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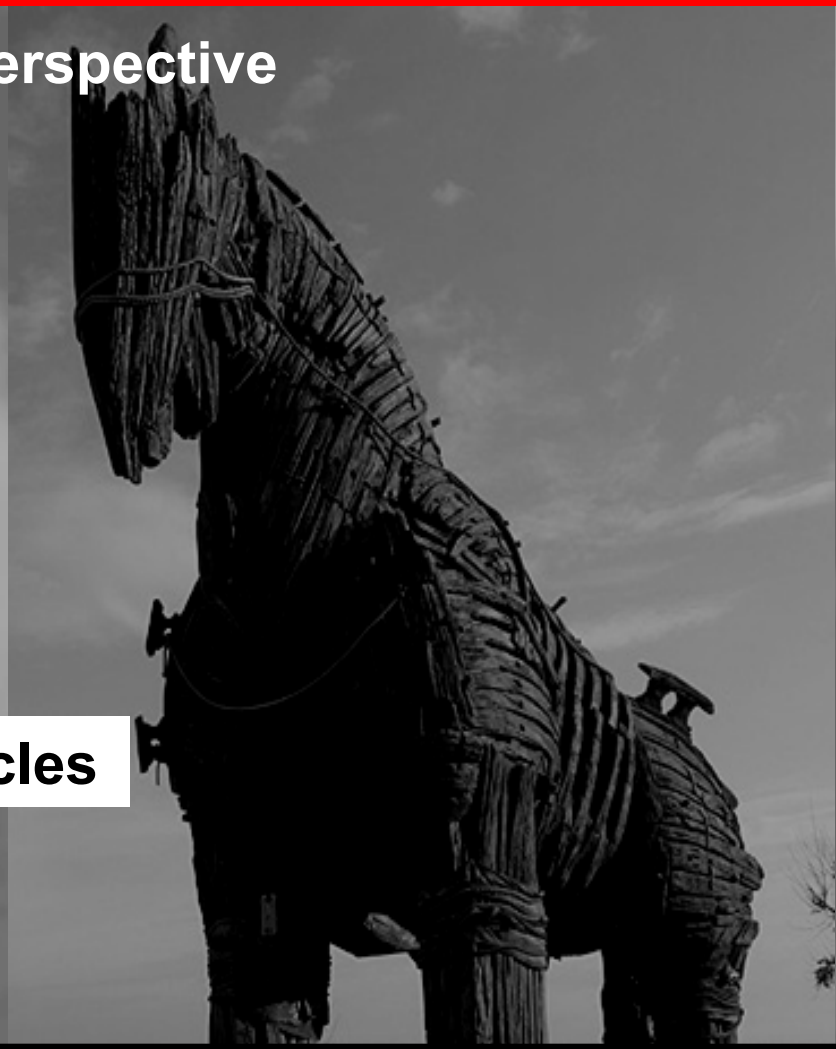
Empa
Materials Science and Technology

The chemistry of nanoparticle adsorbates from diesel and gasoline combustion engines

The Trojan Horse effect, from a chemists perspective

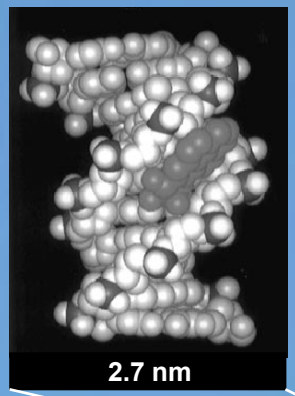


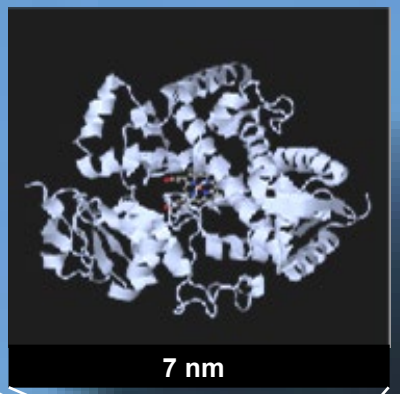
- **Adsorbate chemistry**
  (A quick tour)
- **Chemistry in particle filters**
  (PFs – ideal chemical reactors)
- **Genotoxic particles from gasoline vehicles**
  (a global threat)

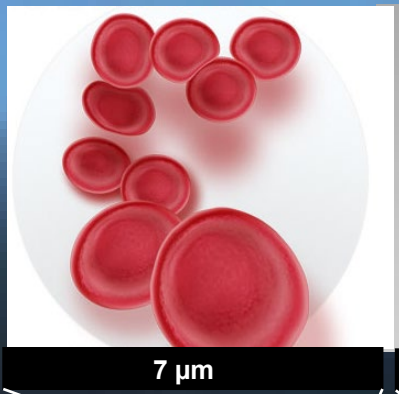
23id ETH Conference on Combustion Generated Nanoparticles

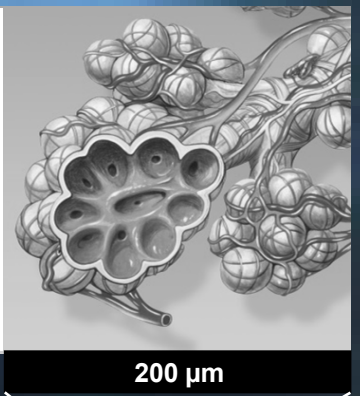
Zürich, June 17th – 20th, 2019

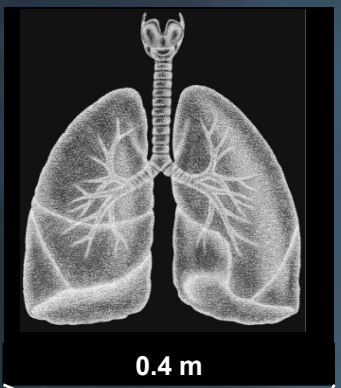
Particle and molecular dimensions and biological receptors


