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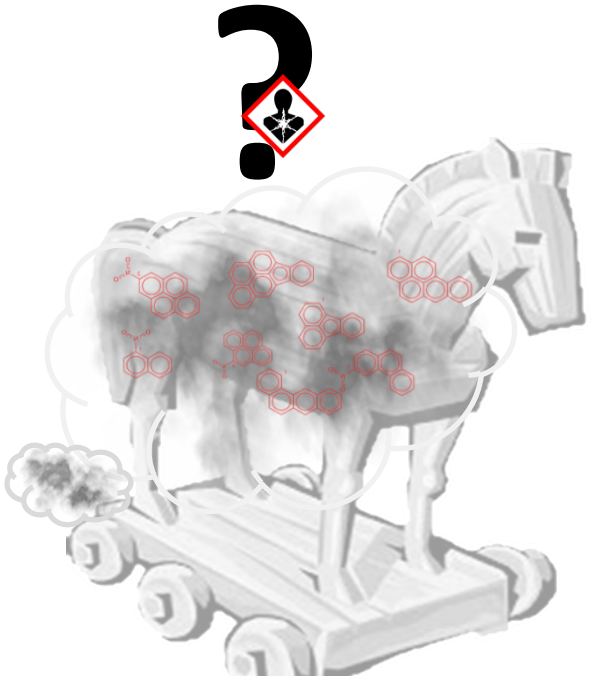
Materials Science and Technology

The co-release of genotoxic PAHs and nanoparticles from GDI vehicles supports the Trojan-horse effect



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Motivation and objectives

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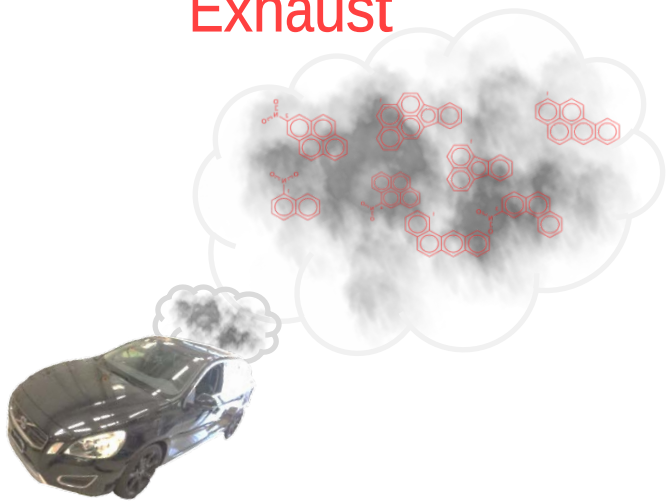
Gasoline Direct Injection Vehicle Exhaust



In our research, we observed:

- $2.5x10^{12}$ #/km GDI fleet (n=7)
- 430-460 ng TEQ PAHs/km
- Much higher than the diesel with DPF

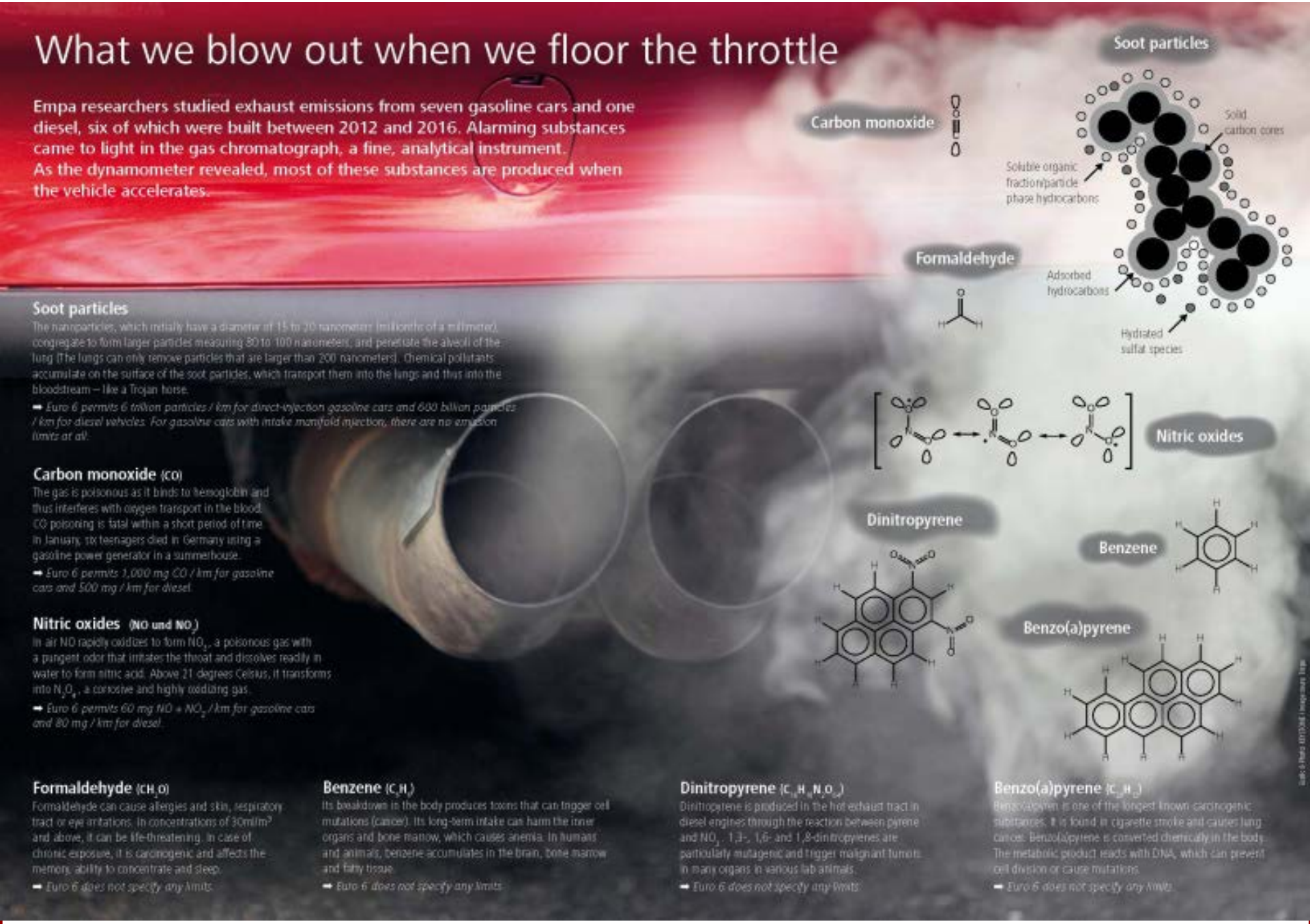
But……

Are PAHs co-released/formed with nanoparticles?

?

What we blow out when we floor the throttle

Empa researchers studied exhaust emissions from seven gasoline cars and one diesel, six of which were built between 2012 and 2016. Alarming substances came to light in the gas chromatograph, a fine, analytical instrument. As the dynamometer revealed, most of these substances are produced when the vehicle accelerates.



Soot particles

The nanoparticles, which initially have a diameter of 15 to 20 nanometers (millionths of a millimeter), congregate to form larger particles measuring 80 to 100 nanometers, and penetrate the alveoli of the lung (The lungs can only remove particles that are larger than 200 nanometers). Chemical pollutants accumulate on the surface of the soot particles, which transport them into the lungs and thus into the bloodstream – like a Trojan horse.

➡ *Euro 6 permits 6 trillion particles / km for direct-injection gasoline cars and 600 billion particles / km for diesel vehicles. For gasoline cars with intake manifold injection, there are no emission limits at all.*

Carbon monoxide (CO)

The gas is poisonous as it binds to hemoglobin and thus interferes with oxygen transport in the blood. CO poisoning is fatal within a short period of time. In January, six teenagers died in Germany using a gasoline power generator in a summerhouse.

➡ *Euro 6 permits 1,000 mg CO / km for gasoline cars and 500 mg / km for diesel.*

Nitric oxides (NO und NO_2)

In air NO rapidly oxidizes to form NO_2, a poisonous gas with a pungent odor that irritates the throat and dissolves readily in water to form nitric acid. Above 21 degrees Celsius, it transforms into N_2O_4, a corrosive and highly oxidizing gas.

