Next-generation GPFs: Impact on genotoxic compounds, risks for secondary poisoning

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Our hypothesis: Any particle filter is a chemical reactor!

Chemistry matters, it determines toxicity

Our hypothesis: Any particle filter is a chemical reactor!

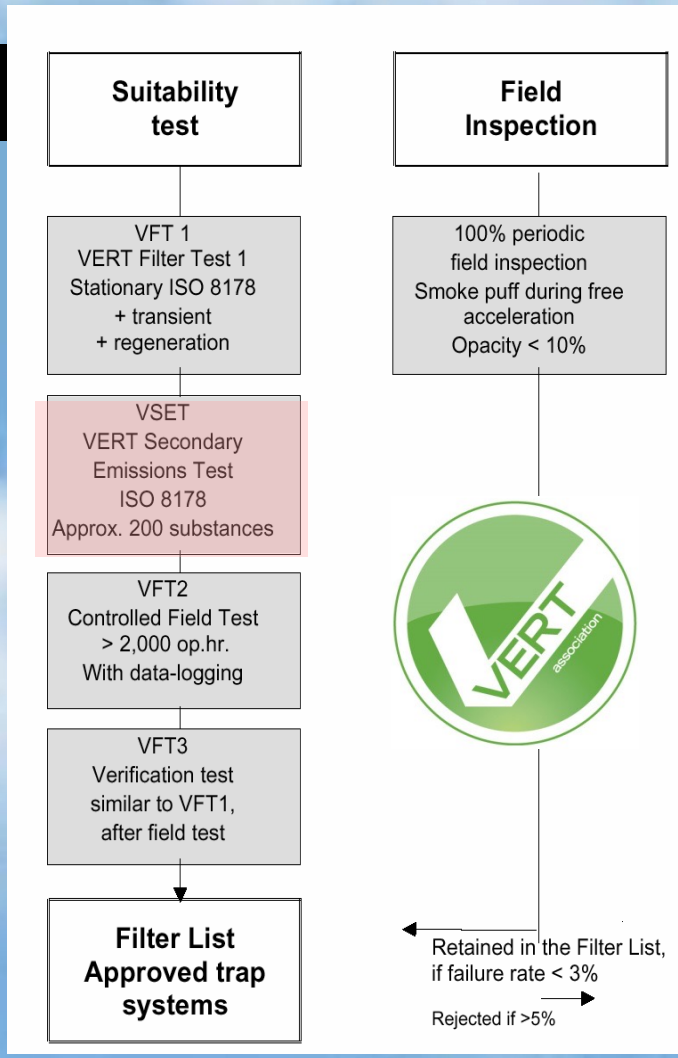
Are particle filters safe to operate them in tunnels?

VERT secondary emissions test (VSET)

Approved filters should:

- Reduce PM- & PN-emissions (>98%)
- Reduce toxic compounds a.m.a.p.
- Low risks for secondary emissions

Are emissions after a PF safe?

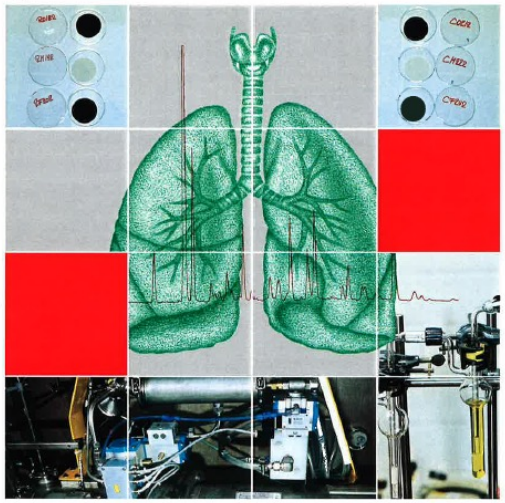


27 years VERT Filter test

The 1st, 2nd and 3id DPF tested and reported were operated with fuel borne catalyst

EMPA-Research report Nr. 167985

EMPA



Influence of particulate trap systems on the composition of Diesel engine exhaust gas emissions

(Includes tests on possible *de novo* synthesis of PCDD/F in particulate trap Systems)

released January, 1998

Author:

Ce-, Fe-FBC-DPF

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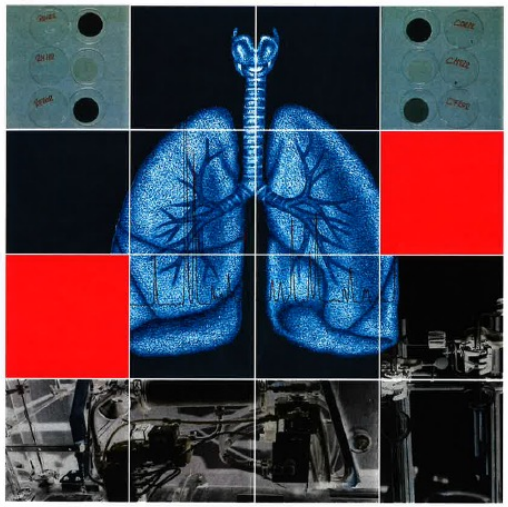
Includes tests with copper containing fuel additives
Extension of research report 167985

EMPA



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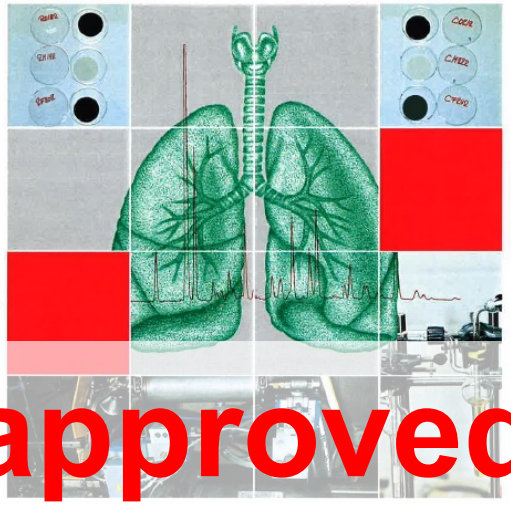

approved

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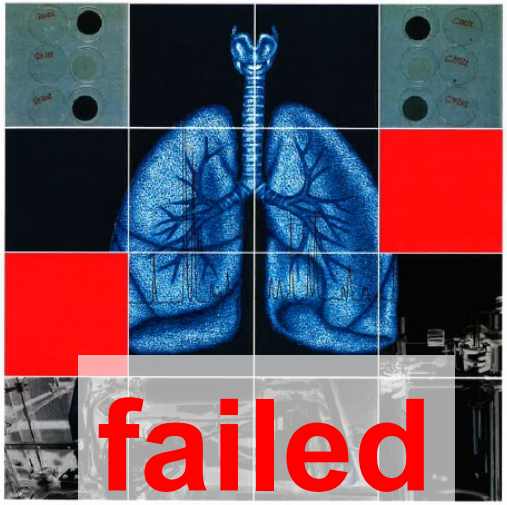

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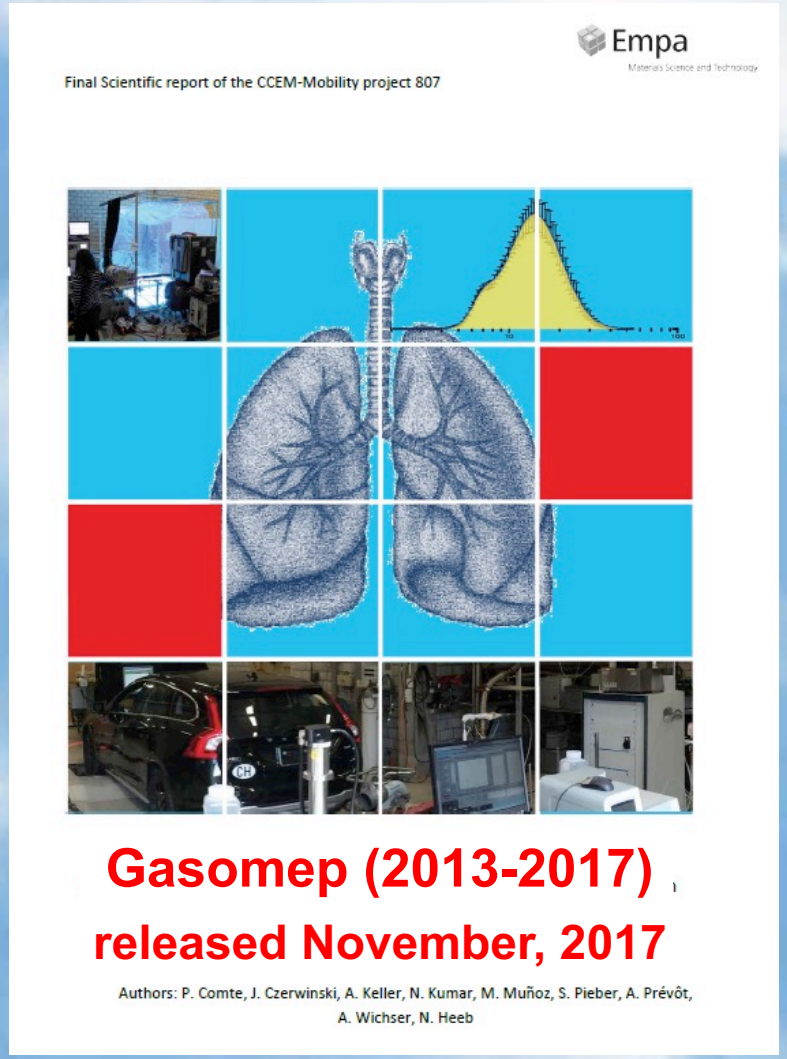
The first- and second-generation gasoline particle filters (GPFs) tested



Gasomep (2013-2017)

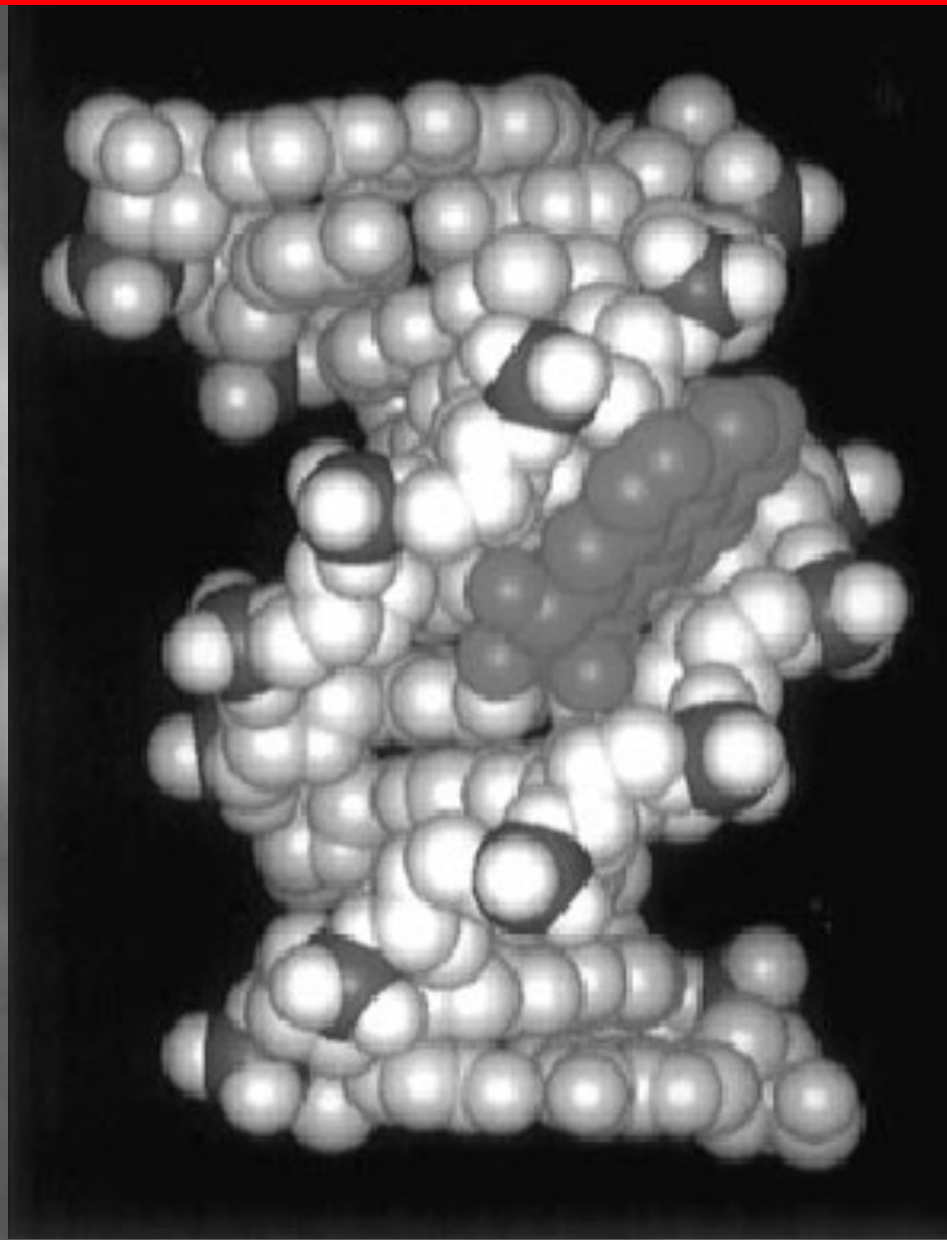
released November, 2017

Aerosolfd (2023-2025)

released January, 2025

Carcinogenesis of aryl hydrocarbons

Metabolically activated
benzo(a)pyrene ($C_{20}H_{12}$) bound to DNA



Chemical composition of adsorbates determines toxicity

Nanoparticles as carriers of toxic compounds

The Trojan horse effect

- Nanoparticles aggregate and adsorb semi-volatile compounds
- Nanoparticles penetrate cell membranes (alveoli, placenta, blood cells) acting like a Trojan horse

Trojan horse, Harbour of Canakkale, Turkey

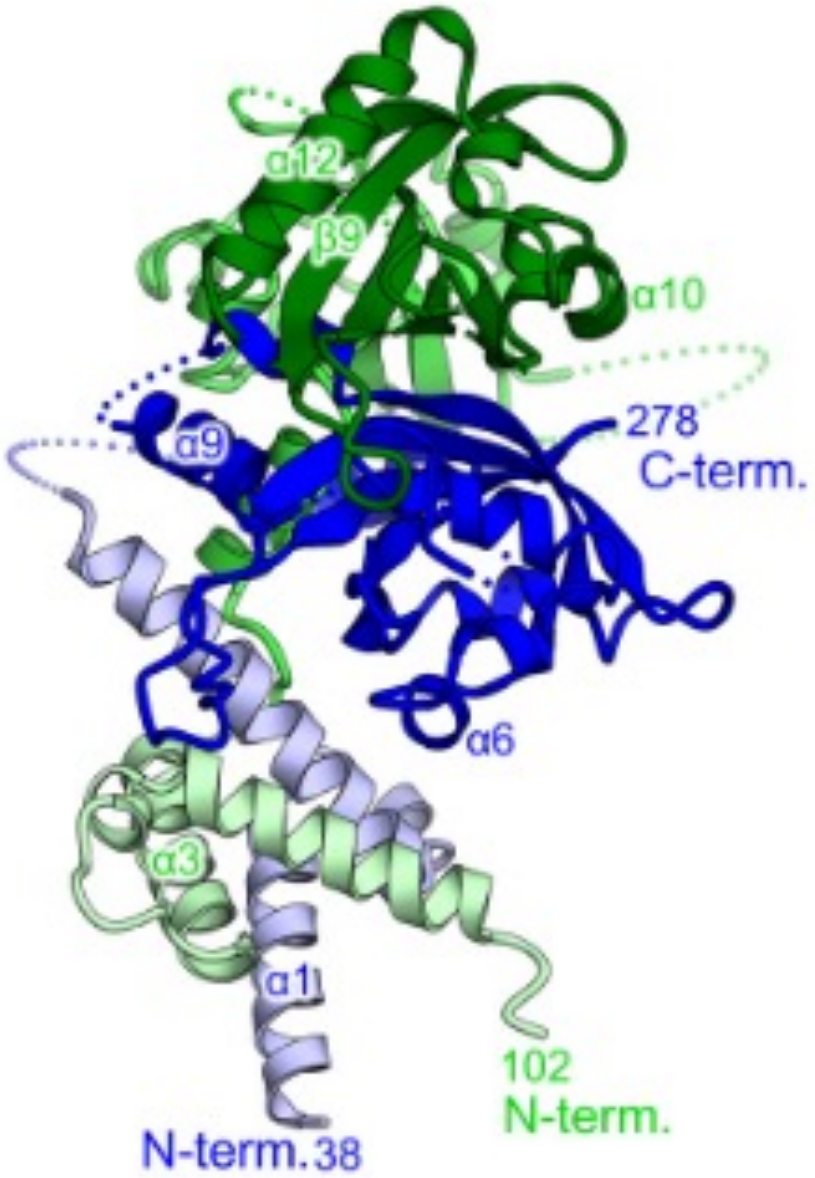
Chemical composition of adsorbates determines toxicity