2.7 nm

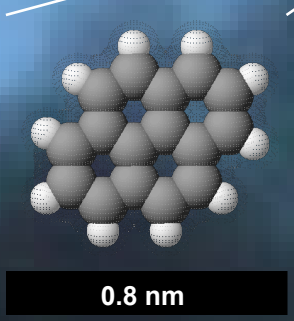

7 nm

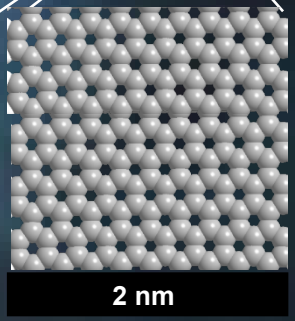

7 µm

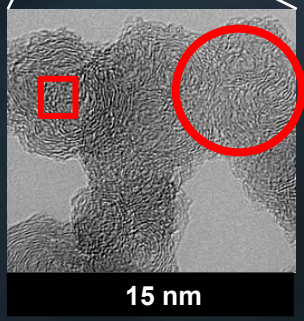

200 µm

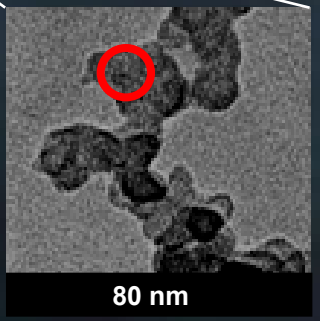

0.4 m

1pm 10 100 1nm 10 100 1µm 10 100 1mm 10 100 1m


0.8 nm


2 nm


