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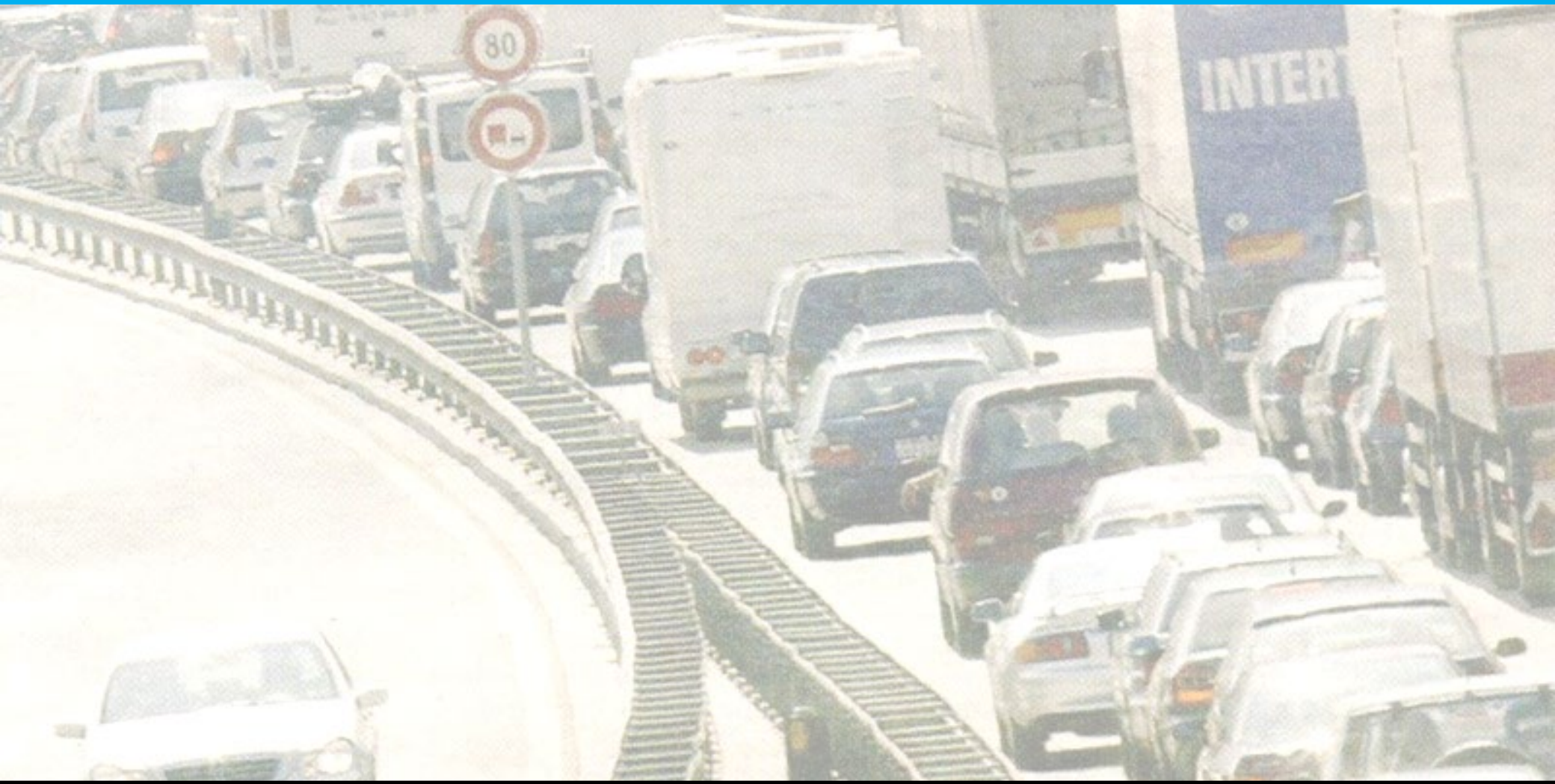
Materials Science and Technology

Secondary emissions test for gasoline direct injection vehicles



13th VERT Forum: New VERT nanoparticle abatement tools

Empa Dübendorf, March 21, 2023

Secondary emissions test for gasoline direct injection vehicles

Something to celebrate!

Outline

- Toxic emissions of GDI vehicles

  GDI vehicles – a massive source for genotoxic nanoparticles

- VSET test on GPF vehicles

  From steady state to transient test cycles

- PFs for gasoline vehicles

  Retro-fit and integrated particle filters for GDI vehicles

13th VERT Forum: New VERT nanoparticle abatement tools

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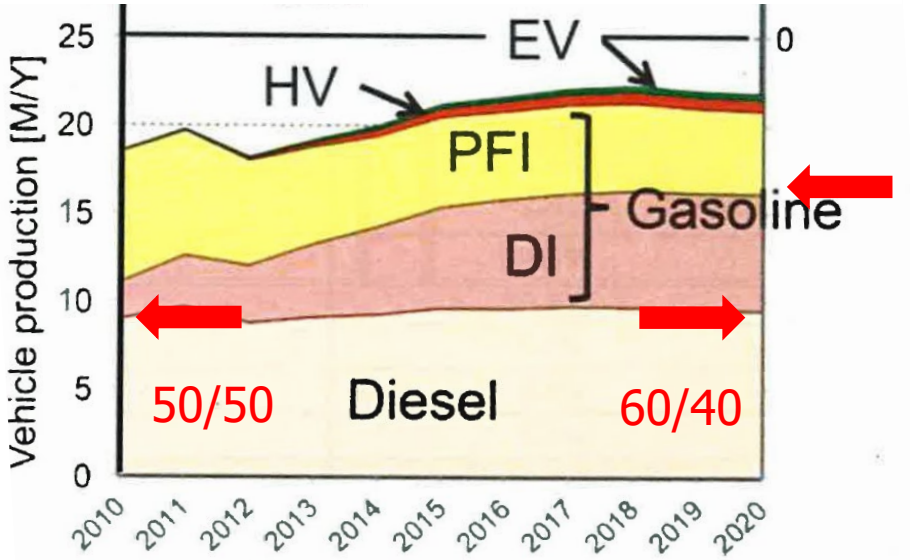
Gasoline direct injection vehicles in the EU

Is there a future for GDI vehicles?

GDI vehicle fleet on the rise

- Gasoline/diesel production: 50/50 in 2010 (18 mio vehicles/y)
- 60/40 in 2020 (22 mio vehicles /y), half of them GDI vehicles



AECC Estimates (Association for Emission Control by Catalyst)

Gasoline direct injection vehicles in the EU

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  half of the gasoline vehicles GDI
- GDI vehicle production,
  2.0 mio vehicles/y in 2010
  6.4 mio vehicles/y in 2020
  53 mio cumulated 2010-2020

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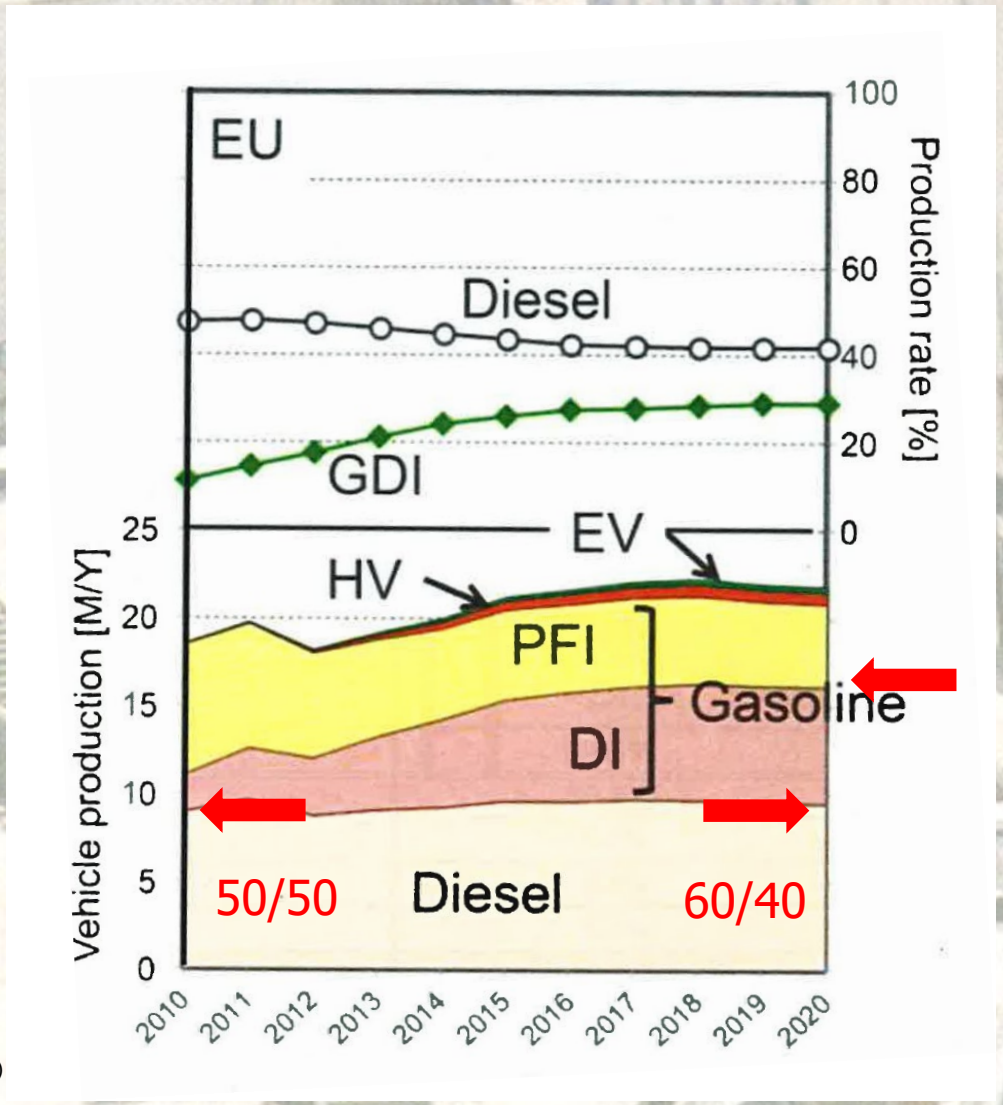

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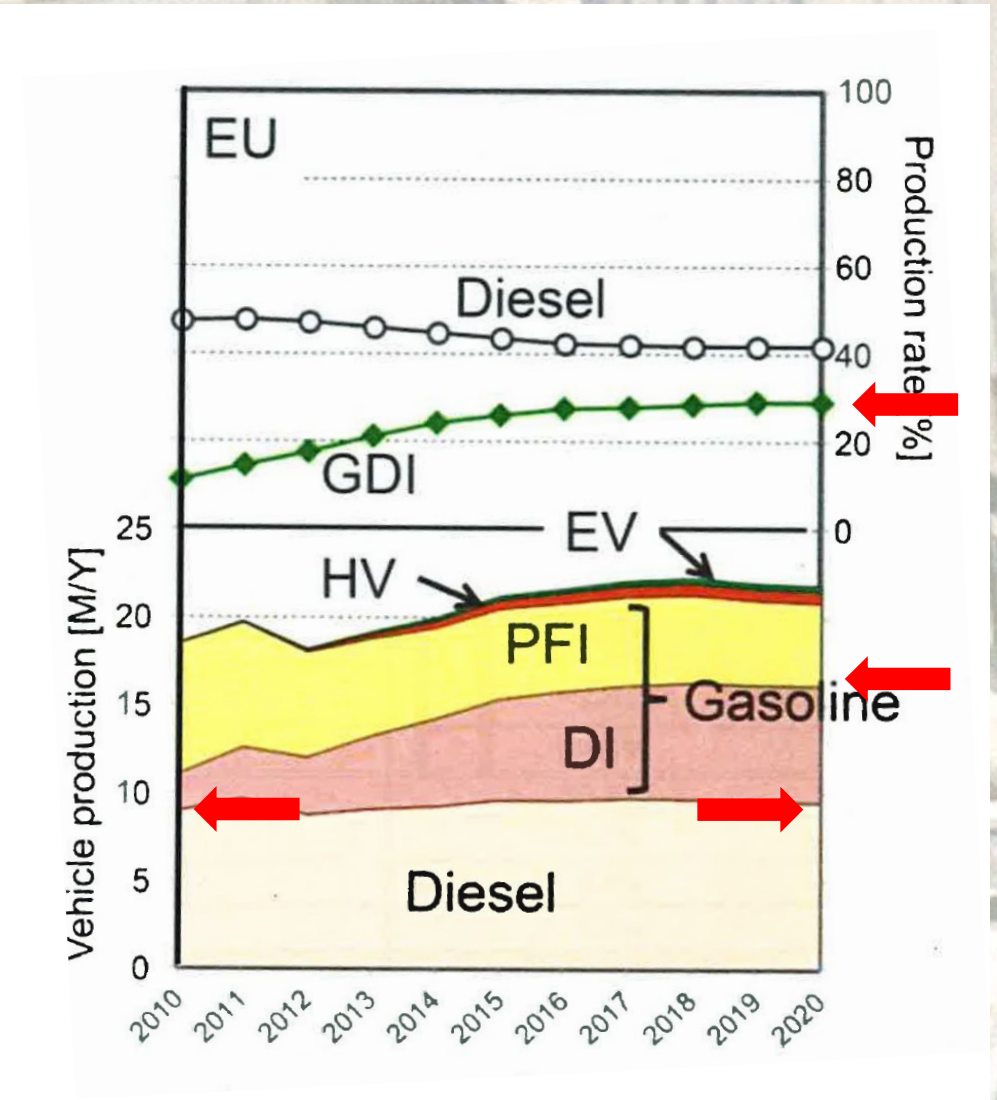

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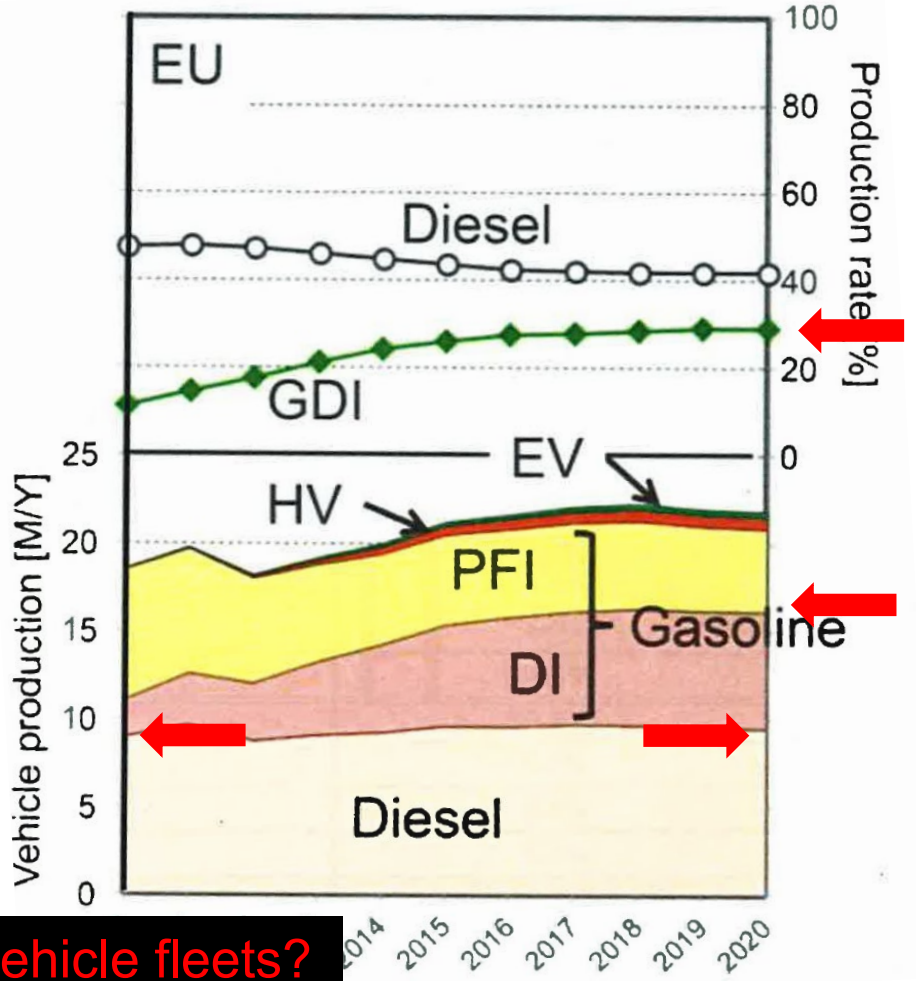

Where are we now with GPFs in our vehicle fleets?

Gasoline direct injection vehicles – the latest source for genotoxic nanoparticles

From sooting diesel to sooting gasoline vehicles – the latest trend on our roads

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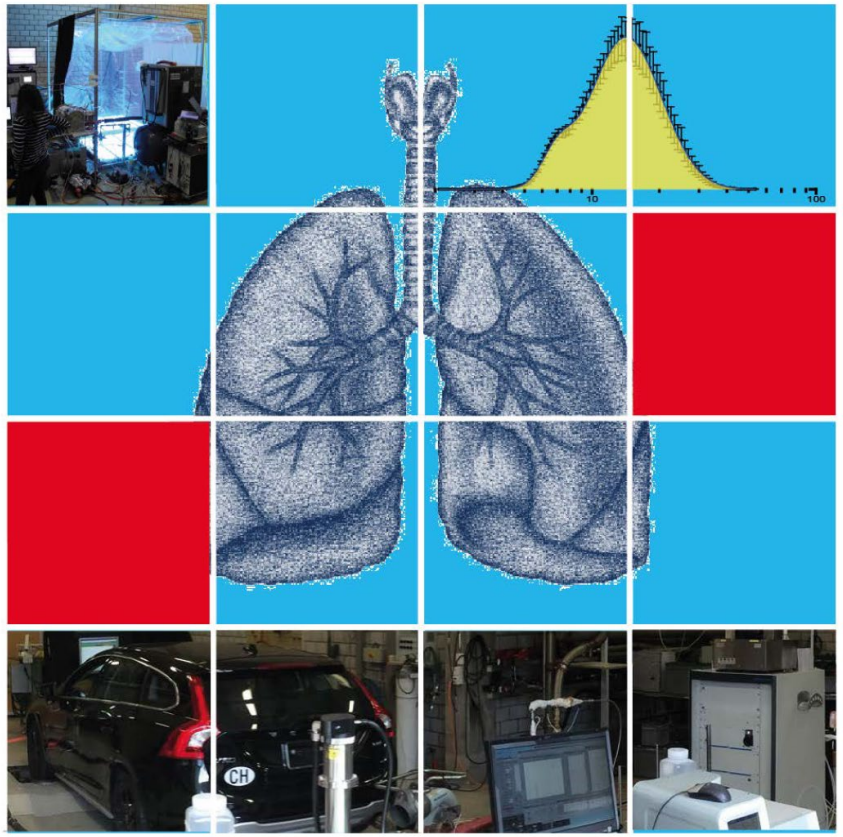
Gasoline direct injection vehicles – the latest source for genotoxic nanoparticles

Lessons learned from the GASOMEP project

GASOMEP project



GASOMEP: Current Status and New Concepts of **Gas**oline Vehicle Emission Control for **O**rganic, **Me**tallic and **P**articulate Non-Legislative Pollutants

https://www.empa.ch/documents/56164/1183406/GASOMEP+Final+Scientific+Report+2017+submitted+Nov.pdf

Authors: P. Comte, J. Czerwinski, A. Keller, N. Kumar, M. Muñoz, S. Pieber, A. Prévôt, A. Wichser, N. Heeb

