Co-formation and co-release of genotoxic PAHs, alkyl-PAHs and soot nanoparticles from gasoline direct injection vehicles

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Abstract

Gasoline direct injection (GDI) vehicles quickly replace traditional port-fuel injection (PFI) vehicles in Europe reaching about 50 million vehicles on roads in 2020. GDI vehicles release large numbers of soot nanoparticles similar to conventional diesel vehicles without particle filters. These exhausts will increasingly affect air quality in European cities. We hypothesized that such particles are released together with polycyclic aromatic hydrocarbons (PAHs) formed under the same combustion conditions. Emission data of a fleet of 7 GDI vehicles (1.2-1.8 L) including Euro-3,-4,-5 and -6 technologies revealed substantial particle emissions on average of $2.5x10^{12}$ particles km^{-1} in the cold worldwide harmonized light vehicle test cycle (cWLTC), the future European legislative driving cycle. Particle emissions increased 2-3 orders of magnitude during acceleration like CO, indicating that transient driving produces fuel-rich conditions with intense particle formation. For comparison, an Euro-5 diesel vehicle (1.6 L) equipped with a particle filter released $3.9x10^{10}$ particles km^{-1} (cWLTC), clearly within the Euro-5/6 limit value of 6.0×10^{11} particles km^{-1} and 64-fold below the GDI fleet average.

PAH and alkyl-PAH emissions of the GDI vehicles also exceeded those of the diesel vehicle. Mean GDI emissions of 2-, 3-, 4-, 5- and 6-ring PAHs in the cWLTC were 240, 44, 5.8, 0.5 and 0.4 µg km^{-1}, those of the diesel vehicle were only 8.8, 7.1, 8.6, 0.02 and 0.02 µg km^{-1}, respectively. Thus mean PAH emissions of the GDI fleet were 2 orders of magnitude higher than the bench mark diesel vehicle. A comparison of the toxicity equivalent concentrations (TEQ) in the cWLTC 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^{-1}. 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. We showed that 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 too for those exposed to them corroborating the progress achieved with current diesel vehicles, now equipped with efficient particle filters.

Keywords

Vehicle emission; Gasoline-direct injection (GDI); Port-fuel injection; Worldwide harmonized light duty test cycle (WLTC); PAH; Genotoxic potential

Highlights

1. GDI vehicles release substantial numbers of persistent soot-like nanoparticles.
2. PN emissions of GDI fleet were 60-700-fold higher than in the diesel vehicle with DPF.
3. PN and CO emissions increase up to three orders of magnitude during acceleration.
4. Genotoxic PAH emissions were 6-40-fold higher than in the diesel with DPF.
5. Inhalation of soot nanoparticles carrying genotoxic PAHs poses major health threat.

1. Introduction

1.1. Fast implementation of gasoline-direct injection vehicles and their impact on nanoparticle emissions

Gasoline and diesel fuels are complex mixtures of hydrocarbons, both derived from petroleum. They differ moderately with respect to their carbon-to-hydrogen ratios and their vapor pressures are quite different. The fuel volatility influences the injection technology to be used. Gasoline is injected in the liquid phase, evaporated in the fuel port and ignited in the engine. Less volatile diesel is directly injected into the cylinder as a liquid spray and self-ignited upon pressurization.

Injection pressures of current diesel engines are over 1000 bar, those of port-fuel gasoline vehicles are around 4-6 bar. The advent of the gasoline-direct injection (GDI) technology now allows injection pressures up to 200 bars as well. With this, manufacturers claim that higher fuel efficiency and increased engine power can be achieved. As a consequence, downsized engines are now implemented in GDI vehicles with reduced fuel consumption and lower CO_2 emissions. Furthermore, vehicles with down-sized engines are often linked to tax benefits in several countries making them even more attractive.

Traditional port-fuel injection vehicles are quickly replaced by the GDI-technology in many markets. It is expected that 50 million GDI vehicles, corresponding to about 30% of the passenger car fleet, will operate on Europe's roads in 2020 (Mamakos, 2012; Zimmerman et al., 2016).

Fuel is injected at higher pressures in GDI engines and mixed less uniformly with the incoming air. Due to this stratified charging in the cylinders, rich mixtures near the spark plug and injector, and leaner mixtures further away are obtained. As a consequence of this inhomogeneous combustion, GDI vehicles release large numbers of soot-like nanoparticles of yet unknown toxicity. These particles are formed in cylinders possibly together with polycyclic aromatic hydrocarbons (PAHs) and are not combusted completely before being released. GDI-particles are agglomerates with diameters of 20-90 nm. They are as small as those of diesel engines.

1.2. Particle number-based legislation to regulate particle emissions of combustion engines.

In 2009, a first particle number-based (PN) emission limit of 10^{12} particles kWh^{-1} for solid particles with a diameter greater than 23 nm was introduced for diesel construction machinery >37 kW in Switzerland (The Swiss Federal Council, 2017). This PN standard has triggered country-wide programs to retrofit such machinery with efficient wall-flow particle filters. Particle emissions of construction machinery applied in two 57 km long tunnels of the new

Swiss railway link through the Alps could be lowered substantially with particle filters which use was mandatory already in 1998 in these construction sites.

Since 2011, a first PN emission standard for Euro-5 diesel passenger cars and light-duty vehicles of 6 x 10^{11} particles km^{-1} was enforced in Europe and since 2013 a limit of 6 x 10^{11} particles kWh^{-1} has been set for Euro-VI heavy-duty vehicles (Commission Regulation, 2008). PN emissions are not regulated in the U.S.A, neither for diesel construction engines nor for on-road diesel and gasoline vehicles. In Europe, PN-based legislation was an important step to initiate and enforce the implementation of efficient particle filters for all diesel applications.

PN emissions of gasoline vehicles have only recently been addressed and are since 2014 regulated in Europe, but only for GDI vehicles. An attempt to limit PN emissions of Euro-5 GDI vehicles at 6 x 10^{11} particles km^{-1}, in accordance with the respective diesel legislation failed, possibly due to the findings that many GDI vehicles could not comply with this limit (Commission Regulation, 2012a). Some recent studies proved that new GDI vehicles tested under the regulatory cycles have PN emissions below the new Euro 6 limit (6 x 10^{11} particles/km), however failed during real driving emissions (RDE). An added gasoline particle filter reduced the emissions below the limit (Chan et al., 2016; Demuynck et al., 2017). First generation of Euro-3 GDI vehicles was introduced by Mitsubishi already in 2000 which released up to 10^{12} particles km^{-1}, exceeding those of diesel vehicles equipped with filters by orders of magnitude (Mohr et al., 2006; Ulrich et al., 2012). A 10-fold less stringent limit of 6 x 10^{12} particles km^{-1} was set for GDI-vehicles valid from 2014 until 2017 which will be lowered to the diesel limit thereafter.

In other words, particle emissions of today's Euro-5/6 diesel vehicles are orders of magnitude lower than those of respective GDI-vehicles due to more stringent PN limits and efficient filter technologies which were already implemented in certain diesel vehicles in 2000 (Commission Regulation, 2008) but are absent in gasoline vehicles.

A recent study on air quality in Europe showed that the PM2.5 limit was exceeded in 10% and the PM10 limit in 43% of the traffic-influenced monitoring sites (Guerreiro et al., 2014). It is estimated that road traffic might contribute more than 50% of the global PM emissions around 2020 (Yan et al., 2011), so the impact of vehicle technologies on PM burdens is substantial and efficient measures for PM and PN reduction are urgent.

1.3. Genotoxic properties of non-filtered diesel exhausts

Particles released from non-treated diesel- and GDI-vehicles are agglomerates of soot-like nanoparticles formed in the engine under high pressures. In 2012, the World Health Organization (WHO) classified non-treated diesel exhaust as carcinogenic to humans (class 1 carcinogen) (Claxton, 2015). Among other facts, the WHO referred to a comprehensive study on the health impact of diesel exhaust on 12315 U.S. miners (Silverman et al., 2012). The authors reported 198 cases of lung cancer death in the observed cohort and concluded that exposure to diesel exhaust not only poses a severe health risk for exposed miners but also for the general population which is also exposed to lower doses of non-filtered diesel exhausts. No diesel particle filters (DPFs) were used in these mines but as mentioned, filter use was mandatory for all diesel engines operated in the long railway tunnels in Switzerland where workers wore exposed for extended periods of time (1998-2017).

Due to striking similarities of GDI- and diesel-particles concerns rise as GDI-exhausts may also be carcinogenic to humans and detailed studies are urgently needed to carefully assess the genotoxicity of such exhausts.

Polycyclic aromatic hydrocarbons (PAHs) are released from various combustion processes and are present in non-filtered and filtered diesel exhausts (Heeb et al., 2010; Heeb et al., 2008). Some PAHs and their alkyl- and nitro-derivatives are genotoxic either acting as direct mutagens or carcinogens or as precursors for carcinogens (WHO, 1998, 2004). Apart from their toxic and carcinogenic properties, PAHs are also considered as intermediates for soot formation (Raj et

al., 2009). Due to low vapour pressures and similar chemical structures with extended aromatic systems, PAHs tend to adsorb on soot and are co-released with soot at lower temperatures.