15 nm

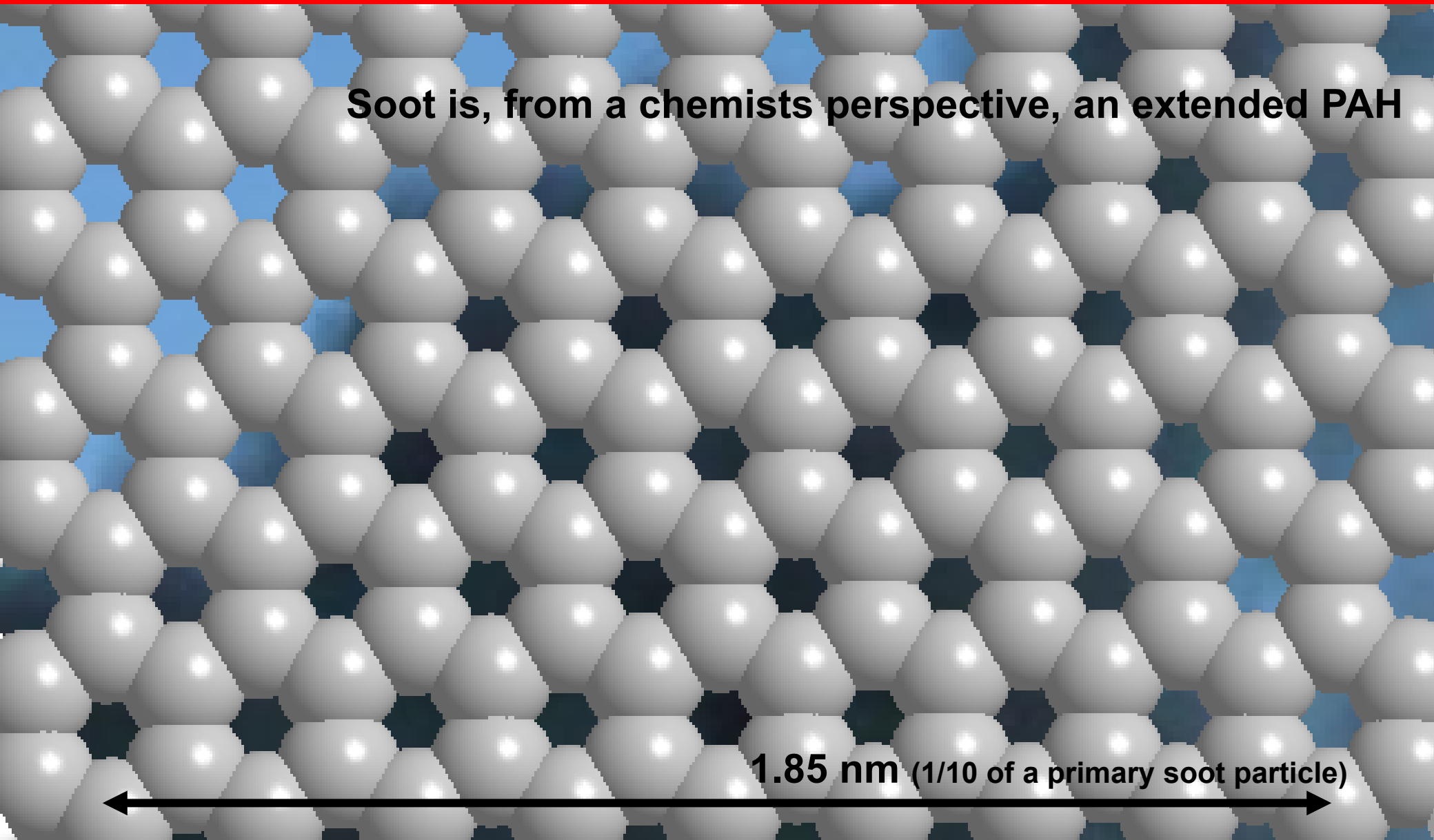

80 nm

PM 10 inhalable < 10 µm

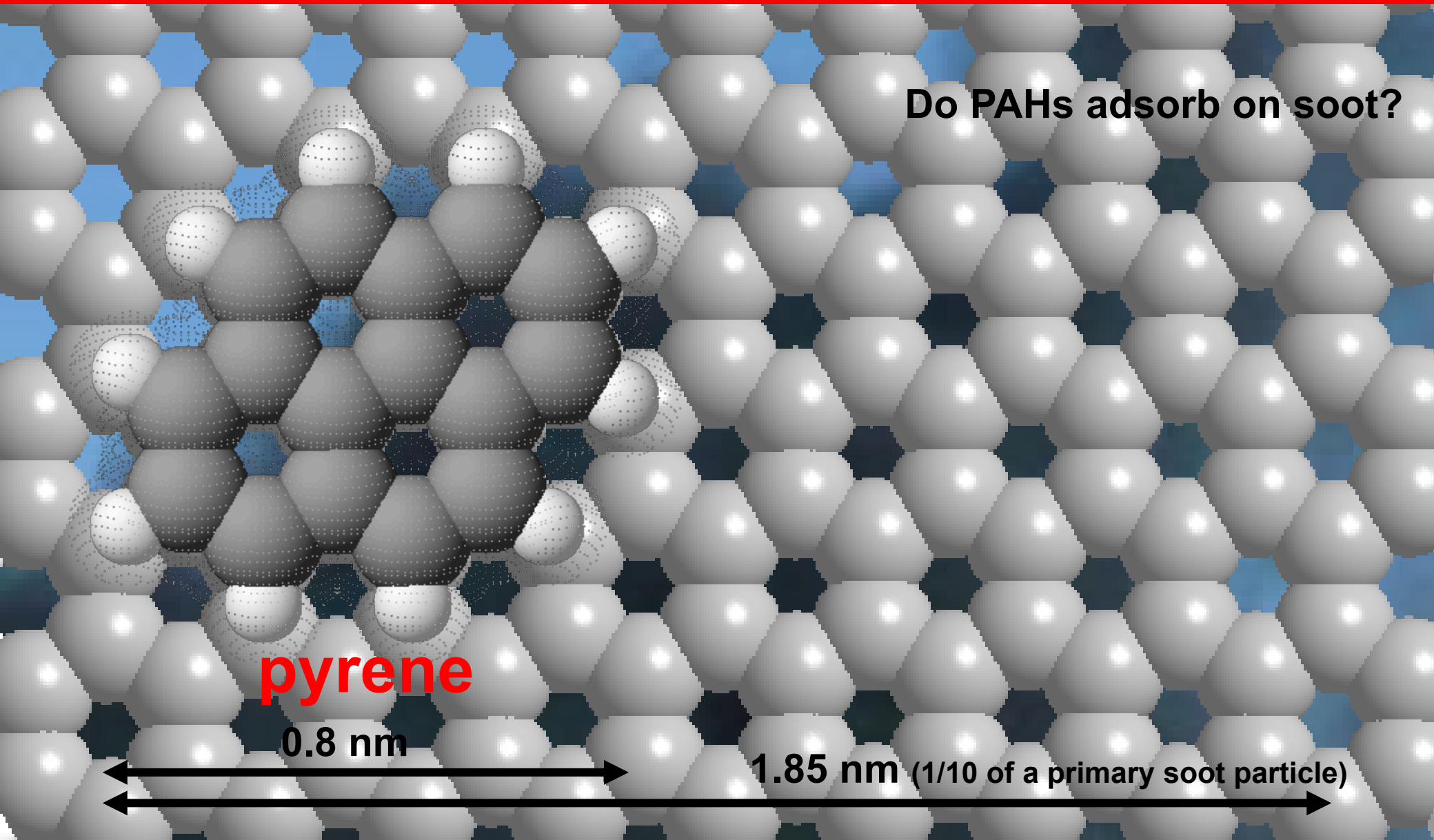
PM 1 reaches alveoli < 1 µm

PM 0.1 can cross membranes < 0.1 µm

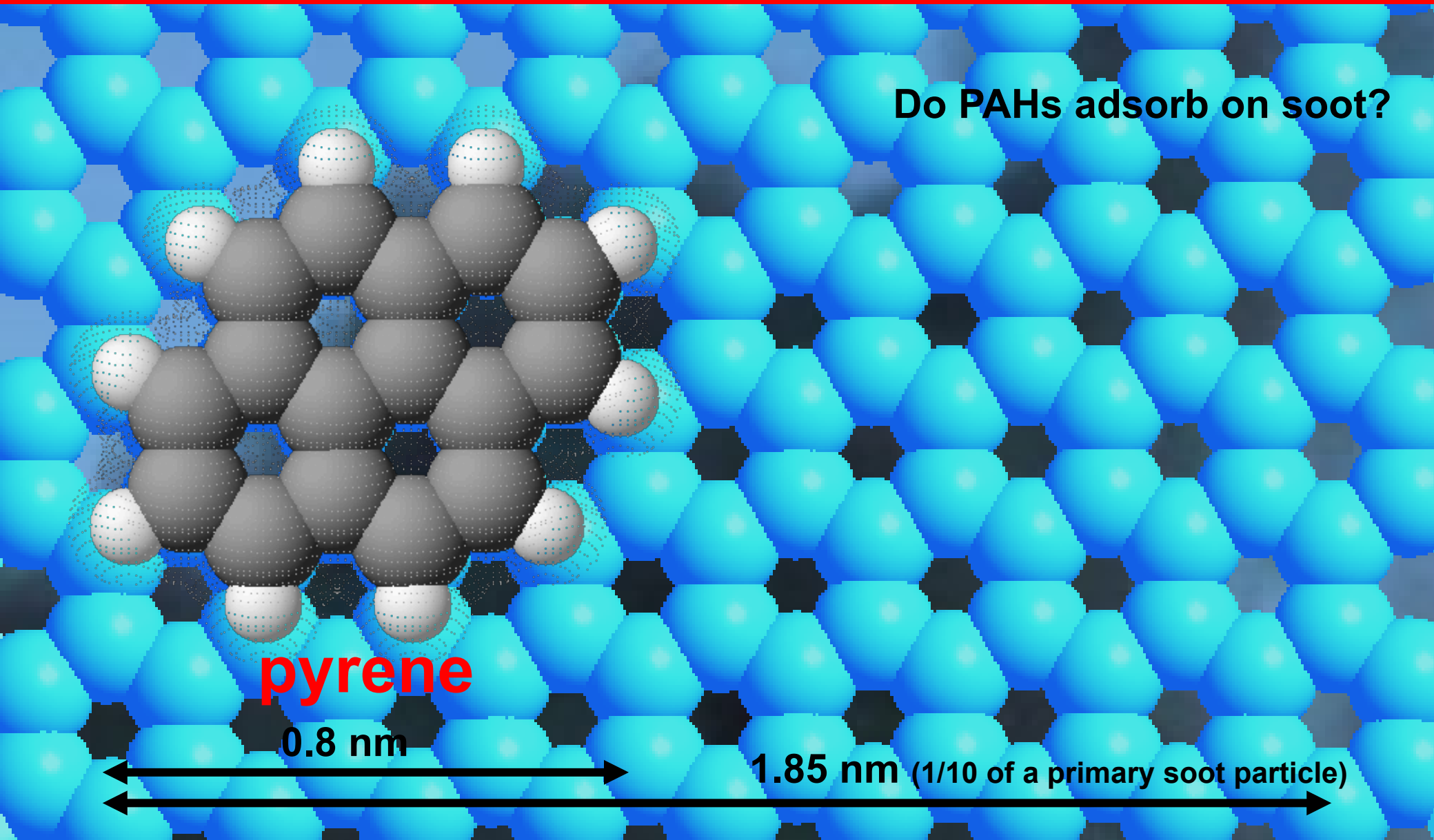
Soot and soot adsorbates