➡ *Euro 6 permits 60 mg NO + NO_2 / km for gasoline cars and 80 mg / km for diesel.*

Formaldehyde (CH_2O)

Formaldehyde can cause allergies and skin, respiratory tract or eye irritations. In concentrations of 30ml/m³ and above, it can be life-threatening. In case of chronic exposure, it is carcinogenic and affects the memory, ability to concentrate and sleep.

➡ *Euro 6 does not specify any limits.*

Benzene (C_6H_6)

Its breakdown in the body produces toxins that can trigger cell mutations (cancer). Its long-term intake can harm the inner organs and bone marrow, which causes anemia. In humans and animals, benzene accumulates in the brain, bone marrow and fatty tissue.

➡ *Euro 6 does not specify any limits.*

Dinitropyrene ($C_{16}H_8N_2O_4$)

Dinitropyrene is produced in the hot exhaust tract in diesel engines through the reaction between pyrene and NO_2. 1,3-, 1,6- and 1,8-dinitropyrenes are particularly mutagenic and trigger malignant tumors in many organs in various lab animals.

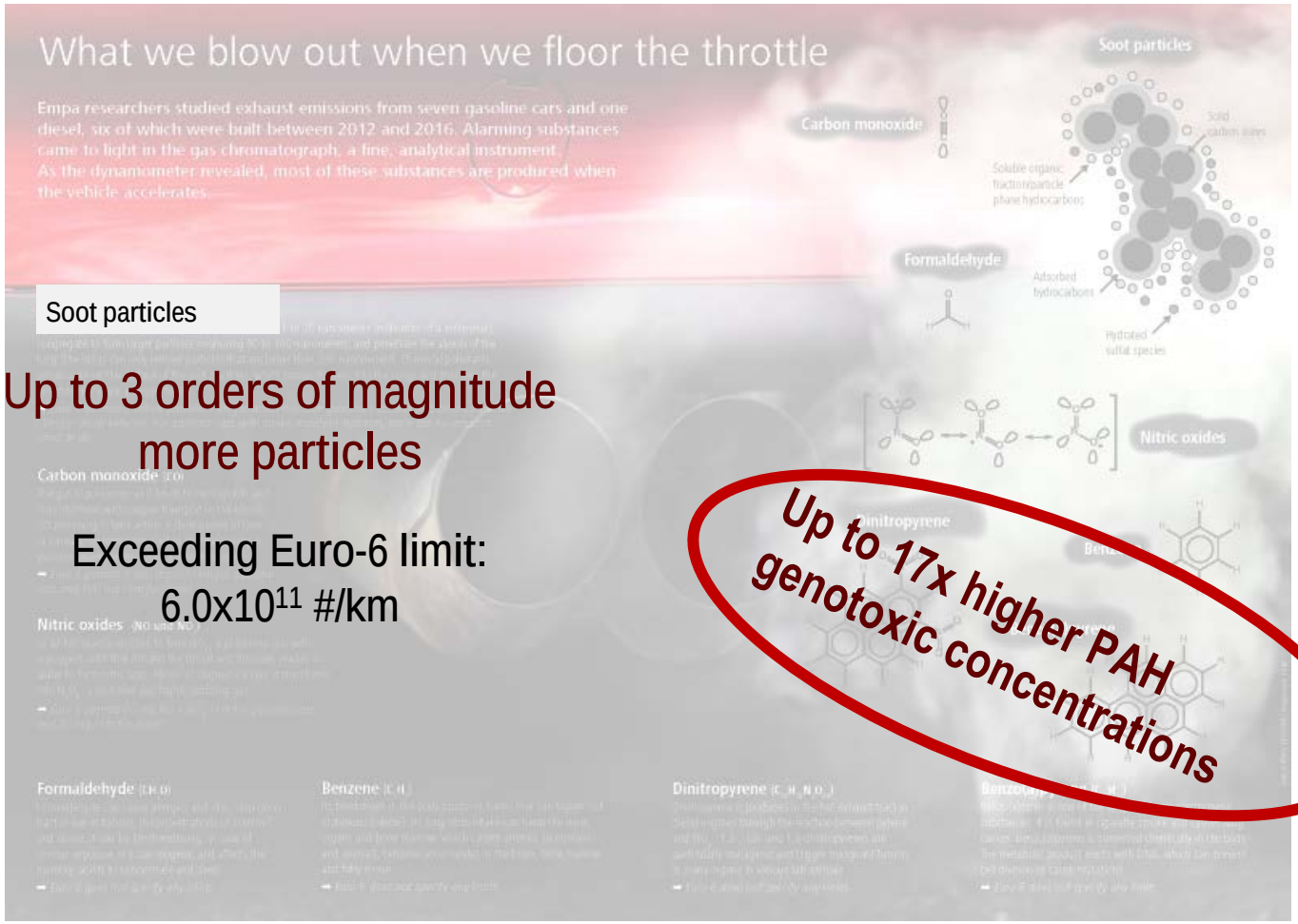
➡ *Euro 6 does not specify any limits.*

Benzo(a)pyrene ($C_{20}H_{12}$)

Benzo(a)pyren is one of the longest known carcinogenic substances. It is found in cigarette smoke and causes lung cancer. Benzo(a)pyrene is converted chemically in the body. The metabolic product reacts with DNA, which can prevent cell division or cause mutations.

➡ *Euro 6 does not specify any limits.*

In comparison with diesel…
GDI vehicles emit….



On the one hand, we have the PARTICLES

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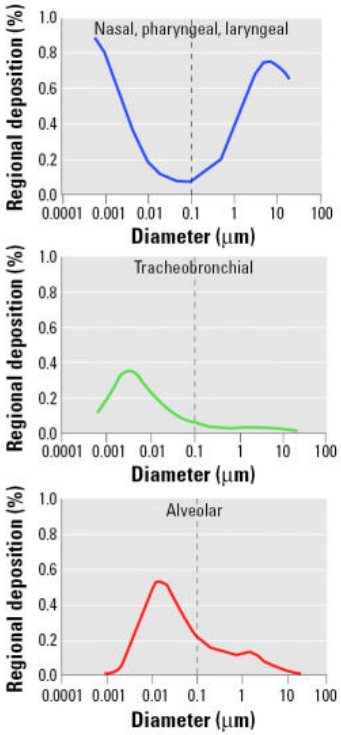
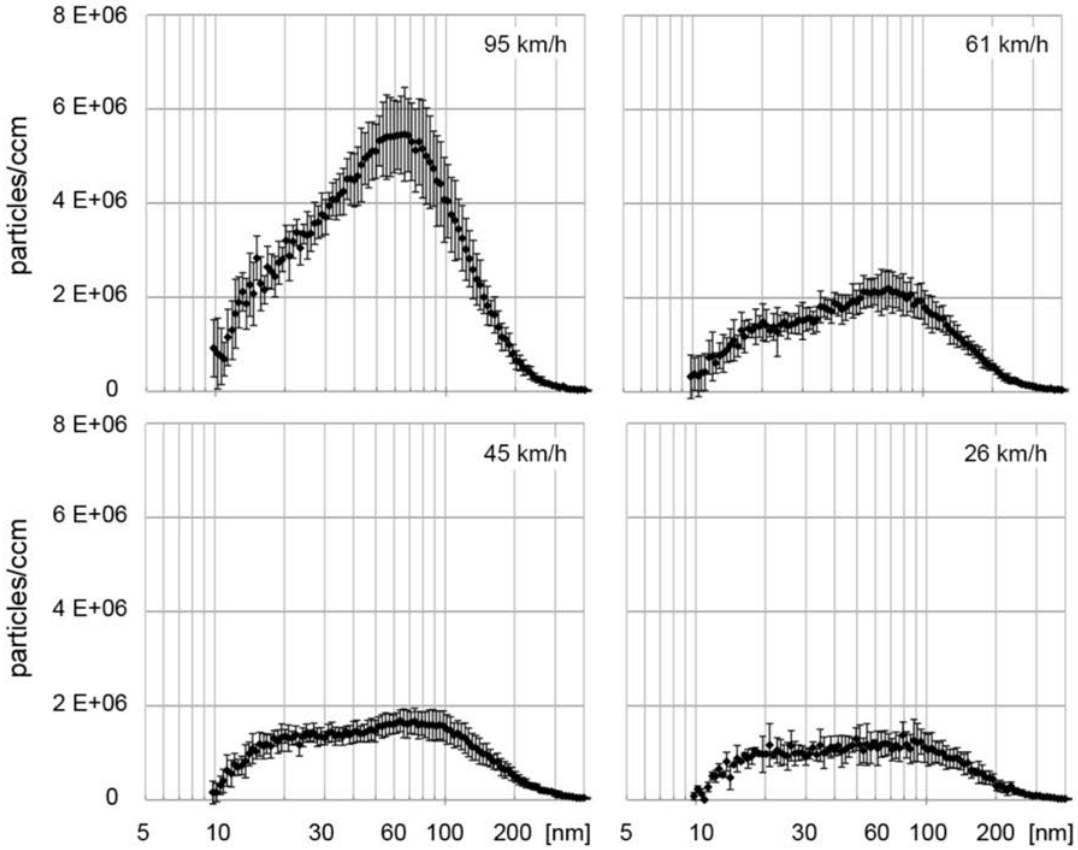


