



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

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Advanced Analytical Technologies

Empa, Dübendorf



Motivation and objectives



International Agency for Research on Cancer



**In 2012
DIESEL ENGINE EXHAUST...**

**... is classified as
Carcinogenic to humans
(Group 1)**

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

Gasoline Direct Injection



30% of EU fleet will be
GDI in 2020



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

Recent press release (May 2017)

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 11 to 20 nanometers (millionths of a millimeter), coagulate 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 3,000 mg CO / km for gasoline cars and 500 mg / km for diesel.

Nitric oxides (NO and NO₂)

In air NO rapidly oxidizes to form NO₂, 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 N₂O₃, a corrosive and highly oxidizing gas.

→ Euro 6 permits 60 mg NO + NO₂ / km for gasoline cars and 80 mg / km for diesel.

Formaldehyde (CH₂O)

Formaldehyde can cause allergies and skin, respiratory tract or eye irritations. In concentrations of 30mlm³ 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 (C₆H₆)

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 (C₁₆H₈N₂O₄)

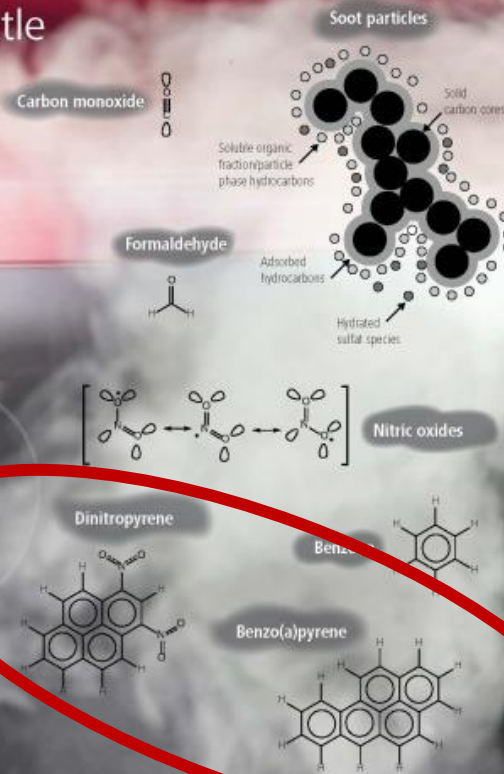
Dinitropyrene is produced in the hot exhaust tract in diesel engines through the reaction between pyrene and NO_x. 1,3-, 1,6- and 1,8-dinitropyrenes are particularly mutagenic and trigger malignant tumors in many organs in various lab animals.

→ Euro 6 does not specify any limits.

Benzo(a)pyrene (C₂₀H₁₂)

Benzo(a)pyrene is one of the most potent 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.



Link: <https://www.empa.ch/empas-press-releases>

In comparison with diesel....

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

Up to 3 orders of magnitude more particles

Exceeding Euro-6 limit:
 $6.0 \times 10^{11} \text{ \#/km}$

3- to 9-fold higher PAH genotoxic concentrations

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 high concentrations and even at lower levels a headache is common.

→ Euro 6 permits 1000 mg CO / km for gasoline cars and 500 mg / km for diesel.

Formaldehyde (CH₂O)

Formaldehyde can cause allergies and skin, respiratory tract and eye irritation. In concentrations of 300 mg / 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 limit.

Benzene (C₆H₆)

Its breakdown in the body produces toxins that can trigger cell mutations (cancer). Its long-term intake can harm the immune system 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 limit.

Dinitropyrene (C₁₂H₆N₂O₄)

Dinitropyrene is produced in the hot exhaust tract in diesel engines through the reaction between pyrene and NO₂. 1,2-, 1,6- and 1,8-dinitropyrenes are particularly mutagenic and trigger malignant tumors in many organs in various lab animals.