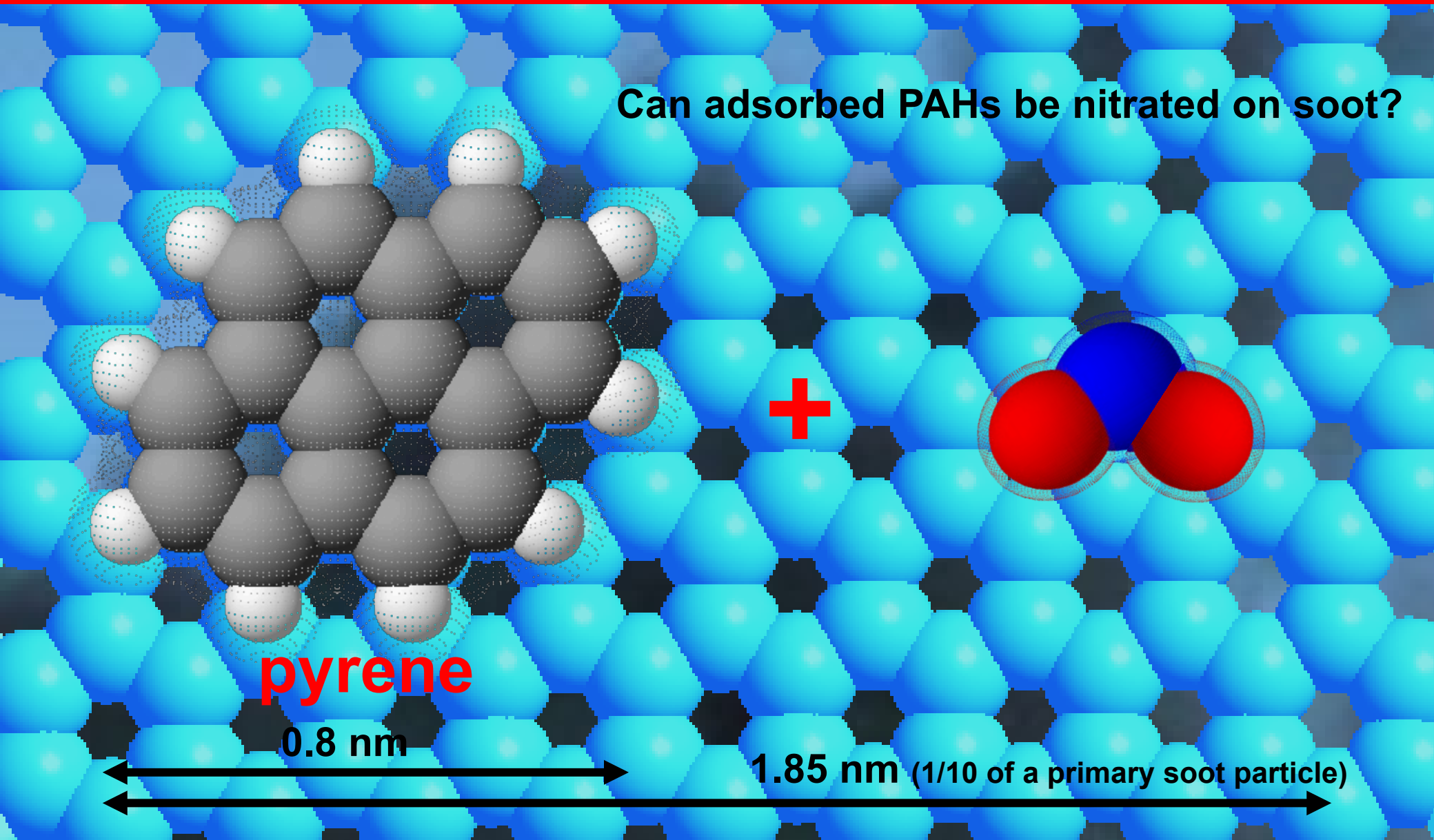
Soot and soot adsorbates



Soot and soot adsorbates



Soot catalyzed nitration of PAHs



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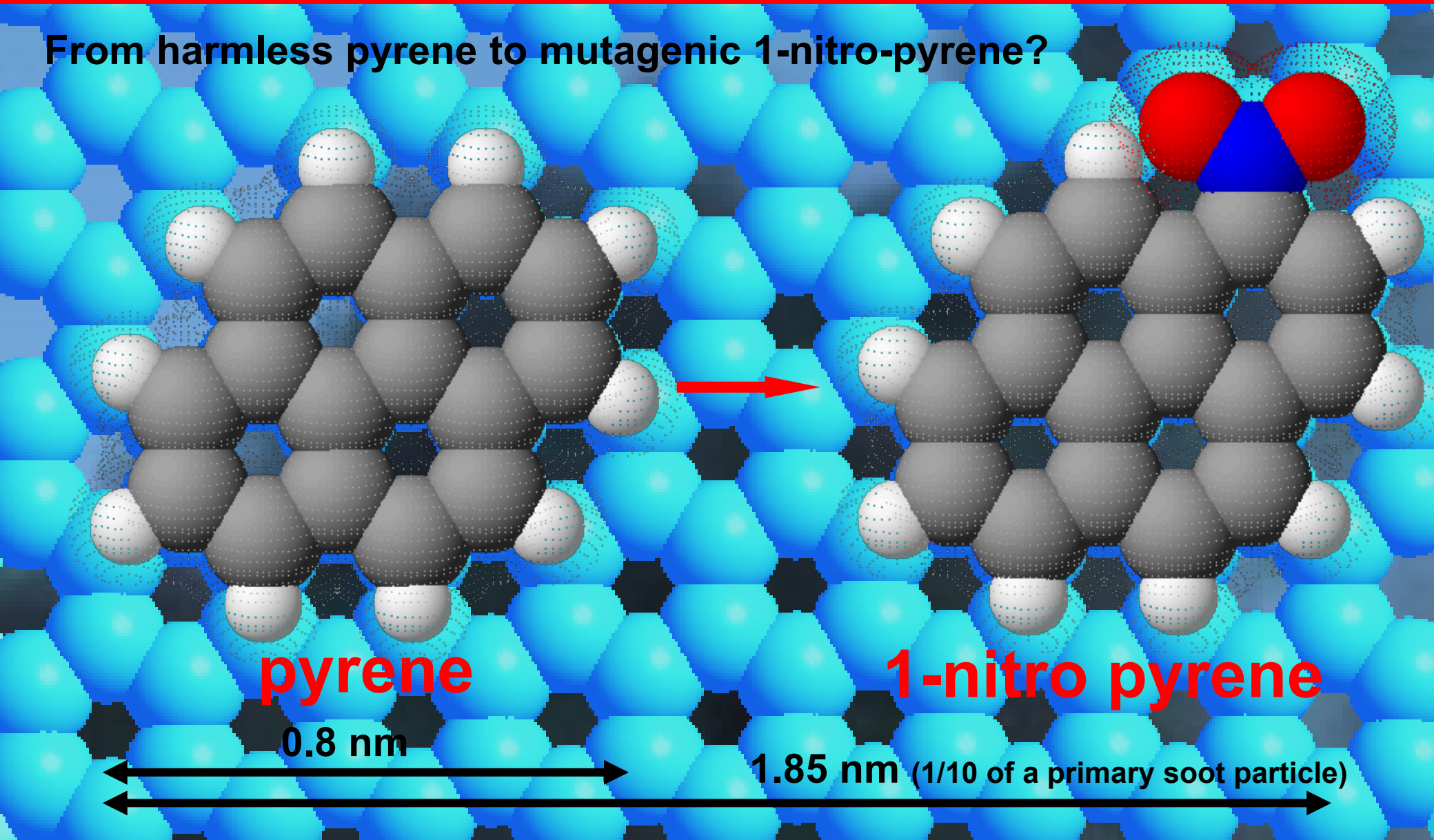
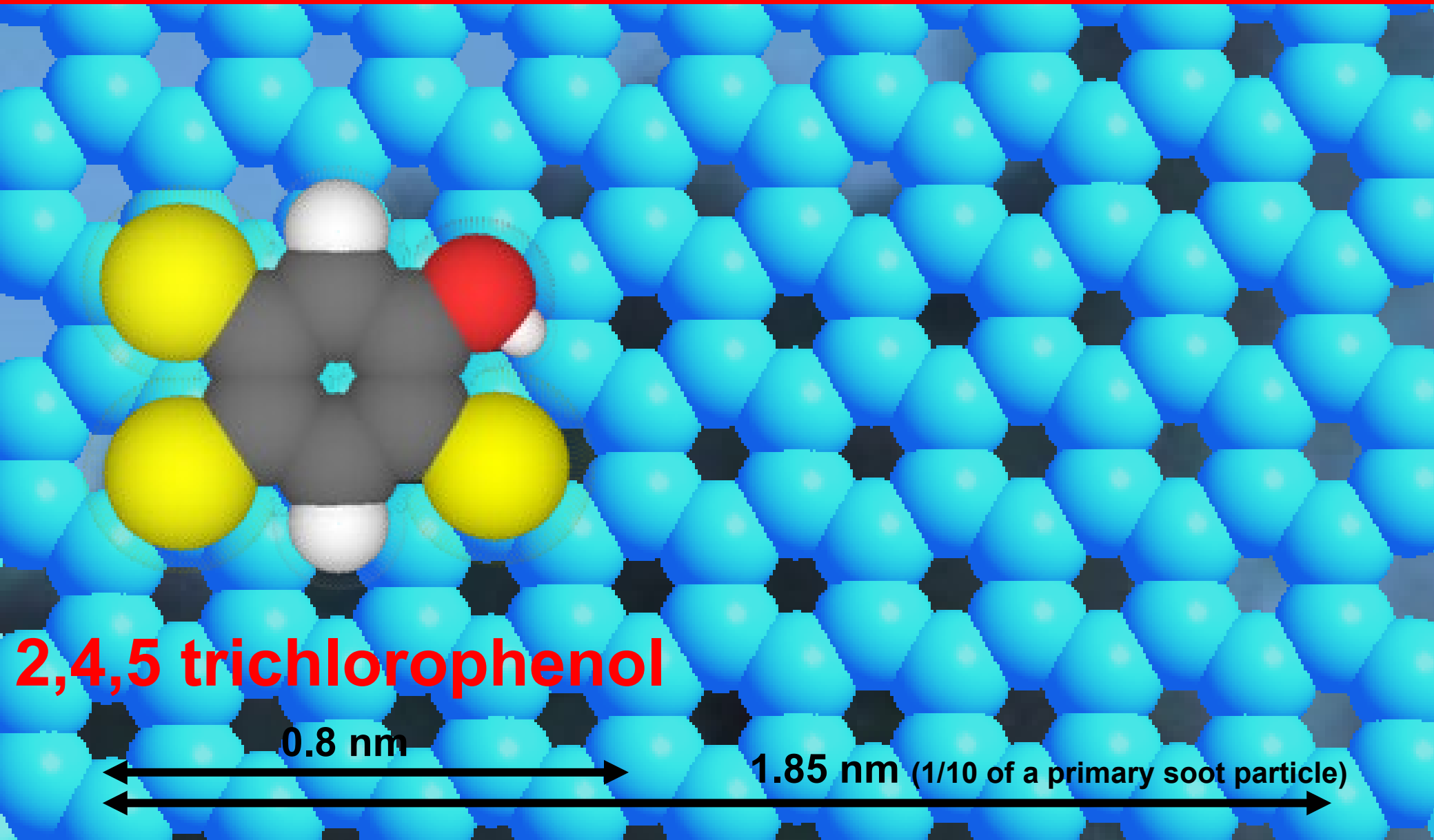