Regional deposition of particles in
(Sierra-Vargas et, 2012; International Commissi

From a tested GDI vehicle

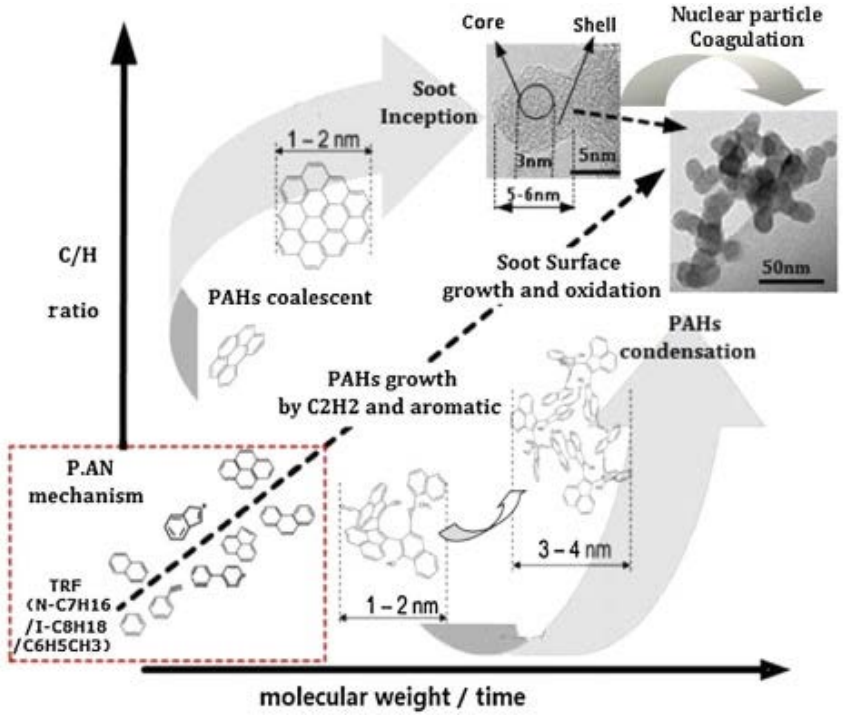


- Substantial contribution in the smallest particle size range, below 23 nm
- Sub-23 nm accounted for about 20 % in all velocities
- High proportion of particles entering the alveolar region??

Then, on the other hand…

We have PAHs ...

PAHs are genotc



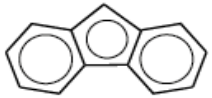
liates for soot formation

Yan-zhao An, Xiang Li, Sheng-ping Teng, Kun Wang, Yi-qiang Pei, Jing Qin, Hua Zhao,
Development of a soot particle model with PAHs as precursors through simulations and experiments, Fuel, Volume 179,2016

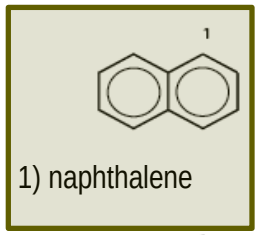
Focus on PAHs

AGENTS CLASSIFIED BY THE *IARC MONOGRAPHS*, VOLUMES 1–111

Group 1	*Carcinogenic to humans*	116 agents
Group 2A	*Probably carcinogenic to humans*	70
Group 2B	*Possibly carcinogenic to humans*	285
Group 3	*Not classifiable as to its carcinogenicity to humans*	506
Group 4	*Probably not carcinogenic to humans*	1



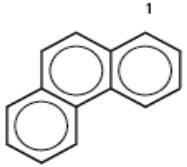
International Agency for Research on Cancer
World Health Organization

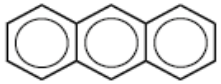

1) naphthalene

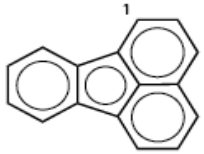

2) acenaphthylene

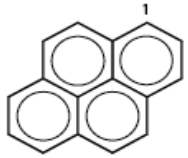

3) acenaphthene

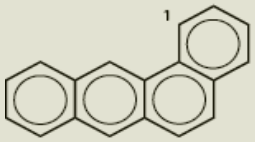
4) fluorene

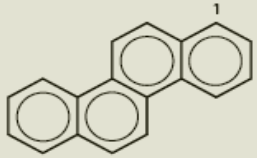

5) phenanthrene


6) anthracene

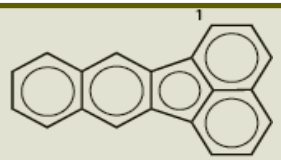

7) fluoranthene


8) pyrene

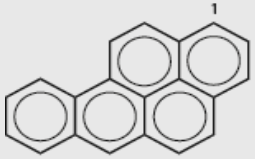

9) benzo(a)anthracene

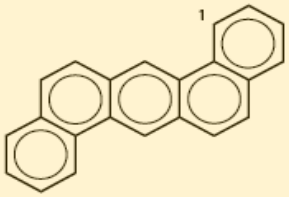

10) chrysene

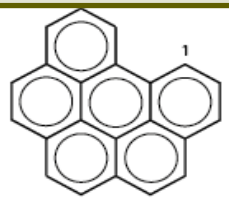

11) benzo[b]fluoranthene

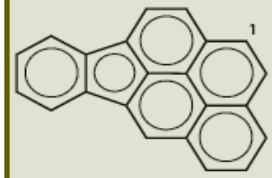

12) benzo[k]fluoranthene

↑ MW
↓ vapor pres. andsolubility


13) benzo[a]pyrene

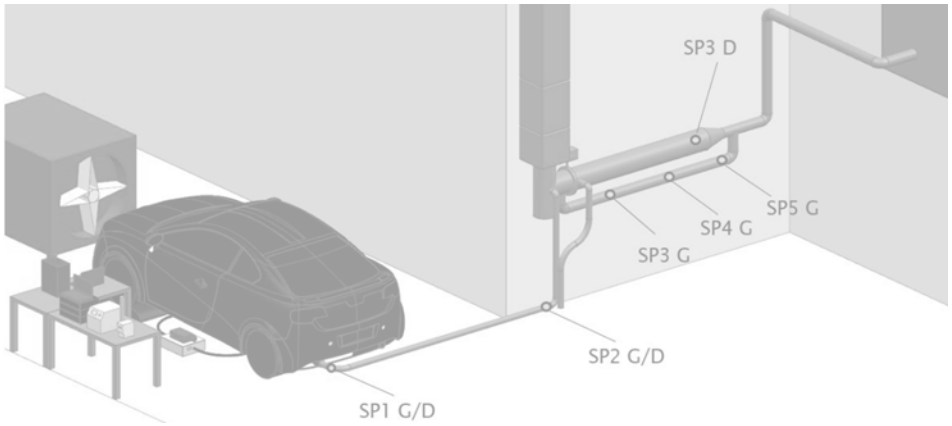

14) dibenz[ah]anthracene


15) benz[ghi]perylene


16) indeno(1,2,cd)pyrene

Group 1 Group 2A Group 2B

TESTS



GDI FLEET (n = 7)