The GDI fleet

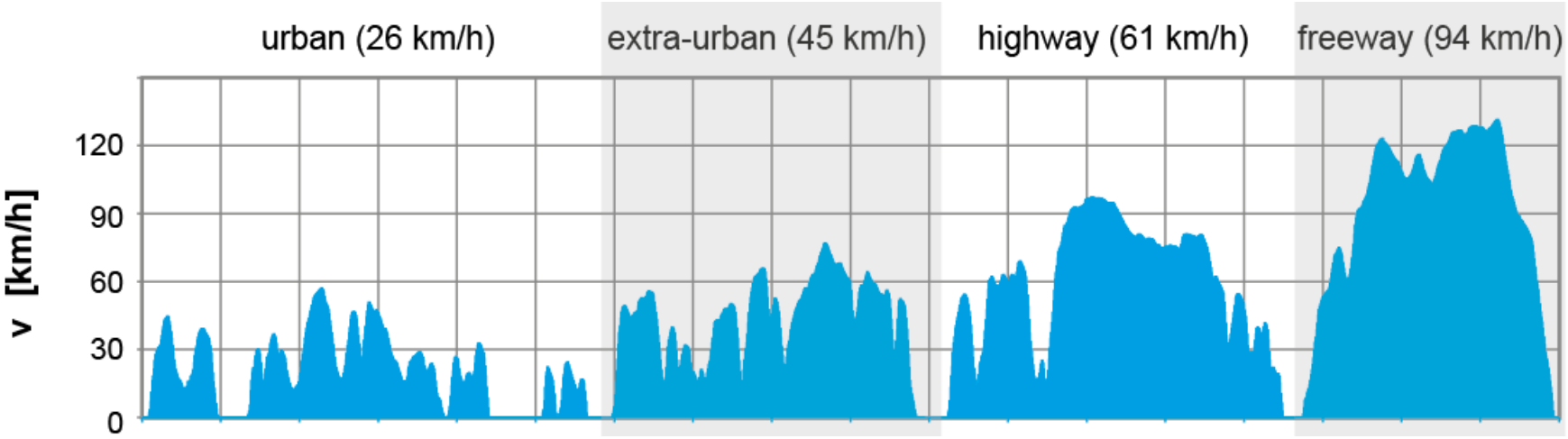
The GASOMEP fleet (n=7)

GDI-1:	Mitsubishi Carisma (1.8 L, the first GDI vehicle)	Euro-3
GDI-2:	VW Golf (1.4 L)	Euro-4
GDI-3:	Opel Insignia (1.6)	Euro-5
GDI-4:	Volvo V60 T4F (1.6 L, GDI reference vehicle	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
DI:	Peugeot 4008 (1.6 L, DPF, benchmark vehicle)	Euro-5

4 generations of vehicle technologies

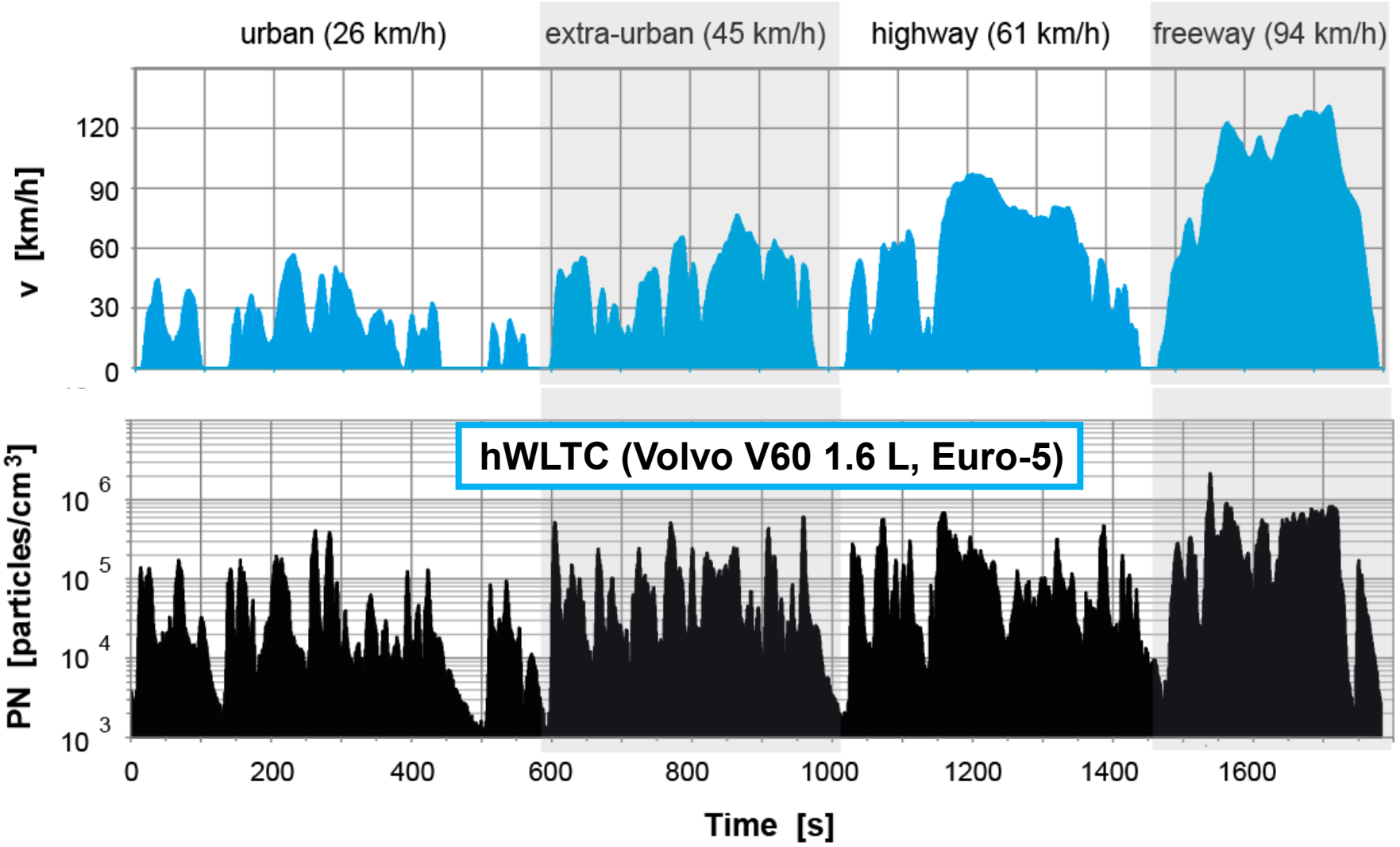
Nanoparticle emissions of GDI vehicles

The WLTC, a realistic test cycle with many transients



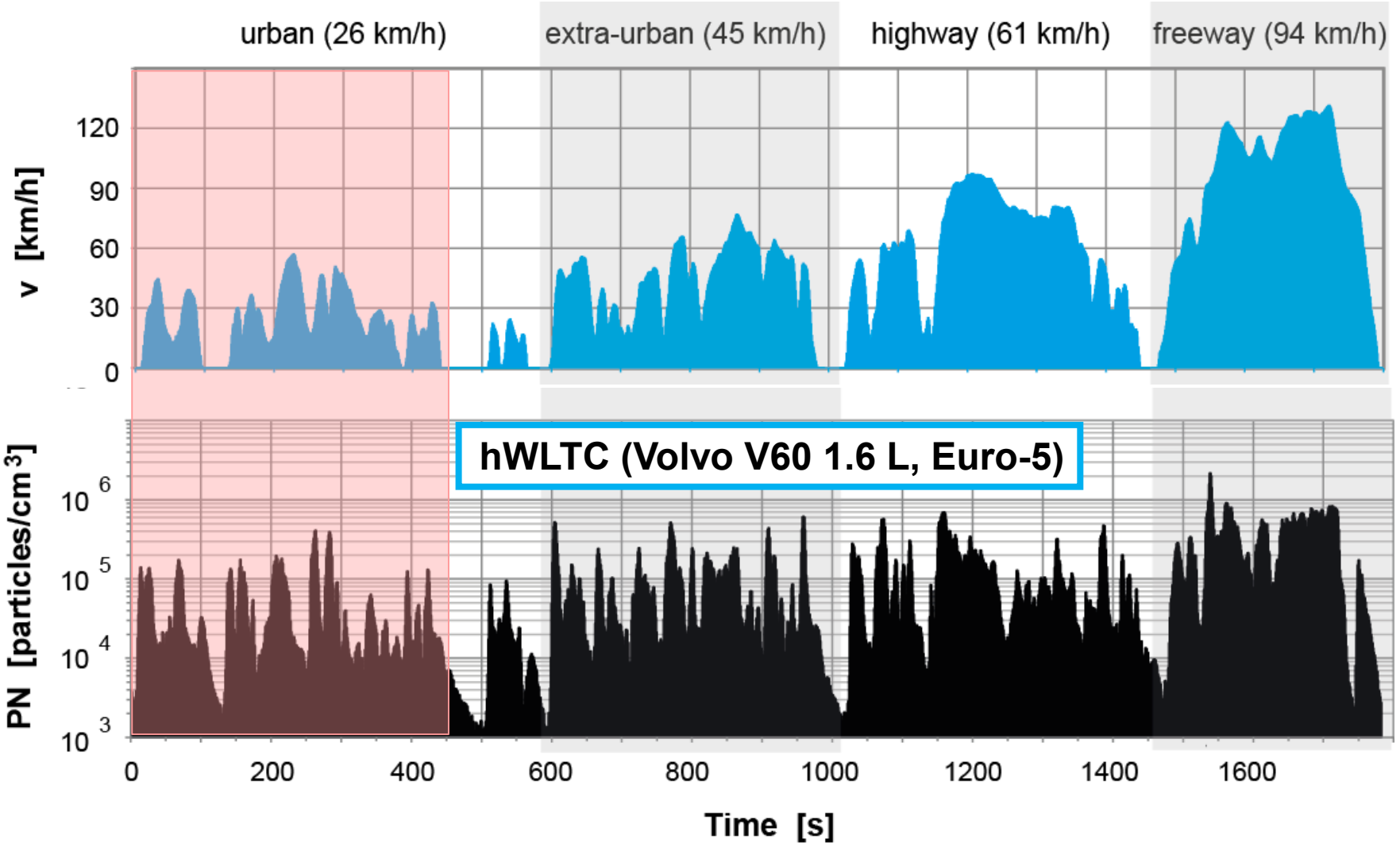
Nanoparticle emissions of GDI vehicles

High numbers of particles are released, where ever you drive!



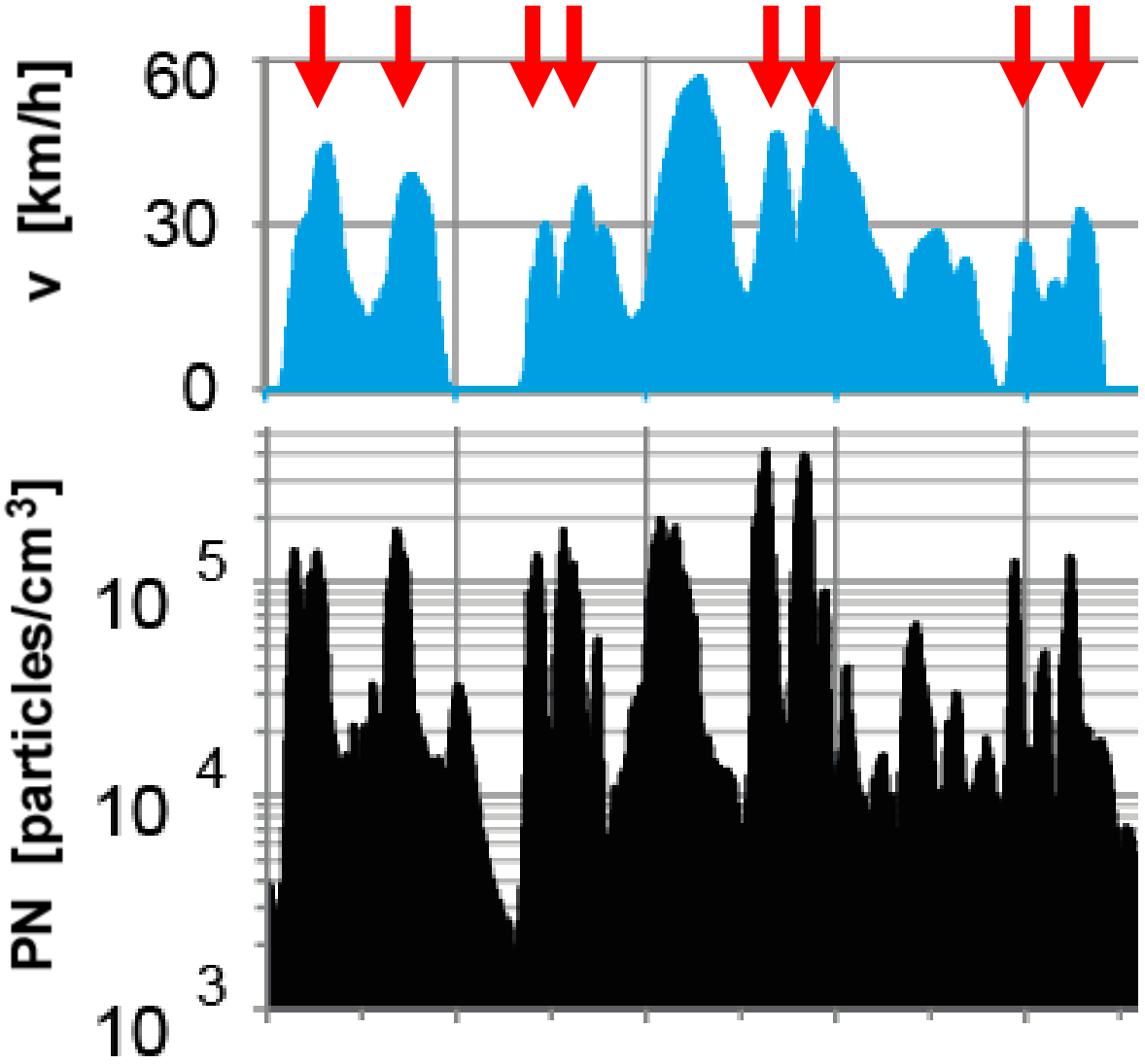
Nanoparticle emissions of GDI vehicles

Every acceleration induces the release of millions of particles



Nanoparticle emissions of GDI vehicles

Particle number emissions (PN) increase 2-3 orders of magnitude

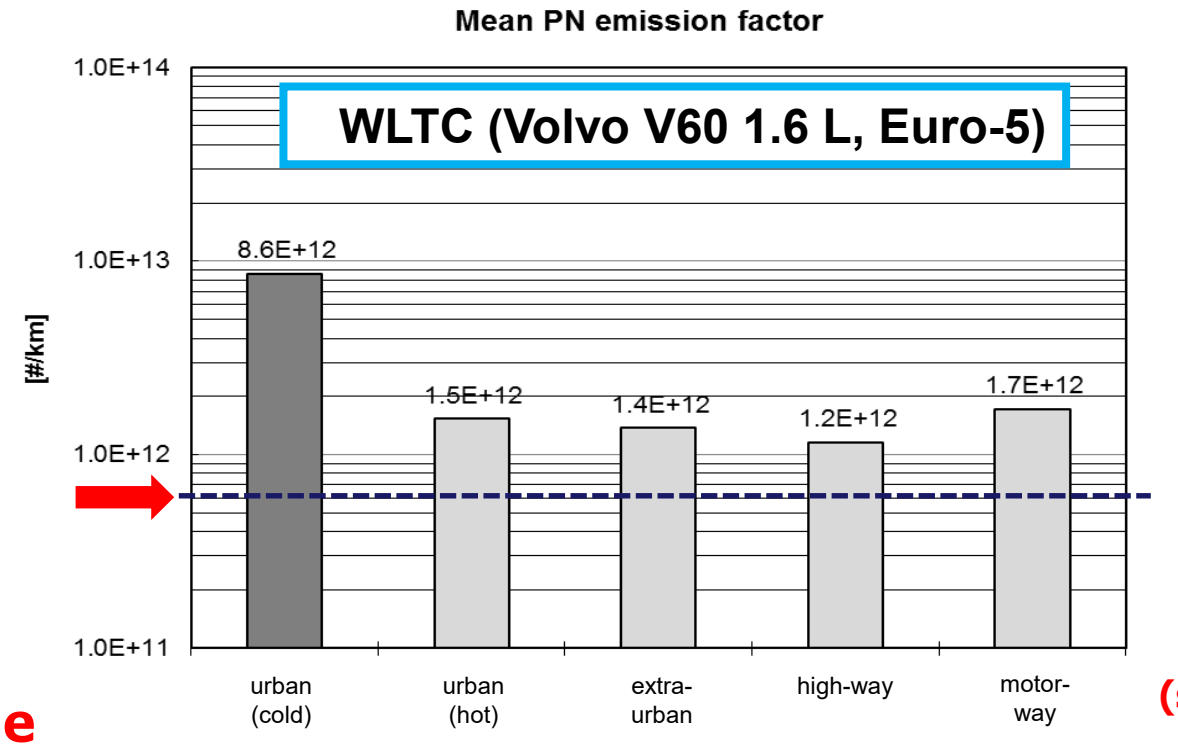


10-fold diluted GDI exhaust contains up to 10e6 particles/ccm

Exhaust of a Swiss municipal waste incinerator contains less than 10e3 partiles/ccm

Nanoparticle emissions of GDI vehicles

More than 1 trillion particles/km, where ever you drive



600 billion particles/km is the legal limit!

Euro-5/6 diesel **(since 2011)**

This Euro-5 GDI vehicle was 2-12x above the limit for diesel vehicles!

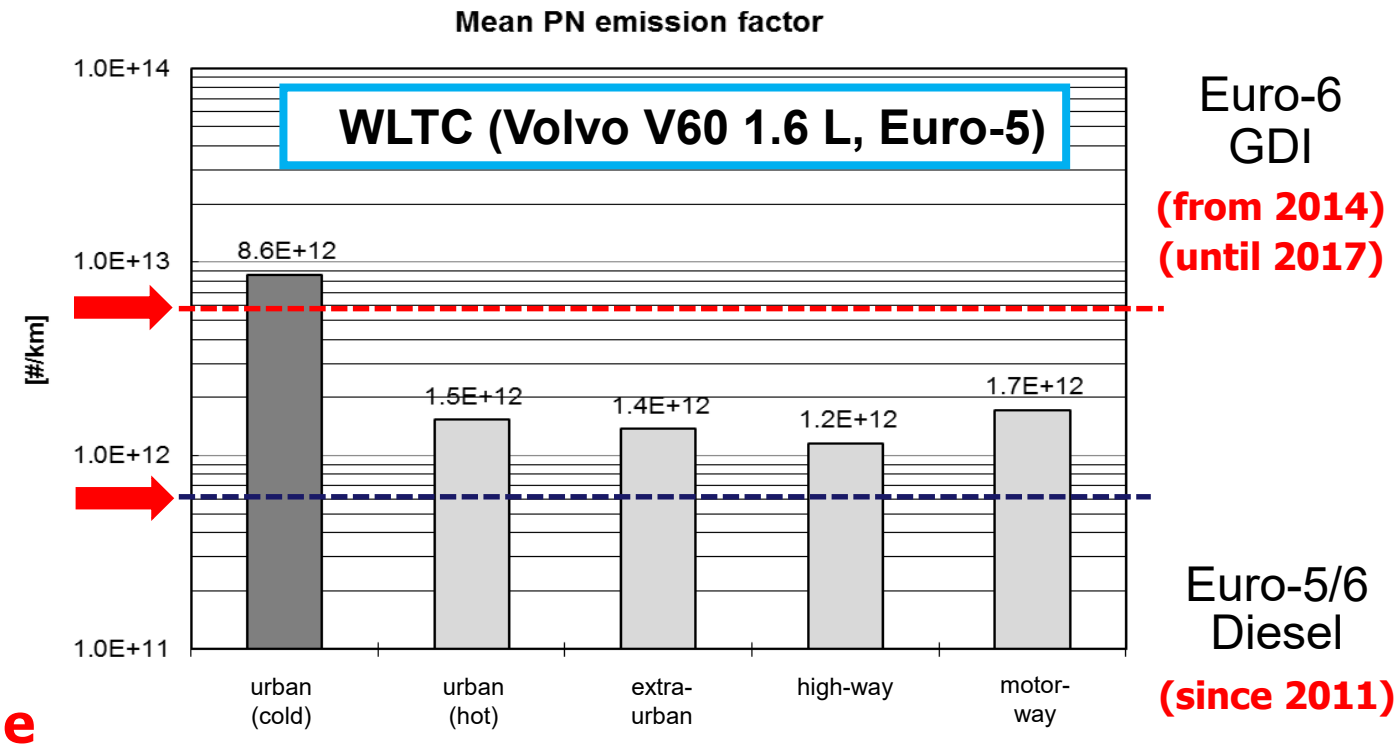
Nanoparticle emissions of GDI vehicles

More than 1 trillion particles/km, where ever you drive

6 trillion particles/km was legal

10x

600 billion particles/km is the legal limit!



