Effects of four prototype gasoline particle filters (GPFs) on nanoparticle and genotoxic PAH emissions of a gasoline direct injection (GDI) vehicle

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ABSTRACT

The fast replacement of traditional gasoline port-fuel injection (PFI) technology with gasoline direct-injection (GDI) vehicles is expected to have a substantial impact on urban air quality. Herein we report on effects of four prototype gasoline particle filters (GPFs) on exhausts of a 1.6 L Euro-5 GDI vehicle. Two non-coated and two filters with catalytic coatings were investigated. These filters, on average, lowered PN emissions 4-7-fold to 4.0-6.8 x 10^{11} particles/km. Genotoxic PAHs were lowered 2-5-fold too with GPF-1-3, with GPF-1 having the highest efficiency, 79% and resulting in 45 ng toxic equivalent concentration (TEQ)/km. Thus particle filtration efficiencies and reduction of the genotoxic potentials are correlated. GPF-4 showing the poorest particle filtration efficiency (66-78%) also released exhausts with...
highest genotoxic potential of 240-530 ng TEQ/km. We recently reported particle-number
(PN) emissions of four generations of GDI vehicles (Euro-3 to Euro-6) which released, on
average, 2.5 x 10^{12} \pm 1.8 x 10^{12} particles/km exceeding the current European limit of 6.0
x10^{11} particle/km. Thus the implementation of filters to GDI vehicles requires best-available
technology (BAT) with PN efficiencies >98% and catalytic activity, to avoid store-and-
release of genotoxic PAHs. In-series applications of BAT-filters to GDI vehicles can lower
genotoxic PAHs and soot nanoparticles.
INTRODUCTION

Particle and Genotoxic PAH Emissions of GDI Vehicles

First emission regulations for vehicles were introduced in 1970 when specific limits were set for CO, hydrocarbons and nitrogen oxides with the implementation of the US Clean Air Act. Latter, particle emissions of diesel vehicles have been regulated too. Particle mass (PM) is limited in the US, Japan, Europe and most other countries. Since 2011, the European Union (EU) and Switzerland also introduced particle number (PN) limits, first for diesel vehicles only and since 2014 also for gasoline-direct injection (GDI) vehicles. PN regulations limited emissions of light-duty vehicles (i.e., passenger cars and light-duty trucks) to $6 \times 10^{11}$ particles/km which were emitting more particles than gasoline port-fuel injection vehicles. These PN limits forced manufacturers to apply particle filters. In 2000, Peugeot implemented first in-series diesel particle filters (DPFs) for passenger cars. Nowadays, best-available-technology (BAT) filters have been successfully introduced in construction machinery, passenger cars, light- and heavy-duty vehicles, busses etc., whenever diesel engines are applied. Meanwhile, other combustion engine technologies were arising. In 2000, Mitsubishi introduced a first in-series GDI engine (1.8 L, 90 kW) in a Euro-3 vehicle. Enhanced engine power, better fuel efficiency and lower CO$_2$ emissions were claimed in comparison with traditional port-fuel injection (PFI) engines. GDI vehicles are now quickly replacing other gasoline and diesel vehicles in many markets. It is estimated that two thirds of the gasoline vehicles sold in Europe in 2016 were equipped with GDI engines and that up to 60% of all new gasoline vehicles were powered by GDI engines in 2017. However, it has been shown that GDI vehicles produce more particles than traditional PFI vehicles and orders of magnitude more particles than comparable diesel vehicles which are today equipped with BAT DPF. Lately, we compared PN emissions of a fleet of GDI vehicles covering Euro-3,
-4, -5 and Euro-6 technology. On average, this fleet released $2.5 \pm 1.8 \times 10^{12}$ and $2.0 \pm 1.6 \times 10^{12}$ particles/km in the cold and hot world light-duty vehicle test cycle (WLTC) which is since 2017 the prescribed homologation cycle in Europe $^{8,10,11}$. We concluded that these GDI vehicles exceeded PN emissions of a benchmark Euro-5 diesel vehicle equipped with a filter by 2-3 orders of magnitude $^{10,12}$.

Furthermore, we concluded that these soot-like nanoparticles $^{13-15}$ are formed and released together with genotoxic polycyclic aromatic hydrocarbons (PAHs) and reported mean genotoxic PAH emissions $480 \pm 360$ and $430 \pm 630$ ng TEQ/km in the cWLTC and hWLTC. Genotoxic emissions in toxic equivalent concentration (ng TEQ/km) are obtained by multiplying the concentration in ng/km by the respective toxicity equivalent factor (TEF). Thus the genotoxic potential of these GDI vehicle exhausts is 21- and 19-fold higher than that of the benchmark diesel vehicle with DPF.