Euro-3 Euro-4 Euro-5 Euro-6

GDI (n=7)
Direct injection

GASOLINE PARTICLE FILTERS

4 particle filters tested

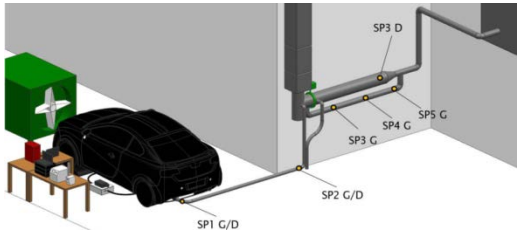
2 coated and 2 non-coated

REFERENCE VEHICLE
Euro 5

DIESEL BENCH MARK WITH DPF

Euro-5

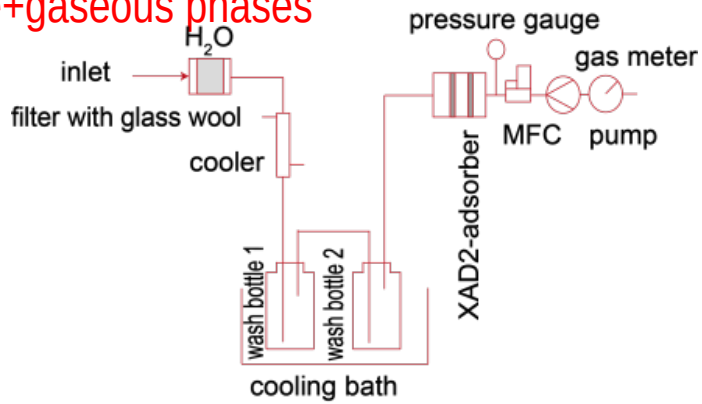
Sampling



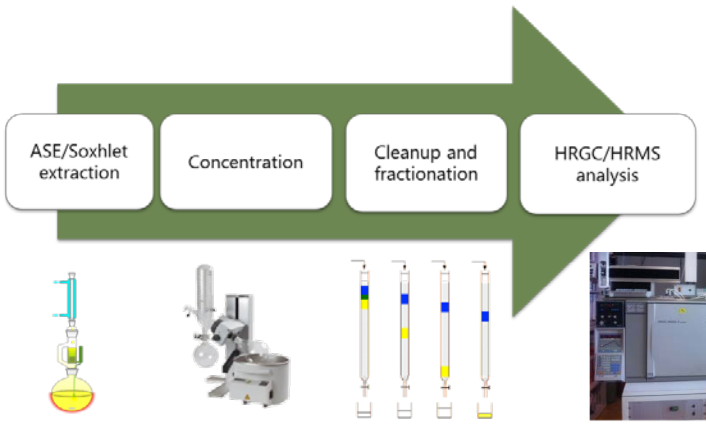
- Chassis dynamometer of the UASB
- 2 transient driving cycles (WLTC)
  - Cold and hot
- SSC
- Diluted exhaust --- CVS tunnel:

solid + condensed + gaseous phases

→ PAH particulate+gaseous phases

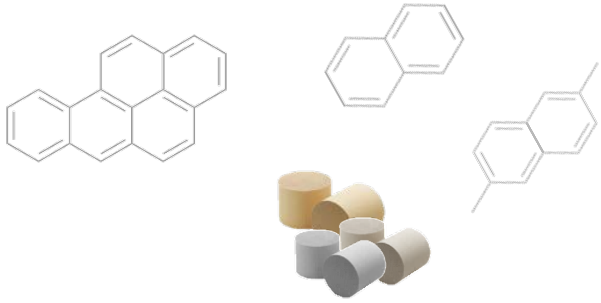


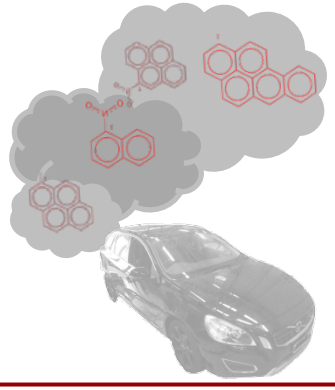
Laboratory analysis



R=120000

RESULTS





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Atmospheric Environment 178 (2018) 242–254

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

Maria Muñoz[a,*], Regula Haag[a], Peter Honegger[b], Kerstin Zeyer[b], Joachim Mohn[b], Pierre Comte[c], Jan Czerwinski[c], Norbert V. Heeb[a]

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Environmental Science & Technology

Article

pubs.acs.org/est

Bioethanol Blending Reduces Nanoparticle, PAH, and Alkyl- and Nitro-PAH Emissions and the Genotoxic Potential of Exhaust from a Gasoline Direct Injection Flex-Fuel Vehicle

Maria Muñoz,*[,†] Norbert V. Heeb,[†] Regula Haag,[†] Peter Honegger,[‡] Kerstin Zeyer,[‡] Joachim Mohn,[‡] Pierre Comte,[§] and Jan Czerwinski[§]

[†]Laboratory for Advanced Analytical Technologies and [‡]Laboratory for Air Pollution/Environmental Technology, EMPA, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland
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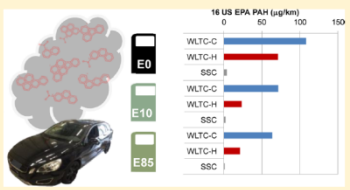
Supporting Information

ABSTRACT: Bioethanol as an alternative fuel is widely used as a substitute for gasoline and also in gasoline direct injection (GDI) vehicles, which are quickly replacing traditional port-fuel injection (PFI) vehicles. Better fuel efficiency and increased engine power are reported advantages of GDI vehicles. However, increased emissions of soot-like nanoparticles are also associated with GDI technology with yet unknown health impacts. In this study, we compare emissions of a flex-fuel Euro-5 GDI vehicle operated with gasoline (E0) and two ethanol/gasoline blends (E10 and E85) under transient and steady driving conditions and report effects on particle, polycyclic aromatic hydrocarbon (PAH), and alkyl-



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

Maria Muñoz[a], Regula Haag[a], Kerstin Zeyer[b], Joachim Mohn[b], Pierre Comte[c], Jan Czerwinski[c], Norbert V. Heeb[a].

Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Advanced Analytical Technologies[a], Laboratory for Air Pollution/Environmental Technology[b], Überlandstrasse 129, CH-8600 Dübendorf, Switzerland.UASB, University of Applied Sciences Bern[c], Laboratory for Exhaust Emission Control, Gwerdtstrasse 5, CH-2560 Nidau, Switzerland.

Submitted to ES&T (June 2018)