Nanoparticles as carriers of toxic compounds

The Trojan horse effect

- Nanoparticles aggregate and adsorb semi-volatile compounds
- Nanoparticles penetrate cell membranes (alveoli, placenta, blood cells) acting like a Trojan horse
- AHR-mediated transport of chemicals to the cell nucleus with direct contact to the genetic material (DNA, mRNA)

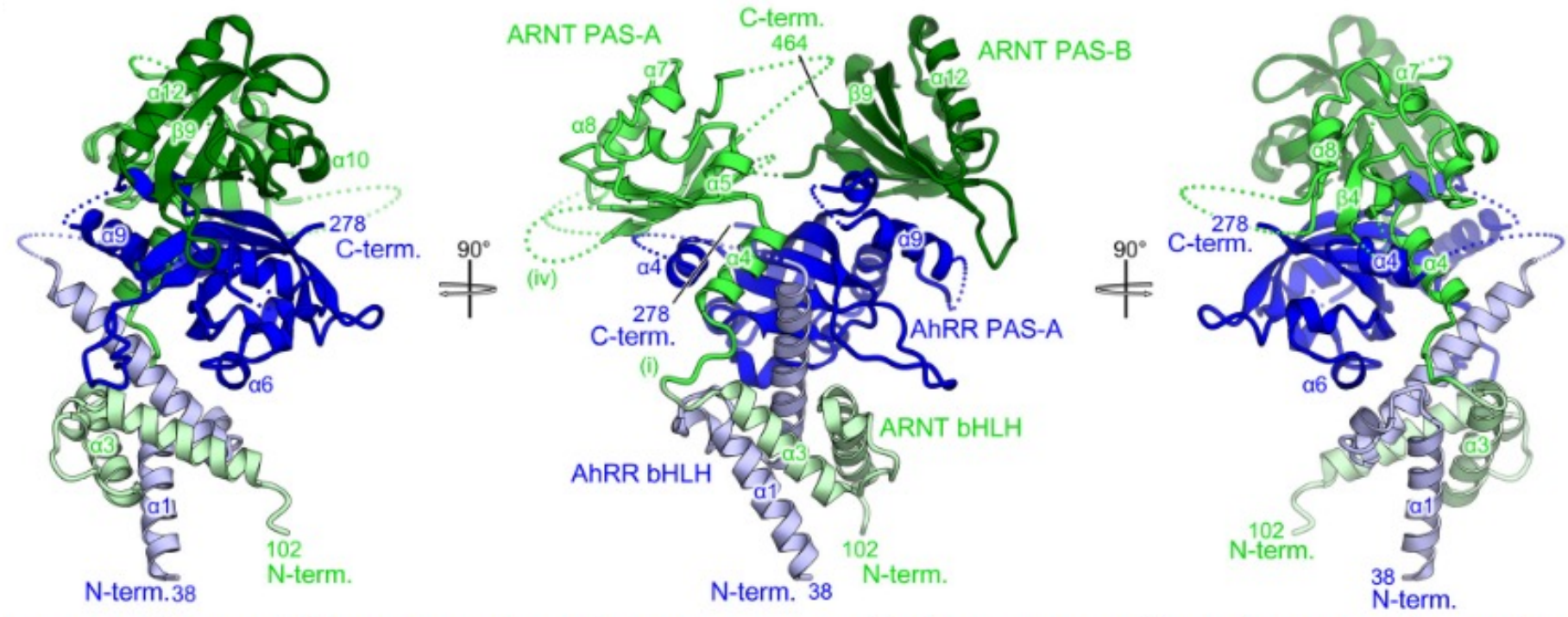
Sakurai et al. 2017 J. Biol. Chem. 292 17609 –17616



The aryl hydrocarbon receptor (AHR)

The shuttle of genotoxic compounds into the cell nucleus to the genetic material

DNA-binding transcription factor:



Crystal structure of the AHRR- (blue) ARNT- (green) complex

Sakurai et al. **2017** J. Biol. Chem. 292 17609 –17616

AHR-TF: AHR-mediated transcription factor

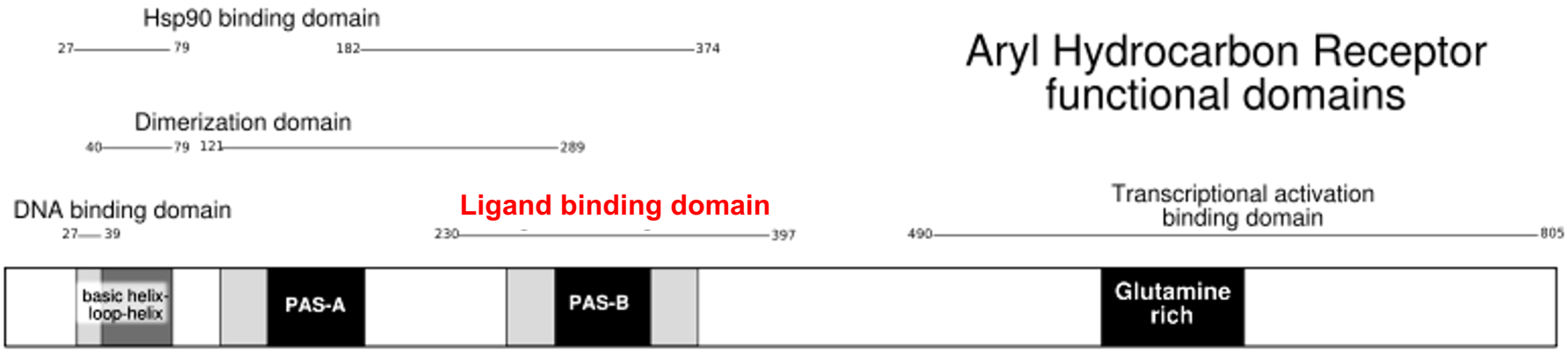
ARNT: AHR nuclear translocator

The aryl hydrocarbon receptor (AHR)

The shuttle of genotoxic compounds into the cell nucleus to the genetic material

DNA-binding transcription factor:

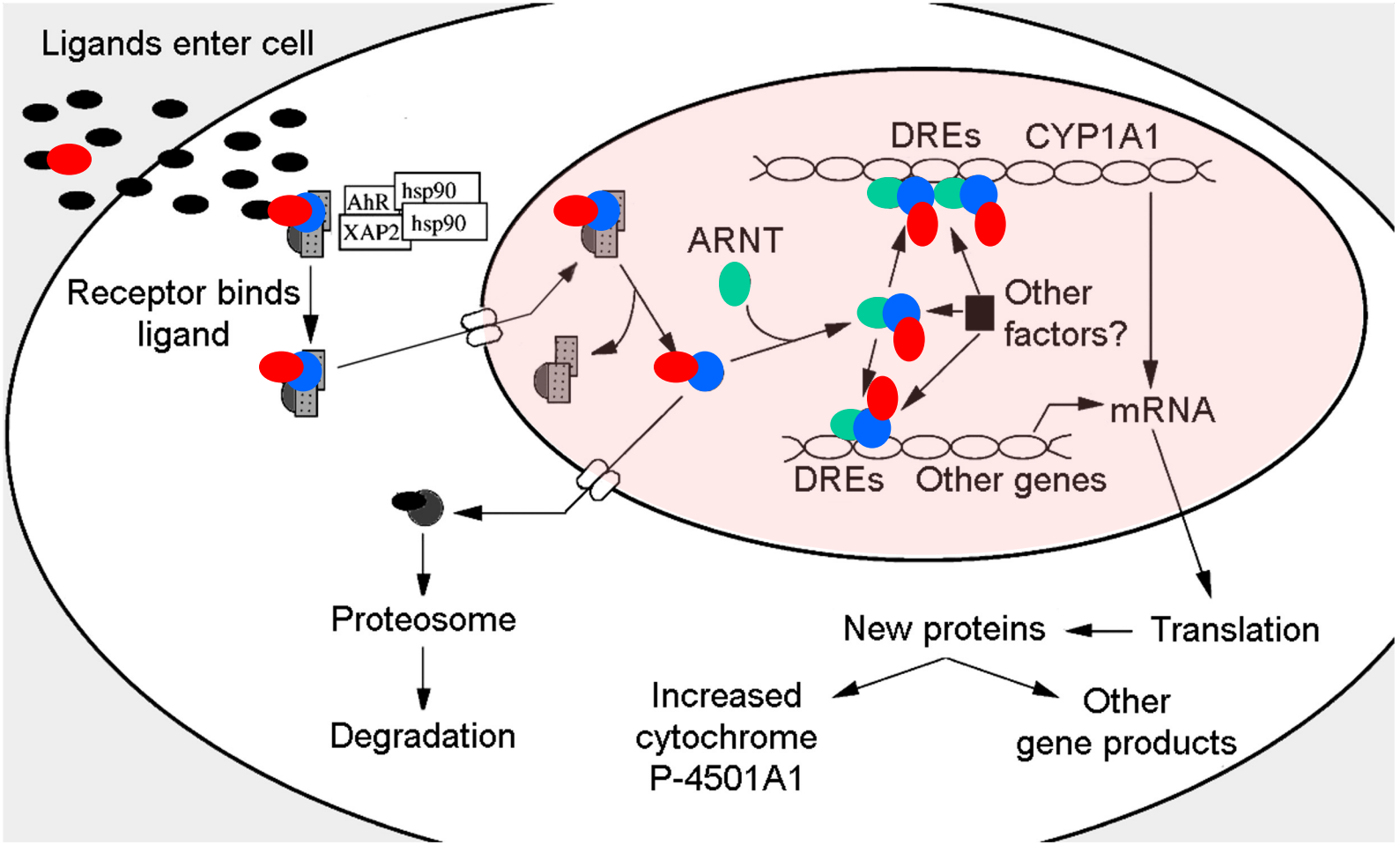
- Cyctosolic transcription factor (DNA-binding protein, 805 AAs, ~90'000 mu, basic helix-turn-helix motive)
- Ligand-binding domain (PAS-B, AS230-397)
- Ligand-AHR complex migrates to nucleus and binds DNA



To compare with naphthalene (128 mu), benzo(a)pyrene (252 mu)

The AHR mode of action

Ligand binding to the AHR triggers a cascade of fundamental reactions



AHR-TF: AHR-mediated transcription factor

ARNT: AHR nuclear translocator

Specific molecular recognition

We do know now the protein structure and some of the keys that bind to the AHR

The key-lock principle:

Specific molecular recognition

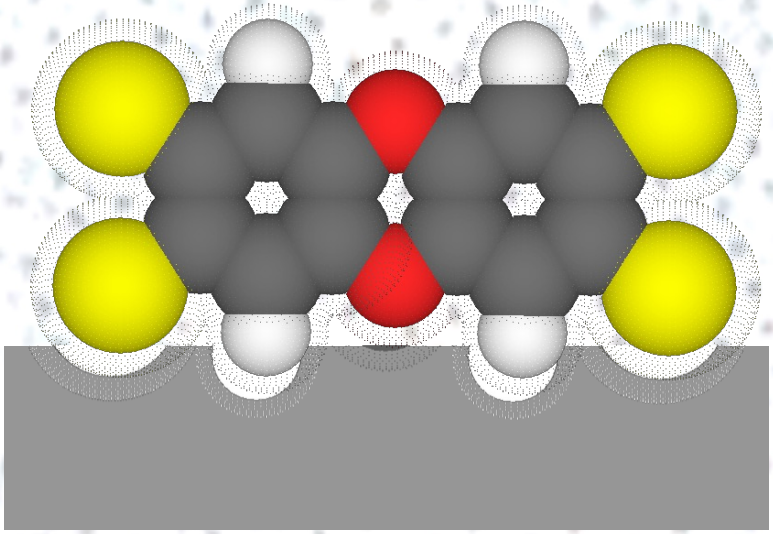
We know some of the keys so we can guess how the lock looks like?

The key-lock principle:

Specific molecular recognition

2,3,7,8-TCDD, the so-called Seveso dioxin, is the ligand with the highest AHR affinity

The key-lock principle:



Specific molecular recognition

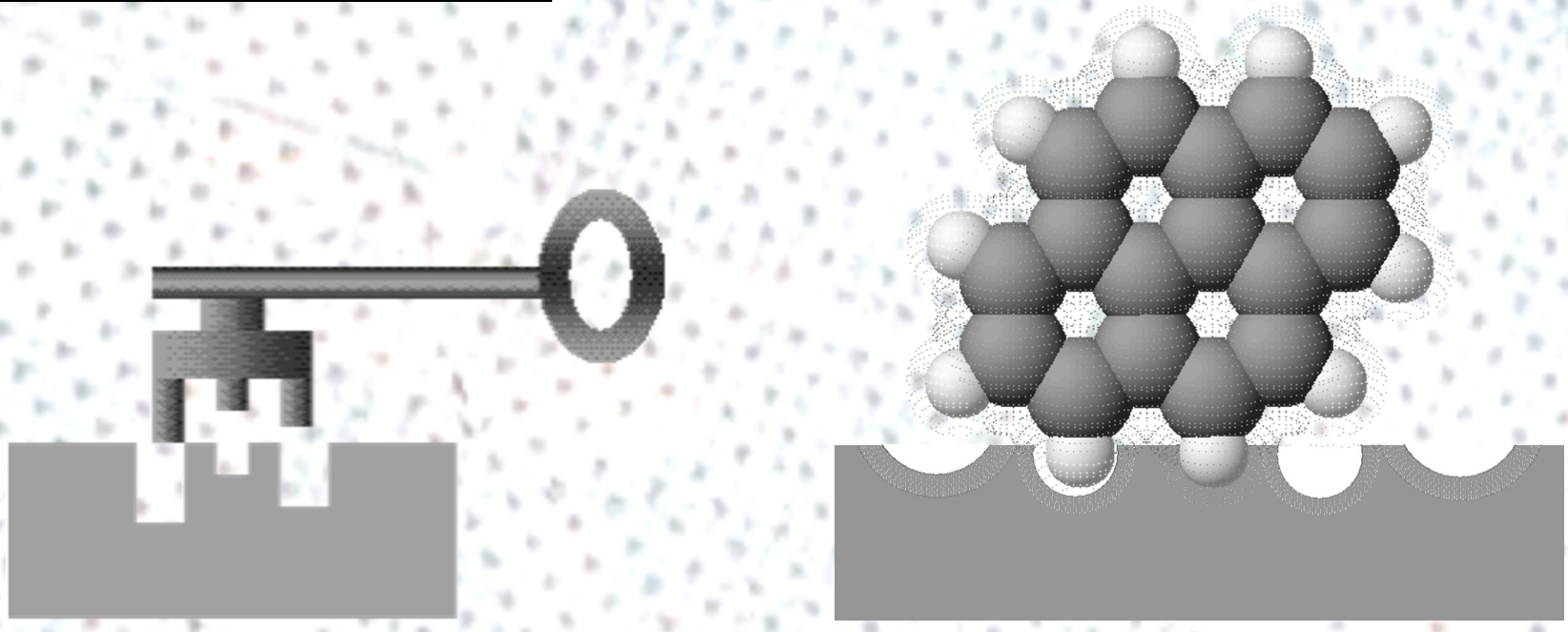
We know some of the keys so we can guess how the lock looks like?