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Nitroarenes

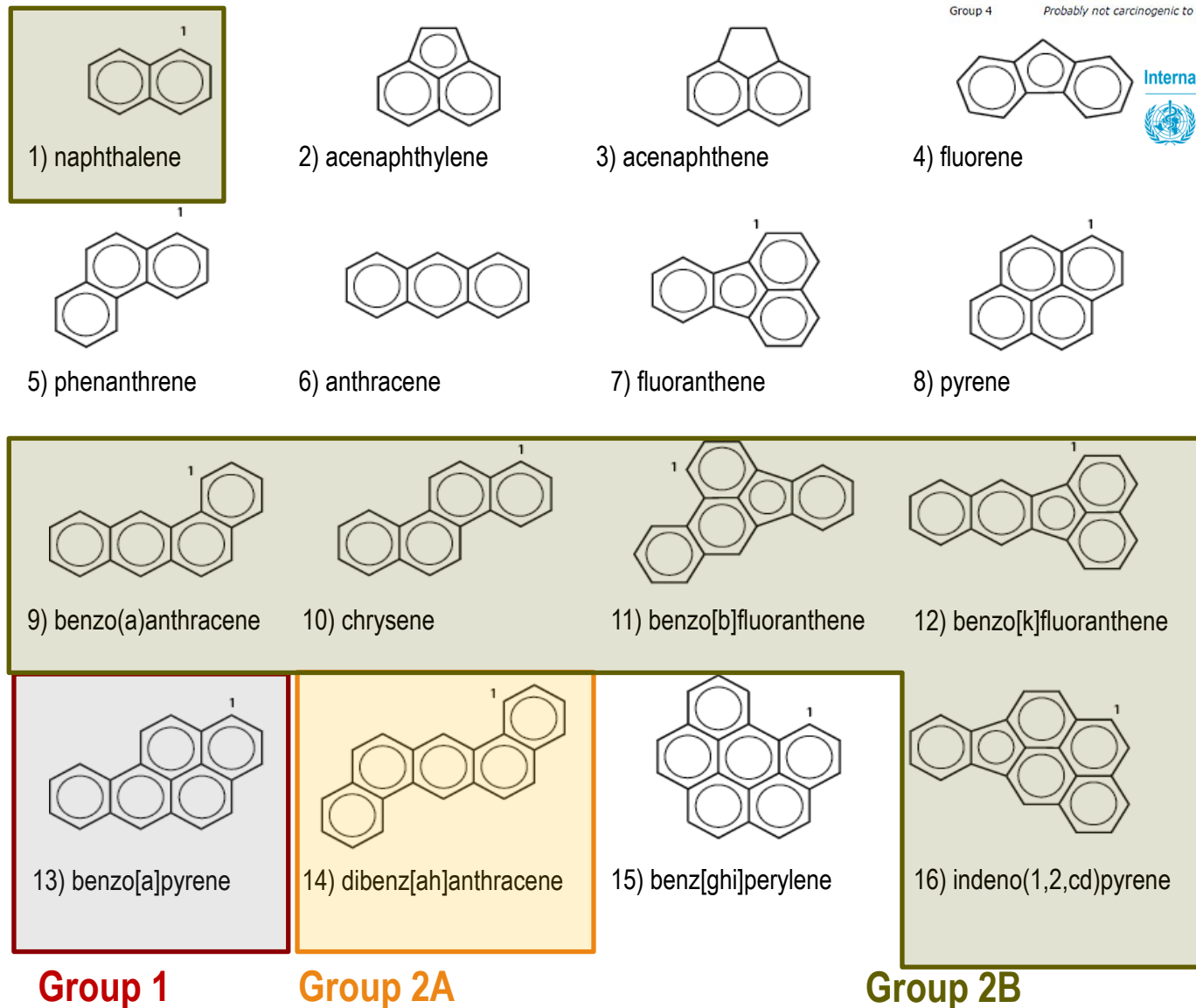
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Carcinogenic PAHs