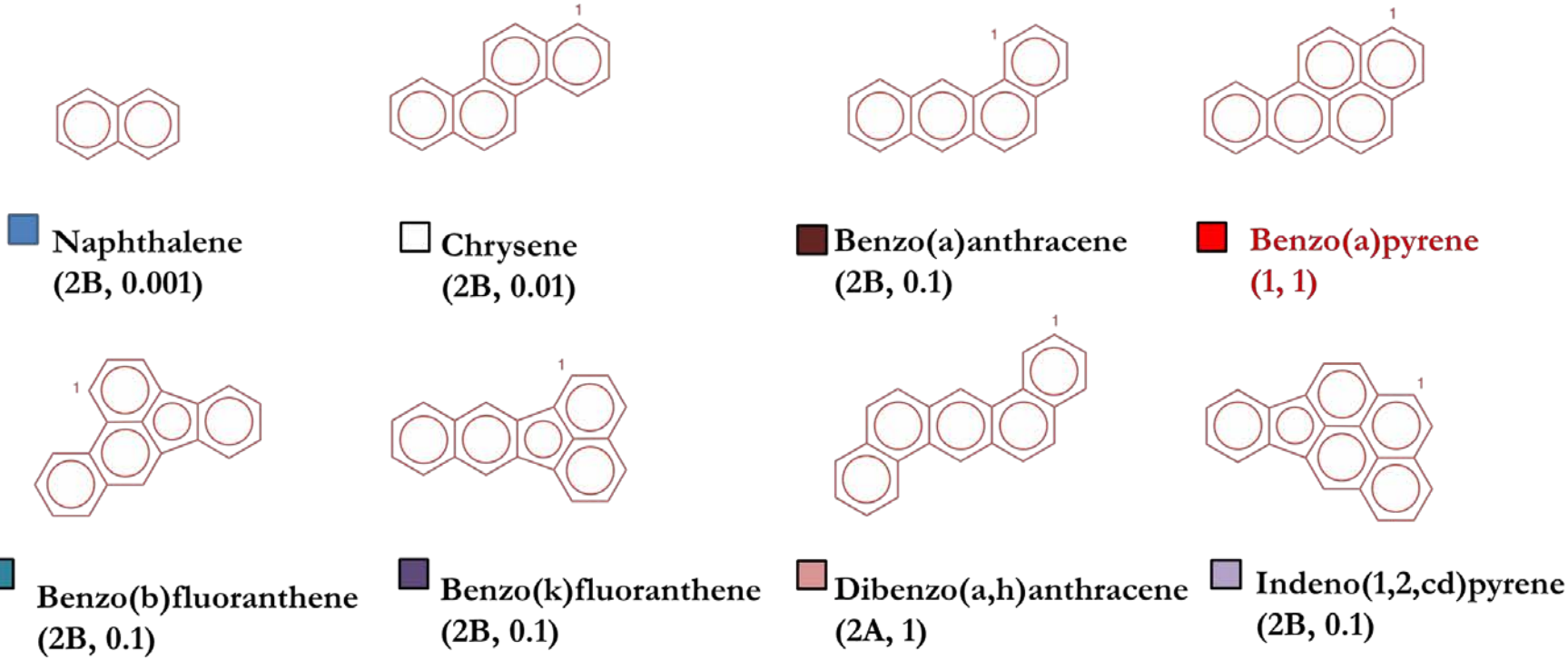
Gasoline (GDI) vs Diesel with DPF

Data reported in ng TEQ/m^3

TEF X C(ng/Nm^3)

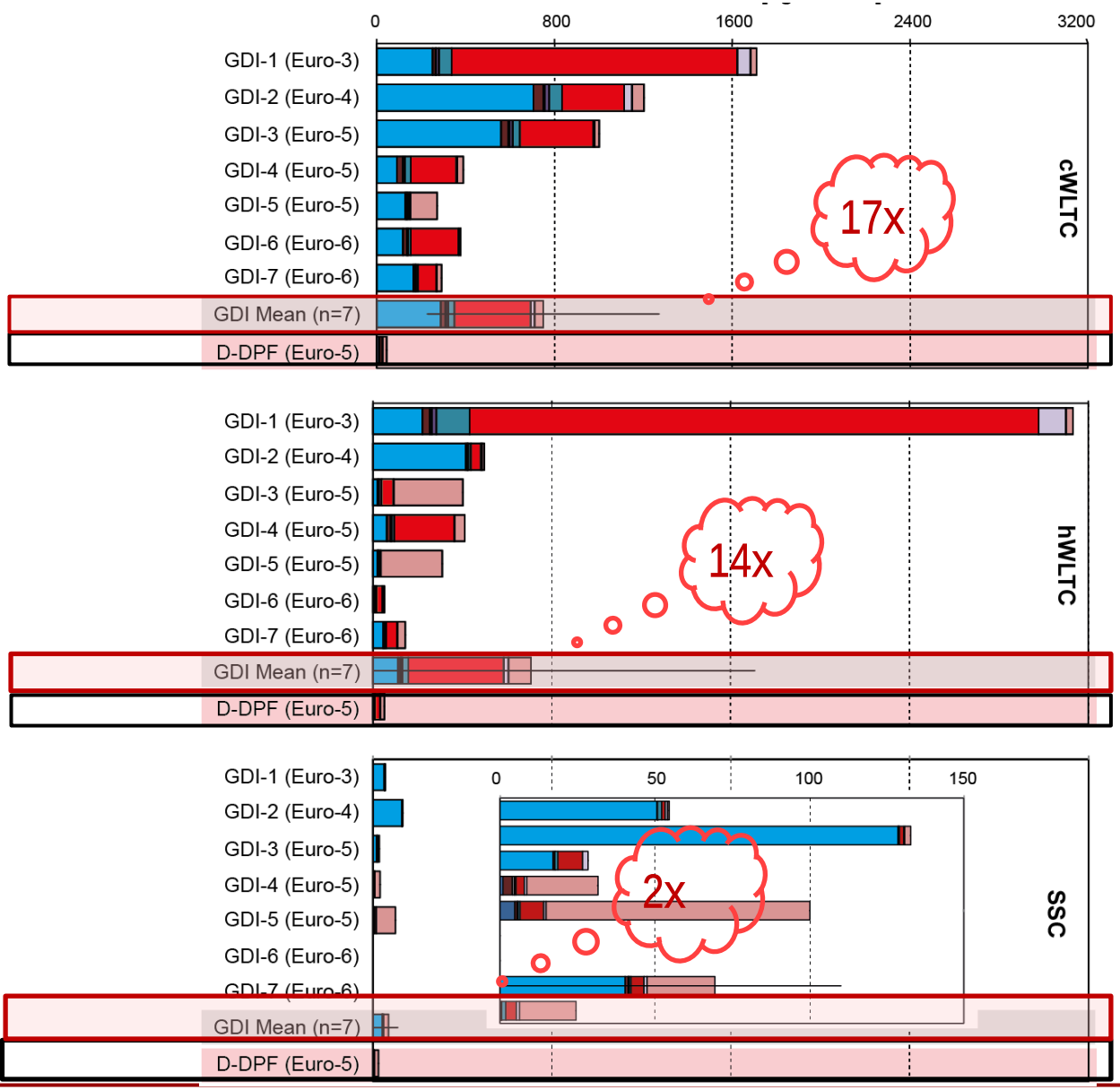
Toxic equivalency concentration (ng TEQ/m^3)

TEF: Toxic Equivalent Factor



Chemical structures and names of the 8 genotoxic PAHs. IARC carcinogenic group and TEFs are indicated in brackets according to I.C. Nisbeth, P.K.L. Regul Toxic Pharmacol. 16:290-300; 1992.

Gasoline vs Diesel-DPF emissions (ng TEQ/m^3, 8 genotox PAHs)