The key-lock principle:

Specific molecular recognition

Pyrene is a poor ligand with a 70’000 fold weaker AHR-affinity than 2,3,7,8-TCDD

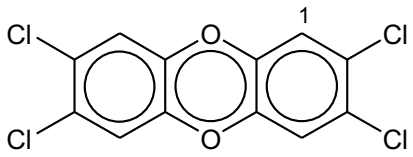
The key-lock principle:



Specific molecular recognition

We know some of the keys and their affinity to the AHR. They are PAH-like!

Affinity of some aryl hydrocarbons:



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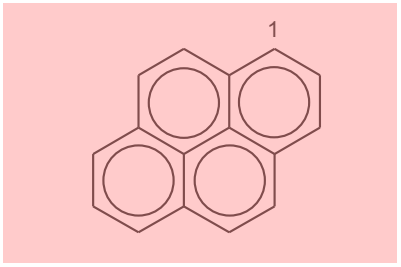

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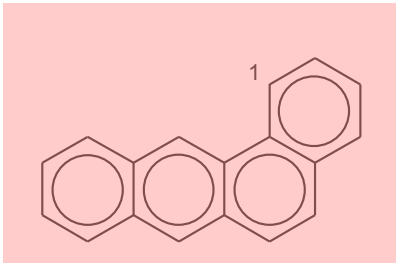
(1/70’000)



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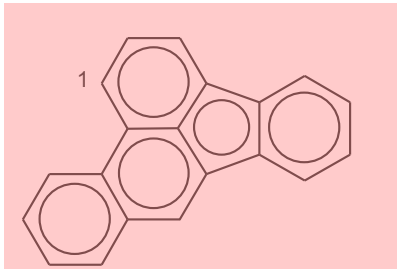

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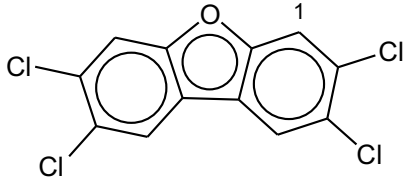

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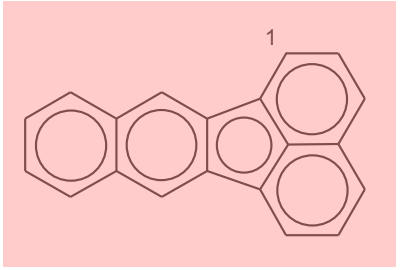

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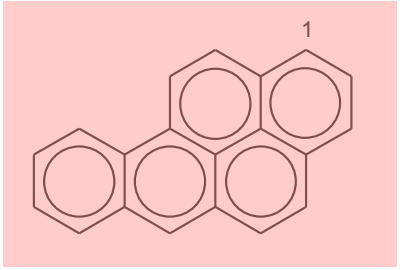

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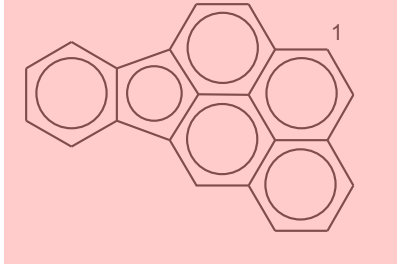


0.0041
(1/240)

Aryl hydrocarbons, another expression for PAHs

Attempted assassination of Viktor Yushchenko, former President of the Ukraine

What happened during the 2004 presidential election campaign in the Ukraine?

Before

Attempted assassination of Viktor Yushchenko, former President of the Ukraine

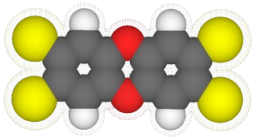
What happened during the 2004 presidential election campaign in the Ukraine?

Before and after the severe dioxin poisoning

Attempted assassination of Viktor Yushchenko, former President of the Ukraine

What happened during the 2004 presidential election campaign in the Ukraine?

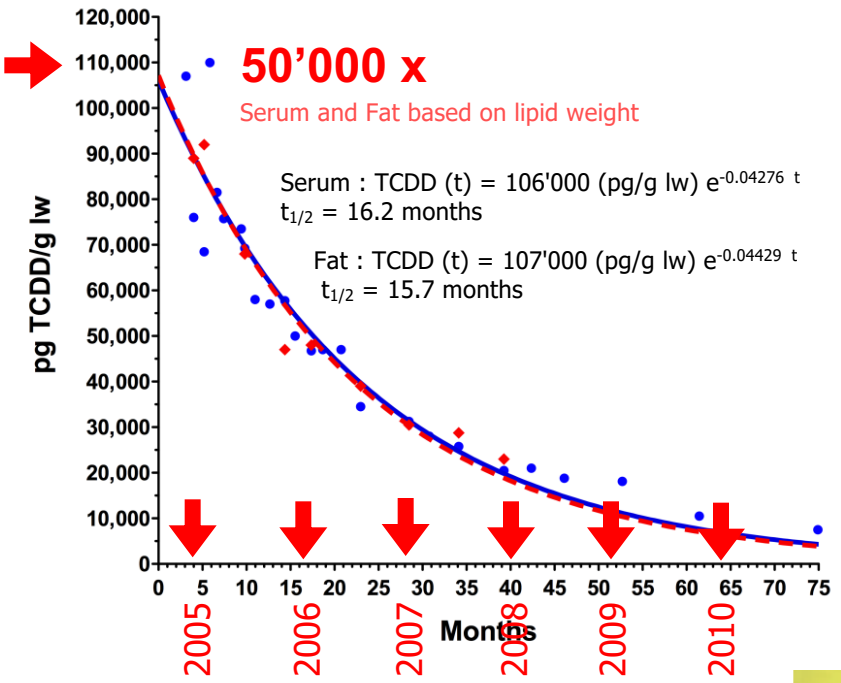
2,3,7,8-TCDD, the only congener found



- Poisoned Sunday, Sept 5, 2004 Dinner with SBU (Ukrainian National Security)
- Uptake of approximately 1-2 mg TCDD !
- Second highest TCDD serum level in a human body ever measured
- 50‘000 x more than the normal population (2 pg/g lipid)
- Nov 23, J. Henry, St. Mary‘s Hospital, London suggests dioxin poisoning
- Dec 17, two independent laboratories confirmed that exclusively 2,3,7,8-TCDD was found in the blood (108’000 and 109‘000 ng/kg lipid)

Viktor Yushchenko was poisoned with synthesized material, PCDD/Fs formed in combustion reactions, e.g. in certain active DPFs produce quite different pattern!

Sorg, O., Zennegg, M. Schmid, P. et al. The Lancet, 2009, 9696, 1179-85



Attempted assassination of Viktor Yushchenko, former President of the Ukraine

What happened during the 2004 presidential election campaign in the Ukraine?

Before and after the severe dioxin poisoning

Do not mess around with your AHR!

The gasoline vehicle fleet (GDI and MPI)

GDI- (n=8) and MPI- (n=1) vehicles from the GASOMEP- and Aerosolfd-projects

GDI-1:	Mitsubishi Carisma (1.8 L, the first GDI vehicle)	Euro-4
GDI-2:	VW Golf (1.4 L)	Euro-5
GDI-3:	Opel Insignia (1.6)	Euro-3
GDI-4:	Volvo V60 T4F (1.6 L)	Euro-5
GDI-5:	Opel Zafira (1.6 L)	Euro-5
GDI-6:	Citroën C4 Cactus (1.2 L)	Euro-6
GDI-7:	VW Golf VII (1.4 L)	Euro-6

4 generations of vehicle technology

DI: Peugeot 4008 (1.6 L, DPF, benchmark vehicle) — Euro-5





The gasoline vehicle fleet (GDI and MPI)

GDI-8: VW Golf TSI (1.4 L, 72’000 km)

MPI-1: Fiat 500X (1.6 L, 49’500 km)

The gasoline vehicle fleet (GDI and MPI)

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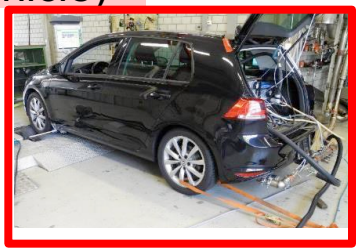
GDI-6:	Citroën C4 Cactus (1.2 L)	Euro-6
GDI-7:	VW Golf VII (1.4 L)	Euro-6
GDI-8:	VW Golf TSI (1.4 L, 72'000 km)	Euro-6b
MPI-1:	Fiat 500X (1.6 L, 49'500 km)	Euro-6b
DI:	Peugeot 4008 (1.6 L, DPF, benchmark vehicle)	Euro-5

4 generations of vehicle technology

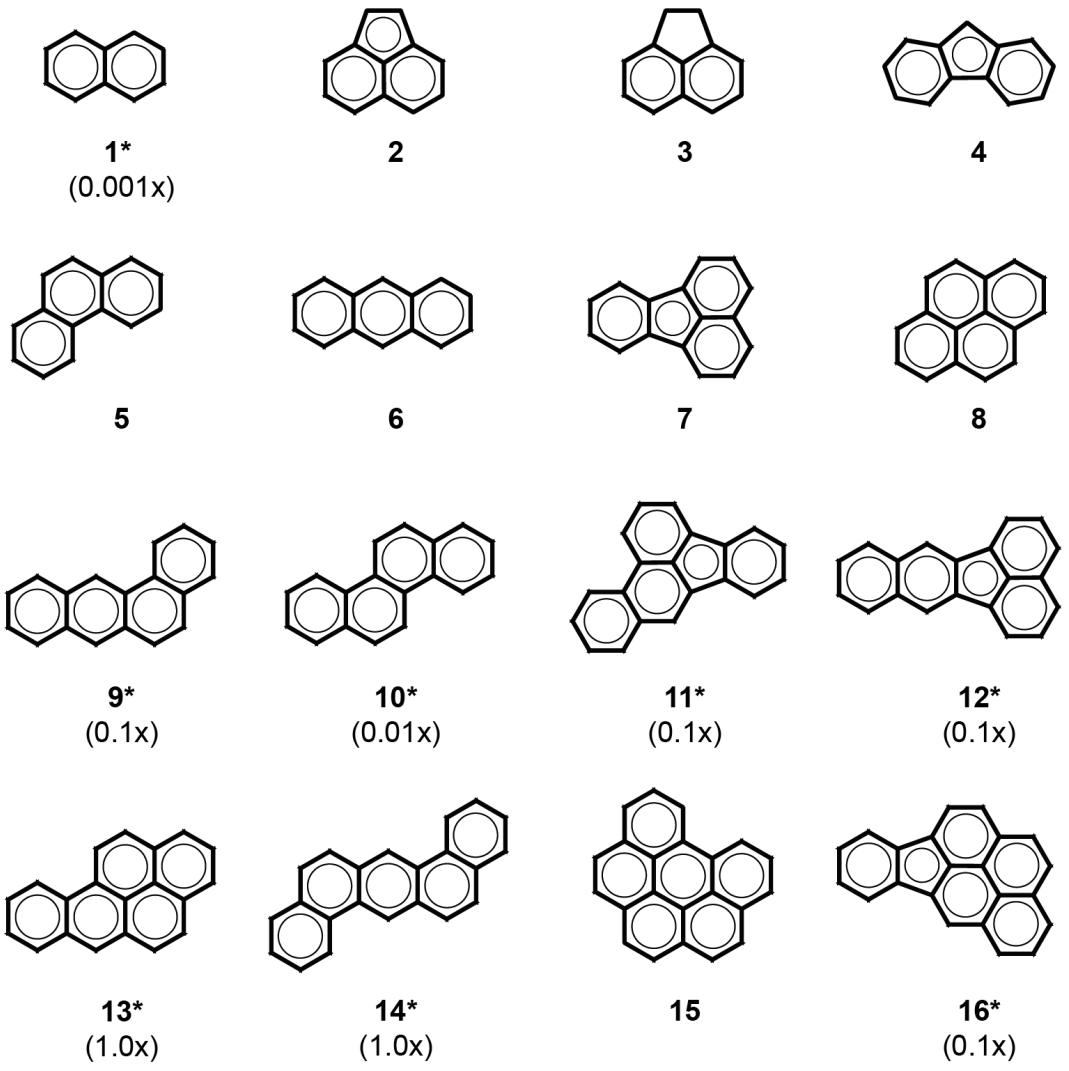






Polycyclic aromatic hydrocarbons (PAHs) (Aryl hydrocarbons)

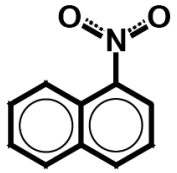
All PAHs are potential AHR ligands, eight labeled with asterisks are carcinogenic



Nitrated PAHs (Nitro-PAHs)

Nitro-PAHs are potential AHR ligands too, and some are mutagenic as well

Some nitro-PAHs do form in non-catalyzed DPFs (secondary poisoning)



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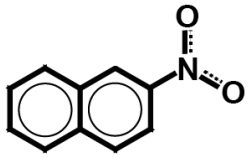

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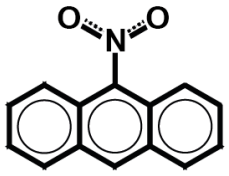

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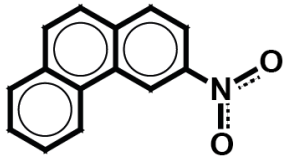

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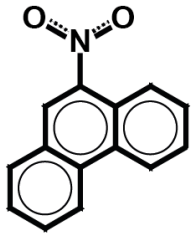

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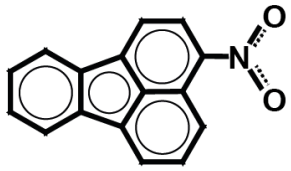

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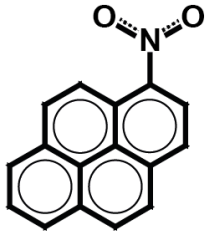

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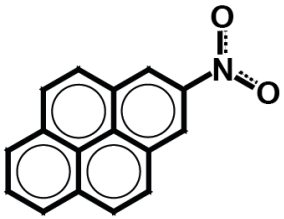
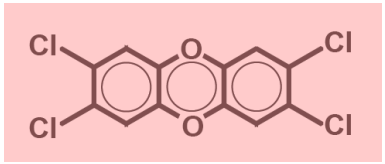


24

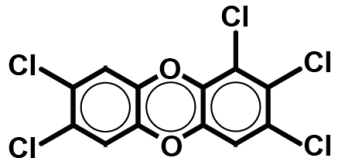
Polychlorinated dibenzodioxins (PCDDs)

All 2,3,7,8-PCDDs are AHR ligands with relative receptor affinities of 0.001 to 1.0

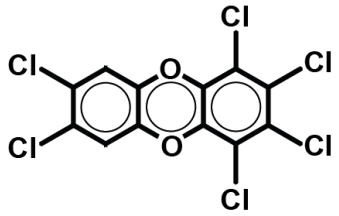
2,3,7,8-TCDD is the strongest AHR ligand!