Figure 1 displays chemical structures and numbering of those PAHs studied herein. Benzo(a)pyrene (22) is a class 1 carcinogen. PAHs 1, 18, 19, 20, 21, 23 also highlighted in Fig. 1 are class 2A, probably carcinogenic to humans and PAH 24 is a class 2B carcinogen, possibly carcinogenic to humans. PAH 13 and 16 are precursors of carcinogenic derivatives. According to the US EPA, 16 PAHs are priority pollutants and 8 of them are carcinogenic (Fig. 1, asterisk). In the Gothenburg Protocol (United Nations Economic Comission for Europe, 2013) and the following directives and amendments the EU and its member states agreed to curtail long-range transboundary air pollutants. Emission ceilings have been defined for a variety of air pollutants including particulate matter and a few genotoxic compounds. Since 2004, an EU directive limits mean annual benzo(a)pyrene ambient air levels to 1 ng/m^3 (European Parlament, 2004). It has been estimated recently that 20% of the European population is exposed to benzo(a)pyrene levels above the target value and 35% of all monitoring stations reported exceedances (European Environment Agency, 2016). It can be questioned, if benzo(a)pyrene levels will remain at current levels or increase in the next years due to additional emissions of the GDI technology. The Swiss occupational health and safety organization limits BaP exposure to 0.002 mg m^{-3} per work shift (Swiss National Accident Insurance Organization, 2016).

We hypothesized that soot and PAHs are formed in parallel in GDI engines. Therefore we investigated particle, PAH- and alkyl-PAH emissions of seven in-use GDI vehicles representing four vehicle legislations (Euro-3 to -6) and studied effects of transient and steady driving under hot- and cold-start conditions on these critical pollutants. The findings show that the release of PAHs and particles indeed is correlated indicating a simultaneous formation of these pollutants. PAH emission levels and patterns are comparable to those of non-filtered diesel exhausts, the latter are considered as class-1 carcinogen by the WHO.

On a long term, the transformation of fleets which were dominated by PFI-vehicles in the past to fleets with millions of GDI-vehicles is expected to increase atmospheric PN and PAH burdens and related to this the genotoxic potential of ambient air in traffic-affected environments.

2. Methodology

2.1. Vehicles, fuels, test cycles

Seven GDI passenger cars representing Euro-3, -4, -5 and -6 technologies were studied together with a Euro-5 diesel vehicle with integrated diesel particle filter (DPF) which was tested as a bench mark. Table 1 summarizes the characteristics of these vehicles.

Table 1. Characteristics of the tested vehicles

	GDI-1	GDI-2	GDI-3	GDI-4	GDI-5	GDI-6	GDI-7	D-DPF
Name	Mitsubishi Carisma	VW Golf Plus	Opel Insignia	Volvo V60	Opel Zafira	Citröen C4	VW Golf VII	Peugeot 4008
Displacement (L)	1.834	1.390	1.598	1.596	1.598	1.199	1.395	1.560
Injection type	GDI	GDI	GDI	GDI	GDI	GDI	GDI	DI
Legislation	Euro-3	Euro-4	Euro-5	Euro-5	Euro-5	Euro-6	Euro-6	Euro-5
Power (kW)	90 (5500 rpm)	118 (5800 rpm)	125 (6000 rpm)	132 (5700 rpm)	125 (6000 rpm)	81 (5500 rpm)	110 (6000 rpm)	84 (3600 rpm)

GDI engines were all but one forced induction type (turbocharger). The Mitsubishi Carisma was a naturally aspired engine. Gasoline and diesel fuels were taken from the Swiss market and are in compliance with SN EN228 (Schweizerische Normen Vereinigung, 2010a) and SN EN 590 class-0 (Schweizerische Normen Vereinigung, 2010b). Details of the fuel parameters can be found in Tables S2 (Supporting Information). All vehicles were tested at the chassis dynamometer (Schenk 500 G5 60) of the University of Applied Sciences Bern (Nidau, Switzerland). Two driving cycles representing transient and steady conditions were used. The world harmonized light vehicle test cycle (WLTC) representing real-world driving conditions

was used (Fig. 2) (UNECE, 2013) . The WLTC was driven under cold-start (cWLTC) and hot engine/catalyst conditions (hWLTC). It includes urban, extra-urban, highway and motorway driving at mean velocities of 26, 45, 61 and 94 km h^{-1} with a total cycle time of 30 min. The steady-state cycle (SSC), represents steady driving at mean velocities of the four WLTC phases and an idling phase. Each phase is driven for 20 minutes (Fig. S1). During SSC runs, the cruise control of the vehicle was used to keep the speed constant. If this was not available, a rod between the steering wheel and the gas pedal was used.

2.2. Analysis of regulated pollutants and particles

Carbon monoxide (CO) and carbon dioxide (CO_2) were investigated by IR spectroscopy (Horiba MEXA-9400H, Japan). Total hydrocarbons (THC) were analyzed with flame ionization detection and nitrogen oxides (NO_x) with chemiluminescence detectors (Horiba). PN emissions were determined from dilute exhaust with a condensation particle counter (TSI 3790, Minnesota, USA) following the PMP protocol (Commission Regulation, 2008).

2.3. Exhaust sampling, work-up and PAH analyses

Diluted exhausts were sampled from a constant volume sampling (CVS) tunnel with an all-glass sampling device including filter-, condenser- and adsorber units (XAD2) according to the filter/condenser method described in the European standard EN-1948-1 (European Committee for Standardization, 1996). This allows quantitative sampling of complete exhausts including particle-bound, liquid and gaseous fractions. An approximated scheme of the set-up is given elsewhere (Heeb et al., 2010; Heeb et al., 2007).

Prior to sampling, the glass apparatus was cleaned and heated to 450 °C overnight. Aliquots of $^{13}C_6$-naphthalene (1), $^{13}C_6$-phenanthrene (7) and $^{13}C_3$-pyrene (13) were placed on quartz swab and given to the condensate separator prior to sampling. These compounds were used to calculate losses during sampling and work-up.

Samples were analyzed for PAHs and alkyl-PAHs following a multistep cleanup procedure described before (Muñoz et al., 2016). Analysis of 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 of compounds 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 for PAH quantification. Five concentrations containing deuterated compounds, 16 native PAHs (Supelco, Bellefonte, USA) and a SRM mix of 18 methyl-substituted PAH 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 the PAH or alkyl-PAH with closest chromatographic retention time.

2.4. Toxicity evaluation assessment

Toxicity equivalency factors (TEFs) are used to compare the cumulated toxicity of multicomponent mixtures with similar mode of action. TEFs for PAHs are used to assess carcinogenic risks of PAH mixtures (Pufulete et al., 2004; Schorny and Poirier, 1993). The use of TEFs for assessment is discussed controversially and some authors prefer to use the terms potency equivalency factor (PEFs) (OEHHAA, 2011) or estimated order of potential potency for such cancer risk assessments. We used TEFs widely accepted in the literature (Bandowe et al., 2014; Tomaz et al., 2016). Table S7 (SI) lists TEFs proposed by Nisbeth and LaGoy (1992), Duran et al. (1996) and the Office of Environmental Health and Hazard Assessment of USA, (2011). Benzo(a)pyrene is assigned as the reference compound with a TEF of 1, being the most carcinogenic PAH (Petry et al., 1996; Pufulete et al., 2004). TEFs are assigned to other PAHs according to their carcinogenic potential related to benzo(a)pyrene. Overall, the genotoxic

potential corresponds to the sum of individual PAH emission factors (ng km^{-1}) multiplied by its TEF. Thus, the total genotoxic potential (TEQ) is calculated as the sum of those 8 genotoxic PAHs marked in Fig. 1. Note that the total TEQ is expected to be higher due to the presence of other genotoxic PAHs.

3. Results and Discussion

Table 1 reports the characteristics of the investigated vehicle fleet. Respective emission factors for major exhaust constituents are given in Table S3 (SI). The fleet consisted of a mix of seven in-use Euro-3, -4, -5 and -6 vehicles including a Mitsubishi Carisma (GDI-1) representing the first GDI vehicle produced in series. Engine displacement and power rating are displayed in Table 1. Average engine size and power of the GDI fleet were 1.5 ± 0.19 L, 110 ±18 kW.

Vehicles were tested in the cold- and hot-started transient cycle (cWLTC and hWLTC respectively in Fig. 2) and a steady state cycle (SSC, Fig. S1) consisting of four phases of constant driving at 94, 61, 45, 26 km h^{-1} and an idle phase representing mean velocity values of the freeway, highway, extra-urban and urban part of the WLTC.

3.1. Increased Particle Emissions in Fuel-rich Combustion during Acceleration.

Compared to traditional port fuel injection gasoline vehicles, in GDI vehicles with turbocharger engines the injection of gasoline at high pressures allows charging the piston with more fuel enabling lean combustion. The very efficient intake of more fuel and air and the relatively high compression ration provide increased power output with better fuel efficiency. In other words, a better performance can be achieved with down-sized engines. The fleet which was equipped with 1.2-1.8 L engines (mean 1.5 ± 0.19 L, 110 ± 18 kW) when operated smoothly under steady conditions, close to ideal combustion stoichiometry, had lowest fuel consumption (5.7 ± 1.0 L 100 km^{-1}) and PN emissions ($6.6x10^{12}$ ± $1.4x10^{13}$ particles km^{-1}). But in transient engine operation, with fast and frequent load changes and increased energy demand, non-ideal combustion conditions are frequent with a substantial impact on PN and CO emissions (Fig.2).

