TEST RESULTS OF EMISSIONS FOR PAH, NITRO-PAHS, NH_3, N_2O AND NANOPARTICLES

WP1, TASK 1.3

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TABLE OF CONTENTS

1. INTRODUCTION 11
  1.1. PURPOSE AND TARGET GROUP 11
  1.2. CONTRIBUTIONS OF PARTNERS 12
2. OBJECTIVES AND EXPECTED IMPACT 12
  2.1. OBJECTIVES 13
  2.2. EXPECTED IMPACT 13
3. DESCRIPTION OF TECHNICAL/SCIENTIFIC ACTIVITIES 13
  3.1. BACKGROUND AND NORMATIVE REQUIREMENTS 13
    3.1.1. VSET VERT SECONDARY EMISSIONS TEST OBJECTIVES**Fehler! Textmarke nicht definiert.**
  3.2. AVAILABLE INFORMATION 14
    3.2.1. GENERATION OF PCDD/F WHEN USING A COPPER-ADDITIVE 15
    3.2.2. GENERATION OF PAH AND NITRO PAH IN PETROL ENGINES 15
  3.3. TEST VEHICLES 16
  3.4. FUEL AND LUBRICANTS 18
  3.5. TEST FILTER 18
  3.6. TEST CYCLE 19
  3.7. TEST BENCH AND MEASUREMENT TECHNOLOGY 20
    3.7.1. MEASURING EQUIPMENT FOR EXHAUST EMISSIONS, ROLLER TEST BENCH 20
    3.7.2. MEASURED SUBSTANCES AND PARAMETERS, CHASSIS DYNAMOMETER 21
  3.8. SAMPLING AND ANALYSIS 21
    3.8.1. SAMPLING EQUIPMENT FOR SECONDARY EXHAUST EMISSIONS, EMPA .. 21
4. RESULTS AND DISCUSSION 21
    4.1.1. LEGALLY LIMITED EMISSIONS AND FUEL CONSUMPTION FIAT 500X 21
    4.1.2. LEGALLY LIMITED EMISSIONS AND CONSUMPTION GOLF (7) 24
  4.2. SECONDARY EMISSIONS (PCDD/F, PAH AND NITRO-PAH) AND NON-LIMITED TOXINS 27
    4.2.1. MEASUREMENT METHODS FOR TOXIC TRACE SUBSTANCES AND SECONDARY EMISSIONS 28
    4.2.2. RESULTS OF EMISSIONS OF TRACE SUBSTANCES AND SECONDARY EMISSIONS 29
5. DEVIATIONS FROM THE PLAN 29
6. LINKS WITH OTHER WPS 29

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7. CONCLUSIONS AND RECOMMENDATIONS 29
8. BIBLIOGRAPHY 30
9. ANNEX 31
  9.1. FIAT 500X, TWC, W/O GPF, FUEL: E10. 31
  9.2. FIAT 500X, TWC, WITH GPF, FUEL: E10. 32
  9.3. VW GOLF TSI, TWC, W/O GPF, FUEL: E10. 33
  9.4. VW GOLF TSI, TWC, WITH GPF, FUEL: E10. 34
  9.5. DETAILED SECONDARY EMISSIONS REPORT EMPA 35

LIST OF TABLES

Table 1 Contribution from Partners 12

Table 2: Technical data of the tested vehicles. 17

Table 3 Measurement methods for toxic trace substances and secondary emissions 28

Table 4: Emissions and fuel consumption during WLTC driving cycle with cold start. 31

Table 5: Emissions and fuel consumption during WLTC driving cycle with warm start. 31

Table 6: Emissions and fuel consumption during SSC driving cycle. 31

Table 7: Emissions and fuel consumption during WLTC driving cycle with cold start. 32

Table 8: Emissions and fuel consumption during WLTC driving cycle with warm start. 32

Table 9: Emissions and fuel consumption during SSC driving cycle. 32

Table 10: Emissions and fuel consumption during WLTC driving cycle with cold start. 33

Table 11: Emissions and fuel consumption during WLTC driving cycle with warm start. 33

Table 12: Emissions and fuel consumption during SSC driving cycle. 33

Table 13: Emissions and fuel consumption during SSC driving cycle, repetition. 34

Table 14: Emissions and fuel consumption during WLTC driving cycle with cold start. 34

Table 15: Emissions and fuel consumption during WLTC driving cycle with warm start. 34

Table 16: Emissions and fuel consumption during SSC driving cycle. 35

LIST OF FIGURES

Figure 1: Formation of Dioxins in a catalytically active particulate trap 15

Figure 2: Cumulative + weighted genotoxic potential of GDI and Diesel exhaust (ng TEQ/m3) 16

Figure 3: Fiat 500X to the left, & VW Golf (7) to the right.. 16

Figure 4: Multicell Wall-Flow Filter Cordierite, Courtesy CORNING.. 18

Figure 5: Delayed separation effect with the DPF and time behavior with the APT filter........... 18

Figure 6: The top diagram represents the WLTC cycle and the one just above the SSC cycle. 19

Figure 7: Sampling and measurement set-up for gaseous exhaust and PN emissions............. 20

Figure 8: Limited exhaust emissions emitted by the Fiat 500X w/o and with GPF during the cold and hot WLTC cycles. CO_2 in g/km, rest in mg/km 22

Figure 9: particle number (TPN) w/o and with GPF and filtration efficiency (FE) during the cold and hot WLTC cycles. Fiat 500X... 22

Figure 10: CO and CO_2 emissions emitted by the Fiat 500X w/o and with GPF during the SSC cycle. CO in mg/km or mg/min in idling, CO_2 in g/km or g/min in idling. 23

Figure 11: HC and NOx emissions emitted by the Fiat 500X w/o and with GPF during the SSC cycle. Idling in mg/min, rest in mg/km. 23

Figure 12: *Particle number (TPN) w/o and with GPF and filtration efficiency (FE) during the SSC cycles. Fiat 500X.* 24

Figure 13: Limited exhaust emissions emitted by the VW Golf TSI w/o and with GPF during the cold and hot WLTC cycles. CO_2 in g/km, rest in mg/km... 24

Figure 14: Particle number (TPN) w/o and with GPF and filtration efficiency (FE) during the cold and hot WLTC cycles. VW Golf TSI. 25

Figure 15: CO and CO_2 emissions emitted by the VW Golf TSI w/o and with GPF during the SSC cycle. CO in mg/km or mg/min in idling, CO_2 in g/km or g/min in idling.............................. 26

Figure 16: HC and NOx emissions emitted by the VW Golf TSI w/o and with GPF during the SSC cycle. Idling in mg/min, rest in mg/km. 26

Figure 17: Particle number (TPN) w/o and with GPF and filtration efficiency (FE) during the SSC cycles. VW Golf.. 26

LIST OF ABBREVIATIONS

ACRONYM	DESCRIPTION
AFHB	Particle Measurement Pgm; University of Applied sciences Biel CH
BAFU	Bundesamt für Umwelt, (Swiss EPA)
CLD	Chemiluminescence Detector
CPC	Condensation Particle Counter
DI	Direct Injection
DPF	Diesel Particle Filter
DMA	Differential Mobility Analyzer
EC	Elemental Carbon, European Community
EMPA	Federal Laboratories for Materials Testing and Research
FE	Filtration Efficiency
FID	Flame ionization detector
FOEN	Federal Office of Environment (FOEN = BAFU)
IARC	International Agency for Research on Cancer - part of WHO
LRV	Air Pollution Control Ordinance, Switzerland
MPI	Multipoint Injection
NP	Nanoparticles = particles < 0,1 µm
OBD	On-Board diagnostics
OC	Organic carbon
OEM	Original Equipment Manufacturer
PAH	Polycyclic Aromatic Hydrocarbons
PAS	Photoelectric Aerosol Sensor
PCDD/F	Polychlorinated dibenzodioxin/furan
PM	Particulate matter, particle mass

PMP	Particulate Measurement Programme
PN	Particle No.: Concentration per cc or per km of per kWh
SMPS	Scanning Mobility Particle Sizer
SSC	Steady State Cycle for testing Secondary Emissions and particle size Distribution
SUVA	Swiss. Accident Insurance Institution
TEQ	Toxicity Equivalent
TWC	Three Way Catalyst (John J. Mooney, Engelhard 1978)
TRL-8	Technology Readiness Level - 8
TTM	Technology Thermal Machines
VERT	Association; Verified Emission Reduction Technology; Reduction of emissions from real machines in tunnel construction
VFT1	VERT Filter Test Phase 1
VSET	VERT Secondary Emission Test
WHO	World Health Organization
WLTC	Worldwide Harmonized Light Duty Test Cycle
WLTP	Worldwide Harmonised Light Vehicles Test Procedure
WP1	Work Package 1

LIST OF SYMBOLS

SYMBOL	DESCRIPTION
µ	Micron

PUBLISHABLE SUMMARY

This document serves the purpose of documenting that no secondary emissions are measured/detected because of installing the retrofit solution proposed in work package 1. The background is that extensive experience with diesel engines has shown that catalytic converters and filters can also have a negative impact on the chemical processes in the exhaust tract. For example, highly toxic substances such as dioxins and furans, PAHs and nitro-PAHs can be formed because of the long residence times of separated soot with accumulated hydrocarbons, metal oxides and chlorides [4,8]. EU legislation does not take this risk into account yet, although the US Clean Air Act already drew attention to it in the 1970s [1]. Swiss legislation, however, explicitly requires corresponding proof [2,9], which is anchored in the Swiss standard SN 277206 [3] with a list of 35 highly toxic trace substances. This has contributed to the worldwide ban on hazardous technologies such as the use of copper-containing additives.