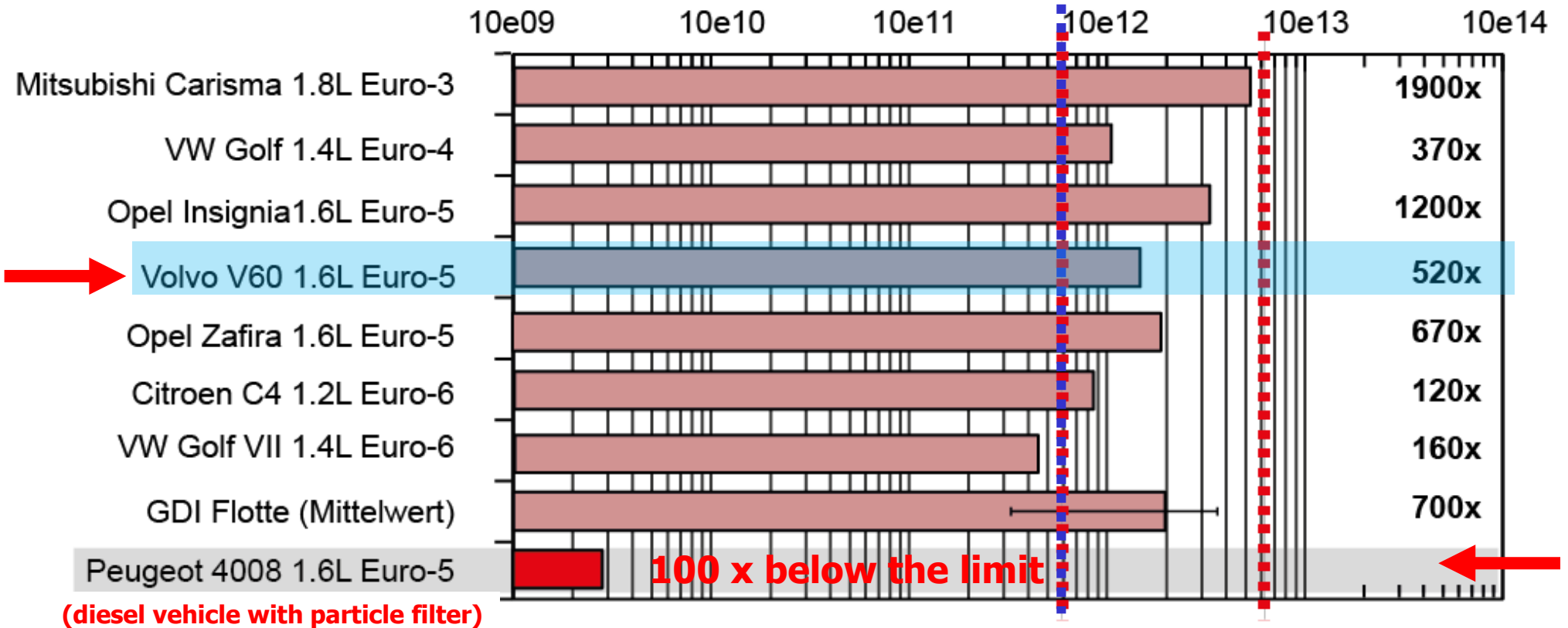
This Euro-5 GDI vehicle was 2-12x above the limit for diesel vehicles!

The European solution to the problem: PN limit for GDI was 10x higher!

Nanoparticle emissions of GDI vehicles

GDI release 120 – 1900 x more particles in the hWLTC than the diesel vehicle with DPF

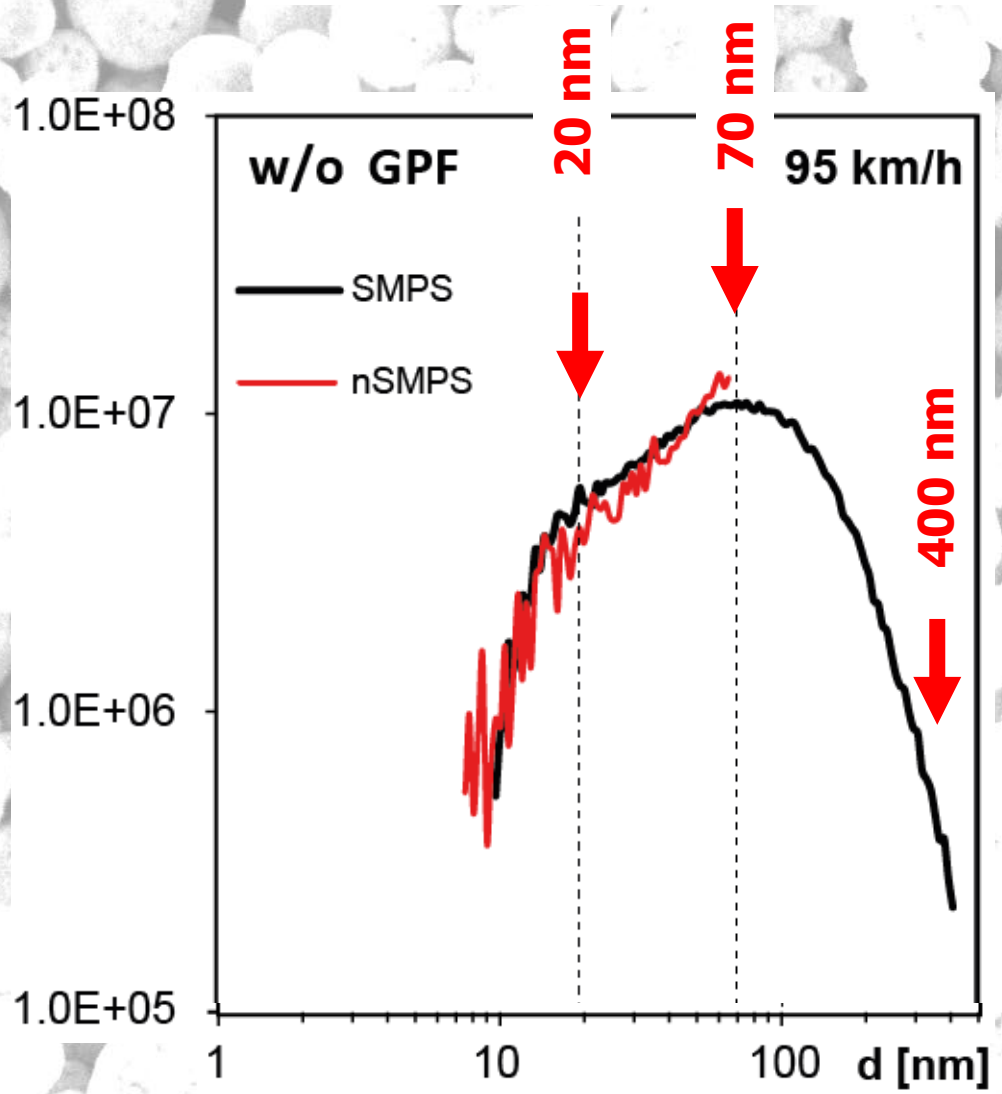
PN emissions (23-400nm) of GDI vehicles (particles/km, hWLTC)
(since 2018 EU limits for diesel- and GDI-vehicles: 600 billion particles/km)



Munoz et al. Atm. Env., **2018**, 178, 242-254

Nanoparticle emissions of GDI vehicles

Two kinds of GDI particles, some with 20 nm others with 70 nm diameter



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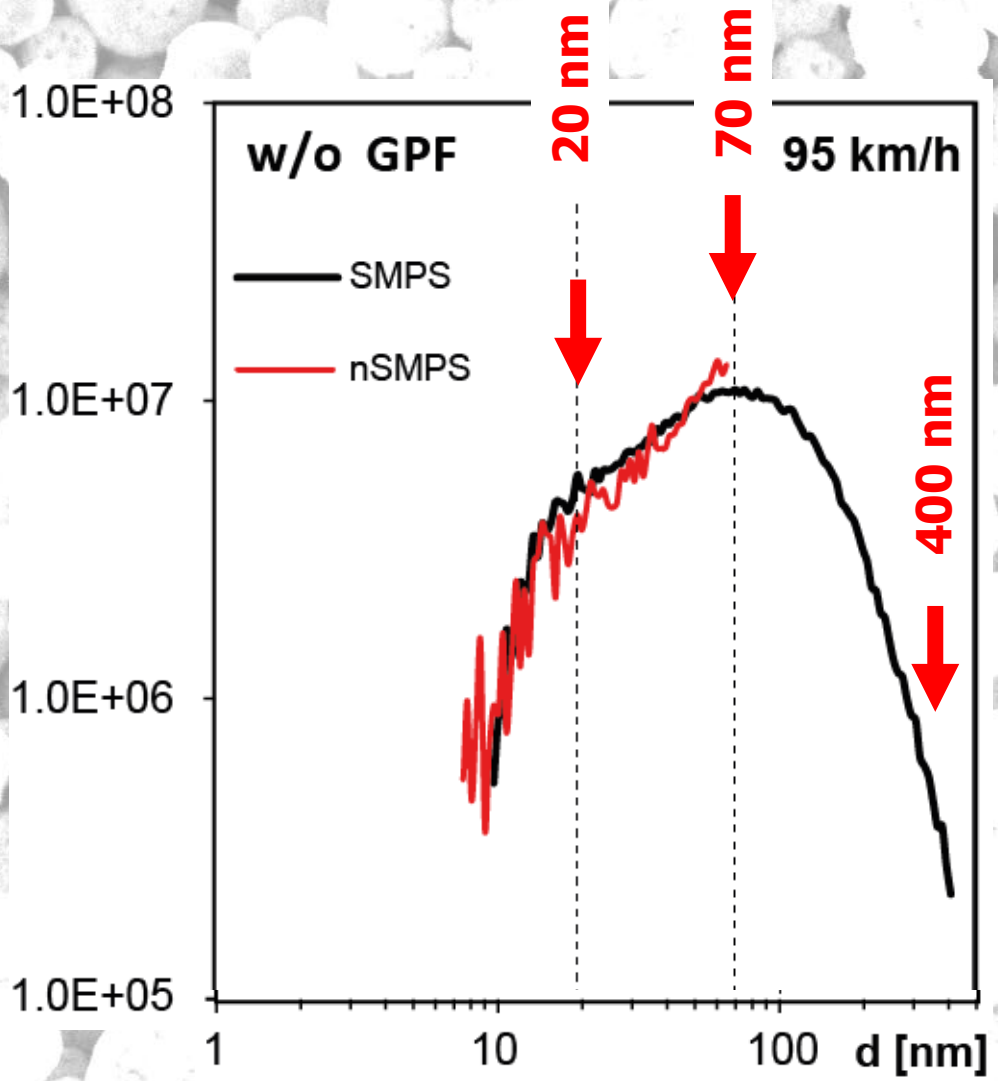

GDI particles are nanoparticles !

All GDI particles below 400 nm!

GDI particles are small enough to reach the alveoli of the lung, just like diesel particles, and are deposited.

They may even penetrate the alveolar membrane.

Nanoparticle emissions of GDI vehicles

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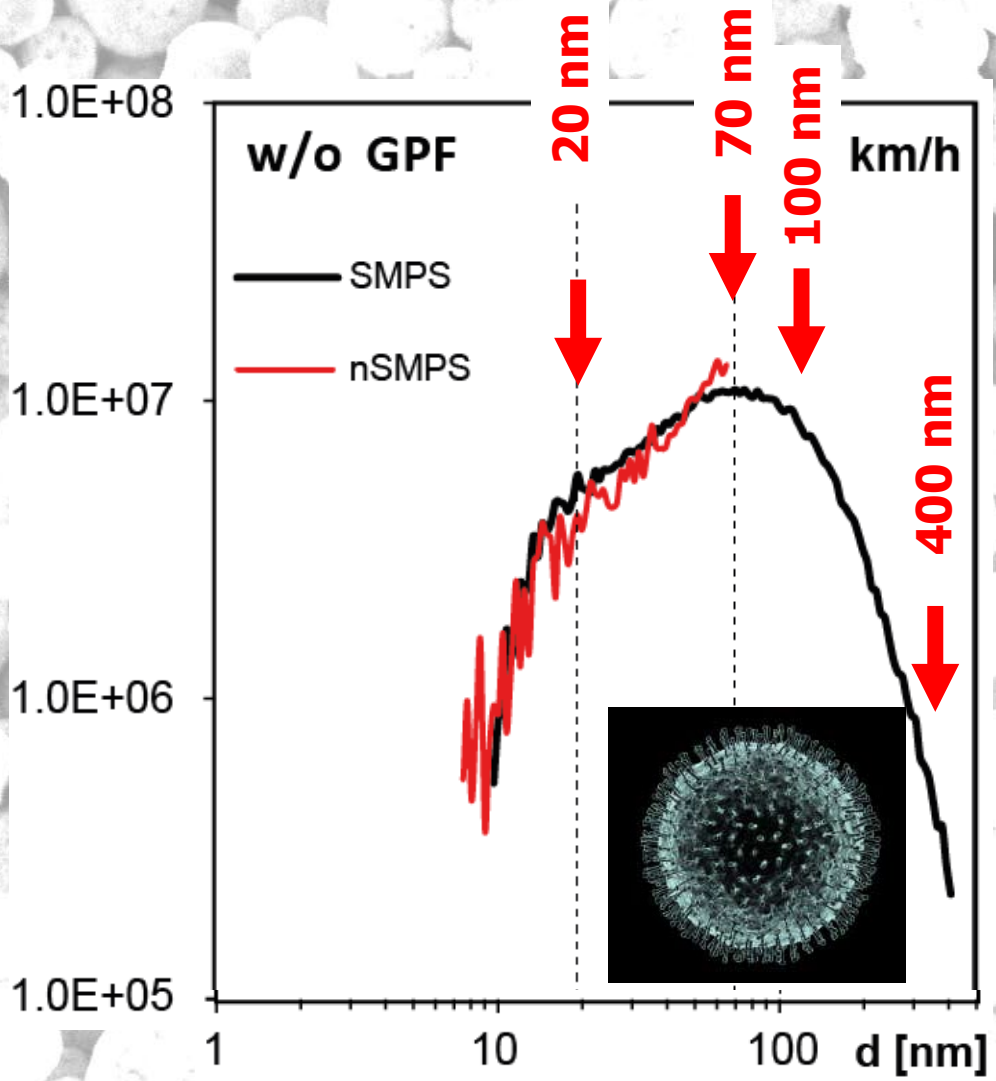

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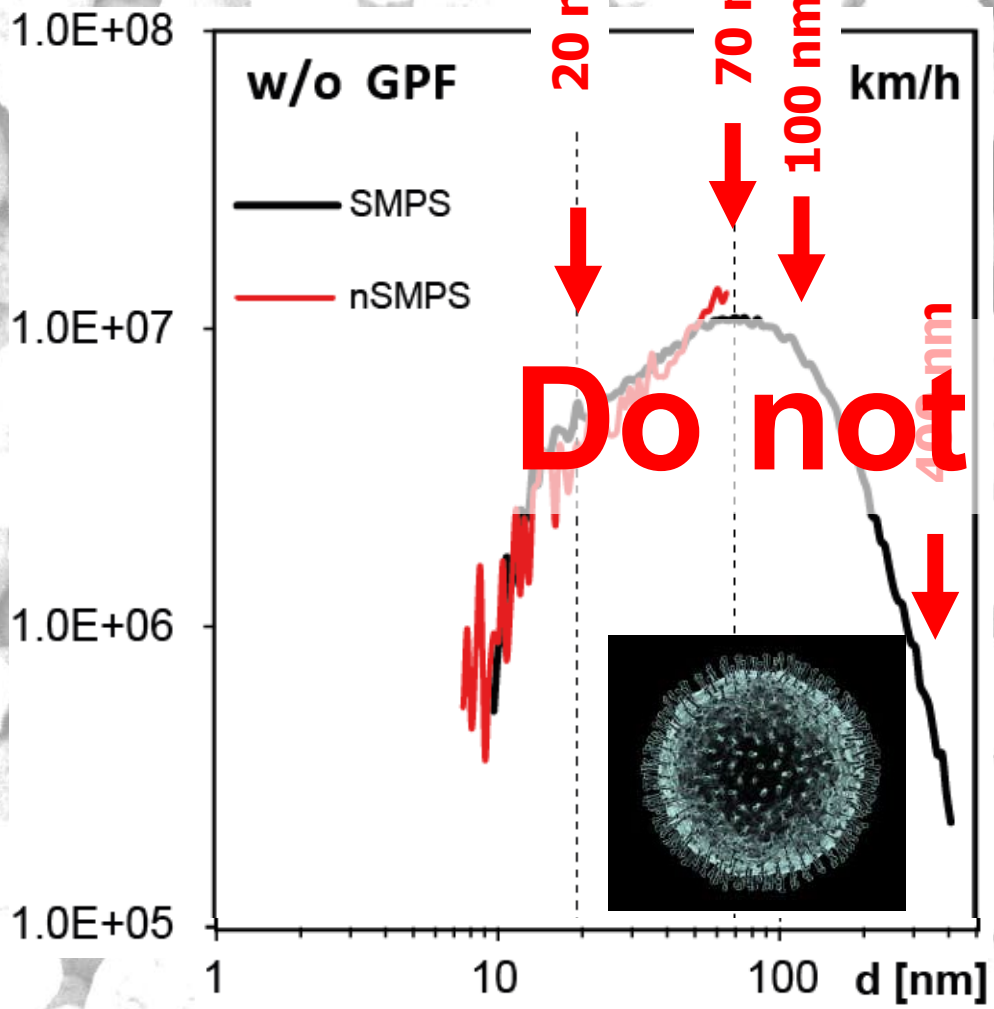

Do not inhale!

