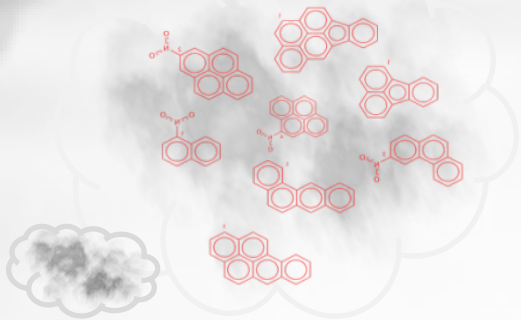
Comparison of genotoxic potentials of diesel and gasoline vehicles



Maria M[a]. Muñoz, R. Haag[a], K. Zeyer[b], J. Mohn[b], P. Comte[c], J. Czerwinski[c], N. Heeb[a]

Empa, Laboratory for Advanced Analytical Technologies[a], Laboratory for Air Pollution/Environmental Technology[b].

UASB Laboratory for Exhaust Emission Control[c]

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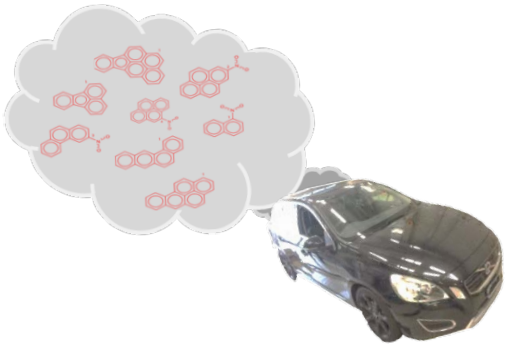
Empa, Dübendorf

Motivation and objectives

International Agency for Research on Cancer
World Health Organization

Miners study, Silverman et al. JNCI, 104(11), 2011

Gasoline Direct Injection



30% of EU fleet will be GDI in 2020

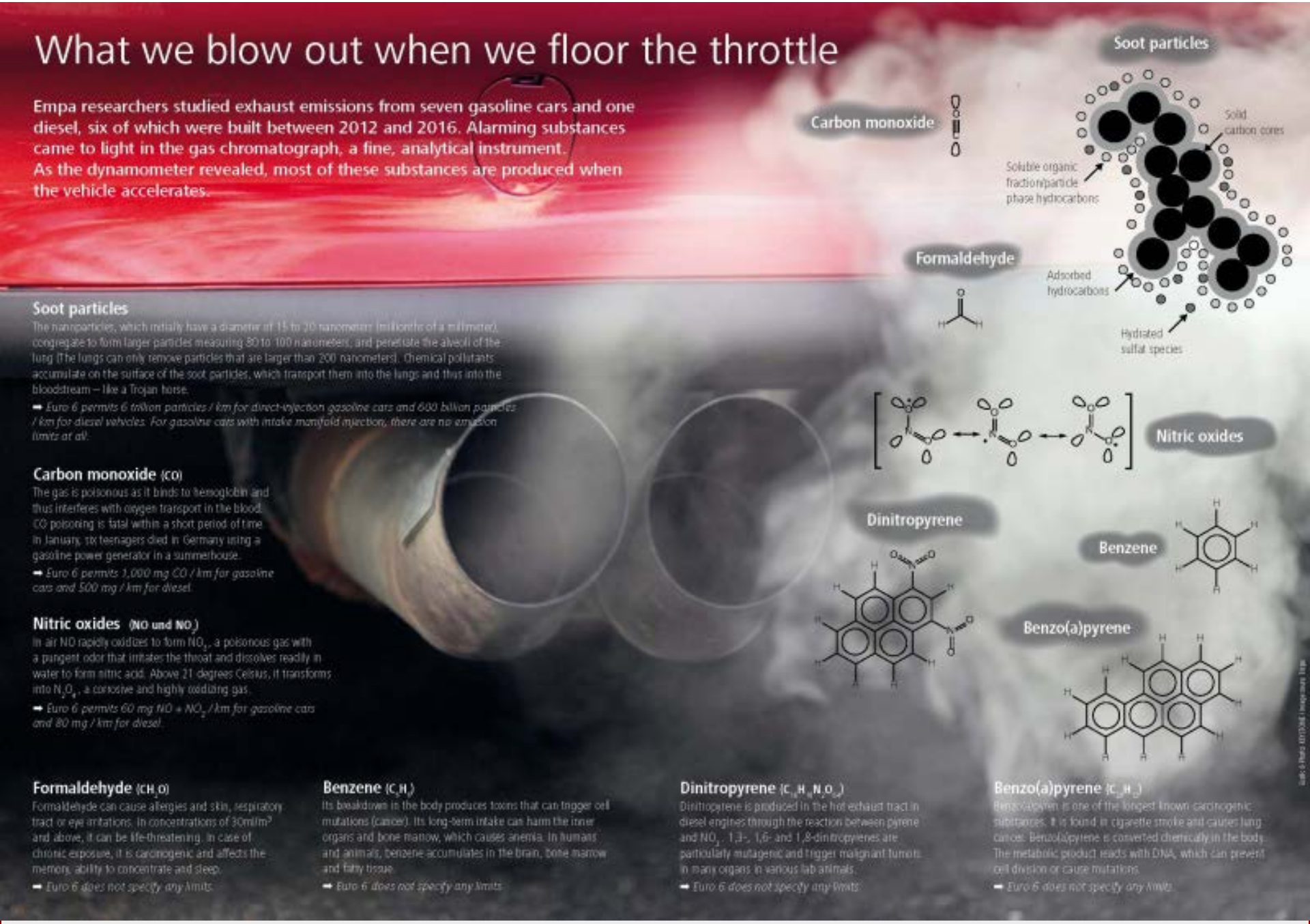
?

GDI vehicle exhaust vs diesel exhaust

Most genotoxic?

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.

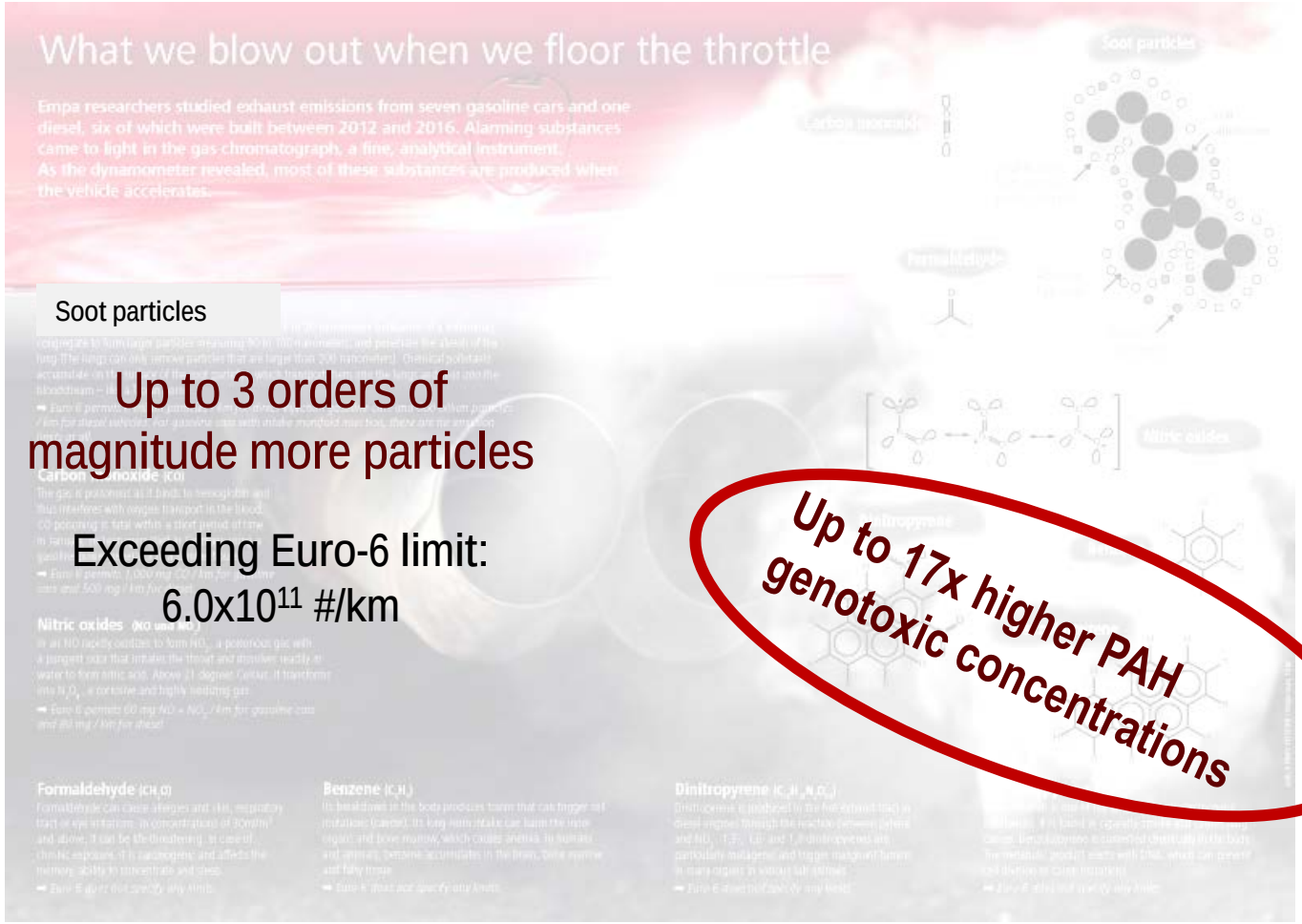
➡ *Euro 6 does not specify any limits.*

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.*

GDI exhaust in comparison with diesel….

