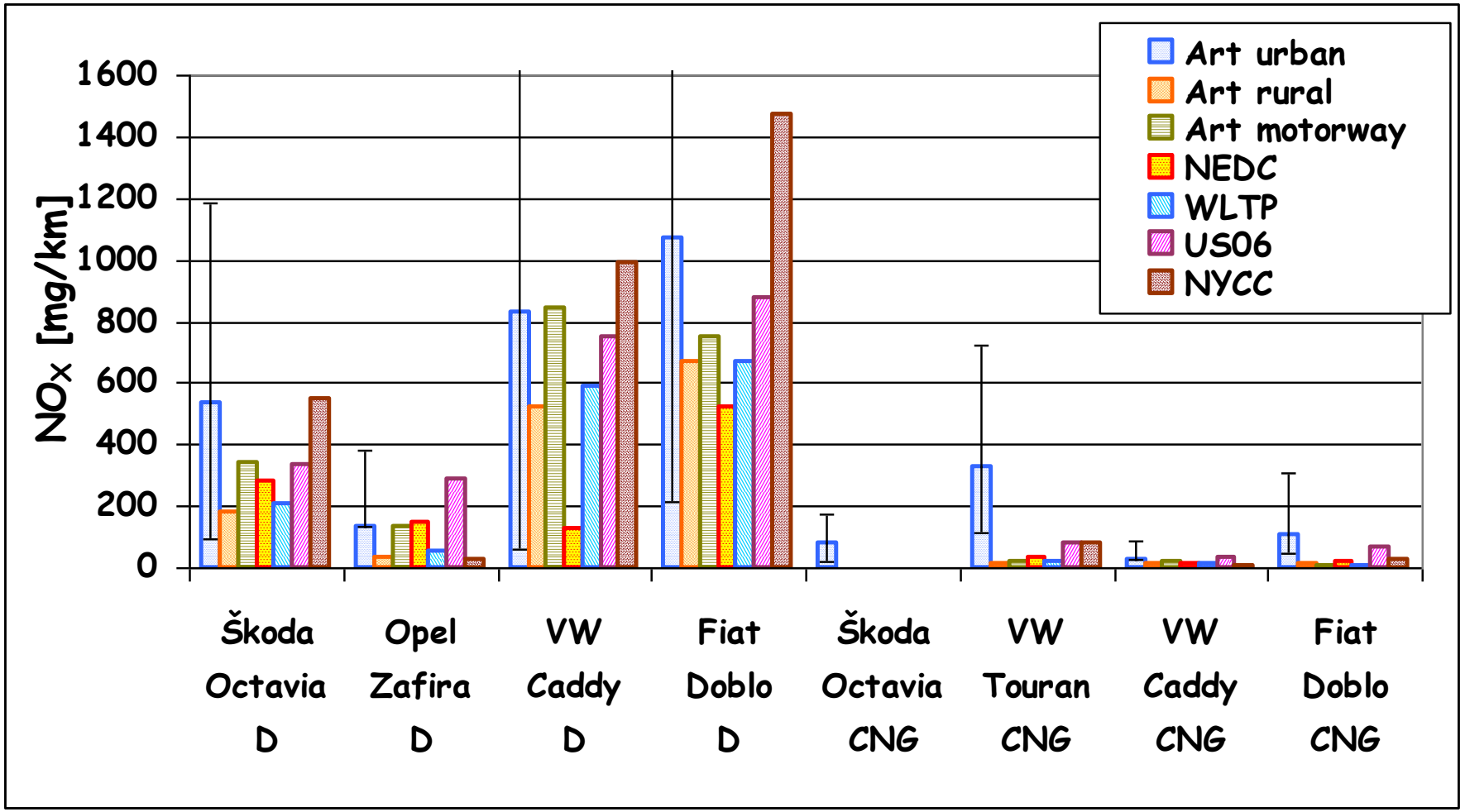
In this test, NEDC run not „as per type approval“,
but with a hot start (engine at operating temperature).
Results vary… (limits: EU 6 cars: 80 mg/km, EU 5 (Caddy) 180 mg/km)