For gasoline engines, it is known from previous VERT research that they can emit up to 40 times more genotoxic PAH despite TWC and GPF [5], often attached to very small particles, which promotes the so-called Trojan Horse effect of toxins being translocated into the blood stream, even in the heart, brain and placenta, a particularly high health risk for unborn. Therefore, a test on non-legislated toxic trace emissions and secondary emissions, following VERT standards, was relevant and necessary to be performed with the technical solution proposed in the AeroSolfd project.

The testing and subsequent analysis for the 2 vehicle emissions, showed similar results with high Particle number filtration efficiencies (over 95%), and no increase in toxic trace substances. Dioxins and furans remained below the detection limit and there was no nitration of PAHs.

The results therefore fulfil the expectation that the tail pipe retrofit technology proposed in WP1 as a TRL-8 product should have no adverse environmental effects, no fuel penalty, hence CO_2 increasing implications and no secondary emissions. Subsequent commercialisation should therefore not have any adverse environmental technical and chemical implications.

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1. INTRODUCTION

Extensive experience with diesel engines has shown that catalytic converters and filters can also have a negative impact on the chemical processes in the exhaust tract. For example, highly toxic substances such as dioxins and furans, PAHs and nitro-PAHs can be formed because of the long residence times of separated soot with accumulated hydrocarbons, metal oxides and chlorides [4,8]. EU legislation does not take this risk into account, although the US Clean Air Act already drew attention to it in the 1970s [1]. Swiss legislation, however, explicitly requires corresponding proof [2,9], which is anchored in the Swiss standard SN 277206 [3] with a list of 35 highly toxic trace substances. This has contributed to the worldwide ban on hazardous technologies such as the use of copper-containing additives.

For gasoline engines, it is known from previous VERT research that they can emit up to 40 times more genotoxic PAH despite TWC and GPF [5], often bound to very small particles, which promotes the so-called Trojan Horse effect of toxin storage in the tissue and therefore a secondary emission test with the technical solution proposed in the AeroSolfd project was relevant and necessary. The expectation is that the tail pipe retrofit technology proposed in WP1 as a TRL-8 product should have no adverse environmental effects and no secondary emissions should be detected. Subsequent commercialisation should therefore not have any negative technical and chemical implications.

Two typical vehicles, a direct-injection VW Golf and an intake manifold-injection Fiat 500X, were tested with and without the non-catalysed AeroSolfd particulate filters in accordance with the VERT secondary emission protocol. For this purpose, 5 operating conditions typical for the WLTP were selected and driven constantly for 20 minutes each, so that sufficient aliquots of samples could be collected for the subsequent chemical analysis. On this occasion, the limited emissions were of course also recorded and the particle size distribution determined. The samples were then processed by EMPA and analysed using gas chromatography and high-resolution mass spectrometry.

1.1.PURPOSE AND TARGET GROUP

The purpose was to test non-legislated trace toxins and secondary emissions after retrofitting of non-catalyzed gasoline particle filter. Target groups are policymakers, stakeholders in the automotive industry and end users of petrol driven passenger cars.

1.2.CONTRIBUTIONS OF PARTNERS

The contribution of the different partners is detailed in Table 1.

Table 1 Contribution from Partners

PARTNER SHORT NAME	CONTRIBUTIONS
AFHB	University of Applied Sciences Biel/Bienne. Responsible for conducting vehicle Emissions testing, data collection and reporting on Regulated emissions
EMPA	Eidgenössische Materialprüfungs- und Forschungsanstalt, Responsible for analyzing and reporting secondary emissions measuremnts
VERT- SC	VERT Scientific Committee responsible of data collection, analysis, compiling and reporting
VERT	Work package leader and AeroSolfd reporting

2. OBJECTIVES AND EXPECTED IMPACT

The goal is to develop and demonstrate on a fast track a cost-efficient retrofit solution for the direct injected European gasoline fleet segment which currently drives without any filter technology (EURO 6c and earlier). The developed product will replace the middle car silencer and be prepared to have a later type-approval to address broad engine/vehicle families across multiple markets. The designed retrofit solutions in TRL 8 will be approved and ready for commercialisation in Europe and Israel. For this, the following specific objectives are defined:

1. To match the retrofit solutions to representative gasoline passenger car type families. For this, high efficient gasoline particle filters (GPFs,) known from latest OEM Euro 6d technology, will be adapted via system design to a representative fleet with 4 engine families.

2. To experimentally validate 4 vehicles/engine types and to test the adapted retrofit filter solutions in typical urban driving cycles.

3. To measure toxic secondary emissions substances like PAH, Nitro-PAH, NH_3, N_2O using 2 exemplary vehicles to evaluate the impact of the retrofit filter.

4. To carry out field tests for min. 6 months with up to 50 vehicles split into 3 fleets (Switzerland, Germany and Israel). Performance will be constantly measured with a datalogging system measuring back pressure, exhaust temperature and surface temperature.

5. To measure particle number emissions of 1,000 cars during their regular PN-PTI emission check to determine the current PN emission status of a European gasoline fleet and identify the share of high emitting gasoline cars.

2.1.OBJECTIVES

Specific objective (3) is related to task 1.4 and this D1.3 is to measure secondary emissions (i.e. PAH, Nitro-PAH, NH_3, N_2O) using 2 exemplary vehicles to evaluate the impact of the retrofit filter by M22. Ref. Objective 1.4)

2.2.EXPECTED IMPACT

AeroSolfd will bring cost-efficient and environmentally friendly retrofit solutions for tailpipe, brake and closed environment emission up to TRL 8 until the project's end. By 2025, these effective transition technologies will be available on the market to deliver clean air to European Cities and beyond in further world markets. Impact of this specific deliverable will have the impact that a non-catalysed GPF is a solution to the elimination of particles emitted from petrol engines without causing any adverse effect in the form of regulated or non- regulated secondary emissions

3. DESCRIPTION OF TECHNICAL/SCIENTIFIC ACTIVITIES

In WP1, 4 vehicles have been used for testing at the laboratories of AFHB. 2 vehicles were used to conduct testing on filtration efficiency of particle number and other 2 vehicles used to conduct the measurement and analysis of secondary emissions. The following will focus on the 2 vehicles used for secondary emissions testing. For filtration efficiency testing, methods, equipment and results please refer to D.1.2 submitted in November 2023.

3.1.BACKGROUND AND NORMATIVE REQUIREMENTS

EU legislation limits exhaust emissions from combustion engines in an almost negligent manner to the gas CO, the group NO+NOx, (NO_2) which are summarized without weighting their very different toxicity, the group of all hydrocarbons, whose very different toxicity is assigned to the substance normal hexane in the definition of the FID measuring method (proportional to the sum of the organically bound C atoms) and the particles according to the mass PM and number PN, again without taking their toxicity into account. This has not changed with the introduction of catalysts and particle filters even not on the level of Euro-7.

In contrast, the US Clean Air Act Section 202 already stipulated a broader definition from 1970: "Standards are applicable **to the emissions of any air pollutant** which may reasonably be anticipated to endanger public health and no emission control device, system, or element of design shall be used in a new motor vehicle or new motor vehicle engine for purposes of complying with requirements prescribed under this title if such device, system, or element of design will cause or contribute to an unreasonable risk to public" [1]

The first regulation issued by the Swiss FDJP (Federal Department of Justice and Police) on 7 August 1990, based on Art. 84 para.1 BAV states "Vehicles in circulation and new vehicles type-approved without particulate filters can be retrofitted with particulate filters (...), whereby it must be proven that a risk to health and the environment due to additional reaction products is excluded". [2]

Based on this, the VERT filter-system specification requires that "there shall be no clearly detectable and relevant increase of emissions compared to the initial engine conditions", where "relevant" is defined by the SUVA MAK-threshold levels at the working place and the general Swiss threshold levels for ambient air. [10].

This requirement is described in detail in the Swiss Filter Testing Norm SN 277206 (2009), where the targeted 35 substances are listed, and the analytical methods are defined. [3]

3.1.1. VERT SECONDARY EMISSIONS TEST OBJECTIVES

During a worst-case test-cycle providing long residence time periods at conditions where such substances may be produced, the following investigations shall be performed:

- Particle size analysis over 10-500 nm:
  - soot particle number concentrations must be reduced by >95 % in any size class
  - overall filtration efficiency for additive ash particles must be at least as good as for soot particles
- PCDD/F-analysis for gaseous and particle-bound substances:
  - none of the individual toxic PCDD/F-substances shall exceed the engine-out level nor shall the Toxicity-Equivalent (TEQ)-sum exceed engine-out TEQ-sum even with increased Cl-content as high as 10 ppm in fuel.
- PAH-analysis for gaseous and particle bound-substances:
  - the sum of carcinogenic PAH as defined by US-EPA or IARC shall not exceed the engine-out concentration, nor shall any individual PAH-substances significantly exceed engine-out levels
- Nitro-PAH-analysis for gaseous and particle bound-substances:
  - emissions of 2-ring-, 3-ring- or 4-ring-Nitro-PAH shall be identified and shall not exceed engine-out emission levels significantly
- Monitoring of legally limited gaseous emissions and solid nanoparticles: no peaks of CO, HC or PN are permitted which increase the overall test-cycle emissions by more than one standard deviation.