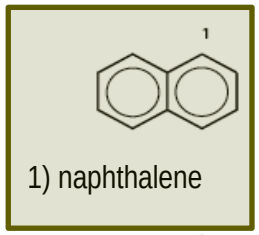


Focus on PAHs

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

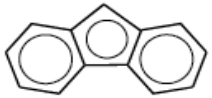
Group 1	*Carcinogenic to humans*	116 agents
Group 2A	*Probably carcinogenic to humans*	70
Group 2B	*Possibly carcinogenic to humans*	285
Group 3	*Not classifiable as to its carcinogenicity to humans*	506
Group 4	*Probably not carcinogenic to humans*	1

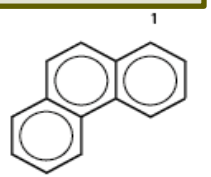
International Agency for Research on Cancer
World Health Organization

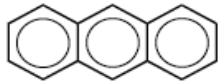

1) naphthalene

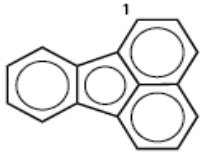

2) acenaphthylene

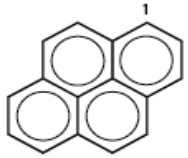

3) acenaphthene

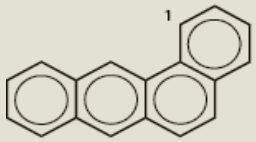

4) fluorene

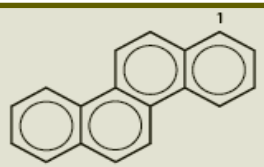

5) phenanthrene


6) anthracene

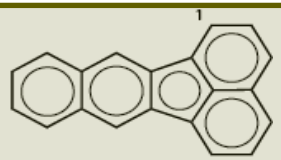

7) fluoranthene


8) pyrene

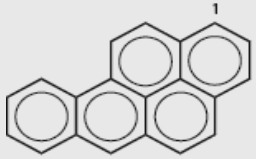

9) benzo(a)anthracene

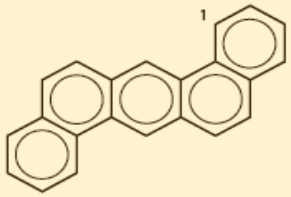

10) chrysene

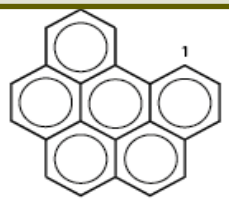

11) benzo[b]fluoranthene

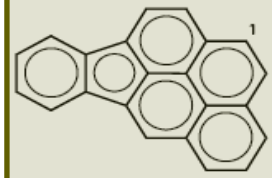

12) benzo[k]fluoranthene

↑ MW
↓ vapor pres.
andsolubility


13) benzo[a]pyrene


14) dibenz[ah]anthracene

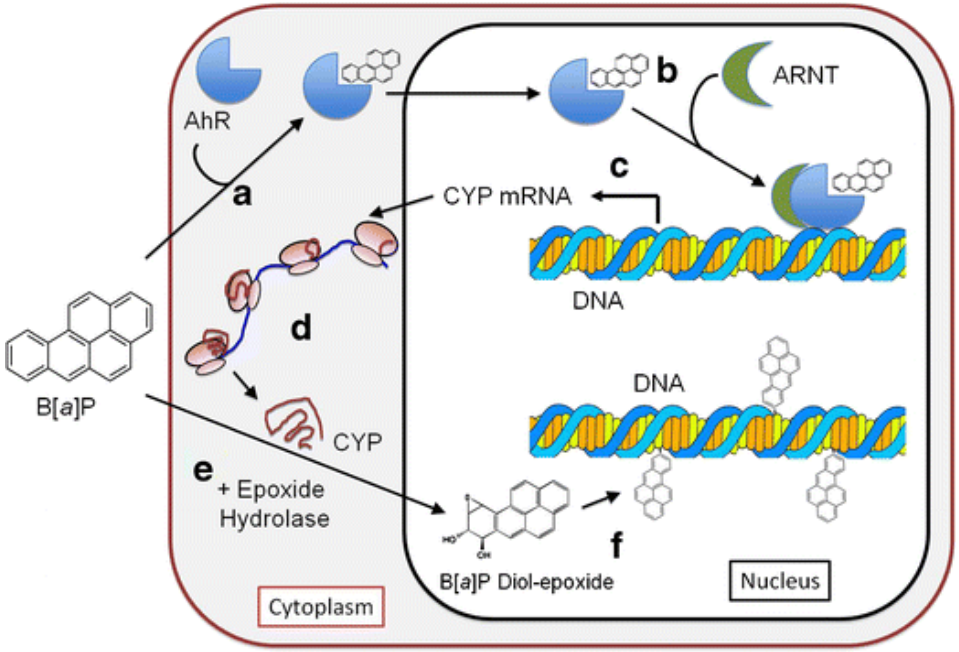

15) benz[ghi]perylene


16) indeno(1,2,cd)pyrene

Group 1 Group 2A Group 2B

Genotoxicity

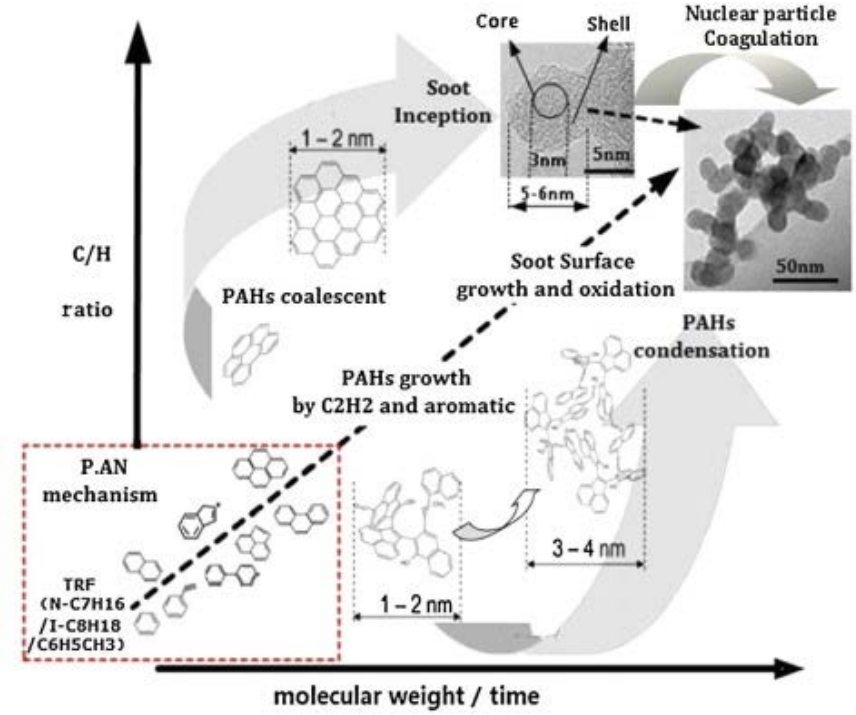
In genetics, genotoxicity describes the property of some chemical agents that damages the genetic information within cells causing mutations which may lead to cancer.



