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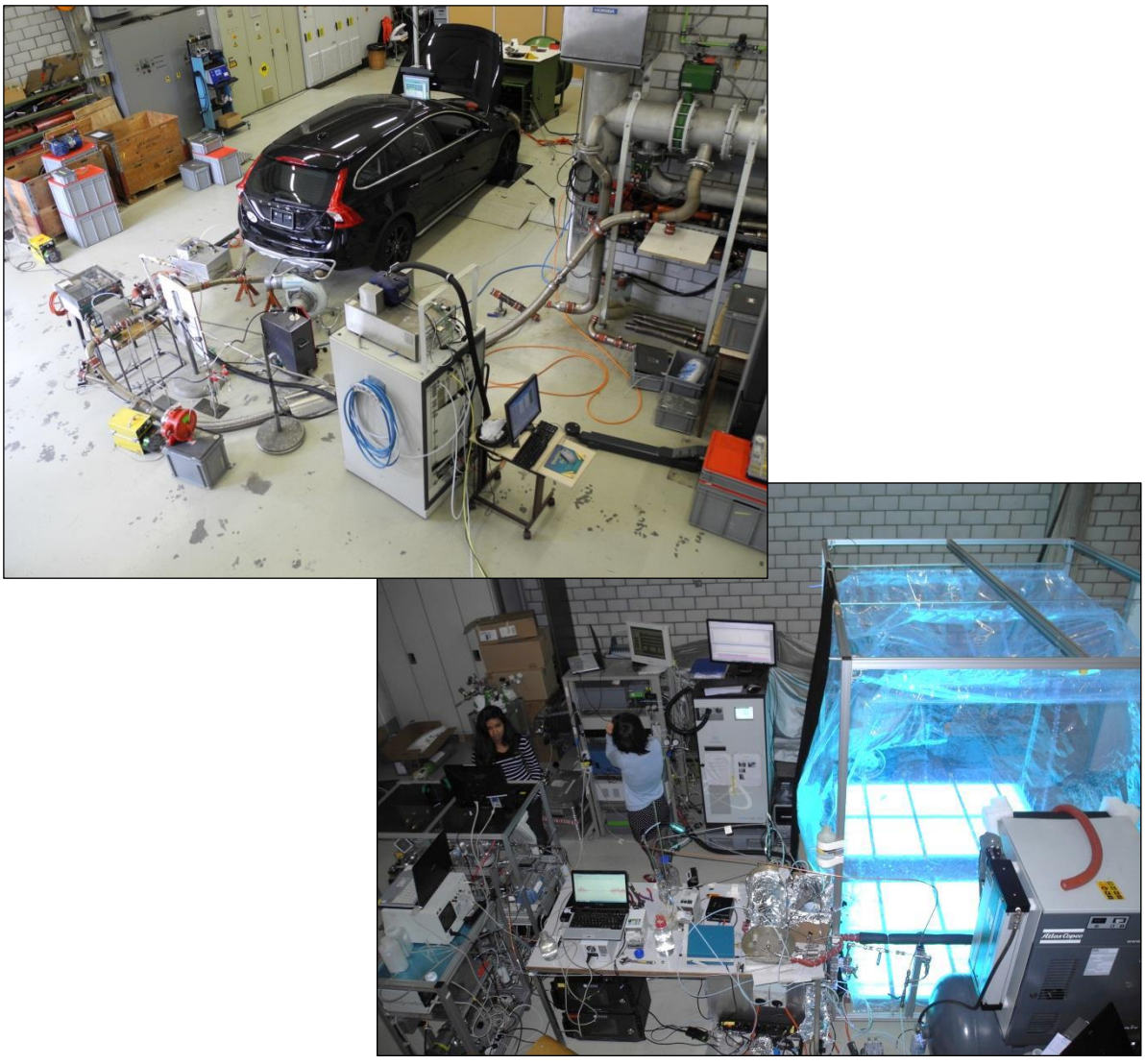
Final report

EmGasCars

Research of Nanoparticles and of Non-Legislated Emissions from GDI Cars.



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The author of this report bears the entire responsibility for the content and for the conclusions drawn therefrom.

Zusammenfassung

Der vorliegende Bericht zeigt die wichtigsten Resultate über die Nanopartikel (NP) und nicht limitierte Abgasemissionen verschiedener DI Benzinpersonenwagen. Die in den Projekten EmGasCars und GasOMeP von der AFHB erarbeiteten Resultate bestätigen, dass manche Fahrzeuge recht hohe Partikelzahlen (PN) emittieren und dass diese sehr effizient mit einem Partikelfilter (GPF) eliminiert werden können. Es wurden auch die Einflüsse von alkoholhaltigen Mischkraftstoffen und vom erhöhten Schmierölverbrauch auf die Emissionen untersucht.

Résumé

Ce rapport présente les résultats d'études sur les émissions de nanoparticules et les émissions gazeuses de différents véhicules à injection directe d'essence. Les résultats obtenus par l'AFHB dans les projets EmGasCars et GasOMeP confirment les émissions élevées au niveau du nombre de particules (PN) de certains véhicules, ainsi que la possibilité d'une réduction très efficace des ces particules à l'aide d'un filtre (GPF). L'influence de carburants contenant de l'alcool ainsi que les influences d'une surconsommation d'huile de lubrification ont également été étudiées.

Summary

The present report summarizes the results concerning the nanoparticles (NP) and the non-legislated emissions from different DI Gasoline Passenger Cars. The results obtained by AFHB in the projects EmGasCars and GasOMeP confirm high particle number emissions of some vehicles and the possibility to efficiently remove these particles by means of a gasoline particle filter (GPF). Influences of alcohol-blend fuels and of the increased lube oil consumption on emissions were also investigated.

Appendix *)

Supplementary information from project partners about GasOMeP:

A1 GasOMeP: Reduction of gasoline vehicle emissions for organic, metallic and particulate non-legislative pollutants. Poster Dr. A. Ulrich 2013

A2 GasOMeP: Current Status an New Concepts of Gasoline Vehicle Emission Control for Organic, Metallic and Particulate Non-Legislative Pollutants. Poster Dr. N. Heeb 1014

A3 GasOMeP, Status Report 2014. Dr. N. Heeb

A4 GasOMeP, Status Report 2015. Dr. N. Heeb

A5 Comparison of PAH Levels and Mutagenicity of GDI and Diesel Vehicle Exhausts and Impact of (Bio)Ethanol. Poster Dr. M. Muñoz, NPC ETHZ 2016.

*) Appendices see at the end of the report

Contents

*) Appendices see at the end of the report

List of abbreviations

AFHB	Abgasprüfstelle FH Biel, CH
ASET	Aerosol Sampling & Evaporation Tube
ASTRA	Amt für Strassen (CH)
BAFU	Bundesamt für Umwelt, (see FOEN)
BfE	Bundesamt für Energie (FOE)
CLA	chemiluminescent analyzer
CPC	condensation particle counter
CS	cold start
CVS	constant volume sampling
DF	dilution factor
DI	Direct Injection
DMA	differential mobility analyzer
DPF	Diesel particle filter
ECE	Economic Commission for Europe
ECU	electronic control unit
EGR	exhaust gas recirculation
EMPA	Eidgenössische Material Prüf- und Forschungsanstalt
EUDC	Extra Urban Driving Cycle
EV	Erdöl Vereinigung
FFV	flex fuel vehicle
FHNW	Fachhochschule Nord-West Schweiz
FID	flame ionization detector
FOE	Federal Office of Energy
FOEN	Federal Office for Environment
FTIR	Fourier Transform Infrared analyzer
GasOMeP	Gasoline Organic & Metal Particles
GDI	gasoline direct injection
GPF	gasoline particle filter
H	high (ash/metal content)
HC	unburned hydrocarbons
HCHO	Formaldehyde
HCN	Hydrocyanic Acid
HNCO	Isocyanic Acid
L	low (ash/metal content)
MD	minidiluter
MeCHO	Acetaldehyde
MFS	mass flow sensor
MS	mass spectroscopy
N_2O	nitrous oxide
NEDC	New European Driving Cycle
NH_3	Ammonia
NO	nitrogen monoxide
NO_2	nitrogen dioxide

NO_x	nitric oxides
NP	nanoparticles < 999 nm
nSMPS	nano SMPS
OAPC	CH: Ordinance of Air Protection Control
OBD	on-board diagnostics
PC	particle counts (integrated)
PCFE	particle counts filtration efficiency
PM	particle mass
PMP	Particle Measuring Program of the GRPE
PN	particle numbers
PSD	particle size distribution
PSI	Paul Scherrer Institute
SEM	scanning electron microscopy
SMPS	scanning mobility particle sizer
SP	sampling position
SSC	steady state cycle
TC	thermoconditioner
Texh	Exhaust gas temperature at tailpipe
THC	total hydrocarbons
TPN	total particle number
TTM	Technik Thermische Maschinen
TWC	three way catalyst
ULSD	ultra low sulphur Diesel
V	vehicle
VERT	Verification of Emission Reduction Technologies
VSS	Verband der Schweizerischen Schmierstoffindustrie
WLTC	Worldwide Light Duty Test Cycle
WLTP	worldwide harmonized light duty test procedure
3WC	three way catalyst

1. Introduction & preliminary information

1.1. Nanoparticles GDI cars

The nanoaerosol in vehicle exhaust is known to be a complex mixture of different volatile and non-volatile species often showing a bimodal particle size distribution with a nucleation mode smaller than 20 nm and a larger accumulation mode that mainly contains aggregates of primary particles.

The larger accumulation mode is usually composed of more graphitic soot particles with an elemental carbon (EC) structure, whereas the particles in the nucleation mode are reported to be mainly volatile organics, especially when sulphur is absent from fuel and lubrication oil, [1-4]. However, recent studies detected also low-volatility particle fractions in the ultrafine size range when sampling was carried out according to PMP protocol at 300 °C, [5-7].

These particles are suspected to be nucleated metal oxides originating from metal additives in lubrication oil or fuels [8-11]. The formation of this particulate fraction was especially observed when the soot content was low as in idle condition of diesel vehicles. These particles mainly appear in the ultrafine size rage <23 nm. While the mass contribution of these ultrafine particles in vehicle emissions is very low, their contribution to the number concentration is significant. Moreover, these ultrafine particles may contribute to the surface composition of the aerosol and have therefore a significant impact on health effects associated with pollution.

Knowledge about the emission level, chemistry and formation mechanisms of these particles is an important objective in order to assess their toxic potential, and to propose effective measures to reduce these emissions.

Studies for gasoline fuelled internal combustion engines pointed out that also this vehicle class can emit remarkable amounts of particles, [6, 12, 13]. Especially gasoline direct injection technology (GDI) shows particle number (PN) emissions significantly higher than modern diesel cars equipped with best available DPF technology. Since the trend for gasoline vehicles with GDI technology is increasing, a significant rise in emission is predicted in the near future.

The nanoparticles emissions are produced especially at cold start and warm-up conditions and at a dynamic engine operation, [14]. The lube oil contributes to this emission in the sense of number concentrations in nuclei mode and composition, [8, 9, 10].

The investigations of morphology of the nanoparticles from gasoline direct injection engine revealed principally graphitic structures, which can store some metal oxides in certain conditions and can be overlapped by condensates, [15, 16].

Car manufacturers and suppliers of exhaust aftertreatment technology offer several mature solutions of GPF for efficient elimination of the nanoparticles from DI SI-engines, [17, 18].

1.2. Operation with Ethanol blends

Thanks to the considerable progress and development of very powerful and reliable electronic control systems. In the last years, a gasoline-Ethanol operation up to E85*) is possible in the Flex Fuel Vehicles (FFV). The engine electronic control unit recognizes automatically the portion of Ethanol and adapts the parameterization of the engine calibration, respectively to obtain the desired performances, and the emissions below the legal limits. The information about Ethanol content after each tank filling is provided by an Ethanol-sensor, [19] together with the OBD-control of the Lambda regulation, [20, 21, 22]. In the tested vehicle in this work no Ethanol-sensor, but a PE (Percentage Ethanol) adaptive algorithm of the ECU was used.

Several manufactures introduced the FFV variants and published extensive information about their R&D and performances: GM / Saab [20, 21]; Toyota [22]; VW [23].

The durable operation with Ethanol needs several precautions: improvements of materials and surfaces of parts of combustion chamber, all plastic materials having contact with fuel, fuel & injection system, functions of the electronic control of the engine, problems of lube oil degradation, [24, 25, 26], deposits formation, [27, 28] and cold startability, [29].

Cold start and especially winter cold start is more difficult with higher Ethanol content in the fuel. The solutions are: double-tank-system (Brazilian market), or electrical preheating of engine and of the fuel system (EU & US markets), [21, 29].

1.3. Butanol for IC-engines

Butanol ($CH_3(CH_2)_3OH$) has a four-carbon structure and is a higher-chain alcohol than Ethanol, as the carbon atoms can either form a straight chain (n-Butanol) or a branched structure (iso-Butanol), thus resulting in different properties. Consequently, it exists as different isomers depending on the location of the hydroxyl group (-OH) and carbon chain structure, with Butanol production from biomass tending to yield mainly straight chain molecules. 1-Butanol, better known as n-Butanol (normal Butanol), has a straight-chain structure with the hydroxyl group (-OH) at the terminal carbon.

n-Butanol is of particular interest as a renewable biofuel as it is less hydrophilic, and possesses higher energy content, higher cetane number, higher viscosity, lower vapour pressure, higher flash point and higher miscibility than Ethanol, making it more preferable than Ethanol for blending with diesel fuel. It is also easily miscible with gasoline and it has no corrosive, or destructing activity on plastics, or metals, like Ethanol or Methanol.

Several research works were performed with different Butanol blends BuXX, [30-36].

Generally there are advantages of higher heat value (than Ethanol). The oxygen content of Butanol has similar advantages, like with other alcohols: tendency of less CO & HC, but possibility of increasing NO_x (depending on engine parameters setting).

The good miscibility, lower hygroscopicity and lower corrosivity make Butanol to an interesting alternative.

The trend of downsizing the SI-engines in the last years implies much higher specific torques and with it an aptitude of knocking and mega-knocking at high- and full load. The alcohols have a higher Octane Numbers (RON), are more resistant to knocking and are a welcomed solution for this new technology of engines, [30].

A basic research of butanol blends Bu20 & Bu100 was performed on mono-cylinder engines with optical ac-cess to the combustion chamber, [31, 32]. One of the engines was with GDI configuration. It was demonstrated, that the alcohol blend improved the internal mixture preparation and reduced the carbonaceous compounds formation and soot.

Concerning the characteristics of combustion Bu100 was similar to gasoline. This research considered only little number of constant operating points.

The alcohol blend fuels E85 & Bu85 were tested on a vehicle with 3WC in road application and with on-board measuring system for exhaust emissions, [33]. It was stated for butanol, that it has no significant influence on CO & HC, but it increases strongly NO_x.

Nevertheless, this is due to the limits of Lambda regulation and as effect of it to the production of too many lean Lambda excursions during the transients.

The warm operation with Bu85 was with no problems, the cold startability and emissions were not investigated.

Butanol is easy miscible with diesel fuel and can con-tribute to the advantages similarly to other oxygenated compounds. In an extensive study of published results, [34], it was confirmed that butanol lowers the PM- and CO-production, has tendencies of increasing HC and no clear tendency concerning NO_x. These are statistical statements concerning different diesel engines with different technical state of the art. The influences on nanoparticle emissions were mentioned as an open field for further investigations.

Another studies on single-cylinder diesel engines with older technology and Bu10 remark no substantial differences between the results with neat diesel fuel and with Bu10, [35, 36].

1.4. Non-legislated emissions of gasoline cars

The most important non-legislated emission components in present discussions are: the nanoparticles (NP), Ammonia (NH_3), nitrous oxide (N_2O), Formaldehyde (HCHO) and Acetaldehyde (MeCHO).

The nanoparticles (NP) became an important research topic, since the first introduction of legal nanoparticle counts limits (Euro 5b) for DI SI passenger cars in EU beginning of 2013.

In this situation the NP and especially the metal oxides emissions from additive packages of lube oils and fuels, become an important topic for all kinds of engines. Lube oil contributes to the NP-emission especially at cold start [37, 38, 39].

Further gaseous substances, which may be present under certain conditions in very low concentrations in the exhaust gases are considered to be potential candidates for future legal limitation. These non-legislated emission components are: Ammonia (NH_3), Nitrogen Dioxide (NO_2), Nitrous Oxide (N_2O), Formaldehyde (HCHO) and Acetaldehyde (MeCHO) – all of them quite easy to be measured and indicated with FTIR.

Production of Ammonia (NH_3) in the exhaust of gasoline cars with 3WC was demonstrated in [40] and [41] – this especially at transient operation with rich excursions of Lambda.

The other components were little investigated in connection with E85-operation. From the research of the authors can be stated, that with a correctly working 3WC (at warm operation) there are usually no measurable concentrations of NO_2 and N_2O and the HCHO – values show a noise below 1ppm, [42].

2. Participating institutions & persons

EMPA	Dr. A. Ulrich † , initial project leading Dr. N. Heeb, project leading Dr. M. Muñoz, analytics of traces, PAH Mr. A. Wichser, analytics of particle mass Mrs. K. Zeyer, analytics Mr. J. Mohn, analytics
PSI	Dr. A. Prevot, secondary organic aerosols (SOA) Ms. S.Pieber, PhD candidate Ms. N. Kumar, PhD candidate
FHNW	Prof. Dr. H. Burtscher, measuring technics for nanoparticles, aerosol ageing tunnel Dr. A. Keller, analytics
AFHB	Prof. Dr. J. Czerwinski, DI P. Comte, DI Y. Zimmerli, Mr. Ph. Wili, Mr. Clénin – vehicles, fuels, lube oils, chassis dynamometer, emissions: standard,nanoparticles, size selective sampling, FTIR
TTM	Dr. A. Mayer, TTM – contacts industrial partners, research material.

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For the support of the EmGasCars-activities thanks are given to: BfE, BAFU, Swiss-Oil (EV) and Swiss-Lubes (VSS).

3. Test methods and Instrumentation

The vehicles were tested on a chassis dynamometer at constant speeds and in the dynamic driving cycles WLTC and NEDC, with cold & warm engine.

3.1 Chassis dynamometer

The following test systems were used:

- roller dynamometer: Schenk 500 GS 60
- driver conductor system: Tornado, version 3.3.
- CVS dilution system: Horiba CVS-9500T with Roots blower
- air conditioning in the hall automatic (intake- and dilution air).

The driving resistances of the test bench were set according to the legal prescriptions, responding to the horizontal road.