Beside of these requirements particulate trap-systems must comply with existing legislation with respect to noise emission, safety aspects [7] and new-substance-regulations [9].

3.2.AVAILABLE INFORMATION

Research on trap systems has revealed that traps can become highly active chemical reactors because of the extremely high specific surface of deposited soot particles (200 m^2/g). They can adsorb any substances offered by the exhaust gas, extent their residence time under high temperature conditions and thereby create products which did not exist in the exhaust before or in much lower concentrations. This chemical activity can be increased by the presence of catalysts originating from fuel, lube-oil, additives or coatings. It has been shown that extremely toxic substances can be created such as PCDD/F*) in very high concentrations [8]. This has prompted the introduction of a so-called VERT-Secondary-Emission-Test VSET, which must be performed routinely during VERT filter system certification in all cases where such catalytic means are used.

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Examples from earlier VSET's demonstrate how strong such effects may be, thus supporting the need of this kind of test, as shown below.

3.2.1. GENERATION OF PCDD/F WHEN USING A COPPER-ADDITIVE

When using the copper additive, the trap immediately became active, increasing the PCDD/F-emission by about one order of magnitude at limited chlorine content but by more than 3 orders of magnitude for increased chlorine whereas in the case of the Fe- and Ce-additives the PCDD/F-concentration was not influenced with the trap-system (**Fehler! Verweisquelle konnte nicht gefunden werden.**).

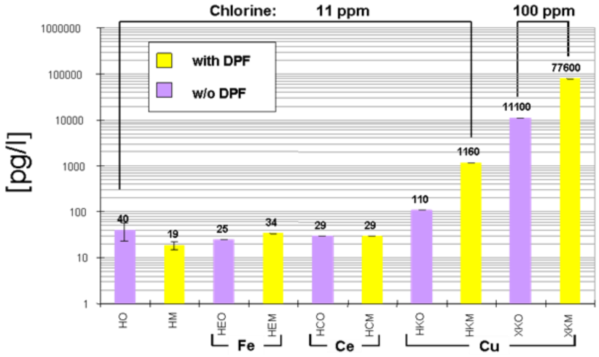

Figure 1: Formation of Dioxins in a catalytically active particulate trap

This would never happen in an exhaust system without filter since residence time would be too short, but the filter with long time deposits permits such detrimental processes. While this was a result with a diesel, petrol engines using high chlorine content in so-called scavenger fuel additives which might still be used in some countries, may produce even stronger effects.

3.2.2. GENERATION OF PAH AND NITRO PAH IN PETROL ENGINES

PAH in gaseous form will be converted to uncritical substances when passing the TWC very efficiently. Heavier PAH however, formed during the combustion process in low oxygen areas are deposited on soot particles and these particles travel through the cells of the TWC without being converted since they are not touching the walls because of their inertia. It can be speculated that we will find more such 3-ring and 4-ring PAH in the petrol engine compared to the Diesel engine, because the oxygen content is lower, and the specific surface of the particles is larger since they are smaller than Diesel soot particles. Once ended up on a filter surface and sitting there for a while they could even be nitrated in Diesel engines, but not so much in petrol engines. Depending on temperature they may be burned together with the particles, but they may also be desorbed and produce high concentration of emissions during this phase as previous VERT research has shown.

During the VERT/EMPA-Project GASOMEP 2017/18 [4] PAH-emissions of the 7 GDI vehicles with OE-GPF were investigated and compared to a Diesel vehicle. Mean PAH emissions of the GDI fleet were 2 orders of magnitude higher than the benchmark diesel vehicle. A comparison of the toxicity equivalent concentrations (TEQ) of the GDI fleet and the diesel vehicle revealed that GDI vehicles released 200-1700 ng TEQ/m^3 genotoxic PAHs, being 6-40 times higher than the diesel vehicle with 45 ng TEQ/km. The co-release of genotoxic PAHs adsorbed on numerous soot nanoparticles is critical due to the Trojan Horse Effect describing, the property of sub-200 nm particles being deposited in the alveoli, transporting genotoxic compounds into the lung. These nanoparticles are persistent and may eventually penetrate the alveolar membrane reaching the blood circulation system. All GDI vehicles tested released large numbers of nanoparticles carrying substantial loads of genotoxic PAHs. If non-treated diesel exhaust is considered as class-1 carcinogen by the WHO inducing lung cancer in humans, these GDI vehicle exhausts may be a major health risk.

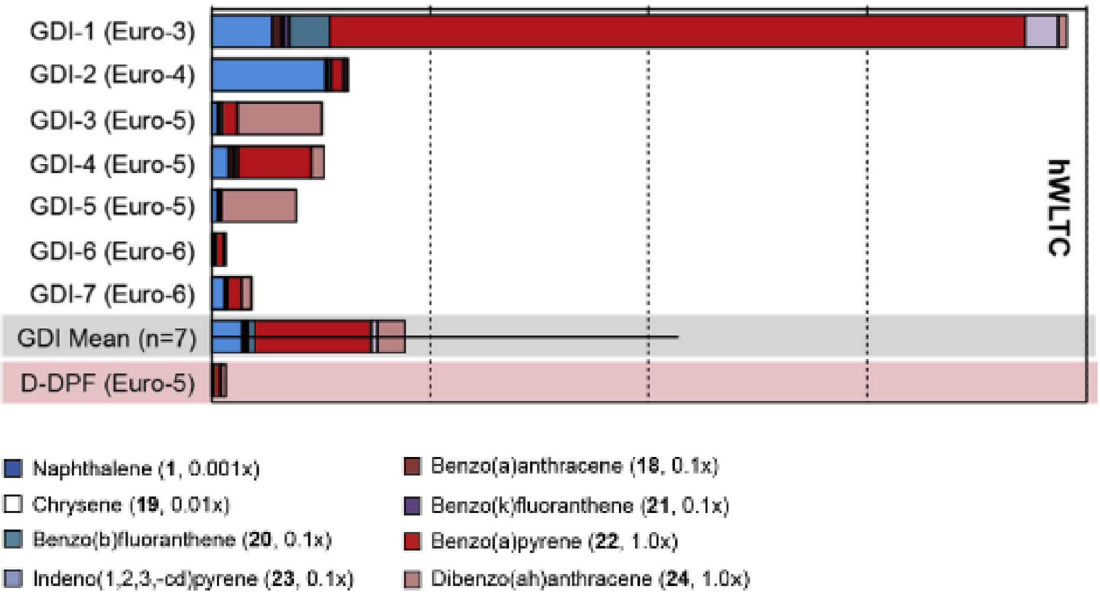

Figure 2: Cumulative + weighted genotoxic potential of GDI and Diesel exhaust (ng TEQ/m3)

3.3.TEST VEHICLES

Two petrol vehicles are being studied for the AeroSolfd project, one of which is Direct Injection (DI) and the other has a Manifold multi point injection[1] (MPI).

Figure 3 shows the tested vehicles and Table 2 present their most important technical data.

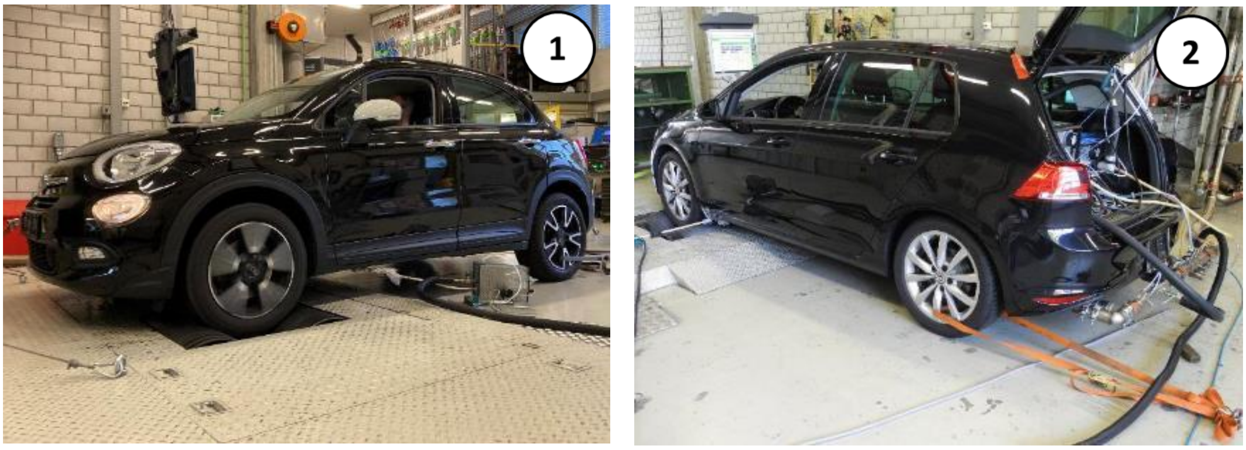

Figure 3: Fiat 500X to the left, & VW Golf (7) to the right

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[1] Also known as Port Fuel Injection

Table 2: Technical data of the tested vehicles.