Metal catalyzed dioxin formation on soot



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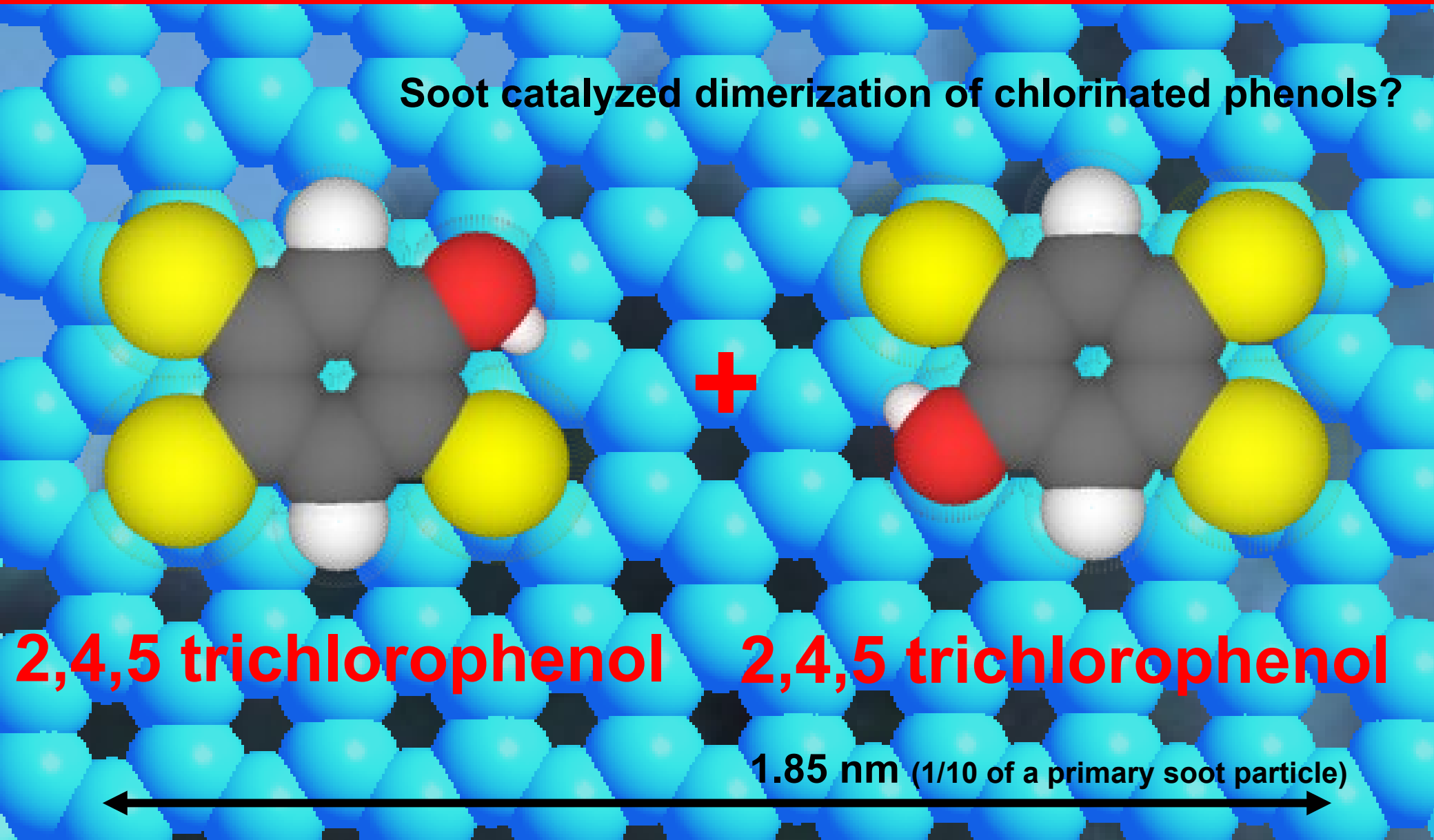

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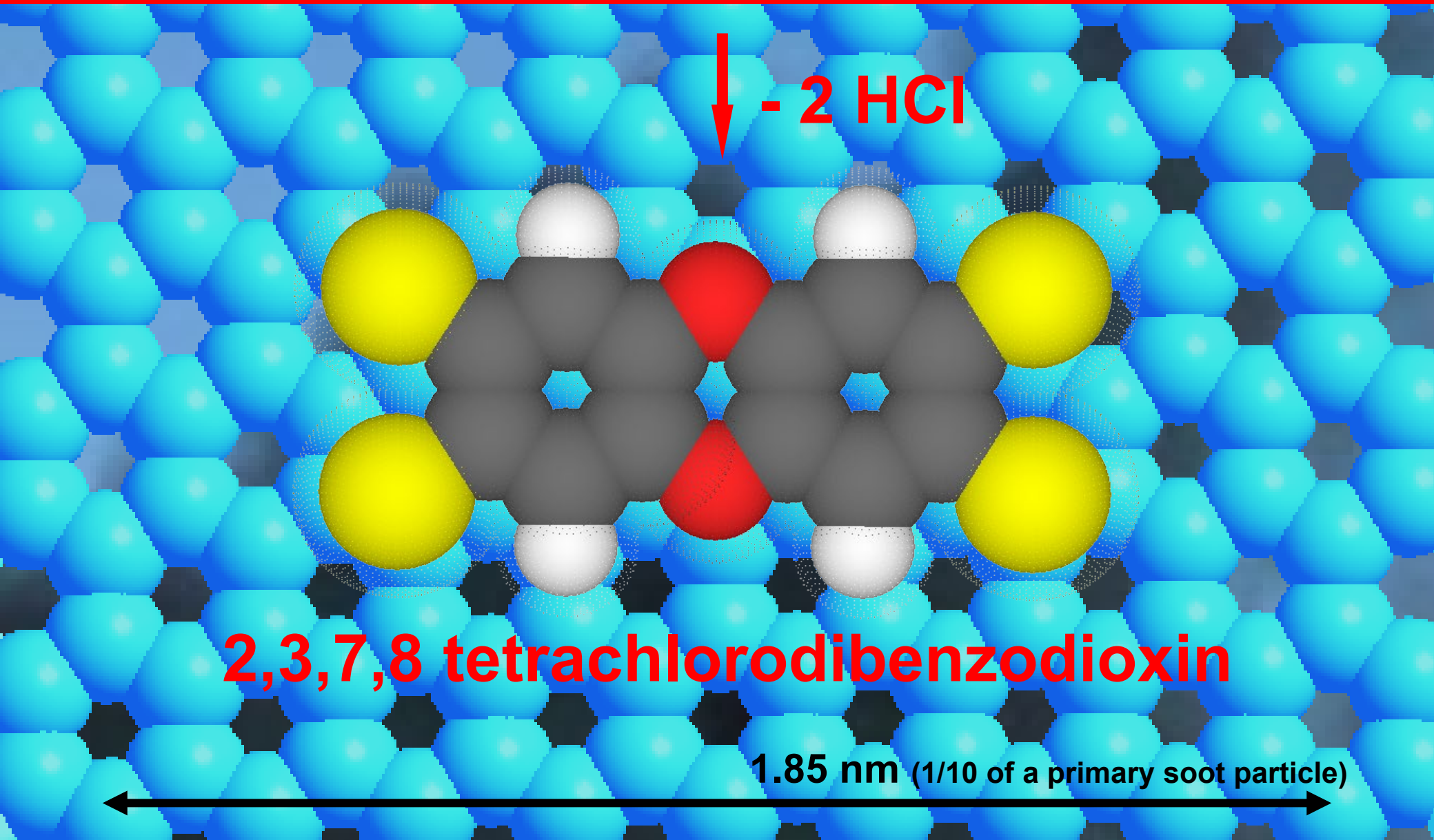
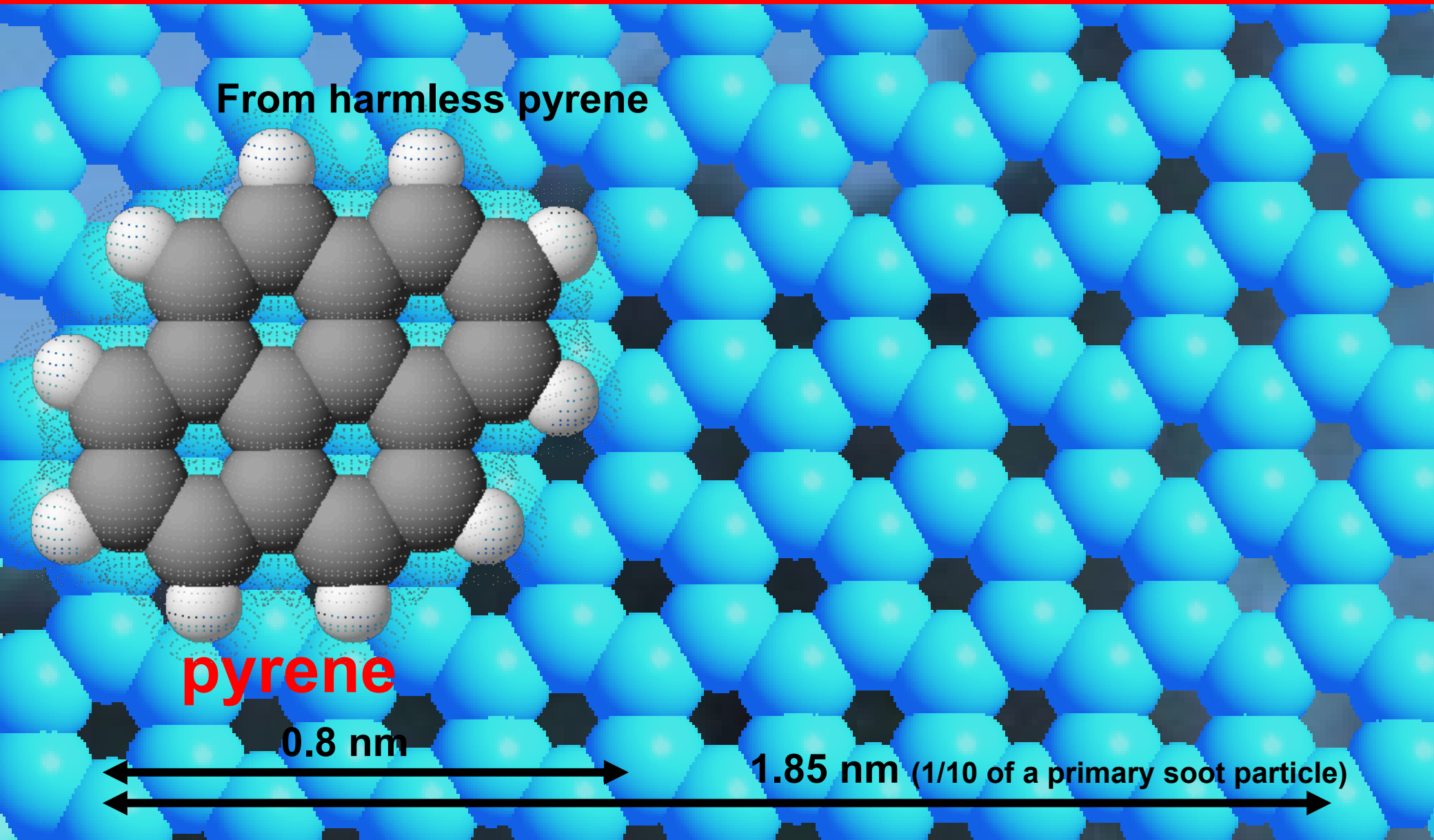