3.2 Nanoparticle analysis

The measurements of NP size distributions were conducted with different SMPS-systems, which enabled different ranges of size analysis:

- SMPS: DMA TSI 3081 & CPC TSI 3772 (10 - 429 nm)
- nSMPS: nDMA TSI 3085 & CPC TSI 3776 (2 - 64 nm)

For the dilution and sample preparation an ASET system from Matter Aerosol was used, (ASET … aerosol sampling & evaporation tube). This system contains:

- Primary dilution - MD19 tunable rotating disc minidiluter (Matter Eng. MD19-2E)
- Secondary dilution - dilution of the primary diluted and thermally conditioned sample gas on the outlet of evaporative tube.
- Thermoconditioner (TC) - sample heating at 300°C

In the tests the gas sample for the NP-analysis was taken from the undiluted exhaust gas at tailpipe for stationary operation (SMPS) or from the diluted exhaust gas in CVS-tunnel at transient operation (CPC).

3.3 Driving cycles

The vehicles were tested on a chassis dynamometer at constant speeds (SSC) and in the dynamic driving cycles (WLTC & NEDC).

The steady state cycle (SSC) consists of 20 min-steps at 95, 61, 45, 26 km/h and idling, performed in the sequence from the highest to the lowest speed.

Fig. 1 shows the steady state cycle (SSC) with the resulting tailpipe temperatures (t_{exh}) for gasoline.

The approach to find a homogenized world-wide driving cycle was successfully finished with the development of the homogenized WLTP world-wide light duty test procedure. The WLTC (world-wide light duty test cycle) represents typical driving conditions around the world, Fig. 2.

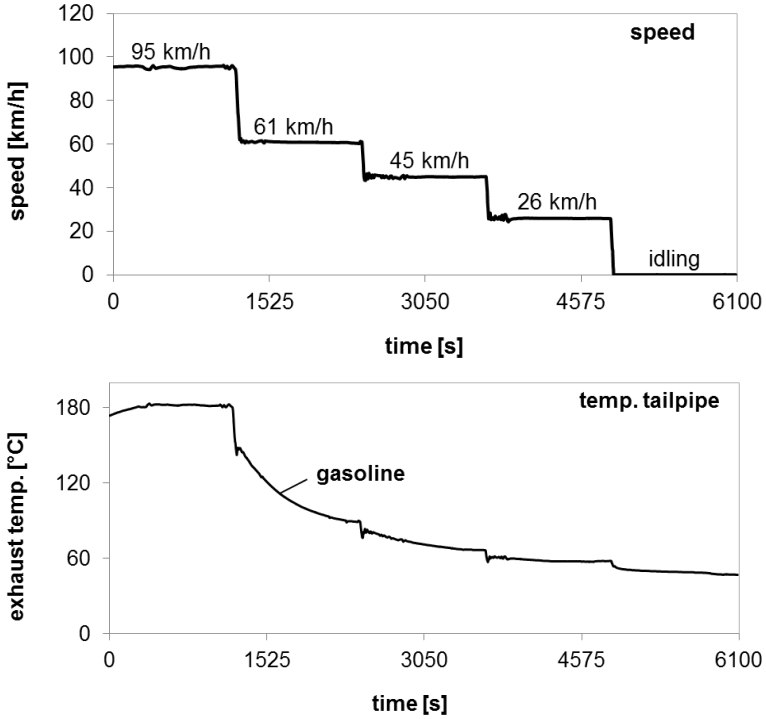

Figure 1: SSC steady state cycle and tailpipe temperature of vehicle 1

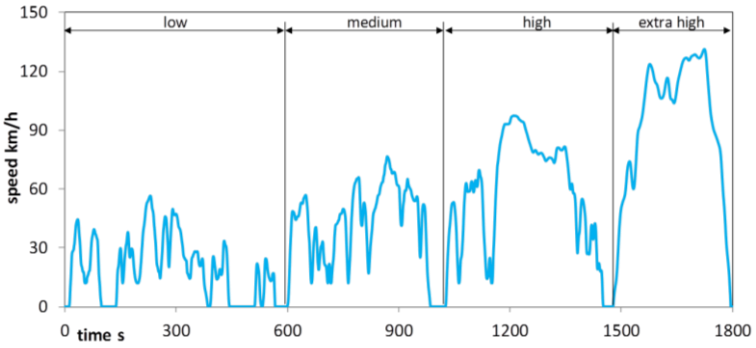

Figure 2: WLTC driving cycle

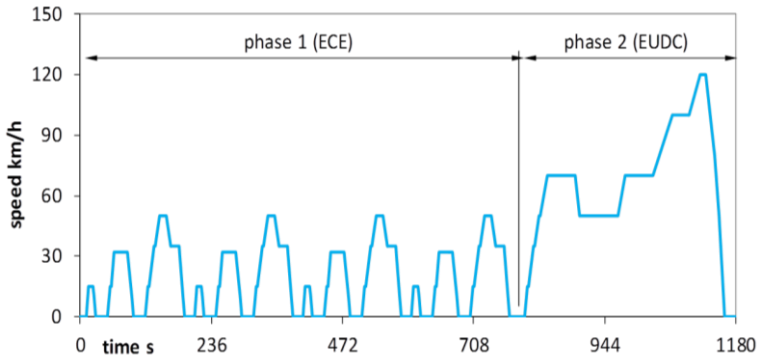

Figure 3: NEDC driving cycle

3.4 Different sampling positions (SP)

The exhaust gases were measured for certain tasks at different sampling positions (SP) along the gas way.

Fig. 4 represents the sampling positions for gasoline vehicles. SP0, SP1 & SP2 are for undiluted and SP3, SP4 & SP5 for diluted gas. In present work the mostly used sampling positions were: after 3WC (SP0), tailpipe (SP1) and CVS at the end (SP5).

At constant operation the measuring system was switched from SP to SP.

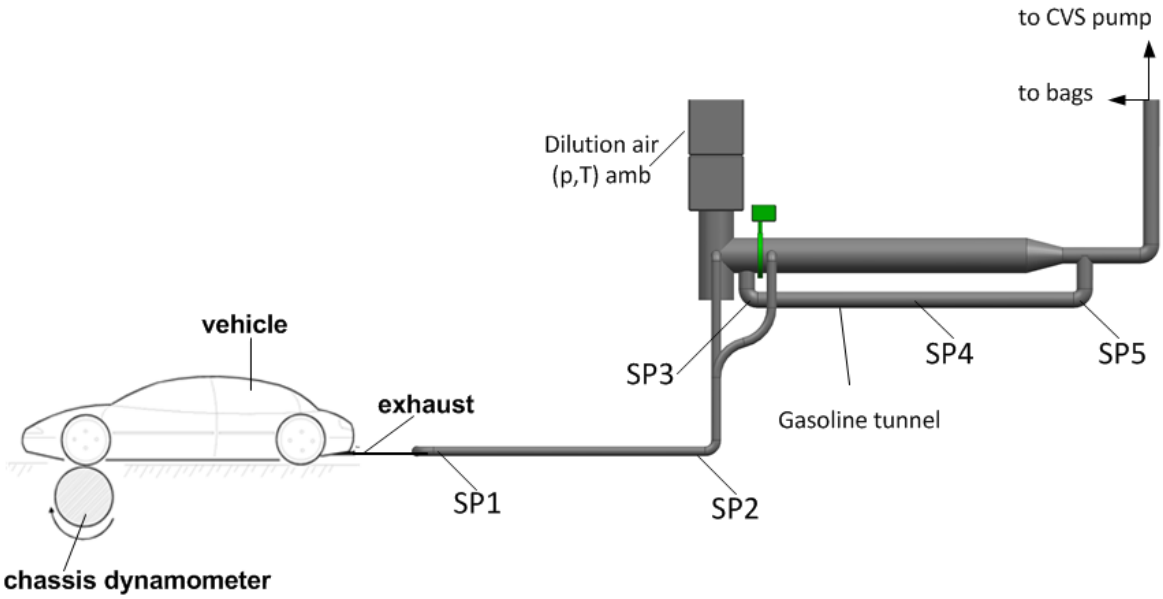

Figure 4: Sampling positions (SP) for testing the emissions along the gas way.

3.5 Size-selective NP-sampling & analytics

In several tests the ELPI-instrument (electrical low pressure impactor) was used to collect size-specific samples for follow-up chemical analysis with respect to the collected substances. The whole range from 30 to 10'000 nm is split into 13 stages (13 impactors + filter for the rest). After the test the collected material is available on these 13 deposition discs, it can be weighed to determine the mass and can be analyzed. In order to improve the quality of the chemical analysis special deposition films were used on these discs, consisting of Polycarbonate, which proved to be a very pure material.

Fig. 5 shows an example of soot deposits on an ELPI filter plate.

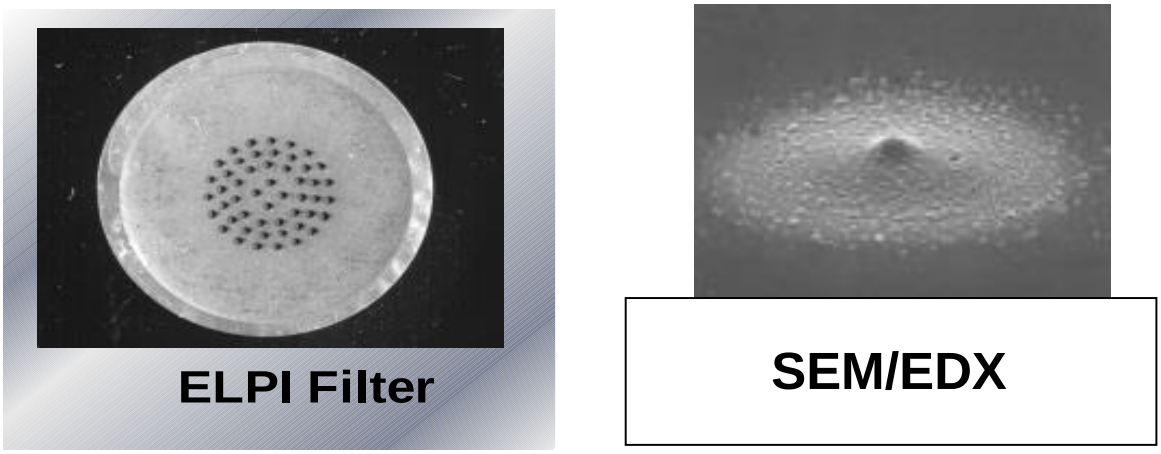

Figure 5: typical appearance of soot deposits on ELPI filter plates

The size-fractionated metal analysis of the collected aerosols on the impactor filter plates was performed according to a microwave-assisted acid digestion procedure with subsequent ICP-MS analysis (inductively coupled plasma mass spectrometry).

This analytical technique is extremely sensitive: detection limit for Pt as well for Pd is on the impressively low level of 0,0004 µg / ELPI-stage and 0,0006 µg / ELPI-stage respectively.

Reliable results can only be achieved if the detection limit of the entire procedure, including sampling, sample preparation and analysis are determined. Therefore, blanks of fresh filter material and field-blanks (processed similarly to field sampling filters) need to be sampled, digested and determined, [5].

4. Results

Most important examples of results from the publications of AFHB are given in this section.

4.1 Nanoparticle emissions of different gasoline cars, [43]

Test vehicles

The research of NP-emissions of a vehicle with MPI (older technology) and of the recent vehicles with GDI was performed on Renault 18, Audi A3, Volvo V60 and Citroën C5, Tab. 1.

The gasoline used was from the Swiss market, RON 95, according to SN EN228. In the present tests the lube oils were not changed and not analyzed.

Vehicle	**Renault 18 Break ①**	**Audi A3 2.0 TFSI ②**	**Volvo V60 T4F ③**	**Citroën C5 ④**
Engine code	J7T-718	BWA	B4164T2	EP6CDT (5F02)
Number and arrangement of cylinders	4 / in line	4 / In line	4 / in line	4 / In line
Displacement cm^3	2164	1984	1596	1598
Power kW	74 @ 5000 rpm	147 @ 6000 rpm	132 @ 5700 rpm	115 @ 6000 rpm
Torque Nm	162 @ 2000 rpm	280 @ 1800 rpm	240 @ 1600 rpm	240 @ 1400 - 4000 rpm
Injection type	MPI	DI	DI	DI
Curb weight kg	1110	1530	1554	1515
Gross vehicle weight kg	1585	1920	2110	1951
Drive wheel	Front-wheel drive	Front-wheel drive	Front-wheel drive	Front-wheel drive
Gearbox	m5	m6	a6	a6
First registration	01.04.1985	01.12.2006	27.01.2012	2013
Exhaust	EURO 0	EURO 4	EURO 5a	EURO 5a
VIN	VF1135B00 F0000505	WAUZZZ8P 17A042987	YV1FW075BC 1043598	VF7RD5FV ABL503114

Table 1: Data of the investigated gasoline cars

Steady state operation

SMPS particle size distributions (PSD) of all tested vehicles at tailpipe are represented exemplary at similar constant part load operation of the engine in Fig. 6.

The PSD's were measured with two SMPS-systems in different size ranges: SMPS [9.8–429nm] and nSMPS [6.85–85nm], which for vehicle 1 gives a very complementary picture of PSD's.

It can be remarked, that vehicle 1, the older model with MPI, has a clearly bimodal shape of PSD with maximum in nuclei mode, which is up to 4 orders of magnitude higher, than the lowest emissions of vehicle 2.

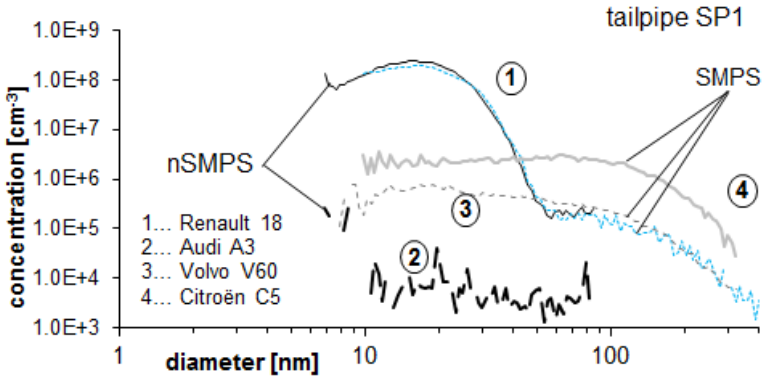

Figure 6: Particle size distributions of different vehicles at tailpipe & 40 km/h

The NP-emissions of vehicle 2 are at the ambient level and show stochastic peaks at different particle sizes, but no regular PSD.

The PSD's of vehicles 3 & 4 show no increased nuclei mode (< 50 nm). In the accumulation mode (> 50 nm) the particle count concentrations (PC) of vehicle 3 are nearly identical with vehicle 1 and for vehicle 4 the PC's are up to 1 order of magnitude higher.

How can the differences be explained? There are different interacting processes during mixture preparation, combustion and gas flow in the exhaust system, which sensitively influence the generation of nanoparticle emissions. The following discussion gives some ideas and hypotheses:

For the older vehicle it is clear that it has higher lube oil consumption than the other new vehicles. The lube oil consumption in such self-aspirating engine can be provoked by the valve shafts and by the used piston segments and cylinder walls. We can suppose the presence of both reasons: the lube oil from intake valves shafts will be carried with the fuel (MPI) into the combustion chambers, the thicker lube oil layer on the combustion chamber walls will contribute to higher induction of oil into the combustion. Both effects work similarly like the blending of lube oil into the fuel for lost-oil-lubrication of small 2-stroke engines and increases strongly the NP-emissions, [44, 45]. This increase is caused on the one hand by metal and metal oxides from the additive packages, which during the spontaneous condensation produce primary particles in nano-, or sub-nano scale. These primary particles are on the other hand "seeding kernels" for the condensation of heaviest HC-compounds from the lube oil, which can pyrolize and cannot be eliminated by the catalytic or thermal striping used in the present measuring systems.

Another question is the mixture preparation: the ideal mixture preparation should atomize and evaporate all the used fuel and bring it as homogenously premixed, as possible into the combustion chamber.

For MPI there is usually a portion of fuel deposited on the walls of the intake port, which can arrive in the combustion chamber as liquid non-premixed droplets. A part of this “unprepared” fuel burns heterogeneously and is a source of soot-production.

These effects are stronger in DI technology and especially, when the liquid fuel arrives at the wall and interacts with the lube oil layer, the production of nanoparticles is particularly increased, [46, 47].

The chemistry of oil and fuel, their HC-matrix and additive packages have a significant influence on the NP’s.

The passage of aerosol through the exhaust system, the history of temperature drop, catalysis, chemistry, spontaneous condensation and store/release effects have finally influences on “what will be measured at tailpipe”.

The processes influencing NP-production depend on engine operating conditions. With no doubt the NP-emissions vary with the operating point and are increased at transient operation.

Several measurements were performed with vehicle 4 at three sampling positions (SP) in the gas path: directly after 3WC SP0, at tailpipe SP1 and at the end of CVS-tunnel (SP5).

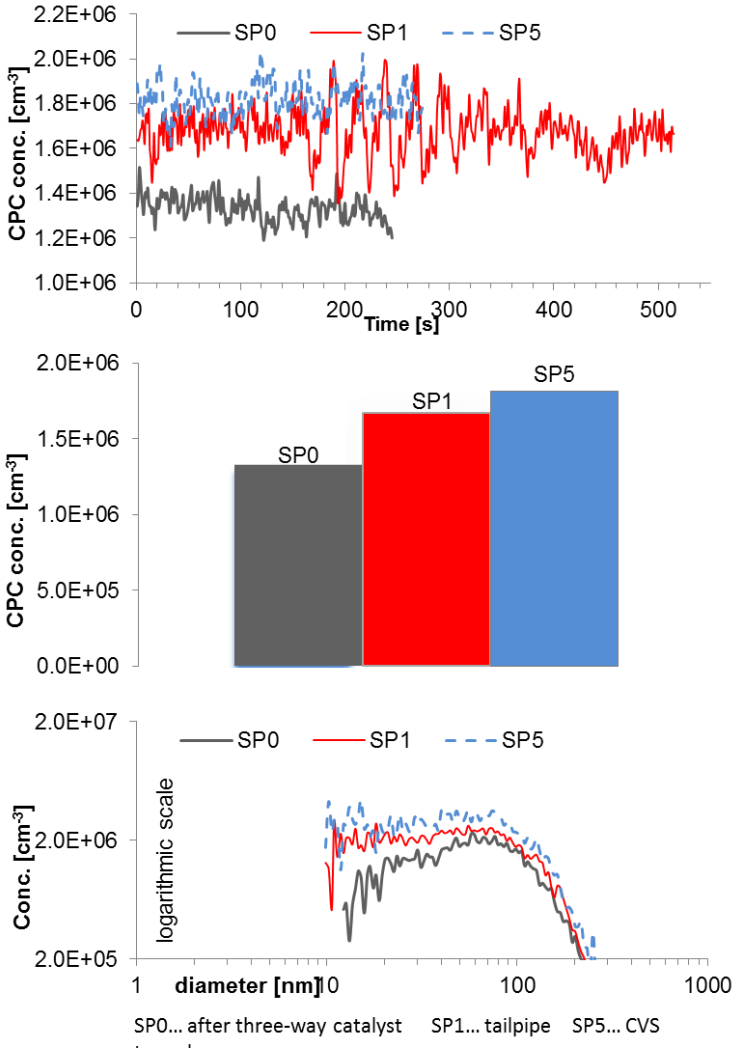

Figure 7: NP-Emissions at different sampling positions (SP). Vehicle 4; 40 km/h; 2nd gear.