Most commonly accepted mechanism for PAHs metabolism and genotoxicity in a typical vertebrate cell (Mesquita, L. van Drooge et al. 2014)

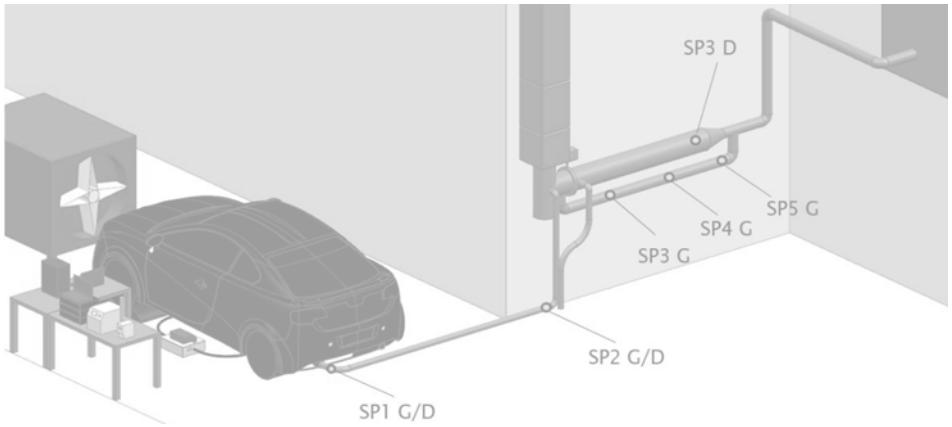
Apart from their genotoxicity…..

PAHs are also considered as intermediates 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

TESTS



GASOLINE VEHICLES

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

GDI (n=7) Direct injection

MPFI (n=1) Multipoint

GASOLINE PARTICLE FILTERS

4 particle filters tested

2 coated and 2 non-coated

REFERENCE VEHICLE
Euro 5

2 particle filters tested

1 coated and 1 non-coated

DIESEL BENCH MARK WITH DPF

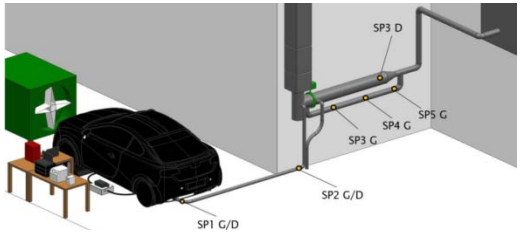
Euro-5

BIOFUELS

4 Ethanol and butanol blends

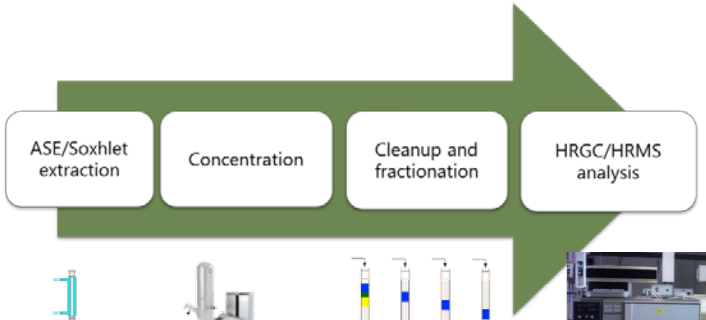
REFERENCE VEHICLE
Euro 5

Sampling



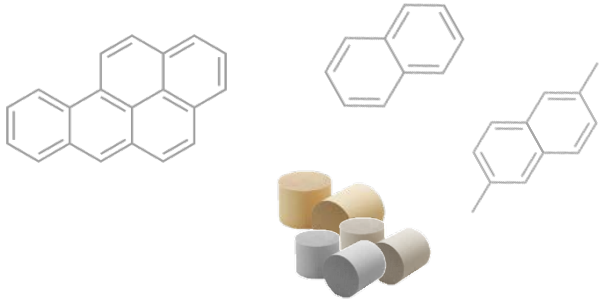
- Chassis dynamometer of the UASB in Nidau
- 2 transient driving cycles:
  - cWLTC and hWLTC)
- and SSC
- Diluted exhaust --- CVS tunnel:
  solid + condensed + gaseous phases
  → PAH particulate+gaseous phases

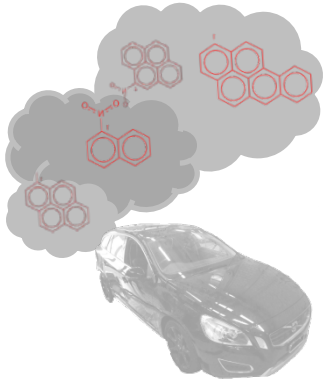
Laboratory analysis



R=120000

RESULTS





?

Environmental Science & Technology
Article
pubs.acs.org/est

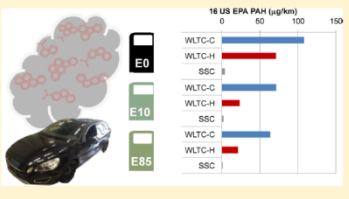
Bioethanol Blending Reduces Nanoparticle, PAH, and Alkyl- and Nitro-PAH Emissions and the Genotoxic Potential of Exhaust from a Gasoline Direct Injection Flex-Fuel Vehicle

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
[§]UASB, University of Applied Sciences Bern, Laboratory for Exhaust Emission Control, Gwerdtstrasse 5, CH-2560 Nidau, Switzerland

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-



Atmospheric Environment 178 (2018) 242–254
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journal homepage: www.elsevier.com/locate/atmosenv

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]

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

2018-01-0363

PN-Emissions of Gasoline Cars MPI and Potentials of GPF

J. Czerwinski, P. Comte, D. Engelmann, AFHB
N. Heeb, M. Muñoz, EMPA
P. Bonsack, BAFU
V. Hensel, A. Mayer, VERT Association

Abstract

Further efforts to reduce the air pollution from traffic are undertaken worldwide and the filtration of exhaust gas will also be increasingly applied on gasoline cars (GPF*) … gasoline particle filter).

the surface composition of the aerosol and have therefore a significant impact on health effects associated with pollution.

Studies for gasoline fueled internal combustion engines pointed out that also this vehicle class can emit remarkable amounts of particles, [13-16]. Especially gasoline direct injection technology (GDI) shows particle number (PN) emissions significantly higher than modern

SAE Technical Paper

Effect of coated and non-coated particle filters (GPFs) on nanoparticle and genotoxic emissions of a gasoline direct injection vehicle (GDI)

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.

To be submitted to ES&T

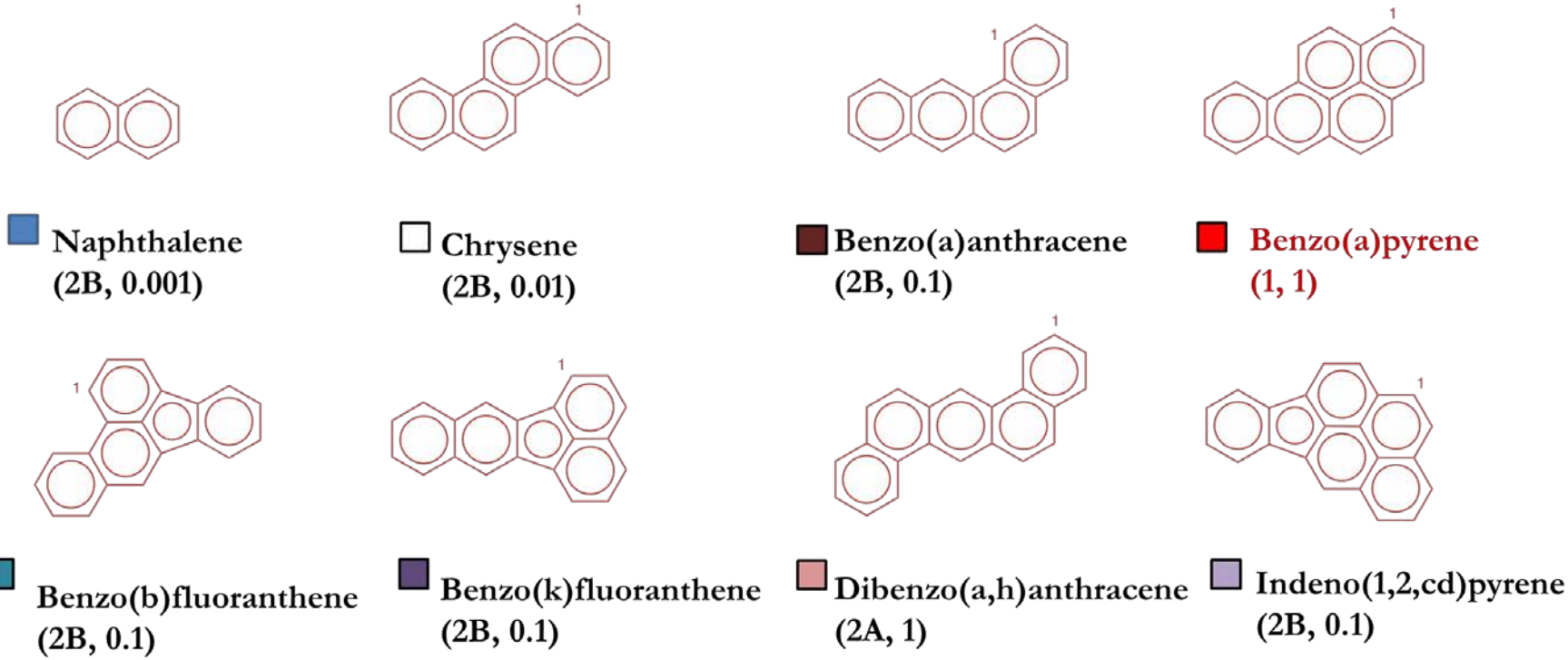
Gasoline (GDI + MPFI) vs Diesel with DPF