In conclusion, non-treated GDI exhausts substantially contribute to both, particle number and genotoxic PAH burdens of ambient air in traffic-affected areas and hence represent a relevant health risk. However, the GDI technology is still evolving, making it difficult to predict particle emissions of future GDI vehicles.

In other words, most of the Euro-3 to Euro-6 GDI-vehicles in operation today cannot fulfil the particle number limit of $6 \times 10^{11}$ particles/km, valid for diesel passenger cars since 2009 $^{2}$ and in force for new GDI vehicles in 2017 $^{3}$. In response to recent scandals with regard to high on-road NOx emissions of diesel vehicles, EU legislators modified current regulations for type approval $^{16,17}$. Type approval for future vehicle will require meeting the Euro-6b PN standard of $6 \times 10^{11}$ particles/km by October 2019 and is based on the WLTC, used herein. Countries like China will also implement a PN limit in 2020 (China 6a). However, other countries like the U.S.A. and Japan have not implemented PN-based standards and are not regulating nanoparticle emissions of GDI vehicles. It can be argued that light-duty vehicles
(i.e., passenger cars and light-duty trucks) are of lesser importance in the U.S. and many Asian countries because their market shares are low. However, diesel trucks, buses and increasingly GDI vehicles will contribute to traffic-related nanoparticle emissions.

GDI engines are designed to either work in a stratified lean mode or in a stoichiometric mode with homogeneous charging. Thus, fuel is injected at high pressures in such engines and mixed less uniformly with the entering air. As a consequence, soot formation can occur due to the stratification which leads to fuel-rich areas promoting particle formation. Furthermore, spray fuelling causes droplet formation which produce particles and hydrocarbons like PAHs during combustion. Various methods for stratified charging (wall guided, spray guided and air guided) can be used. Due to the high power output of spray-guided GDI technology, it is anticipated that such technology will replace wall-guided systems in the near future.

The vehicle tested in this research, the VOLVO V60, was a most common concept with no stratification (homogeneous GDI), which has both a spray and wall-guided injection. Independently of the direct injection type, the manufacturer should use the best available technology. An implementation of filter technology to new GDI or retrofitting of in-use GDI vehicles could help to close the gap between diesel and GDI vehicle particle emissions.

**Impact of Particle Filters on Diesel and GDI Vehicle Exhaunts.**

Particle filters are widely used for different diesel engines applications. Since its first implementation in 2000 in a Euro-3 passenger car (Peugeot 607), DPFs have proven their effectiveness reaching particle filtration efficiencies of more than 98% and working properly even under harsh conditions in tunnel construction sites. DPFs have been implemented in construction machinery in the long New Railway Link through the Alps, the NEAT tunnels already in 1998. In 2009, a first PN limit of $10^{12}$ particles/kWh and requirements for DPFs have been set for construction machinery (>47 kW) in the Swiss clean air act.
After the implementation of a PN emission limit of $6 \times 10^{11}$ particles/km, diesel passenger cars and diesel light-duty vehicles produced for European markets are equipped with DPFs. In 2012, the WHO classified non-treated diesel exhaust as group 1 carcinogen inducing lung cancer in humans. Due to the striking similarities, concerns rise that GDI exhausts might also be carcinogenic to humans. Therefore, detailed studies on the genotoxic potential of GDI-vehicle exhausts are urgently needed to assess these new risks.

The physical and chemical properties of GDI-particles resemble those released from diesel engines. They are agglomerates of soot-like nanoparticles formed in the engine under high pressure. Particularly those nanoparticles with diameters $<100$ nm are of concern for human health. They are predominantly deposited in the alveoli of the lung carrying genotoxic PAHs. Sub 100 nm particles may even penetrate the alveolar membrane and enter the circulatory system, whereby they may be deposited in other vital organs. PAHs, including several genotoxic ones, are bound to such particles and can migrate with them (Trojan horse effect). We have shown that genotoxic potentials of GDI vehicle exhausts, on average, exceed those of a diesel vehicles with DPF 6-40 times.

In order to reduce particle and PAH emissions, we consider particle filters as a promising environmental technology that should be implemented in GDI vehicles. Whether gasoline particle filters (GPFs) are efficient or not in GDI vehicles, removing both nanoparticle and PAH emissions is not yet known. To answer these questions we have investigated four prototype ceramic wall-flow particle filters, two were non-coated and two were coated with catalysts, and studied their effects on the exhaust composition of a Euro-5 GDI vehicle. Our findings indicate that GPFs have the potential to lower both, PN and genotoxic PAH emissions.

METHODOLOGY

**Vehicles, Test Cycles and Gasoline Particle Filters**
Emissions of a Euro-5 GDI-vehicle (Volvo V60, 132 kW) with a 1.6 L engine were investigated without and with 4 prototype particle filters. This vehicle from a fleet of 7 Euro-3 to Euro-6 vehicles was chosen as reference. The gasoline, taken from the Swiss market, was in compliance with SN EN228. Moreover, a Euro-5 diesel vehicle (Peugeot 4008, 1.6 L, and 84 kW) with integrated DPF was tested as benchmark vehicle. Diesel fuel was also taken from the Swiss market and was in accordance to SN EN 590 class-0. Additional information about the vehicles tested can be found in Table S2 in supporting information.