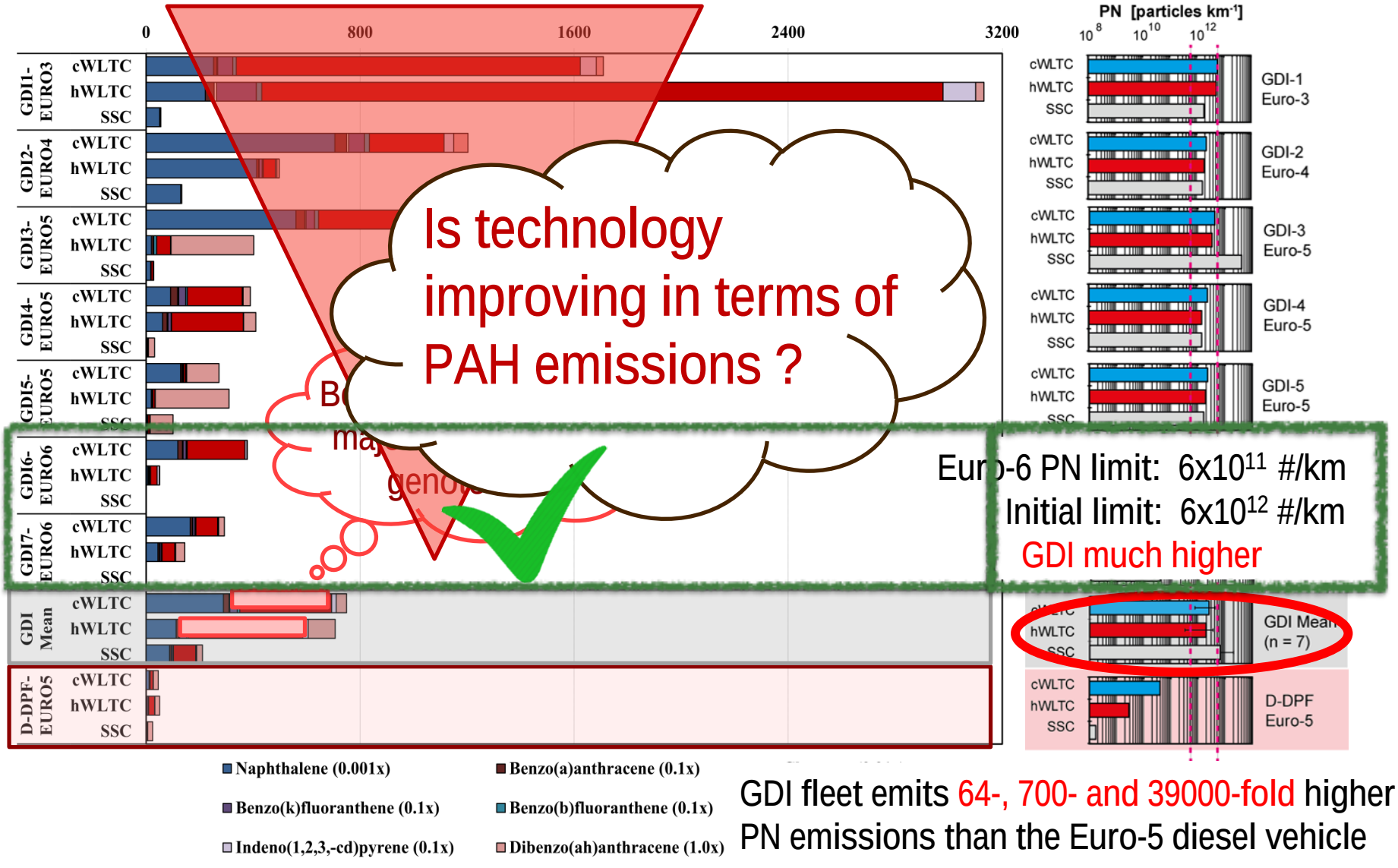
Transient

Oldest technologies

Steady state

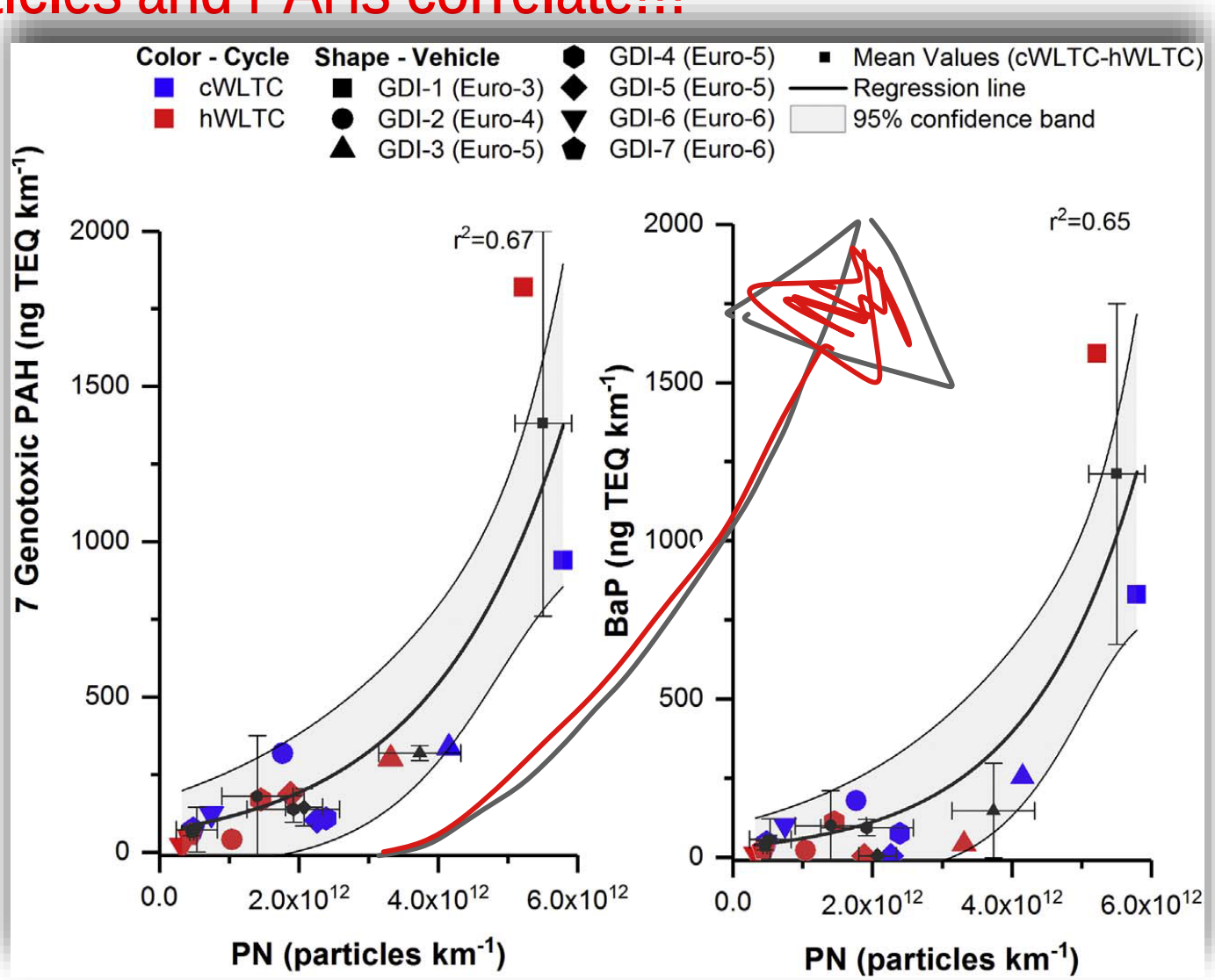
Newest technologies

Lowest emitter (PN and PAHs) → newest technology (Euro 6)



GDI fleet emits 64-, 700- and 39000-fold higher PN emissions than the Euro-5 diesel vehicle

Particles and PAHs correlate!!!



Muñoz, M., R. Haag, P. Honegger, K. Zeyer, J. Mohn, P. Comte, J. Czerwinsk and N. V. Heeb (2018). "Co-formation and co-release of genotoxic PAHs, alkyl-PAHs and soot nanoparticles from gasoline direct injection vehicles." Atmospheric Environment.

Solutions are needed to lower emissions…
at least to diesel with DPF levels

Aftertreatment:

Prototype GPFs → BAT FILTERS ??

GDI with GPF

Euro-5 REF Vehicle

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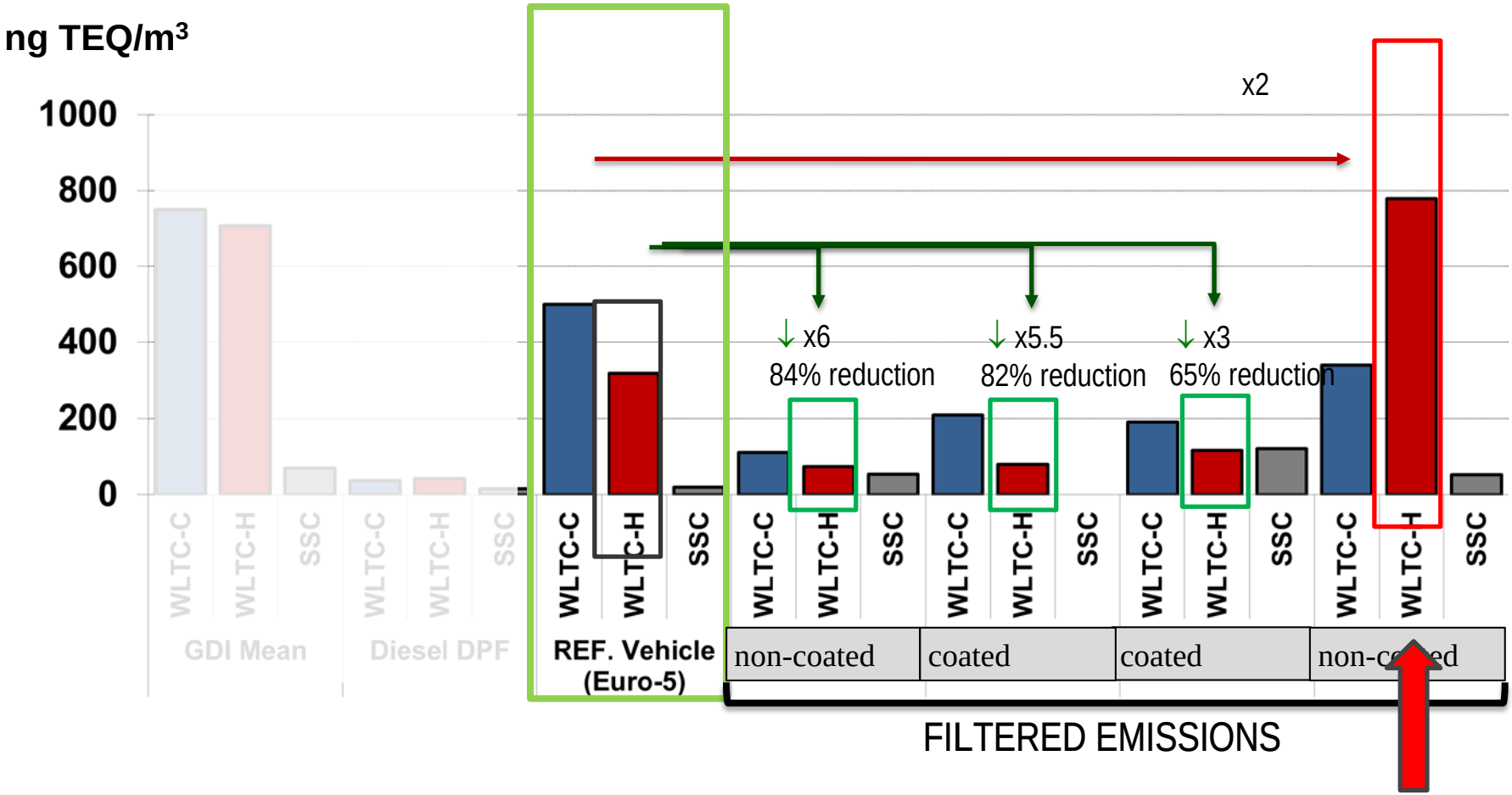
2 coated + 2 non-coated filters