Data reported in ng TEQ/m^3

TEF X C(ng/Nm^3)

Toxic equivalency concentration (ng TEQ/m^3)

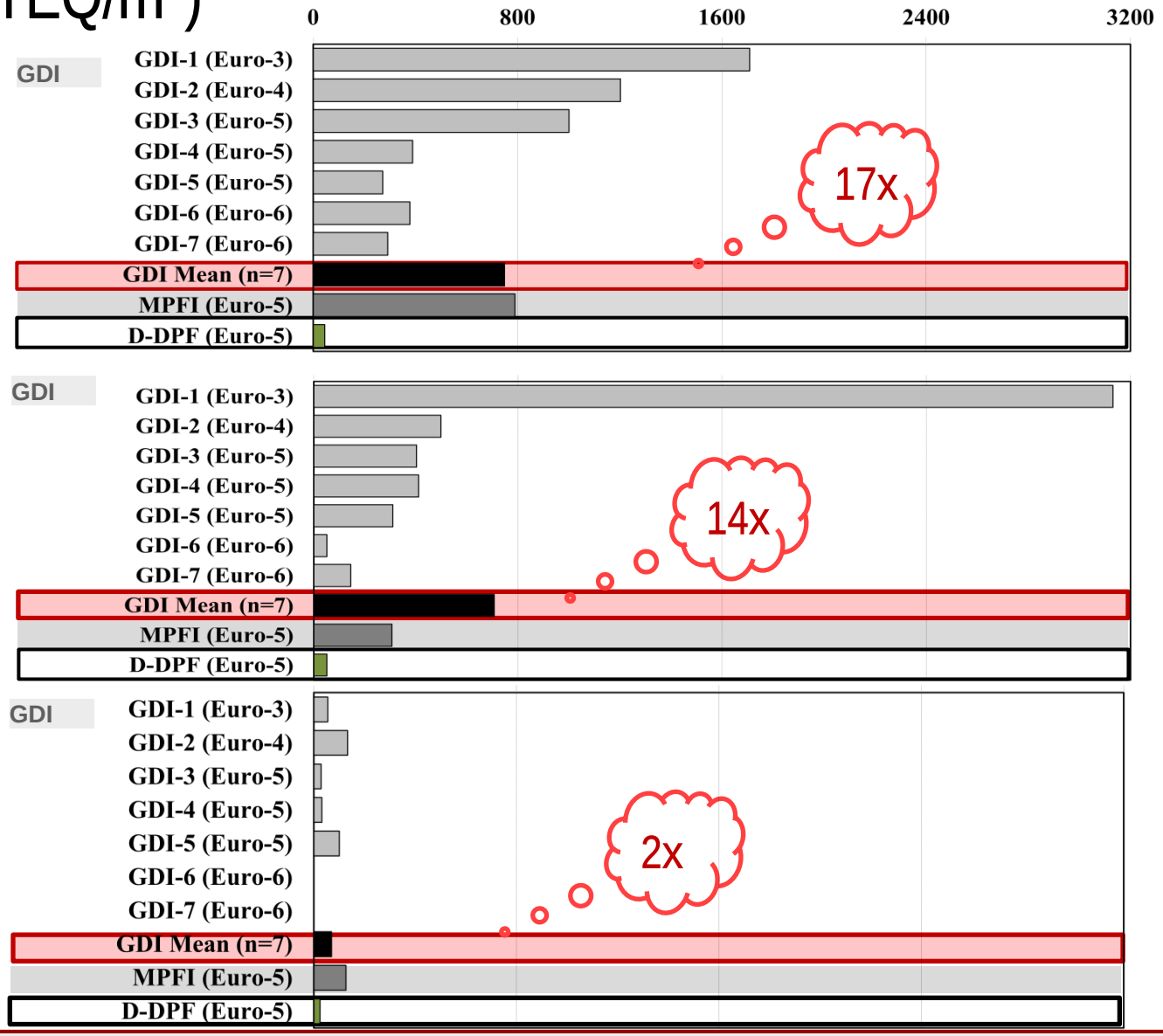
TEF: Toxic Equivalent Factor



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/m³)