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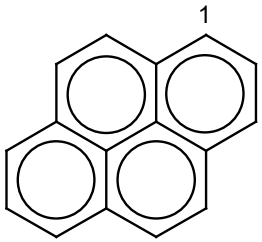
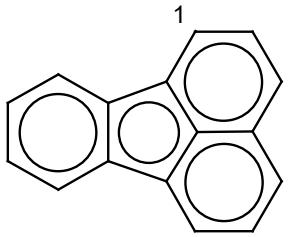
Genotoxic PAHs

Six PAHs are carcinogenic according to the WHO

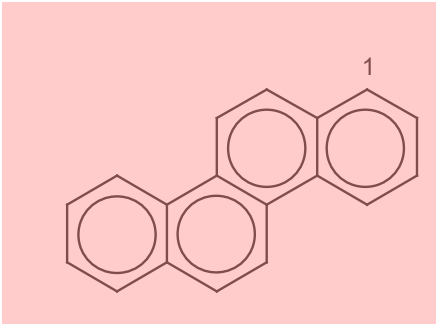
Carcinogenic PAHs



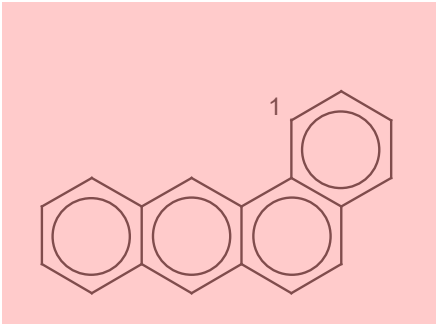
Pyrene



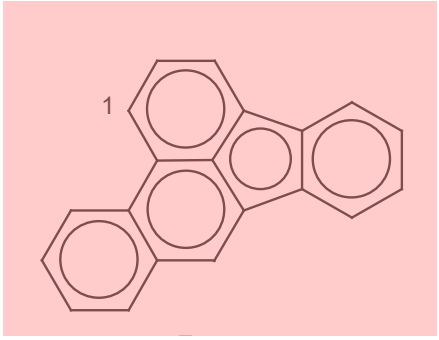
Fluoranthene



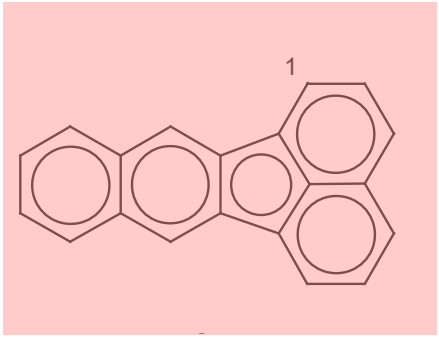
Chrysene



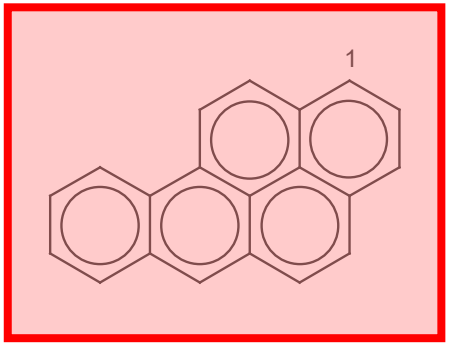
Benz(a)anthracene



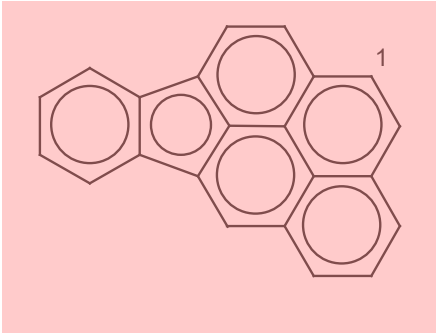
Benzo[b]-
fluoranthene



Benzo[k]-
fluoranthene



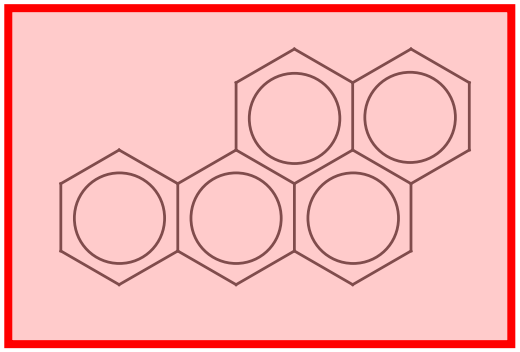
Benzo[a]-
pyrene



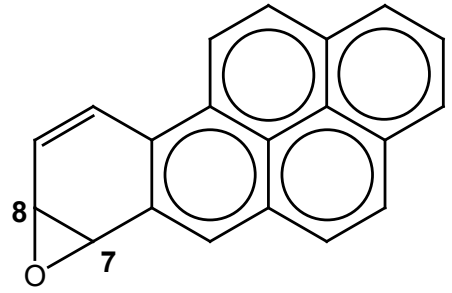
Indeno(1,2,3-cd)-
pyrene

Carcinogenesis of benzo(a)pyrene

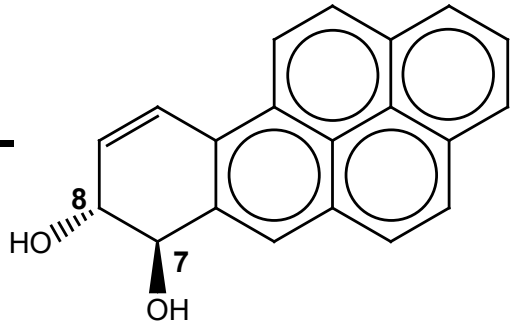
Oxidative metabolic activation of benzo(a)pyrene



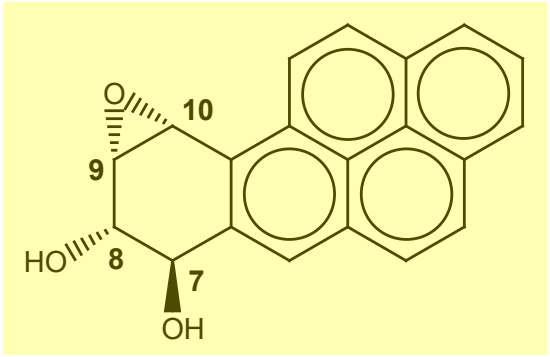
Benzo(a)pyrene (BP)



(+/-) 7,8 BP-oxide



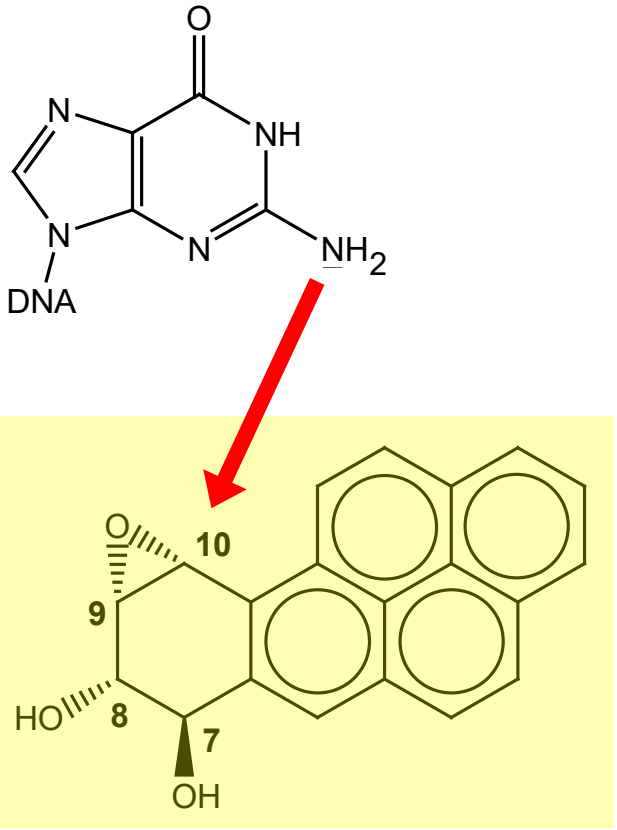
(+/-) 7,8 BP-dihydrodiol



(+) anti 7R,8S,9S,10R-BP-dihydrodiol-epoxide

Carcinogenesis of benzo(a)pyrene

Stereoselective formation of benzo(a)pyrene-DNA adducts



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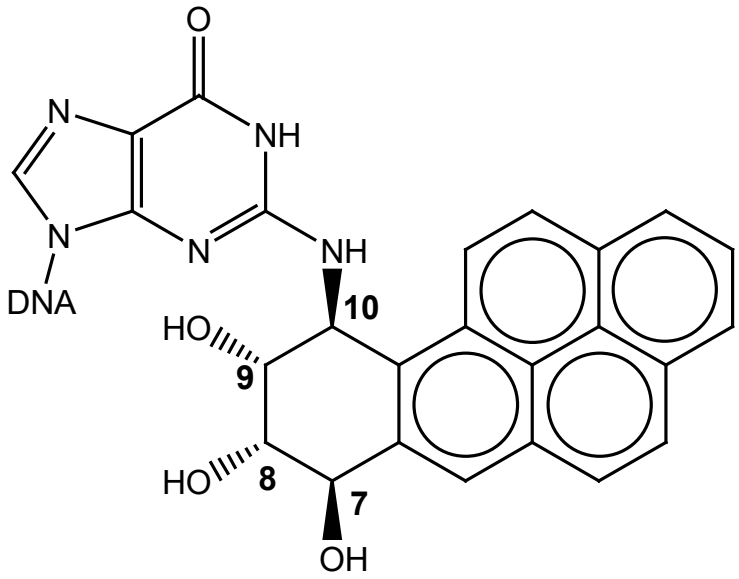
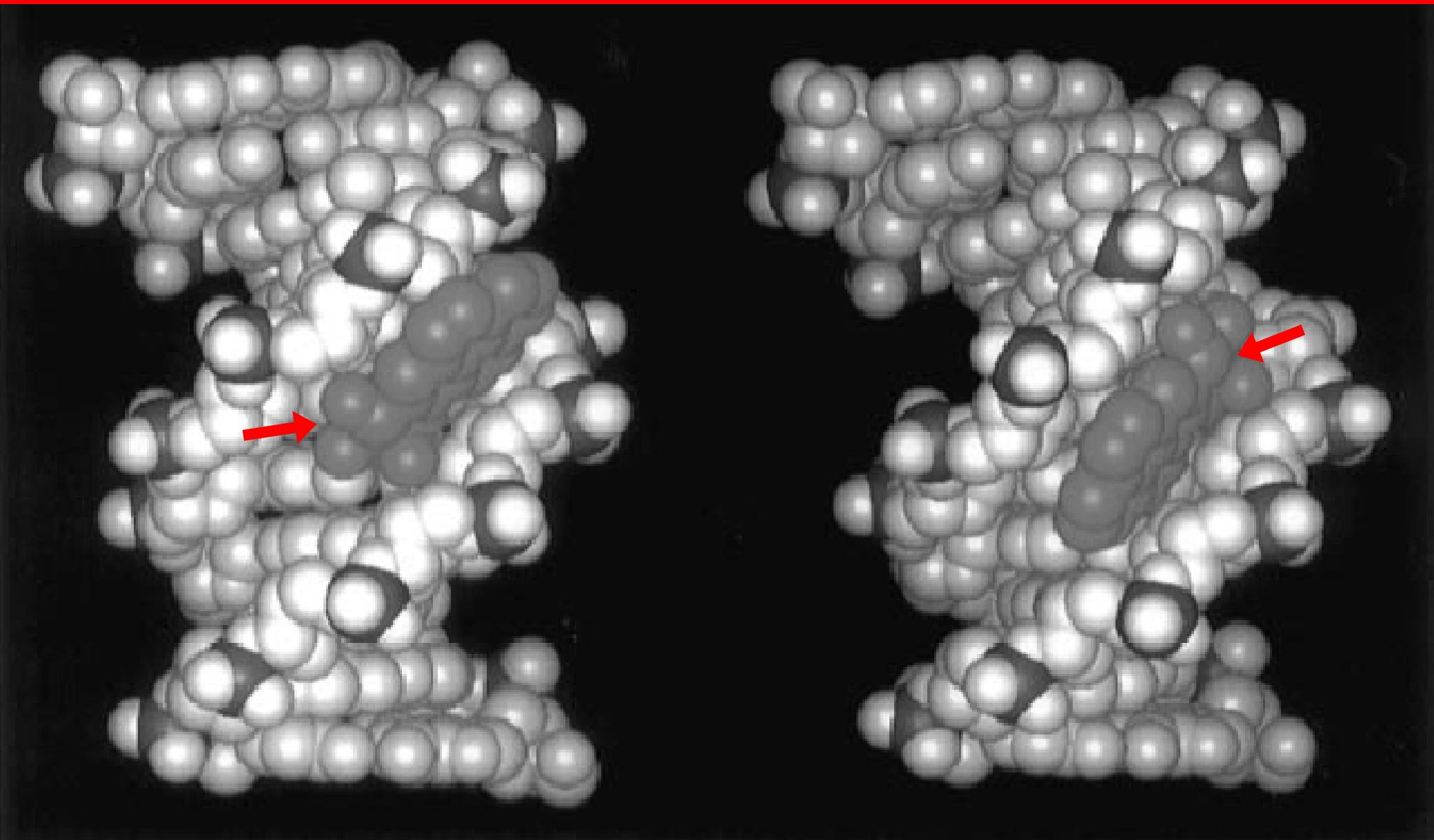


(-) 10R trans-anti-[BP]-triol-N2-deoxy-guanosine-adduct

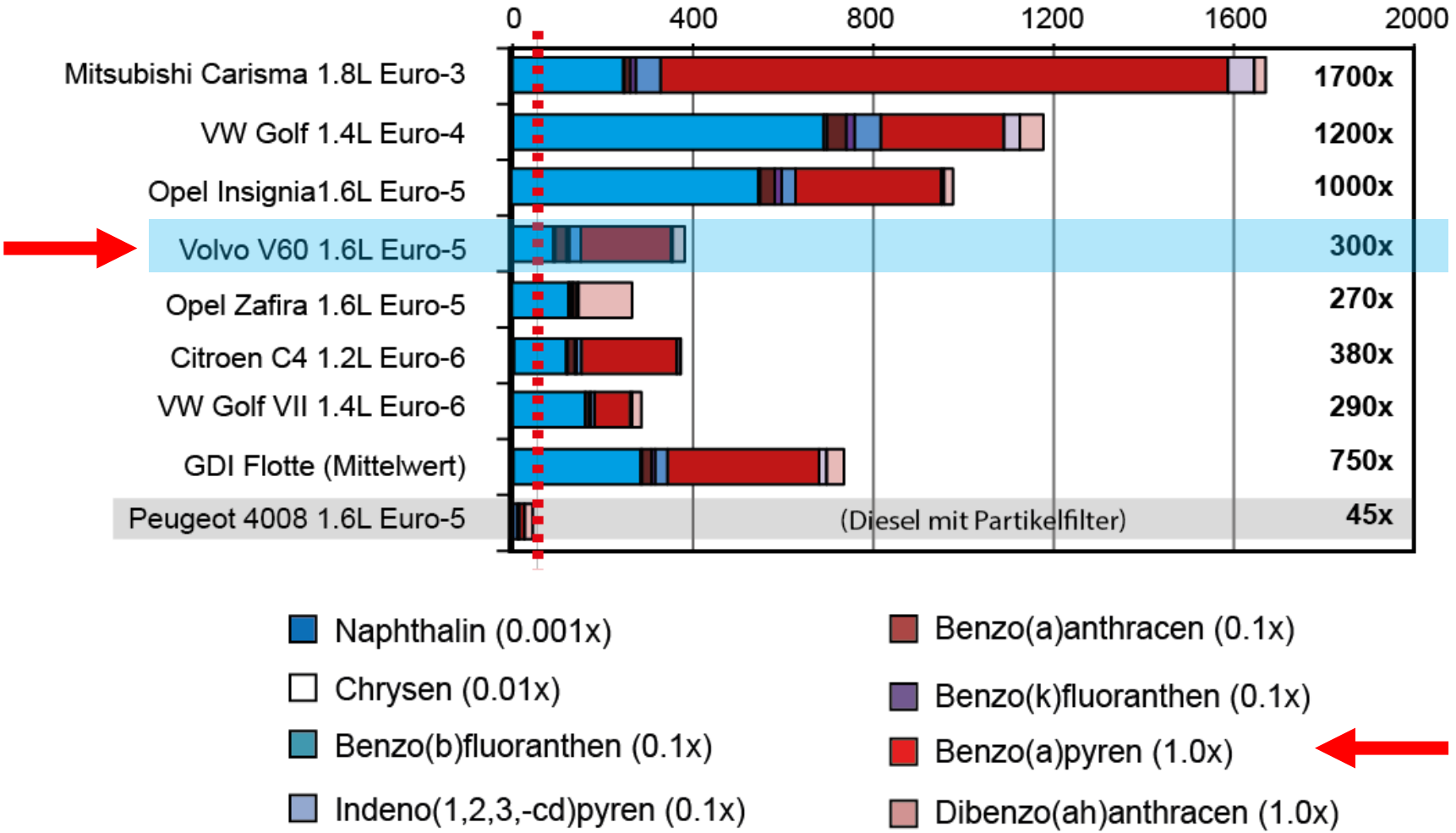
Carcinogenesis of benzo(a)pyrene



Genotoxic emissions of GDI vehicles

Genotoxic potential of GDI vehicle exhausts (ngTEQ/m³, cWLTC)

(EU ambient air limit: 1 ng benzo(a)pyrene/m³, yearly mean)



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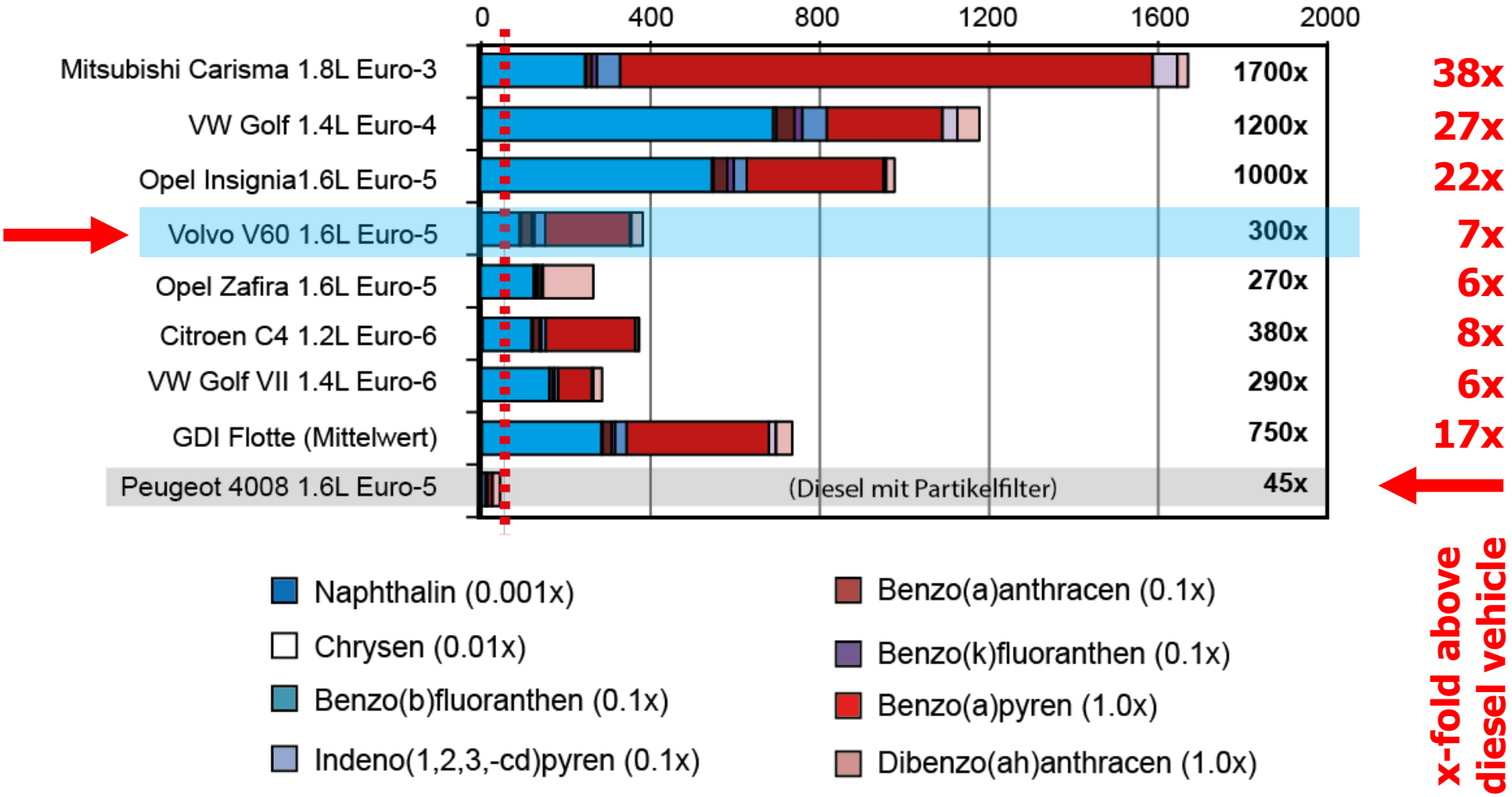

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GDI-vehicle exhausts are not classified yet, even though we are exposed to them every day!

What do we know about GDI-exhausts after 20 years of application?

- contain billions of soot nanoparticles
- EU limit for GDI vehicles of 6 x 10e11 particles/km is very high
- PN emissions are not at all limited outside Europe (US, Japan)

Are they class 1 carcinogens causing lung cancer?