The time-velocity diagram of the WLTC is displayed in Fig. 2. This cycle replaces the European driving cycle (EDC) in 2017 as the new legislative cycle for type approval. The WTLC includes more transients and is better representing real world driving than the EDC. Fig. 2 (bottom) also includes a plot of the positive acceleration x velocity (m^2 s^{-3}) versus time (s) to emphasize those transients in the cycle that are related to increased fuel demand and emissions. Furthermore, Fig. 2 displays concentrations of CO_2 (%v, red), CO (ppmv, orange) and particle number (PN, particles cm^{-3}, black) in diluted exhaust of a CVS system of an Euro-5 vehicle (GDI-4, Volvo V60, 1.6 L, 132 kW) during a hot-started WLTC.

It is evident that each positive acceleration event immediately induces an increase in CO_2 emissions and related to this higher fuel consumption. The comparison of CO emissions with positive acceleration reveals a strong correlation. CO is released throughout the entire cycle, but increased 100- to 1000-fold when accelerating the vehicle. Particle number emissions are also strongly correlated with positive acceleration, also increasing 100 to 1000-fold (logarithmic scales).

We conclude that incomplete combustion conditions are prevailing, whenever the vehicle is accelerated. Based on the chemical composition of these exhausts, one has to assume that fuel-rich and oxygen-deficient conditions prevail when accelerating the vehicle. This is frequently happening during the transient mode. In other words, rich conditions local in time and space occur more frequently during acceleration events. We hypothesize that a better mixing of air and fuel to reduce this non-homogeneity through better injection systems or a re-design of the engine control system would probably improve this phenomenon. Accordingly, CO and PN emissions increase 2 to 3 orders of magnitude in these transients due to sub-stoichiometric combustion.

As shown in Fig. S1, time-resolved CO (orange) and CO_2 (red) emissions under the SSC remained one to two orders of magnitude below those at transient with positive accelerations (Fig. 2).

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304 **3.2. Regulated Pollutants and Fuel Consumption.**

305 Figure 3 displays mean fuel consumption (FC), CO_2, CO, NO_x, and PN emission factors of the
306 seven GDI vehicles in the cold- (blue) and hot-started (red) WLTC (Fig. 2). For comparison,
307 mean SSC emission factors (gray) representing constant vehicle operation at 94, 61, 45 and 26
308 km h^{-1} and idling are also given. Fig S1 (SI) displays the time-velocity diagram of the SSC and
309 Table S1 reports respective values. Mean (n=7) emission factors (± standard deviation) of the
310 GDI fleet and the Euro-5 diesel vehicle (D-DPF, Peugeot 4008, 1.6 L) used as bench mark are
311 also given. The diesel vehicle, which was equipped with a particle filter, is representing the
312 status in European markets since the introduction of a PN limit in 2009.
313 Fuel consumption of the seven GDI vehicles varied from 5.7 - 9.5 L 100 km^{-1} with mean values
314 of 7.6±1.3 and 7.4±1.3 L 100 km^{-1} in the cold and hot WLTC and 5.7 ± 1.0 L 100 km^{-1} under
315 steady driving (SSC). This corresponds to mean CO_2 emissions of 174 ± 28, 171 ± 28 and 132 ±
316 24 g km^{-1}, respectively. There are some extra CO_2 emissions due to the cold start but most CO_2
317 is released due to the transient driving in the WLTC compared to the SSC. Fuel consumption of
318 the bench mark diesel vehicle was 5.8, 5.5 and 4.3 L 100 km^{-1} corresponding to 151, 145 and
319 110 g CO_2 km^{-1} and meaning 16%, 15% and 13% lower emissions than the diesel vehicle. In
320 other words, CO_2 emissions released from these GDI vehicles are substantial and for example at
321 the level of the Swiss average passenger car fleet which released 177 g CO_2 km^{-1} in 2015
322 (including diesel passenger cars) and much above the target value of 95 g CO_2 km^{-1} of the
323 European Union for 2020 (FOEN, 2010) .
324 As shown in Fig. 2, CO emissions strongly increase during positive acceleration together with
325 particle emissions. Four GDI vehicles released CO emissions above the Euro-5/6 emission limit
326 of 1.0 g km^{-1} in the cWLTC and both Euro-6 and the Euro-3 vehicles, were below this limit.
327 A trend toward lower PN emissions was observed for both Euro-6 vehicles, in the cold and the
328 hot WLTC. In all but one case (Fig.3), PN emissions were lower in the SSC than in the WLTCs

indicating the impact of transient driving. Overall, PN emissions in the SSC were 1-4-fold lower than those of the WLTC (cWLTC and hWLTC average). A Euro-6 vehicle (GDI-7) showed even 15-fold lower emissions in the SSC compared to WLTC. The exception was one of the Euro-5 vehicles (GDI-3), with 11-fold higher emissions in the SCC. Noteworthy to mention is the large difference of emissions in the transient and the steady state cycle of the diesel vehicle, with more than 120-fold lower emissions in the SSC.

However, the PN emissions of all GDI vehicles, both in transient and steady state conditions, are substantially higher than those of the diesel vehicle. On average, the GDI fleet released $2.51x10^{12} \pm 1.75x10^{12}$, $1.95x10^{12} \pm 1.63x10^{12}$ and $6.60x10^{12} \pm 1.38x10^{13}$ particles km^{-1} during the cWLTC, hWLTC and SSC respectively. This means that GDI fleet emits 64-, 700- and 39000-fold higher PN emissions than the Euro-5 diesel vehicle. Thus, all GDI vehicles release substantial numbers of particles at or above the PN-limit of $6.0x10^{11}$ particles km^{-1} which applies for diesel passenger cars since 2009. Both Euro-6 GDI vehicles seem to be optimized to this limit, while the Euro-3, -4 and -5 technology is emitting close to the PN limit of 6.0×10^{12} particles km^{-1} valid for the time period 2014-2017. However, this new Euro-6 legislation which temporally loosened the limit to of $6x10^{12}$ particles/km in 2014 has entered into force for all new GDI vehicles in September 2017 with $6x10^{11}$ particles km^{-1} (Commission Regulation, 2012b)

All GDI vehicles comply with the NO_x limit of 80 (Euro-4) and 60 mg km^{-1} (Euro-5/6), even the oldest Euro-3 vehicle (GDI-1, Mitsubishi Carisma, 1.8 L) is at the Euro-3 NOx limit of 150 mg km^{-1}. However, the bench mark diesel vehicle with NO_x emissions of 641 and 643 mg km^{-1} in the cold and hot WLTC exceeded the Euro-5 NO_x limit of 180 mg km^{-1} for diesel vehicles by a factor of 4. At steady driving NO_x emissions were much lower.

Comparing PN emissions of GDI- and diesel vehicles, it is obvious that the particle filter technology which is now a standard in diesel light- and heavy-duty vehicles has the potential to lower particle emissions by 1-2 orders of magnitude below the current PN limit. Considering the

substantial health threat of persistent soot nanoparticles, it is difficult to understand, why this efficient abatement technology, which was already introduced into diesel passenger cars already in 2000, is not implemented in GDI vehicles. Below, we investigate the chemical composition of GDI exhausts with a focus on genotoxic PAHs which are expected to be formed in GDI engines and adsorb onto soot nanoparticles.

3.3. PAH and alkyl-PAH emissions of GDI vehicles at transient and steady state driving conditions

Figure 4 displays emission factors (EFs) in ng km^{-1} of the sum of the 16 US EPA priority PAHs and the sum of 7 genotoxic PAHs (Fig. 1, 18-24) for individual vehicles and driving cycles. GDI fleet mean values are also given. Emission factors for 34 PAHs and alkyl-PAHs are given in Tables S4-S6 (SI) for the cWLTC, hWLTC and SSC.

EFs of 16 US EPA sum in the cWLTC ranged from $9.1x10^4$ to $6.3\ x10^5$ ng km^{-1} with a mean (± standard deviation) of $2.4x10^5 \pm 1.9x10^5$ ng km^{-1} which compares with the diesel vehicle releasing $1.8x10^4$ ng km^{-1}. EFs in the hWLTC are lower than in the cWLTC in all but one case, on average $9.6x10^4 \pm 9.5x10^4$ ng km^{-1}. Mean EFs in the SSC were $2.6\ x10^4 \pm 2.4x10^4$ ng km^{-1} meaning approximately 17-fold lower than in the WLTC (cWLTC and hWLTC average). Therefore, the difference between transient and SSC emissions is even larger for PAH than for PN emissions as shown above. This indicates that transient driving also leads to increased PAH emissions compared to steady vehicle operation, as observed before for particle emissions (Fig. 3). Once again, differences between WLTC and SSC emissions in GDI vehicles are relatively small if compared with GDI emissions and diesel emission, as shown below.

Vehicle-to-vehicle variations are substantial and a trend towards lower PAH emissions from Euro-3 and -4 towards Euro-5 and -6 technologies could be observed. This decreasing trend is also show in literature for older Euro legislation vehicles (Caplain et al., 2006).

Considering the sum of seven genotoxic PAHs (Fig.1, 18-24), the Euro-3 vehicle (GDI-1) is releasing most genotoxic compounds, 1.9×10^3 and 4.2×10^3 ng km^{-1} in cWLTC and hWLTC, respectively, being 41 and 70 times higher than the diesel vehicle with emissions of 48 and 60 ng km^{-1}, respectively. On average, the GDI fleet (n=7) emitted 19- and 15-fold more genotoxic PAHs in the cWLTC and hWLTC than the diesel vehicle. Cold start PAH emissions are often higher than those of the hot start when considering the EPA sum, but cold start effects are smaller for genotoxic PAHs, where average cold and hot start emissions are similar.