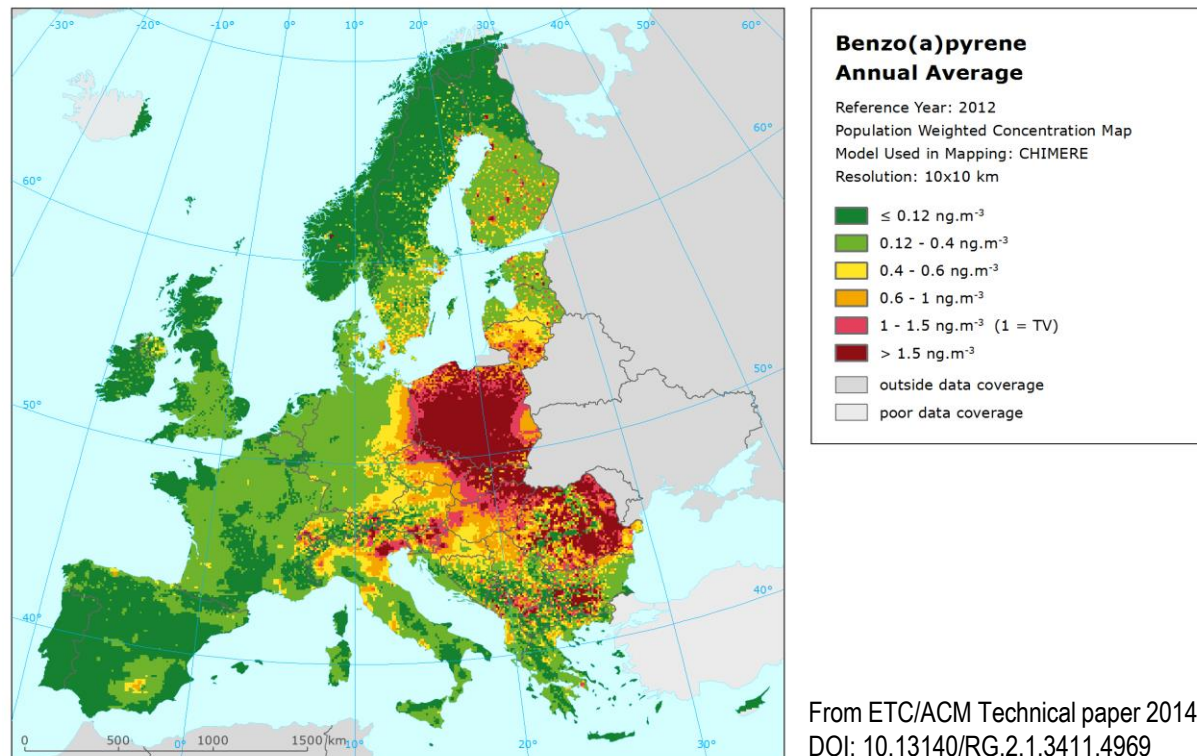
Group 1	Carcinogenic to humans	116 agents
Group 2A	Probably carcinogenic to humans	70
Group 2B	Possibly carcinogenic to humans	285
Group 3	Not classifiable as to its carcinogenicity to humans	506
Group 4	Probably not carcinogenic to humans	1

International Agency for Research on Cancer
World Health Organization

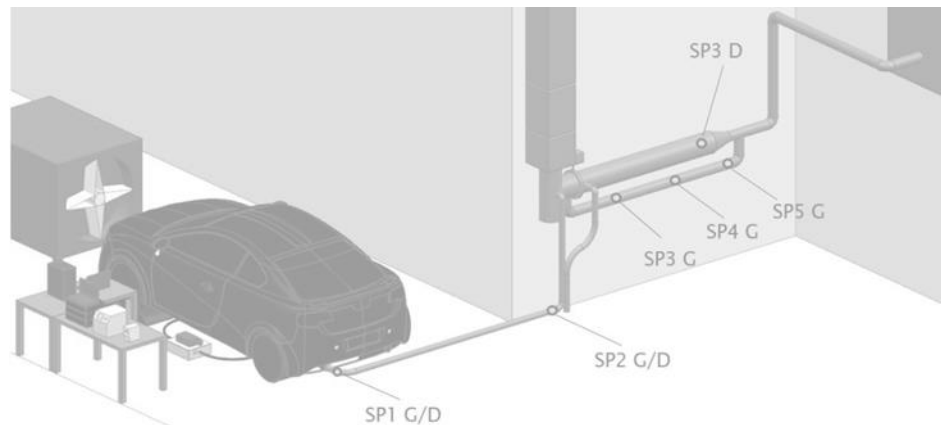


↑ MW
↓ vapor pres.
and solubility

- BaP is a marker for total exposure to carcinogenic PAHs
- Air Quality in Europe – 2016 Report (EEA):
 - In 2014, **1/3 of the BaP** measurement stations in Europe **exceed the target value (1ng/m^3 , annual average , 2014/107/EC Directive)**
 - Only 12% of the population are exposed to the estimated reference level of 0.12 ng/m^3 (WHO)
 - Emissions of BaP in the EU-28 **increased by 1%** (2000-2014)



EXPERIMENTAL SETUP



Experimental procedure

GD1 Fleet (n=7)