Storage / Release ?

GDI with GPF vs Diesel with DPF

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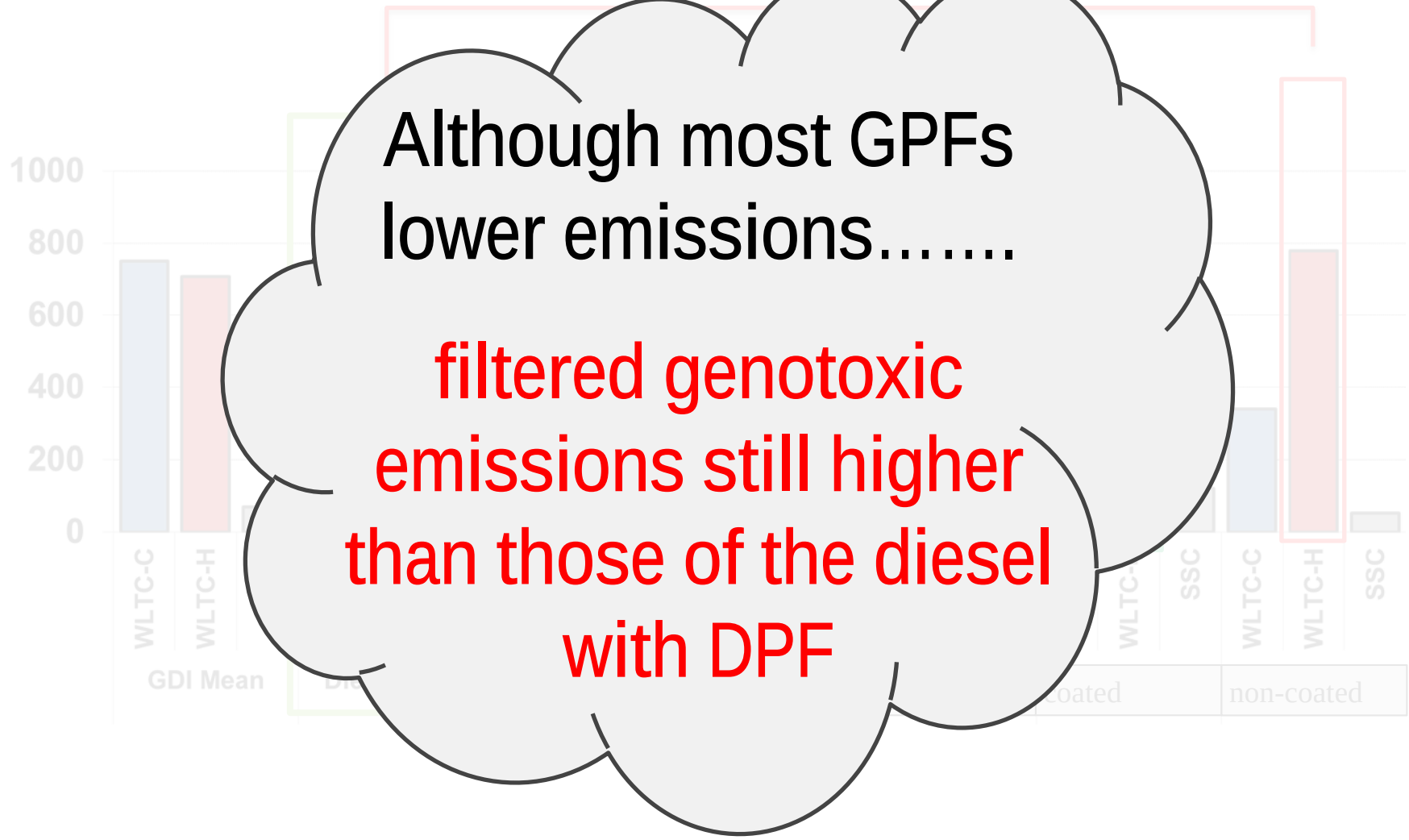
FILTERS: 2 coated + 2 non-coated



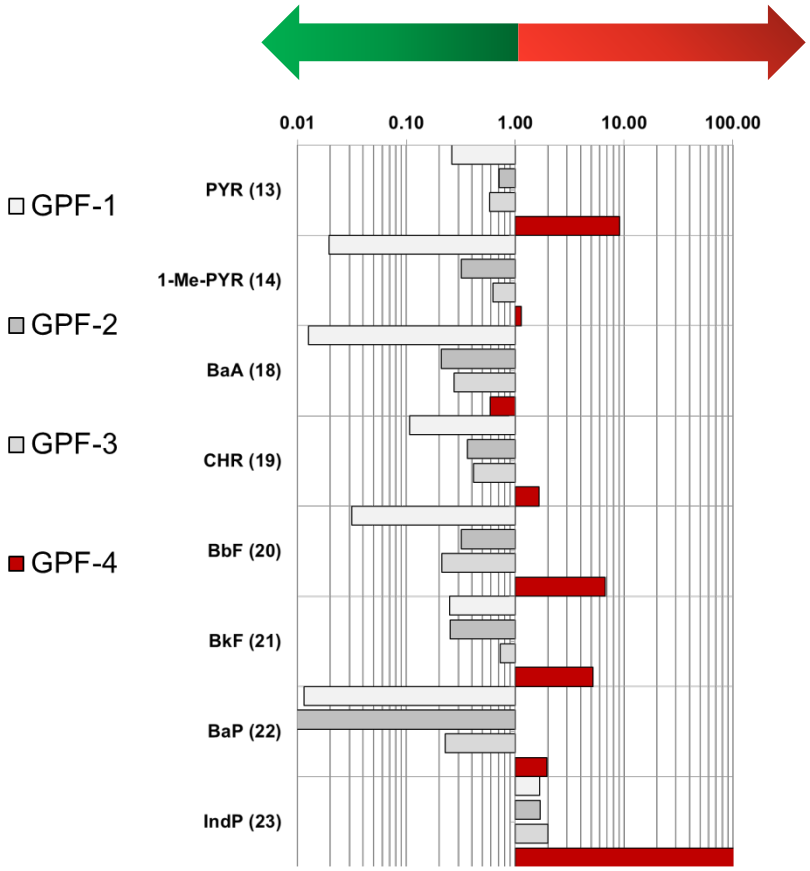
Best filter

GPF-1: 75-99%

GPF-2 and -3: 20-90%

Worse filter

GPF-4: 2-100x increase



COATED: 2 and 3

Genotoxic compounds reduced

86% GPF-1

82% GPF-2

65% GPF-3

For individual PAHs

20-99% with most around 60-75%

However, GPF need to improve…..