Share of NO_2 in NO_x

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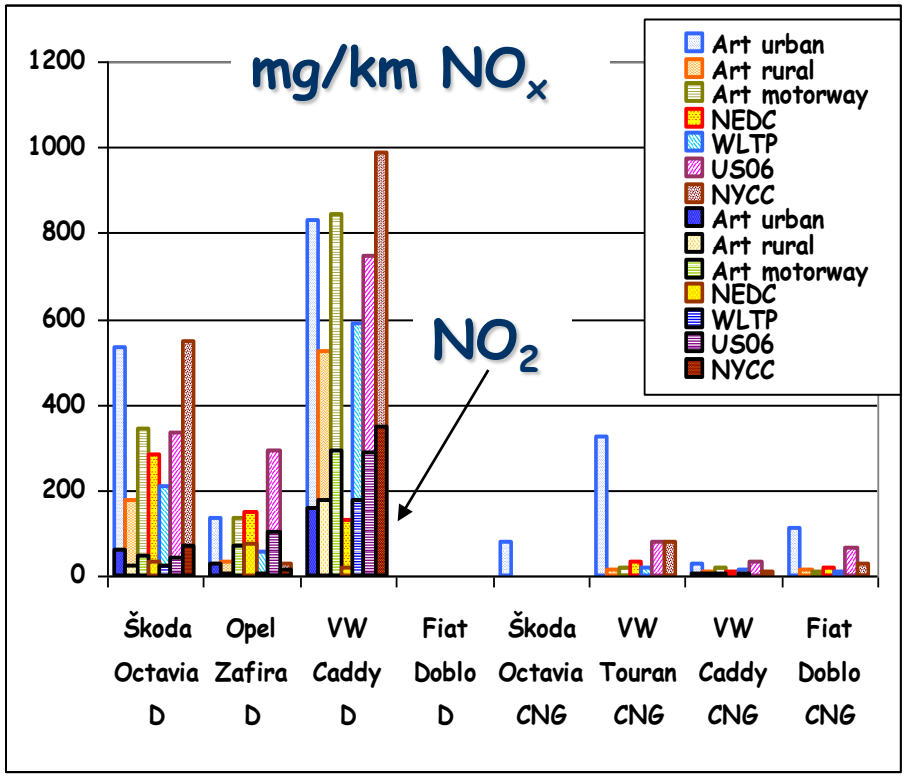
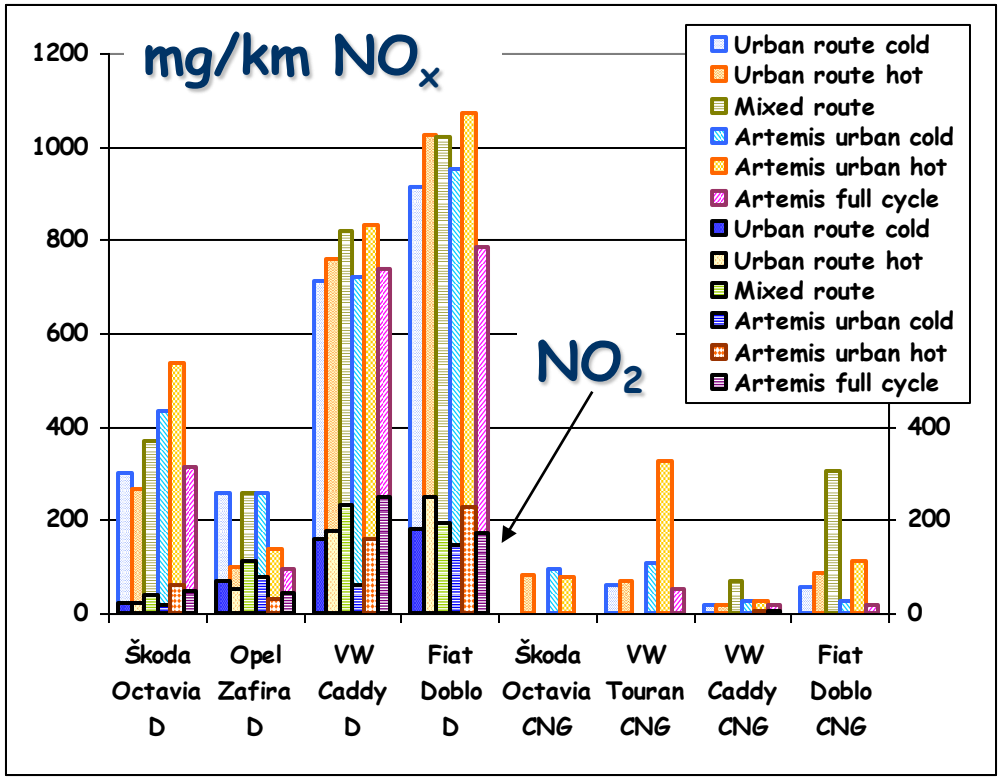
CNG – Negligible