		FIAT	VW
Model		500X	Golf TSI
Model year		2016	2016
Gearbox		m5	m6
Mileage		49396 km	71789 km
First registration		27.10.2016	05.04.2016
Engine type		55263842	CZCA
Number of cylinders / arrangement		4 / in-line	4 / in-line
Displacement		1598	1395
Nominal power	cm3	91	92
Nominal power speed	kW	5500	5000
Maximum torque	min-1	152	200
Speed of the max. torque	Nm	4500	1400
Engine cooling system	min-1	liquid	liquid
Injection system		MPI	DI
Empty weight		1350	1247
Total weight	kg	1875	1770
Maximum speed	kg	180	204
Exhaust aftertreatment systems	km/h	TWC	TWC
Fulfilled exhaust emission standard		EURO 6b	EURO 6b

3.4.FUEL AND LUBRICANTS

Fuel: Commercially available fuels were used for the tests. These correspond to Swiss market quality (petrol: SN EN 228).

Lubricating oil: The lubricating oils used comply with the vehicle/engine manufacturer's recommendations.

3.5.TEST FILTER

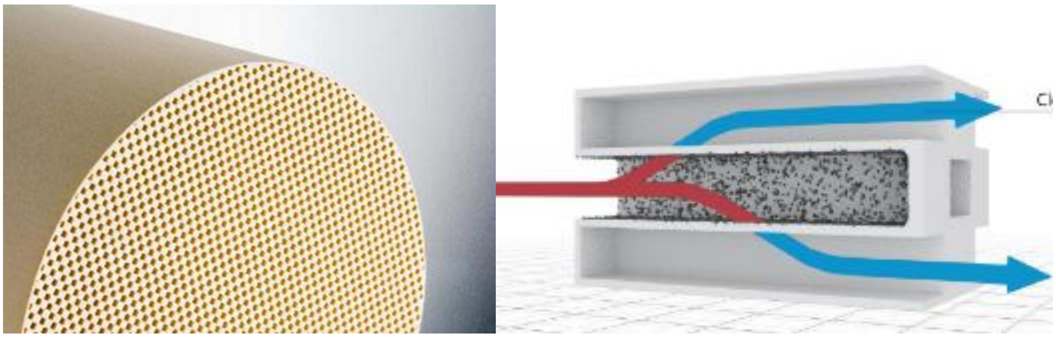

Figure 4: Multicell Wall-Flow Filter Cordierite, Courtesy CORNING

These filters were developed back in the 1980s for use in diesel engines and, with more than 300 million vehicles, are now state of the art for diesel. They achieve separation efficiencies of over 99% thanks to the soot cake that forms on the surface of the filter wall after 20-30 minutes, but no such soot cake is produced in petrol engines as the soot burns away continuously, and the particles are even smaller, so the separation efficiencies remain in the range of 80% or less [11]

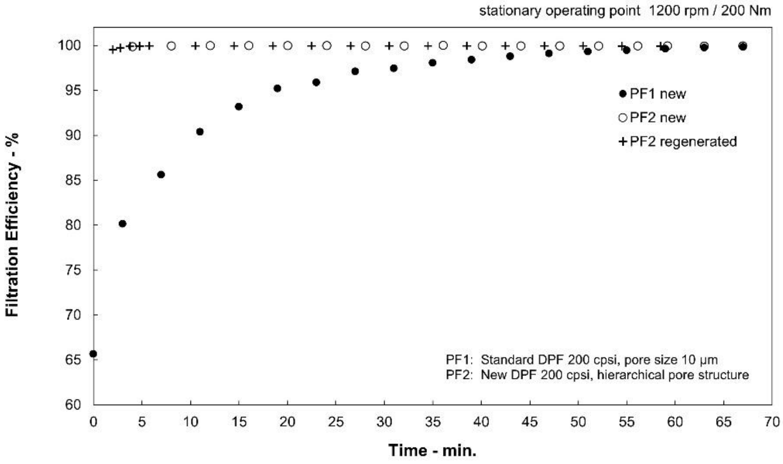

Figure 5: Delayed separation effect with the DPF and time behavior with the APT filter

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To improve this situation, CORNING has developed a new pore structure, called hierarchical pore structure or APF technology[2], and contributed these new filters to the AeroSolfd project as a project partner.

Material: Cordierite - basic porosity 55% with APT technology.
Diameter and length: 2 variants 132mm x 120mm = 1.64l and 103mm x 139mm = 1.16l).

3.6.TEST CYCLE

Figure 6 shows the WLTC (World Harmonized Light Duty Test Cycle) and the SSC (Steady State Cycle), applied for the secondary emission measurements – since we need constant conditions for the sampling as well as for the particle size distribution.

The SSC driving cycle consists of 20 min. steps at constant vehicle speeds 95, 61, 45, 26 km/h and idling, which are driven from the highest to the lowest speed. These vehicle speeds respond to the average speeds in the WLTC.

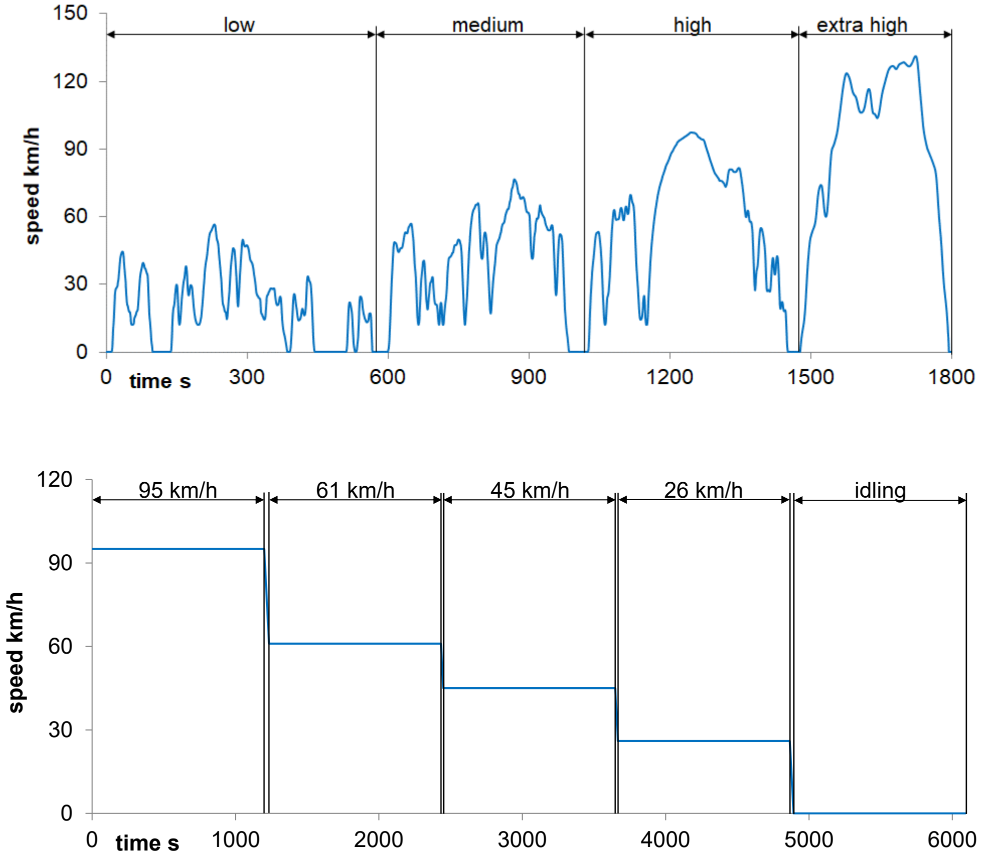

Figure 6: The top diagram represents the WLTC cycle and the one just above the SSC cycle.

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[2] Trade name: Corning DuraTrap GC 2.0 APT 200/8 (200 CPSI / 8 mil wall thickness

3.7.TEST BENCH AND MEASUREMENT TECHNOLOGY

The measurement setup of the chassis dynamometers is shown in Figure 7. The nanoparticle measurements are carried out according to the EU-PMP method.

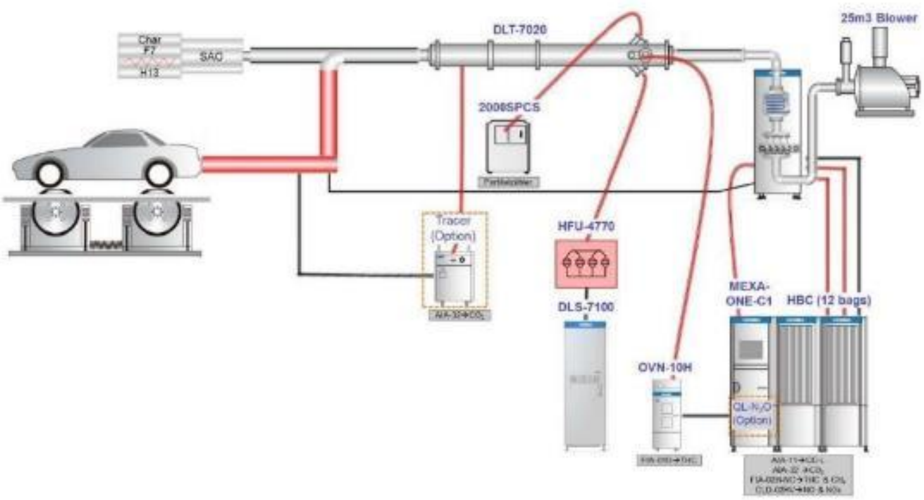

Figure 7: Sampling and measurement set-up for gaseous exhaust and PN emissions.

3.7.1. MEASURING EQUIPMENT FOR EXHAUST EMISSIONS, ROLLER TEST BENCH

The exhaust emissions emitted by the vehicle are diluted in a CVS system (CVS: Constant Volume Sampling) and measured by means of the exhaust gas analyser. These meet the technical requirements of UNECE Regulation No. 83 and are suitable for measuring vehicle exhaust emissions in Switzerland and the European Union.