Figure 5 shows EFs (ng km^{-1}) in the cWLTC of a selection of 2- to 6-ring PAHs, from naphthalene, the most volatile PAH with a boiling point (BP) of 218 °C, to benzo(a)pyrene with a BP of 495 °C. All genotoxic PAHs (1, 18-24) are included besides several non-toxic alkyl-PAHs. EF of single vehicles varied to some extent, therefore mean EFs (black) of the GDI fleet (n=7) are compared with those of the bench mark diesel vehicles (red highlighted).

Naphthalene, 1-methyl-naphthalene and 2-methyl-naphthalene EFs are high for all GDI vehicles, often an order of magnitude higher than the diesel vehicle. This is also shown in the literature for spark-ignition and diesel vehicles (Zielinska et al., 2004). The fold increase of mean GDI EFs compared to the diesel vehicle is varying from 0.6 to 47 (Fig. 5).

Even when considering the scatter of the data it can be concluded that for 19 out of 24 PAHs mean GDI-EFs exceeded those of the diesel vehicle. The other 5 PAHs (9, 10, 11, 13, 16) were released at comparable levels.

Mean benzo(a)pyrene (22), benzo(b)fluoranthene (20) and benzo(k)fluoranthene (21) EFs of 210 ± 260, 170 ± 140 and 60 ± 40 ng km^{-1} were found, which compare with respective emissions of the diesel vehicle of 5.5, 8.0 and 1.3 ng km^{-1}. In other words, genotoxic BaP (22), BbF (20) and BkF (21) emissions of the GDI fleet are, on average, 40-, 22- and 47-fold higher than those of the diesel vehicle. Of the genotoxic PAHs, benzo(a)pyrene, benzo(b)fluoranthene,

benzo(a)anthracene and chrysene are predominant which partially agrees to other studies (Aakko-Saksa et al., 2014).

We conclude that emissions of genotoxic PAHs and most other investigated PAHs are up to 47 times higher for the GDI fleet than for the diesel vehicle. For most PAHs, emissions decrease when comparing Euro-3, -4, -5 and -6 technologies. Similar trends have been observed for PN emissions.

GDI exhaust concentrations of the 16 US EPA PAHs ranged from 140 to 990 μg m^{-3} in the cWLTC and from 30 to 530 μg m^{-3} in the hWLTC, whereas concentrations of 10 and 36 μg m^{-3} were found for the diesel vehicle, respectively. Therefore, mean GDI fleet values for the 16 US EPA PAHs were 370, 170 and 120 μg m^{-3} respectively. Values found in literature from older port-fuel injection vehicles were lower, ranging from 93 to 170 μg m^{-3} (Wei et al., 2015).

It should also be noted that in other studies with heavy-duty diesel engines without filter technology emissions of 8.8 mg km^{-1} (14.1 mg $mile^{-1}$) of the 16 US EPA PAHs were found in transient operation (Hu et al., 2013). Different after treatment devices including a DPF lowered PAH emissions to values of 0.038-0.113 mg km-1, which agrees with values reported herein, revealing that PAH emissions of GDI vehicles are close to those of diesel vehicles without DPFs.

3.4. Genotoxic potential of GDI exhausts

Figure 6 shows the weighted and cumulated genotoxic potential of GDI exhausts (ng m^{-3}) for the sum of 8 genotoxic PAHs (Fig.1, 1, 18-24). Only those PAHs classified as group 1, 2A and 2B carcinogens were, if detected, considered to assess the genotoxic potential. For this, concentrations of single PAHs (ng m^{-3}) were multiplied with the respective toxicity equivalence factors and summed up to the total genotoxicity equivalence (TEQ).

Highest TEQ-values were found for the GDI-1 (Euro-3) vehicle, being 38- and 70-fold higher than for the diesel vehicle in the cWLTC and hWLTC, respectively. On average, TEQ values of

the GDI fleet in the cWLTC and hWLTC were 750 ± 520 and 710 ± 1000 ng TEQ m^{-3} being 17- and 16-fold higher than the diesel vehicle. A trend towards lower TEQ-values was observed when comparing Euro-3, -4, -5 and -6 technologies, while cold start effects, on average, were low.

As observed for PN and CO (Fig. 3), also PAH emissions including those rated genotoxic increase substantially at transient vehicle operation. In other words, particle and PAH emissions are correlated, with highest emissions observed at transient and lowest at steady driving.

All this indicates that PAHs and soot nanoparticles are possibly formed together in the engine, in fuel-rich and oxygen-deficient zones, where incomplete combustion is prevailing. Upon cooling, less volatile compounds, including most genotoxic PAHs, adsorb on these surface-rich nanoparticles. From a chemical point of view, GDI exhausts are very similar to those released from diesel vehicles without particle filters. From a health perspective, these exhausts are critical too. Benzo(a)pyrene, a class-1 carcinogen, widely used as an indicator PAH for genotoxicity, substantially contributes to the total genotoxic equivalent concentration (Fig. 6, red bars).

3.5. Pattern changes and characteristic PAH ratios

Figure 7 describes some characteristic PAH patterns and ratios found in GDI and diesel vehicle exhausts of cold and hot WLTCs.

The benzo(a)pyrene and benzo(ah)anthracene proportions are displayed in Fig. 7a with TEFs of 1.0 assigned to both compounds. In general, benzo(a)pyrene (red) predominates over benzo(ah)anthracene (pink) accounting, on average, for more than 90%, with the exception of two Euro-5 vehicles (GDI-3 and GDI-5) which showed a preference for benzo(ah)anthracene. BaP proportions in GDI-vehicle exhausts are slightly higher than in the diesel vehicle.

Fig. 7b compares four genotoxic PAHs with TEFs of 0.1, all are group-2B carcinogens. It was observed that benzo(b)fluoranthene proportions (blue) mostly exceed those of benzo(k)fluoranthene (violet), on average 75-81% (cWLTC and hWLTC respectively. Proportions of benzo(a)anthracene (brown) and indeno(1,2,3-cd)pyrene (lila) are similar accounting for about 20-40%. These GDI-pattern were similar to those found in diesel exhaust with a predominance of benzo(b)fluoranthene both, in cWLTC and hWLTC exhausts.

Fig. 7c displays fluoranthene (brown) and pyrene (light brown) proportions which, on average, were about 40% and 60% in GDI exhausts and closer to 50% and 50% in the diesel exhaust.

Fig. 7d compares naphthalene and alkyl-naphthalene proportions. Naphthalene accounts for about 80%, while 1- and 2-methyl-naphtalenes account for 15-20%, with low dimethyl-naphthalene proportions (<5%). These patterns were similar for all GDI vehicle exhausts and also resembled those found in diesel exhausts.

Overall one can conclude that patterns of characteristic PAHs in GDI exhausts are very similar to those found in diesel exhaust. This indicates that combustion conditions in GDI and diesel engines must be similar, allowing a simultaneous formation of PAHs and soot nanoparticles. The latter can be considered as agglomerates of extended PAHs. Furthermore, we conclude that the reaction mechanism leading to comparable PAH patterns, must be similar as well.

3.6. PAH and PN correlations

Figure 8 shows the correlated data between the weighted concentration of the 7 genotoxic PAHs and benzo(a)pyrene (ng TEQ km^{-1}), the most carcinogenic PAH, with the PN (particle km-1) of the 7 GDI vehicles. Regression factors of r^2 = 0.67 and 0.65 have been determined. The exponential regression indicates that whereas PN is reaching a PN limit the genotoxic potential still increasing. Results showed above in Figures 2-8 support the proposed hypothesis that soot and PAHs are formed in parallel in GDI engines.

Figure 8 also shows and confirms that vehicles with the oldest technologies (Euro 3-4) are emitting the highest concentrations of PAHs. Moreover, black points indicate mean values within cold and hot WLTC, showing that highest deviations are found with the oldest vehicles and therefore highest differences between cold and hot emissions.

4. Conclusions

The GDI technology quickly replaces port-fuel injection vehicles and will soon dominate car fleets in many European countries. Whereas CO, NO_x and hydrocarbon emissions of these vehicles, which are equipped with close-coupled three-way catalysts, are at levels of port-fuel injection vehicles of the same legislation, those of particles are not. PN emissions of the examined GDI vehicle fleet during transient driving in the WLTC exceeded those of a Euro-5 diesel vehicle, equipped with a particle filter, by up to three orders of magnitude.

It has to be expected that with increasing shares of GDI vehicles also soot nanoparticle emissions of gasoline vehicles will become a major contributor to road emissions, increasing ambient air particle number concentrations in traffic affected areas. As shown herein, these nanoparticles are formed and co-released together with PAHs including several genotoxic PAHs. PAH emissions of the GDI fleet exceeded those of the diesel vehicle and genotoxic potentials of different GDI vehicle exhausts were, on average, 16-17-fold higher than those of the diesel vehicle.

With respect to particle and PAH emissions, GDI vehicle exhausts resemble those of non-filtered diesel vehicles which are rated as class-1 carcinogen, inducing lung cancer in humans. Based on the similar chemical composition and the co-existence of large numbers of soot-like nanoparticles and relevant quantities of genotoxic PAHs, GDI vehicle exhausts have to be considered as dangerous too. A further increase of GDI vehicle shares is therefore considered as a critical impact on air quality. The precaution principle, which is an important concept to regulate the exposure to genotoxic compounds at workplaces, has been applied in the past, to

force the implementation of particle filters in poorly vented tunnel construction sites in Switzerland to better protect workers, exposed to diesel engine exhausts. With similar reasons, the implementation of filters could be forced for GDI-vehicles. It is strongly recommended that filter technologies are also implemented in GDI-vehicles, even though the overall health impact of GDI-engine exhausts on general and sensitive population is not yet known.