(as expected from stoichiometric operation & three-way catalyst)

Diesel – tens of percent (as expected from many types of DOC)

Problem: We have as much NO2 as we „expected" to have NOx (when Euro legislation enacted) – NO2 worse than NO – now we have concentrated NO2 in the streets …





Greenhouse gases – Artemis urban, urban on-road

CENTRUM VOZIDEL UDRŽITELNÉ MOBILITY

CH_4: 28x higher 100-yr global warming potential vs. CO_2 (IPCC)

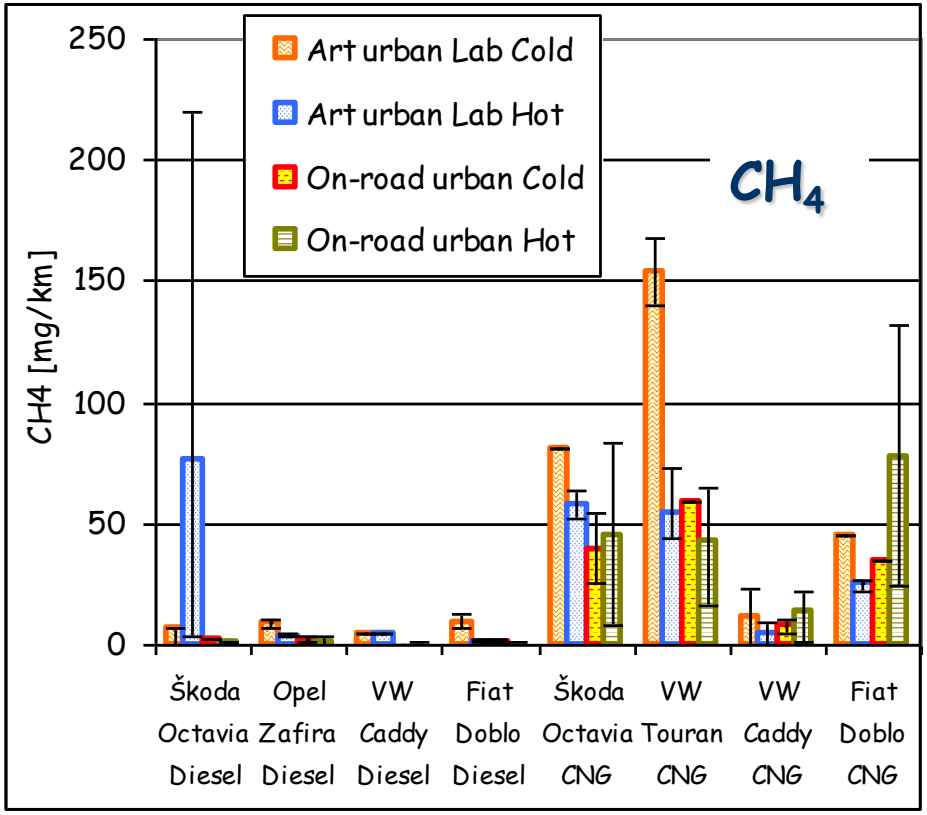
CNG – corresponds to < 1 g/km CO_2

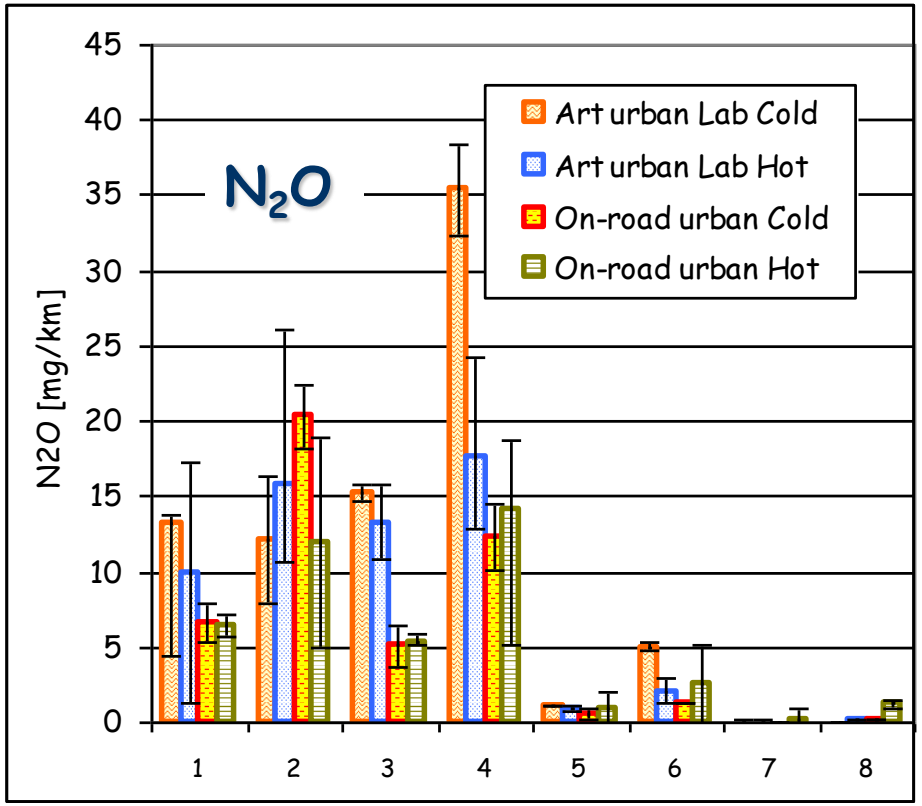
Diesel – essentially limited to DPF and LNT regeneration