Fig. 7 shows some results at 40 km/h. There is an increase of summary PC's over the gas way, both: in undiluted gas (SP0 to SP1) and in diluted gas (SP1 to SP5).

These effects are clear and repetitive. It must be supposed that in the undiluted part the nucleation and the spontaneous condensation are more pronounced, than in the diluted part of the gas line. In the last one, the agglomeration and the diffusion loses are slowed down due to the dilution.

In the SMPS particle size distributions represented at the bottom of this figure. the supplementary particle generation in nuclei mode is visible. At SP1 & SP5 the measuring system detects smaller NP's as at SP0.

Transient operation

Following figures represent some results of summary NP-counts, measured with CPC in the legal driving cycles NEDC & WLTC.

Particles from 10 repeated NEDC's with vehicle 3 were collected on ELPI-stages and the size-selective analysis of collected substances was performed at the EMPA Analytical Laboratory.

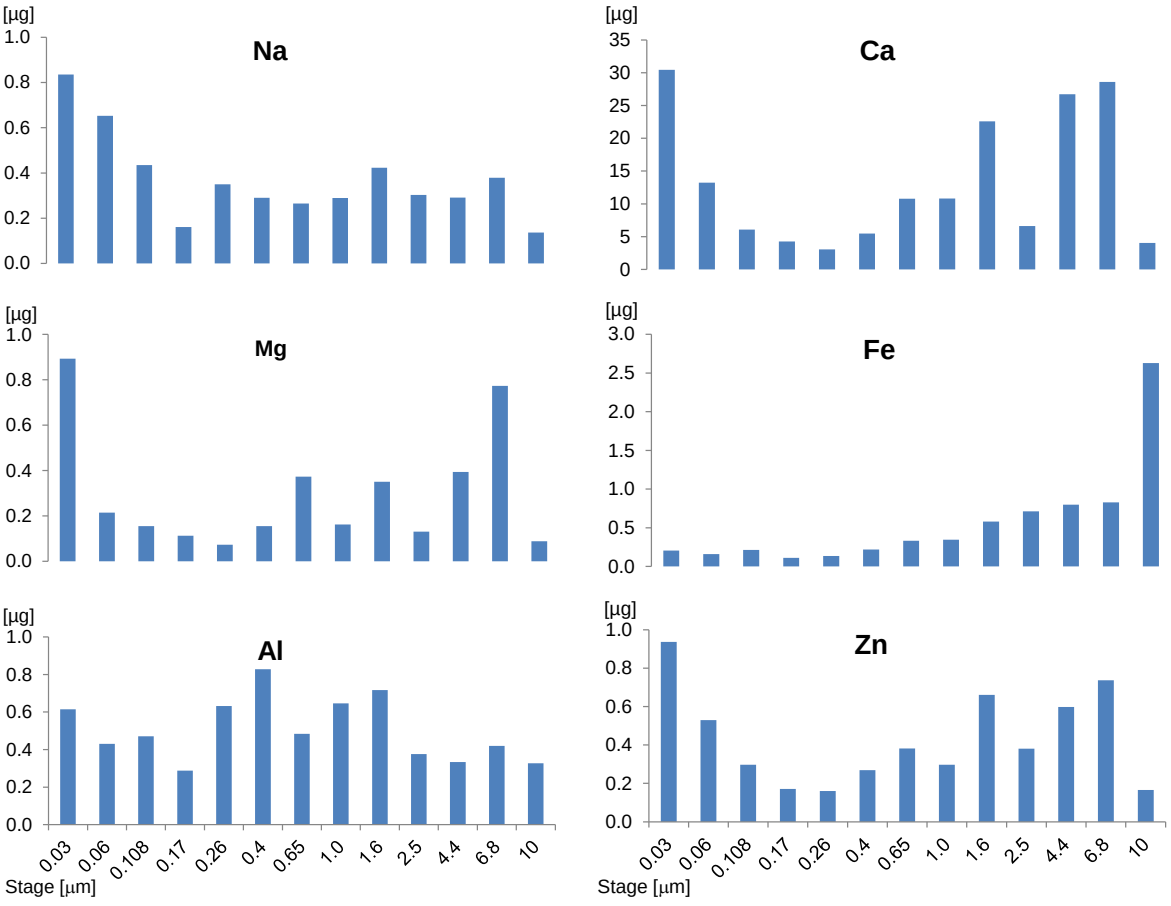

Figure 8: Major elements found on the ELPI-stages after 10 NEDC's. Vehicle 3; CVS tunnel.

Fig. 8 shows the most important substances, which were found on the ELPI-stages after the 10 NEDC's.

It can be remarked that there is a highest amount of Ca (in average 10 to 15 times more, than other substances). A clear increase of amount in the lowest size range show Na, Mg, Ca & Zn, while Al & Fe do not show this effect. There are also some sporadic peaks in higher size classes. This can be partly explained by the mechanism of particle production. While the nano-size particles originate from "atomary procedures" (like combustion, nucleation, agglomeration, condensation), the micro-size particles are coming from the mechanical wear.

The maximum values of Ca are at 30 µg/filter and for the other elements at 1 µg/filter.

Five WLTC's – 1 cycle with cold start and 4 cycles with warm start – were performed with the objective of indicating the repetitivity of NP-emissions.

The nanoparticles were measured on line with CPC at the end of CVS-tunnel (according to the PMP-method).

Fig. 9 compares the total particle number emissions TPN of all vehicles in the driving cycles NEDC & WLTC "hot". In both phases of NEDC vehicle 1 has the highest emissions.

Regarding from phase 1 (ECE) to phase 2 (EUDC with higher load) the relationship of vehicles 2, 3 & 4 inverts.

In WLTC vehicle 2 becomes in some phases of the cycle higher emitting than the other vehicles, in spite of showing previously very low emissions at constant speeds (see Fig. 6). It is visible that the NP-emissions of each vehicle depend on the dynamics and power of the used driving cycle. The consideration of SMPS PSD's at certain constant operation (like in Fig. 6) is not sufficient to see the relationships at transient operation in the presented driving cycles.

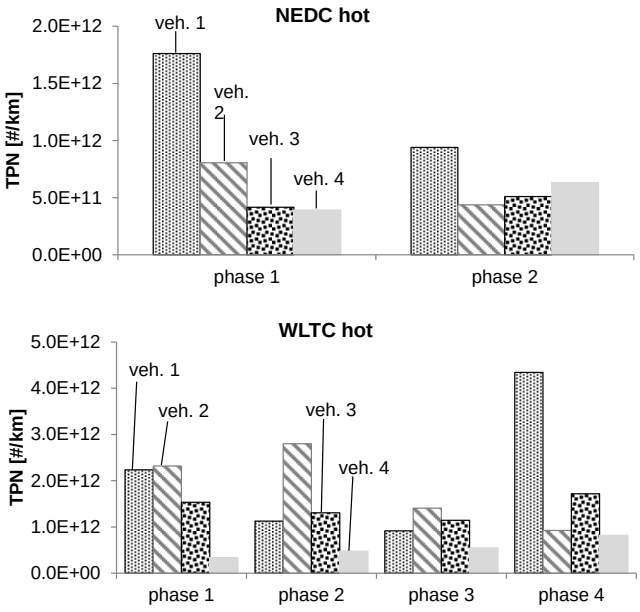

Figure 9: Comparisons of NP-results in NEDC hot. CVS tunnel; gasoline

Conclusions

The most important statements from this part of tests can be summarized as follows:

- the older model with MPI (vehicle 1) emits at the stationary part load operation up to 4 orders of magnitude more nanoparticles,
- for the low-emitting vehicle there are sporadic PN-emission peaks and no clear shape of particle size distribution,
- for the vehicles with DI (vehicle 2, 3 & 4) there is no increase of PC's in nuclei mode (below 10 nm) at the measured constant speeds,
- the NP emitted at cold start (20-25°C) of a NEDC, or WLTC are roughly 4 to 5 times higher than with the hot start,
- in the last phases of WLTC with higher accelerations, with higher speeds and more energy needed for accelerations, there is a highest level of PN-emissions,
- there is a good repeatability of the average emissions in the "warm" driving cycles,
- 10 NEDC's allow the accumulation of enough particles on the ELPI-stages, to enable the size-selective substance analysis,
- the most important substances found after 10 NEDC's in the 3 lowest stages (sizes: 0,03; 0,06; 0,108; µm) were: Na, Mg, Ca and Zn,
- there is an increase of particle counts along the gas way due to the increasing nuclei mode,
- due to the electronic regulation of the engine the PN-emission of some vehicles (here vehicle 3 & 4) are periodically fluctuating,
- comparing the NP-emissions of different vehicles with SMPS PSD's at constant operation gives only a limited information about the relationships of emissions measured with CPC in dynamic driving cycles.

4.2 Results with/without GPF and with Diesel car, [48]

Test vehicles

Tables 2 & 3 summarize the most important vehicle data. As a reference of the best available technology, concerning the reduction or elimination of PM- and PN-emissions a modern Diesel passenger car (vehicle 6) with a high-quality DPF was included in the tests.

Vehicle ①②③	① **Volvo V60 T4F**	② **Opel Insignia 1.6 EcoFlex**	③ **Mitsubishi Carisma 1.8 GDI**
Number and arrangement of cylinders	4 / in line	4 / in line	4 / in line
Displacement cm^3	1596	1598	1834
Power kW	132 @ 5700 rpm	125 @ 6000 rpm	90 @ 5500 rpm
Torque Nm	240 @ 1600 rpm	260 @ 1650-3200 rpm	174 @ 3750 rpm
Injection type	DI	DI	DI
Curb weight kg	1554	1701	1315
Gross vehicle weight kg	2110	2120	1750
Drive wheel	Front-wheel drive	Front-wheel drive	Front-wheel drive
Gearbox	a6	m6	m5
First registration	27.01.2012	2014	05.2001
Exhaust	EURO 5a	EURO 5b+	EURO 3

Table 2: Data of investigated cars

Vehicle ④⑤⑥	④ **Opel Zafira Tourer**	⑤ **VW Golf Plus**	⑥ **Peugeot 4008 1.6HDi STT**
Number and arrangement of cylinders	4 / in line	4 / in line	4 / in line
Displacement cm^3	1598	1390	1560
Power kW	125 @ 6000 rpm	118 @ 5800 rpm	84 @ 3600 rpm
Torque Nm	260 @ 1650-3200 rpm	240 @ 1500 rpm	270 @ 1750 rpm
Injection type	DI	DI	DI
Curb weight kg	1678	1348 - 1362	1462
Gross vehicle weight kg	2360	1960 - 1980	2060
Drive wheel	Front-wheel drive	Front-wheel drive	Front-wheel drive
Gearbox	m6	m6	m6
First registration	22.07.2014	01.02.2010	12.04.2013
Exhaust	EURO 5b+	EURO 4	EURO 5b

Table 3: Data of investigated cars

Steady state operation (SSC)

Fig. 10 represents exemplary the SMPS particle size distributions (PSD) of all tested vehicles (V1 to V5) at tailpipe without GPF at the same constant speeds and idling.

At 95 and 45 km/h the maxima of PSD's show the particle counts concentrations (PC) in the range of 106 to 107 #/cm3, which is similar as for Diesel engines. At idling, the PC values are roughly one order of magnitude lower.

For vehicle 3, strong fluctuations of the PC-concentration during the period of scanning (over the size range) are visible. During the constant speed operation of this vehicle (at 95 and 45 km/h), periodic fluctuations of gaseous emissions (CO, HC, NO_x) were observed (not represented here) and confirmed a continuous switching of the operation between lean and rich. This means that for this vehicle, changing between the stratified (lean) and homogenous (rich) operating strategies, it also implies the switching of parameters, like ignition timing, injection timing, injection quantity and eventually EGR. This has the influence on NP-emission as demonstrated.

The relationships of NP-emissions between different vehicles can vary depending on operating condition. As example: vehicle 2 has at 95 km/h the lowest and at 45 km/h and idling the highest particle counts concentrations.

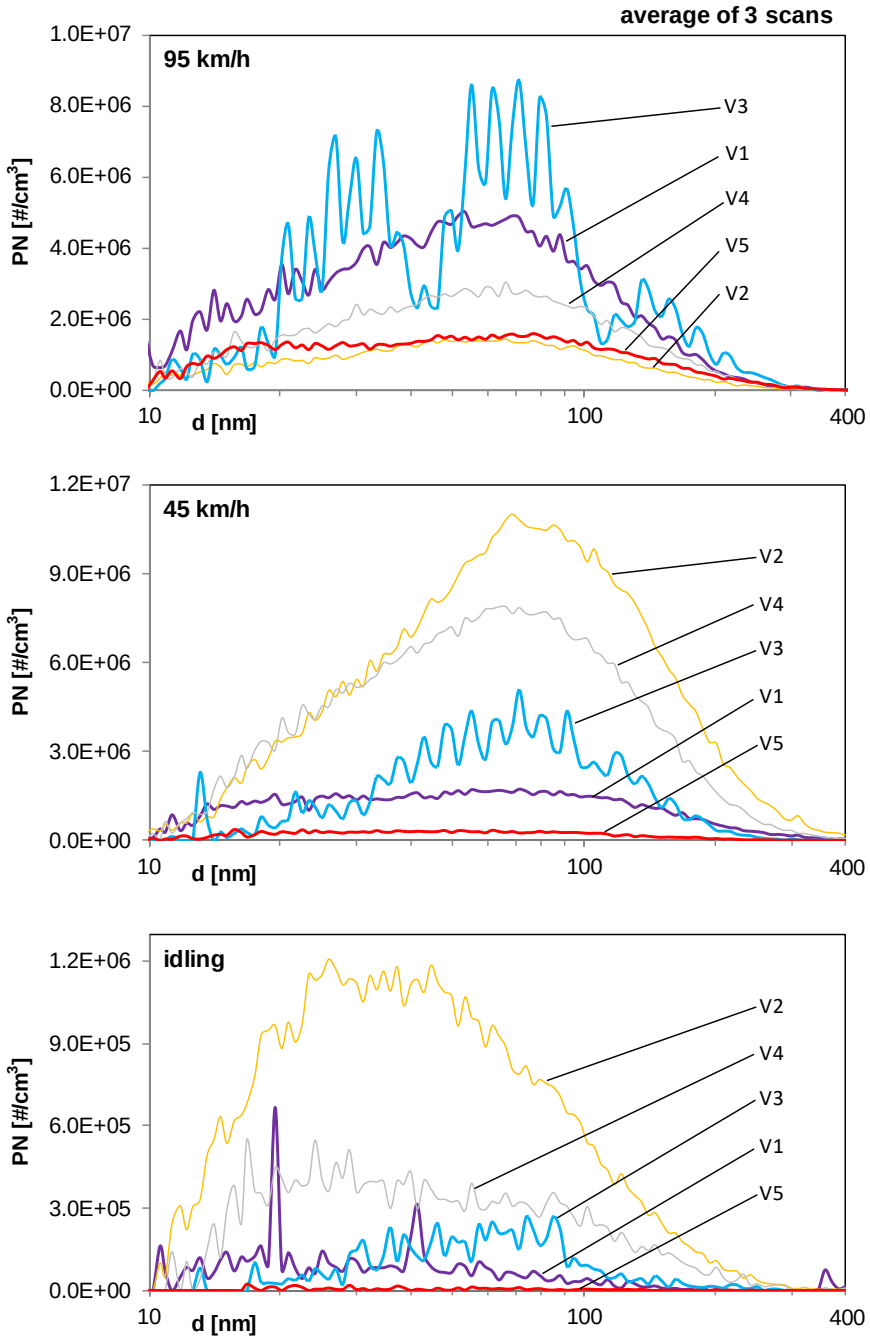

Figure 10: SMPS particle size distributions at constant speeds with different GDI vehicles (w/o GPF).

Transient operation

All mechanisms influencing the NP-production in combustion chambers and in the exhaust system are at transient operation variable and mostly overlapping each other. A known and accepted fact is that the peak values of NP-emissions coincide with the acceleration, or deceleration events in the driving cycle.

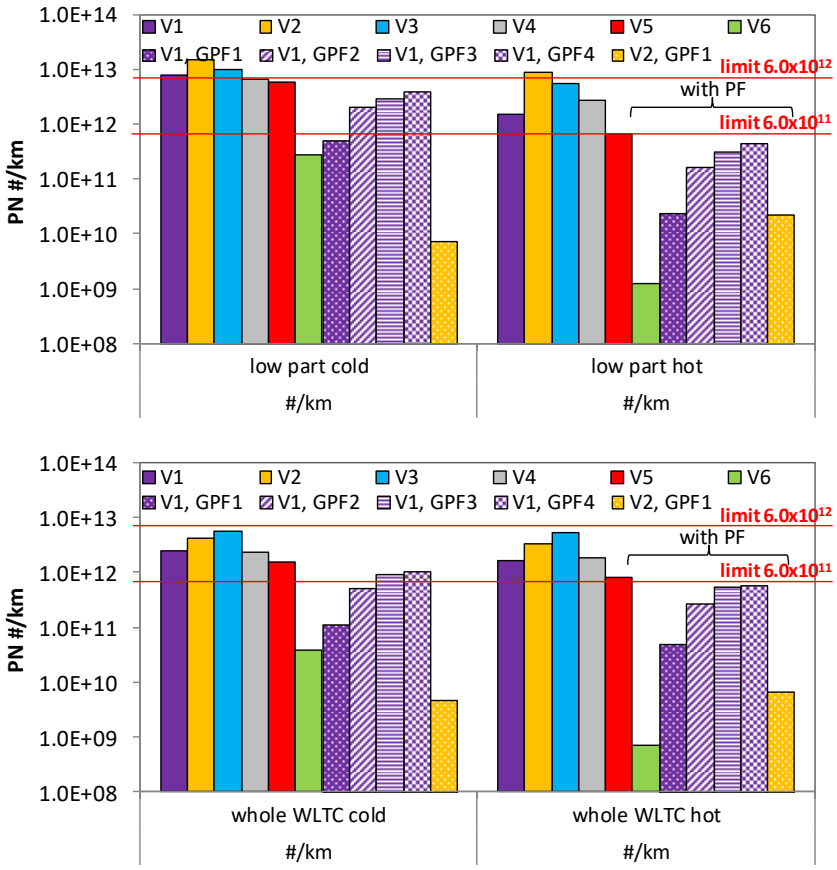

Figure 11: Comparison of PN-emissions in WLTC cold and hot for different vehicles

Fig. 11 summarizes the average PN emissions in WLTC cold and hot. The emission level of “hot” cycles is generally lower than the emission level of “cold” cycles. Vehicles which are equipped with GPF have, as expected, lower PN-emissions. Vehicle 6 is a Diesel car with original DPF of a very good quality; it sets a quality level, which is only roughly attained by the vehicle 2 with GPF1.