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- soot nanoparticles mainly deposit in the alveoli of the lung
- sub-100 nm particles may penetrate the alveolar membrane transporting adsorbates into the body (Trojan horse effect)

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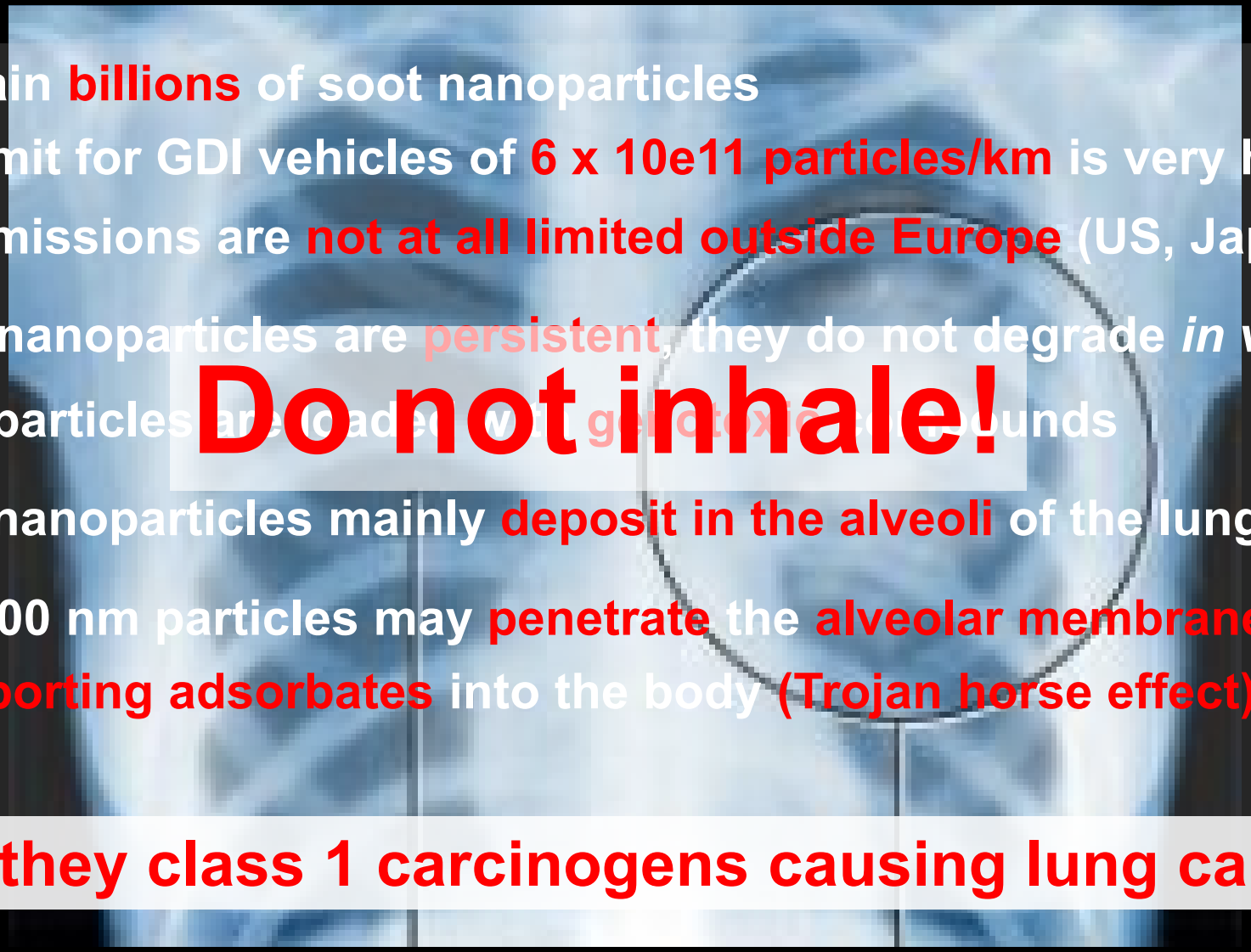

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Do not inhale!

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25 years VERT filter tests

How to test GPFs, the VERT approach

- VSET test on GPF vehicles

Something to celebrate!

13th VERT Forum: New VERT nanoparticle abatement tools

Empa Dübendorf, March 21, 2023

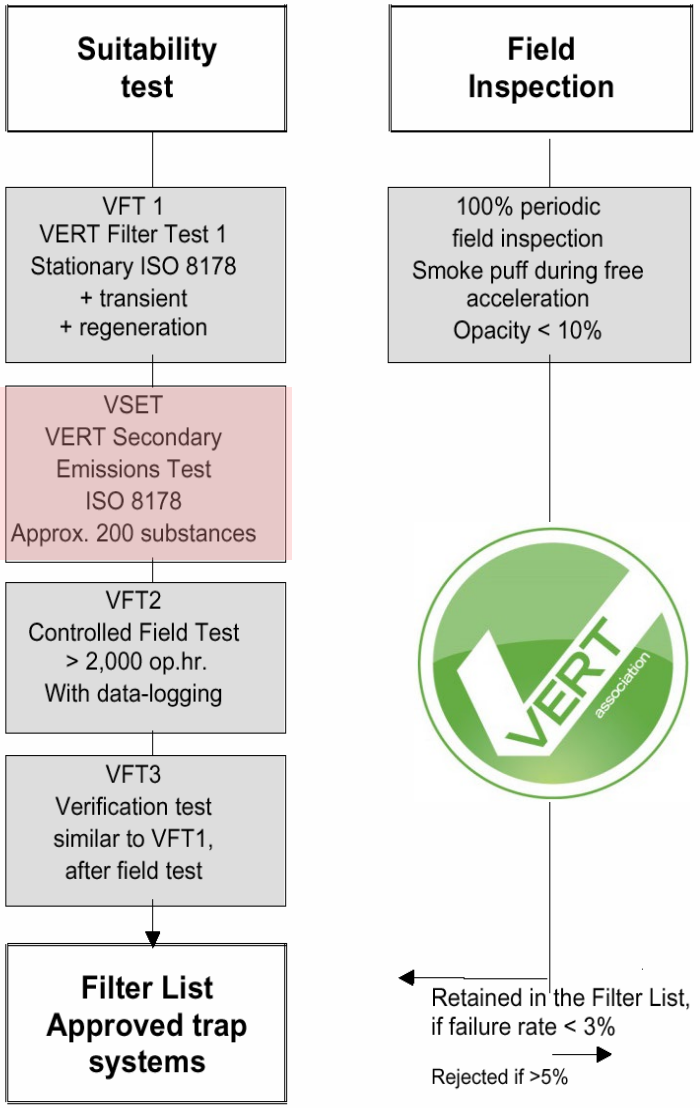
25 years VERT filter tests

How to test PFs, the VERT approach

Approved filters have to:

- Reduce PM- & PN-emissions (>98%), both in new and aged conditions (VFT1, VFT3)
- Reduce toxic compounds a.m.a.p.
- Low risks for secondary emissions (VSET)

Are all particle filters safe?



Lessons learned from GASOMEP project

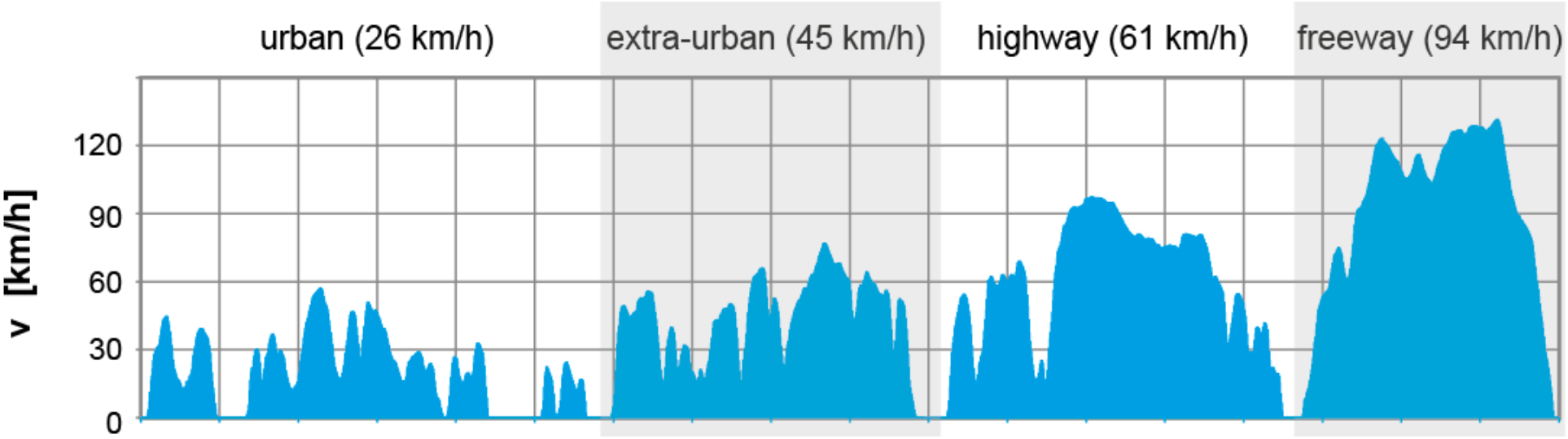
Testing of GPF on vehicles, on a chassis dynometer

GPF testing on vehicles at UASB Nidau

- GDI vehicles with integrated GPFs will be tested in the **EU AeroSolfd project**
- Bench mark GDI vehicle without GPF (Volvo V60. 1.6L, Euro-5)
  (was and can be used to test prototype retrofit GPFs)

Transient cycle used in the GASOMEP project

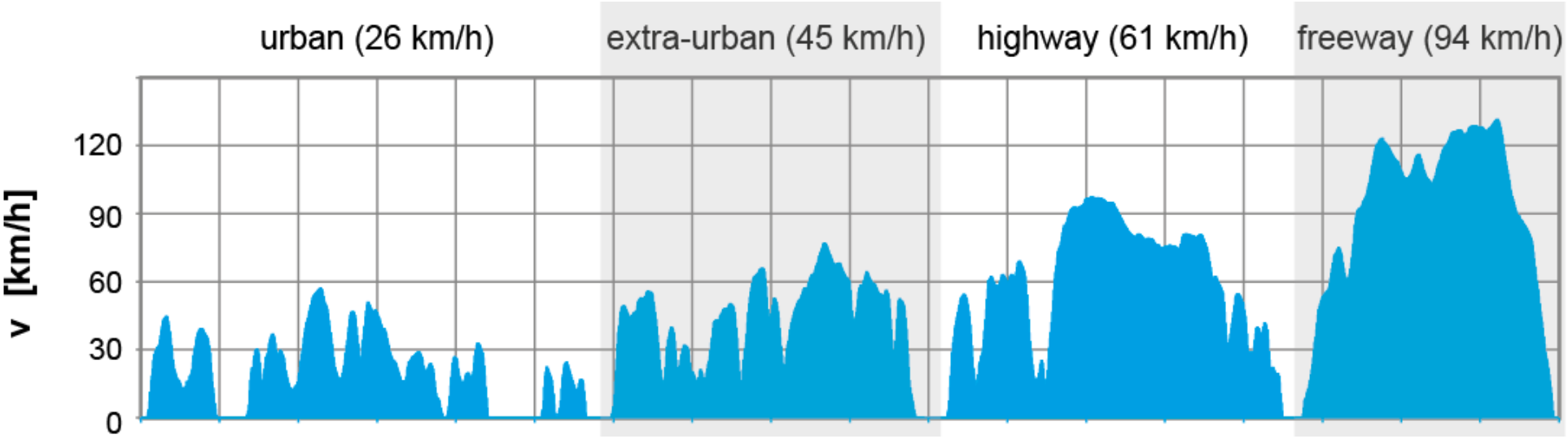
The WLTC is a legal and realistic test cycle with many transients



WLTC: 4 phases, 30 minutes per cycle, cold / hot starts

Transient cycle used in the GASOMEP project

The WLTC, a realistic test cycle with many transients



WLTC: 4 phases, 30 minutes per cycle, cold / hot starts

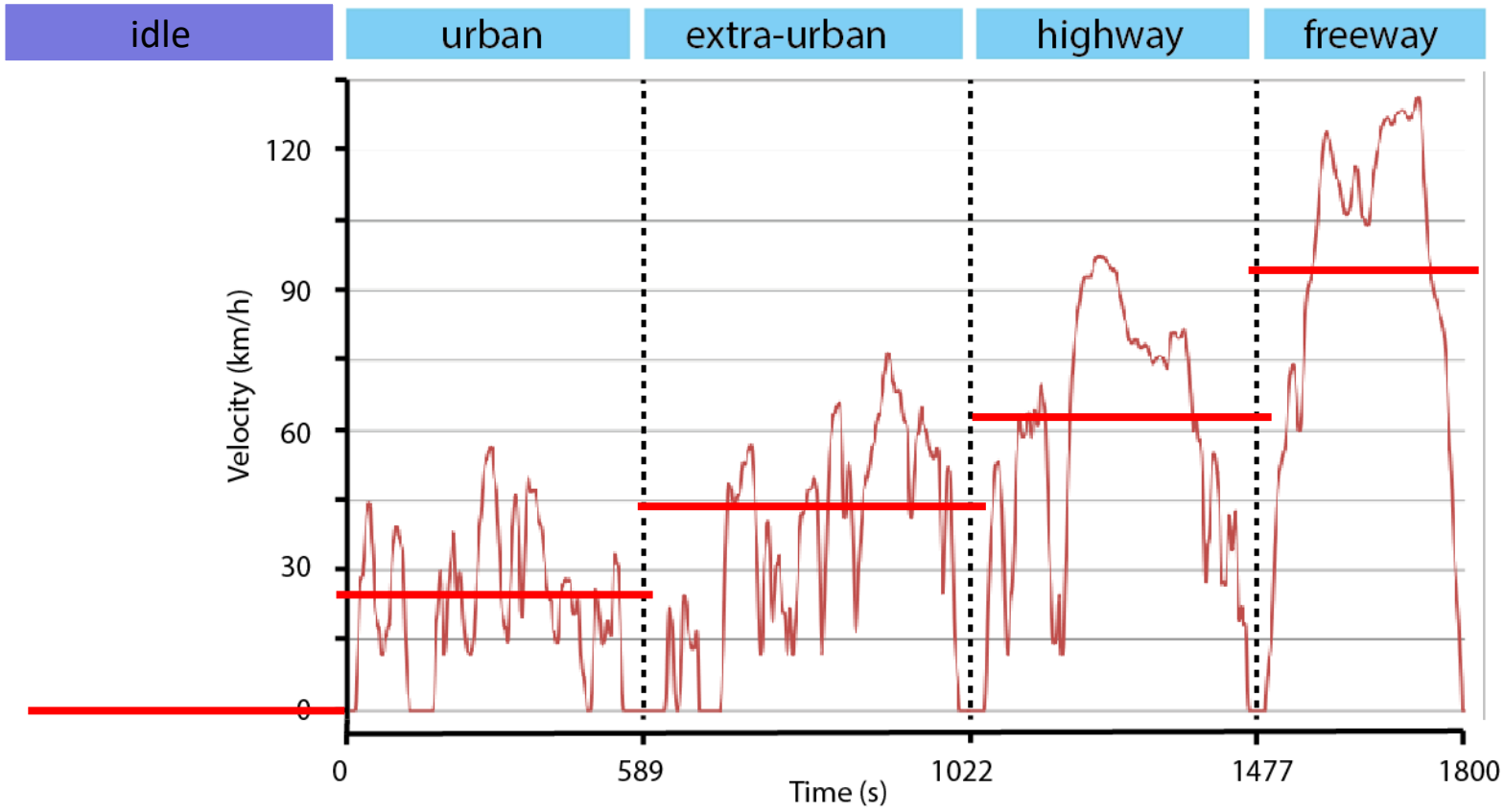
Furthermore, we developed a steady state cycle (SSC) to study:

particle size distributions and filtration efficiencies at

different space velocities

Steady state cycle used in the GASOMEP project

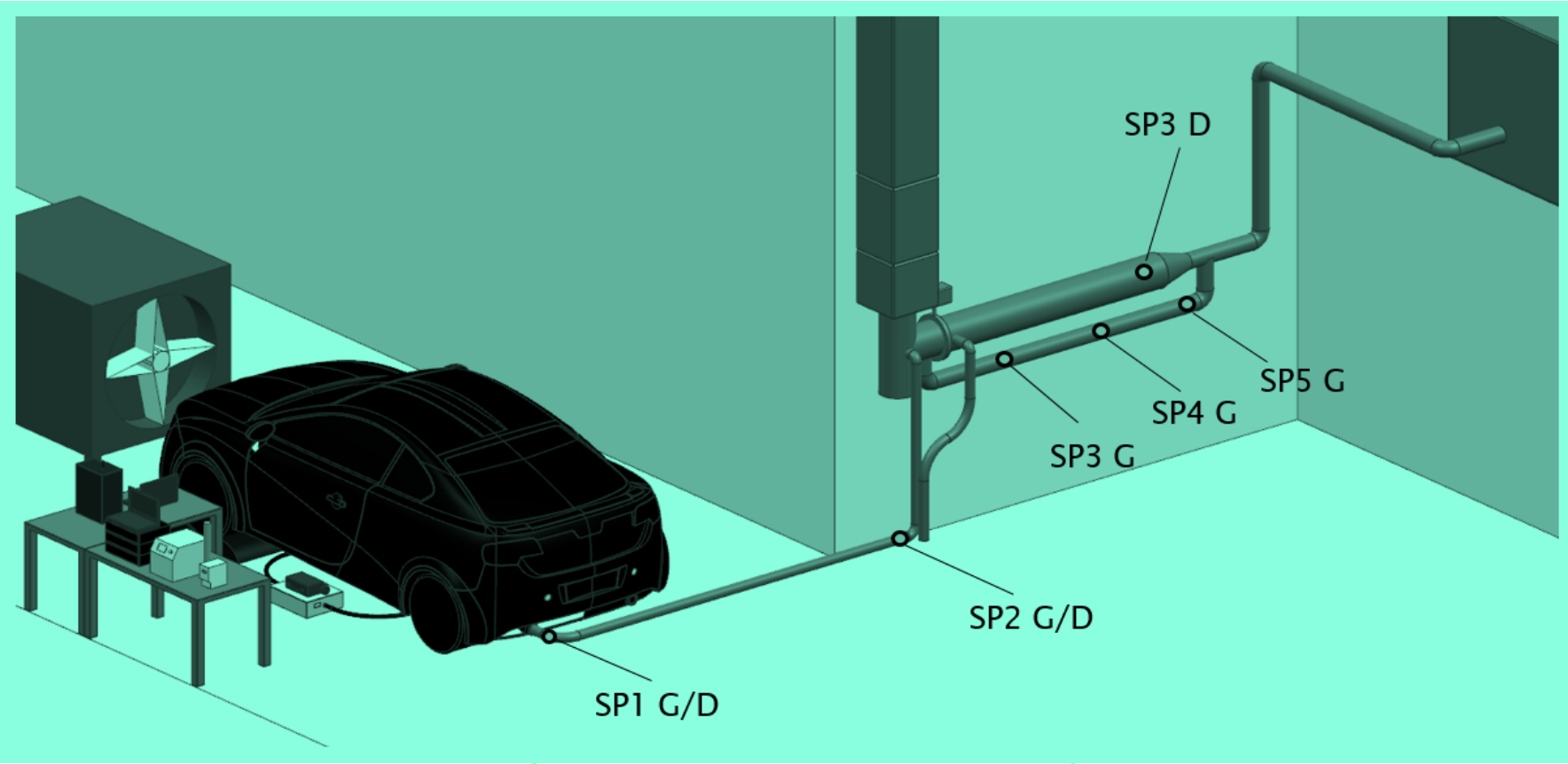
SSC: 5 conditions, 20 minutes per phase, hot conditions