25*
(1.0x)

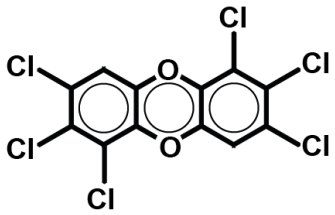


26*
(0.5x)



27*
(0.1x)

the Seveso dioxin



28*
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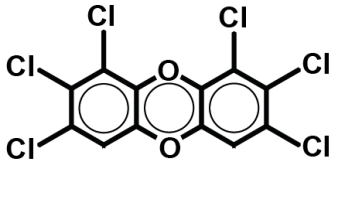

29*
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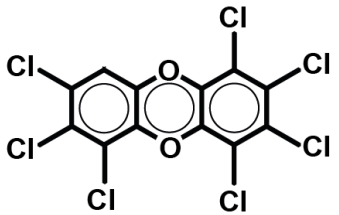

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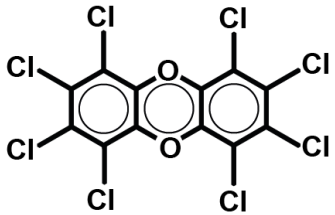
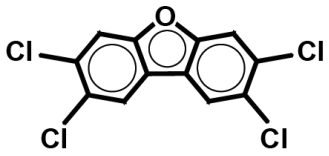


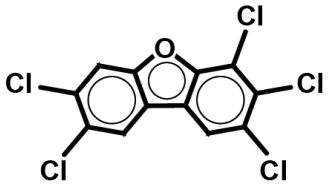
31*
(0.001x)

Polychlorinated dibenzofurans (PCDFs)

All 2,3,7,8-PCDFs are AHR ligands with relative receptor affinities of 0.001 to 0.1



32*
(0.1x)



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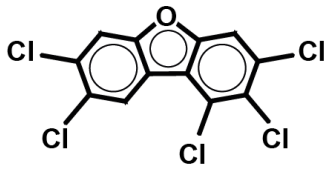

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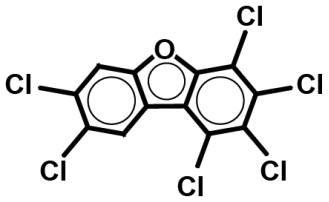

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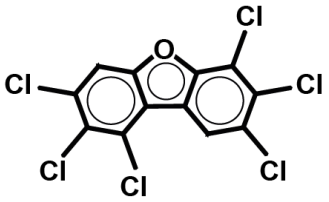

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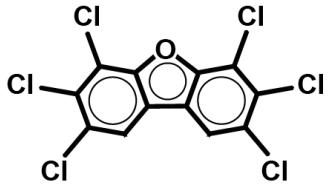

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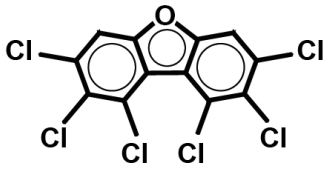

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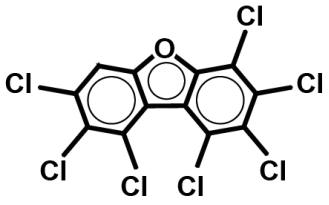
(0.1x)



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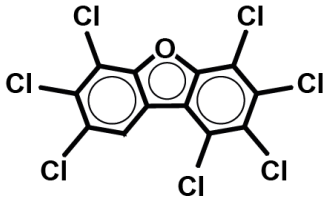
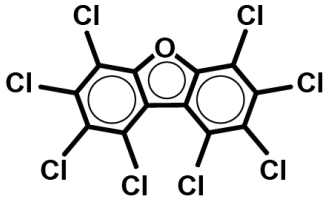
(0.01x)



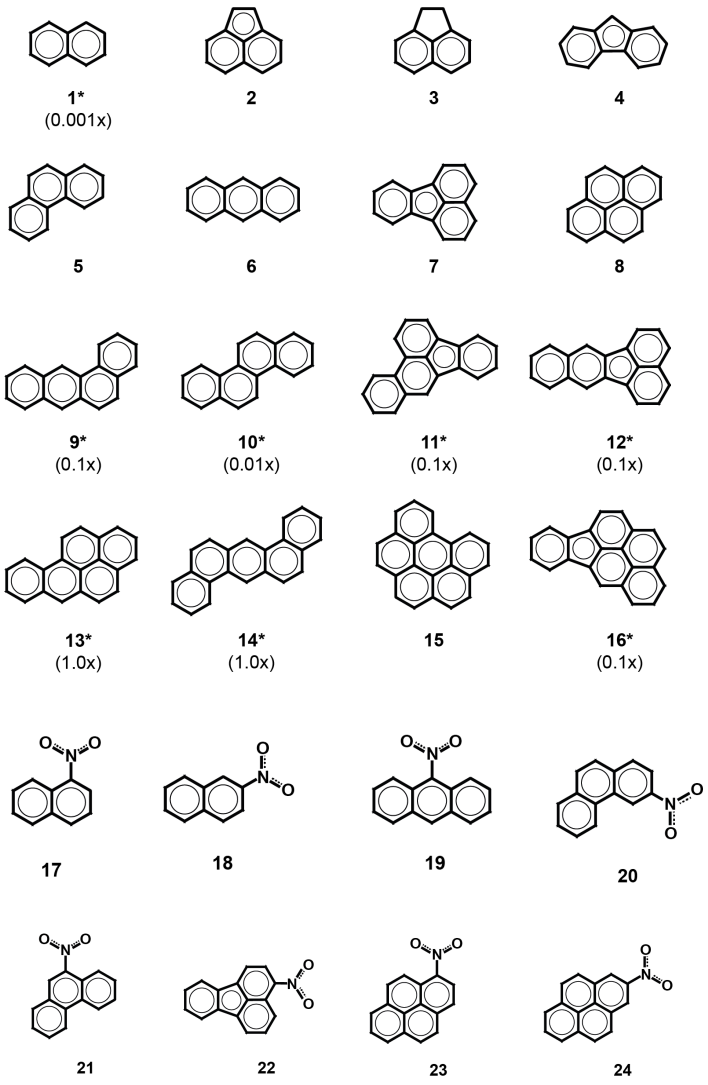
40*
(0.01x)

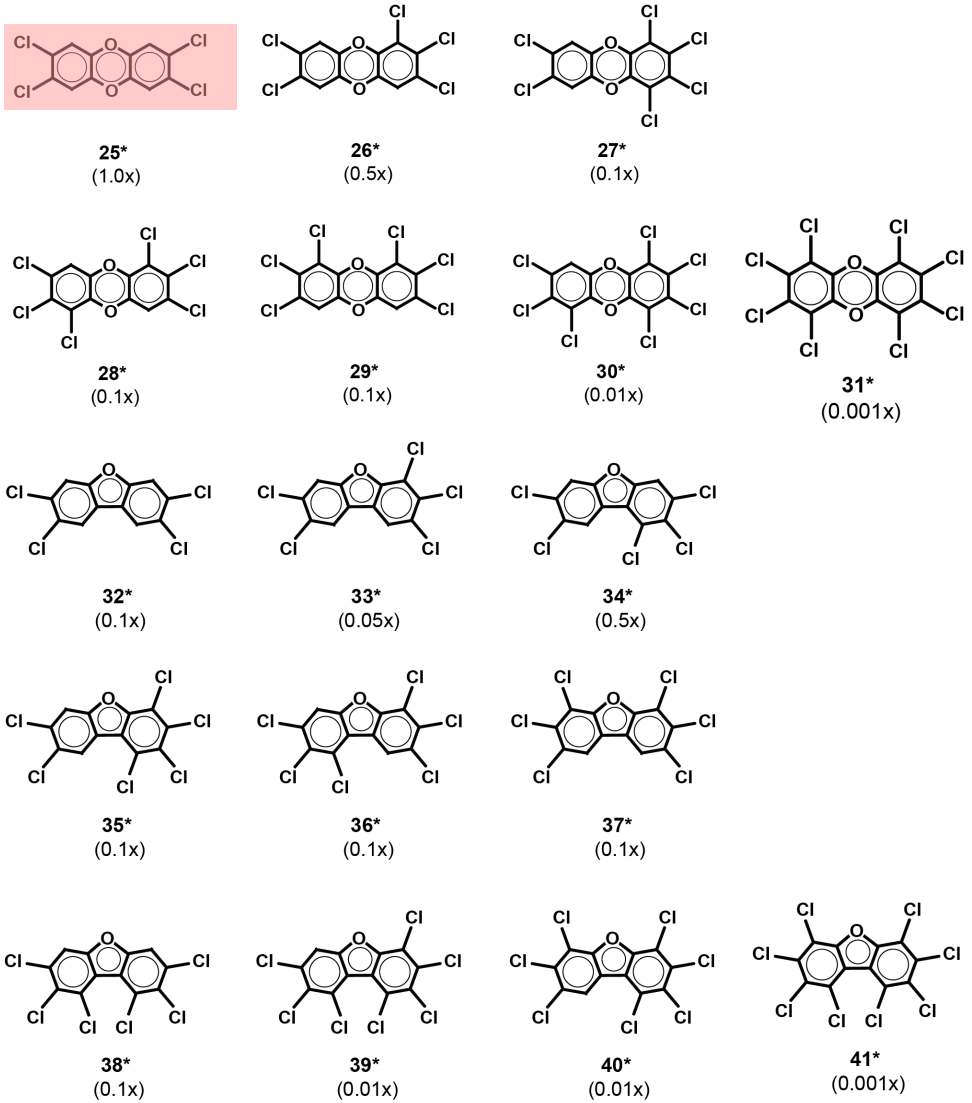


41*
(0.001x)

Aryl hydrocarbon receptor ligands

Gasoline vehicle exhausts were tested for the presence of 41 AHR ligands

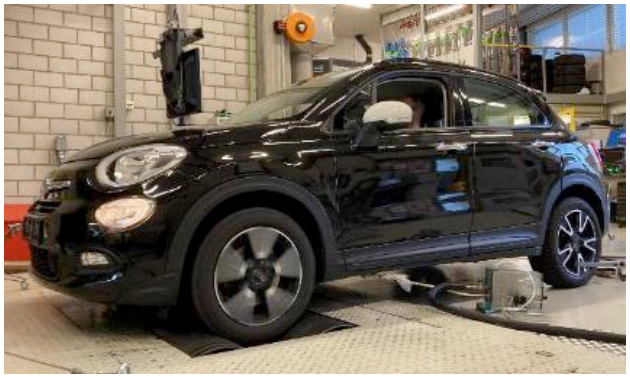


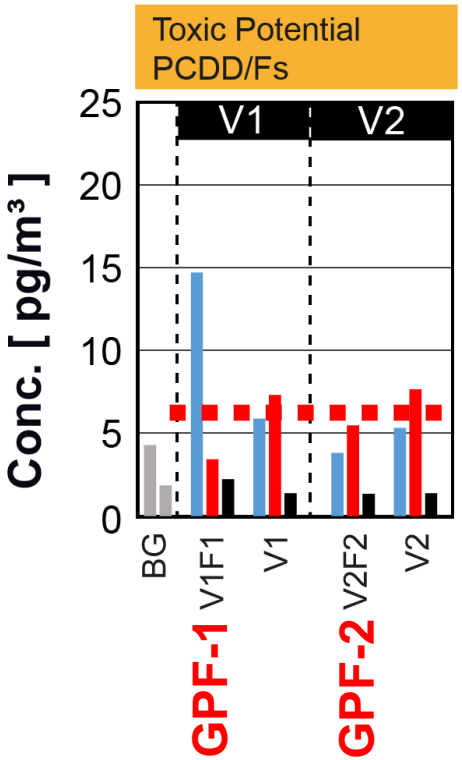


Polychlorinated dibenzodioxins (PCDFs)

No indications for a GPF-induced formation of PCDD/Fs under best case conditions.

PCCD/Fs



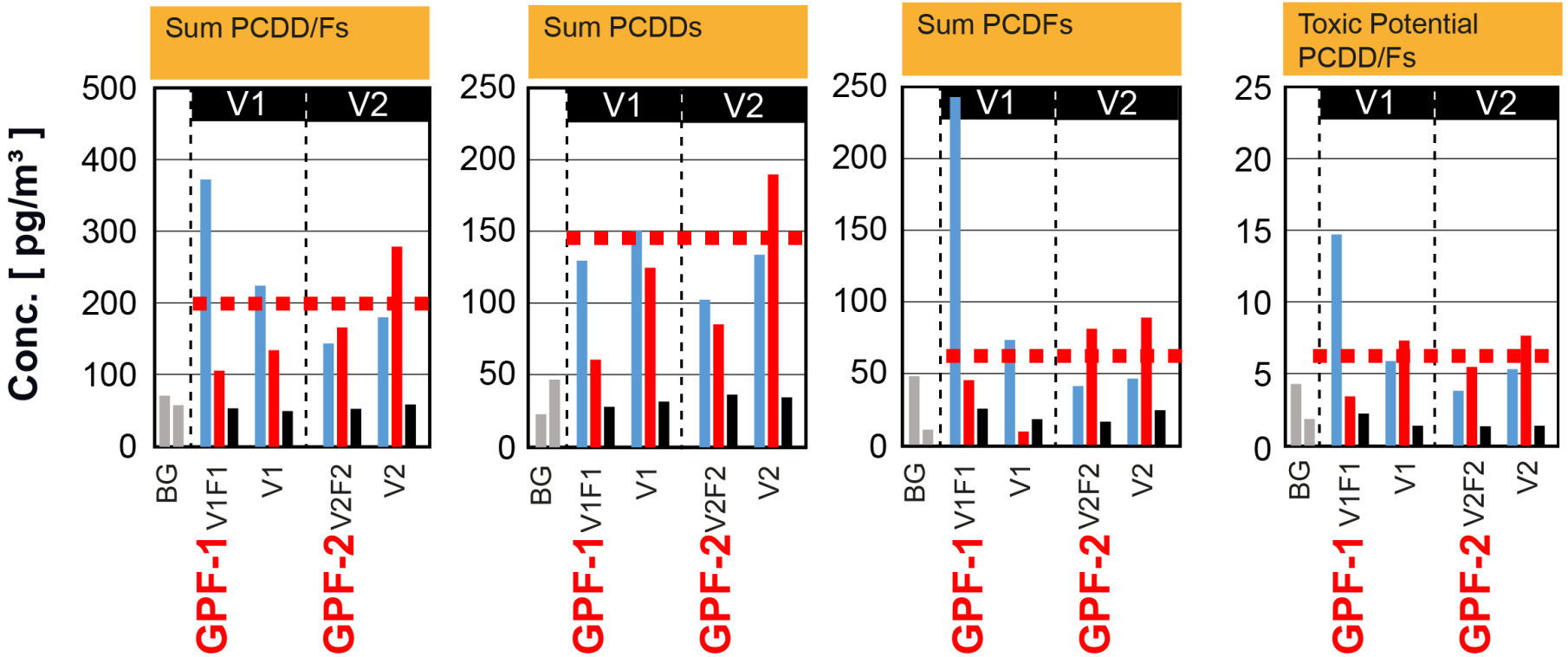


V1: MPI Fiat 500X (1.6 L, 49’500 km) **V2: GDI** VW Golf TSI (1.4 L, 72’000 km)

Polychlorinated dibenzodioxins (PCDFs)

No indications for a GPF-induced formation of PCDD/Fs under best case conditions.