4 particle filters tested

2 coated and 2 non-coated



Diesel bench mark

Euro-5

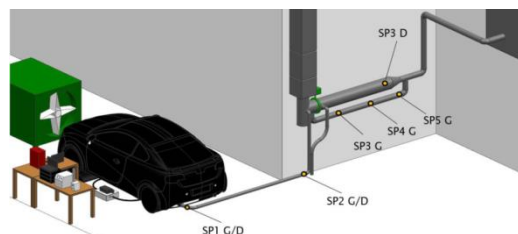


Biofuels

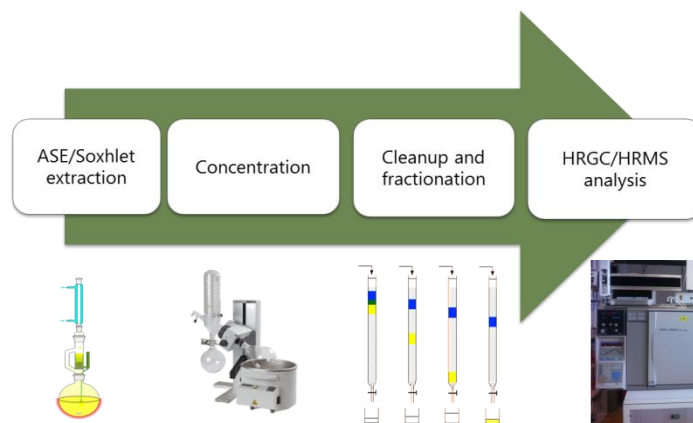


Ethanol and butanol blends

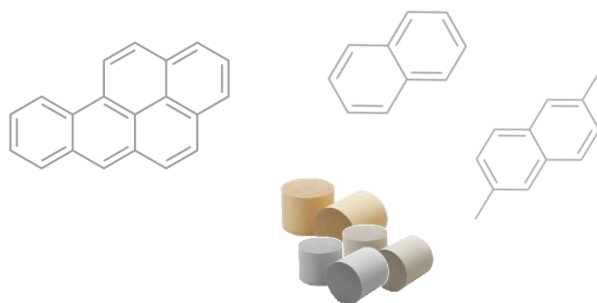
Laboratory analysis



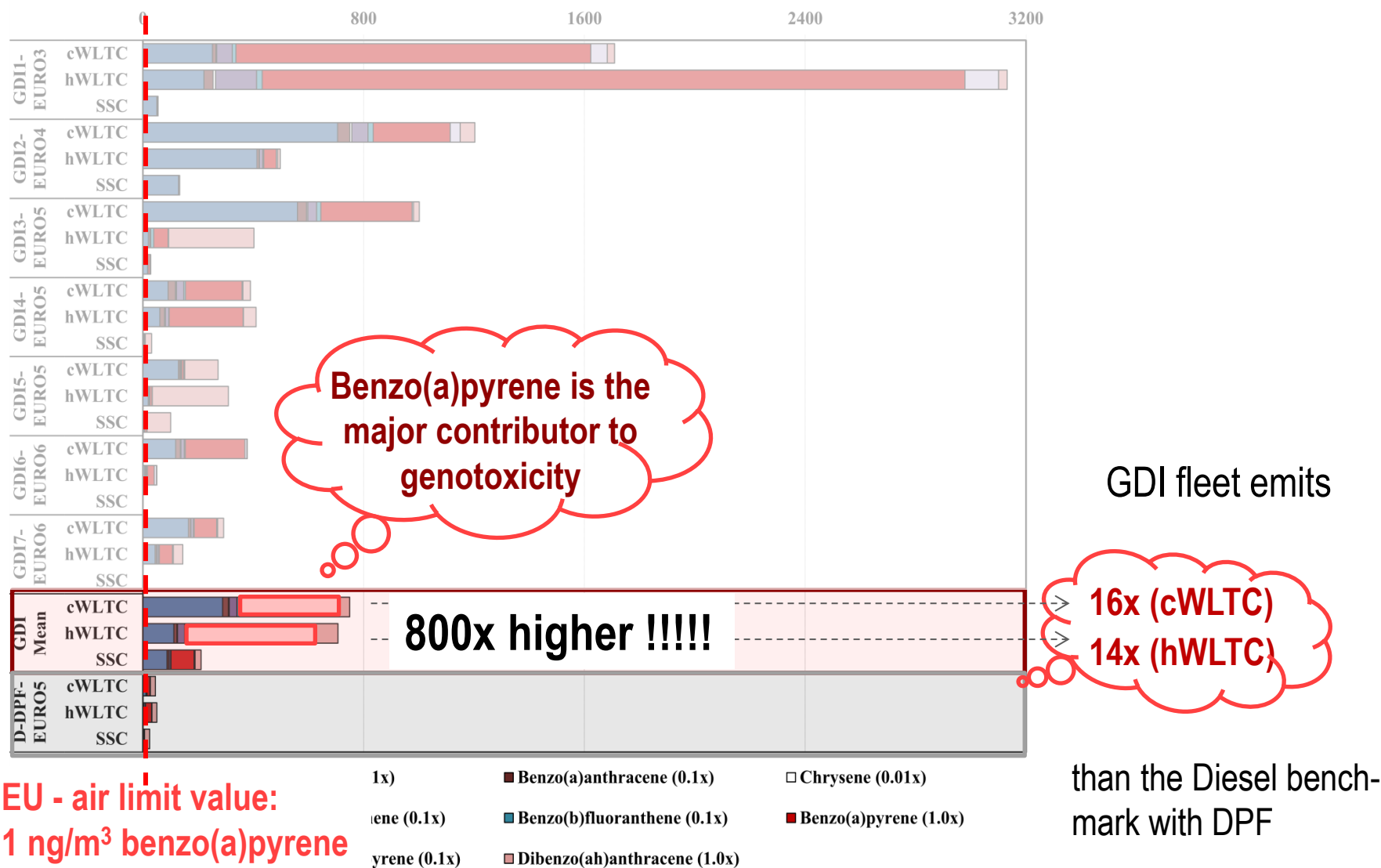
- Chassis dynamometer of the UASB in Nidau
- 2 transient driving cycles (cWLTC and hWLTC) and SSC
- Diluted exhaust --- CVS tunnel:
solid + condensed + gaseous phases