Oxidation of PAHs on soot



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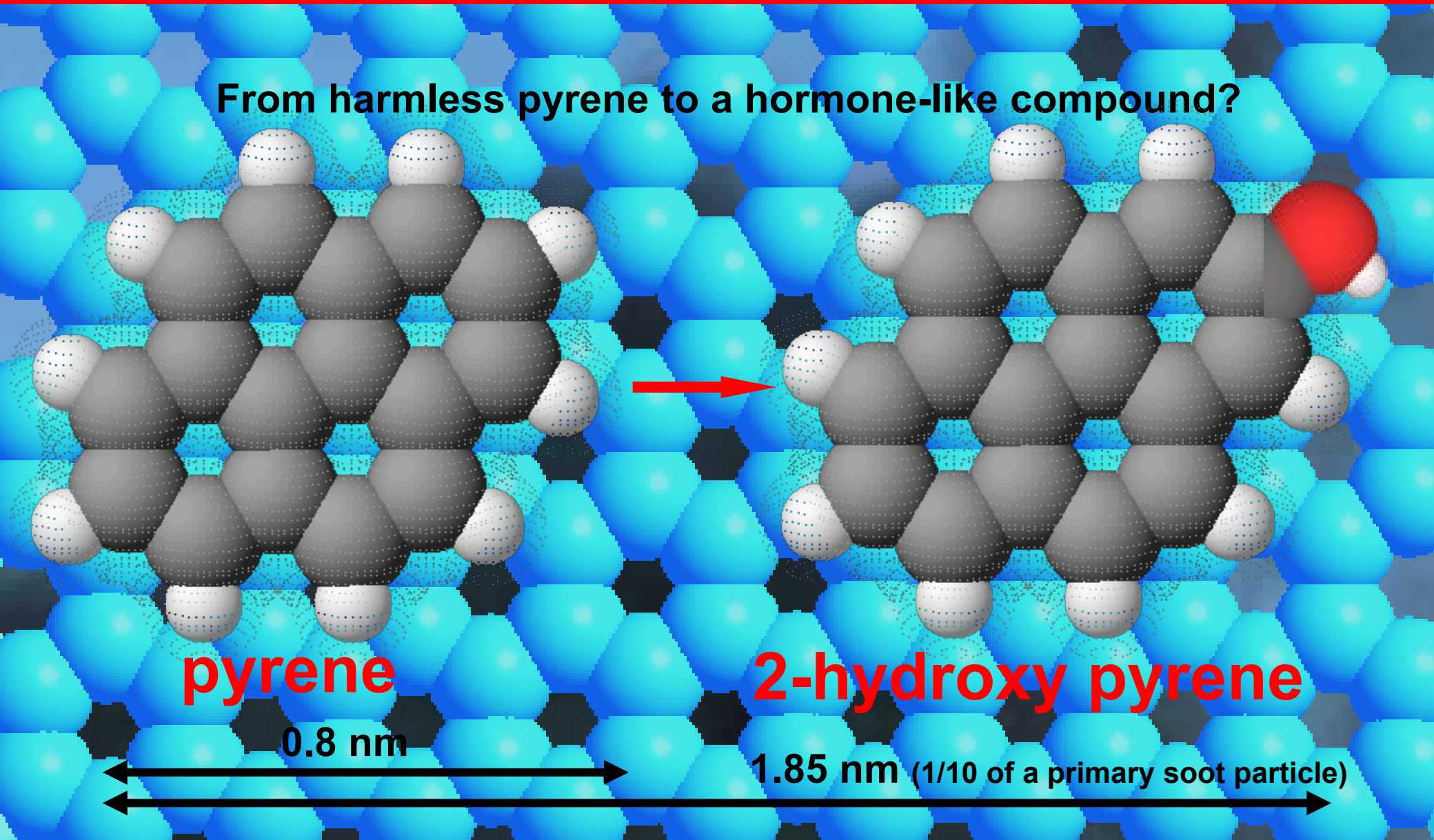
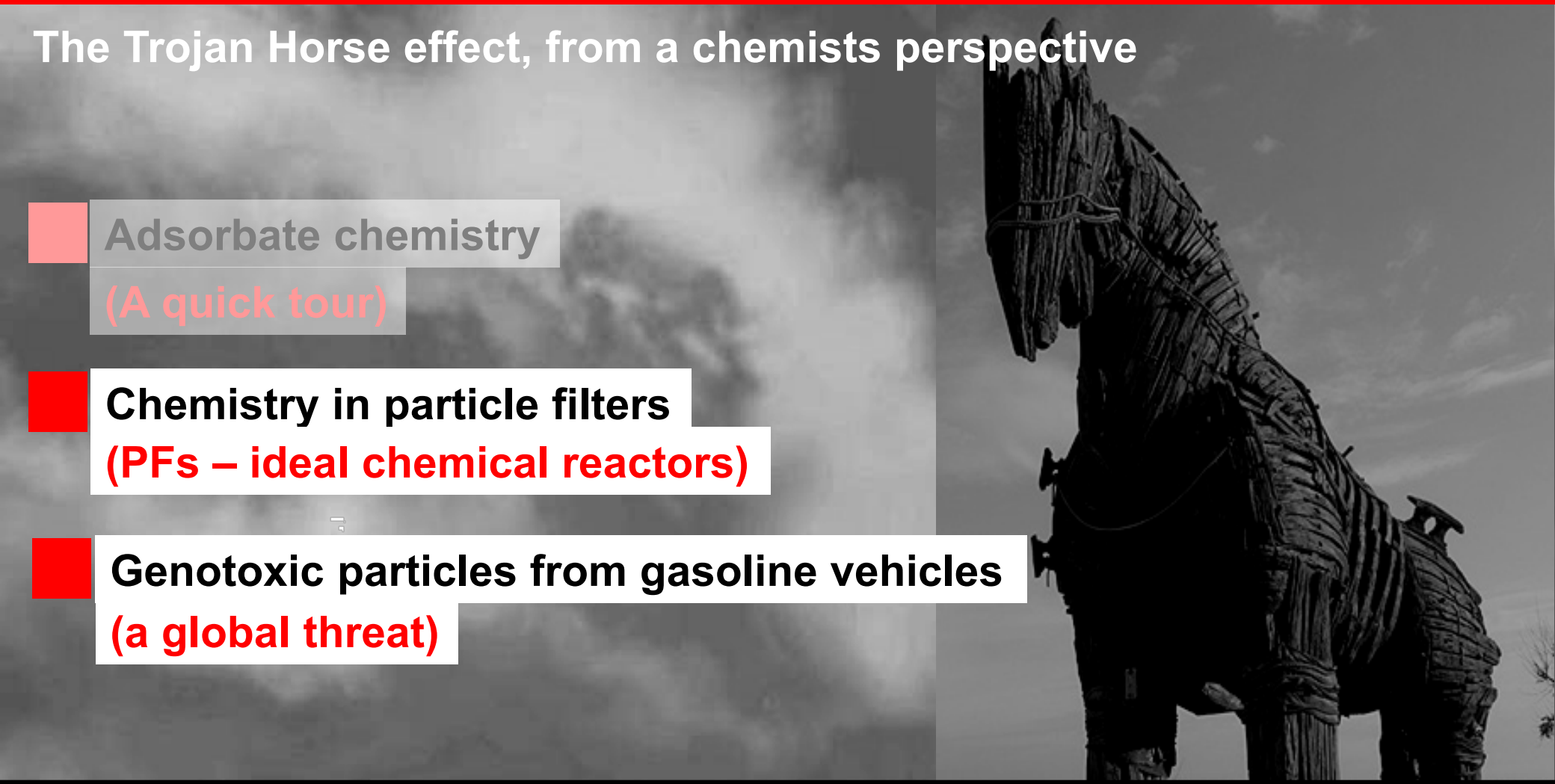