N_2O: 265x higher 100-yr global warming potential vs. CO_2 (IPCC)

Diesel – corresponds to several g/km CO_2e, CNG – negligible

??? Will diesel N_2O increase once SCR will be really put to work ???



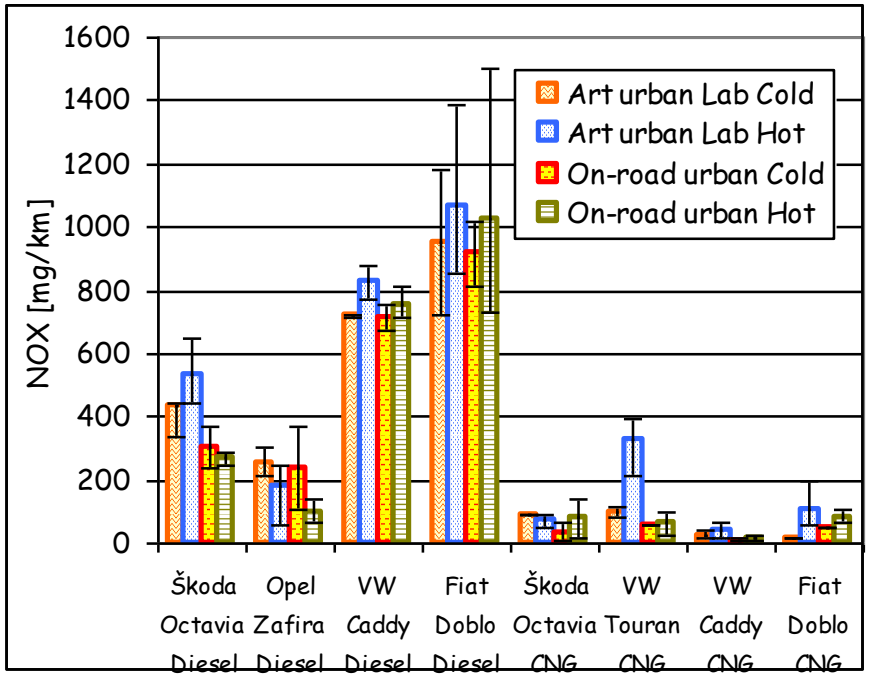


Legal disclaimer about „excess NOx"

On no vehicle, malfunction was indicated or noticed by the test personnel (all with degrees in automotive engineering).

The vehicles were rented from rental fleets and tested as received.

The authors were not in a position to determine whether the malfunction leading to excessive NOx was "unintended" or deliberately created at the factory or by „aftermarket" tampering.