RESULTS



On average,



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

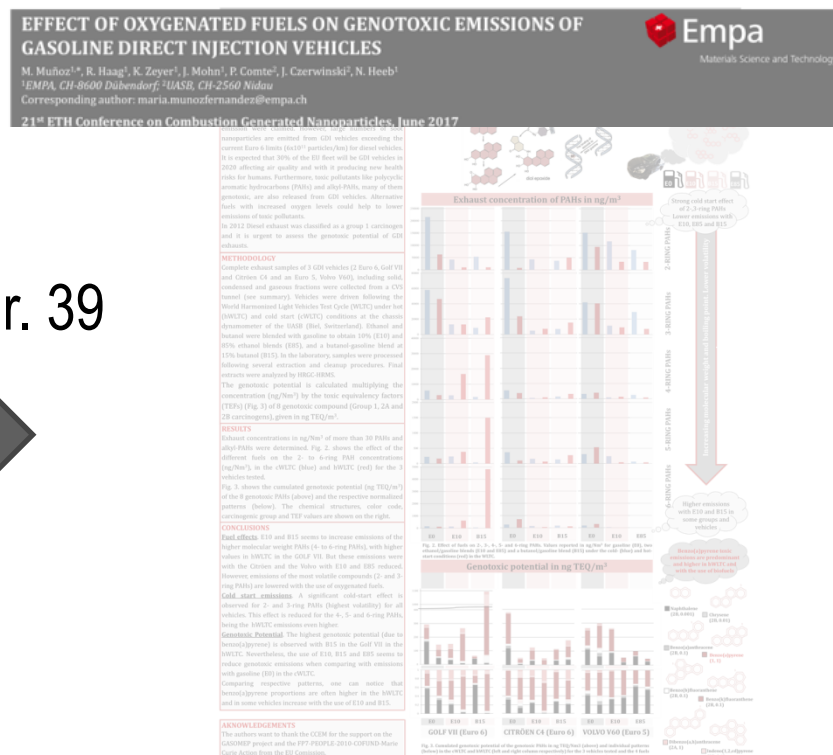
Aftertreatment:

Filters

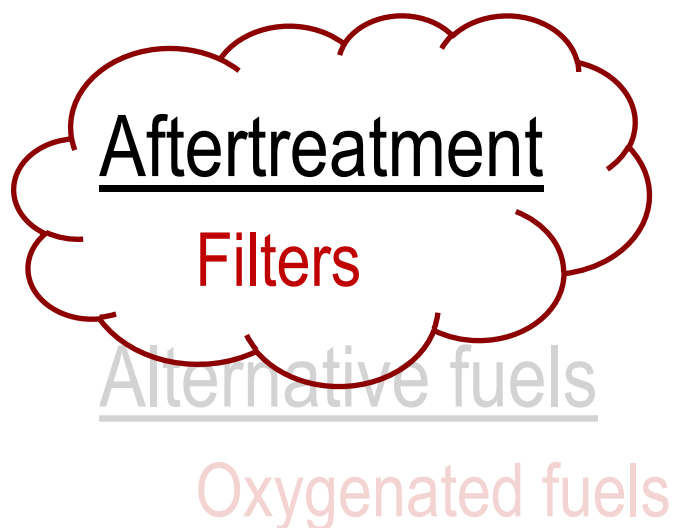
Alternative fuels

Oxygenated fuels

Poster Nr. 39



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



Poster Nr. 39

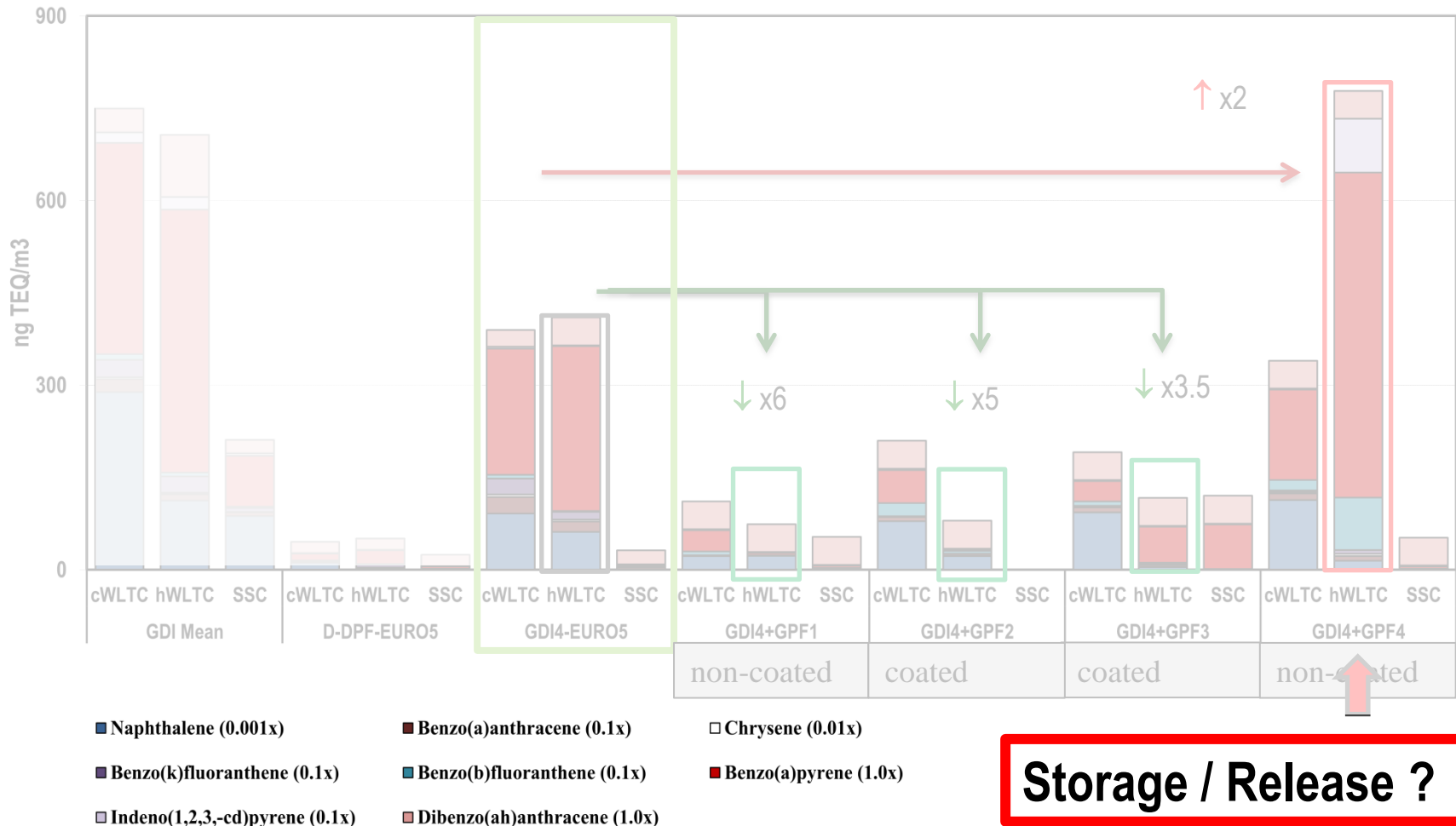