Vehicles were tested on the chassis dynamometer (Schenk 500 G5 60) of the University of Applied Science Bern (Nidau, Switzerland). Two driving cycles simulating transient and steady driving, were applied. Detailed information is found in SI. The worldwide harmonized light-duty vehicle test cycle was used (Fig. S1, Supporting Information). The WLTC including urban, extra-urban, highway, and motorway driving was driven under cold (cWLTC) and hot-start conditions (hWLTC). Furthermore, a steady-state cycle (SSC) representing mean velocities of the four WLTC phases and an idle phase was applied (Fig. S1, Supporting Information). In 2017, the WLTC applied herein was implemented as the new type approval cycle. By 2019, all vehicles approved for Europe must be certified according to the WLTC procedure.

Four prototype ceramic wall-flow filters (GPFs), provided by industrial partners, were tested on the reference vehicle and installed approximately 60 cm downstream of the three-way catalyst. Two filters were coated with noble metals to support oxidation (GPF-2, GPF-3); two were non-coated filters (GPF-1, GPF-4).

Additional measurements have shown that a build-up of a detectable soot cake in the prototype filters could not be observed. Thus no additional measures had to be foreseen to actively induce filter regeneration. Nevertheless, we had continuously regeneration due to the
highest exhaust gas temperature of the gasoline engine and due to the availability of oxygen
during the transients.

These prototype filters were only tested over short periods of time and not long term
operation effects have been addressed. An in-series application of such filters also needs a
better implementation and test on durability and long term performance of GPFs including
studies on soot and ash loading.

Exhaust Sampling and Analysis

Carbon monoxide (CO) and carbon dioxide (CO₂) were measured by IR spectroscopy
(Horiba MEXA-9400H, Japan). Total hydrocarbons (THC) were analyzed with flame
ionization detection and nitrogen oxides (NOx) with chemiluminescence detectors (Horiba).
PN emissions were determined from dilute exhaust with a condensation particle counter
(CPC, TSI 3790, Minnesota, USA) following the Particle Measurement Programme (PMP)
protocol ², ²⁹. A scanning mobility particle sizer (SMPS, DMA TSI 3081 and CPC TSI 3772)
was used to determine particle number size distributions under steady operating conditions.
An all-glass sampling device including filter-, condenser- and adsorber units (XAD2) was
used to sample PAHs and alkyl-PAHs of diluted exhausts from a constant volume sampling
(CVS) tunnel, according to the filter/condenser method described in the European standard
EN-1948-1 ³⁰. A similar scheme of the set-up is given elsewhere ³¹, ³². This method provides
quantitative sampling of complete exhausts including particle-bound, liquid and gaseous
fractions.

PAH and alkyl-PAH emissions were determined following a multistep cleanup procedure
described before ¹¹. Analysis of individual PAHs is performed by gas chromatography (Fisons
Instruments HRGC Mega 2, Rodano, Italy) on a 30 m x 0.25 μm x 0.10 μm capillary column
(Restek, Bellefonte, USA). Detection and identification were achieved by high resolution
mass spectrometry (Thermo Finnigan MAT 95, Bremen, Germany) in electron-impact ionization mode (GC/EI-HRMS).

The internal standard method is used to quantify PAHs. Five concentrations containing deuterated PAHs, 16 native PAHs (Supelco, Bellefonte, USA) and a standard reference material (SRM) mix of 18 methyl-substituted PAHs from methyl-naphthalene to methyl-chrysene (LGC Standards, Switzerland) were analyzed to determine respective calibration curves and response factors. For compounds identified by mass spectrometry but not present in labelled form, quantification was performed with relative response factors of PAHs or alkyl-PAHs with closest chromatographic retention time. Aliquots of $^{13}$C$_6$-naphthalene, $^{13}$C$_6$-phenanthrene and $^{13}$C$_3$-pyrene were placed on quartz swab and given to the condensate separator prior to each sampling. These compounds were used to calculate losses during sampling and work-up. CVS blank samples were also collected to determine background air concentrations and with it detection limits of the methodology.