PCCD/Fs

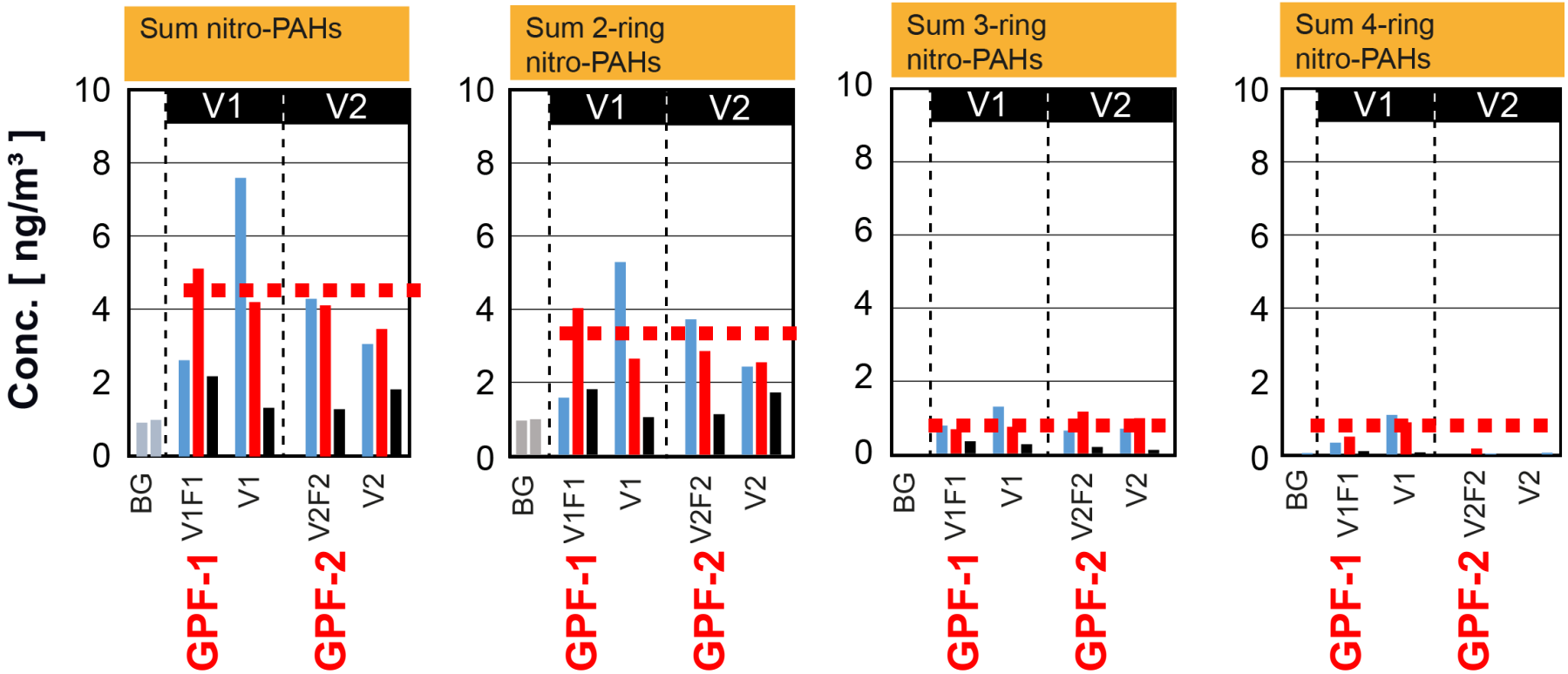


V1: MPI Fiat 500X (1.6 L, 49’500 km) **V2: GDI** VW Golf TSI (1.4 L, 72’000 km)

Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs)

No indications for a GPF-induced formation of nitro-PAHs.

Nitro-PAHs



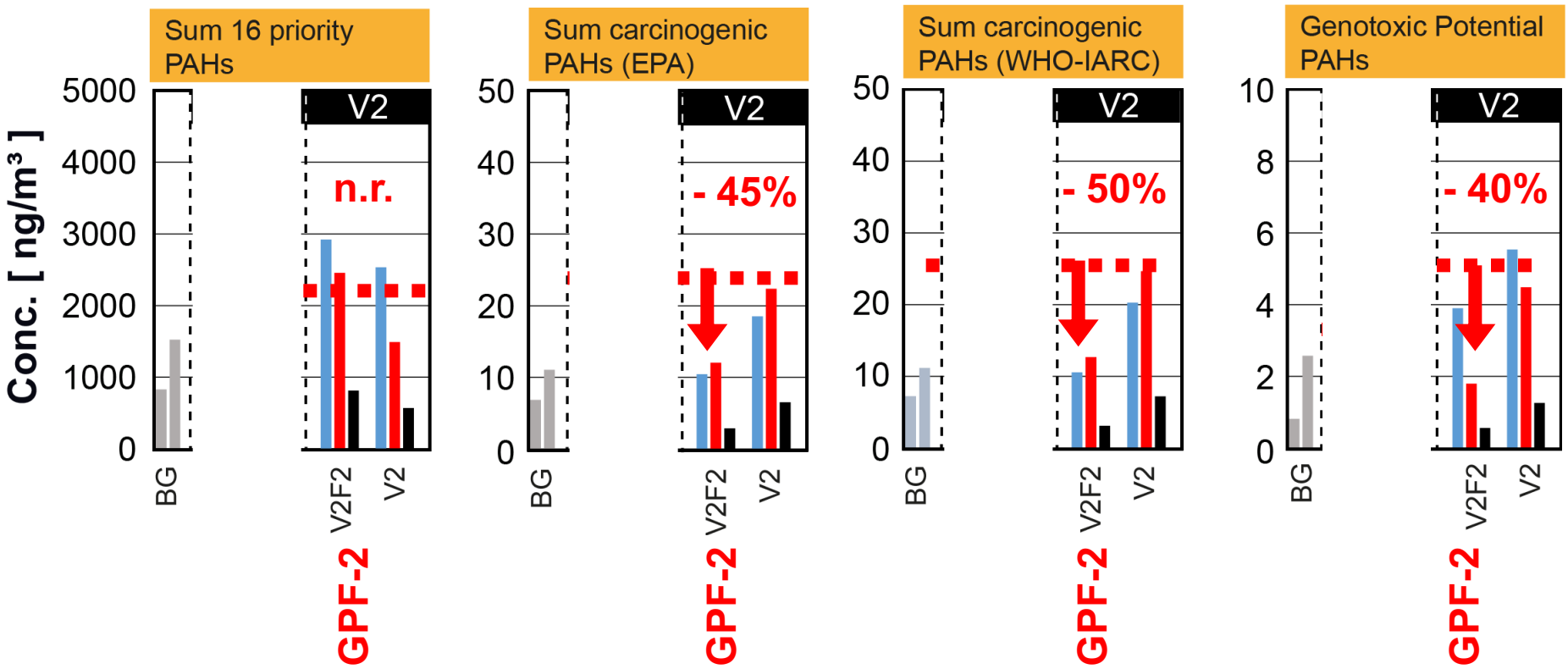
V1: MPI Fiat 500X (1.6 L, 49’500 km) **V2: GDI** VW Golf TSI (1.4 L, 72’000 km)

Polycyclic aromatic hydrocarbons (PAHs) (Aryl hydrocarbons)

No indications for a GPF-induced formation of PAHs

Reduction of genotoxic PAHs of GPF-2 on the GDI-vehicle (VW Golf)

PAHs



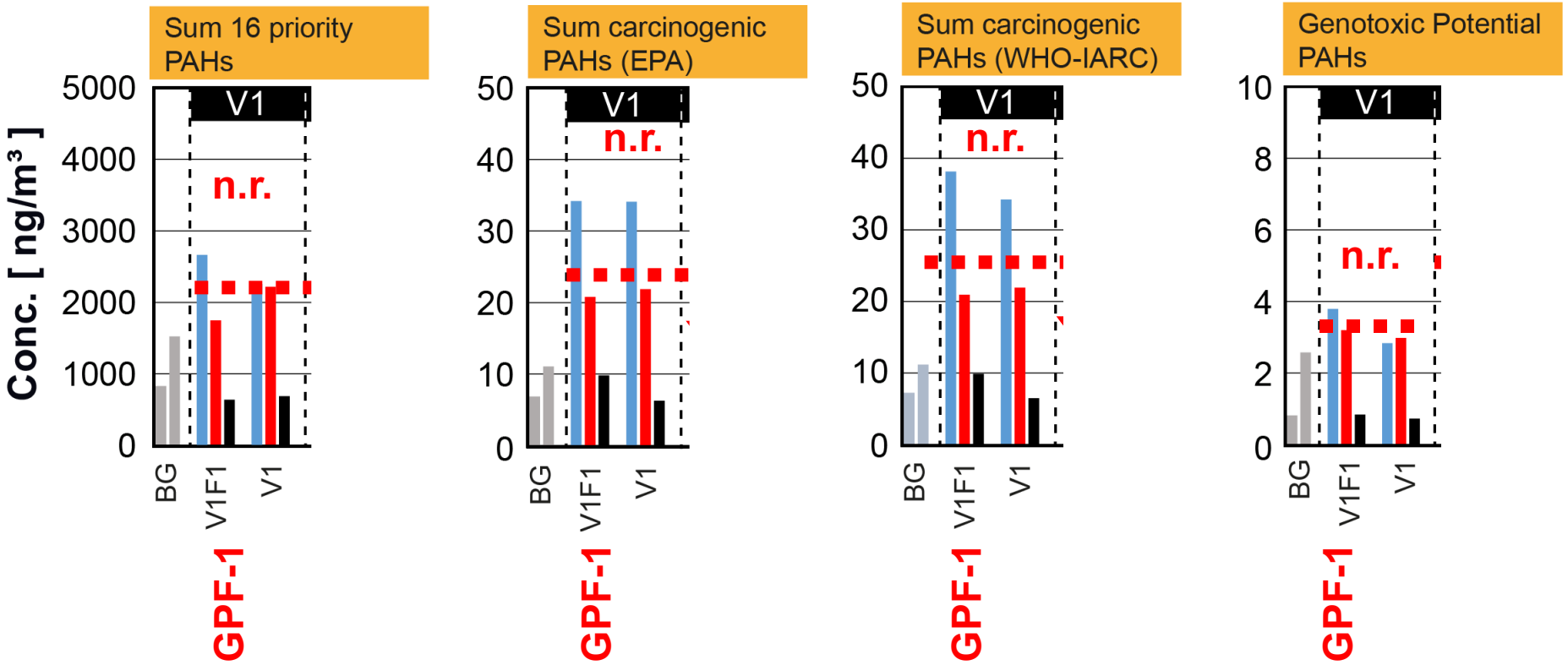
V1: MPI Fiat 500X (1.6 L, 49’500 km) **V2: GDI** VW Golf TSI (1.4 L, 72’000 km)

Polycyclic aromatic hydrocarbons (PAHs)

No indications for a GPF-induced formation of PAHs

PAHs

No reduction of genotoxic PAHs of GPF-1 on the MPI-vehicle (Fiat 500X)



V1: MPI Fiat 500X (1.6 L, 49'500 km) **V2: GDI** VW Golf TSI (1.4 L, 72'000 km)

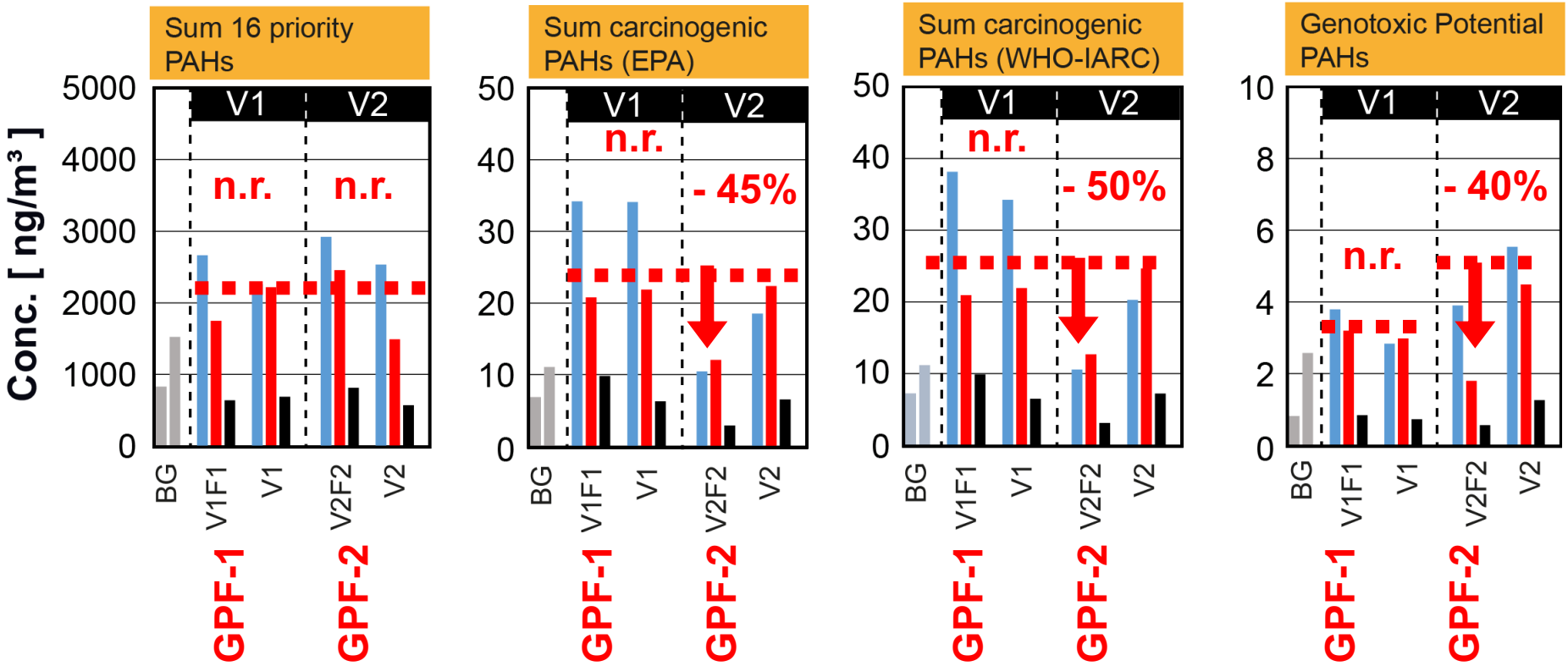
Polycyclic aromatic hydrocarbons (PAHs)

No indications for a GPF-induced formation of PAHs

Reduction of genotoxic PAHs of GPF-2 on the GDI-vehicle (VW Golf)

No reduction of genotoxic PAHs of GPF-1 on the MPI-vehicle (Fiat 500X)