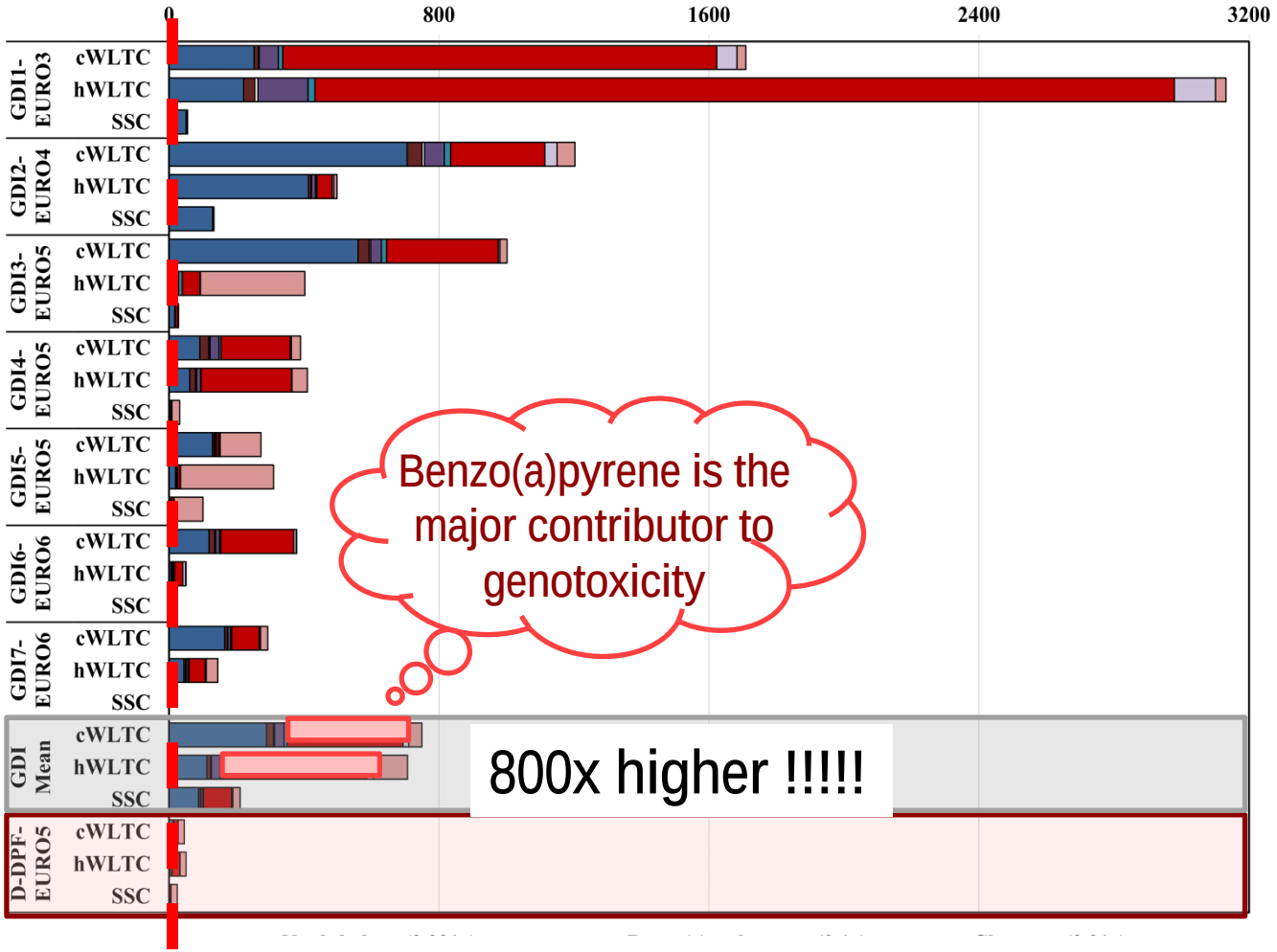
Sum of 8 genotoxic PAHs

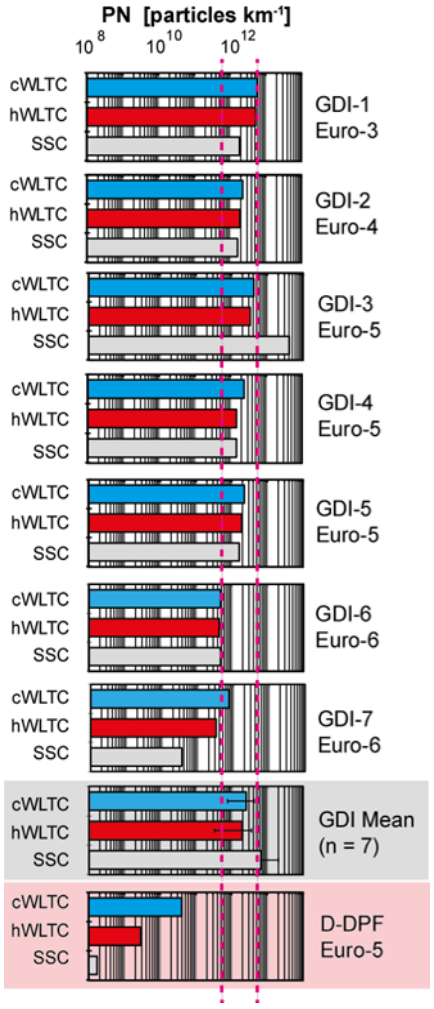


cWLTC

hWLTC

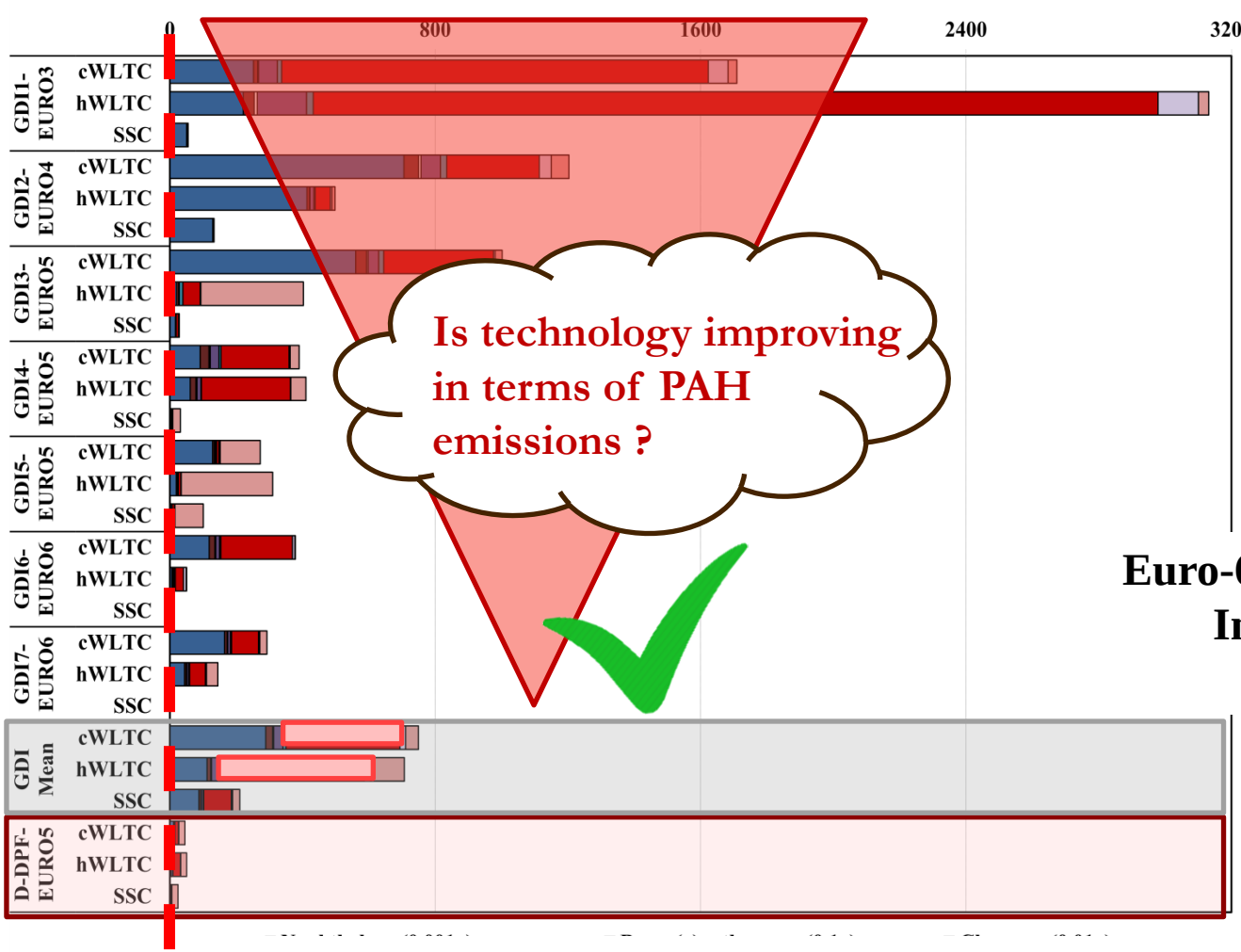
SSC

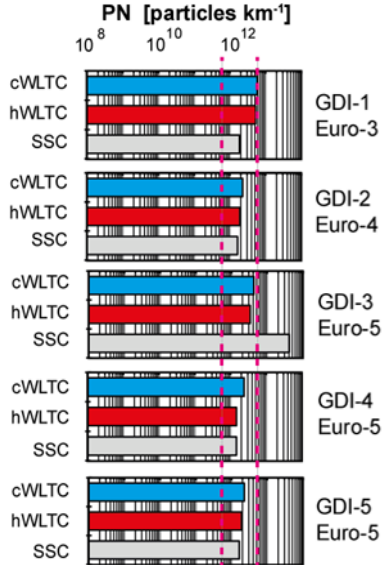




EU - air limit value:
1 ng/m^3 benzo(a)pyrene (2014/107/EC Directive)

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

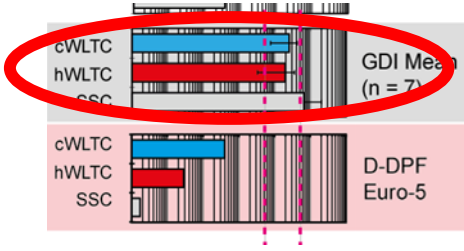




Euro-6 PN limit: $6x10^{11}$ #/km

Initial limit: $6x10^{12}$ #/km

GDI much higher



EU - air limit value:
1 ng/m^3 benzo(a)pyrene (2014/107/EC Directive)

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

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

Aftertreatment:

- Filters

Alternative fuels

- Oxygenated fuels

Empa
Materials Science and Technology

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

Aftertreatment

Filters

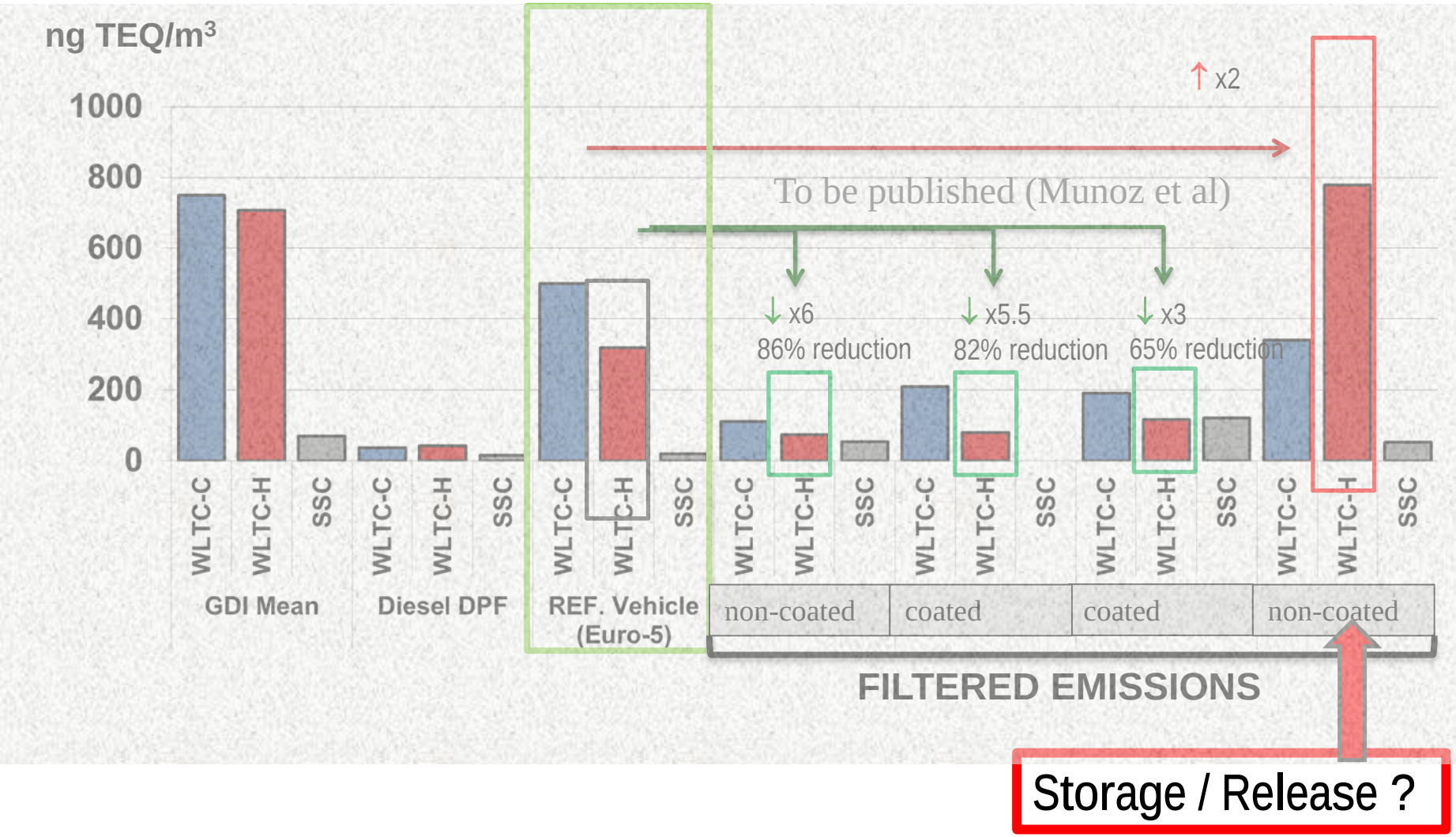
Alternative fuels

Oxygenated fuels

GDI with GPF

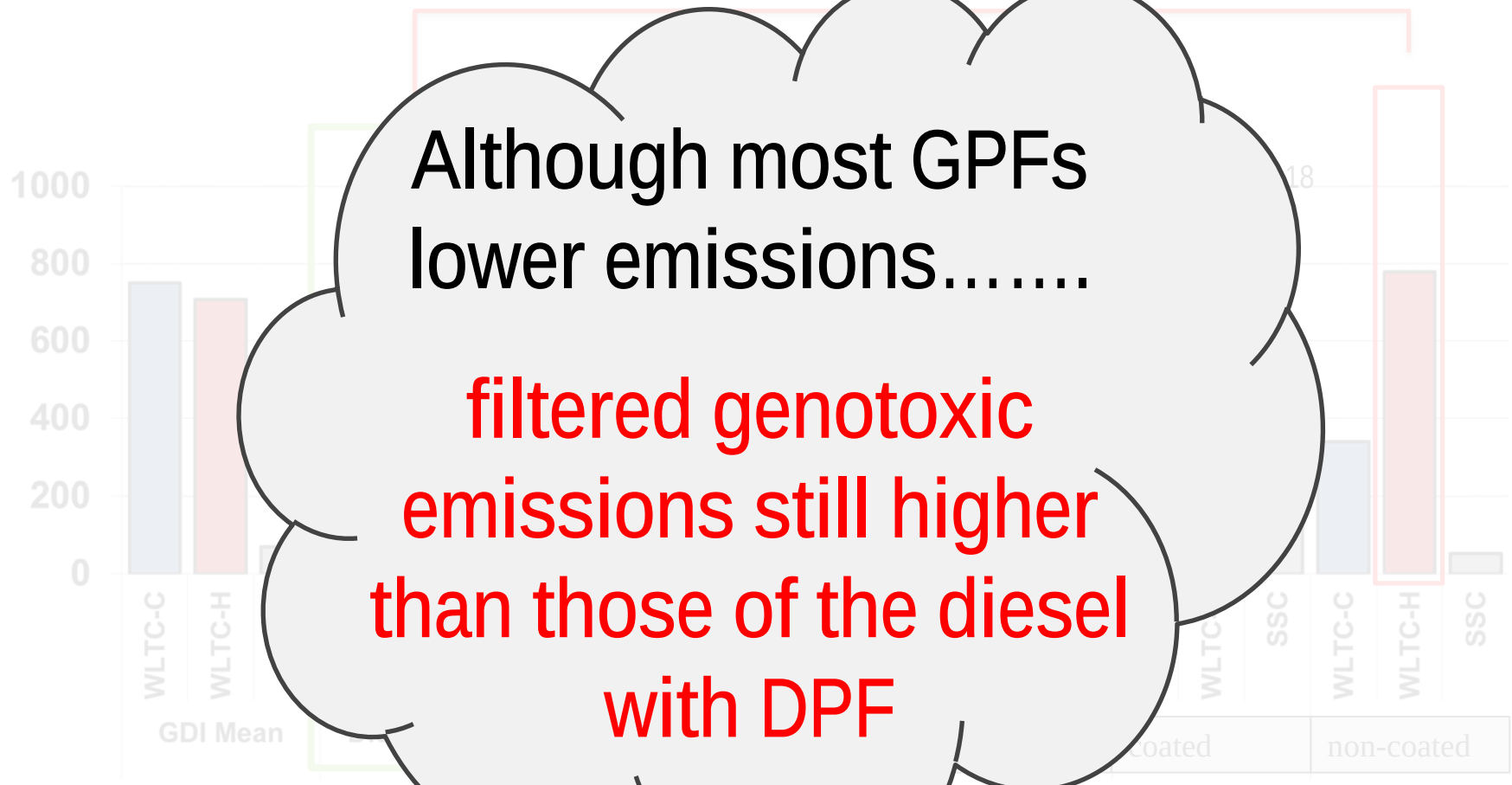
Euro-5 REF Vehicle

2 coated + 2 non-coated filters



GDI with GPF vs Diesel with DPF

FILTERS: 2 coated + 2 non-coated



Although most GPFs lower emissions…….

filtered genotoxic emissions still higher than those of the diesel with DPF

GPF need to improve…..