Genotoxic concentration

Euro-5

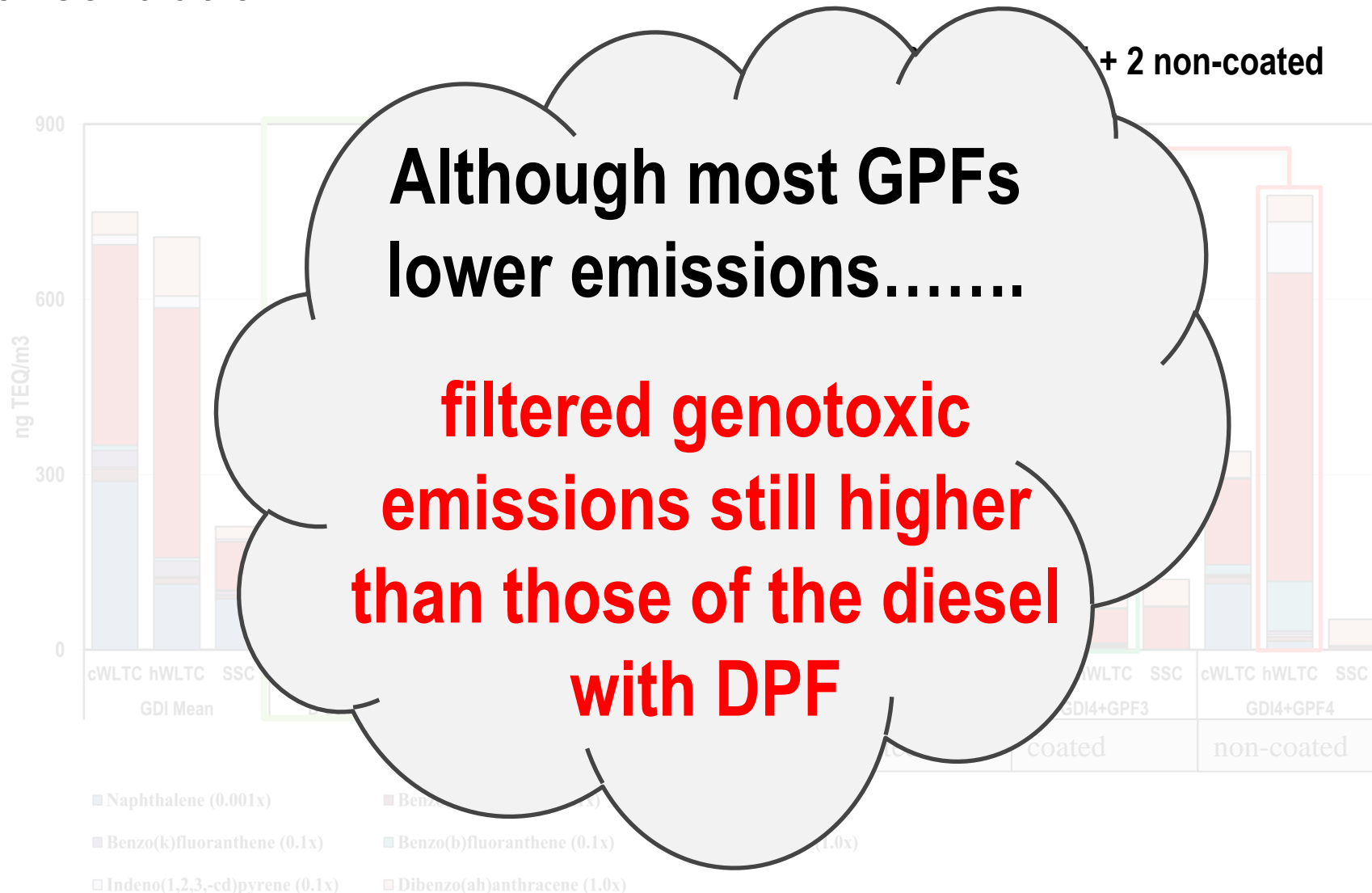


FILTERS: 2 coated + 2 non-coated



*I.C. Nisbeth, P.K.L. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAH). Regul Toxic Pharmacol. 16:290-300; 1992