The dilution ratio in the CVS plant is variable and can be controlled by means of CO_2 analyser.

The volatile exhaust components are measured with HORIBA analysers, which have the measuring principles shown below:

CO, CO_2	NDIR analyser
THC	FID analyser for the total of hydrocarbons
CH_4	FID analyser for methane $(CH)_4$
NO/NOx	CLA analyser

Particulate Number (NP) emissions are measured using TSI's (EECPC), model 3790 (4WD RP) or Horiba's MEXA-2100SPCS (2WD RP). For the SSC cycle, particle size distribution is additionally measured using TSI's SMPS systems.

Figure 7 shows the sampling and measurement setup during the tests. Sampling was done in the CVS tunnel with a thermo-conditioner (TC) heated to 300°C / 350 °C.

The non-limited emissions are determined by means of an FTIR analyser. The description of the analyser can be found in Annex A2 from the AeroSolfd-Report TR-3.

3.7.2. MEASURED SUBSTANCES AND PARAMETERS, CHASSIS DYNAMOMETER

- CO, CO_2, HC, CH_4 , NOx diluted exhaust gas (bag).
- Recording (1 Hz) of diluted exhaust emissions and roller speed.
- Recording (1 Hz) of the nanoparticle concentration NP values (CPC). The sampling point is located directly at the CVS tunnel.
- Recording of OBD parameters such as vehicle speed, engine speed, coolant temperature and throttle position.

3.8.SAMPLING AND ANALYSIS

3.8.1. SAMPLING EQUIPMENT FOR SECONDARY EXHAUST EMISSIONS, EMPA

Diluted exhaust gases have been sampled from the CVS tunnel for all vehicle configurations. For this purpose, aliquots of diluted exhausts have been collected in all-glass sampling devices to collect complete exhaust samples including solid, condensed (liquid) and gaseous exhaust constituents.

The sampling device consisted of a sampling probe, energy cooler, condensate separator, filter stage and two-stage adsorber unit (XAD-2). The sampling apparatus was extensively cleaned and heated to high temperatures prior to each sampling.

The same sample was used to determine the contents of PCDD/F, PAH and Nitro-PAH. With respect to the different concentrations 10 %-aliquots of the extract were used for the PAH and Nitro-PAH analysis, the rest for the PCDD/F-analysis.

13C-marked PCDD-, naphthalene-, phenanthrene- and pyrene-standards were placed on quartz swab and put into the condensate separator prior to each sampling to test recovery.

Quantitative PCDD/F-analysis was obtained by adding an aliquot of a mixture of 13 C-labelled 2,3,7,8-PCDD/F-standard compounds prior to sample purification. The 17 toxicologically relevant PCDD/F isomers were separated using capillary gas chromatography followed by high resolution mass spectrometry (typical mass resolution 6000-10'000).

After a chromatographic work up, the quantitative analysis for the PAH and Nitro-PAH were also performed using capillary gas chromatography high resolution mass spectrometry at a typical mass resolution of 6000-10'000. Both the PAH and the Nitro-PAH were detected using electron impact ionization mass spectrometry (EI-MS).

For more details see the full EMPA-report by Norbert Heeb attached as Annex 9.5.

4. RESULTS AND DISCUSSION

In the next two sections results from the two different test vehicles are discussed. Section 4.2 will discuss other secondary emissions analyzed.

4.1.1. LEGALLY LIMITED EMISSIONS AND FUEL CONSUMPTION **FIAT 500X**

In the following sub-section results from the FIAT 500X generated from the 2 different test cycles are presented, i.e. steady state (SSC) and transient test cycle (WLTC).

WLTC Cycles

The comparison of the measurement results of the limited components from the CVS analysis is unremarkable overall. All differences between the OEM and GPF measurements are within the tolerance of the individual measurement results. For the Fiat 500X, the use of the retrofitted GPF in the WLTC can be described as emission-neutral. The CO_2 emissions are at the same level within the measurement dispersion, which means that the use of the GPF is fuel consumption-neutral.

With the Fiat 500X, the PN separation efficiency achieves an average value of 95.5% for the two WLTC cycles.

Figure 8: Limited exhaust emissions emitted by the Fiat 500X w/o and with GPF during the cold and hot WLTC cycles. CO_2 in g/km, rest in mg/km

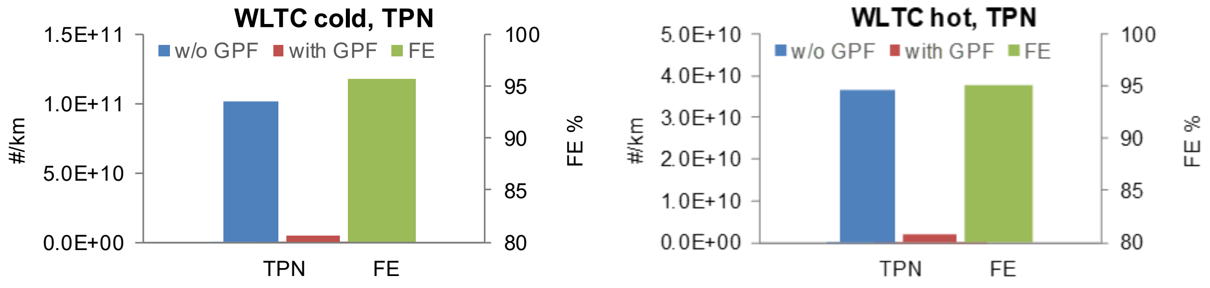

Figure 9: particle number (TPN) w/o and with GPF and filtration efficiency (FE) during the cold and hot WLTC cycles. Fiat 500X.

SSC Cycle

As before, the CO_2 emissions remain neutral within the measurement uncertainty. The particle filtration efficiency levels vary between 67% at idling speed and 89% at 45 km/h. The fluctuating and apparently low filtration efficiency levels **are an artefact** since the PN concentrations downstream the filter is very low around 1.1E+08 particles/km. At these low PN concentrations the effect of system-background noise (Rauschen) becomes apparent, since we cannot exclude that some particles deposited by diffusion and thermophoresis on the walls of the whole system from the exhaust probe to the sensor when dirty gases are measured are stochastically released. This is a small effect for normal PN-measurement, but becomes obvious if the gas is very clean. In a time resolved measurements we observe these irregular peaks, which integrated increases the average PN-value downstream high efficient DPF/GPF much more than upstream thus reducing the calculated value for efficiency. In the case of gaseous limited gas emissions, a halving of CO emissions at 26 and 45 km/h can be seen with the use of the GPF. However, as mentioned in the TR-6 report, CO emissions are generally at a low level. With regards to the emission neutrality of the Fiat 500X in the WLTC and RDE tests, the result can also be rated as neutral.

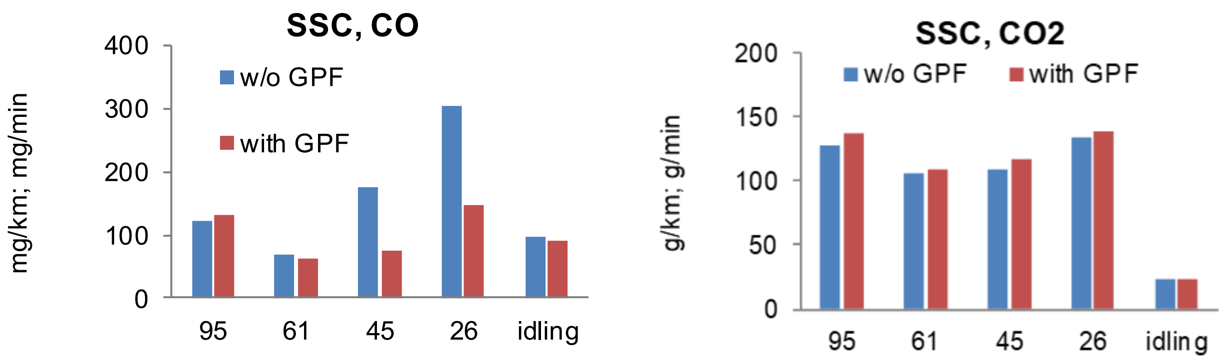

Figure 10: CO and CO_2 emissions emitted by the Fiat 500X w/o and with GPF during the SSC cycle. CO in mg/km or mg/min in idling, CO_2 in g/km or g/min in idling.

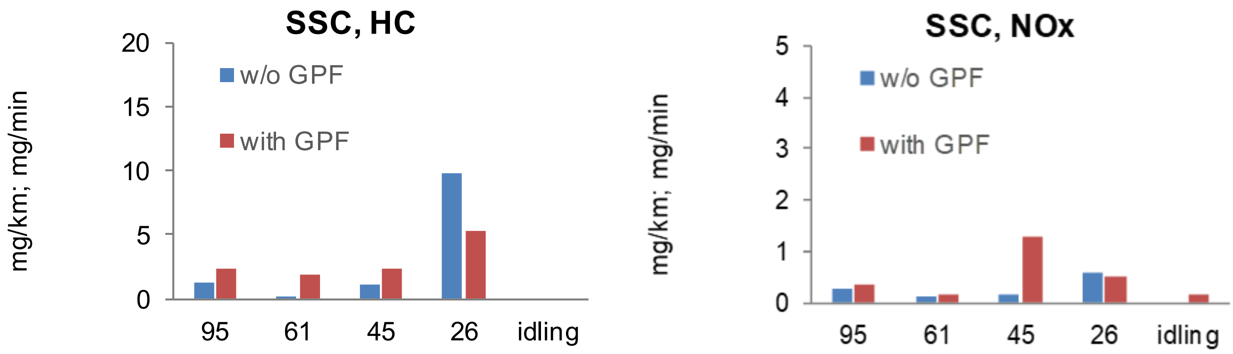

Figure 11: HC and NOx emissions emitted by the Fiat 500X w/o and with GPF during the SSC cycle. Idling in mg/min, rest in mg/km.