Genotoxic compounds reduced

86% GPF-1

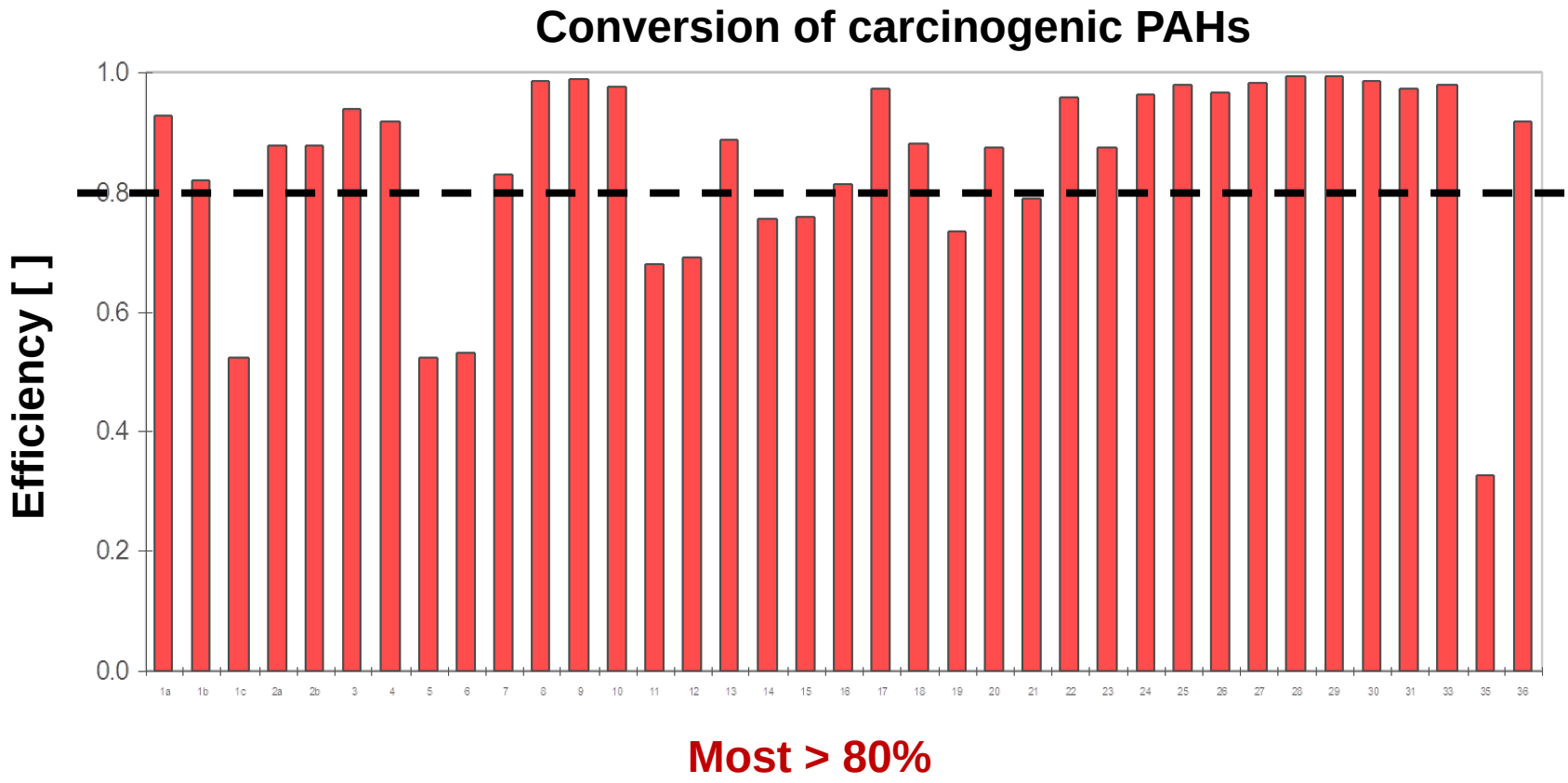
82% GPF-2 (coated)

65% GPF-3 (coated)

0% GPF-4

Likewise a DPF does:

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



Most > 80%

The benzo(a)pyrene example (less volatile, carcinogenic)

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Euro-5 GDI vehicle

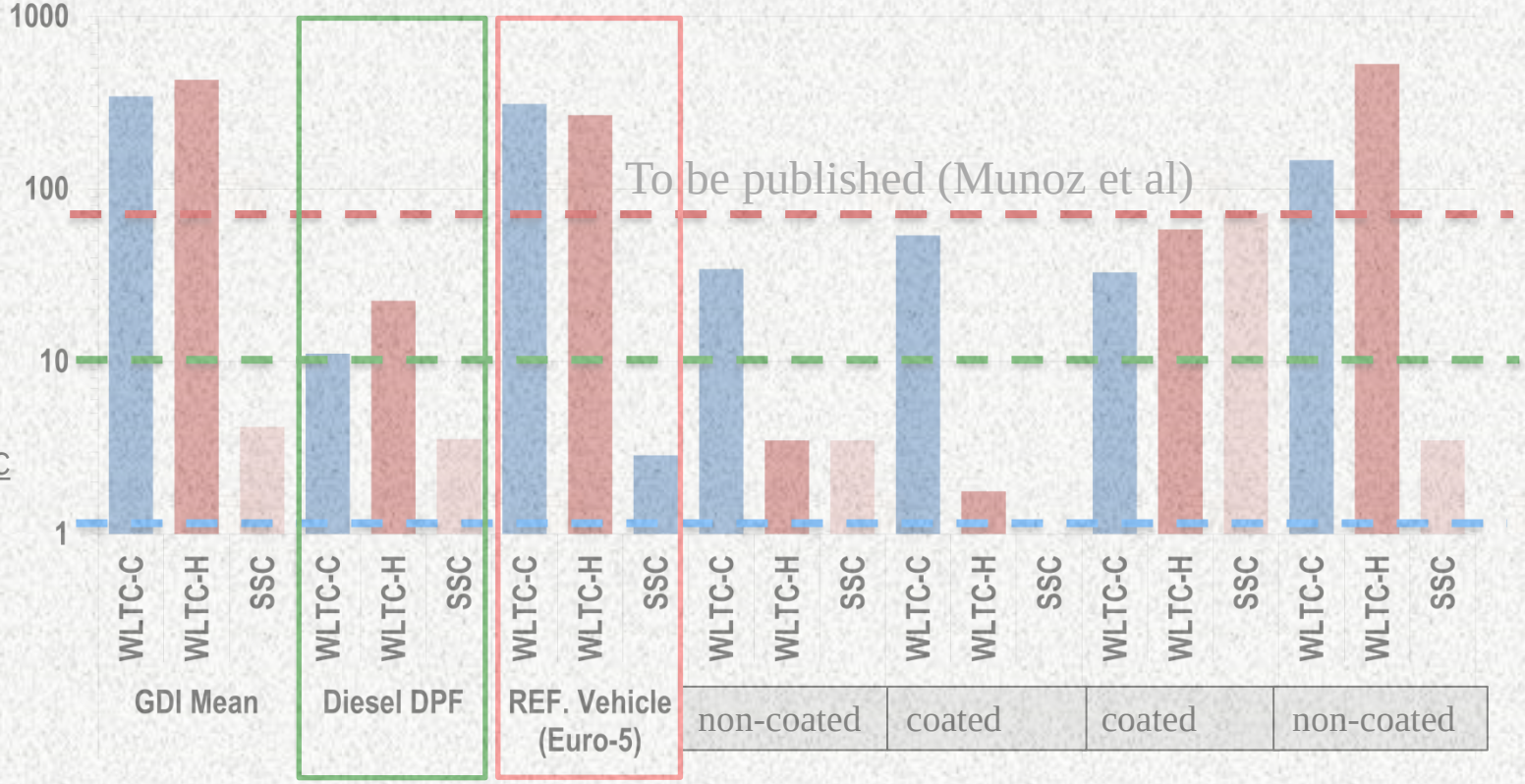
ng/Nm^3 Benzo(a)pyrene

~ 1000x higher

Diesel emissions
BaP
78-92 ng/Nm^3
without DPF

< 10 ng/Nm^3 with DPF
(Mean values)

Directive 2004/107/EC
BaP target value in ambient air: 1 ng/m^3



MPFI with GPF

ng TEQ/m^3)

Empa
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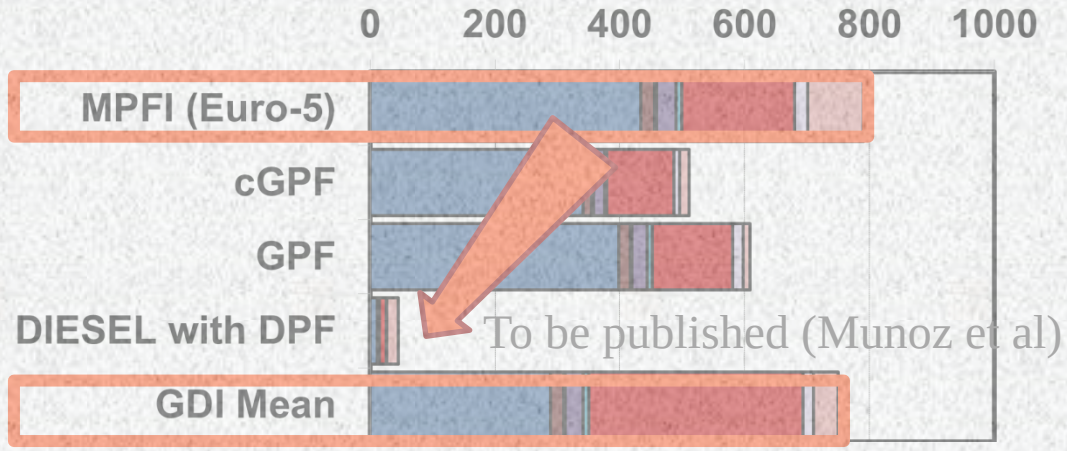
cWLTC