The chemistry of nanoparticle adsorbates from diesel and gasoline combustion engines



The Trojan Horse effect, from a chemists perspective

- Adsorbate chemistry
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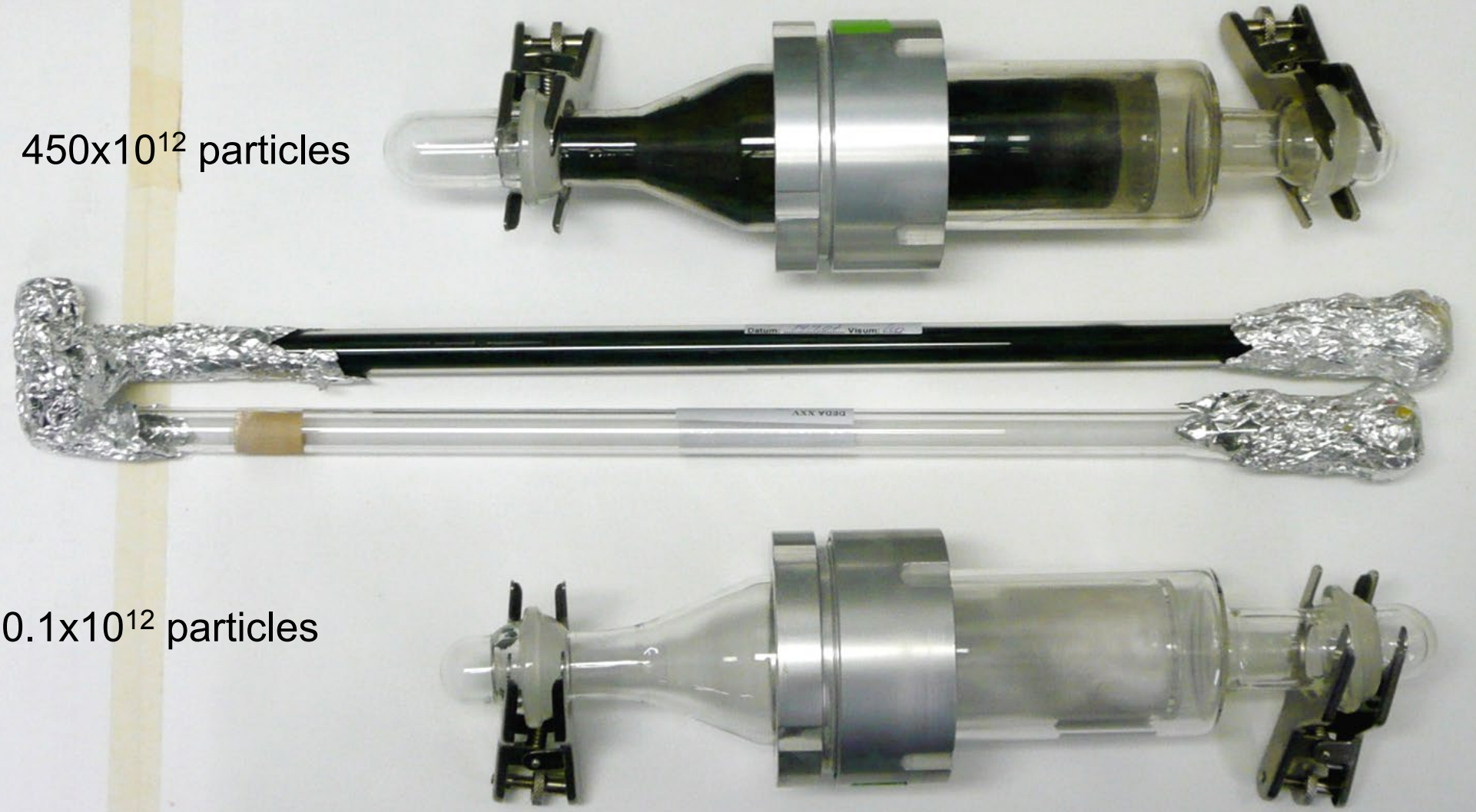
The visible effect of a DPF

7 m^3 exhaust (2 minutes of an Euro-3 diesel engine (6.1 L, 105 kW)



The chemistry of soot adsorbates

High quality filters are efficient sinks for soot. How about adsorbates?