**Assessment of Genotoxic Potential**

Toxicity equivalence factors (TEFs) are used to compare the cumulative toxicity of multicomponent mixtures with similar modes of action. TEFs for individual PAHs are used to assess carcinogenic risks of mixtures\(^{33, 34}\). Table S7 (Supporting Information) shows those TEFs used and proposed by different authors\(^{35-37}\). Benzo(a)pyrene and dibenzo(a,h)anthracene are assigned with a TEF of 1, being the most carcinogenic PAHs\(^{34, 38}\). TEFs are assigned to other PAHs according to their carcinogenic potential relative to benzo(a)pyrene. Overall, the genotoxic potential of an exhaust corresponds to the sum of individual PAH emission factors (ng/km) multiplied by its TEF. Thus, the total genotoxic potential (TEQ) is calculated here as the sum of those 8 genotoxic PAHs marked in Fig. 1.
RESULTS AND DISCUSSION

Particle Number and CO Emissions of a GDI Vehicle

Gasoline-direct injection engines allow combustion of gasoline at higher pressures (up to 200 bars) in smaller engines (1.0-1.6 L). Higher fuel charging of down-sized engines results in higher power output. Another consequence is the appearance of fuel-rich combustion zones and subsequent formation of soot particles and, as previously shown, of polycyclic aromatic hydrocarbons (PAHs) including those displayed in Fig. 1. In other words, insufficient in-cylinder residence time prevents full fuel spray evaporation and mixing with air, which in turns leads to particle formation during the combustion. In homogeneous GDI vehicles large droplets and spray impingement may also lead to more soot formation. Therefore, large numbers of nanometer-sized soot-like particles are formed together with PAHs and co-released from such GDI-engines (Fig. 2, lower left).

Fig. 2 and Table S3 (Supporting Information) report particle number emissions (PN) of a Euro-5 GDI vehicle (Volvo V60, 1.6 L) of $3.0 \pm 0.9 \times 10^{12}$ and $3.0 \pm 0.76 \times 10^{12}$ particles/km comparable during a cold- (blue) and hot- (red) started WLTC, indicating that particles are formed and released under all engine conditions not just at engine start. This differs from hydrocarbon emissions which are mainly released from a cold-started engine/catalyst.

This vehicle was chosen as the reference from a fleet of seven vehicles to study effects of four prototype gasoline particle filters (GPFs). Particle emissions of this vehicle were close to mean values of the fleet (n=7) which consisted of Euro-3, Euro-4, Euro-5 and Euro-6 technology. This fleet, on average, emits $2.5 \pm 1.8 \times 10^{12}$ and $2.0 \pm 1.6 \times 10^{12}$ particles/km in the cWLTC and hWLTC, respectively (Table S3). The reference vehicle released $2.0 \pm 0.4 \times 10^{12}$ particles/km in the SSC which compares with the GDI fleet mean value of $0.7 \pm 1.4 \times 10^{13}$ particles/km.
In conclusion, the chosen reference vehicle is representative for GDI-technology currently operated on European roads. Its PN emissions are above the PN limit of $6.0 \times 10^{11}$ particles/km, valid for diesel vehicles since 2009 and new GDI vehicles since September 2017 (Euro 6b)\textsuperscript{3}.

Fig. 2 also displays CO emissions which remained below the limit value of 1000 mg/km in all configurations without and with GPFs. It was found that transient driving in the WLTC results in higher emissions of particles and CO. As observed before\textsuperscript{11}, PN and CO emissions are correlated, indicating that both pollutants are formed under oxygen-deficient conditions which are frequent under transient engine operation in the WLTC.

Table S3 (Supporting Information) lists PN and CO emission factors of the GDI vehicle without and with four prototype GPFs together with THC, NO\textsubscript{x}, CO\textsubscript{2} and fuel consumption (FC) data. FC of the Euro-5 GDI vehicle (1.6 L) was not affected to a long extend by the applied filter technology. On average $7.8 \pm 0.1$ and $7.6 \pm 0.2$ L gasoline/100 km ($3.3 \pm 0.04$ and $3.23 \pm 0.10$ gallons/100 miles) were consumed in the cWLTC and hWLTC in runs with filters, corresponding to $181 \pm 3$ and $176 \pm 5$ g CO\textsubscript{2}/km. This compares with FC of $8.0 \pm 0.10$ and $7.8 \pm 0.10$ L/100 km without filter corresponding to CO\textsubscript{2} emissions of $187 \pm 3.0$ and $182 \pm 2.0$ g/km. Thus the implementation of these filters on these GDI vehicles, did not increase fuel consumption which is in accordance with previous findings for diesel particle filters\textsuperscript{31}. However, more studies on FC effects are needed for well-integrated GPFs.