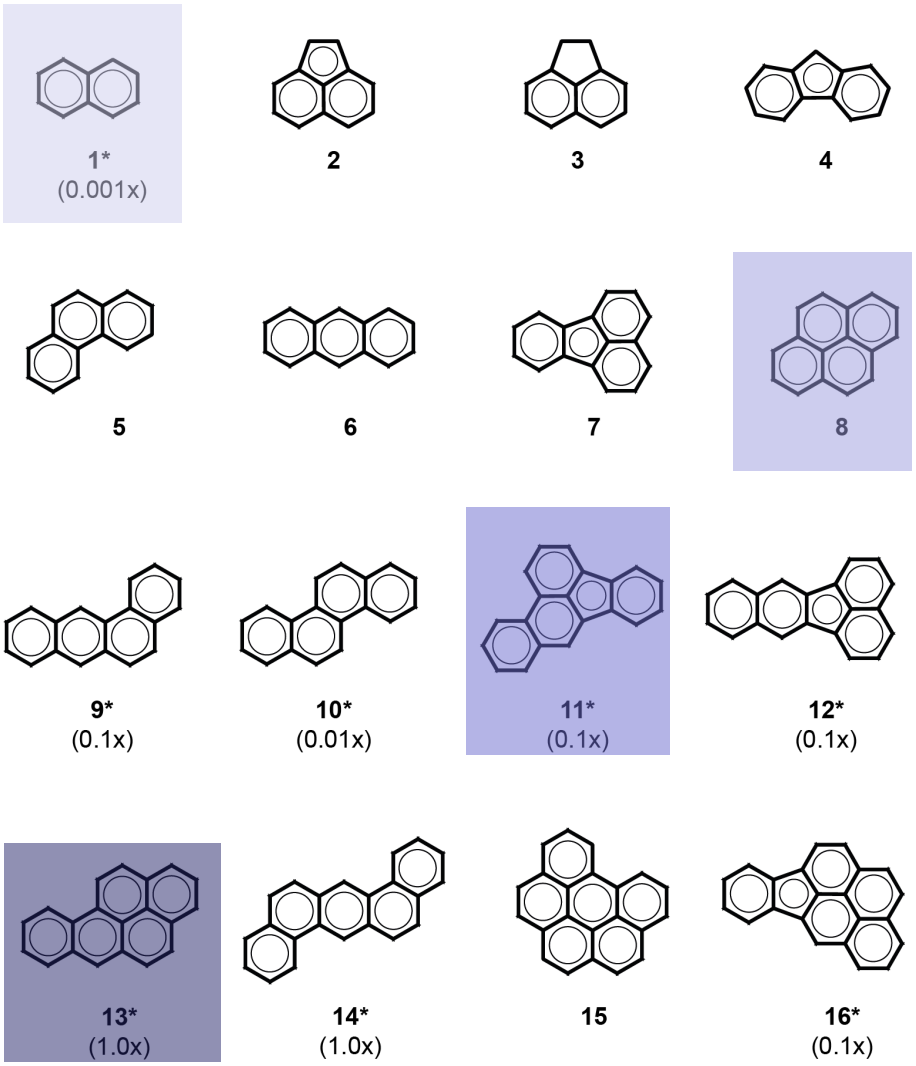
PAHs

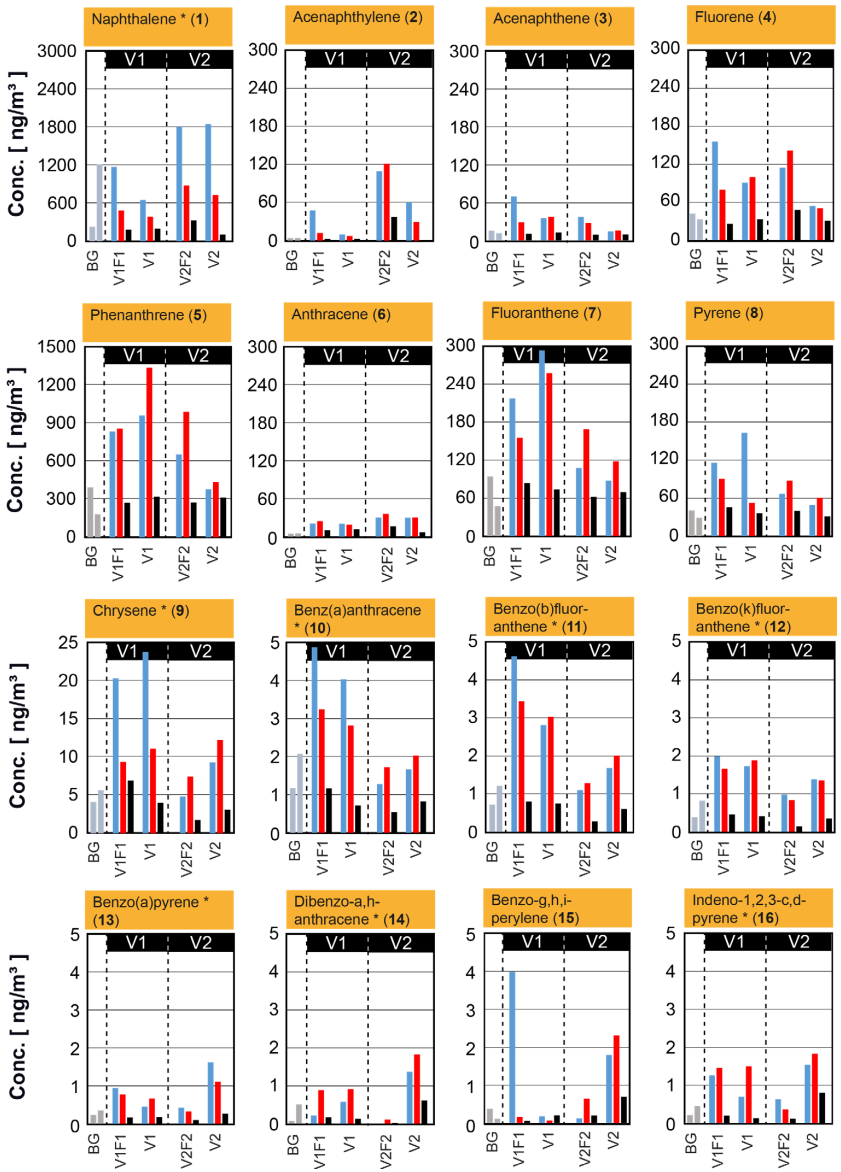


V1: MPI Fiat 500X (1.6 L, 49’500 km) **V2: GDI** VW Golf TSI (1.4 L, 72’000 km)

Polycyclic aromatic hydrocarbons (PAHs)

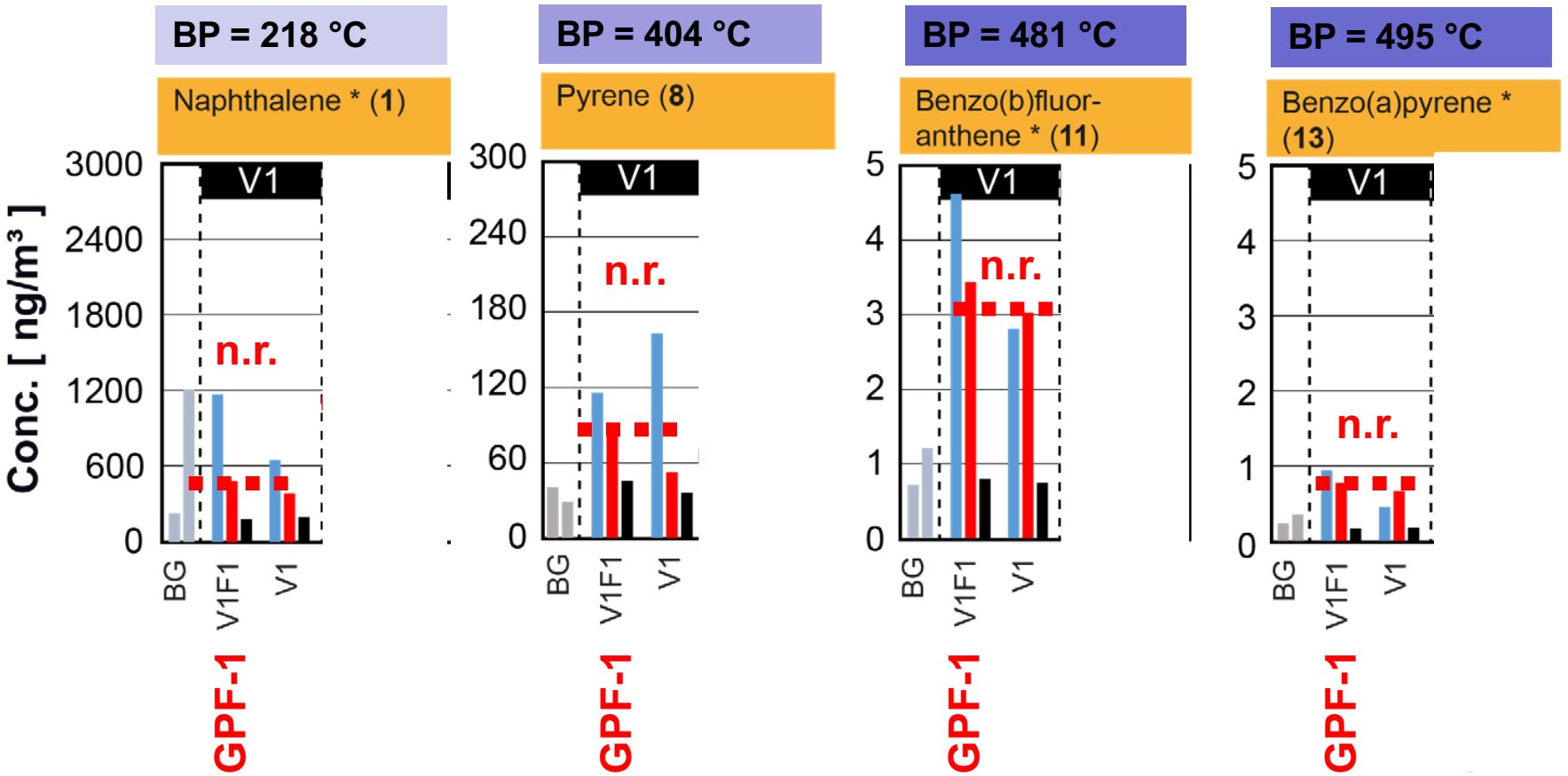
What about individual PAHs?





Polycyclic aromatic hydrocarbons (PAHs)

No PAH-reduction with GPF-1 on the MDI vehicle (Fiat 500X)

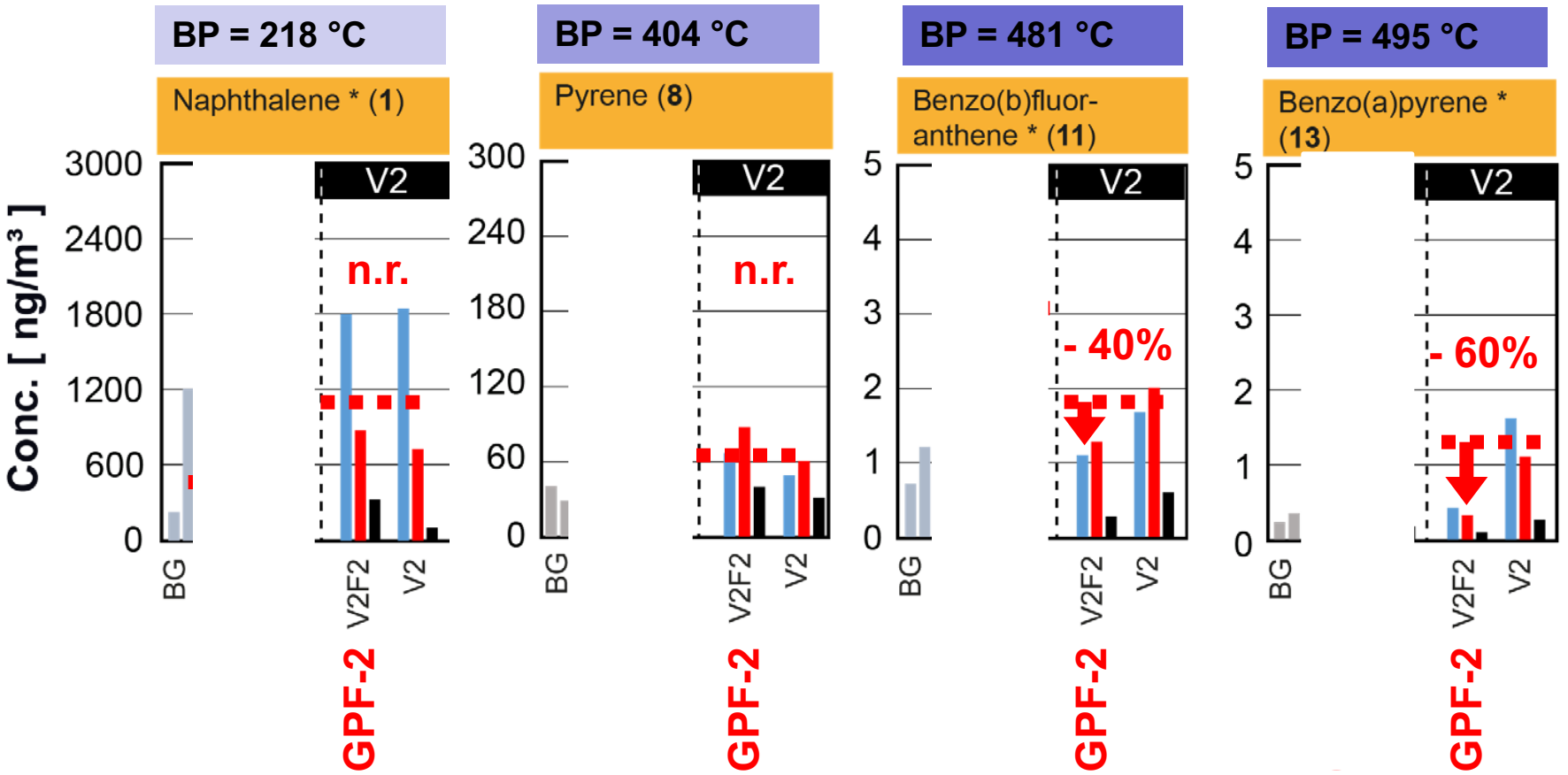


V1: MDI Fiat 500X (1.6 L, 49’500 km) **V2: GDI** VW Golf TSI (1.4 L, 72’000 km)

Polycyclic aromatic hydrocarbons (PAHs)

No PAH-reduction with GPF-1 on the MDI vehicle (Fiat 500X)

Some reduction of high boiling PAHs (>450 °C) with GPF-2 on the GDI vehicle (VW Golf)



V1: MDI Fiat 500X (1.6 L, 49'500 km) **V2: GDI** VW Golf TSI (1.4 L, 72'000 km)

Polycyclic aromatic hydrocarbons (PAHs)

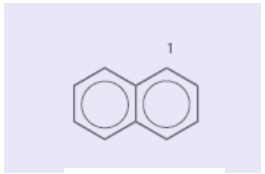
PAHs - a diverse class of compounds with variable physico-chemical properties

2- to 6-ring PAHs

Volatile PAHs penetrate PFs

Semi-volatile PAHs are stored, but can be released again

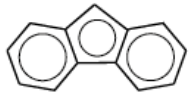
Non-volatile PAHs are stored like soot



218 °C

2

3



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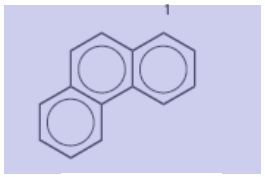
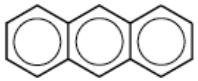


340 °C



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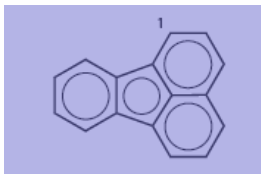
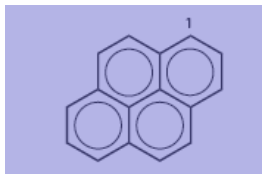
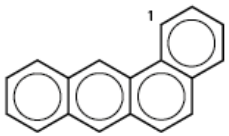