Velocity (km/h)	0	25.7	44.5	60.8	94.0

Exhaust gas sampling points

Sampling points for raw and CVS exhausts

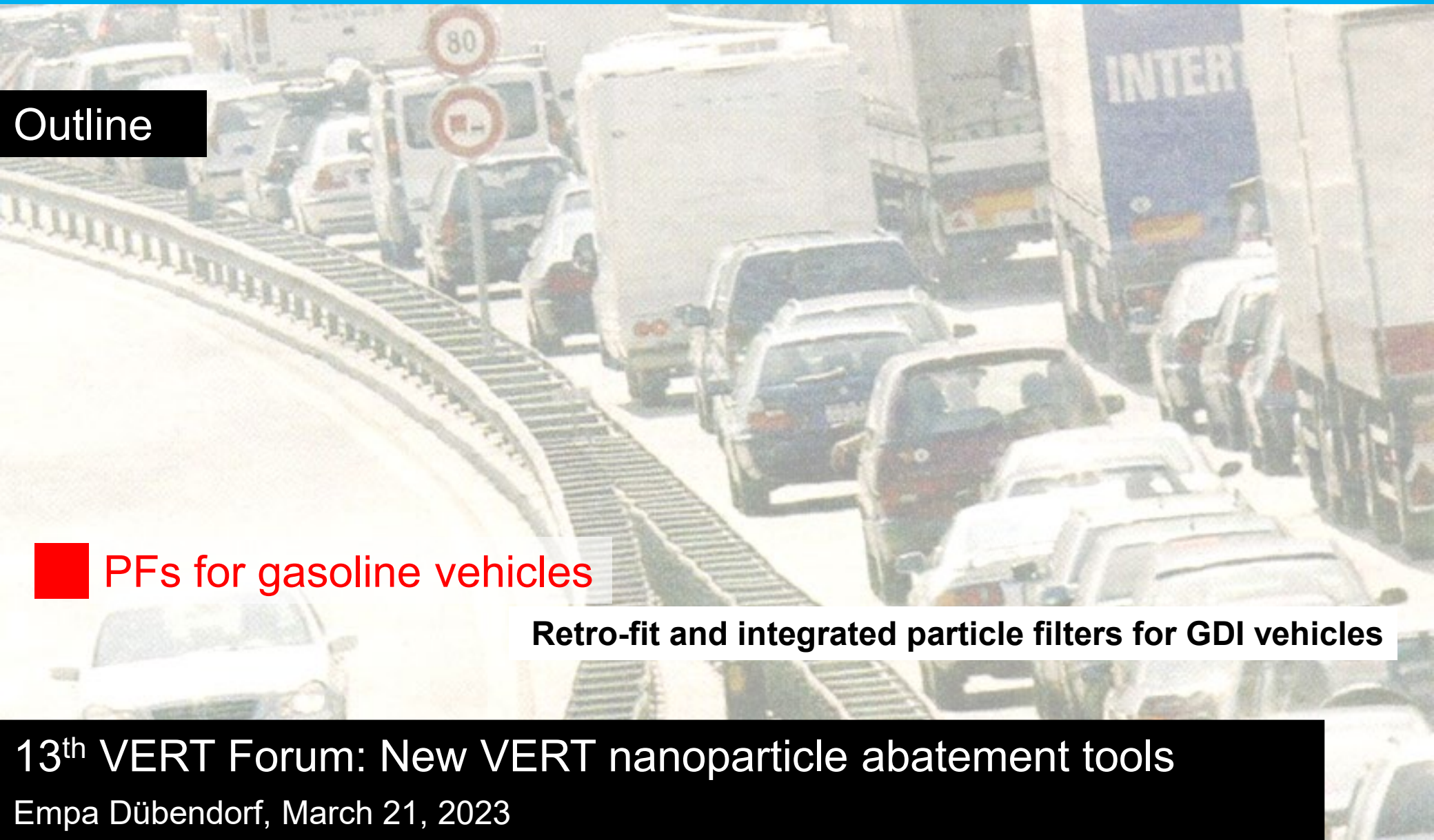


Bezeichnung Benzin	Messstelle
SP1 G	Nach Endtopf
SP2 G	Vor CVS-Tunnel

Bezeichnung Benzin	Messstelle
SP3 G	Anfang CVS-Tunnel
SP4 G	Mitte CVS-Tunnel
SP5 G	Ende CVS-Anlage

Bezeichnung Diesel	Messstelle
SP1 D	Nach Endtopf
SP2 D	Vor CVS-Tunnel
SP3 D	Ende CVS-Tunnel

Secondary emissions test for gasoline direct injection vehicles



Outline

- PFs for gasoline vehicles

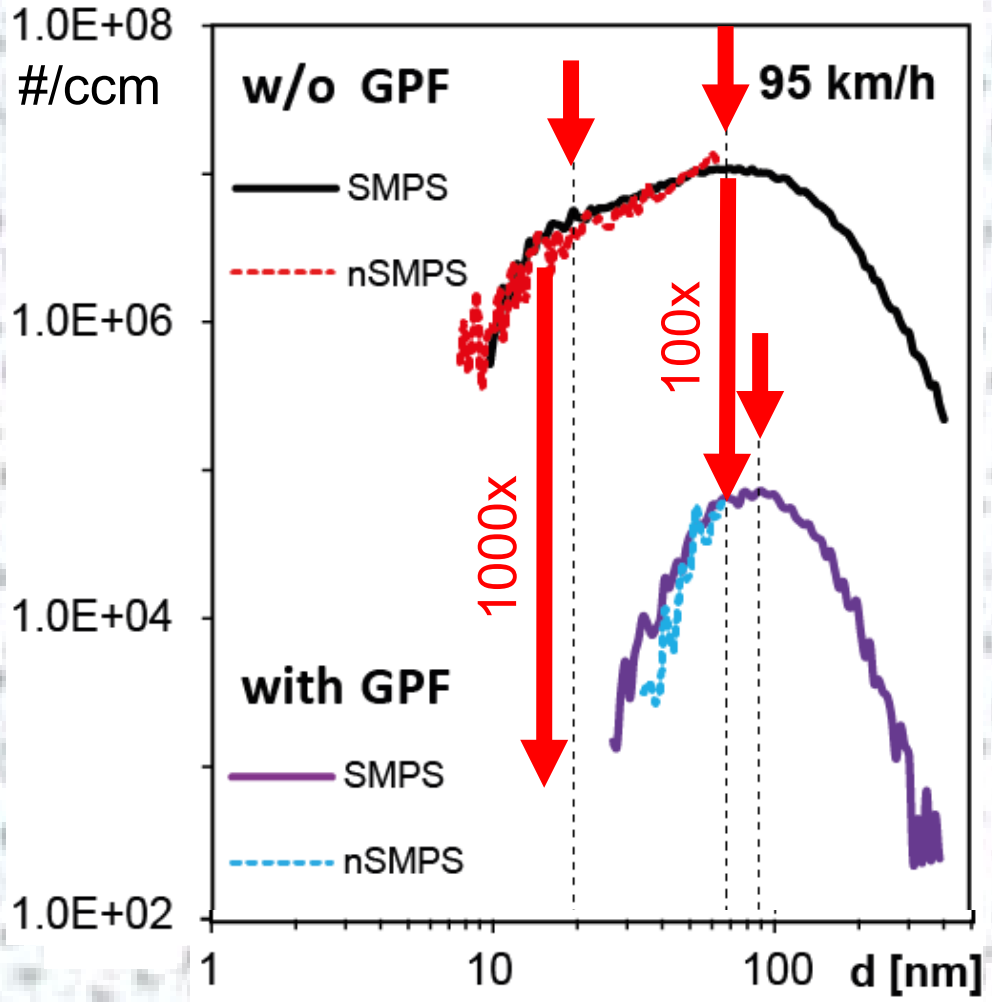
Retro-fit and integrated particle filters for GDI vehicles

13th VERT Forum: New VERT nanoparticle abatement tools

Empa Dübendorf, March 21, 2023

First-generation particle filters (GPFs) for GDI-vehicles

After the GPF only one kind of particles at 90 nm detected



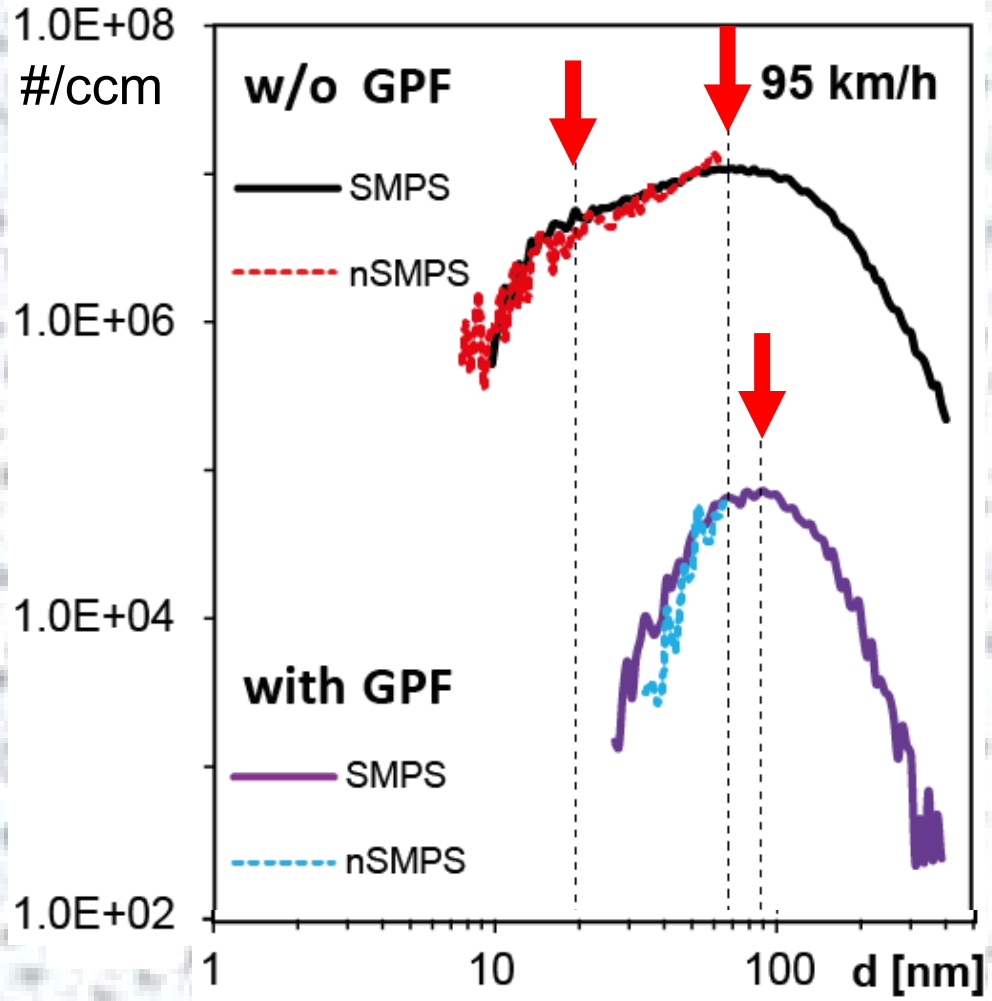
Even prototype filters can lower particle emissions by 2-3 orders of magnitude.

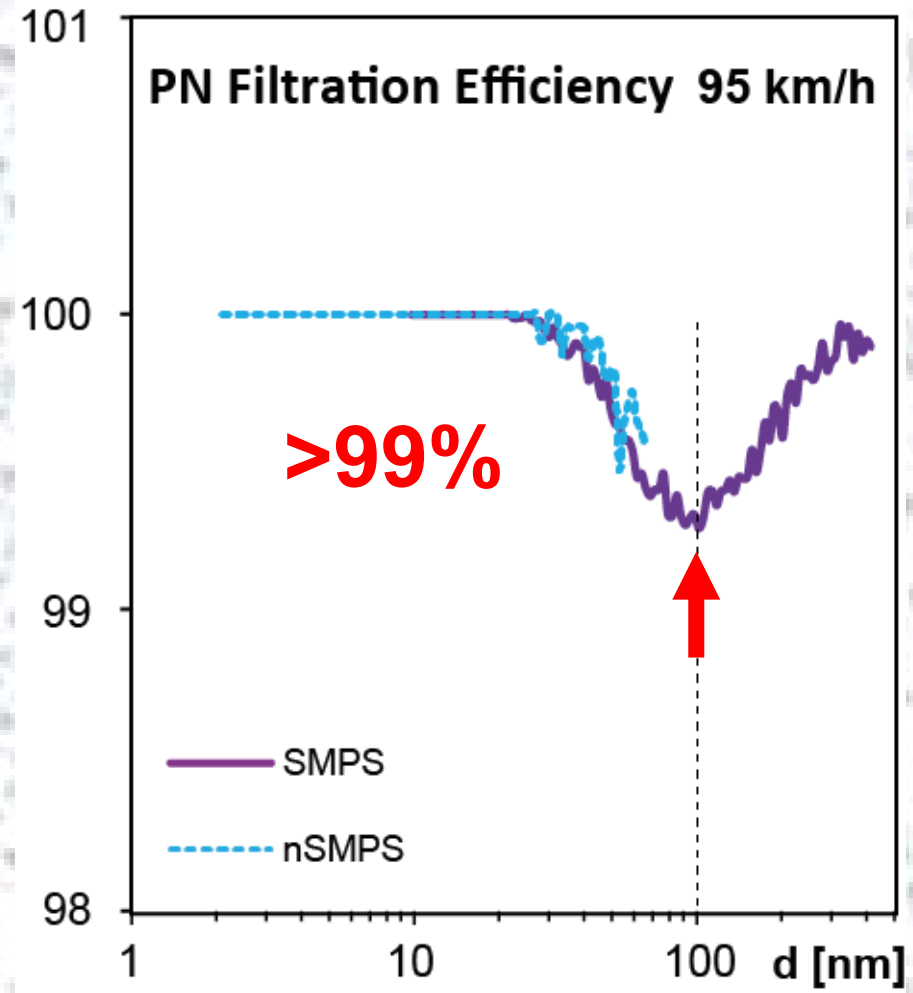
20 nm particles are removed most efficiently

Munoz et al. ES&T., **2018**, 52, 10709-10718

Particle filters for GDI-vehicles (GPFs)

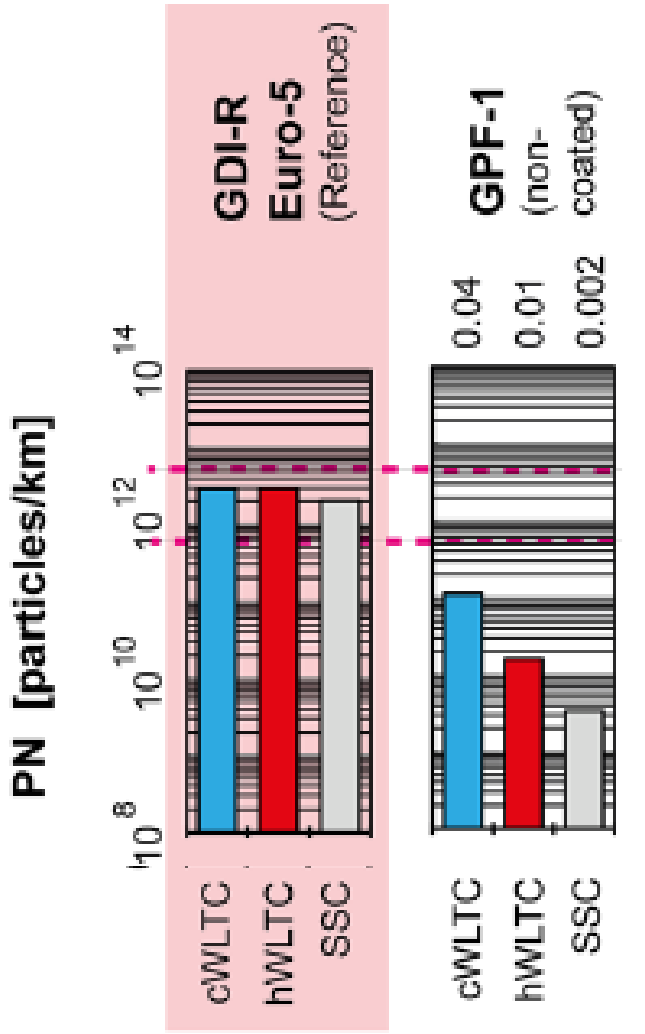
GPFs can be as efficient as best availible DPF technology (>98%)





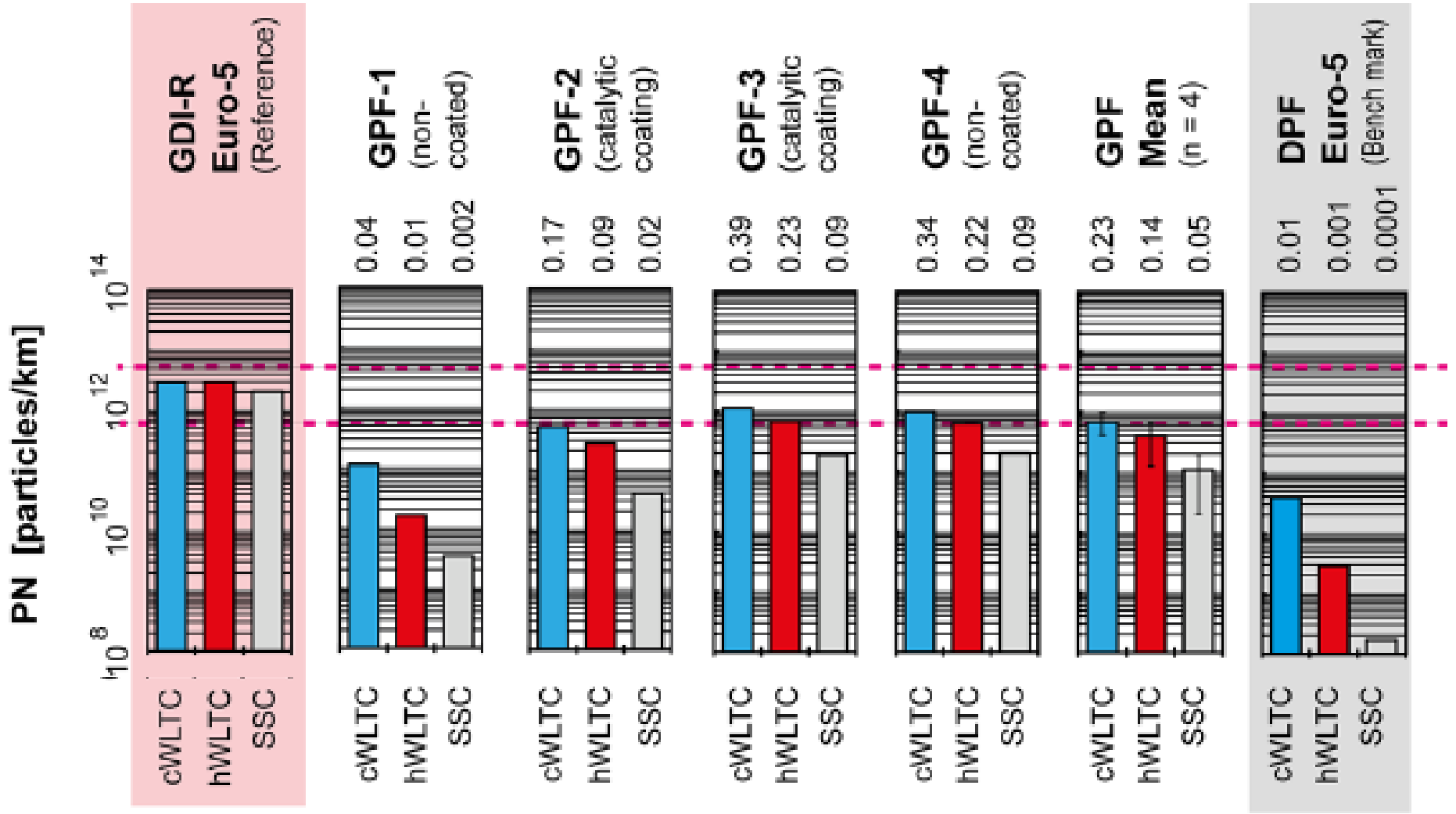
Particle filters for GDI-vehicles (GPFs)

Filtration efficiency of GPFs (transient) versus DPFs (steady state)



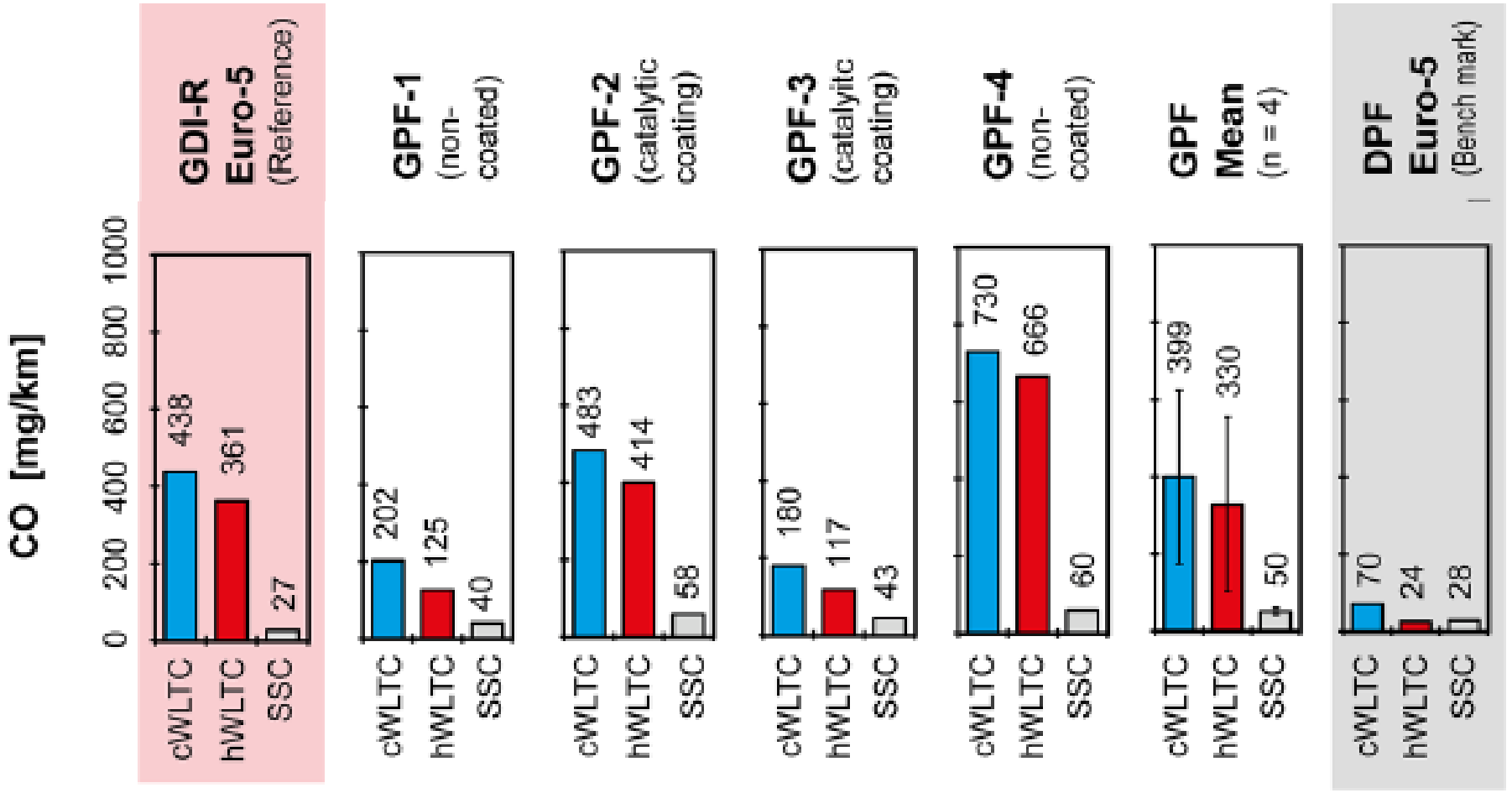
Particle filters for GDI-vehicles (GPFs)

Filtration efficiency of GPFs (transient) versus DPFs (steady state)



Particle filters for GDI-vehicles (GPFs)

High or low oxidation potential GPFs?