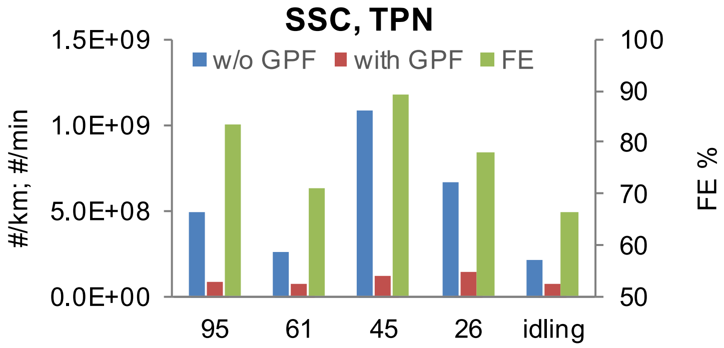

Figure 12: Particle number (TPN) w/o and with GPF and filtration efficiency (FE) during the SSC cycles. Fiat 500X.

4.1.2. LEGALLY LIMITED EMISSIONS AND CONSUMPTION **GOLF (7)**

WLTC Cycles

Table 10 and Table 11 for the vehicle without GPF and Table 14 and Table 15 with GPF, as well as Figure 13 andFigure 14, provide a quick overview of the emission results from the measurements on the chassis dynamometer with the CVS measuring system. The particle filter reduces the PN very well. For the two WLTC cycles, the reduction in PN is 98% on average.

Except for the CO_2 emissions, which show a maximum difference of 2% in the cold state for the variants with and without GPF, the gaseous emissions with PFF are always lower than those without GPF.

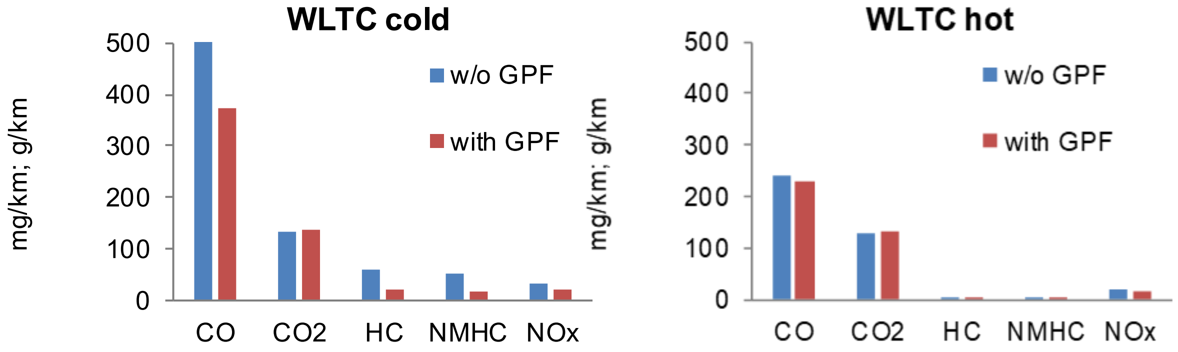

Figure 13: Limited exhaust emissions emitted by the VW Golf TSI w/o and with GPF during the cold and hot WLTC cycles. CO_2 in g/km, rest in mg/km.

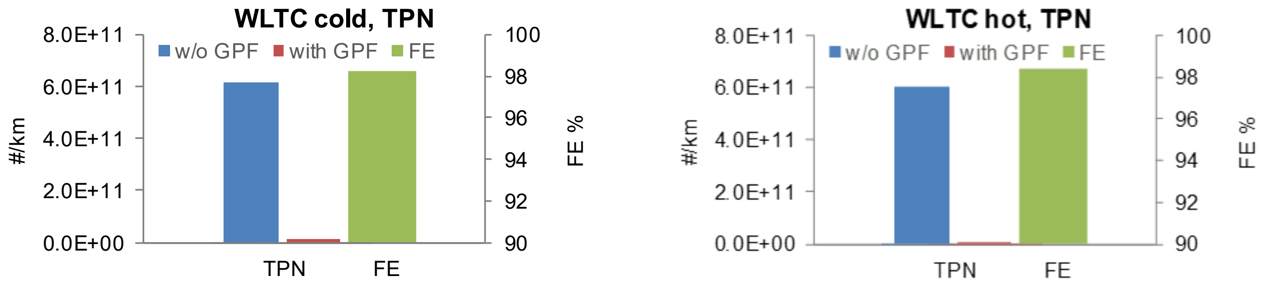

Figure 14: Particle number (TPN) w/o and with GPF and filtration efficiency (FE) during the cold and hot WLTC cycles. VW Golf TSI.

SSC Cycle

The results of the SSC tests for the VW Golf are summarized in Table 12 and Table 13 for the vehicle without GPF and Table 16 for the vehicle with GPF, as well as in Figure 15 to Figure 17. All exhaust emissions except for particle number emissions, shown at the 95 km/h driving point are higher with the GPF than without the GPF. To maintain the speed of 95 km/h, the cruise control of the vehicle was switched on. For unknown reasons, this switched off after about two minutes of driving in the SSC cycle, so that an employee of the laboratory had to intervene and set the speed back to 95 km/h. This readjustment led to a few pollutant peaks, which are responsible for the recorded difference between the variants with and without GPF. At the other speed levels and when idling, small differences between the variants with and without GPF are minor and can be attributed to the natural fluctuations in emissions and the measurement accuracy of the system.

The filtration rates of the particulate filter, which were calculated from the values of the CVS analysis, show different values for the various operating points. While the separation rate at idling speed is around 34% for the reasons mentioned above, it is around 99% from 45 km/h and remains stable at higher speeds in the cycle.

The PN capture efficiency has an average value of 99.5% when calculated from the cumulative PN emissions over the entire SSC cycle.

A repetition of the test at constant speed (SSC cycle), without particulate filter, was carried out on the same day, approximately one hour after the end of the first test. During the first speed stage at 95 km/h, apart from the CO_2 emissions, which remained the same in both tests, a difference was recorded in all limited emissions. The reason for this difference is not known. The other speed levels and idling show identical results for both CO_2 emissions and limited emissions. The results can be found in Table 13 in the annex.

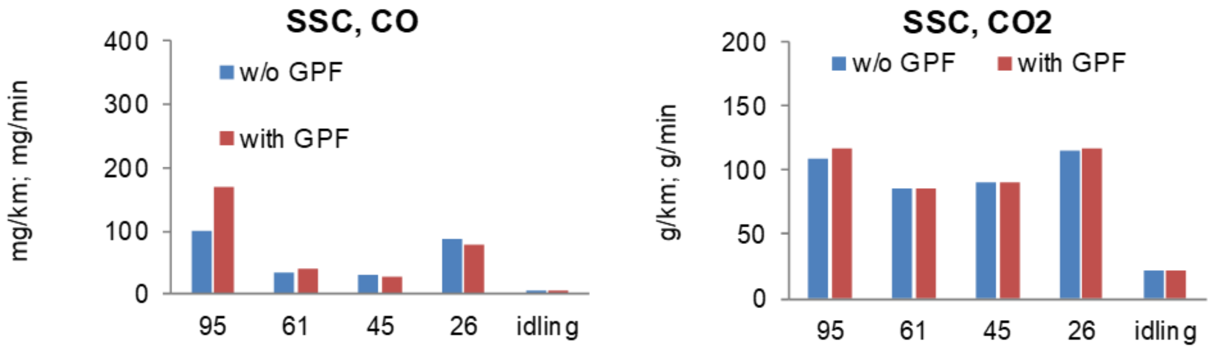

Figure 15: CO and CO_2 emissions emitted by the VW Golf TSI w/o and with GPF during the SSC cycle. CO in mg/km or mg/min in idling, CO_2 in g/km or g/min in idling.

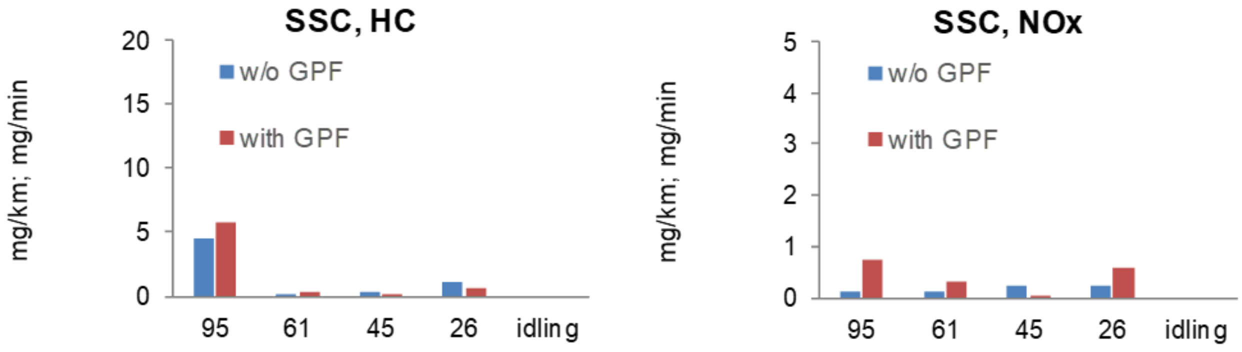

Figure 16: HC and NOx emissions emitted by the VW Golf TSI w/o and with GPF during the SSC cycle. Idling in mg/min, rest in mg/km.