From all variants with GPF’s the GPF3 and GPF4 have the highest emissions. These two filters also have the lowest average filtration efficiencies, Fig. 12.

Finally, it can be concluded that the PN-emission level of the investigated GDI cars in WLTC without GPF is in the same range of magnitude very near to the actual limit value of 6.0 x 10^{12} #/km. With the GPF’s with better filtration quality it is possible to lower the emissions below the future limit value of 6.0 x 10^{11} #/km.

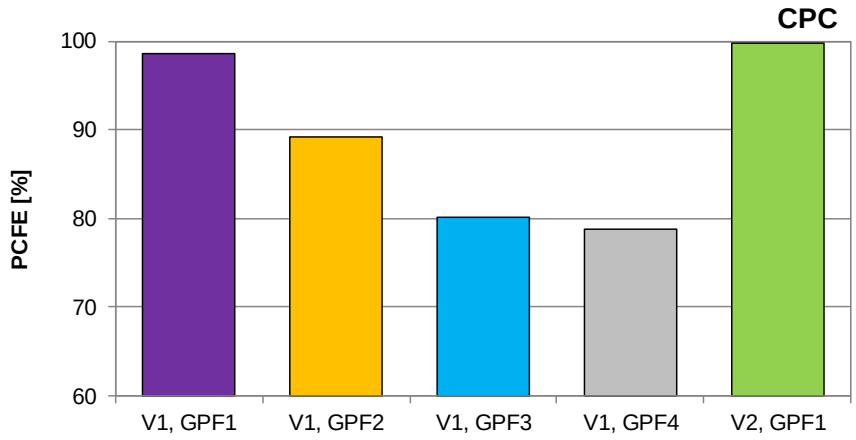

Figure 12: PCFE's of the investigated GPF's in WLTC hot

Conclusions

The results from these tests confirm the previous findings and they can be summarized as follows:

- the PN-emission level of the investigated GDI cars in WLTC without GPF is in the same range of magnitude very near to the actual limit value of 6.0 x 1012 #/km,
- with the GPF's with better filtration quality it is possible to lower the emissions below the future limit value of 6.0 x 10^{11}#/km,
- the filtration efficiency of GPF can attain 99% but it can also be optimized to lower values – in this respect the requirement of "best available technology for health protection" should be considered,
- the relationships of NP-emissions between different vehicles can vary depending on operating condition,
- generally there is a very good accordance of PSD's measured with both systems SMPS and nSMPS in the common size range (10-64 mm),
- for the vehicles with gasoline DI, there is no increase of PC's in nuclei mode (below 10 nm) at the measured constant speeds, the particle counts below 10 nm are negligible,
- due to the electronic regulation of the engine the NP-emission of some vehicles (here vehicle 3) are periodically fluctuating,
- there is a good repeatability of the average emissions in the "warm" driving cycles.

4.3 Influences of fuels E0/E10/E85, [49]

As example the effects of Ethanol blend fuels E10 & E85 on the emissions of a flex fuel passenger car (FFV, vehicle 1, see Table 2, chap. 4.2) are presented and discussed:

Fig. 13 gives the comparisons of average emission values from the operation with gasoline, E10 and E85 in WLTC warm. These results are averages of 2 cycles. The warm-up procedure was always by means of a preliminary cold started WLTC.

The particle counts emissions are generally significantly reduced with Exx (more than 1 order of magnitude). There is a clear increase of NH_3 with E85 and an insignificant tendency of increasing NH_3 with E10.

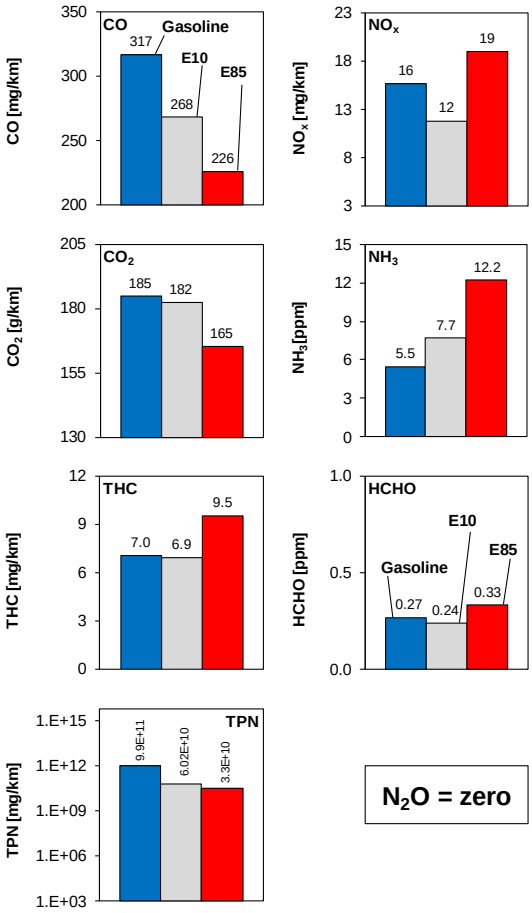

Figure 13: Average emissions in WLTC warm, with gasoline E10 & E85 Volvo V60 T4F, 3WC

There are no significant emissions and no increasing tendencies of average values HCHO Formaldehyde (at a level of fraction of ppm) with higher Ethanol content.

CO-emissions are clearly reduced with increasing Exx-content. For HC- & NO_x no regular tendencies with E10 & E85 are visible. It can be stated, that with E10 there are no changes of HC & NO_x, but with E85 a slight increase of these compounds is noticed. This nevertheless, especially NO_x is dependent very much on the electronic control of this FFV and the indicated differences of few [ppm] can also be an effect of emitting dispersion.

Fig. 14 represents the respective SMPS particle size distributions at different constant speeds. The drastic reduction of NP count concentrations with E10 & E85 is demonstrated. It is interesting to remark, that already the lower Ethanol content (E10) contributes significantly to the reduction of PC-concentrations at all driven vehicle speeds.

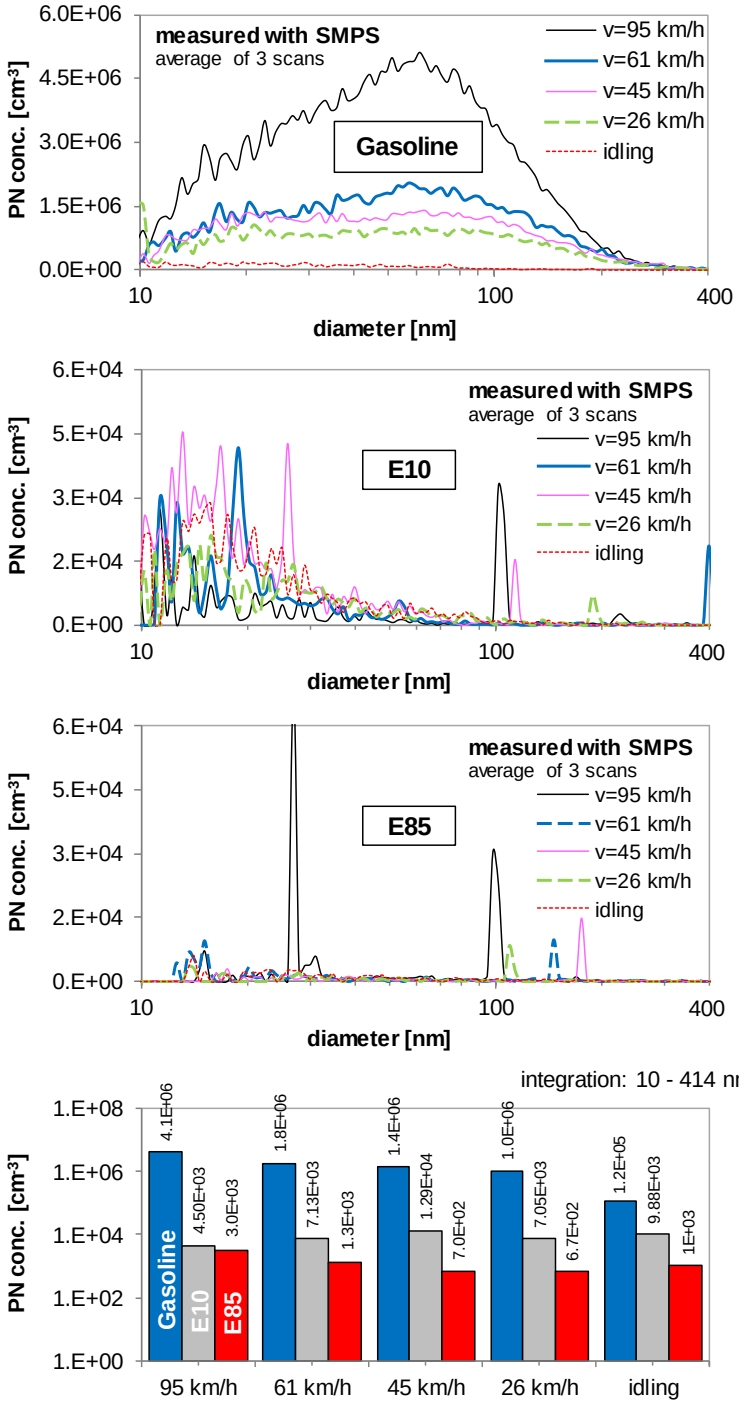

Figure 14: Particles size distributions (PSD) and integrated particle counts during the driving cycle SSC Volvo V60 T4F; 3WC

Conclusions

The main results obtained from the investigated test vehicle are:

- the particle counts emissions are generally significantly reduced with Ethanol blend fuels at all operating conditions,
- in WLTC there is a clear increase of NH_3 with E85 and an insignificant tendency of increasing NH_3 with E10,
- with all fuels (E0, E10 & E85) there are no emissions of N_2O and no increase of HCHO (below 1 ppm), in WLTC warm.

4.4 Cold start with Ethanol and Butanol blend fuels, [50]

Test vehicle

The tests were performed with a new (Euro 5) flex fuel vehicle Volvo V60 (GDI), which is a reference vehicle for several projects concerning NP-research from gasoline engines, (vehicle 1, chap. 4.2).

E0, E10 / E85

The emission results are represented as time-courses during the cold start (CS) and warm-up phase until 10 min after start. Each configuration of CS was performed at least 3 times and the represented plots are averages from 3 attempts.

The results from single days (not represented here) show repetitive tendencies with certain fluctuation of the peak values.

Fig. 15 & Fig. 16 show the gaseous emissions, comparing Ethanol blend fuels E0 / E10 / E85 in two temperature domains of the CS: 0°C and 20°C.

The values of CO, HC, HCHO (Formaldehyde) and ETOH (Ethanol) have generally a strong peak in the first 60-80 s after start. At higher start temperature (20°C) these peak values are lower.

For CO & HC there is no tendency of the peak values considering the fuel quality (E0 / E10 / E85). The peak values of HCHO and of ETOH nevertheless are with E85 the highest.

NH_3 is zero at start, but it increases during the warm-up period up to 6 ppm after 10 min. Exception is with E85 at 20°C, where NH_3 has a stronger increase (up to 13 ppm). This is due to random conditions promoting NH_3-production, like: dispersion of the engine emission profile, store-release effects in the exhaust system, local enrichment regions in the catalyst and/or heterogeneous heating up of the catalyst. It is known from the previous research, [51], that certain NH_3-peaks appear randomly even in repetitive driving conditions at warm operation.

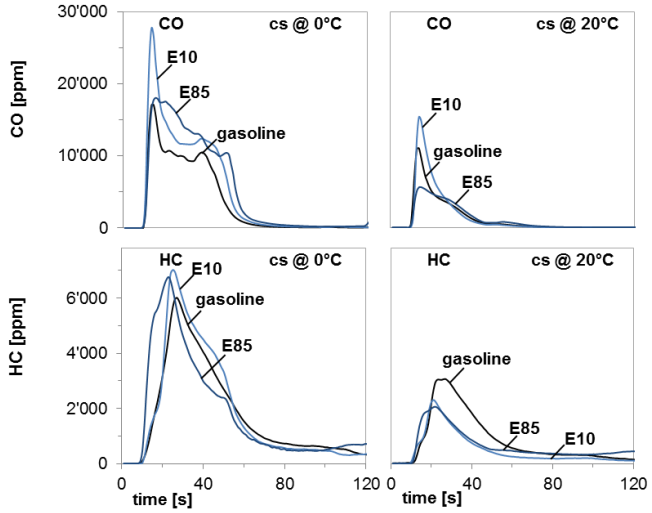

Figure 15: Comparison of the gaseous emissions during cold start at idling with different fuels, measured with FTIR at tailpipe

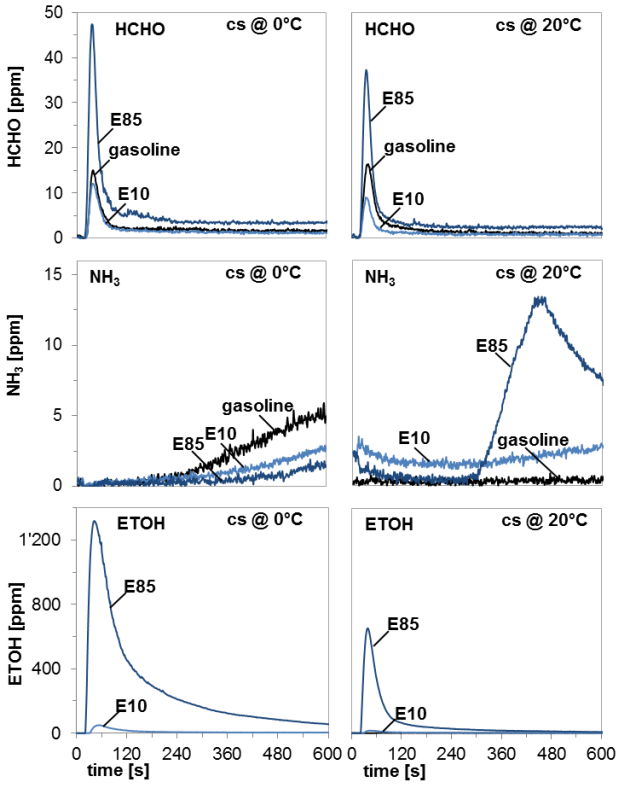

Figure 16: Comparison of the gaseous emissions during cold start at idling with different fuels, measured with FTIR at tailpipe.

E0, E10 / Bu15

Fig. 17 & Fig. 18 summarize the emissions as integral average values in the 1st two minutes after CS. For CO, HC and NO_x the emissions are lower at the higher temperature of start. With increasing Ethanol content the NO_x-values decrease; with Bu15 the NO_x-values are similar like with E10.

For non-legislated gaseous components there is a finding of considerable increased values of MeCHO and HCHO with E85. Bu15 yields in this respect similar results as E10.

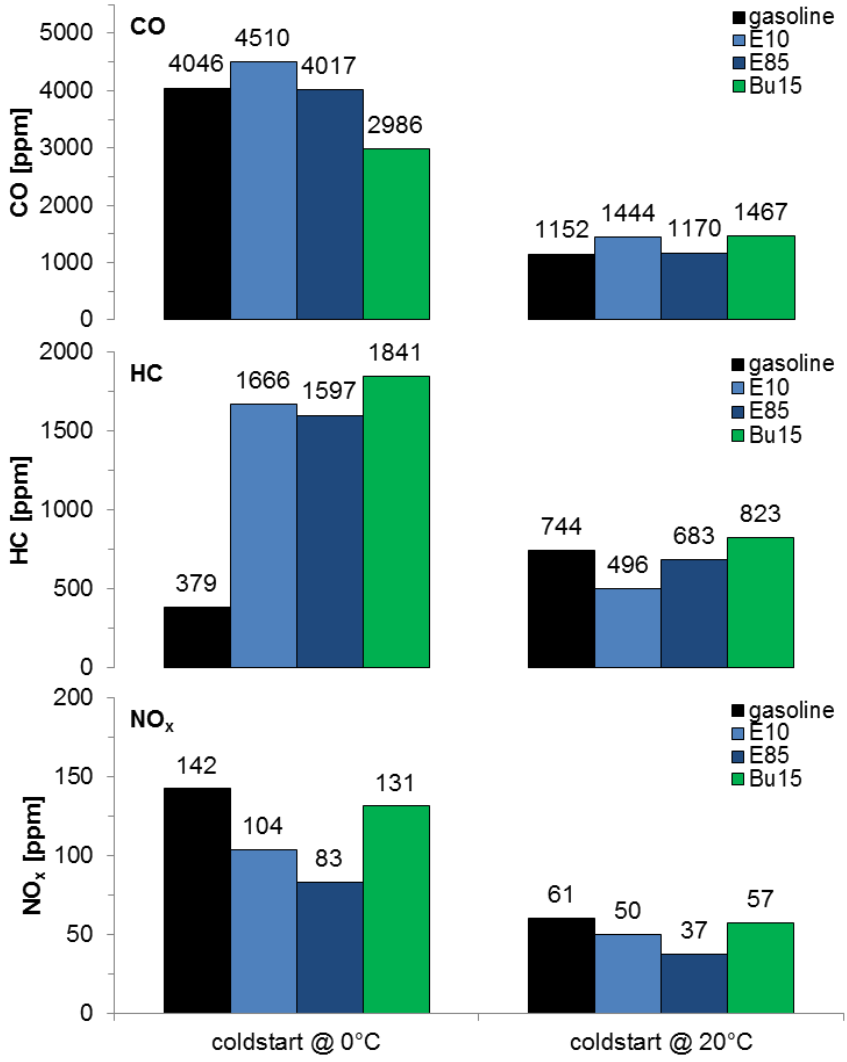

Figure 17: Integral average values of exhaust emissions with different fuels in the first 2 min. after cold start (0°C & 20°C) at idling

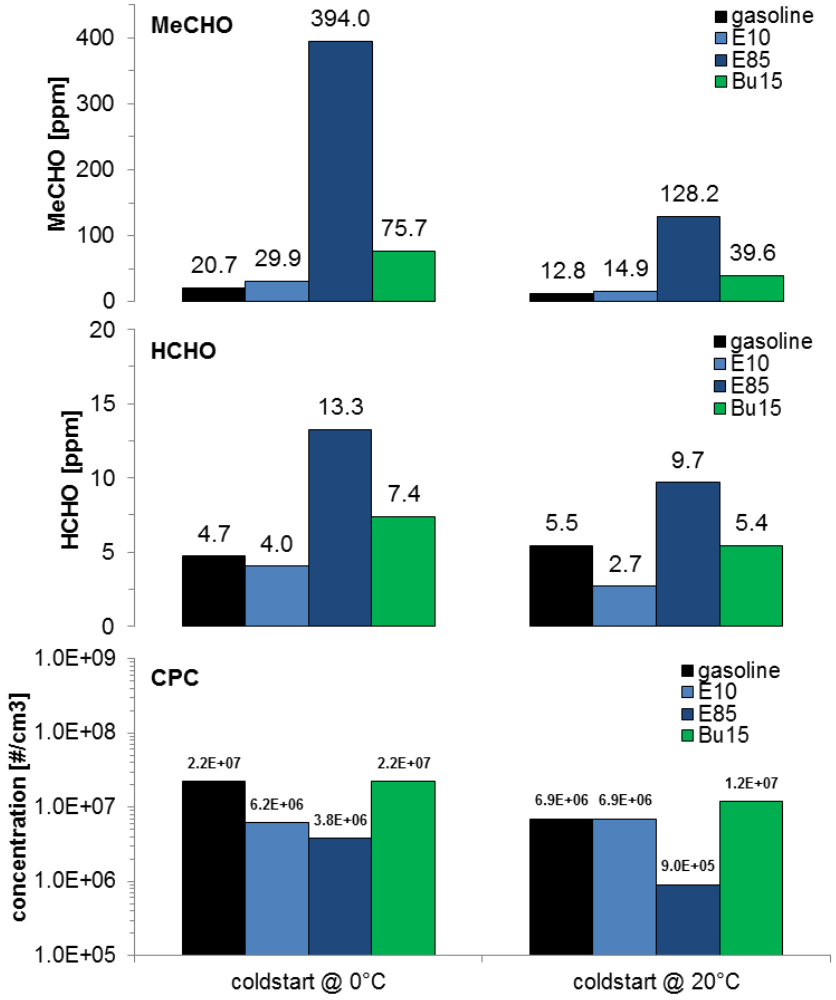

Figure 18: Integral average values of gaseous- and nanoparticles emissions with different fuels in the first 2 min. after cold start (0°C & 20°C) at idling

Conclusions

From the cold start tests following statements have to be mentioned:

With higher Ethanol content there are:

- higher peaks of Formaldehyde (HCHO) and of Acetaldehyde (MeCHO) at start,
- lower increase of NH_3 after 600s at 0°C and higher increase of NH_3 after 600s at 20°C
- lower NP-value, both: average of CPC-and average of SMPS-signals.