**Impact of Prototype GPFs on PN and CO Emissions of a GDI Vehicle**

PN emissions after four prototype-GPFs were, on average $7.0 \pm 3.0 \times 10^{11}$ and $4.0 \pm 3.0 \times 10^{11}$ particles/km in the cWLTC and hWLTC, respectively, thus 77% and 87% below those of non-filtered exhausts. Under steady-state driving, filter efficiencies were highest, reaching 95% reduction. Thus efficiencies of GPFs at transient operation in the WLTC were lower in
all cases. GPF-1 reached lowest PN emission levels of $1.1 \pm 0.1 \times 10^{11}$ and $1.6 \pm 0.1 \times 10^{11}$ particles/km in the cWLTC and hWLTC and $3.4 \pm 3.3 \times 10^{9}$ particles/km in the SSC. This compares with even lower PN emissions of the Euro-5 bench mark diesel vehicles (Peugeot 4008, 1.6 L) which released $4.0 \pm 2.6 \times 10^{10}$, $2.8 \pm 6.0 \times 10^{9}$ and $1.7 \pm 1.3 \times 10^{8}$ particles/km in the cWLTC, hWLTC and SSC (Fig. 2, Table S3).

Only GPF-1 and GPF-2 are able to lower PN emissions to the future limit of $6 \times 10^{11}$ particles/km. However, only the best filter GPF-1 could come close to the low particle emissions of the bench mark diesel vehicle with well-integrated filter.

Fig. 2 also displays particle number size distributions (lower left) obtained by SMPS measurements under steady driving at 95 km/h. A bimodal size distribution with two maxima at 20 and 70 nm is observed without filter. Down-stream of GPF-1, particle number and size distribution changed remarkably. Filtration efficiencies of particles <30 nm were close to 100% (Fig. 2, lower right). Slightly lower efficiencies of 99% were observed for 80-100 nm particles. Overall, GPF-1 was highly efficient also at higher space velocities at highway driving of 95 km/h (59 miles/h). In conclusion, all tested prototype filters lowered PN emissions with strongest effects during the steady driving and the lower transient mode.

According to Swiss particle filter standards for construction machinery, filtration efficiencies above 98% must be achieved under all conditions in a particle size-range of 23-400 nm as specified in the Swiss Clean Air Act since 2009. CO emissions can be affected by different parameters. In case of the reference vehicle transient driving has the strongest effect with CO emissions exceeding those at steady conditions (SSC) 13-16-fold. Well-designed particle filters with high enough substrate porosities should not build up relevant exhaust backpressures. Increased back pressure of a
filter can affect combustion in the engine and lead to increased CO emissions (more fuel consumed).

CO emissions after 3 of 4 filters remained at or below the levels of the reference vehicle. However, CO emissions after the GPF-4 were increased to some degree and increased back-pressure of the filter could possibly have an influence in this case. In conclusion, in-series application of filters for GDI vehicles would also need a careful integration of the system, avoiding increased back pressures under all driving conditions with low and high soot and ash loadings.

**Effects of Particle Filters on PAH emissions**

We have already reported substantial effects of diesel particle filters on PAH emissions\(^{31, 42}\). Respective DPFs were high-quality wall-flow filters with efficiencies above 98%, as required by the Swiss Clean Air Act. As discussed above, only one of the four prototype GPFs reached comparably high filtration efficiencies and hence PN emissions close to the low level of the bench mark diesel vehicle. Below we report on effects of the prototype GPFs on PAH emissions with a focus on genotoxic PAHs.

Fig. 3 displays emission factors (EFs, ng/km) in the hWLTC of selected 2- to 6-ring PAHs ranging from naphthalene (1), the most volatile PAH with a boiling point (BP) of 218 °C, to dibenzo(a,h)anthracene (24) with a BP of 524 °C. Genotoxic PAHs (Fig. 1, 1, 18, 19, 20, 21, 22, 23, 24) are indicated with an asterisk. Respective EFs are reported in Tables S4-S6 (Supporting Information).

Emissions of the reference vehicle (GDI-R, highlighted in red) without and with filters are compared. GPF-2 and GPF-3 are coated with catalytic material; GPF-1 and GPF-4 are non-coated filters. PAH EFs of the bench mark diesel vehicle (highlighted in gray) with an integrated DPF are always lower than those of the GDI vehicle without filters with one
exception. Highest emissions from the GDI vehicle without GPF were in the range of $10^3$-$10^4$ for naphthalene (1*), 1-methyl naphthalene (2), 2-methyl naphthalene (3), phenanthrene (7) and pyrene (13) which were observed in other GDI vehicles (43, 44).

PAH emissions are lowered to some degree with filters, however only GPF-1 has a clear impact on PAH emissions. As shown in Fig. 4, emissions of benzo(a)pyrene (22), one of the most genotoxic PAH, were reduced by 89%, 83% and 88% with GPF-1, GPF-2 and GPF-3 in the cWLTC and 99%, 99% and 77% in the hWLTC. It can be observed in Fig. 4 that as boiling points of PAHs increase, their filtration efficiencies increase too. GPF-4 had the poorest PAH filtration efficiency in the cWLTC. Emissions of certain PAHs were even higher after GPF-4 in the hWLTC. For example, pyrene (13) increased 9-fold, fluoranthene (16) 2-fold and the sum of genotoxic PAHs 19-fold. GPF-4 is a non-coated filter also showing poorest particle filtration efficiencies. We assume that a storage-and-release phenomenon can explain these observations. Hence, semi-volatile material is stored during the cold driving cycle and released to some degree during the hot cycle. GPF-2 and GPF-3 are filters coated with catalytic material. In this regards, it is not clear, if coated catalysts were able to convert PAHs or not.