From our findings, it is clear that GDI vehicles would need efficient catalytic filters in order to reduce the emission of nanoparticles and genotoxic PAHs to levels of current diesel vehicles. Four prototype gasoline particle filters have recently been investigated. Preliminary results support the conclusion that gasoline particle filters could lower PN and PAH emissions.

Moreover, legislation should implement equal PN limits for all gasoline and diesel vehicles as they release substantial numbers of particles. Vehicle emissions legislation should also include a limit or target value for benzo(a)pyrene and other genotoxic PAHs as exhausts of GDI- and non-filtered diesel vehicles exceed the ambient air target value of 1 ng/m^3 by two to three orders of magnitude.

Acknowledgements

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Appendix: Supplementary data

Supplementary data associated with this article can be found in the online version.

Legends

Fig. 1. Chemical structures and numbering of PAHs and alkyl-PAHs. Genotoxic compounds are labelled with asterisks and respective names, numbers and abbreviations are given. Naphthalene (**1***, NAP), 1-methylnaphthalene (**2**, 1-MeNAP), 2-methylnaphthalene (**3**, 2-MeNAP), 1,2-dimethylnaphtphalene (**4**, 1,2-diMeNAP); 1,6-dimethylnaphthalene (**5,** 1,6-diMeNAP), 2,6-dimethylnaphthalene (**6**, 2,6-diMeNAP), phenanthrene (**7**, PHEN),1-methylphenanthrene (**8**, 1-MePHEN), 2-methylphenanthrene (**9**, 2-MePHEN),3-methylphenanthrene (**10**, 3-MePHEN), 9-methylphenanthrene (**11**, 9-MePHEN), 1,7-dimethylphenanthrene (**12**, 1,7-diMePHEN), pyrene (**13**, PYR), 1-methylpyrene (**14**, 1-MePYR), 4-methylpyrene (**15**, 4-MePYR), fluoranthene (**16**, FLT), 3-methylfluoranthene (**17**, 3-MeFLT), benzo(a)anthracene (**18*,**BaA), chrysene (**19*,** CHR), benzo(b)fluoranthene (**20***, BbF), benzo(k)fluoranthene (**21***, BkF), benzo(a)pyrene (**22***, BaP), indeno(1,2,cd)pyrene (**23***, IndP), dibenz(ah)anthracene (**24***, DBahA). Carcinogenic PAHs are shaded in red. Benzo(a)pyrene (22) is a class 1 carcinogen. PAHs 1, 18, 19, 20, 21, 23 are class 2A, probably carcinogenic to humans and PAH 24 is a class 2B carcinogen, possibly carcinogenic to humans.

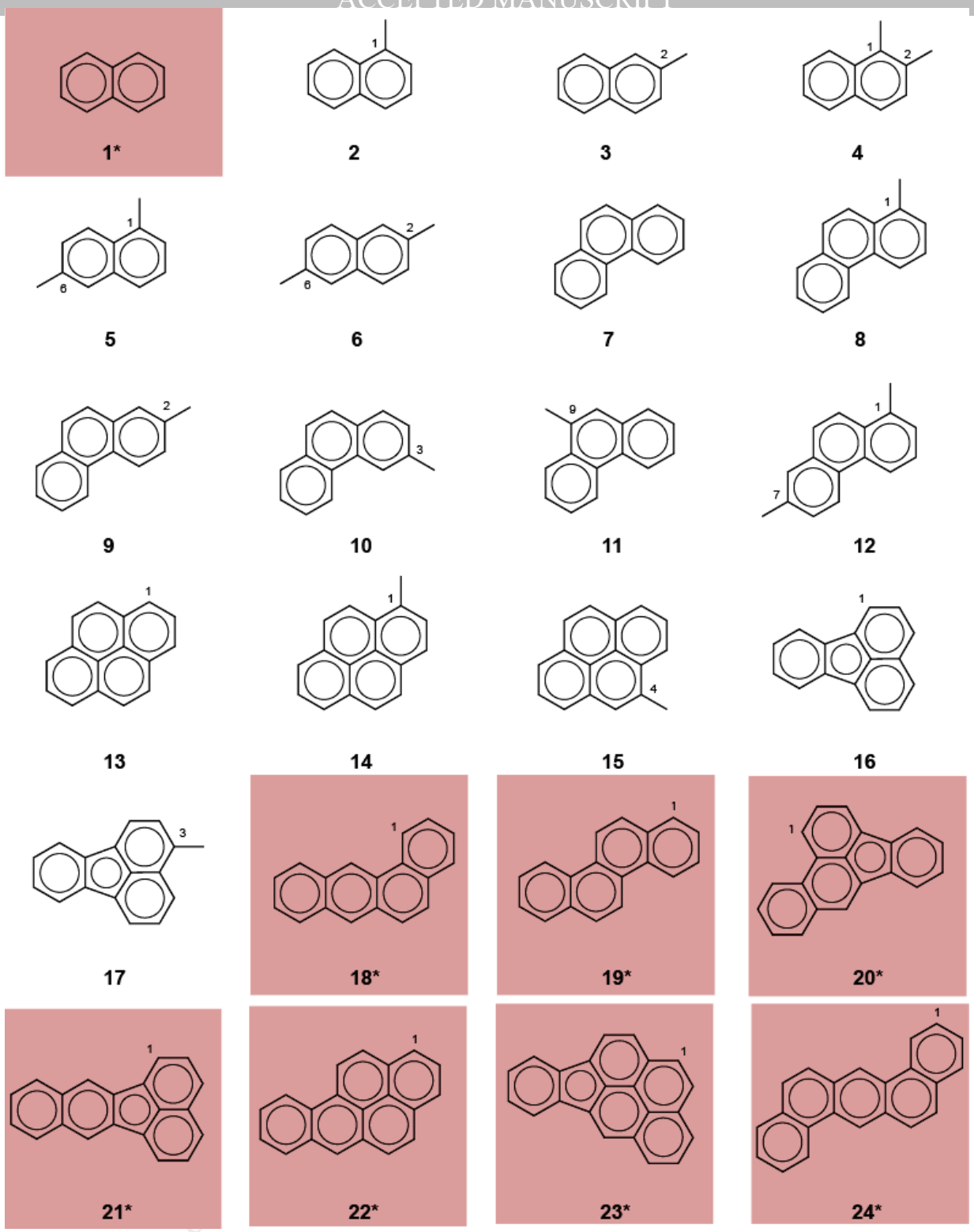

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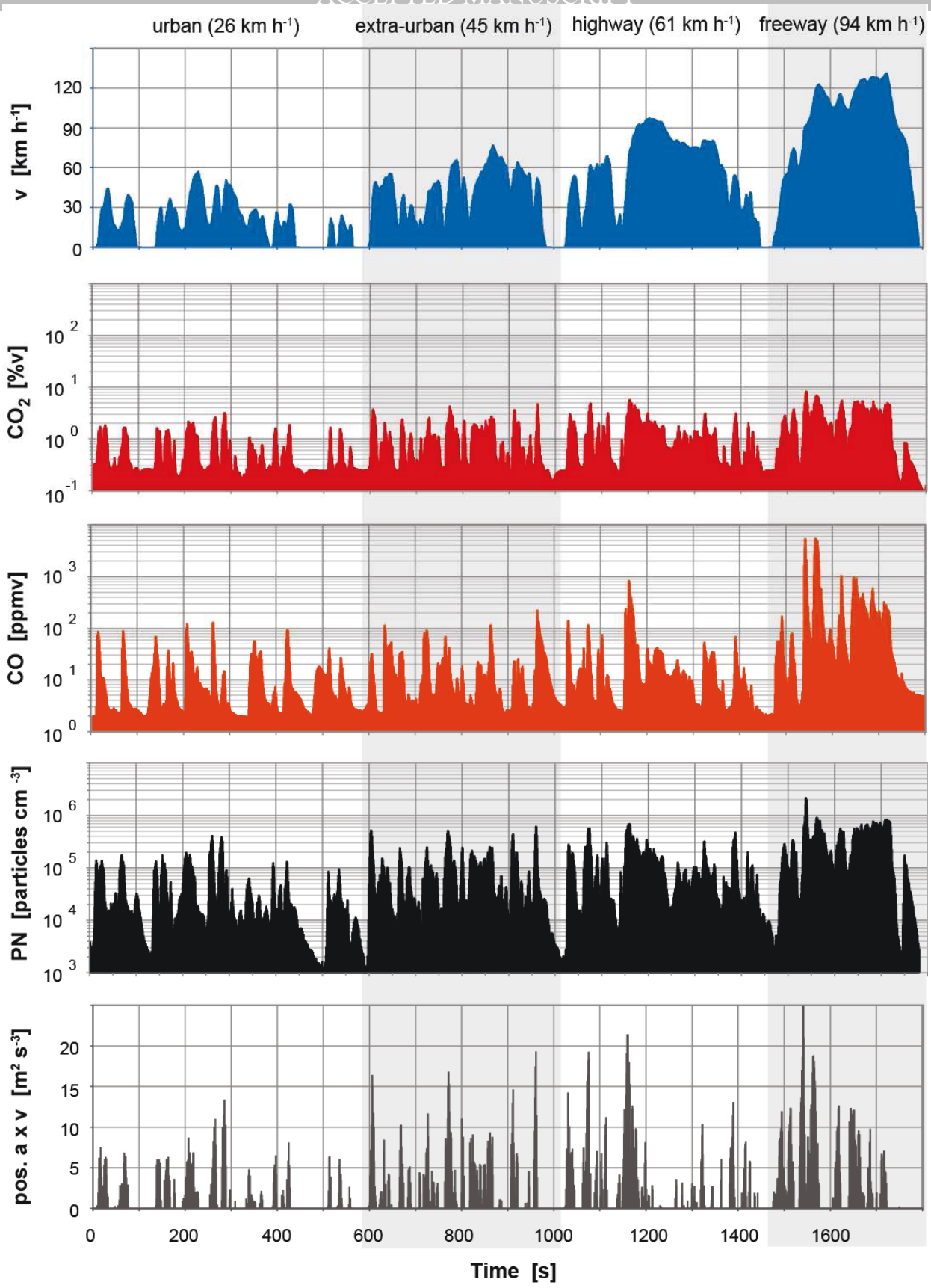
Fig. 2. Time-resolved (1Hz) exhaust concentrations (logarithmic scales) of CO_2 (%v, red), CO (ppm, orange) and particle number (PN, particles cm^{-3}, black) of a Euro-5 vehicle (GDI-4, Volvo V60, 1.6 L) in the hWLTC. Diluted exhausts of the CVS system were studied. The velocity-time diagram (blue) of the WLTC and a plot of the product of positive acceleration and velocity (a x v, $m^2 s^{-3}$, grey) are also given and the four WLTC phases and their mean velocities (km h^{-1}) are indicated.