Comparing Bu15-results with E10 – both fuels with similar O_2-content – it can be remarked that with E10 comparing to Bu15 there are:

- higher peak values of CO and ETOH and
- lower peak values of MeCHO, HCHO and nanoparticles (both CPC & SMPS).

These tendencies can be found at both temperature levels: 0°C and 20°C.

With increased temperature at start (20°C instead of 0°C) there are:
- lower peaks of CO & NO_x,
- lower peaks of MeCHO and of HCHO,
- lower peaks of ETOH,
- lower peak values of N_2O after start,
- lower peaks of CPC and mostly lower SMPS PC-concentrations.

With progressing warm-up generally the emission level is reduced. Only NH_3 behaves inversely, increasing after 540s in some test series up to max. 6 ppm.

4.5 Investigations of NH_3 at different sampling positions, [51]

Test vehicle

The tests were performed with a new (Euro 5) flex fuel vehicle Volvo V60 (GDI), which is a reference vehicle for several projects concerning NP-research from gasoline engines, (vehicle 1, chap. 4.2).
The vehicle was operated with gasoline, with Butanol blend Bu 30 and Ethanol blend fuel E85. The emissions were measured at different sampling positions (SP, siehe Fig. 4).

Steady state and WLTC

Fig. 19 shows an example of time courses of diluted and undiluted emissions of NH_3 and N_2O during the test of vehicle 1 at v=30km/h. The time intervals of measurements and of switching the sampling sonde between the sampling positions (SP's) are visible. The undiluted values are obtained by multiplying the diluted values with DF.
At 50 km/h two CVS flows and consequently two dilution factors DF have been applied – Fig. 20 represents the integral average values. It can be seen, that with a double DF the values at SP3 to SP5 and bag are also nearly doubled. This means, that the low NH_3-values which were measured in diluted gas were at the detection limit of the FTIR and did not represent the real NH_3-concentrations any more.

This influence – measurements at the detection limit – is believed to be the major reason of non-valid results from diluted gas. The other postulated reasons – inhomogeneities in the flow, reactivity and store-release of NH_3 – are at these low concentrations most probably of lower importance.

Test were also performed in transient operation (WLTC). Concentrations were measured at different sampling positions in undiluted (SP1 and SP2) and in diluted (SP3, 4 and 5) exhaust gas. There are some high peaks of NH_3, which occur systematically in all tests of the same vehicle and in the same operating profile of the cycle. These peaks are the results of rich Lambda-excursions connected with higher exhaust gas temperatures. Another type of NH_3-spikes arrive randomly (only in one measurement) and are an effect of stochastic "release" from the exhaust system. They are originating from the store-release effects of NH_3 and/or of NH_3 precursor substances.

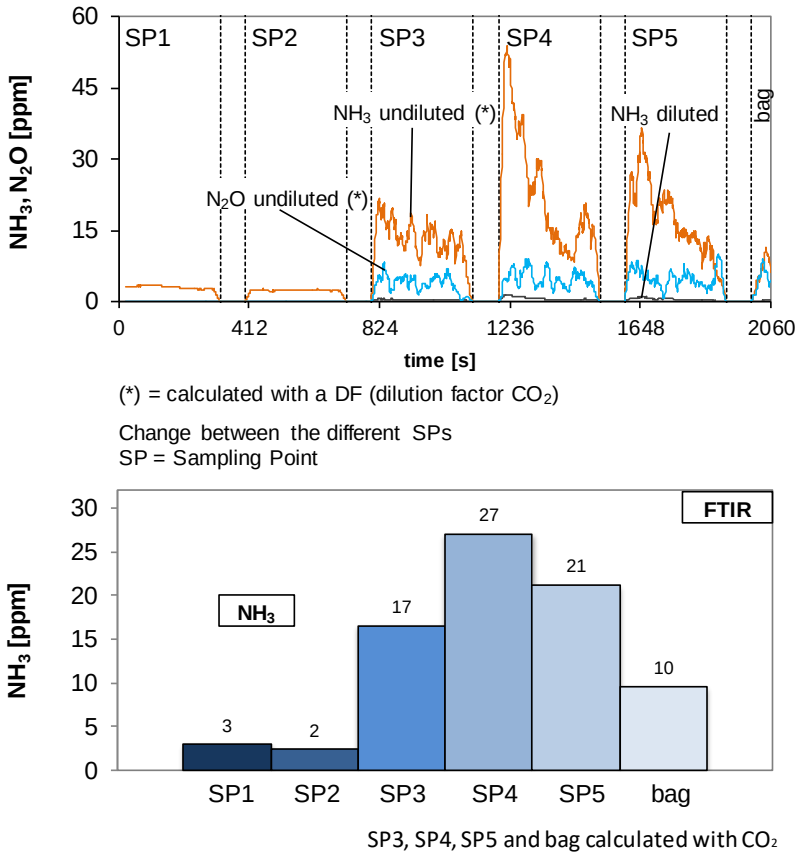

Figure 19: Influence of dilution on NH_3-emissions at v=const 30 km/h vehicle 1; DF: 34.1

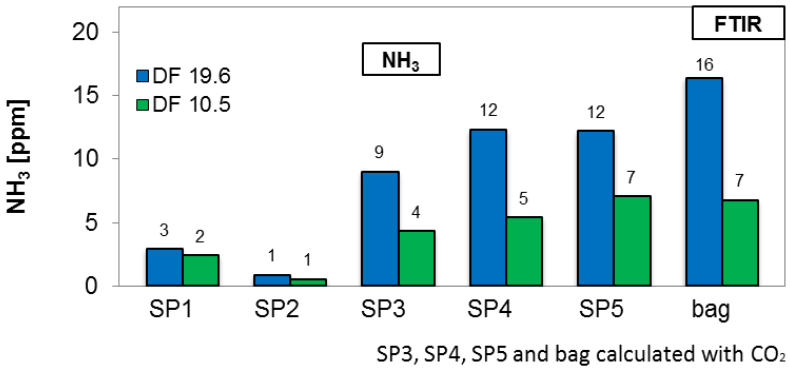

Figure 20: Influence of dilution factors on NH_3-emissions at v=const 50 km/h vehicle 1; DF: 19.6 and 10.5

Gasoline / Bu30 / E85

Fig. 21 represents the comparisons of NH_3-emissions with gasoline, Bu30 and E85 at 30km/h, 50 km/h and in WLTC.
At constant speeds there are no clear repetitive tendencies. In WLTC warm, nevertheless, the increase of NH_3 with the oxygenated fuels B30 and E85 becomes quite clear, although overlapped by the stochastic emission effects. This increase can be explained with stronger Lambda-excursions, which happen with higher Oxygen content of fuel. NH_3 is produced especially at rich Lambda

deviations with a hot exhaust system, a situation which happens regularly in the high-speed part of WLTC (at 1200s).
E85 has a 3 times higher Oxygen content, than Bu30 and there is also higher NH_3 with E85.

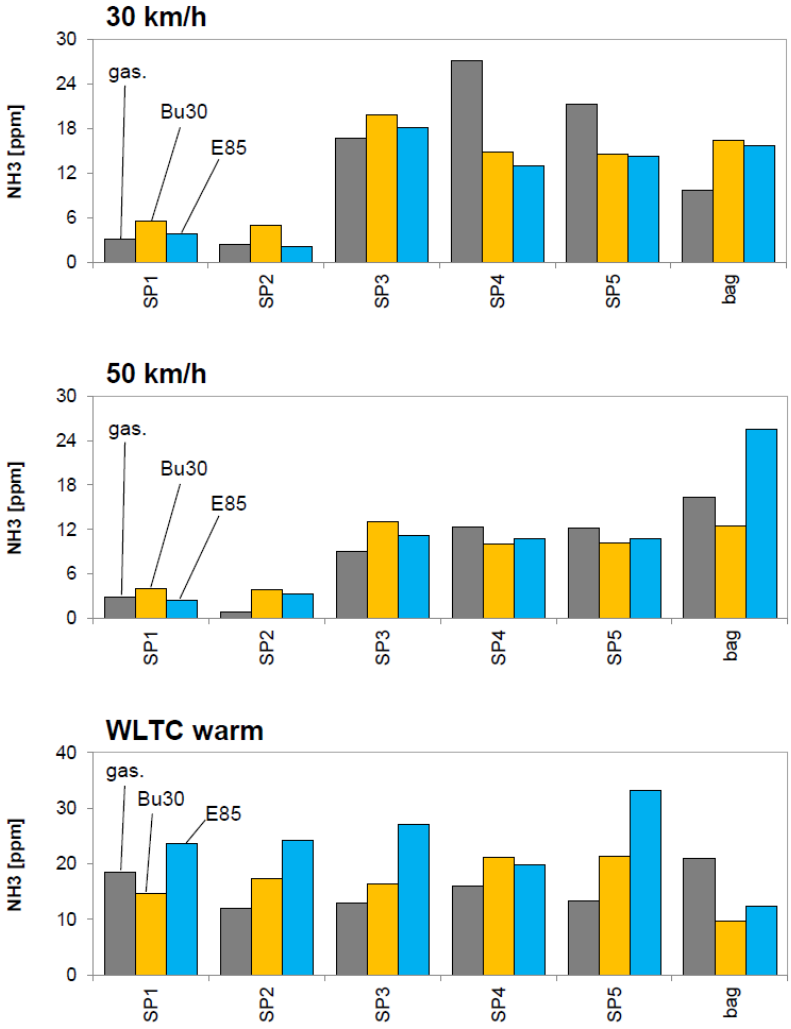

Figure 21: comparisons of NH_3-emissins with gasoline, Bu30 and E85 at constant speeds and in WLTC warm.

Conclusions

The most important experiences from the NH_3-research with different vehicles can be summarized as follows:

- The vehicle with older technology had an approximately 10x higher NH_3-emission level, than the newer vehicles.
- In single phases of the WLTC the relationships of bag-values and the average SP-values are varying: there is a tendency of lower NH_3 in the bag for high emitting case and a tendency of slight increasing NH_3 in the bag for the low emitting cases.
- The results from diluted gas (also bag-values) in WLTC correspond better with the results from undiluted gas than at constant speeds; this is because of different emission profiles and different estimates of dilution factors in both operating modes.

- In certain acceleration events of WLTC high peaks of NH_3 emissions are observed; some of these peaks are repetitive (originating from rich Lambda-excursions) and some of them are stochastic (originating from store-release effects of NH_3, or NH_3-precursors).
- Emission level of newer vehicles, regarded as average of all SP's, is mostly below 20 ppm NH_3.
- The NH_3-concentrations in diluted exhaust gas in CVS-tunnel (SP3, SP4, SP5) and in bag are for modern, low-emitting vehicles close to the detection limit of FTIR and the results are biased from detector noise.
- The direct, undiluted measurement of NH_3 at tailpipe (SP1) can be recommended as the best variant. This direct measurement avoids the possible problems of: detection limit, contamination from dilution air, adsorption/desorption in CVS-tunnel and artefacts in the bag.
- E85 has a 3 times higher Oxygen content, than Bu30, this causes more frequent and more intense Lambda rich excursions in the transient operation (WLTC) and consequently a tendency of higher NH_3-emissions,
- the N_2O-emissions of the investigated vehicle 1 are zero and the NO_2 -emissions are negligible (below 1ppm).

4.6 Increased lube oil consumption, [52]

Test vehicle

The tests on gasoline vehicle (GDI) were performed with a Seat Leon 1.4 TSI. This vehicle was operated with gasoline, in original condition (3WC) and with lube oil blended to the fuel, which simulated the increased lube oil consumption.

The vehicle data are presented in Tab. 4.

Vehicle	**Seat Leon 1.4 TSI ST/ 2015**
Number and arrangement of cylinders	4 / in line
Displacement cm^3	1395
Power kW	110 @ 6000 rpm
Torque Nm	250 @ 1500 rpm
Injection type	Gasoline / DI
Curb weight kg	1287
Gross vehicle weight kg	1830
Drive wheel	Front-wheel drive
Gearbox	m6
First registration	13.11.2014
Exhaust	Euro 6b

Table 4: Technical data of tested vehicle

Simulation of lube oil consumption & GPF

The lube oil consumption was simulated by mixing 2% vol. lube oil into the fuel. A non-coated GPF was mounted at tailpipe, so only the filtration effects were indicated. The tests were performed at transient (WLTC) and at stationary (SSC) operating conditions.

The lube oils blended to the fuel were selected in order to enable the testing with high "H" (≤ 1.2%) or with low "L" (≤ 0.5%) content of ashes and metals. They have an unified HC-matrix (hydrocrack) and equal viscosity. This choice makes the influence of ashes and metals on the PN more visible.

Fig.22 represents the comparison of limited gaseous emissions CO, HC, and NO_x in WLTC warm (averages of 3 cycles). The average emission levels with fuels containing lube oil are generally higher than the reference (gasoline). This is to explain with the higher content of heavy HC, their influence on chemistry of exhaust gases and on the Lambda regulation. There are, nevertheless, significant differences of CO- and HC-values between ""2% H" and "2% H + GPF". The questions arise: how repetitive are the CO peak values in WLTC? Can the GPF be responsible for the observed effects?

With this configuration (2% "H" + GPF) 30 WLTC with 3 cold starts were performed in the frame of another project. This gave the opportunity to consider the above questions.

Finally, it could be stated, that the extreme CO-values are not connected to the GPF and they represent some coincidental and random states of the system (mixture preparation, λ-regulation, OBD-control, state of catalyst) of this vehicle. The influence of driver is unlikely, but cannot be excluded.

The results in SSC (not presented in this report) confirm the highest CO & HC values with lube oil "H".

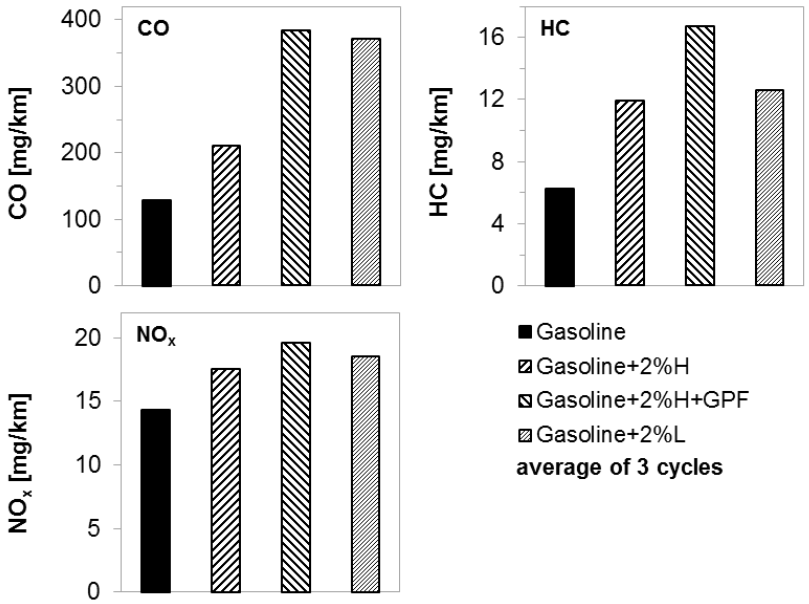

Figure 22: Limited gaseous exhaust emissions in WLTC warm.

Fig. 23 compares the integral average values of non-legislated gaseous components in a single WLTC warm. There is a clear increase of NH_3 with fuels containing lube oil. This is a result from both influences: oil chemistry and impact of the oil on the Lambda regulation (more Lambda rich "excursions" provoke more NH_3).