As mentioned, PAH EFs of the GDI vehicle without filter are in general higher than those of the diesel vehicle with DPF. Even with particle filters, PAH emissions of the GDI vehicle still exceed those of the diesel vehicle.

A well-designed and integrated GPF, as mentioned before, may also require changes in engine calibration to accommodate it, and the addition of air injection upstream of the GPF to affect PAH oxidation may be needed. The lack of catalytic activity may be due in part to significantly lower available exhaust oxygen.

Filtration efficiencies of four prototype filters for selected 2- to 6-ring PAHs in the cold and hot WLTC vary to some degree. Values <1 indicate a reduction, values >1, mainly observed
for GPF-4, indicate a store-and-release phenomenon. Overall, it seems that GPFs showed higher PAH efficiencies in the cWLTC than in the hWLTC. This seems plausible, because a cold, soot-loaded GPF can adsorb more semi-volatile PAHs and can desorb them again at higher temperature. GPF-1 showed the highest filtration efficiency for most PAHs in both cycles. On the other hand, GPF-4 is less efficient under cold conditions (cWLTC) and is even releasing some high molecular weight PAHs in the hWLTC.

**Impact of Filters on Genotoxic PAHs**

Fig. 5 shows the toxicity-weighted genotoxic potential (ng TEQ/km) of GDI vehicle exhausts without (GDI-R) and with filters and the bench mark diesel vehicle with DPF in the cWLTC and hWLTC. It also displays patterns of the genotoxic PAHs (Fig. 5B, toxicity-weighted), of PAHs with TEF=0.1 (Fig. 5C, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene and benzo(a)anthracene), and patterns of naphthalene and its alkyl-derivatives (Fig. 5D and 5E).

Genotoxic PAH emissions of the GDI vehicle were 330 and 220 ng TEQ/km in the cWLTC and hWLTC and are in the same range of a GDI fleet of 7 Euro-3 to Euro-6 vehicles which on average releases genotoxic PAHs of 480 ± 360 and 430 ± 630 ng TEQ/km in the cWLTC and hWLTC respectively. The GDI vehicle, without and with filters, releases considerably more genotoxic PAHs than the bench mark diesel vehicle (Fig. 5A). Genotoxic PAH emissions of the GDI vehicle were 3- to 15- and 2- to 23-fold higher in the cWLTC and hWLTC than the diesel vehicle.

In conclusion, Euro-3, -4, -5 and Euro-6 GDI vehicles without filter release 2-3 orders of magnitude more particles and 1-2 orders of magnitude more genotoxic PAHs than the Euro-5 bench mark diesel vehicle with DPF.
Genotoxic PAH filtration efficiencies of 79-79%, 60-78% and 57-62% were achieved with GPF-1, GPF-2 and GPF-3 in the cWLTC and hWLTC. Efficiencies of GPF-4 are poor in the cWLTC (30%). This filter even produced 2.4-fold higher genotoxic PAH emissions in the hWLTC. GPF-4 also showed lowest particle efficiencies of 61% and 77% in the cWLTC and hWLTC. We conclude that GPF-4 did not convert genotoxic PAHs but stored them and released them again under hot driving conditions. Such store-and-release phenomena have also been observed with non-coated DPFs.

Although genotoxic PAH emissions of the GDI vehicle were lowered with GPF-1, GPF-2 and GPF-3, these emissions still are 2- to 6-fold higher than those of the Euro-5 diesel vehicle with DPF. With GPF-4, are 11 to 23 times higher than the diesel vehicle. Genotoxic PAH emissions in the SSC (Table S4-S6, SI) varied in the range of 10-60 ng TEQ/km, thus at the level of the diesel vehicle with DPF (21 ng TEQ/km). For most PAHs, concentrations in SSC exhausts were at background air level under steady state conditions.

As observed in Figs. 5A and 5B, benzo(a)pyrene emissions (red) mainly contribute to the genotoxic potential together with dibenzo(a,h)anthracene (pink). Emissions decrease in all but one case when filters are used. With GPF-4 a store-and-release phenomenon was observed. Relative proportions of benzo(a)pyrene, one of the most carcinogenic PAH, decreased from 62-84% in non-filtered WLTC exhausts and 31-5%, 26-2% and 17-50% after GPF-1, GPF-2 and GPF-3, respectively (Fig. 5B).