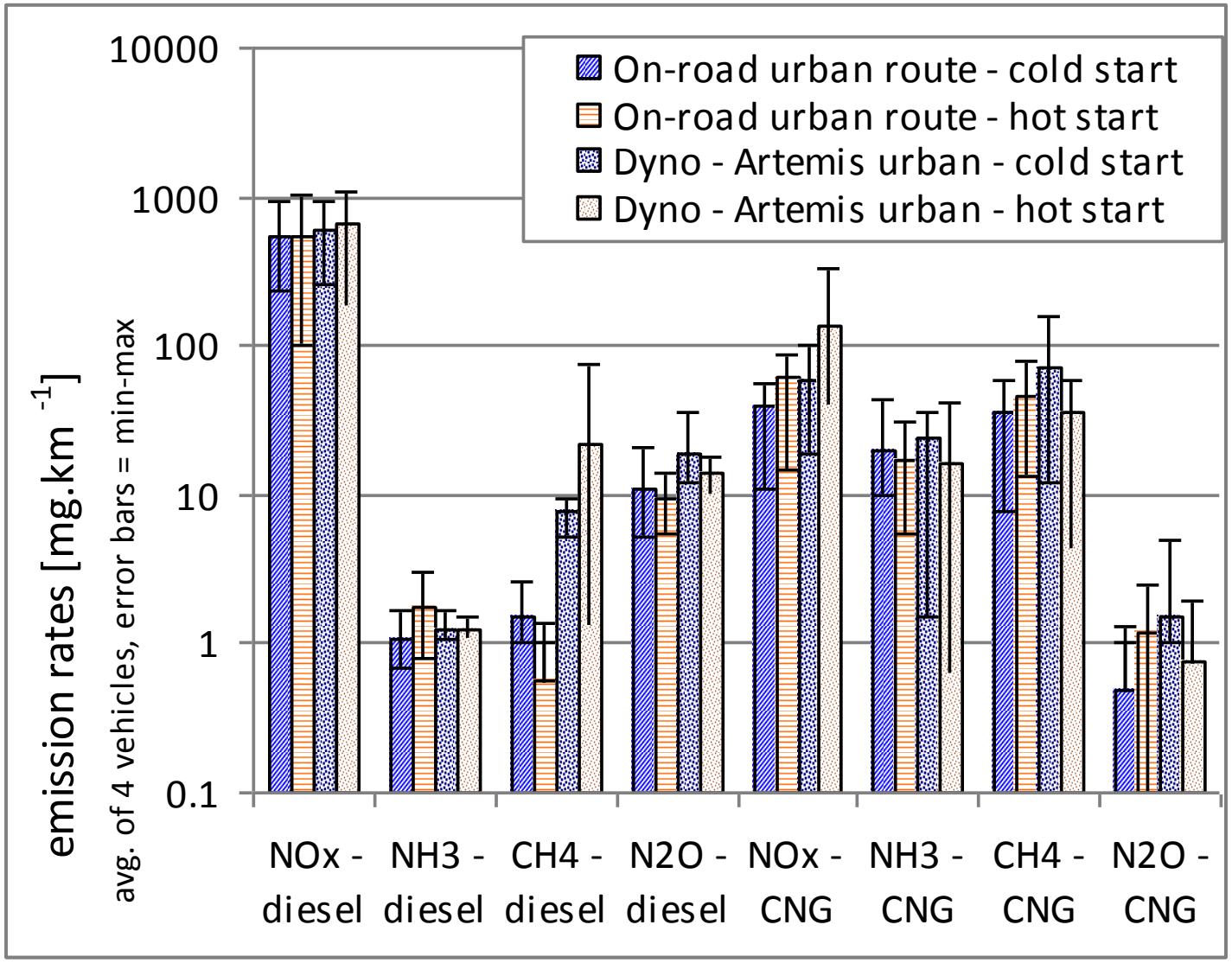


Implications of findings to CNG support policy:

The real benefits of CNG are increased by the „excess" PM caused by non-functional or absent DPF and by the "excess" NOx caused by the "current EU diesel car technology".

Summary of results

(full paper in review at Science of the Total Environment)



Conclusions

- The effects of compressed natural gas (CNG) on emissions addressed.
- Exhaust emissions from 4 diesel and 4 CNG light-duty utility vehicles measured in the laboratory and on the road.
- On-board FTIR used to measure unregulated gaseous pollutants.
- All vehicles – CNG and diesel with DPF – low emissions of non-volatile particles (PN), not clear about nano & volatiles.
- Diesel: non-type-approval NOx order of magnitude higher than Euro 6 limit.
- Diesel: N_2O global warming potential equivalent of several g/km CO_2.
- CNG: Methane emissions equivalent to < 1 g/km CO_2.
- CNG: Non-problematic emissions due to relatively clean burning fuel, stoichiometric air-fuel ratio, three-way catalyst, relatively new engines. Just like with any other engines, quality of design, calibration, maintenance and usage to be monitored and ensured.

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