375 °C



404 °C



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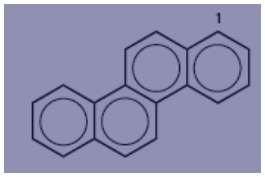
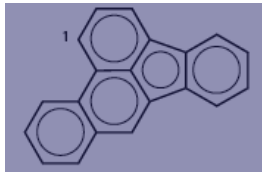
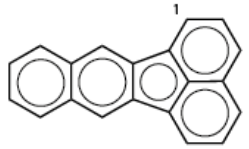


448 °C



481 °C



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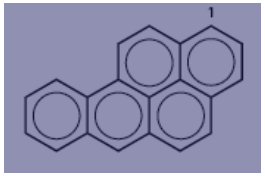
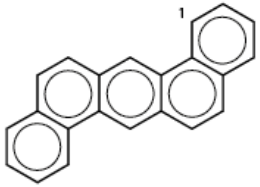


495 °C



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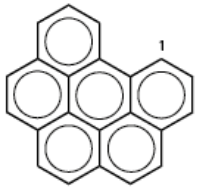

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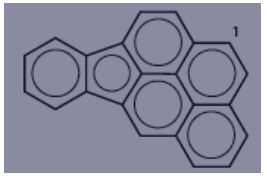
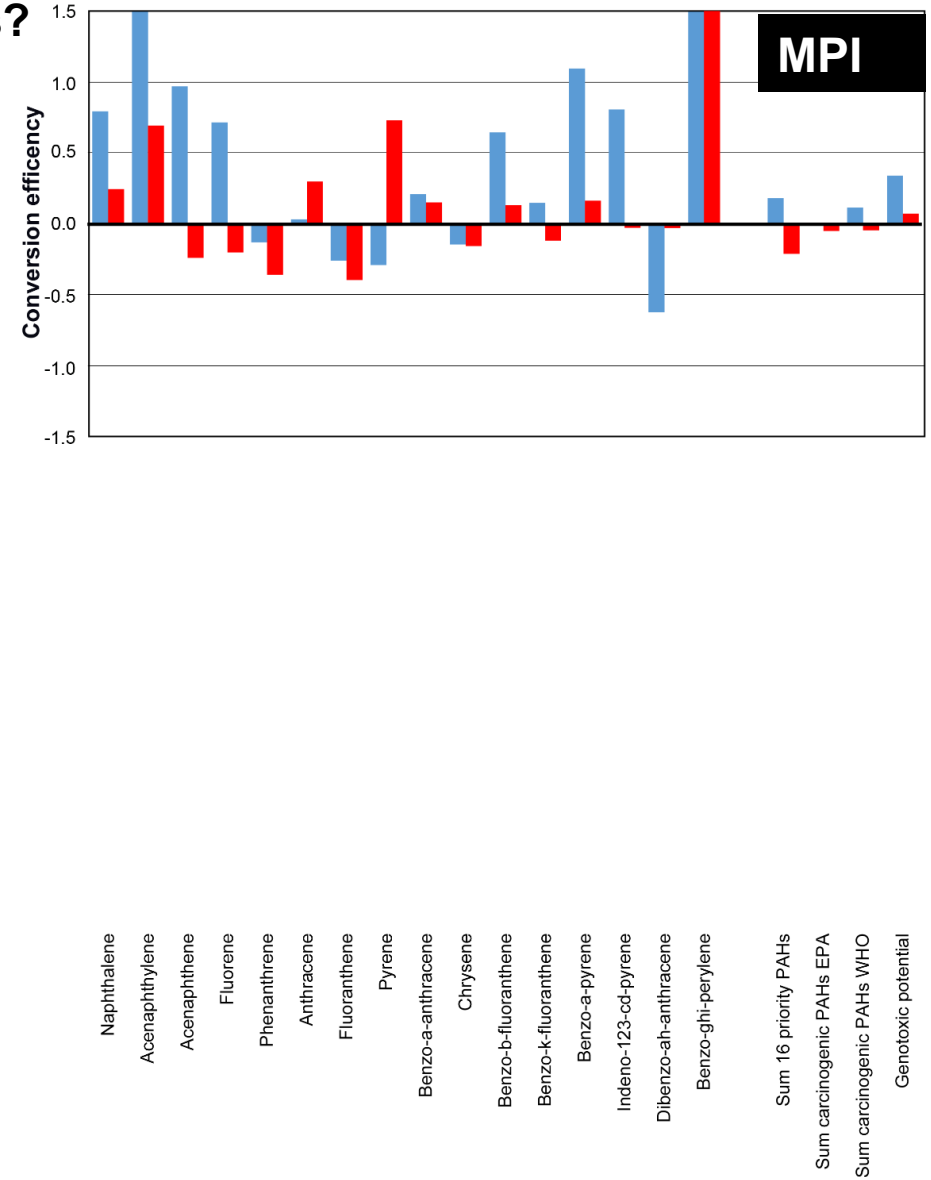


536 °C

Polycyclic aromatic hydrocarbons (PAHs)

Conversion efficiencies of individual PAHs?



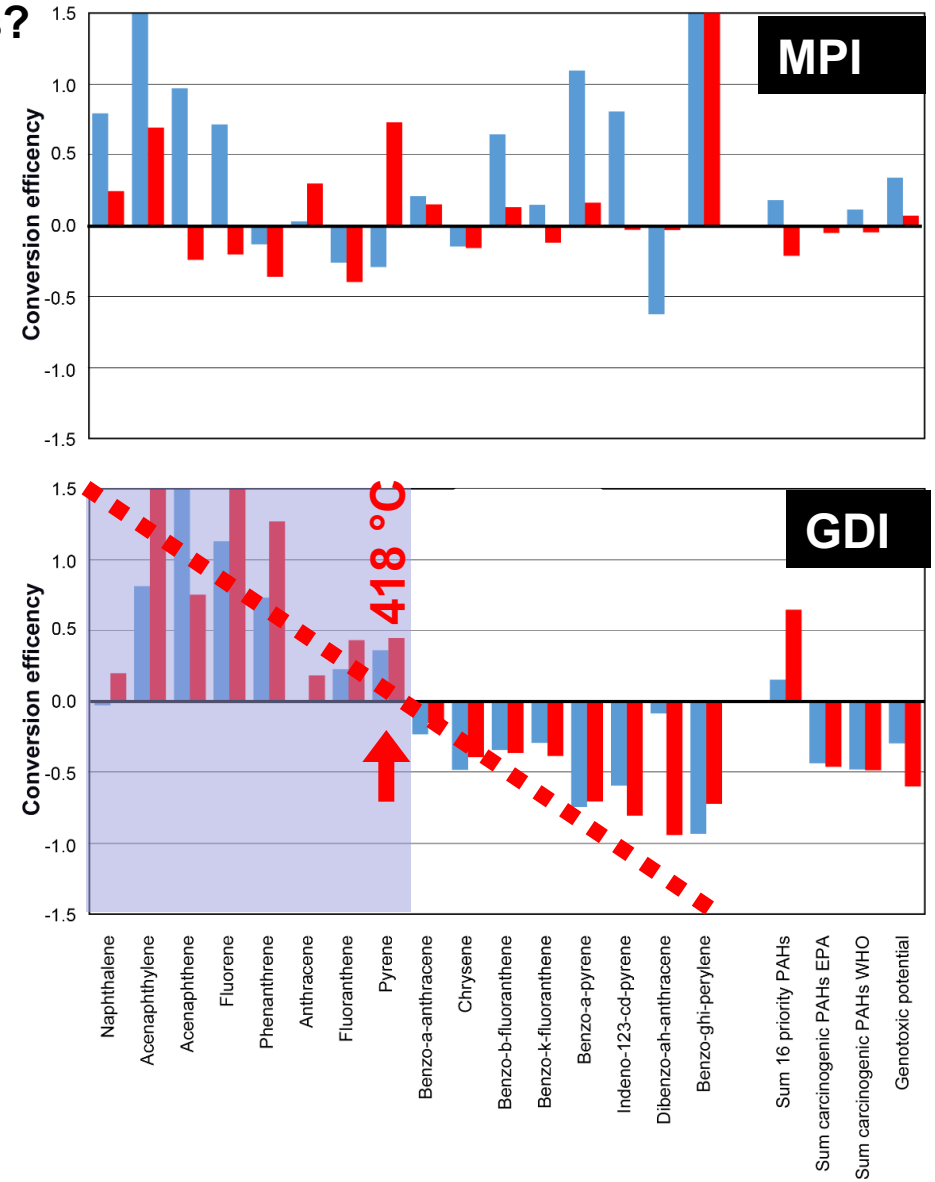
No systematic trend,
all tested PAHs can penetrate
the GPF-1 on the MPI-vehicle V1

Polycyclic aromatic hydrocarbons (PAHs)

Conversion efficiencies of individual PAHs?

**No systematic trend,
all tested PAHs can penetrate
the GPF-1 on the MPI-vehicle V1**

Systematic trend, all semi-volatile PAHs penetrate the GPF-2 on the GDI-vehicle V2



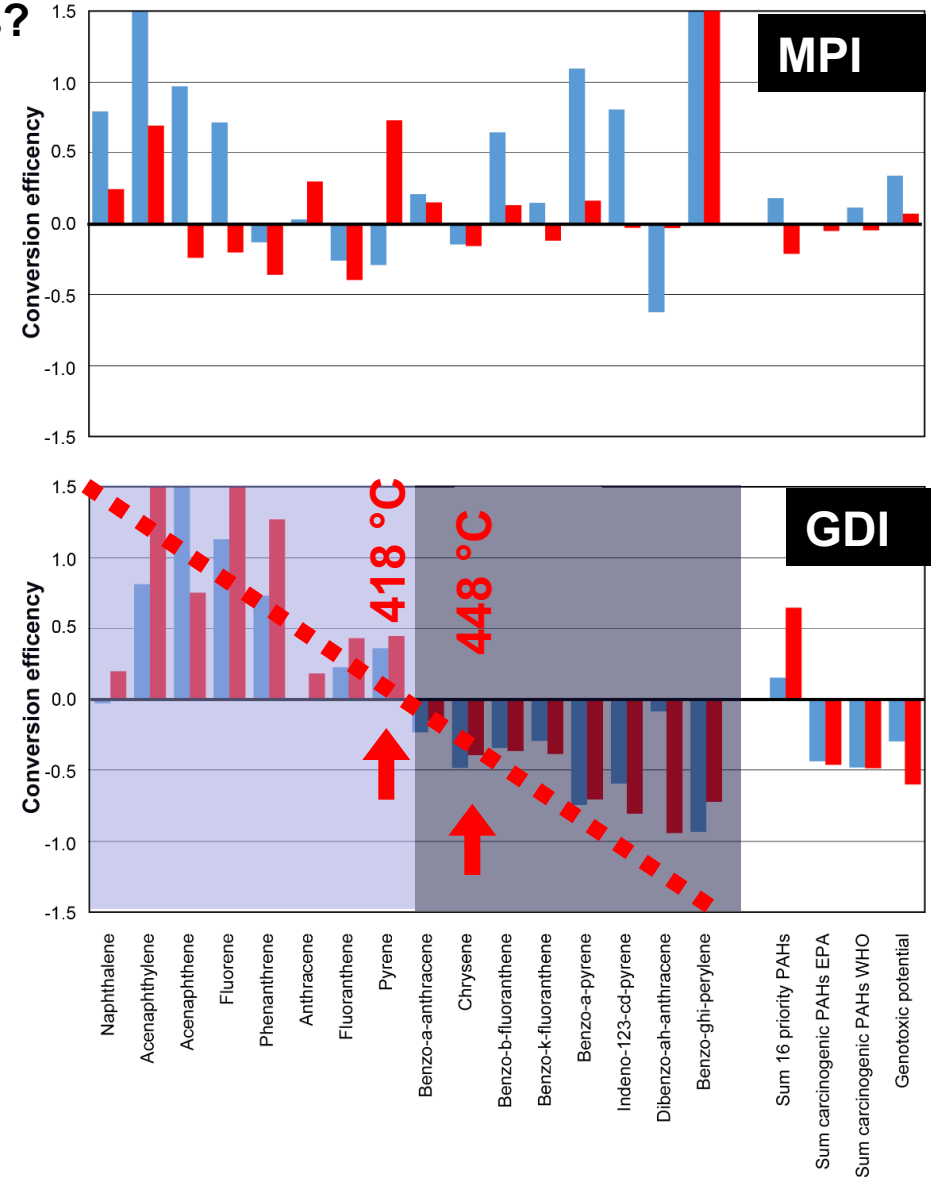
Polycyclic aromatic hydrocarbons (PAHs)

Conversion efficiencies of individual PAHs?

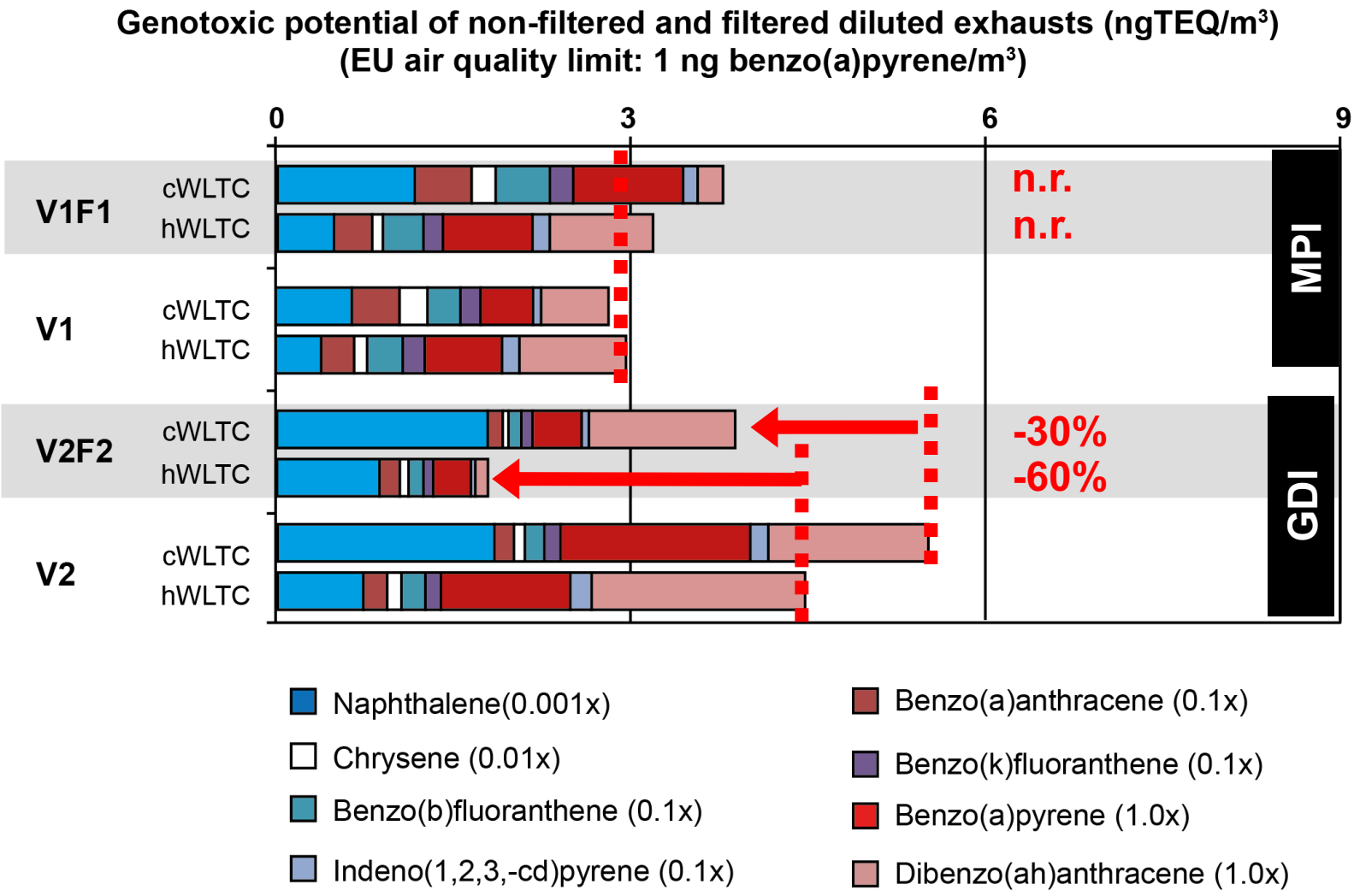
**No systematic trend,
all tested PAHs can penetrate
the GPF-1 on the MPI-vehicle V1**