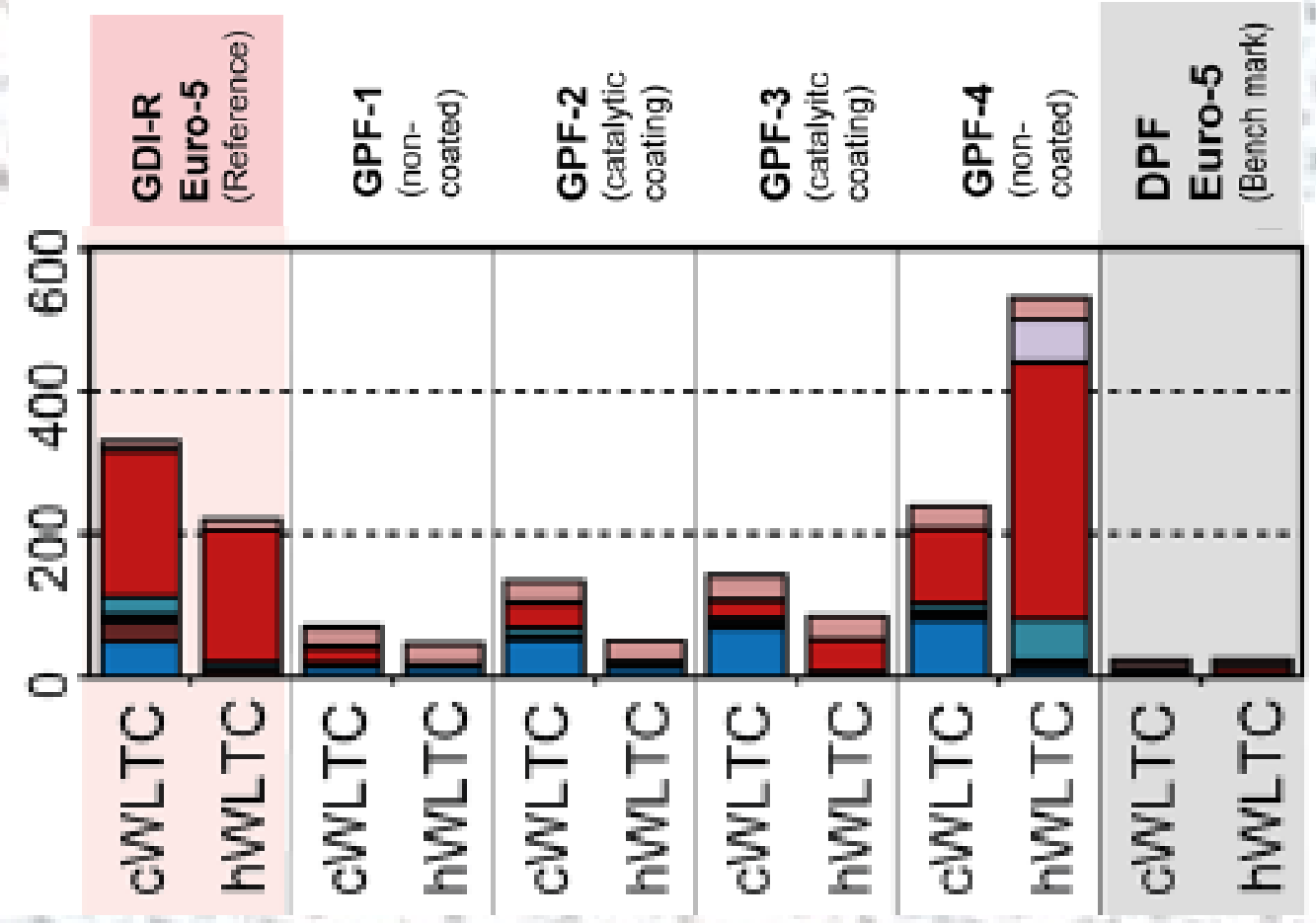


Munoz et al. ES&T., **2018**, 52, 10709-10718

Particle filters for GDI-vehicles (GPFs)

3 of 4 prototype-GPFs reduced genotoxic PAHs

Genotoxic potential (ng TEQ/km)

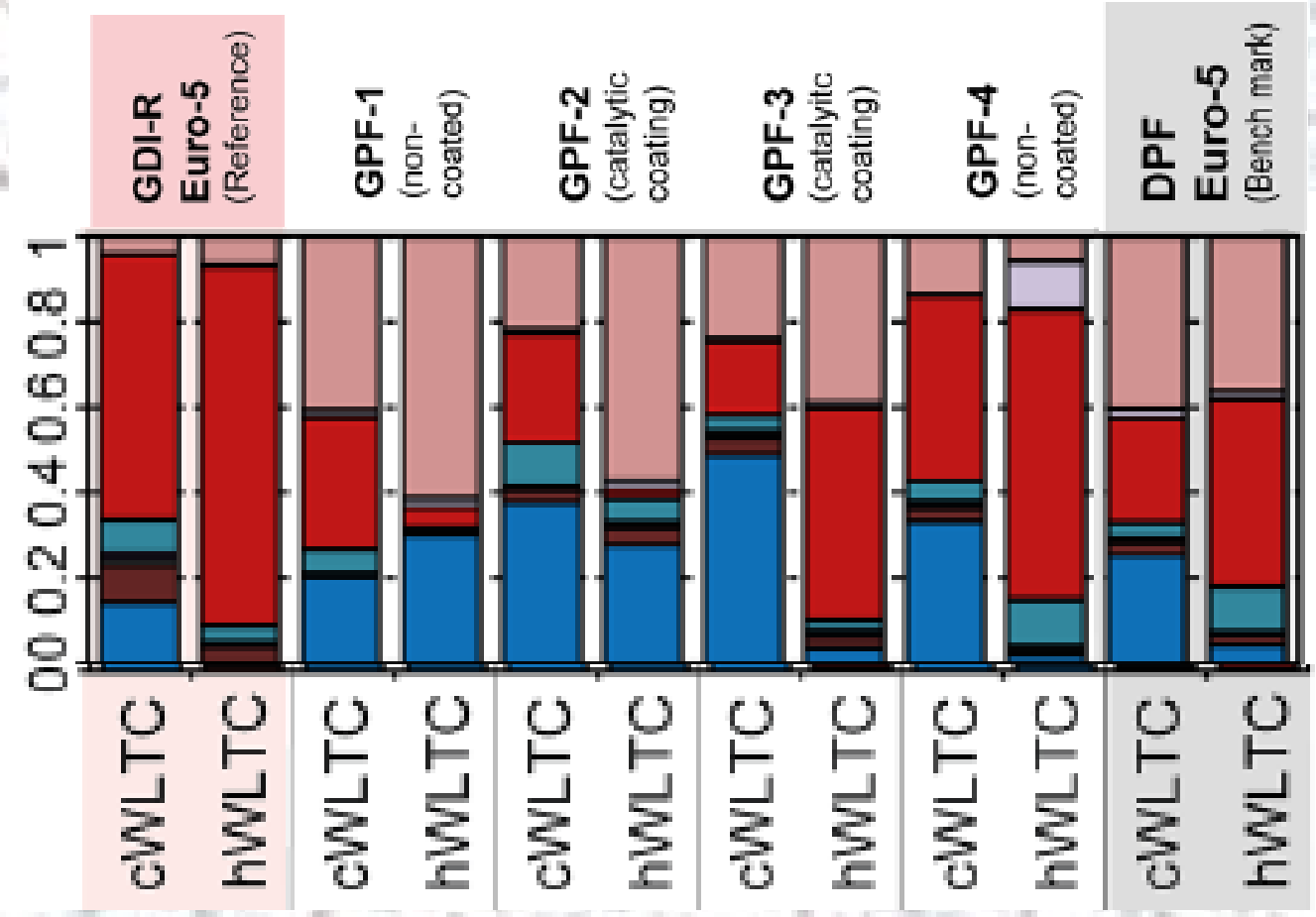


Munoz et al. ES&T., **2018**, 52, 10709-10718

Particle filters for GDI-vehicles (GPFs)

3 of 4 prototype-GPFs reduced genotoxic PAHs

Proportions of genotoxic PAHs



Munoz et al. ES&T., **2018**, 52, 10709-10718

Secondary emissions test for gasoline direct injection vehicles

Something to celebrate!

Outline

- Toxic emissions of GDI vehicles

  GDI vehicles – a massive source for genotoxic nanoparticles

- VSET test on GPF vehicles

  From steady state to transient test cycles

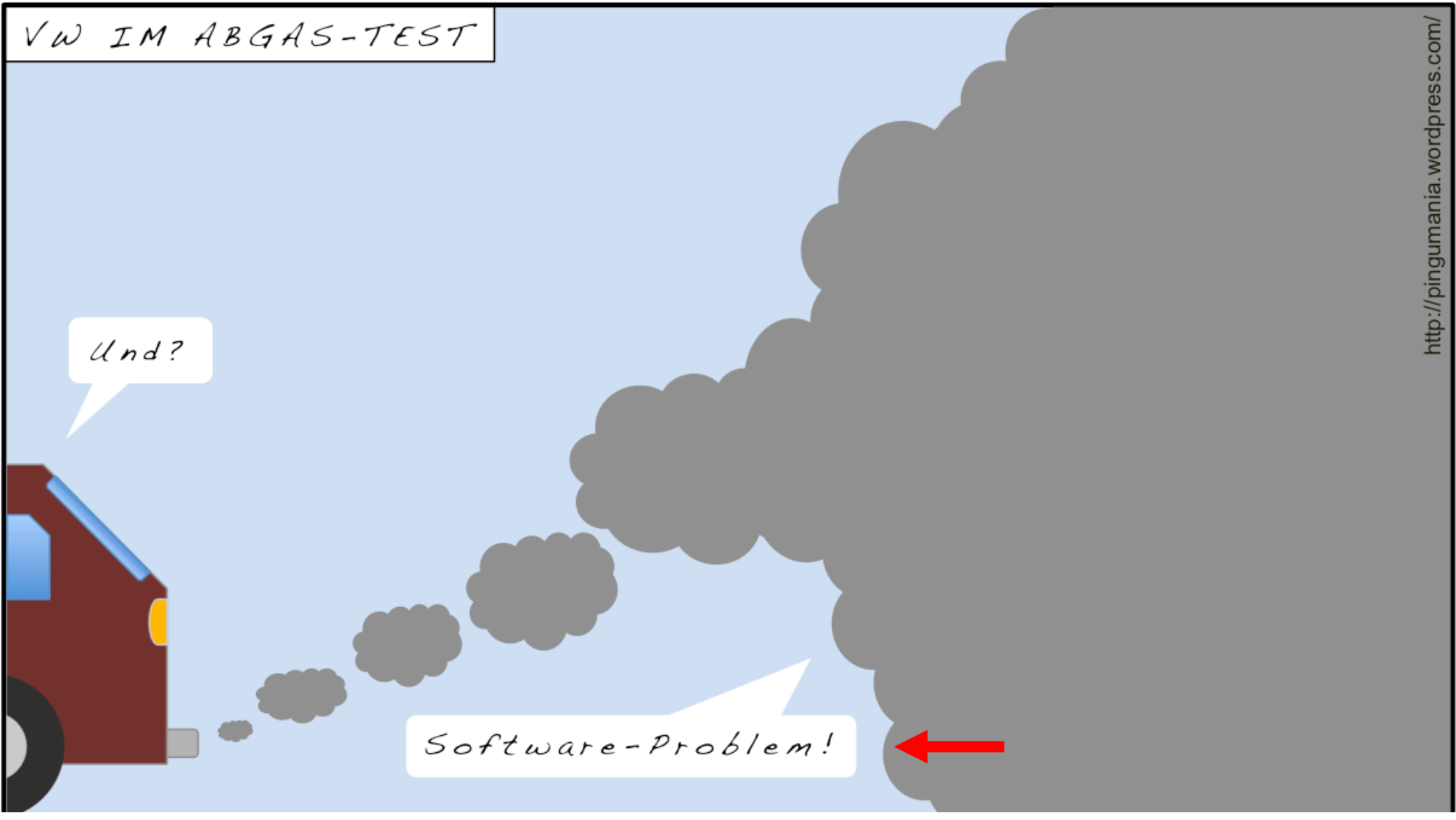
- PFs for gasoline vehicles

  Retro-fit and integrated particle filters for GDI vehicles

13th VERT Forum: New VERT nanoparticle abatement tools

Empa Dübendorf, March 21, 2023

Gasoline direct injection vehicles – the latest source for genotoxic nanoparticles



Gasoline direct injection vehicles – the latest source for genotoxic nanoparticles

GASOMEP: New concepts for gasoline vehicle emission control

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Bundesamt für Umwelt BAFU
Office fédéral de l'environnement OFEV
Ufficio federale dell'ambiente UFAM
Uffizi federal d'ambient UFAM

Dr. Andrea Ulrich

2. Nov. 1961 – 12. März 2013

Dr. Andrea Ulrich

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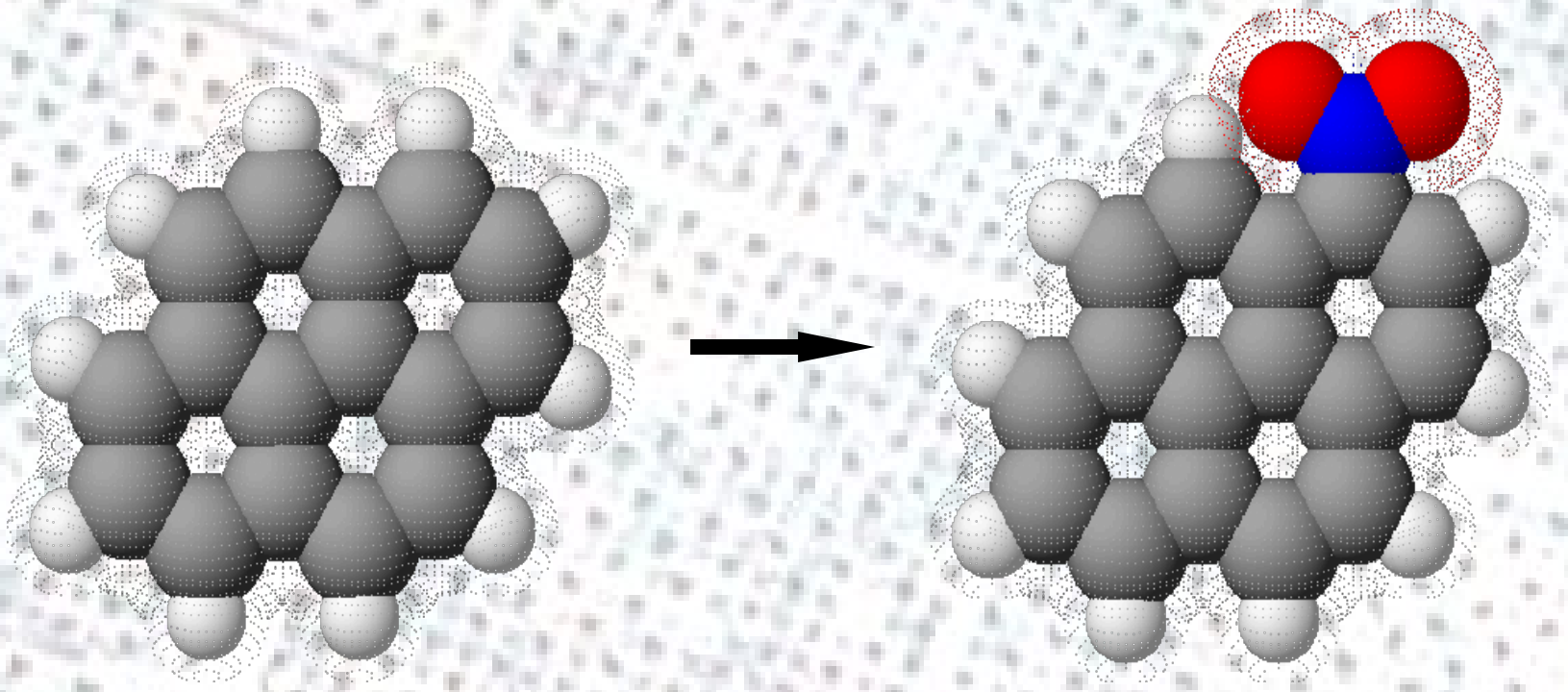
Particle filters are chemical reactors

In one step from a harmless precursor to a mutagen?

Nitration of PAHs

ideal nitration conditions?



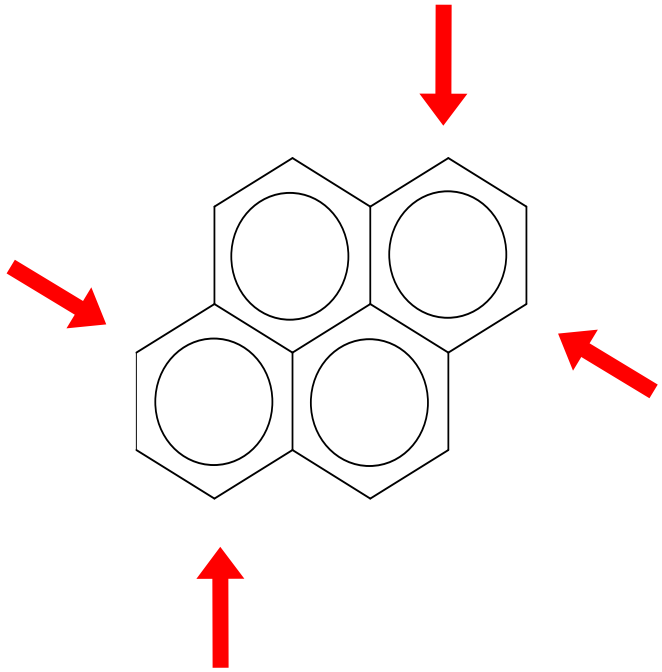
pyrene

1-nitropyrene

Particle filters are chemical reactors

Nitration in alpha-position?