Genotoxic concentration

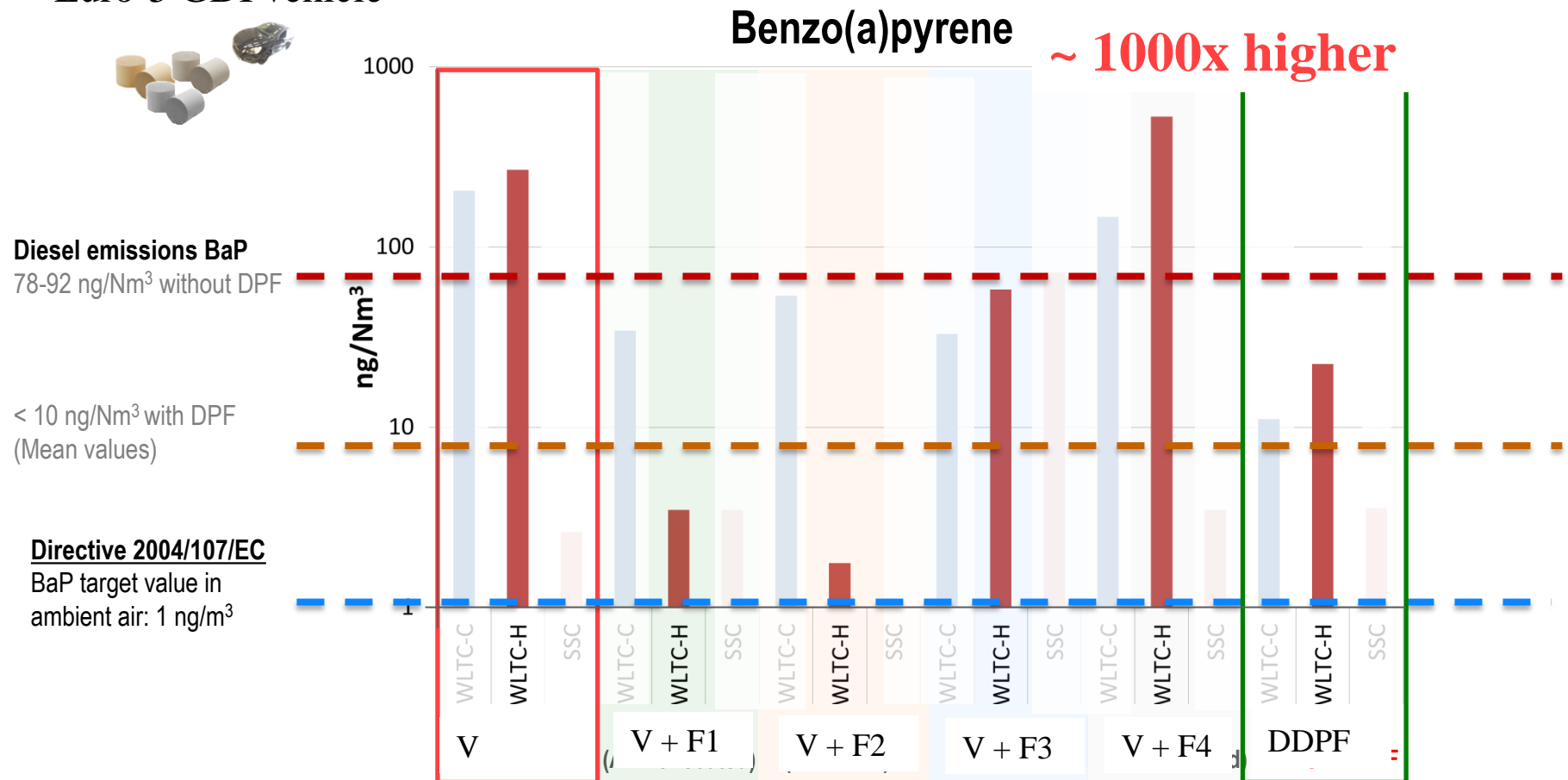


*I.C. Nisbeth, P.K.L. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAH). Regul Toxic Pharmacol. 16:290-300; 1992

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

Materials Science and Technology

Euro-5 GDI vehicle



F1	BRAND A / NON COATED
F2	BRAND A / COATED
F3	BRAND B / COATED
F4	BRAND B / NON COATED

- Benzo(a)pyrene concentrations are 1-3 orders of magnitude higher than EU Target Limit (1 ng/m³)
- Not a big difference between coated and non-coated
- Overall, PAH emissions are lowered with filter (20-80%)
- Filter 4 increases PAH emissions (x2)
- Toxic equivalent concentrations are several times higher in GDI (with and without filter) than in diesel with DPF.

**Are GDI vehicle
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non-treated diesel
exhaust?**

-
- GDI should be equipped with filters
 - GPF should undergo certification procedures like DPF (VERT)
 - New or used filters
 - Analysis of PCDD/Fs



Thank you for your attention



Questions?