Systematic trend, all semi-volatile PAHs penetrate the GPF-2 on the GDI-vehicle V2

Non-volatile PAHs (BP >450 °C) are removed by GPF-2 on the GDI-vehicle V2



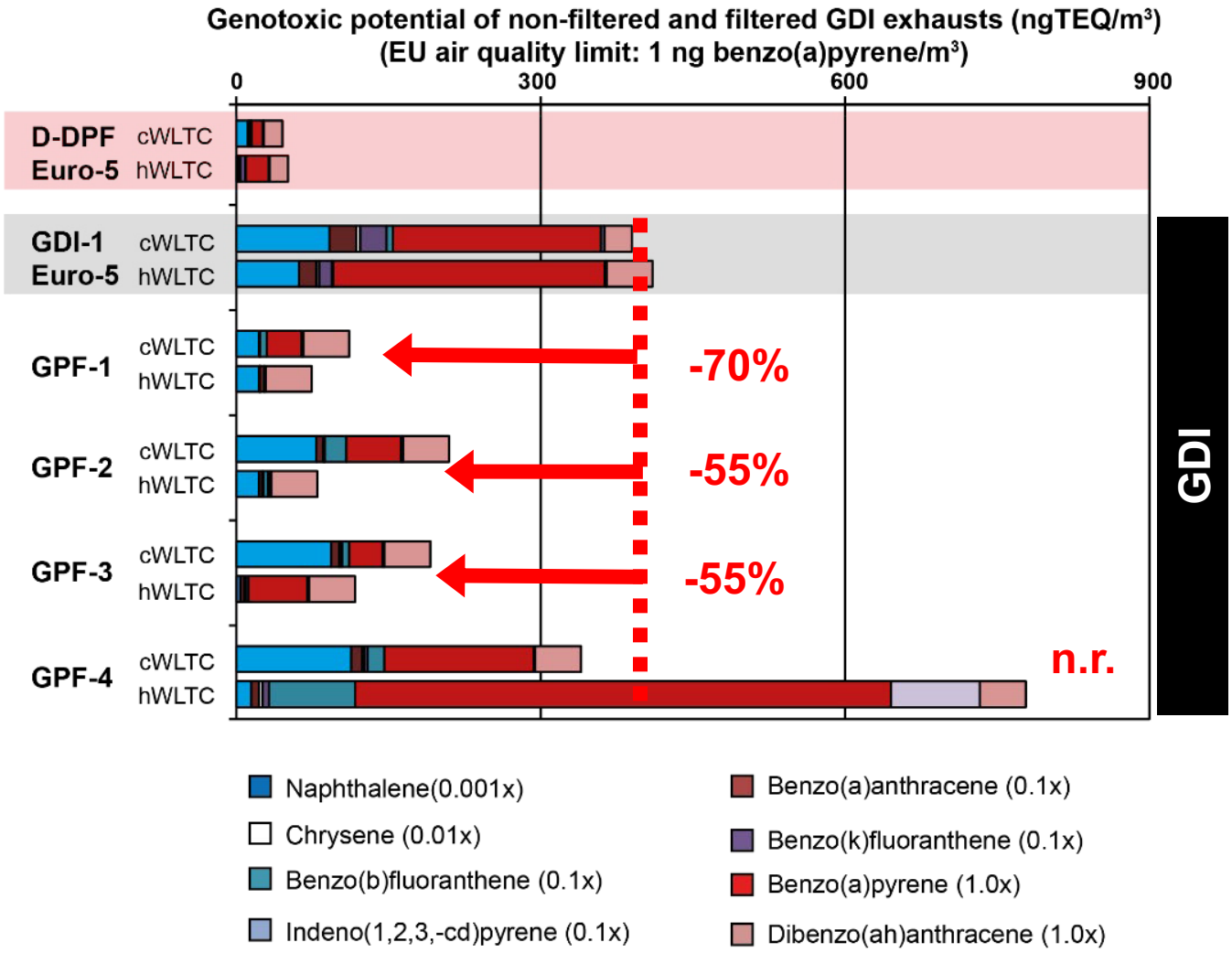
Genotoxic potential of PAHs



V1: MPI Fiat 500X (1.6 L, 49'500 km) **V2: GDI** VW Golf TSI (1.4 L, 72'000 km)

Genotoxic potential of PAHs

Not all GPFs are able to lower the genotoxic potential of gasoline vehicles



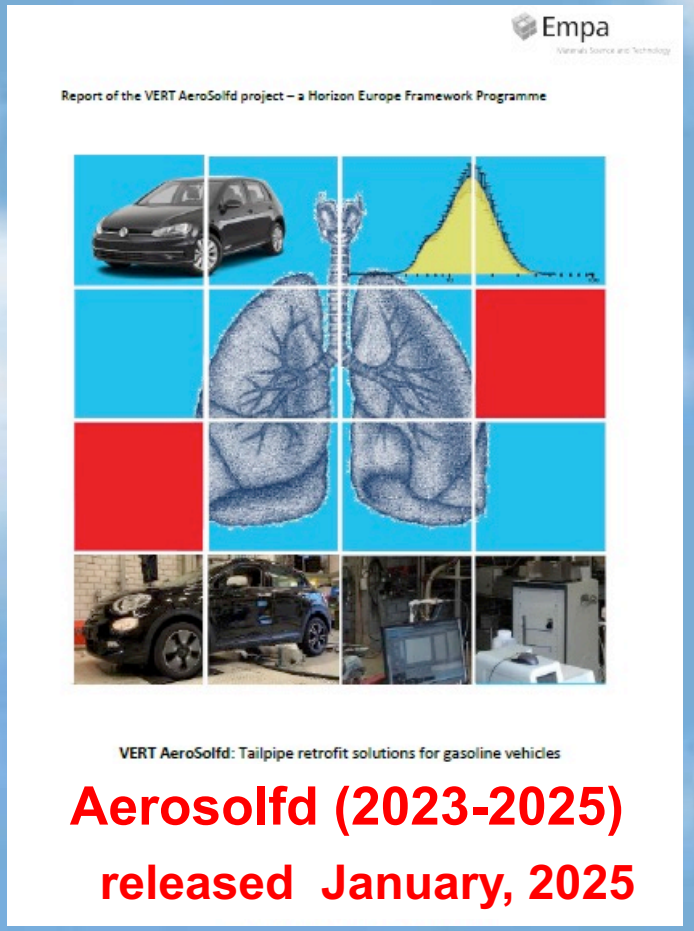
Impact of next-generation GPFs on genotoxic compounds and risks for secondary poisoning

First- and second-generation GPFs tested

GDI vehicle exhausts - at toxic cocktail

- GDI-vehicles release high numbers of NPs which adsorb toxic compounds.
- GDI-NPs small enough to penetrate cell membranes (alveoli, placenta, blood cells) acting like a Trojan horse.
- AHR-mediated transport of chemicals to the cell nucleus with direct contact to genetic material (DNA, mRNA)
- GPFs can lower PN burdens, PAHs and the genotoxic potential.
  No secondary formation of nitro-PAHs and PCDD/Fs observed in GPFs.

GPFs needed to lower PN <1x10e9/km, which should become the new PN limit

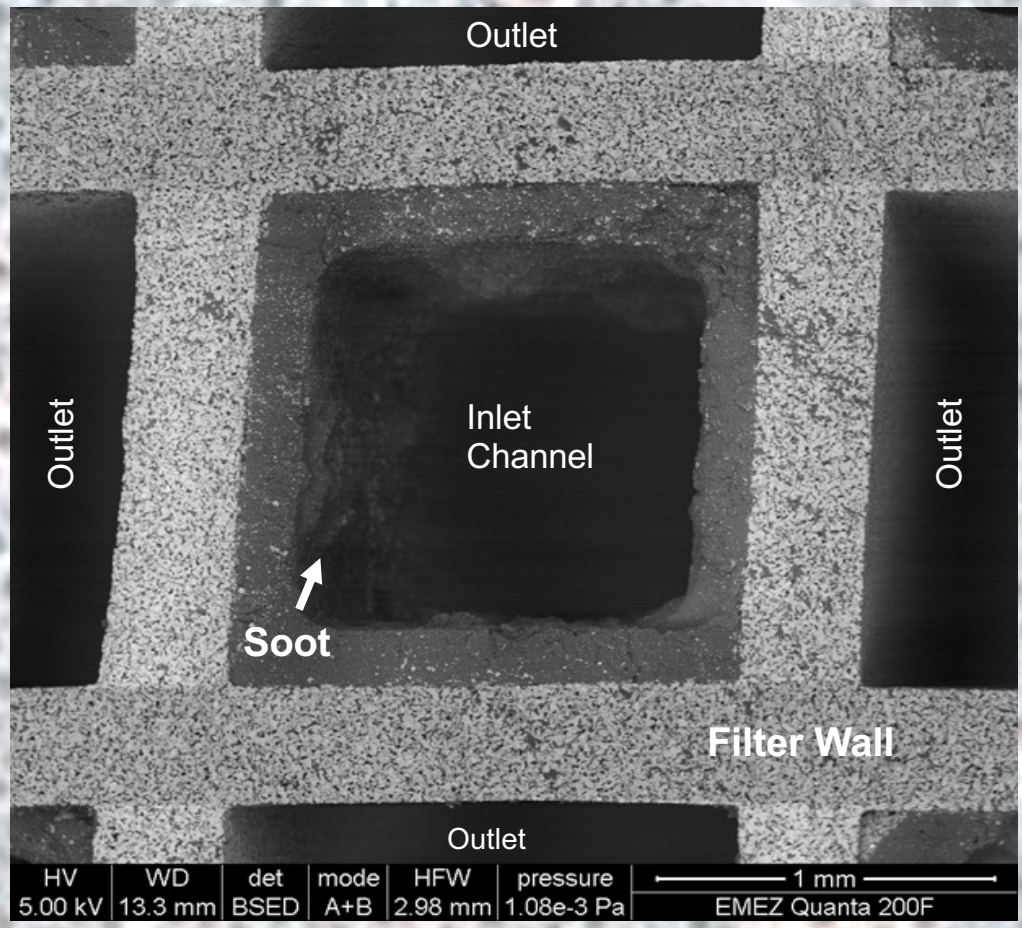


Aerosolfd (2023-2025)

released January, 2025

The visible effect of a DPF

Wall-through filters are highly efficient for soot



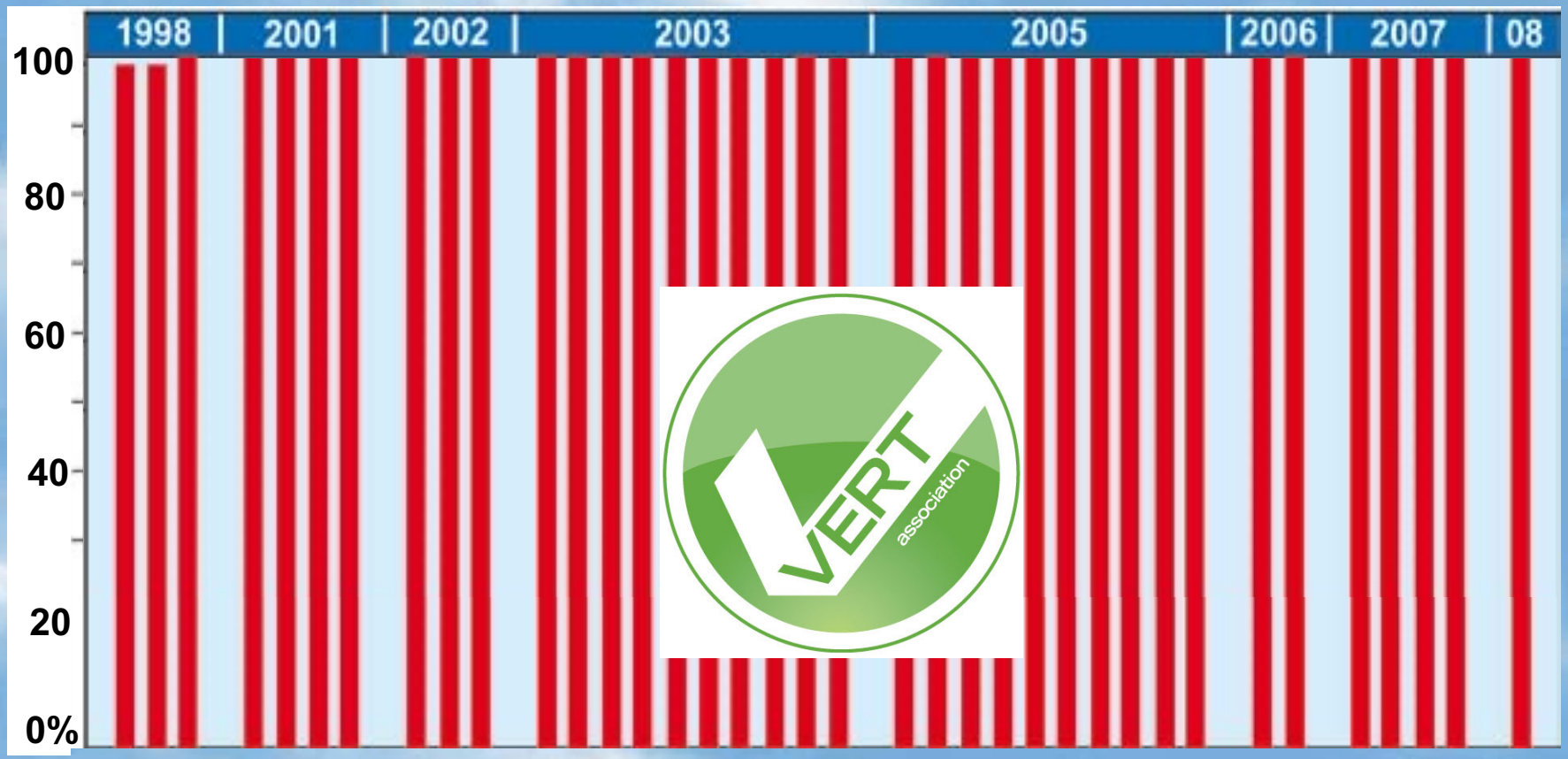
VERT-approved DPFs:

- Reduce PN-emissions (>98%)
- Reduce genotoxic compounds (a.m.a.p.)
- Low risks of toxic secondary emissions

The VERT label for approved particle filter

>60 VERT-approved DPFs available (to use them)

PN filtration efficiencies >98% for all particles (23 – 400 nm)



Mayer et al. MTZ, **2009**, 70, 72-79

VERT approved DPF convert genotoxic PAHs

All VERT approved DPFs convert PAHs, many rather efficient