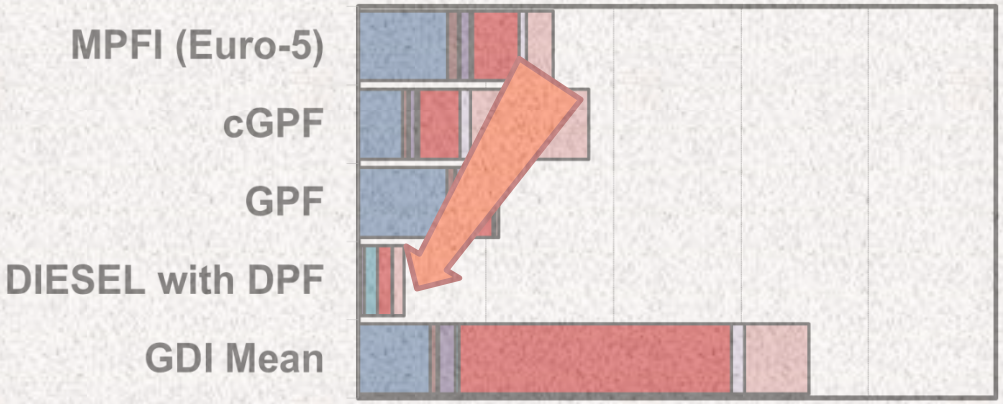


Genotoxic emissions

MPFI ≈ GDI mean in cWLTC

MPFI ≠ DIESEL
. 17x higher (cWLTC)

hWLTC



. 4x higher (hWLTC)

Naphthalene
Benzo(a)nthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Indeno(1,2,3-cd)pyrene
Dibenz(ah)anthracene

MPFI with GPF

ng TEQ/m^3)

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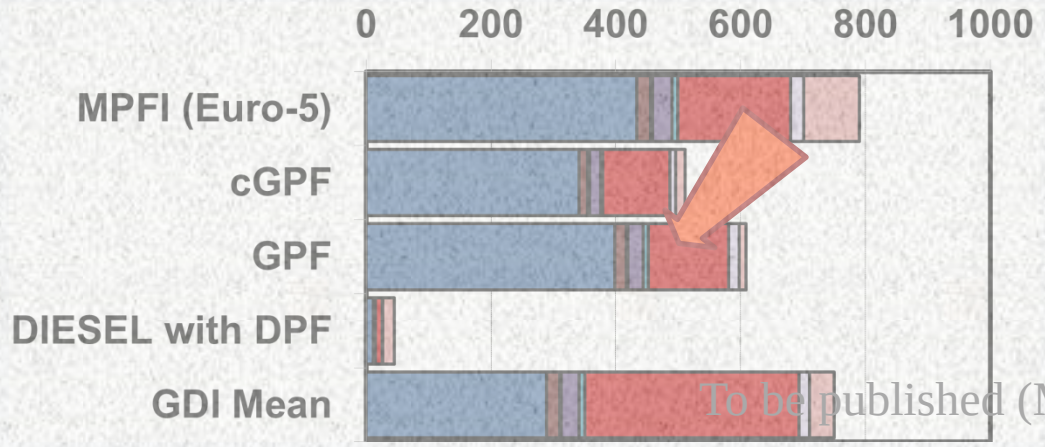
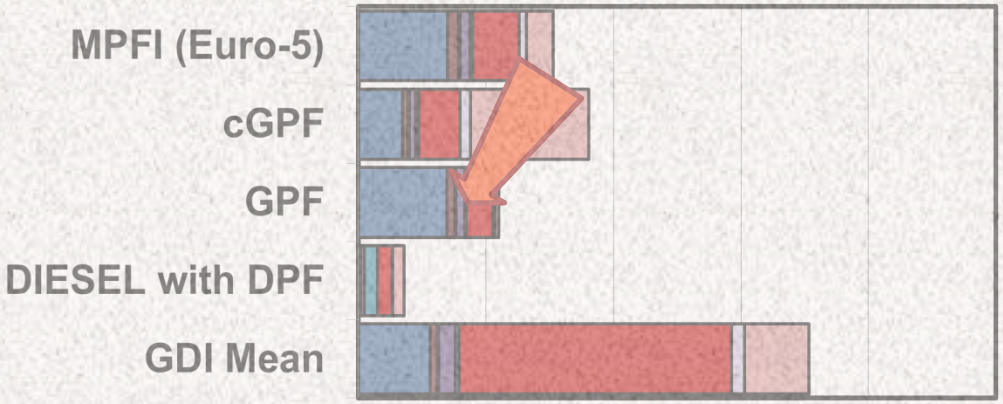


≈ 40% reduction

≈ 20% reduction

To be published (Munoz et al)

hWLTC



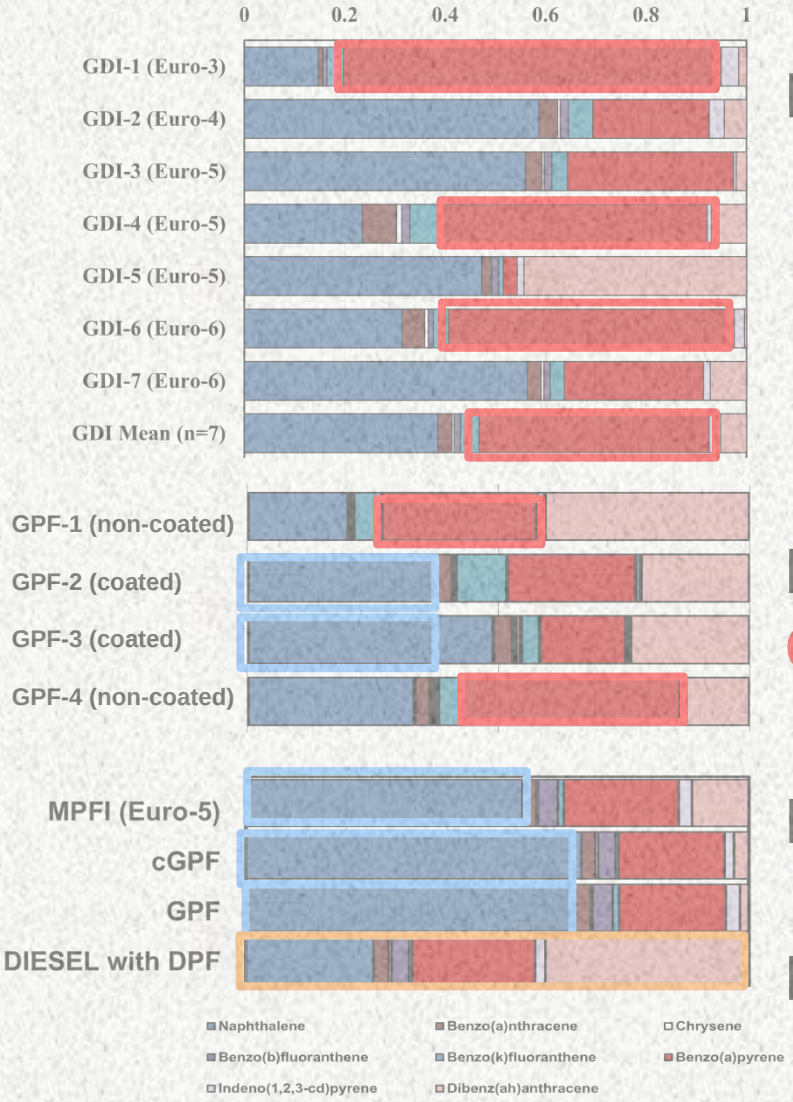
≈ 1.5-fold increase

≈ 30% reduction

Poor coating efficiency

Naphthalene
Benzo(a)nthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Indeno(1,2,3-cd)pyrene
Dibenz(ah)anthracene

Individual patterns



Benzo(a)pyrene dominates in GDI

To be published (Munoz et al)

Naphthalene dominates in GDI- filtered exhaust (with coating)

Naphthalene dominates in MPFI

Different in DIESEL

CONCLUSIONS / SUGGESTIONS

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Are GDI vehicle exhaust genotoxic like non-treated diesel exhaust?

- Toxic equivalent concentrations are several times higher in GDI (with and without fitler) than in diesel with DPF.
- Benzo(a)pyrene concentrations are 1-3 orders of magnitude higher than EU Target Limit (1 ng/m^3)
- Differences in individual patterns: BaP dominates in GDI, NAP in MPFI

To reach DIESEL with DPF levels

- GDI should be equipped with filters – May reduce PAH emissions (20-80%)
- GPF should undergo certification procedures like DPF (VERT)
- Efficient coating
- Use of ethanol/gasoline blends?

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Thank you for your attention

Questions?

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