urban (26 km h-1)
extra-urban (45 km h-1)
highway (61 km h-1)
freeway (94 km h-1)
v [km h-1]
CO2 [%v]
CO [ppmv]
PN [particles cm -3]
pos. a x v [m2 s-3]
Time [s]

553 **Fig. 3.** Fuel consumption (L 100 km^{-1}), CO_2, CO, NO_x (g km^{-1}) and PN emission factors
554 (particles km^{-1}, logarithmic scale) of seven GDI vehicles (GDI-1-GDI-7) in the cold- (blue) and
555 hot-started (red) WLTC and SSC (gray). Mean emission factors (± standard deviation) of the
556 GDI fleet (n=7) are compared with an Euro-5 diesel vehicle with particle filter (D-DPF).
557 Respective Euro-5/6 emission limits of 0.06 and 0.18 g NO_x km^{-1} and 1.0 g CO km^{-1} and 6 x
558 10^{11} and 6 x 10^{12} particles km^{-1} are indicated. In addition, the mean CO_2 emission factor of the
559 entire Swiss passenger car fleet in 2015 of 177 g km^{-1} is also shown.

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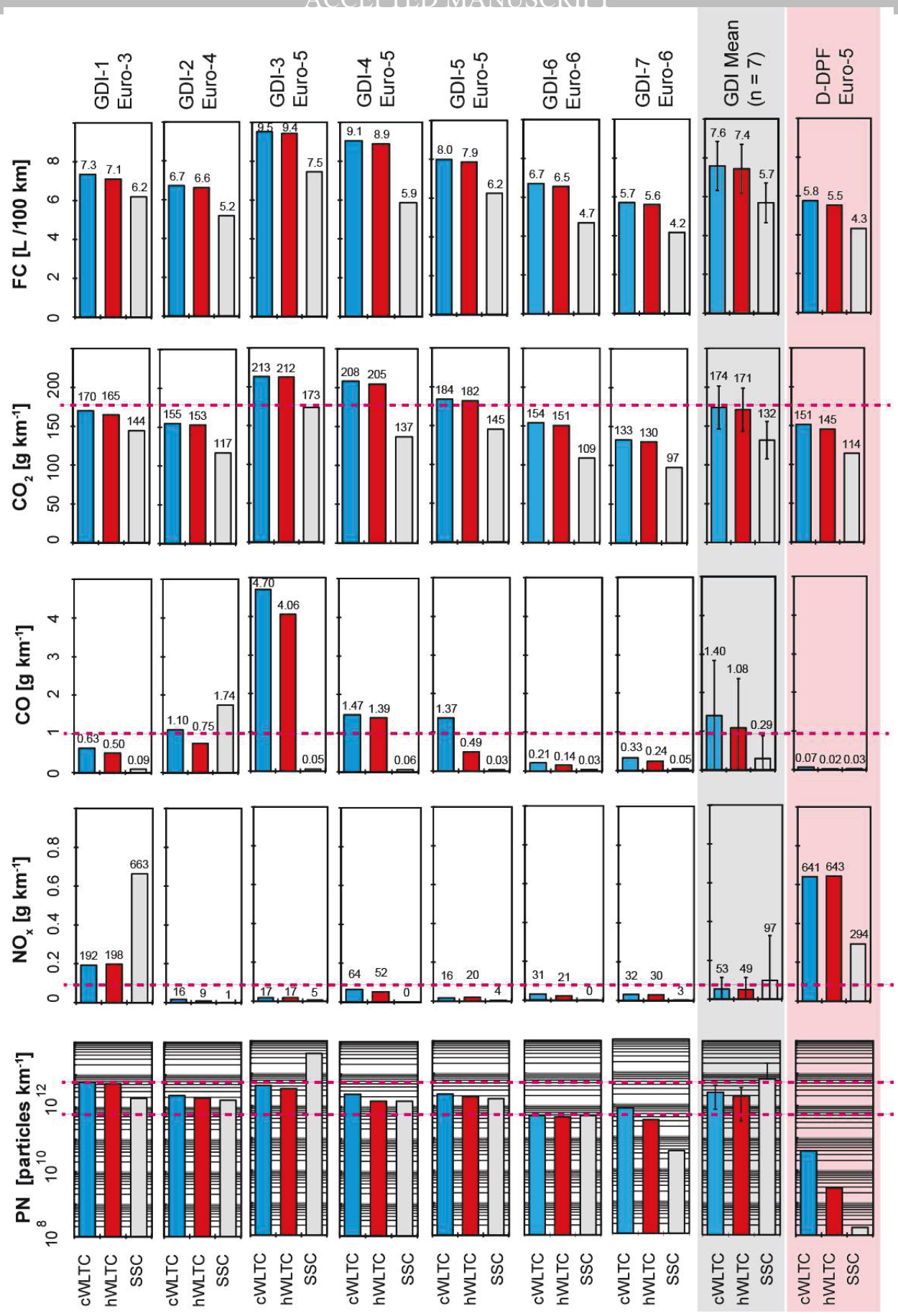
GDI-1 Euro-3
GDI-2 Euro-4
GDI-3 Euro-5
GDI-4 Euro-5
GDI-5 Euro-5
GDI-6 Euro-6
GDI-7 Euro-6
GDI Mean (n = 7)
D-DPF Euro-5
FC [L /100 km]
CO2 [g km-1]
CO [g km-1]
NOx [g km-1]
PN [particles km-1]
cWLTC
hWLTC
SSC

561

562

Fig. 4. Emission factors of the sum of the 16 US EPA PAHs (bottom) and the sum of semi-volatile genotoxic compounds (18-24, top) for all tested vehicles and driving cycles. The fold increase of all vehicle emissions in relation to the bench mark diesel vehicle is also indicated.