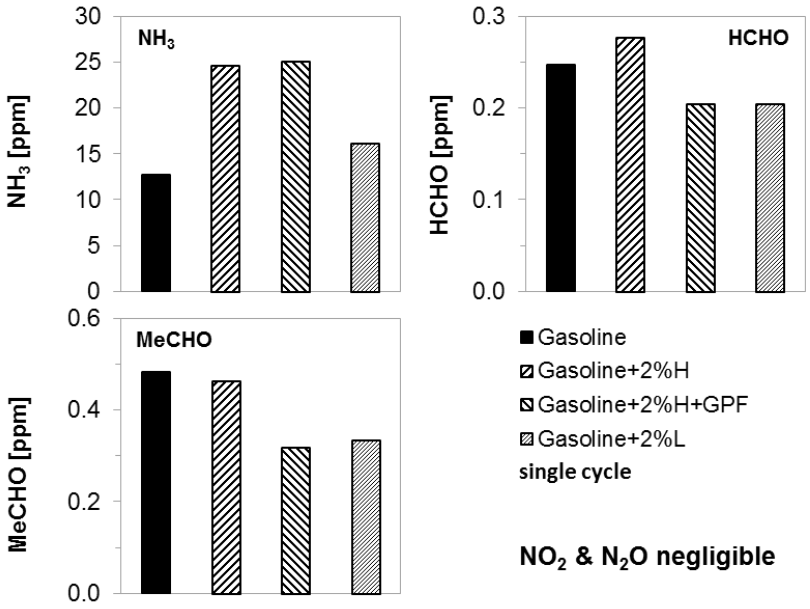

Figure 23: Non-legislated gaseous emissions in WLTC warm.

The emissions of NO_2, N_2O, HCHO and MeCHO are negligible.

In previous research of NH_3 emissions on gasoline vehicles, [51], was found that certain NH_3-peaks in the repeated transient cycle (WLTC) appear randomly, while the NH_3-peaks connected with the acceleration events in the high-speed part of the cycle appear regularly, but of course with an extremely varying intensity. This means that the NH_3-emissions are irregular even in the repeating operating conditions. Additionally to the rich Lambda excursions and high exhaust temperatures further reasons for the NH_3-fluctuations are the store/release effect of NH_3 and NH_3 precursor substances in the exhaust system and especially in the catalyst.
Considering this together with the emission variability observed the authors presume, that the NH_3 values in Fig. 23 are generally overlapped by the emission fluctuation.

Fig. 24 represents the average PN-emission (WLTC averages of 3 cycles, SSC single cycle). It is demonstrated in this figure that the fuel variant "2% H" increases the nanoparticle emissions a little bit more than the fuel variant "2% L". The applied, non-catalytic gasoline particle filter (GPF) eliminates very efficiently the nanoparticle counts. This reduction is by approximately 4 orders of magnitude and sets the particle count concentrations down to or below the ambient level.

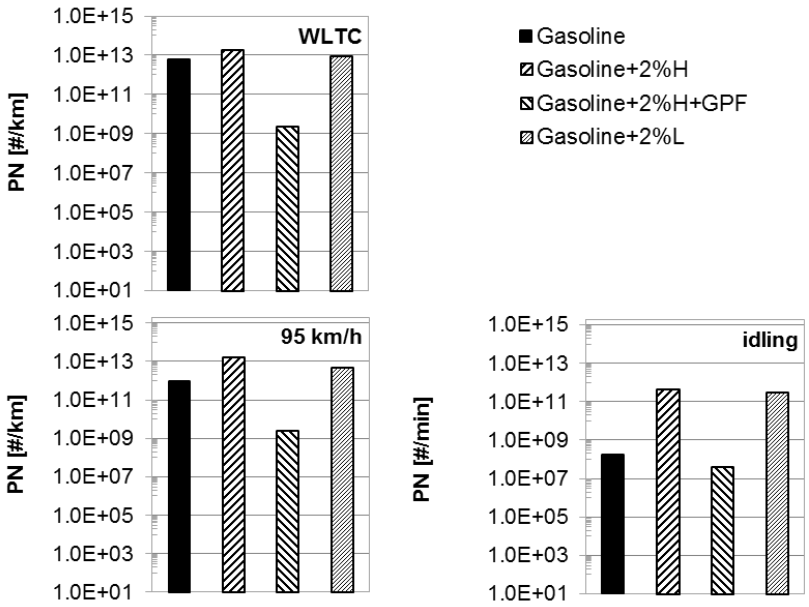

Figure 24: PN emissions during WLTC (3 cycles) and SSC (single) driving cycles warm.

Conclusions

The results obtained in this part of tests allow following summarizing statements:

- the increased lube oil consumption increases emissions of CO and HC, it can have impact on Lambda regulation and contributes to increased NH_3-values,
- with all fuels: gasoline, gasoline +"H" and gasoline +"L" there are no emissions of nitric dioxide NO_2, of nitrous oxide N_2O and negligible emissions (<1ppm) of aldehyde HCHO and of acetaldehyde MeOH,
- with increasing constant speed the NP-emissions increase for the investigated car; at idling there is the lowest NP-emission (1-2 orders of magnitude lower than with engine load),
- with addition of lube oil to the fuel (simulating the increased lube oil consumption) there is an increase of PN-emissions by approximately 2 orders of magnitude,
  - lube oil "H" increases PN by 2 orders of magnitude,
  - lube oil "L" increases PN a little less (1 to 1.5 orders of magnitude),
- the lube oil composition (HC-matrix and content of metals) influences slightly the particle size distributions,
- an efficient GPF eliminates the nanoparticles and lowers PN by 4 orders of magnitude.

5. Conclusions

The detailed conclusions of the presented test topics are given in the respective sections (chap. 4.1. p. 21; chap. 4.2. p. 26; chap. 4.3. p. 29; chap. 4.4. p. 32 and chap. 4.5. p. 36).

Let us recapitulate here the most important facts:

The GDI cars can emit high level of PN-emissions, such as the unfiltered Diesel exhaust, depending on the: engine technology, engine technical state (wear, lube oil consumption) and operating profile. There are also GDI cars, which at certain constant speeds emit no PN at all.

In the operation conditions with higher accelerations, with higher speeds and more energy needed for accelerations, there is a highest level of PN-emissions.

The size-selective metal analysis of the exhaust aerosol from a representative modern car (vehicle 1, Table 2, p. 22) showed that the majority of metals are deposited in the lower particle sizes: the most important substances found after 10 NEDC's in the 3 lowest stages (sizes: 0,03; 0,06; 0,108; µm) were: Na, Mg, Ca and Zn.

With GPF the PN-emission level can be significantly reduced, this below the actual (since 2017) limit value of 6.0×10^{11}#/km.

The filtration efficiency of GPF can attain 99% but it can also be optimized to lower values – in this respect the requirement of "best available technology for health protection" should be considered.

With Ethanol blend fuels the particle counts emissions are generally significantly reduced at all operating conditions.

At cold start there are emission peaks of nanoparticles, but also of the most gaseous emission components. With lower cold start temperature these peaks are higher.

With increased lube oil consumption the PN-emissions increase significantly (approx. 2 orders of magnitude). With an efficient GPF the PN can be impressively eliminated (by 4 orders of magnitude).

For the development and application of the GPF-technology there are still several interesting research questions, which can be addressed in the later common projects.

Emission level of newer vehicles, regarded as average of all SP's, is mostly below 20 ppm NH_3.

In certain acceleration events of WLTC high peaks of NH_3 emissions are observed; some of these peaks are repetitive (originating from rich Lambda-excursions) and some of them are stochastic (originating from store-release effects of NH_3, or NH_3-precursors).

6. Literature

[1] Sgro, L.A., et al., Investigating the origin of nuclei particles in GDI engine exhausts. Combustion and Flame, 2012. 159(4): p. 1687-1692.

[2] Burtscher, H., Physical characterization of particulate emissions from diesel engines: a review. Journal of Aerosol Science, 2005. 36(7): p. 896-932.

[3] Ulrich, A. and Wichser, A.: Analysis of additive metals in fuel and emission aerosols of diesel vehicles with and without particle traps. Analytical and Bioanalytical Chemistry, 2003. 377(1):p.71-81

[4] Hu, S., et al., Metals emitted from heavy-duty diesel vehicles equipped with advanced PM and NO_x emission controls. Atmospheric Environment, 2009. 43(18): p. 2950-2959.

[5] Mayer, A., Czerwinski, J.; Ulrich, A.; Mooney, J.J.: Metal-Oxide Particles in Combustion Engine Exhaust. SAE Technical Paper 2010-01-0792.

[6] Mayer, A.; Czerwinski, J.; Kasper, M.; Ulrich, A.; Mooney, J.J.: Metal Oxide Particle Emissions from Diesel and Petrol Engines. SAE Technical Paper 2012-01-0841.

[7] Ulrich, A., et al., Particle and metal emissions of diesel and gasoline engines are particle filters appropriate measures? Proceedings of the 16th ETH Conference on Combustion Generated Nanoparticles 2012.

[8] Buchholz, B. A.; Dibble R. W.; Rich, D.; Cheng, A.S. (Ed).: Quantifying the contribution of lubrication oil carbon to particulate emissions from a diesel engine. SAE Technical Paper 2003-01-1987.

[9] Sonntag, D. B.; Bailey, Ch. R.; Fulper, C. R.; Baldauf, R.W.: Contribution of Lubricating Oil to Particulate Matter Emissions from Light-Duty Gasoline Vehicles in Kansas City. Environment Science & Technology, 27. Febr. 2012.

[10] Hadler, J.; Lensch-Franze, Ch.; Gohl, M.; Mink, T.: Emission Reduction A Solution of Lubricant Composition, Calibration and Mechanical Development. MTZ, September 2015.

[11] Yinhui, W.; Rong, Z.; Yanhong, Q.; Jianfei, P. ; Mengren, L.; Jianrong, L.; Yusheng, W.; Min, H.; Shijin, S.: The impact of fuel compositions on the particulate emissions of direct injection gasoline engine. Elsevier, Fuel 166 (2016) 543-552. Journal homepage: www.elsevier.com/locate/fuel

[12] Bach, C., “Emissionsvergleich verschiedener Antriebsarten in aktuellen Personenwagen. Untersuchung der Emissionen von aktuellen Personenwagen mit konventionellen und direkteingespritzten Benzinmotoren, Dieselmotoren mit und ohne Partikelfilter, sowie Erdgasmotoren. (Empa Final Report for Novatlantis and Bundesamt für Umwelt BAFU,), in Empa Report 2007 (Novatlantis).

[13] Bielaczyc, P.; Szczotka, A.; Woodburn, J.: An overview of particulate matter emissions from modern light duty vehicles. Combustion Engines, No. 2/2013 (153), 101-108. ISSN 0138-0346.

[14] Chan, T.W.; Meloche, E.; Kubsh, J.; Brezny, R.; Rosenblatt, D.; Rideout, G.: Impact of Ambient Temperature on Gaseous and Particle Emissions from a Direct Injection Gasoline Vehicle and its Implications on Particle Filtration. SAE Technical Paper 2013-01-0527, Detroit, April 2013.

[15] Mathis, U.; Kaegi, R.; Mohr, M.; Zenobi, R.: TEM analysis of volatile nanoparticles from particle trap equipped diesel and direct-injection spark-ignition vehicles. Atmospheric Environment 38 (2004) 4347-4355, April 2004.

[16] Lee, K. O.; Seong, H.; Sakai, St.; Hageman, M.; Rothamer, D.: Detailed Morphological Properties of Nanoparticles from Gasoline Direct Injection Engine Combustion of Ethanol Blends. SAE Technical Paper 2013-24-0185, Napoli, September 2013

[17] Königstein, A.; Fritzsche, J.; Kettenring, K.; Ley, B.; Nolte, R.; Schaffner, P.: Alternatives to Meet Future Particule Emission Standards with a Boosted SIDI Engine. 24th Aachen Colloquium Automobile and Engine Technology, Oct. 2015, p. 1301.

[18] Kern, B.; Kunert, S.: The Potential of Comprehensive Emission Control for Gasoline DI-Engines – A comparison of Different Exhaust System Options and an Outlook on Future Requirements. 24th Aachen Colloquium Automobile and Engine Technology, Oct. 2015, p. 1267.

[19] Fahrenbruch, A.; Bachmann, J.: Ethanolsensoren für den Flex-Fuel-Betrieb.
MTZ Sept. 2008. p. 732.

[20] Bergström, K.; Melin, S.-A.; Jones, C.: The New ECOTEC Turbo BioPower Engine from GM powertrain – Utilizing the Power of Nature's re-sources. 28. Internationales Wiener Motoren-Symposium 2007, Bd.2, p. 47

[21] Bergström, K.; Nordin, H.; Königstein, A.; Marriott, C.; Wiles, M.: ABC – Alcohol Based Combustion Engines – Challenges and Opportuni-ties. 16. Aachener Kolloquium Fahrzeug- und Mo-torentechnik 2007, Bd.2, p. 1031.

[22] Kawai, T.; Tsunooka, T.; Chiba, F.; Uda, H.; Sonoda,Y.: Effect of High Concentration Ethanol on SI Engine Cold Startabillity and Emissions. 16. Aachener Kolloquium Fahrzeug- und Mtoren-technik 2007, Bd.2, p. 1075.

[23] Hadler, J.; Szengel, R.; Middendorf, H.; Sperling, H.; Gröer, H-G.; Tilchner, L.: Der 1.4l 118kW TSI für E85 Betrieb – die Erweiterung der ver-brauchsgünstigen Ottomotorenlinie von Volks-wagen. 32. Internationales Wiener Motorensymposium 2011, Bd.1, p. 263.

[24] Schwarze, H.; Brouwer, L.; Knoll, G.; Longo, C.; Kopnarski, M.; Emrich, S.: Auswirkung von Etha-nol E85 auf Schmierstoffalterung und Verschleiss im Ottomotor. MTZ April 2010, p. 286.

[25] Artmann, Ch.; Rabl, H-P.; Faulstich, M.: Online-Ermittlung der Schmierölverdünnung bei Ottomo-toren. MTZ Januar 2012, p. 70.

[26] Küpper, C.; Artmann, Ch.; Pischinger, S.; Rabl H-P.: Schmierölverdünnung von direktein-spritzenden Ottomotoren unter Kaltstartrandbedingungen. MTZ 09/2013, S.710

[27] DuMont, R. J.; Cunningham, L. J.; Oliver, M. K.; Studzinski, W. M.; Galante-Fox, J. M.: Controlling Induction System Deposits in Flexible Fuel Vehi-cles Operating on E85. SAE Technical Paper 2007-01-4071, Rosemont, Illinois, 2007.

[28] Galante -Fox, J. M.; Von Bacho, P.; Notaro, C.; Zizelman, J.: E-85 Fuel Corrosivity: Effects on Port Fuel Injector Durability Performance. SAE Technical Paper 2007-01-4072, Rosemont, Illinois, 2007.

[29] Greff, A.; Brandl, A.; Schulze, T.; Kapphan, F.: Extended range of optimal combustion in flex-fuel operation. MTZ September 2011, p. 668.

[30] Brassat, A.; Thewes, M.; Müther M.; Pischinger, S.: Massgeschneiderte Kraftstoffe aus Biomasse für Ottomotoren. MTZ 12, 2011, p. 988.

[31] Marchitto, L.; Mazzei, A.; Merola, S. S.; Tornatore, C.; Valentino, G.: Optical Investiga-tions of Combustion Process in SI and CI Engines Fuelled with Butanol Blends. TAE Technische Akademie Esslingen, 9th International Colloquium “Fuels”, Jan. 15-17, 2013.

[32] Irimescu, A.; Tornatore, C.; Merola, S. S.; Valentino, G.: Integrated Diagnostics for Combus-tion Investigation in a DISI Engine Fueled with Butanol and Gasoline at Different Load Settings. TAE Technische Akademie Esslingen, 10th Inter-national Colloquium „Fuels“, Stuttgart/Ostfildern, January 2015, S. 117

[33] Vojtisek-Lom, M.; Pechout, M.; Mazac, M.: Real-Word On-Road Exhaust Emissions from an Ordi-nary Gasoline Car Operated on E85 and on Buta-nol-Gasoline Blend. SAE Technical Paper 2013-24-0102, Napoli, September 2013.

[34] Giakoumis, E. G.; Rakopoulos, C. D.; Dimaratos, A. M.; Rakopoulos, D. C.: Exhaust emissions with ethanol or n-butanol diesel fuel blends during transient operation: A review. Renewable and Sustainable Energy Reviews 17 (2013), p. 170-190.

[35] Shukla, M. K.; Tharke, G. D.; Saxena, R. C.; Sharma, Y. K.; Jain, A. K.; Singal, S. K.: Buta-nol/Diesel Blends as a CI Engine Fuel: Physico-chemical and Engine Performance Characteristics Evaluation. TAE Technische Akademie Esslingen, 9th International Colloquium “Fuels”, Jan. 15-17, 2013.

[36] Anuj, P.; Manisch, V.; Sahil, G.; Naveen, K.: Per-formance and Emission Characteristics of Isobutanol-Diesel Blend in Water Cooled CI Engine Employing EGR with EGR Intercooler. SAE Technical Paper 2013-24-0151, Napoli, September 2013.

[37] Chan, T.W.; Meloche, E.; Kubsh, J.; Brezny, R.; Rosenblatt, D.; Rideout, G.: Impact of Ambient Temperature on Gaseous and Particle Emissions from a Direct Injection Gasoline Vehicle and its Implications on Particle Filtration. SAE Technical Paper 2013-01-0527, Detroit, April 2013.

[38] Sonntag, D. B.; Bailey, Ch. R.; Fulper, C. R.; Baldauf, R.W.: Contribution of Lubricating Oil to Particulate Matter Emissions from Light-Duty Gasoline Vehicles in Kansas City. Environment Science & Technology, 27. Febr. 2012.

[39] Porter, S.: Particle Number Emissions of Gasoline Hybrid Electric Vehicle. MTZ 04/2012.

[40] Heeb, N.; Forss, A-M.; Brühlmann, S.; Lüscher, R.; Saxer, Ch.; Hug, P.: Three-Way Catalyst-Induced Formation of Ammonia – Velocity- and Acceleration-Dependent Emission factors. Elsevier, Atmospheric Environment, 40 (2006) 5986-5997.

[41] Heeb, N.; Saxer, Ch.; Forss, A-M.; Brühlmann, S.: Trends of NO-, NO_2-, and NH_3-Emissions from Gasoline-Fueled Euro-3- to Euro-4-Passenger Cars. Elsevier, Atmospheric Environment, 42 (2008) 2543-2554.

[42] Czerwinski, J.; Comte, P.; Stepien, Z.; Oleksiak, S.: Effects of Ethanol Blend Fuels E10 & E85 on the Non-Legislated Emissions of a Flex Fuel Passenger Car. SAE Technical Paper 2016-01-0977, Detroit, April 2016.

[43] Czerwinski, J.; Comte, P.; Heeb, N.; Mayer, A.: Experiences from Nanoparticle Research on four Gasoline Cars. SAE Technical Paper 2015-01-1079.