On the other hand, relative proportions of dibenzo(ah)anthracene increased from 4-7% without filter to 41-61%, 22-57% and 24-39% after GPF-1, GPF-2 and GPF-3 in WLTC exhausts (Fig. 5B). GPF-4 did not affect benzo(a)pyrene and dibenzo(ah)anthracene proportions which resembled those of the vehicle without filter.
In Fig. 5C, it is observed that relative benzo(a)anthracene proportions (brown) decrease with GPFs compared to the reference vehicle, while those of indeno(1,2,3-cd)pyrene (violet) increased. Benzo(b)fluoranthene proportions exceed those of benzo(k)fluoranthene, both without and with filters. Naphthalene (blue) is predominant compared with alkyl-naphthalenes, as can be seen in patterns displayed in Figs. 5D and 5E, with one exception. The naphthalene content in the hWLTC sample of the reference vehicle was low and the respective pattern is affected by this. However, in all other cases, naphthalene accounts for 60-90% of the sum of naphthalene and alkyl-naphthalenes.

Fig. 5E also distinguishes C1- and C2-naphthalenes (sums of mono- and di-methylated naphthalenes). Relative proportions of 32% and 9% were reported for non-filtered exhausts in the cWLTC. C1- and C2-naphthalene proportions decreased to 22-3%, 20-2% and 11-1% with GPF-1, GPF-2 and GPF-3, respectively, which lowered all PAH and particle emissions. These findings indicate that alkylated naphthalenes are retained more efficiently in filters than naphthalene or that dealkylation reactions may occur in filters. As mentioned before, the coated filters tested contained noble metals, which can support dealkylation reactions. Dealkylation reactions have also been observed in three-way-catalysts of PFI vehicles.

Environmental Impact

We have demonstrated that two out of four tested prototype GPFs lowered particle number emissions of a GDI vehicle by 80-99.9%, even under transient vehicle operation. Filtration efficiencies of GPF-3 and GPF-4 are poor (60-79%), clearly below 98%, which is a requirement for DPFs for construction machinery according to Swiss legislation. In other words, GPF-3 and GPF-4 would not be considered as best-available technology and not recommended for retrofitting. GPF-1 with PN efficiencies of 96-99.8% was the best filter.
tested, lowering PN emissions by 2-3 orders of magnitude, and nearly reaching levels of the bench mark diesel vehicle.

Effects of these prototype-GPFs on semivolatile compounds like PAHs and alkyl PAHs are also promising. GPF-1, GPF-2 and GPF-3 lowered genotoxic PAH emissions by 79-79%, 60-78% and 57-62% in the cWLTC and hWLTC respectively. However, effects on semivolatile compounds are not as strong as for solid particles. This is due to the physicochemical nature of these PAHs, specifically their volatility and reactivity. Volatility is related to the boiling point of these compounds, which range from 218 °C for naphthalene (1) to 536 °C for indeno[1,2,3,cd]pyrene (23). Thus, semivolatile PAHs can escape from a soot-loaded filter at higher temperatures and accumulate in the cold.

Those filters with catalytic coatings (GPF-2, GPF-3) did not remove PAHs to a larger extent than GPF-1, which was not coated but most efficient. Thus a catalytic activity could not be confirmed for those PAHs investigated. On the other hand, non-coated GPF-4, with lowest efficiencies for particles and PAHs, accumulated semivolatile PAHs in the cold and partially released them again in hot conditions.

GPFs have a large potential to lower, particle and genotoxic PAH emissions. The filter technology is well established for diesel vehicles and could be quickly incorporated on every new GDI vehicle. However, this promising environmental technology needs to be carefully integrated in future GDI vehicles or retrofitted to in-use vehicles.

The potential of particle filters has been successfully demonstrated in millions of diesel vehicles which have orders of magnitude lower emissions of soot nanoparticles and genotoxic PAHs than current GDI vehicles. Since 2000, DPFs have been in operation in on-road diesel vehicles. Considering the high particle number emissions of GDI vehicles, which exceed those of current diesel vehicles by 2-3 orders of magnitude and the high genotoxic potential of GDI exhausts, exceeding those of diesel vehicles with DPF by 1-2 orders of magnitude,
one can ask, why filter technology has not been introduced to GDI vehicles in parallel to diesel vehicles. As a matter of fact, BAT filters have been used in diesel passenger cars since 2000 and have been retrofitted to construction machinery (>43 kW) in Switzerland since 1998.

ASSOCIATED CONTENT

Supporting Information.

Additional figures, tables, and descriptions can be found in Supporting Information. Figure S1, Table S1 and Table S2 are providing additional information regarding the driving test cycling. Table S3 reports quantitative results of all regulated pollutants and complements Figure 2. Tables S4-S6 show concentrations of all PAHs in the cycles and support Figures 3-5. Table S7 displays toxicity equivalency factors (TEFs) used to deduce the genotoxic potential given in Figure 5.