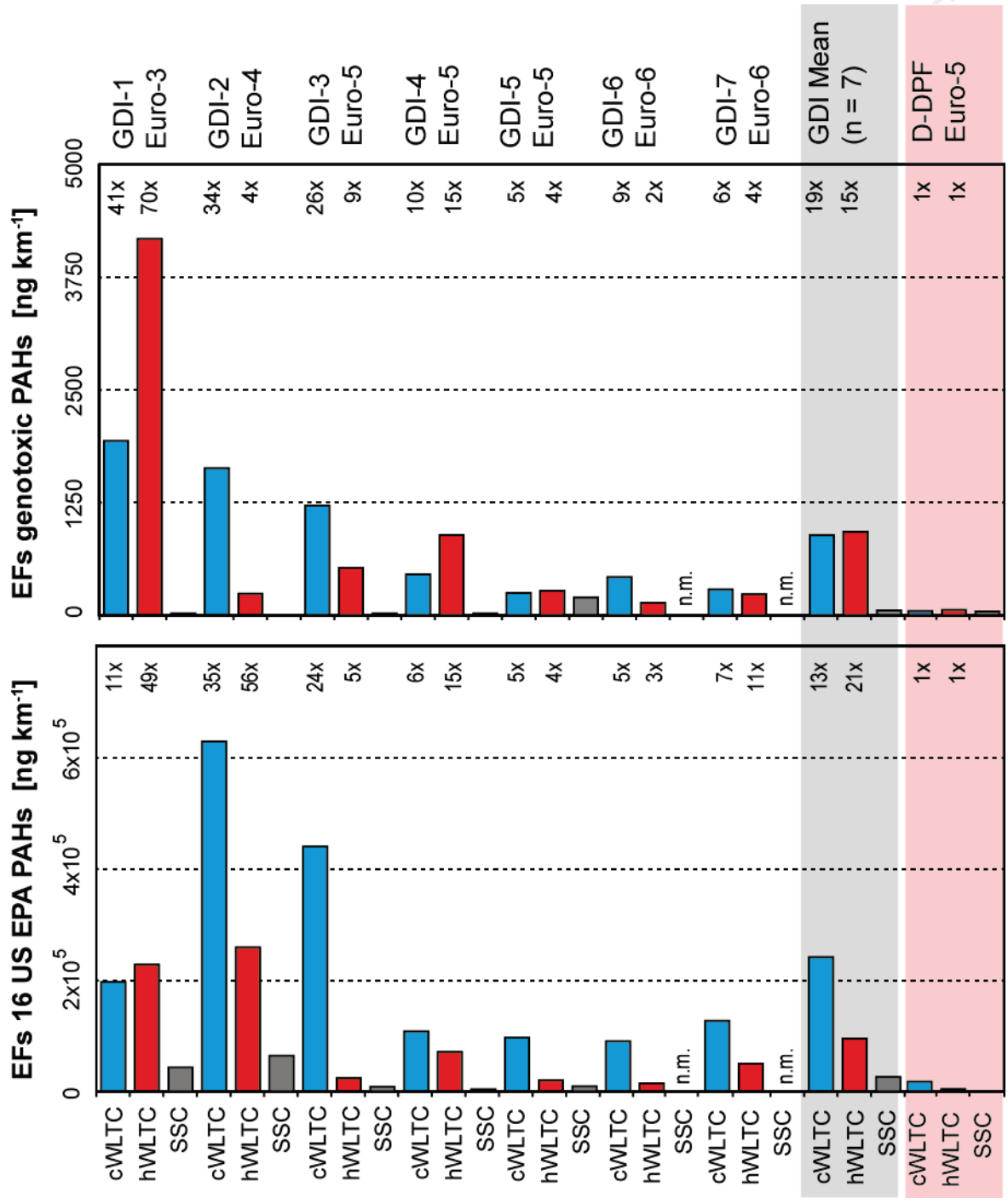

Fig. 5. Emission factors (ng km^{-1}, logarithmic scale) of selected PAH and alkyl-PAHs in the cold started conditions WLTC. The genotoxic compounds (1, 18, 19, 20, 21, 22, 23 and 24) are labeled with an asterisk. Mean values of the GDI fleet (n=7) and the bench mark diesel vehicle with DPF are highlighted in grey and red respectively.

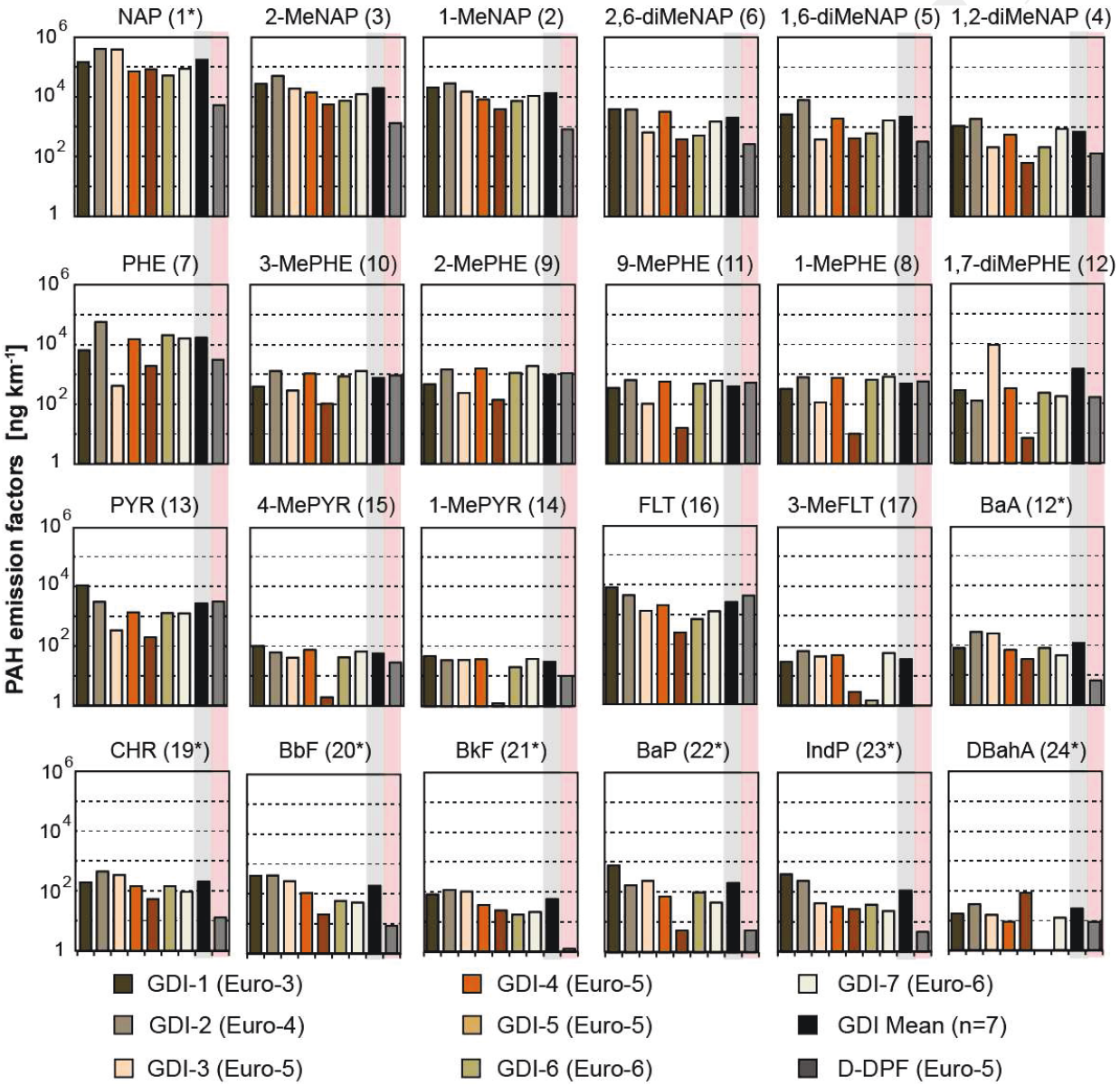

Fig. 6. Cumulated and weighted genotoxic potential of GDI- and diesel vehicle exhausts (ng TEQ m^{-3}) in the cold (upper), hot WLTC (middle) and the SSC (lower diagram. Mean values

(±standard deviation) of the GDI fleet (n=7) and the bench mark diesel vehicle with DPF are highlighted in grey and red. A zoom of the SSC data is also given (bottom).

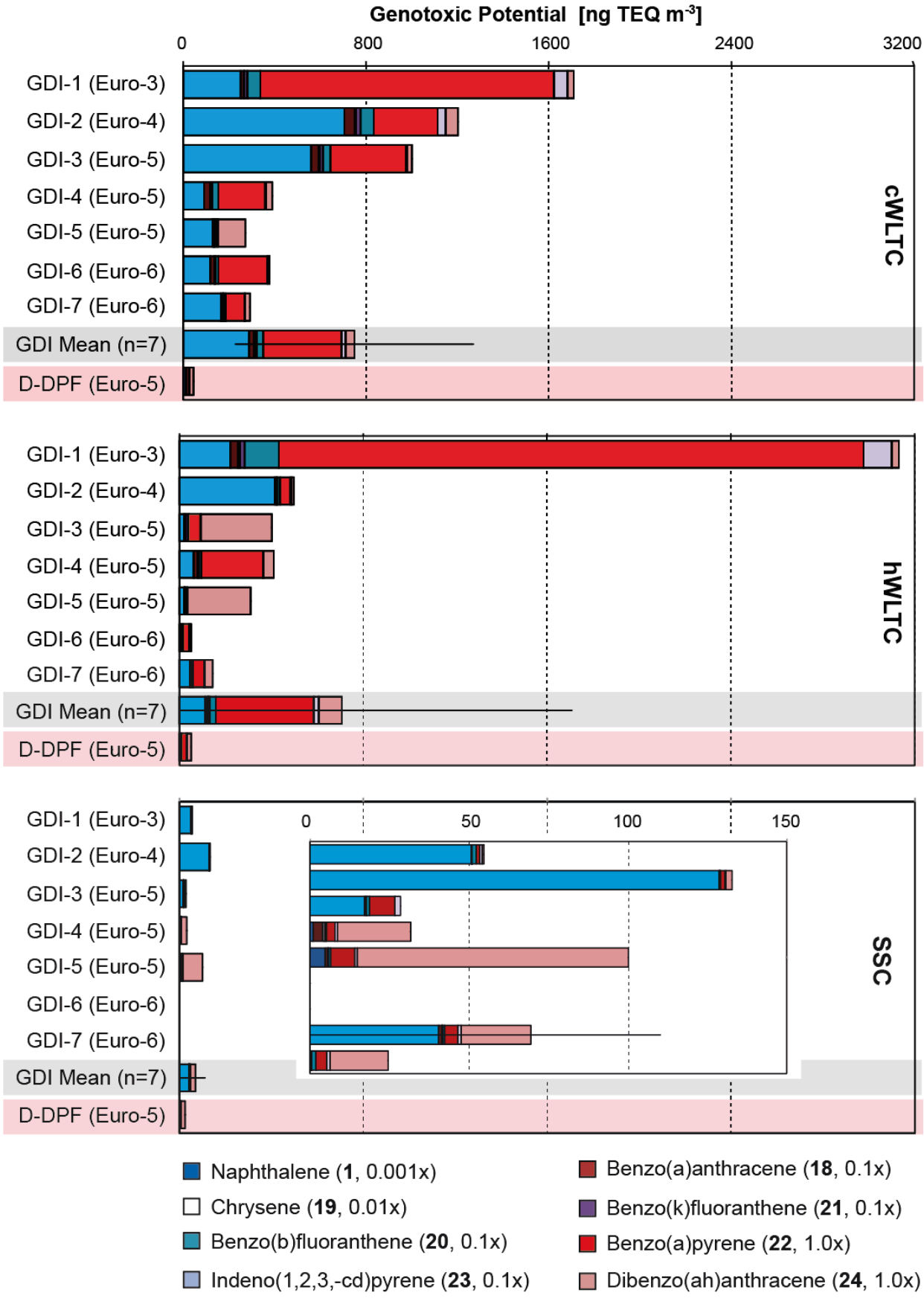

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Fig. 7. Patterns of selected PAHs and alky-PAHs in GDI- and diesel-vehicle exhausts. Proportions of benzo(a)pyrene (red) and dibenzo(ah)anthracene (pink), both having TEF values of 1.0, are given in Fig. 7a in the cold and hot WLTC. Proportions of genotoxic PAHs with TEFs of 0.1 are compared in Fig. 7b. Proportions of fluoranthene (brown) and pyrene (light brown) are given in Fig. 7c and proportions of naphthalene and its alkyl-derivatives are compared in Fig. 7d. Mean GDI pattern (n=7) and patterns of the diesel vehicle with DPF are highlighted in gray and red.