[44] Czerwinski, J.; Comte, P.; Astorga, C.; Rey, M.; Mayer, A.; Reutimann, F.: (Nano) Particle from 2-S Scooters: SOF / INSOF; Improvements of Aftertreatment; Toxicity. AFHB, JRC, TTM, BAFU, SAE Techn. Paper 2007-01-1089.

[45] Martini G.; Bonnel P.; Krasenbrink A.; De Santi G.: Particulate Emissions from Mopeds: Effect of Lubricant and Fuel. EU Joint Research Centre, Ispra. 7th ETH Conference on Combustion Generated Nanoparticles, Zurich, CH, Aug. 2003. (www.nanoparticles.ethz.ch)

[46] Winklhofer, E; Hopfner, W.; Kapus, P.: Euro VI Partikelgrenzwerte – Entwicklungsmethoden für GDI Motoren. AVL List GmbH, Graz, Österreich, 7. Tagung HDT, Berlin, Dez. 2010.

[47] Dyckmans, J.; Arndt, S.; Raatz, T.; Grzeszik, R.; Eilts, P.: Laseroptische Untersuchungen zur Gemischbildung und Verbrennung in Verbindung mit dem Einsatz von Alko-holen als alternativer Krafstoff bei der Benzindirekt-einspritzung. Robert Bosch GmbH, Stuttgart. TU Braunschweig, 7. Tagung HDT, Berlin, Dez. 2010.

[48] Czerwinski, J.; Comte, P.; Heeb, N.; Mayer, A.; Hensel, V.: Nanoparticle Emissions of DI Gasoline Cars with/without GPF. SAE Paper submitted for SAE World Congress, Detroit 2017.

[49] Czerwinski, J., Comte, P., Stepien, Z., and Oleksiak, S.: Effects of Ethanol Blend Fuels E10 and E85 on the Non-Legislated Emissions of a Flex Fuel Passenger Car. SAE Technical Paper 2016-01-0977.

[50] Czerwinski, J., Comte, P., Güdel, M.: Non-Legislated Emissions of a GDI Flex Fuel Passenger Car at Cold Start with Ethanol and Butanol Blend Fuels. Submitted for TAE “Fuels” 2017.

[51] Czerwinski, J.; Comte, P.; Güdel, M.; Lemaire, J.; Mayer, A.; Heeb, N. ; Berger, H. ; Reutimann, F.: Investigations of Emissions of Reactive Substances NO_2 and NH_3 from Passenger Cars. PTNSS Journal Combustion Engines No.3/2016, ISSN 2300-9896

[52] Kurzwart, M.; Czerwinski, J.; Comte, P.; Güdel, M.: PN-Emissions with Increased Lube Oil Consumption of GDI Car with/without GPF. Submitted for TAE “Fuels” 2017.

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GasOMeP

Reduction of **gas**oline vehicle emissions for **o**rganic, **me**tallic and **p**articulate non-legislative pollutants

Starting from Euro 6 not only for diesel but also for gasoline vehicles, a solid particle number emissions limit of 6×10^{11} #/km becomes effective. Recent investigations demonstrated that gasoline vehicles especially with direct injection technology (GDI) require additional after-treatment technology to match these values. Nuclei of metals as well as organics are suspected to significantly contribute especially to the ultrafine particle size fractions, and thus to the ultrafine particle number concentration. Particle filter systems (PFs) are proposed as possible measure also for gasoline vehicles and should be critically evaluated for their efficiency to reduce effectively emissions from current and future gasoline vehicles. Moreover, gasoline driven cars have recently been found in an exemplary study to contribute significantly to organic matter through the oxidation of volatile organic compounds and subsequent condensation on existing particles or formation of new particles. The secondary aerosol production potential (SAPP) was found to be much larger than for diesel vehicles including trucks.

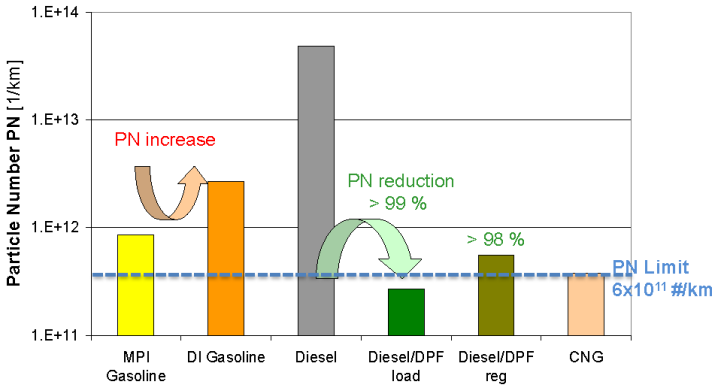

Fig. 1: Particle number concentration (PN) of different vehicle types and PN limit $6x10^{11}$ #/km for Euro 5b diesel and Euro 6 all vehicles
MPI = multiport injection / DI = direct injection / CNG = compressed natural gas
DPF = diesel particle filter (wall flow) / load = loading phase / reg = regeneration phase

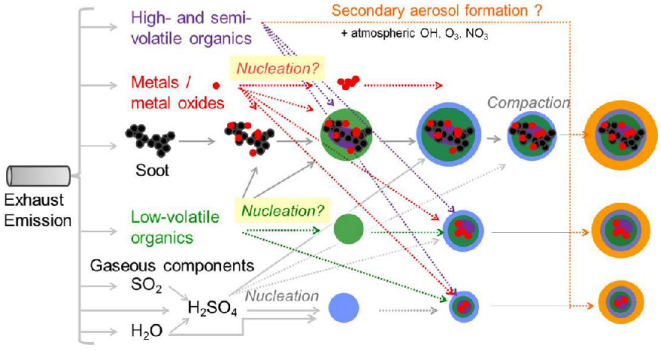

Fig. 2: Schematic mechanisms of emission and particle formation in exhaust (partly adopted from Schneider et al.2006

Project duration: spring/summer 2013 – mid of 2016

Research partners: Empa: A. Ulrich, N.V. Heeb; PSI: A. Prevot, U. Baltensperger
FHNW: H. Burtscher, A. Keller, FH Biel: J. Czerwinski

Industry partners: TSI, NGK, TTM, VERT Association
Authorities: FOEN (Swiss Federal Office for the Environment)

There is only little known on metal emissions and on the SAPP of current gasoline vehicles with variable technology including GDI. It is the main goal of this project to increase the knowledge on species-selective information and the identification of efficient removal measures is the main goal of this project. The project is ordered in three phases of which the first phase focus on the characterization of the emission status of representative current and upcoming gasoline vehicle types (Euro III, IV, V, VI with direct injection DI and indirect MPI)in terms of metallic, organic species and possible nucleation products in the nano-meter size range including ultrafine particles smaller than 23 nm as well as the secondary aerosol production potential following the newly proposed homogenized world-wide low duty driving cycle WLTC. In the second phase, requirements for an effective removal by filtration of the most critical pollutants are proposed, based on the results, a detailed literature survey and in close cooperation with our industry partners. The third phase investigates both the effectiveness of specific pollutant removal from the exhaust gas and the potential to form secondary emissions for the proposed particle filter system.

References

1. A. Ulrich et al, Anal Bioanal Chem, 2003, 377, 7181.
2. J. Schneider et al. Environ. Sci. Technol. 2005, 39, 6153-6161
3. N.V. Heeb, et al. Atm. Env. 45, 2011. 3203-3209
4. A. Ulrich et al. Proceedings of PTNSS Congress 2011, June 2011
5. A. Ulrich et al, Proceedings of the 16th ETH Conference on Combustion Generated Nanoparticles 2012
6. A. Mayer et al, SAE 2012-01-0841
7. S.M. Platt, Atmos. Chem. Phys. Discuss., 12, 28343-28383, 2012

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Networked Research Energy and Mobility

GASOMEP: Current Status and New Concepts of **Gas**oline Vehicle Emission Control for **O**rganic, **Me**tallic and **P**articulate Non-Legislative Pollutants

The GASOMEP project is an interdisciplinary research project which investigates the emission characteristics of current gasoline direct injection (GDI) vehicles and evaluates the potential of gasoline particle filter technology (GPF) which is currently developed by our industrial partners. A wide spectrum of gaseous and particle-bound pollutants are studied for several GDI vehicles which are operated both, without and with filter technology. A detailed characterization of the particle emissions including their size, number and metal content are foreseen. Emissions of genotoxic compounds like PAHs and their nitrated and oxygenated forms will be determined. Furthermore, the secondary organic aerosol (SOA) forming potential of GDI exhausts is investigated with smog chamber experiments and two independent flow reactor approaches.

The three-year project will result in a comprehensive characterization of current GDI vehicle emissions. It will also evaluate the potential of new filter technology to abate these potentially harmful emissions. The project is of general relevance for the public since we all will increasingly be exposed to exhausts of GDI vehicles which in the future are possibly equipped with efficient catalytic filter technology. The project is a joint effort of the industry, regulators, and the Swiss research institutions PSI, the Universities of Applied Sciences Northwestern Switzerland (UASNW) and Biel (UASB) and Empa.

Fig. 1 displays the particle number size distribution of a Euro-5 GDI vehicle (VOLVO V60 T4F, 1.6 l) which was chosen as the reference vehicle in the GASOMEP project. The most prominent particles have diameters around 80 nm like diesel soot particles. **Fig. 2** displays particle number-based emission factors (#/km) over a size range of 23 – 400 nm in the worldwide harmonized light vehicle test cycle (WLTC) for urban (cold and hot started), extra-urban, highway and motorway conditions. Highest PN emissions of 8.6 x 10e12/km were observed under urban cold start conditions. Particle emissions stabilized at 1.2-1.7 x 10e12/km under hot engine conditions. We conclude that the gasoline-fueled Euro-5 vehicle exceeded the threshold limit for diesel passenger cars of 6 x 10e11 #/km. Aliquots of the emitted exhausts are collected in a smog chamber (**Fig. 3**) and aged for 4-5h under conditions similar to the atmosphere. In parallel, two flow reactors are used to determine the SOA potential of the exhausts with accelerated aging. **Fig. 4** gives an impression of the clustering of instruments at the chassis dynamometer of the UASB in Nidau during the first sampling campaign held in spring 2014.

Fig. 1. Particle size distribution

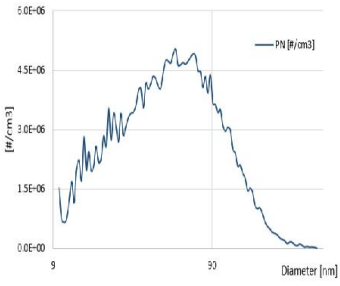


Fig. 2. Particle number emissions

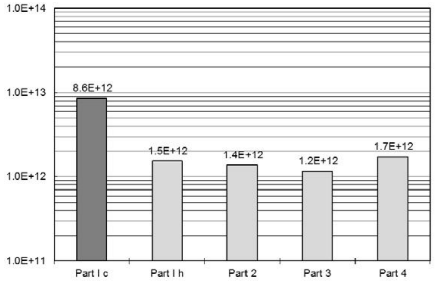
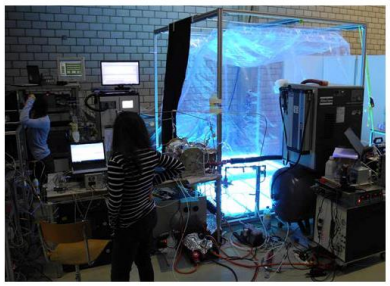


Fig. 3. PSI Smog chamber



Project partners: PSI, UASNW, UASB, Empa

Industry partners: NGK, TTM, VERT Association

PAUL SCHERRER INSTITUT PSI · ETH zürich · EPFL ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE · n|w Fachhochschule Nordwestschweiz Hochschule für Technik · EMPA Materials Science & Technology

GasOMeP

Gasoline Vehicle Emission Control for Organic, Metallic and Particulate Non-Legislative Pollutants

List of abbreviations

GC-HRMS	Gas Chromatography-High Resolution Mass Spectrometry
GDI	Gasoline Direct Injection
GPF	Gasoline Particle Filter
SMPS	Scanning Mobility Particle Sizer
SOA	Secondary Organic Aerosol
SSC	Steady State Cycle
PAH	Polycyclic Aromatic Hydrocarbons
PN	Particle Number
WLTC	World Harmonized Light Vehicle Test Cycle
WP	Work Package

Major partners in the ETH domain

- Empa – Laboratory for Advanced Analytical Technologies
- Empa – Laboratory for Air Pollution/Environmental Technology
- PSI – Laboratory for Atmospheric Chemistry

Main Investigator

Norbert Heeb, Empa

Project Partners

Empa

PSI

UASB

UASNW

FOEN

Time frame of Project

2013–2016

Thematic Relationship to SCCER

Mobility

Scope of project

In the next decades, we will be exposed to exhausts of gasoline direct injection (GDI) vehicles with yet unknown consequences. But we have the choice to equip these vehicles with catalytic filter technology or not. The GasOMeP project will investigate the emission characteristics of various GDI vehicles and evaluate the potential of gasoline particle filters (GPF) currently developed by our industrial partners. A wide spectrum of gaseous and particle-bound pollutants is studied for different GDI vehicles which are operated without and with filter technology and fossil fuels or biofuels. Particle emissions including their size distribution, number and metal content will be characterized in detail. Emissions of semi-volatile compounds including genotoxic constituents like polycyclic aromatic hydrocarbons (PAH), their alkylated, nitrated and oxygenated forms will be studied. These compounds are important precursors of secondary organic aerosols (SOA) which form in the atmosphere. Respective SOA forming potentials will be investigated with smog chamber experiments and two independent flow reactor approaches.

Status of project

The three-year project will result in a comprehensive characterization of GDI vehicle emissions and evaluate the potential of new filter technology to abate potentially harmful exhaust constituents. The project is a joint effort of industry, regulators, and the Swiss research institutions PSI, the Universities of Applied Sciences Northwestern Switzerland (UASNW) and Biel (UASB) as well as Empa.

The project is divided in 5 work packages (WP):

WP 1: regulated pollutants (UASB),
WP 2: nanoparticles (UASB, UASNW),
WP 3: secondary organic aerosols (PSI, UASNW),
WP 4: non-regulated pollutants (Empa),
WP 5: metals (Empa).

All vehicles and vehicle configurations are tested at the chassis dynamometer of the UASB in Nidau. A batch of commercial gasoline is used as reference fuel in the project and blended with biofuel if needed. The world harmonized light vehicle test cycle (WLTC), which includes parts of urban (26 km/h), extra-urban (45 km/h, highway (61 km/h) and motorway (94 km/h) driving, is investigated under cold start and hot engine/catalyst conditions. In addition, a steady state cycle (SSC) covering constant vehicle operation at 26, 45, 61, 94 km/h and at idle conditions is studied.

So far, 6 different vehicle configurations including three different GDI vehicles (Volvo V60 T4F, 1.6 l, Euro-5; Opel Insignia, 1.6 l, Euro-5; Mitsubishi Carisma, 1.8 l, Euro-3), a first GPF contributed by our industry partner, and two different biofuel/gasoline blends (E85 and E10) were investigated.

Main scientific results of workgroups

Current GDI technology

A first set of three different GDI vehicles has been studied. Substantial emission variations were observed. With respect to particle emissions the Euro-3 vehicle (Mitsubishi Carisma, 1.8 l) exceeded those of both Euro-5 vehicles, the Volvo V60 (T4F, 1.6 l), which was chosen as the reference vehicle throughout the project, and the Opel Insignia (1.6 l). Particle emissions of these three GDI vehicles were above the threshold limit for diesel passenger cars of $6 \cdot 10^{11}$ particles/km indicating that particle emissions indeed are an important issue for these GDI vehicles.

Figure 1 displays the particle number size distribution of the reference vehicle (Volvo V60 T4F, 1.6 l) operated with gasoline without particle filter. A nano-SMPS instrument was used to detect the particle size distribution down to 9 nm. The most prominent particles have diameters around 80 nm like diesel particles, but substantial contributions are also found in the smallest size range below 23 nm.

Figure 2 displays particle number-based emission factors (#/km) over a size range of

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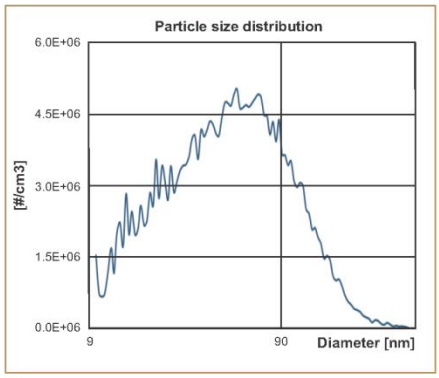

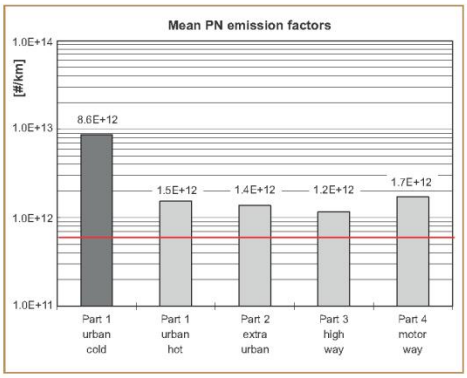

Figure 1 (left):
Particle number size distribution of exhaust of the reference GDI vehicle (Volvo V60, 1.6 l, Euro-5) obtained from an SMPS measurement.

Figure 2 (right):
Particle number emissions (#/km) of the reference GDI vehicle (Volvo V60, 1.6 l, Euro-5) in different parts of the WLTC. The threshold limit of 6 x 10e11 particles/km (red line) valid for Euro-5 diesel vehicles is exceeded in all cycle parts.

23–400 nm (the legally binding size range) in the WLTC. Highest particle number (PN) emissions of $8.6 \cdot 10^{12}$ particles/km were observed under urban cold start conditions. Particle emissions stabilized at $1.2–1.7 \cdot 10^{12}$ #/km under hot engine conditions. We conclude that this gasoline-fueled Euro-5 vehicle exceeded the threshold limit for diesel passenger cars ($6 \cdot 10^{11}$ #/km) 2-fold under hot and 14-fold under cold start conditions.

A first gasoline particle filter tested

A first GPF, developed by one of our industrial partners, was tested successfully showing that substantial reductions of PN emissions are possible with good filter technology.

Impact of (Bio)ethanol on particle emissions

In two additional configurations the impact of (bio)ethanol was studied on particle emissions and emissions of non-regulated pollutants. For this purpose aliquots of emitted exhausts are collected in all-glass sampling devices and are analyzed after a multi-step clean-up procedure with GC-HRMS for PAHs and related compounds. Respective data evaluation is on-going.

Other aliquots of the exhausts are delivered to a smog chamber and aged therein for 4–5 h under conditions similar to the atmosphere to study the extent of secondary aerosol formation. In parallel, two flow reactors are used to determine the SOA potential of these exhausts with accelerated aging at higher time resolution. Figure 3 displays the smog chamber in operation and figure 4 gives an impression of the clustering of instruments at the chassis dynamometer of the UASB in Nidau during the first sampling campaign held in spring 2014.