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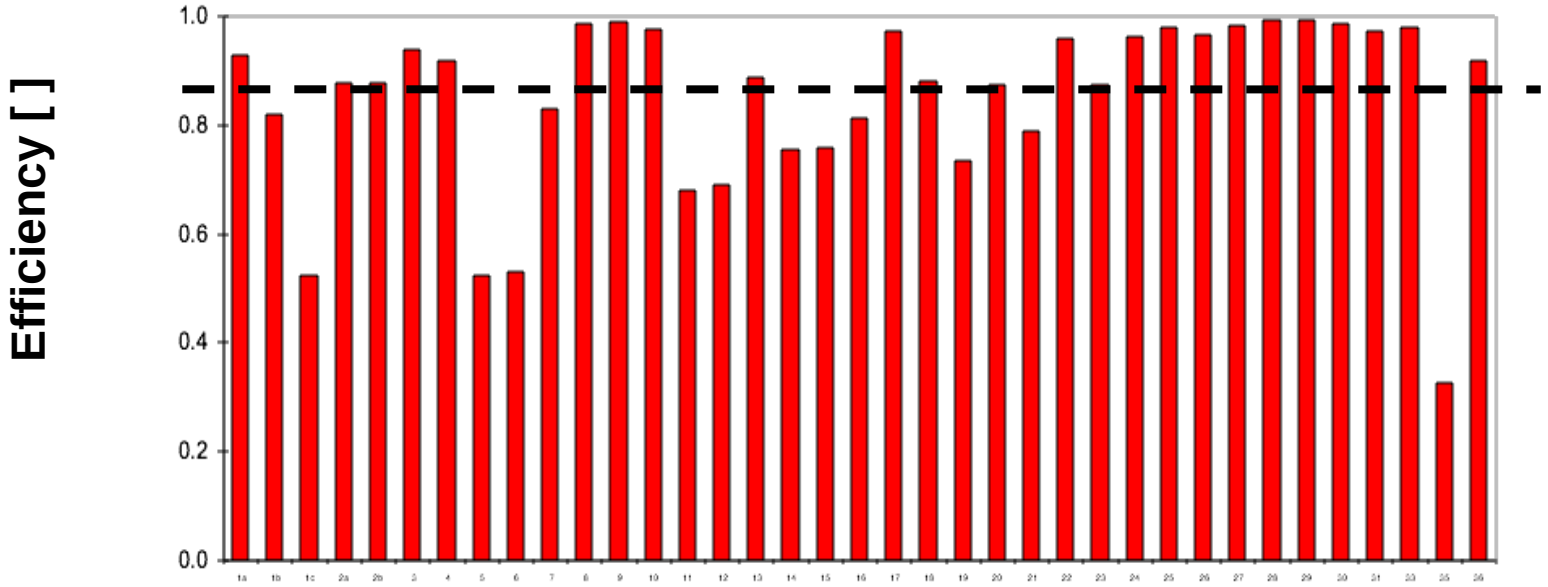
Most DPFs converted 80%

Genotoxic compounds reduced
86% GPF-1
82% GPF-2 (coated)
65% GPF-3 (coated)
0% GPF-4

For individual PAHs
20-99% with most around 60-75%

Conversion of carcinogenic PAHs with DPFs



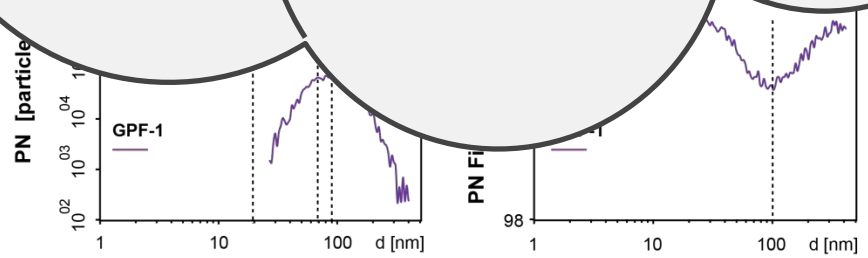
Most > 80%

GPF-1 → highest efficiency, lowest PN

cy, worse filter

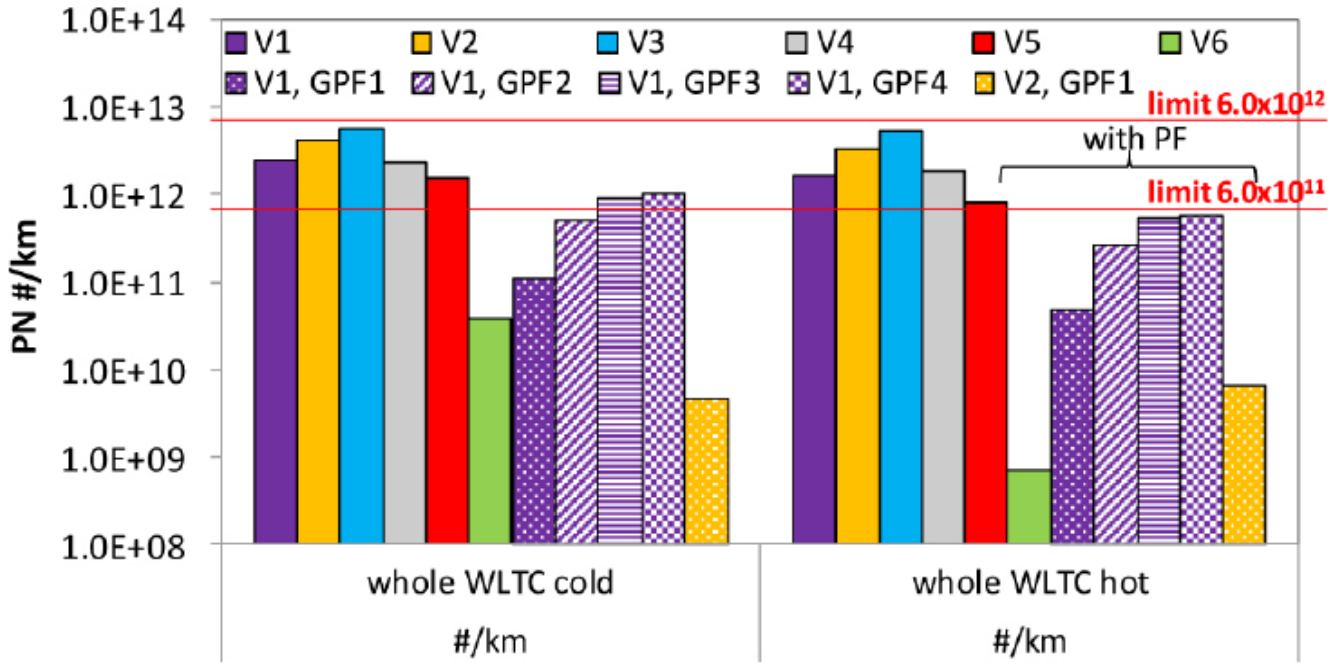
PN results are in accordance with PAH results

Particles and PAHs seem to correlate even with GPFs!!!



Munoz et al. (submitted June 2018)

Newest technology (Euro-6) lowest emissions



Czerwinski, J., Comte, P., Heeb, N., Mayer, A. et al., "Nanoparticle Emissions of DI Gasoline Cars with/without GPF," SAE Technical Paper 2017-01-1004, 2017, doi:10.4271/2017-01-1004.

CONCLUSIONS / SUGGESTIONS

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PAHs are co-formed and co-released with particles

- The higher the PN, the higher the genotoxicity
- they may penetrate the alveoli, supporting Trojan Horse effect

- Toxic equivalent concentrations are several times higher in GDI (with and without filter) than in diesel with DPF.
- Newest technology (Euro-6) shows the lowest emissions of PN and PAH
- GPF-1 → best filter for PN and PAHs // GPF-4 → worse filter

GDI should be equipped with filters – May reduce PAH emissions (20-80%)

GPF should undergo certification procedures like DPF (VERT)

However, BAT filters not yet ready to eliminate genotoxic PAHs

- Efficient coating / Biofuels?

Thank you for your attention

Questions?