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Figure 1. Chemical structures and numbering of PAHs and alkyl-PAHs. Genotoxic compounds are labelled with asterisks, respective names, numbers and abbreviations are given below. Naphthalene (1*, NAP), 1-methylnaphthalene (2, 1MeNAP), 2-methylnaphthalene (3, 2MeNAP), 1,2-dimethylnaphtalene (4, 1,2diMeNAP); 1,6-dimethylnaphthalene (5, 1,6diMeNAP), 2,6-dimethylnaphthalene (6, 2,6diMeNAP), phenanthrene (7, PHEN), 1-methylphenanthrene (8, 1MePHEN), 2-methylphenanthrene (9, 2MePHEN), 3-methylphenanthrene (10, 3MePHEN), 9-methylphenanthrene (11, 9MePHEN), 1,7-dimethylphenanthrene (12, 1,7diMePHEN), pyrene (13, PYR), 1-methylpyrene (14, 1MePYR), 4-methylpyrene (15, 4MePYR), fluoranthene (16, FLT), 3-methylfluoranthene (17, 3MeFLT), benzo(a)anthracene (18*, BaA), chrysene (19*, CRY), benzo(b)fluoranthene (20*, BbF), benzo(k)fluoranthene (21*, BkF), benzo(a)pyrene (22*, BaP), indeno(1,2,3,cd)pyrene (23*, IND), dibenz(ah)anthracene (24*, DBA)
Figure 2. Particle number (particles/km) and CO (mg/km) emissions of an Euro-5 GDI vehicle (Volvo V60, 1.6 L) without and with GPFs. Effects of two non-coated (GPF-1, GPF-3) and two catalytically coated (GPF-2, GPF-4) GPFs.
4) and two filters with catalytic coatings (GPF-2, GPF-3) were studied at transient driving cWLTC (blue bars) and hWLTC (red bars) and steady operation (SSC, gray bars). Emissions of filtered exhausts were compared with non-filtered ones of the Euro-5 GDI vehicle (highlighted in red) and the bench mark Euro-5 diesel vehicle with DPF (Peugeot 4008, 1.6 L, highlighted in gray). PN emissions in relation to the reference vehicle and respective cycle are indicated. The upper pink dashed line indicates the former PN limit of $6 \times 10^{12}$ particles/km while the bottom pink dashed line indicates the current PN limit ($6 \times 10^{12}$ particles/km). Particle number concentrations (particle/cm$^3$) and size distribution (nm) of GDI vehicle exhaust without (GDI-R, black) and with GPF-1 (purple) at 95 km/h are given (lower left). Respective size-dependent particle number filtration efficiencies are also shown (lower right).
Figure 3. Effects of filters on selected PAH and alkyl-PAH emissions during the hWLTC.

Emission factors in ng/km are given for the reference GDI vehicle (Volvo V60, 1.6 L, Euro-5) without and with GPF-1 (non-coated, brown), GPF-2 (coated, dark brown) GPF-3 (coated, light brown) and GPF-4 (non-coated, gray). The reference vehicle without filter (GDI-R) is highlighted in red, the bench mark diesel vehicle with DPF (Peugeot 6008, 1.6 L Euro-5) in grey. Genotoxic compounds NAP (1), BaA (18), CRY (19), BbF (20), BkF (21), BaP (22), IND (23) and DBA (24) are labelled (*). Emission factors at background air levels are indicated (●).
Figure 4. Filtration efficiency of selected PAHs in the cWLTC and hWLTC. Efficiencies are expressed as ratios of emission factors with filter and without filter. Ratios <1 indicate a net reduction of a given PAH in the filter, ratios >1 a net release from the filter (store-and-release phenomenon). Four prototype ceramic wall-flow filters, GPF-1 (non-coated, brown), GPF-2 (coated, dark brown), GPF-3 (coated, light brown) and GPF-4 (non-coated, gray) were studied. Arrows indicate out of scale values.
Figure 5. Cumulated and weighted genotoxic potential (A, ng TEQ/km) of exhausts of the reference GDI vehicle (Volvo V60, 1.6 L, Euro-5) without and with four prototype filters, GPF-1 (non-coated), GPF-2 (coated), GPF-3 (coated), GPF-4 (non-coated) and the bench mark diesel vehicle with DPF (Peugeot 6008, 1.6 L, Euro-5). Toxicity weighted patterns of 8 genotoxic PAHs are also shown (B) together with patterns of different PAH groups. Fig. 5C shows patterns of PAHs with TEF=0.1 (benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, benzo(a)anthracene). Figure 5D displays patterns of naphthalene and five alkyl-naphthalenes. Figure 5E illustrates patterns of naphthalene and sums of C1- and C2-naphthalenes. Indicated are patterns affected by an outlier (●). Naphthalene levels of the reference vehicle in the hWLTC were low, influencing patterns in D and E and to a lower degree also in A and B.