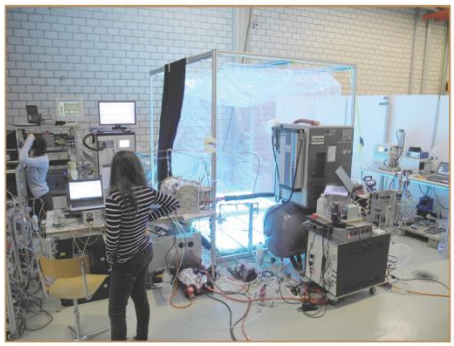

Figure 3 (left):
Mobile Smog chamber of the PSI to study SOA formation of GDI vehicle exhausts.

Figure 4 (right):
Clustering of instruments at the chassis dynamometer of the UASB in Nidau during the spring 2014 campaign.

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List of abbreviations

GDI	Gasoline Direct Injection
GPF	Gasoline Particle Filter
SMPS	Scanning Mobility Particle Sizer
SA	Secondary Aerosol
SOA	Secondary Organic Aerosol
SSC	Steady State Cycle
PAH	Polycyclic Aromatic Hydrocarbons
PN	Particle Number
WLTC	World Harmonized Light Vehicle Test Cycle
WP	Work Package

Major partners in the ETH domain

- Empa – Laboratory for Advanced Analytical Technologies
- Empa – Laboratory for Air Pollution/Environmental Technology
- PSI – Laboratory for Atmospheric Chemistry

Main Investigator

Norbert Heeb, Empa

Project Partners

Empa

PSI

UASB

UASNWS

FOEN

Time frame of Project

2013–2016

Thematic Relationship to SCCER

Mobility

Scope of project

Gasoline direct injection (GDI) vehicles will quickly replace port-fuel injection vehicles in the next years. It is estimated that about 50 million GDI vehicles will be operated on Europe's roads by 2020. In the GASOMEP project, we comprehensively study exhaust composition of various GDI vehicles including particle-bound, condensable and gaseous pollutants. Effects of fuel quality and converter technology, especially the potential of gasoline particle filters (GPFs), which are currently developed by our industrial partners, will be studied. Particle characterization including size distribution, number and metal content as well as the emissions of genotoxic compounds like polycyclic aromatic hydrocarbons (PAHs), their alkylated and nitrated forms are studied. These semi-volatile compounds are expected to penetrate filters to some degree and are important precursors of secondary organic aerosols (SOA) formed upon atmospheric oxidation. Respective SOA forming potentials are investigated in smog chamber experiments and two different flow reactor approaches in the project.

Status of project

After two years we can now look back to four intense sampling campaigns of 3 to 4 weeks each at the chassis dynamometer at the University of Applied Sciences Biel (UASB). One from the PSI, one from the University of Applied Sciences Northwestern Switzerland (UASNW) and one from Empa met the one at the UASB to investigate, according to the different work packages, emissions of regulated pollutants and nanoparticles (UASB, UASWN), non-regulated pollutants and metals (Empa) and secondary organic aerosols (PSI, UASWN).

So far, five different GDI vehicles from Euro-3 and Euro-5 legislation were tested and compared with a Euro-5 diesel vehicle with particle filter as the bench mark vehicle. A flex-fuel vehicle (Volvo V60 T4I, 1.6 l, Euro-5) which was operated with (bio)ethanol/gasoline blends is the reference GDI vehicle available in the 3-year campaign. In addition, two of our industrial partners contributed two coated and two non-coated gasoline particle filters (GPFs). These filters were tested with the reference vehicle in the world harmonized light vehicle test cycle (WLTC), under cold start and hot engine/catalyst conditions and in a steady state cycle (SSC) with constant vehicle operation at 94, 61, 45, 26 km/h and idle.

Main scientific results of workgroups

GDI vehicles release up to 2000 x more particles than current diesel vehicles equipped with filters: The five GDI vehicles studied so far released substantial numbers of nanoparticles (PN) in the range of 7×10^{11} to 2×10^{13} particles/km. Emissions were about 2–10 times higher under cold start conditions. In other words, PN emissions of these GDI vehicles are clearly above the threshold limit for diesel passenger cars of 6×10^{11} particles/km.

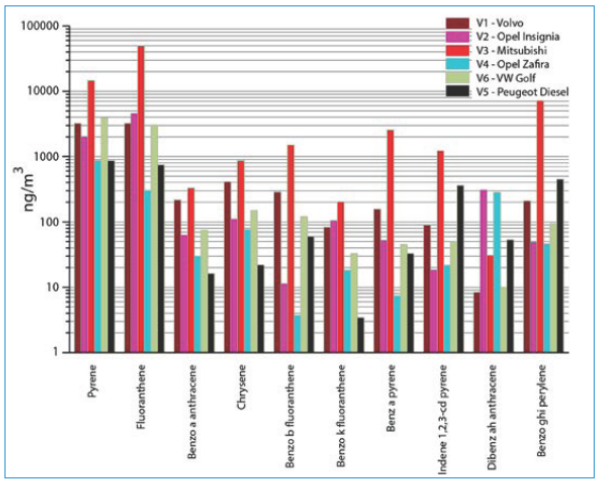

Figure 1 :
Emissions of genotoxic PAHs and precursors for genotoxic nitro-PAHs in GDI vehicle exhausts (ng/m³).

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Comparing these values with those of the benchmark diesel vehicle (Peugeot 4008, 1.6 l, Euro-5), which is equipped with a particle filter, revealed 30–2000-fold higher particle emissions of the GDI technology. This clearly indicates that filters must have a large potential to detoxify GDI vehicles with respect to their high particle emissions.

Comparable emissions of genotoxic PAHs from GDI- and diesel vehicles

Figure 1 displays emission factors (ng/m³) of various 4-, 5-, 6- and 7-ring PAHs, including those PAHs relevant for the genotoxic potential, of five GDI vehicles and the bench mark diesel vehicle equipped with filter (Peugeot 4008, 1.6 l). PAH emissions varied considerably among the different GDI vehicles. They were highest for the oldest vehicle (Mitsubishi Carisma, 1.8 l, Euro-3) but comparable for the Euro-4 and Euro-5 vehicles. In comparison with the diesel vehicle one can state that PAH emissions of the GDI vehicles are at or slightly above those of the diesel vehicle. In other words, GDI vehicle exhausts will also contribute to the overall burden for these genotoxic compounds in areas which are affected by traffic.

Impact of (bio)ethanol on PAH and particle emissions

Figure 2 displays emission factors (µg/km) of various 2-, 3-, 4- and 5-ring PAHs of the reference vehicle (VOLVO V60 T4F, 1.6 l) operated with gasoline (E0) and ethanol/gasoline blends (E10, E85) in the cold and hot started WLTC and the SSC. Transient driving (WLTC) has a substantial impact on PAH emissions which were 1–3 orders of magnitude higher than those under steady state driving. The cold start effect is moderate (< 10 x) whereas blending with ethanol lowered PAH emissions by more than one order of magnitude. Effects tent to be larger with increasing PAH ring number.

For comparison, figure 2 also includes particle number emissions in the WTLC which were 10^{13} particles/km with E0 but only about 10^{11} particles/km with E10 and E85. This indicates that blending of gasoline with ethanol has beneficial effects on particle and PAH emissions including the genotoxic PAHs. However, these promising effects will be verified again in next year's campaign on additional GDI vehicles.

Particle filters for GDI vehicles successfully applied

So far, four different filters, two with catalytic coatings, two non-coated ones, have been tested on the reference vehicle under comparable conditions. Data evaluation is ongoing and will be reported later in the project.

Time-resolved secondary aerosol analysis of GDI vehicles

Time-resolved secondary aerosol analysis of GDI vehicles was conducted using the micro smog chamber. A continuous-flow reactor-tube was applied to study the formation of secondary aerosols (SA) by taking the gas-phase fraction of exhausts and oxidize it with ozone (up to 60 ppm) at residence times of about 10 seconds. Figure 3 displays an example of secondary aerosol emissions (g/lit-fuel) during cold and hot WLTC. In conclusion, the secondary aerosol released per liter of fuel is several orders of magnitude lower than what has been observed in wood burning experiments.

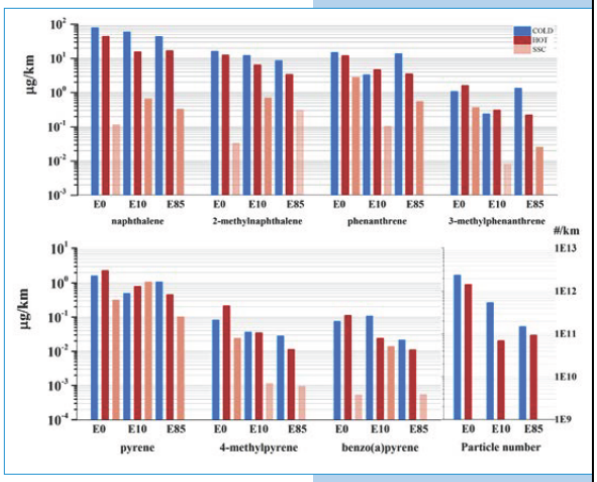

Figure 2 :
Effects of ethanol blending on selected PAH (µg/km) and particle number (#/km) emissions of the reference GDI vehicle (Volvo V60, 1.6 l, Euro-5) in the cold (blue) and hot (red) started WLTC and the SSC (pink). Commercial gasoline (E0) and two (bio) ethanol/gasoline blends (E10 and E85) have been applied.

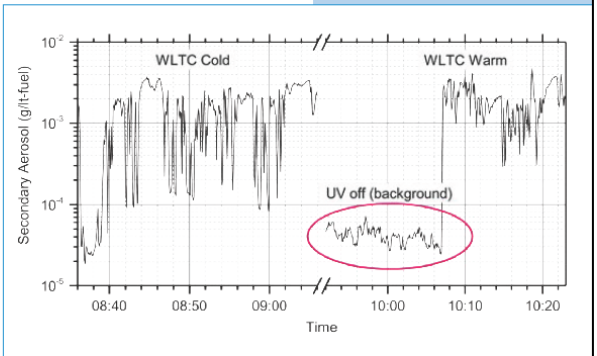

Figure 3:
Secondary aerosols of a GDI vehicle produced in the micro-smog chamber during cold and hot WLTC driving. The mass concentration was derived from the observed number concentration, average mass distributions from the SSC and a particle density ρ = 2000 kg/m³.

COMPARISON OF PAH LEVELS AND MUTAGENICITY OF GDI- AND DIESEL VEHICLE EXHAUSTS AND IMPACT OF (BIO)ETHANOL

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Empa
Materials Science and Technology

BACKGROUND

GDI vehicles appear to be a promising technology for reducing exhaust emissions and fuel consumption. However, several sources reported high emissions of particles exceeding the Euro 6 limit of $6x10^{11}$ particles/km. In addition, increased emissions of genotoxic pollutants (e.g. Polycyclic aromatic hydrocarbons or PAHs) are produced. PAHs are known to induce genotoxic responses inside cells causing mutations, which may lead to cancer. The WHO also classified several PAHs as carcinogenic, like benzo(a)pyrene, a group 1 carcinogen.

METHODOLOGY

Complete exhaust samples sampled from a CVS tunnel (Fig. 1.A), including solid, condensed and gaseous fractions were collected from 5 GDI vehicles. Vehicles were driven following the WLTC (World Harmonized Light Vehicles Test Cycle) under hot (WLTC-H) and cold (WLTC-C) start conditions. Vehicle 1 was also tested with two ethanol blends (E10 and E85). In addition, an Euro-5 diesel vehicle equipped with a filter was tested. Samples went through extraction and cleanup procedures and were analyzed by HRGC-HRMS. Concentrations of the genotoxic PAHs were determined (Fig. 2).

To evaluate the mutagenicity, aliquots of the exhaust extracts (5%) of vehicle 1 in WLTC-H, with E0, E10, E85 and the diesel vehicle were tested for mutagenicity using the bacterial Ames test (Xenometrix, S. typhimurium, strains TA98 and TA100). Different concentrations (C1-C6, two fold dilutions, C1 low to C6 high) of the extracts were directly exposed to the bacteria for 1.5 h, then dispersed in histidine-free medium and incubated for a 48-h period at 37 °C. Exhaust extracts collected in the WLTC-C, for all vehicles were also tested with the mutagenicity Ames test in order to compare the whole GDI fleet with the diesel vehicle.

RESULTS

Fig. 3. shows the effect of the ethanol blends on PAH concentrations (ng/Nm³) and respective patterns for the WLTC-C and WLTC-H. There is a significant decrease on the emissions when ethanol is used. WLTC-H is also decreasing compared to WLTC-C, when ethanol is used. Except for E10, patterns are similar but differ with respect to absolute values. Fig. 4 shows the concentrations in ng/Nm³ and patterns of genotoxic PAHs for all GDI-vehicles and diesel vehicle with filter. Patterns and PAH emission levels differ from vehicle to vehicle. Fig. 5 displays the fold-increase of revertants over the negative control for the samples E0, E10, E85 and diesel in WLTC-H, with the strain TA 98. There were no signs of mutagenicity in the TA100 strain. A three-fold or higher increase in the number of revertants relative to the negative control or a clear dose response suggests mutagenicity. This is the case for E0 at the concentration C6. Regarding the fleet, no significant differences were found in the Ames test.

CONCLUSIONS

Ethanol effect. The concentrations of genotoxic PAHs decrease with increased ethanol contents. This decrease is in accordance with the particle number, which is also reduced.

GDI fleet emissions. All GDI vehicles tested emit more genotoxic PAHs than the diesel vehicle (which included a particle filter), some emitted even 1 order of magnitude higher concentrations.

Ames test results. From all dose-tests performed, only the gasoline sample (E0, WLTC-H) at C6 showed a significant response with TA 98 strain, meaning "probably mutagenic" and being in accordance with the PAH concentration (the highest also in WLTC-H with E0). No significant results were found for other samples. However, these experiments should be reconfirmed with higher doses.

AKNOWLEDGEMENTS

The authors want to thank the CCEM for the support on the GASOMEP project and the FP7-PEOPLE-2010-COFUND-Marie Curie Action from the EU Comission for the support on the genotoxic experiments.

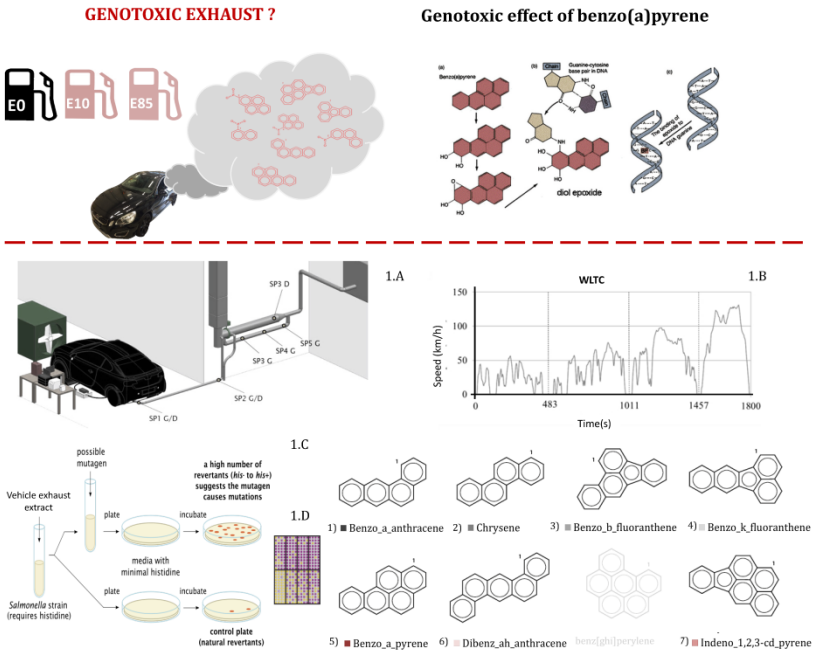

Fig.1. Sampling setup (1.A), driving cycles (1.B) and scheme of Ames test with an example of a mutagenicity test plate (1.C and 1.D)

Fig. 2. The 7 genotoxic PAH. According to the WHO, these PAHs are genotoxic, with benzo(a)pyrene being a class 1 carcinogen.

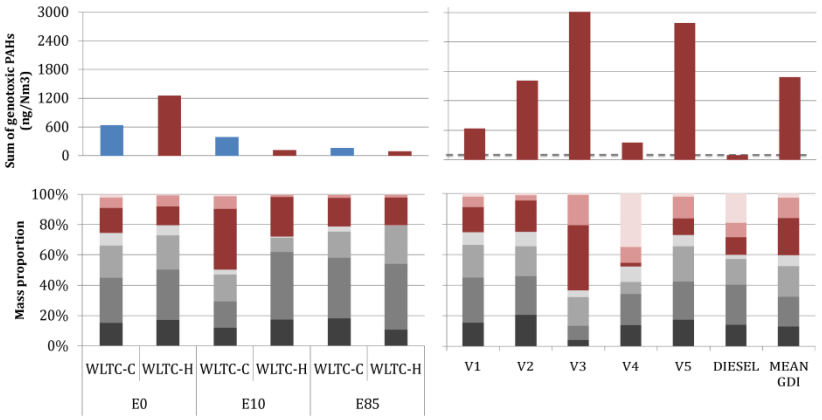

Fig. 3. Ethanol effect on PAH emissions. Concentration of genotoxic PAHs in ng/Nm³ (top, WLTC-C in blue, WLTC-H in red) and respective patterns (bottom, color code in Fig.2).

Fig. 4. Emissions of PAHs of the GDI fleet and comparison with the diesel vehicle. Concentration of genotoxic PAHs in ng/Nm³ (top) and respective patterns (bottom).

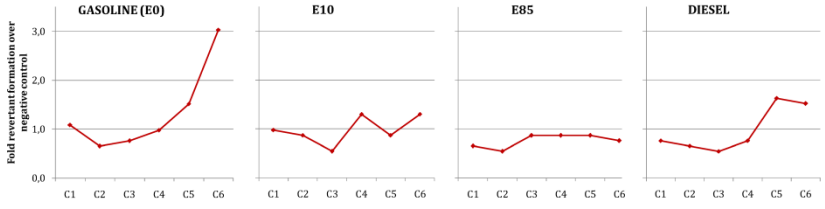

Fig. 5. Exhaust mutagenicity (Ames test, strain TA98, WLTC-H). Fold revertant is obtained by dividing the number of revertants in the sample by the number in the negative control (untreated sample) indicating mutagenicity if higher or equal to 3. C1-C6 correspond to the different concentrations tested, C6 being the highest.