Regioselective nitration of pyrene

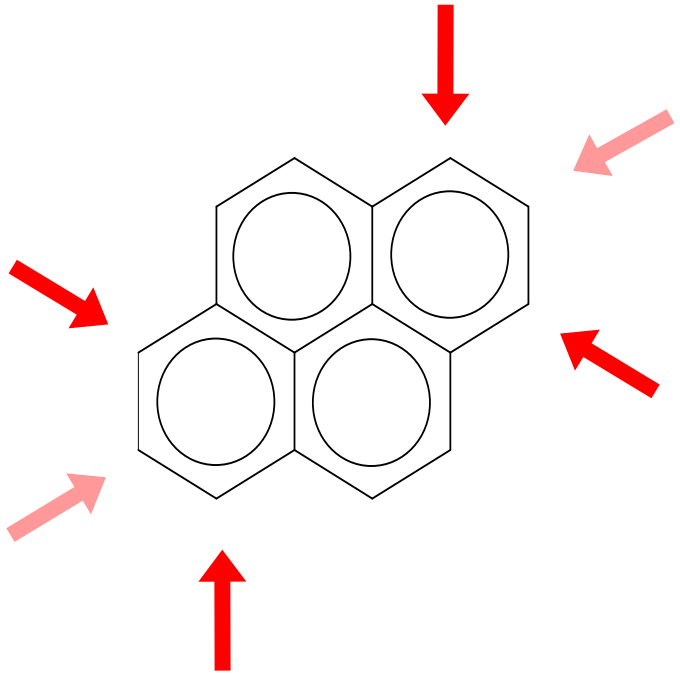


EMPA

Particle filters are chemical reactors

or in beta-position?

Regioselective nitration of pyrene

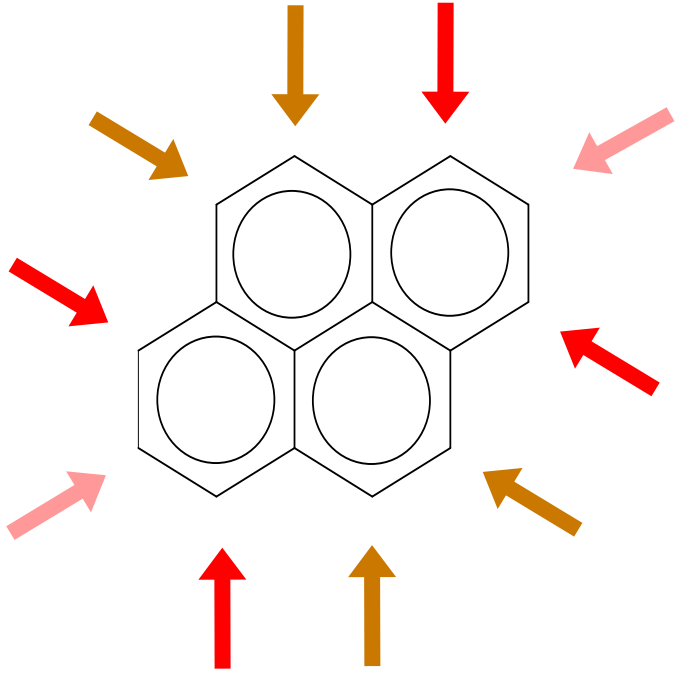


EMPA

Particle filters are chemical reactors

or in gamma-position?

Regioselective nitration of pyrene

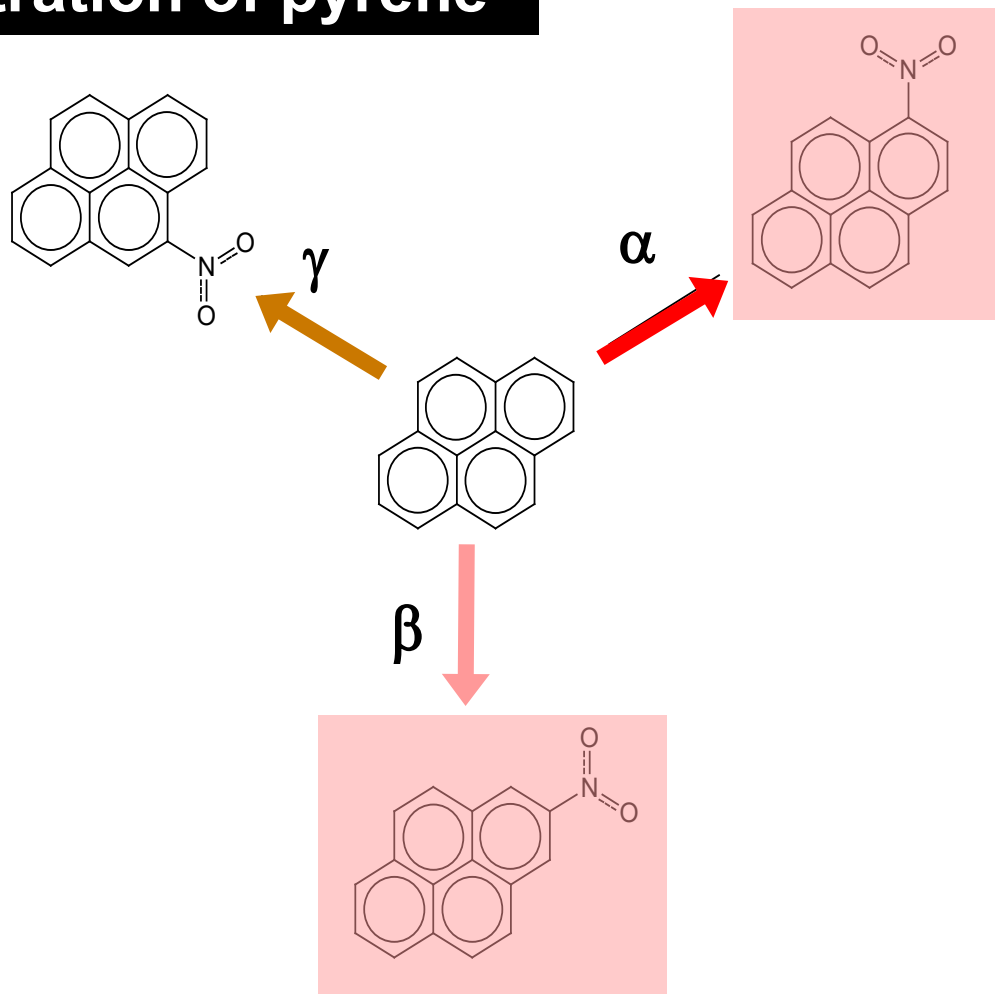


EMPA

Particle filters are chemical reactors

Two of the three isomers are mutagenic.

Regioselective nitration of pyrene

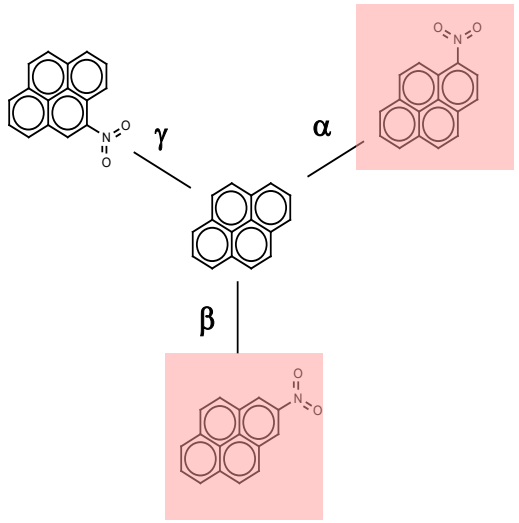


EMPA

Particle filters are chemical reactors

If nitration is possible ones, why not twice?

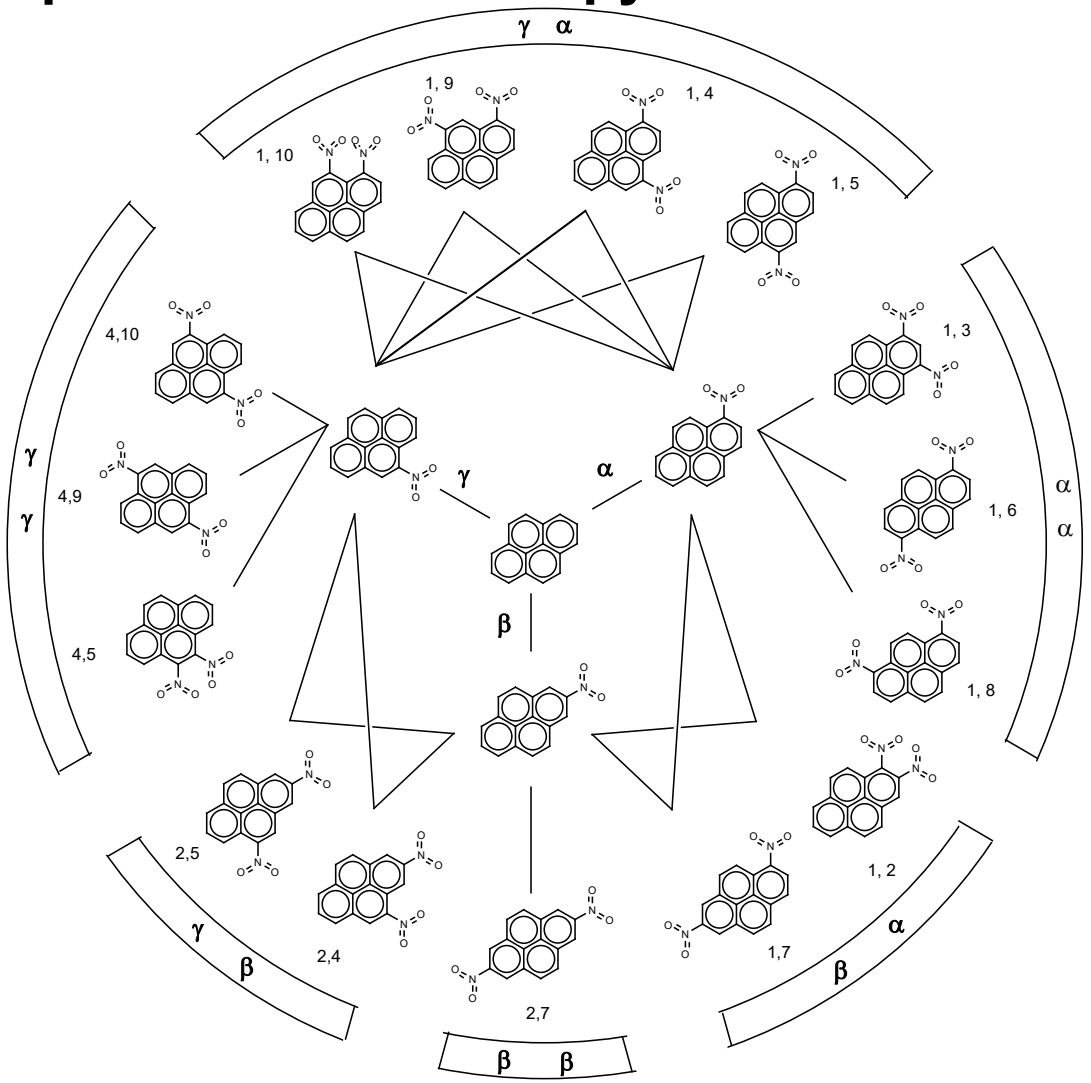
Regioselective nitration of pyrene



EMPA

Particle filters are chemical reactors

From one precursor to 3 nitropyrenes to 15 dinitropyrenes?

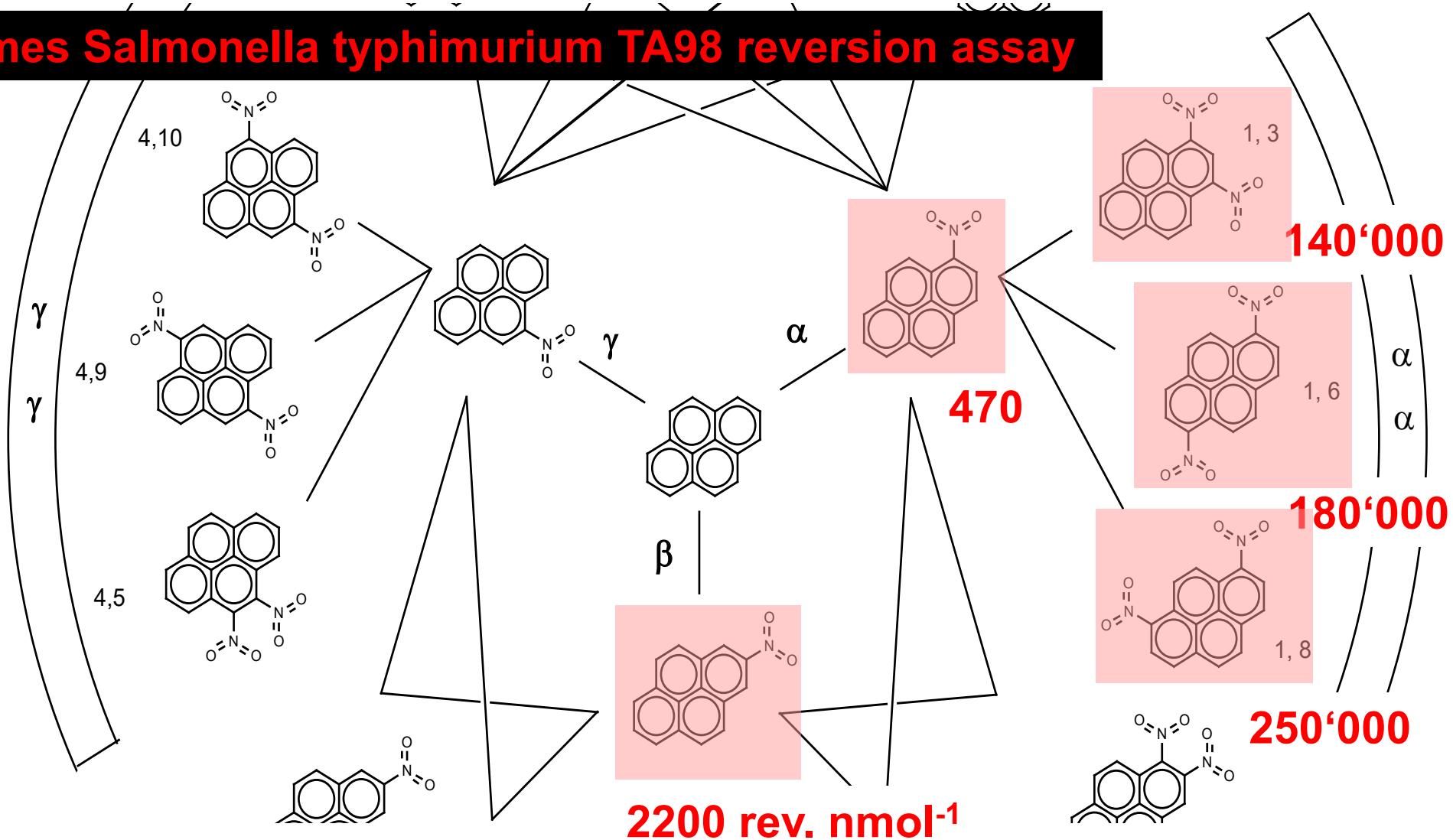


EMPA

Particle filters are chemical reactors

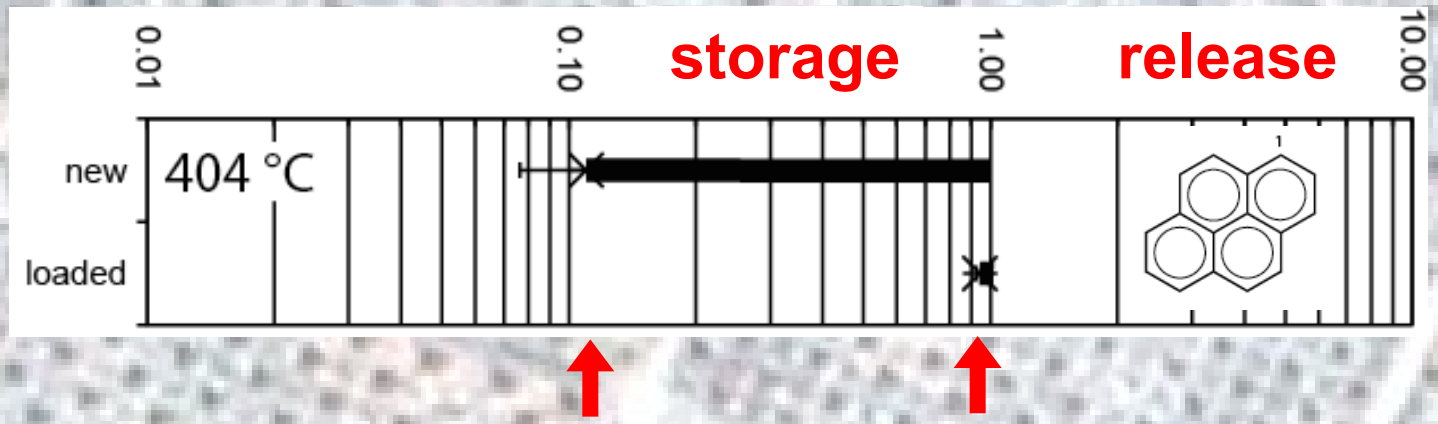
The most potent direct-acting mutagens known are dinitropyrenes

Ames Salmonella typhimurium TA98 reversion assay



Nitro-PAH formation in non-catalyzed DPF

Non-catalyzed filter operated <200 °C to accumulate soot and hydrocarbons

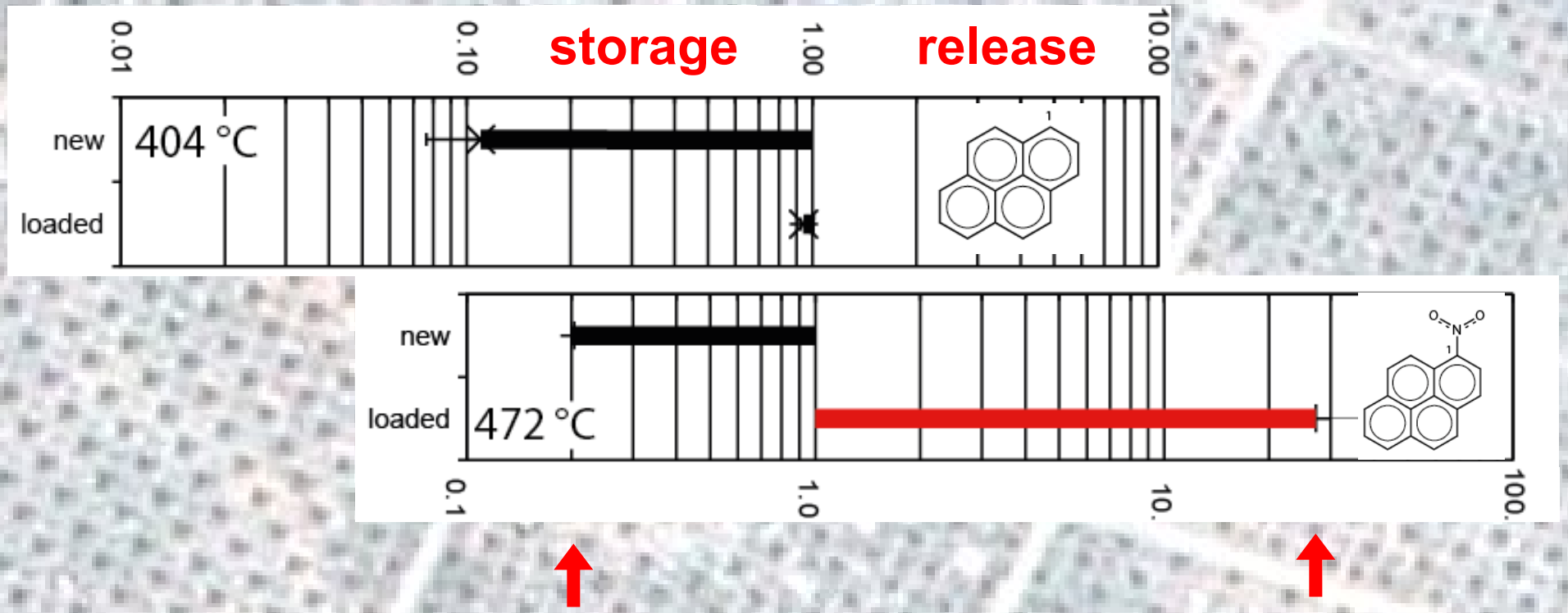


- pyrene is stored in a new, but released from a soot-loaded DPF

Outlet

Nitro-PAH formation in non-catalyzed DPF

Non-catalyzed filter operated <200 °C to accumulate soot and hydrocarbons



- pyrene is stored in a new, but released from a soot-loaded DPF

- 1-nitro pyrene is stored in a new, but formed and released from a soot-loaded DPF (30x)

Swiss road traffic in the future

It’s time to move on without inefficient combustion engines which release toxic exhausts in places we live