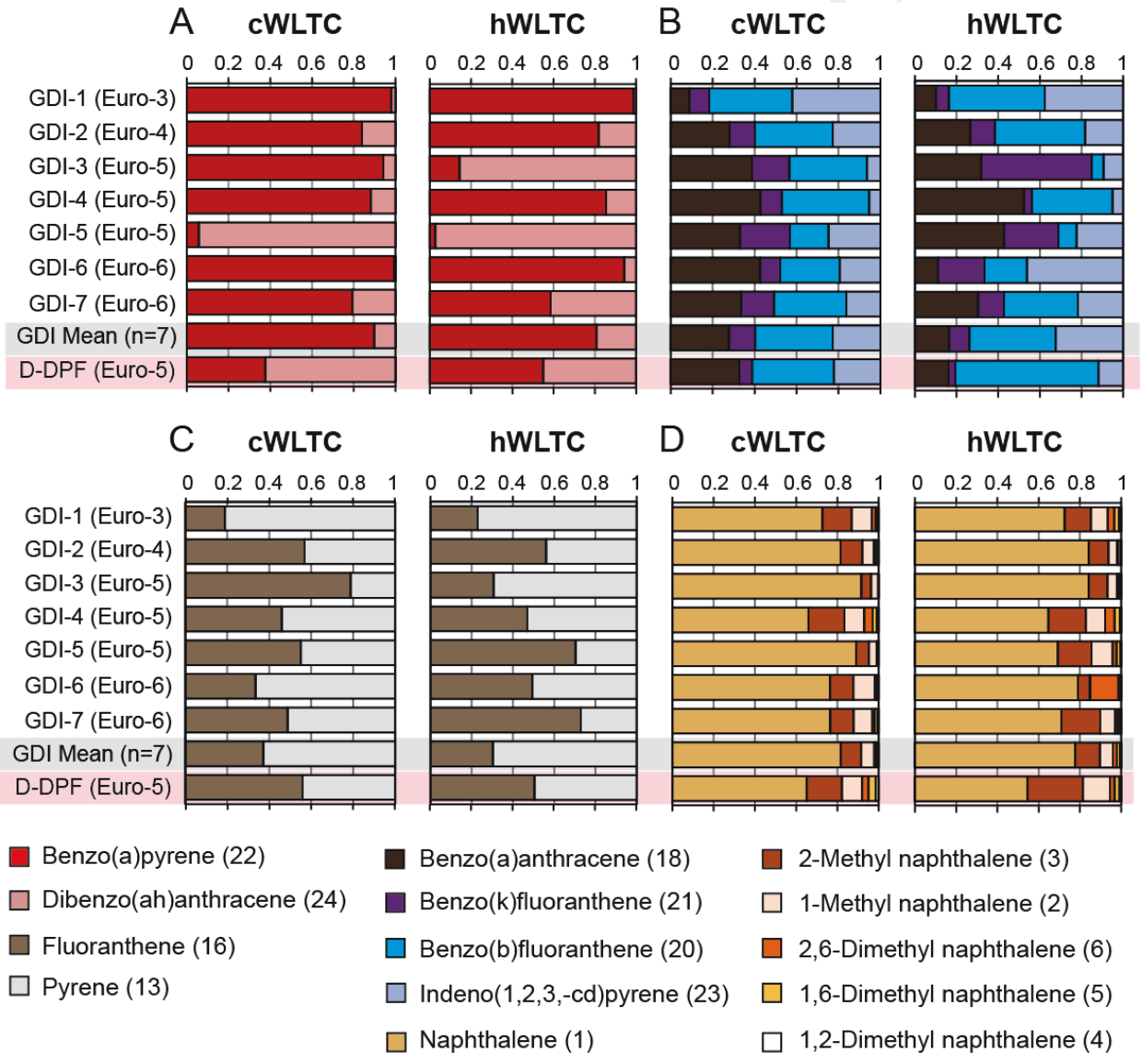
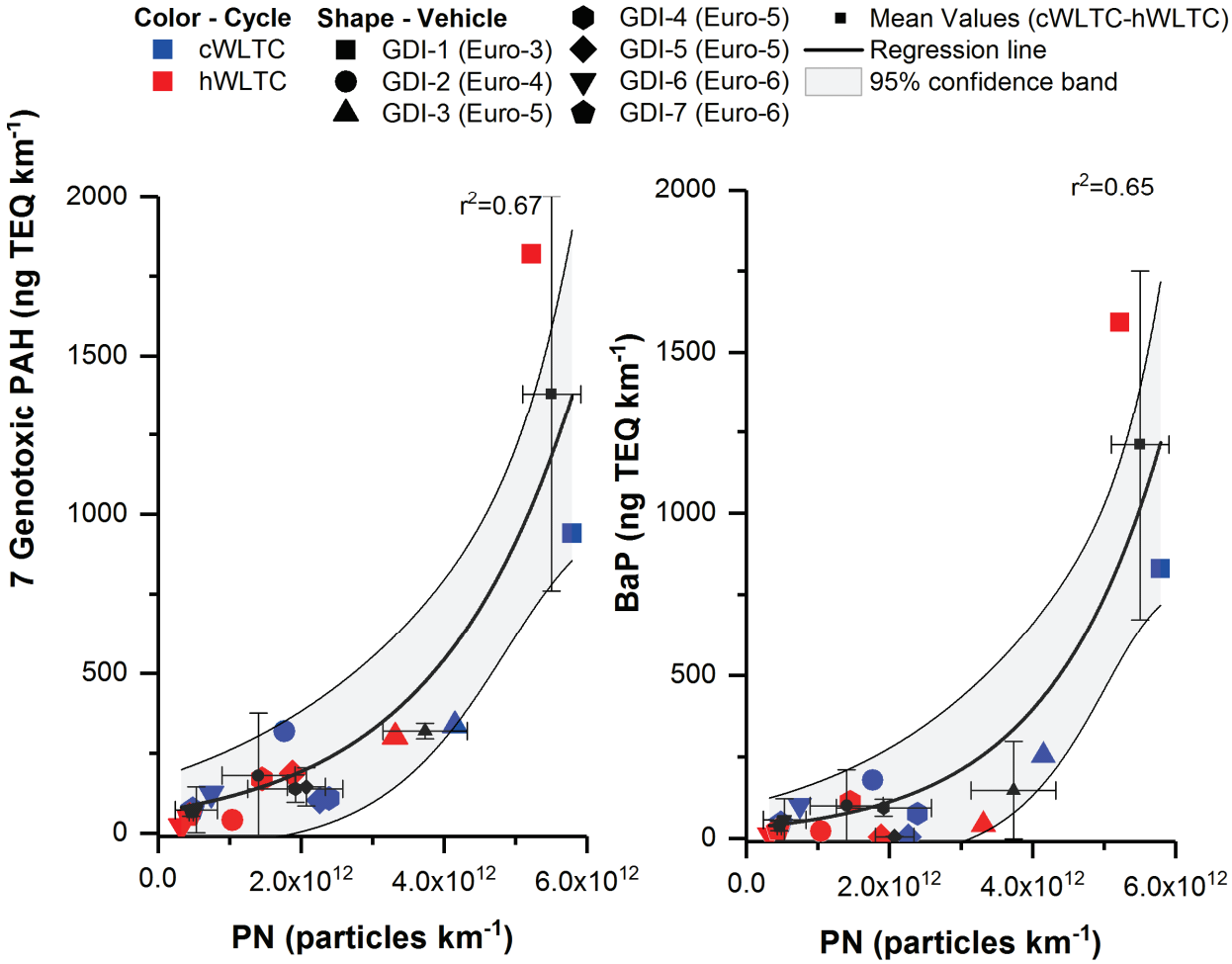


Fig. 8. Correlations of the sum of 7 genotoxic PAHs and benzo(a)pyrene (ng TEQ km^{-1}) and PN (particles km^{-1}) in the cold (blue) and hot WLTC (red) of the 7 GDI vehicles. Mean values of cold and hot WLTC for the individual vehicles are indicated in black with standard deviation bars. Exponential regression curves, uncertainties and r^2 values are also included.



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Highlights

1. GDI vehicles release substantial numbers of persistent soot-like nanoparticles.
2. PN emissions of GDI fleet were 60-700-fold higher than in the diesel vehicle with DPF.
3. PN and CO emissions increase up to three orders of magnitude during acceleration.
4. Genotoxic PAH emissions were 6-40-fold higher than in the diesel with DPF.
5. Inhalation of soot nanoparticles carrying genotoxic PAHs poses major health threat.