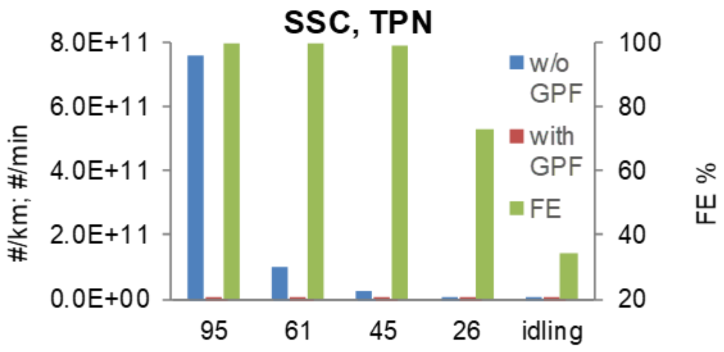

Figure 17: Particle number (TPN) w/o and with GPF and filtration efficiency (FE) during the SSC cycles. VW Golf

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4.2. SECONDARY EMISSIONS (PCDD/F, PAH AND NITRO-PAH) AND NON-LIMITED TOXINS

The following substances have been analyzed from the gas samples of SSC-Testing. The carcinogenic or mutagenic substances are marked with an *:

- Benzene *
- 1.3-Butadiene *
- Formaldehyde *
- Acetaldehyde *
- **PAH * (total)**
- Pyrene
- Fluoranthene
- Chrysene *
- Benz(a)- anthracene *
- Benzo(b)- fluoranthene *
- Benzo(k)- fluoranthene *
- Benzo(a)- pyrene *
- Indene(1,2,3- cd)pyrene *
- **Nitro-PAH (total)**
- 1-nitronaphthalene
- 2-nitronaphthalene
- 3-nitrophenanthrene
- 9-nitrophenanthrene
- 9-nitroanthracene
- 3-nitrofluoranthene *
- 1-nitropyrene *
- PCDD/F (TEQ total)
- 2,3,7,8- TCDD
- 1,2,3,7,8- PCDD
- 1,2,3,4,7,8- HxCDD
- 1,2,3,6,7,8- HxCDD
- 1,2,3,7,8,9- HxCDD
- 1,2,3,4,6,7,8- HpCDD
- **OCDD**
- 2,3,7,8- TCDF
- 1,2,3,7,8- PCDF
- 2,3,4,7,8- PCDF
- 1,2,3,4,7,8- HxCDF
- 1,2,3,6,7,8- HxCDF
- 1,2,3,7,8,9- HxCDF
- 2,3,4,6,7,8- HxCDF
- 1,2,3,4,6,7,8- HpCDF
- 1,2,3,4,7,8,9- HpCDF
- **OCDF**

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4.2.1. MEASUREMENT METHODS FOR TOXIC TRACE SUBSTANCES AND SECONDARY EMISSIONS

The measurement methods for toxic trace substances and secondary emissions are detailed in Table 3.

Table 3 Measurement methods for toxic trace substances and secondary emissions

PARAMETER	SAMPLING	ANALYTICAL METHOD	STANDARD
NO_2	Heated sampling line from undiluted exhaust gas	Chemiluminescence detector (CLD) or Fourier transform infrared spectroscopy (FTIR)	EN 14792 ISO 16000 DIN EN ISO 16017
VOC	From exhaust diluted to a constant volume flow (CVS tunnel)	Gas chromatorgraphy flame ionisation detector (GC-FID)	ISO 16000 DIN EN ISO 16017
VOCOX	From exhaust diluted to a constant volume flow (CV3 tunnel), chemisorption in di9nitrophenylhydrazine solution	Liquid chromatography ultraviolet detector (LC-UV/VIS)	ISO 16000 DIN EN ISO 16017
PAH	Flow proportional sampling from undiluted exhaust, multiple stage glass apparatus based on the filter/condenser method (UNE-EN 1948-1)	Gas chromatography high-resolution mass spectrometry (GC-HRMS) or Liquid chromatography ultraviolet/fluorescence detector (LC-UV/fluorescence)	VDI 3874
Nitro-PAH	Flow proportional sampling from undiluted exhaust, multiple stage glass apparatus based on the filter/condenser method (UNE-EN 1948-1)	Gas chromatography high-resolution mass spectrometry (GC-HRMS)	VDI 3874
PCDD/F	Flow proportional sampling from undiluted exhaust, multiple stage glass apparatus based on the filter/condenser method (UNE-EN 1948-1)	Gas chromatography high-resolution mass spectrometry (GC-HRMS)	UNE-EN 1948
Catalytically active elements (metals)	Flow proportional sampling from undiluted exhaust, size-fractionated sampling with 12-stage electric low-pressure impactor (ELPI) plus backup filter	Microwave digestion, inductively-coupled plasma mass spectrometry (ICP-MS)	DIN EN 13890 DIN 51002-1

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4.2.2. RESULTS OF EMISSIONS OF TRACE SUBSTANCES AND SECONDARY EMISSIONS

There is no significant increase of these toxic substances due to the use of the non-catalysed GPF during the five operation modes of the SSC-Test Cycle. Detailed data will be supplied with Annex 9.

5. DEVIATIONS FROM THE PLAN

This deliverable was originally scheduled for completion in M22 but experienced a delayed due to a serious health issue affecting a key researcher at EMPA. All tests, data collection and analysis were completed in due time, only the final reporting was postponed. The delay was reported to project management and there is no negative impact on other tasks, milestones and or deliverables.

6. LINKS WITH OTHER WPS

No effects on other WPs and or tasks

7. CONCLUSIONS AND RECOMMENDATIONS

Conclusion is that the testing and subsequent data analysis confirmed the original requirement that no secondary emissions should be emitted because of retrofitting the GPF and both the tested vehicles showed the similar picture and the same results with high PN separation efficiencies (over 95%), and no increase in toxic trace substances. Dioxins and furans remained below the detection limit and there was no nitration of PAHs.

This confirms the expectation that the use of non-catalysed GPF in the technical design with regard to the pore structure, as recommended by AeroSolfd, poses no additional risk from secondary pollutants in this test operation.

The question of processes in dynamic operation and during the regeneration of stored soot with deposited substances remains. The following considerations can be made in analogy to the experience with diesel engines:

- In addition to the availability of the reactants, the formation of the substances mentioned requires relatively long residence times; the stationary test is therefore actually the worst case.
- In contrast to diesel engines, regeneration in petrol engines is characterized by the simultaneous presence of very high temperatures and a very high oxygen content. It is therefore to be expected that accumulated substances burn simultaneously with the soot core to form CO2 and H2O.
- A typical risk with diesel is that accumulated PAHs desorb during the long storage phases at medium temperatures and are thus released for emission. This does not apply to gasoline engines if, like all modern gasoline engines, they are operated

stoichiometrically and never form soot cake over a longer period of time in the alternating operation typical of traffic.

Overall, the results and conclusions are coherent and consistent with the goal set for the project and no follow-up actions are needed.

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9. ANNEX

9.1. FIAT 500X, TWC, **W/O GPF**, FUEL: E10.

WLTC cold

Part of driving cycle	**CO**	**CO_2**	**HC**	**NMHC**	**NOx**	**TPN**	**fuel consumption**
	[mg/km]	[g/km]	[mg/km]	[mg/km]	[mg/km]	[TPN/km]	[l/100 km]
low	882.3	242.2	116.1	110.9	112.4	2.5E+11	10.7
medium	329.6	168.1	1.8	2.0	19.6	2.1E+11	7.4
high	360.1	144.7	1.1	1.2	15.3	5.0E+10	6.4
extra high	312.7	166.5	1.0	1.0	16.0	2.8E+10	7.3
whole cycle	406.7	170.2	16.6	15.9	29.4	1.0E+11	7.5

Table 4: emissions and fuel consumption during WLTC driving cycle with cold start.

WLTC warm

Part of driving cycle	**CO**	**CO_2**	**HC**	**NMHC**	**NOx**	**TPN**	**fuel consumption**
	[mg/km]	[g/km]	[mg/km]	[mg/km]	[mg/km]	[TPN/km]	[l/100 km]
low	61.6	219.7	2.0	2.5	17.7	1.4E+11	9.6
medium	96.4	163.6	0.6	0.7	28.1	2.7E+10	7.2
high	116.0	145.0	0.4	0.4	20.4	2.0E+10	6.4
extra high	344.2	167.4	0.7	0.7	20.6	1.7E+10	7.4
whole cycle	185.6	166.7	0.8	0.8	21.7	3.7E+10	7.3

Table 5: emissions and fuel consumption during WLTC driving cycle with warm start.

SSC

Part of driving cycle	**CO**	**CO_2**	**HC**	**NMHC**	**NOx**	**TPN**	**fuel consumption**
	mg/km mg/min	g/km g/min	mg/km mg/min	mg/km mg/min	mg/km mg/min	[#/km] [#/min]	[l/100 km] [l/100 min]
95 km/h	122.3	128.1	1.3	0.5	0.3	4.9E+08	5.6
61 km/h	69.7	106.4	0.2	0.0	0.1	2.6E+08	4.7
45 km/h	175.5	108.6	1.2	0.0	0.2	1.1E+09	4.8
26 km/h	304.5	134.2	9.8	4.6	0.6	6.7E+08	5.9
idling	98.3	23.3	0.0	0.0	0.0	2.1E+08	1.0

Table 6: emissions and fuel consumption during SSC driving cycle.

9.2. FIAT 500X, TWC, **WITH GPF**, FUEL: E10.

WLTC cold

Part of driving cycle	CO	CO_2	HC	NMHC	NOx	TPN	FE	fuel consumption
	[mg/km]	[g/km]	[mg/km]	[mg/km]	[mg/km]	[TPN/km]	[%]	[l/100 km]
low	858.9	243.4	120.3	114.5	98.7	9.4E+09	96.2	10.7
medium	567.1	168.7	2.5	2.5	39.2	9.3E+09	95.6	7.4
high	303.0	145.3	1.5	1.6	11.4	2.7E+09	94.6	6.4
extra high	295.4	168.9	1.6	1.6	19.5	8.4E+08	97.0	7.4
whole cycle	428.4	171.5	17.6	16.8	31.6	4.3E+09	95.8	7.6

Table 7: emissions and fuel consumption during WLTC driving cycle with cold start.

WLTC warm

Part of driving cycle	CO	CO_2	HC	NMHC	NOx	TPN	FE	fuel consumption
	[mg/km]	[g/km]	[mg/km]	[mg/km]	[mg/km]	[TPN/km]	[%]	[l/100 km]
low	60.8	226.1	2.5	3.1	17.6	6.1E+09	95.7	9.9
medium	101.6	164.1	0.8	0.9	18.7	1.1E+09	96.0	7.2
high	98.5	144.7	0.4	0.5	17.6	1.7E+09	91.5	6.4
extra high	294.9	169.3	1.2	1.0	26.8	6.5E+08	96.2	7.4
whole cycle	163.7	168.2	1.1	1.1	21.1	1.8E+09	95.1	7.4

Table 8: emissions and fuel consumption during WLTC driving cycle with warm start.

SSC

Part of driving cycle	CO	CO_2	HC	NMHC	NOx	TPN	FE	fuel consumption
	mg/km mg/min	g/km g/min	mg/km mg/min	mg/km mg/min	mg/km mg/min	[#/km] [#/min]	[%]	[l/100 km] [l/100 min]
95 km/h	130.5	137.1	2.3	1.3	0.3	8.0E+07	83.6	6.0
61 km/h	61.3	109.8	1.8	1.3	0.2	7.6E+07	70.9	4.8
45 km/h	73.8	117.5	2.4	1.8	1.3	1.2E+08	89.4	5.2
26 km/h	147.8	138.8	5.3	2.7	0.5	1.5E+08	78.1	6.1
idling	92.4	23.5	0.0	0.0	0.1	6.9E+07	66.5	1.0

Table 9: emissions and fuel consumption during SSC driving cycle.

9.3.VW GOLF TSI, TWC, **W/O GPF**, FUEL: E10.

WLTC cold

Part of driving cycle	**CO**	**CO_2**	**HC**	**NMHC**	**NOx**	**TPN**	**fuel consumption**
	[mg/km]	[g/km]	[mg/km]	[mg/km]	[mg/km]	[TPN/km]	[l/100 km]
low	2818.1	175.2	401.2	376.7	147.2	4.7E+11	7.9
medium	268.2	128.6	4.8	2.2	15.3	4.6E+11	5.7
high	195.5	115.2	1.6	1.2	13.5	5.0E+11	5.1
extra high	266.0	132.6	6.0	3.8	8.4	8.6E+11	5.8
whole cycle	584.2	132.1	56.9	52.3	29.8	6.2E+11	5.8

Table 10: emissions and fuel consumption during WLTC driving cycle with cold start.

WLTC warm

Part of driving cycle	**CO**	**CO_2**	**HC**	**NMHC**	**NOx**	**TPN**	**fuel consumption**
	[mg/km]	[g/km]	[mg/km]	[mg/km]	[mg/km]	[TPN/km]	[l/100 km]
low	344.0	160.0	6.5	4.6	51.3	3.8E+11	7.0
medium	206.4	125.7	2.5	1.1	35.4	4.4E+11	5.5
high	129.9	113.2	1.0	0.6	10.4	4.2E+11	5.0
extra high	314.0	133.4	10.1	3.6	7.8	9.4E+11	5.9
whole cycle	239.6	129.2	5.3	2.3	20.1	6.1E+11	5.7

Table 11: emissions and fuel consumption during WLTC driving cycle with warm start.

SSC

Part of driving cycle	**CO**	**CO_2**	**HC**	**NMHC**	**NOx**	**TPN**	**fuel consumption**
	mg/km mg/min	g/km g/min	mg/km mg/min	mg/km mg/min	mg/km mg/min	[#/km] [#/min]	[l/100 km] [l/100 min]
95 km/h	100.3	108.8	4.5	3.1	0.1	7.6E+11	4.8
61 km/h	34.4	85.5	0.2	0.1	0.1	1.0E+11	3.7
45 km/h	30.8	90.5	0.3	0.3	0.2	2.7E+10	4.0
26 km/h	88.2	115.6	1.1	0.4	0.2	2.0E+09	5.1
idling	5.7	21.9	0.0	0.0	0.0	3.2E+08	1.0

Table 12: emissions and fuel consumption during SSC driving cycle.

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State Secretariat for Education, Research and Innovation SERI

SSC, repetition

Part of driving cycle	CO	CO_2	HC	NMHC	NOx	TPN	fuel consumption
	mg/km mg/min	g/km g/min	mg/km mg/min	mg/km mg/min	mg/km mg/min	[#/km] [#/min]	[l/100 km] [l/100 min]
95 km/h	78.9	110.0	2.1	1.3	0.1	4.6E+11	4.8
61 km/h	32.3	86.3	0.5	0.4	0.3	9.4E+10	3.8
45 km/h	31.0	91.1	0.5	0.4	0.0	2.6E+10	4.0
26 km/h	83.8	116.3	1.9	1.1	0.6	1.8E+09	5.1
idling	4.7	21.6	0.0	0.0	0.0	2.9E+08	0.9

Table 13: emissions and fuel consumption during SSC driving cycle, repetition.

9.4.VW GOLF TSI, TWC, **WITH GPF**, FUEL: E10.

WLTC cold

Part of driving cycle	CO	CO_2	HC	NMHC	NOx	TPN	FE	fuel consumption
	[mg/km]	[g/km]	[mg/km]	[mg/km]	[mg/km]	[TPN/km]	[%]	[l/100 km]
low	1393.7	187.5	121.4	103.0	75.7	1.1E+10	97.6	8.3
medium	256.6	130.3	4.7	2.6	13.8	9.6E+09	97.9	5.7
high	191.2	116.3	2.1	1.7	13.5	8.7E+09	98.3	5.1
extra high	220.2	133.6	4.7	3.2	6.6	1.3E+10	98.5	5.9
whole cycle	374.9	134.8	19.4	15.9	19.4	1.1E+10	98.3	5.9

Table 14: emissions and fuel consumption during WLTC driving cycle with cold start.

WLTC warm

Part of driving cycle	CO	CO_2	HC	NMHC	NOx	TPN	FE	fuel consumption
	[mg/km]	[g/km]	[mg/km]	[mg/km]	[mg/km]	[TPN/km]	[%]	[l/100 km]
low	276.3	164.5	6.0	3.1	36.4	5.2E+09	98.6	7.2
medium	245.1	127.0	2.9	1.4	25.8	7.0E+09	98.4	5.6
high	182.3	113.7	1.5	1.0	13.5	6.3E+09	98.5	5.0
extra high	242.1	133.8	4.8	2.9	4.6	1.6E+10	98.3	5.9
whole cycle	229.0	130.4	3.5	2.0	15.9	9.6E+09	98.4	5.7

Table 15: emissions and fuel consumption during WLTC driving cycle with warm start.

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State Secretariat for Education,
Research and Innovation SERI

SSC

Part of driving cycle	CO	CO_2	HC	NMHC	NOx	TPN	FE	fuel consumption
	mg/km mg/min	g/km g/min	mg/km mg/min	mg/km mg/min	mg/km mg/min	[#/km] [#/min]	[%]	[l/100 km] [l/100 min]
95 km/h	169.6	117.5	5.7	3.4	0.8	2.8E+09	99.6	5.2
61 km/h	40.4	86.4	0.3	0.2	0.3	3.0E+08	99.7	3.8
45 km/h	28.6	90.6	0.0	0.0	0.0	3.0E+08	98.9	4.0
26 km/h	79.0	116.8	0.6	0.0	0.6	5.3E+08	73.3	5.1
idling	5.4	22.0	0.0	0.0	0.0	2.1E+08	34.1	1.0

Table 16: emissions and fuel consumption during SSC driving cycle.

9.5.DETAILED SECONDARY EMISSIONS REPORT EMPA

The detailed report on vehicle exhaust analysis PCDD/Fs, PAHs, NPAHs is available on the repository Zenodo (AeroSolfd Community) and can be accessed under: Report on Vehicle Exhaust Analysis PCDD/Fs, PAHs, NPAHs.