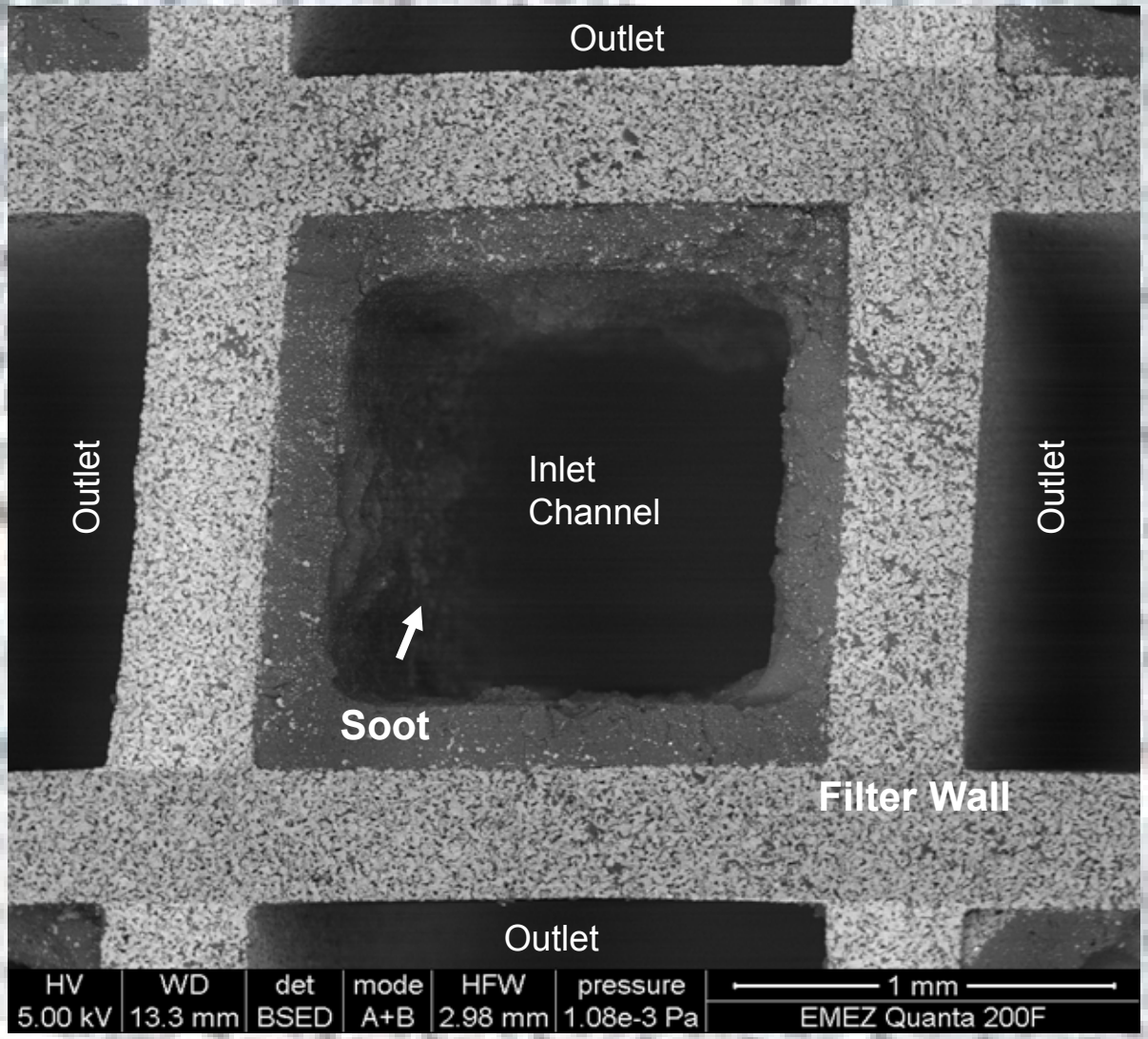
High quality PFs:

accumulate soot and ashes (>98%)

Can adsorbates penetrate soot loaded filters?

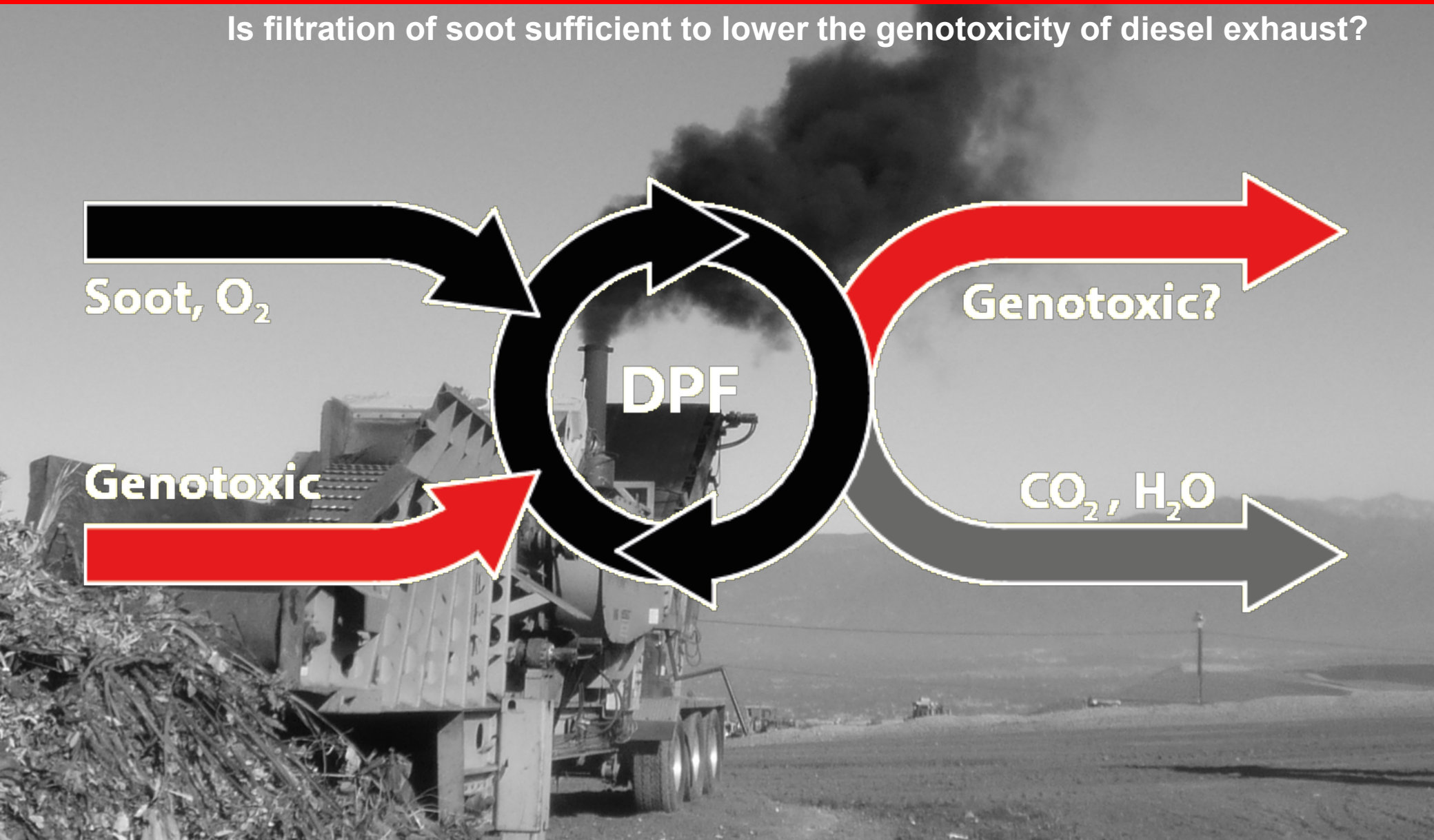
Do filters remove genotoxic compounds a.m.a.p?

Do filters support the formation of new toxic secondary pollutants?



Impact of particle filters on genotoxicity

Is filtration of soot sufficient to lower the genotoxicity of diesel exhaust?

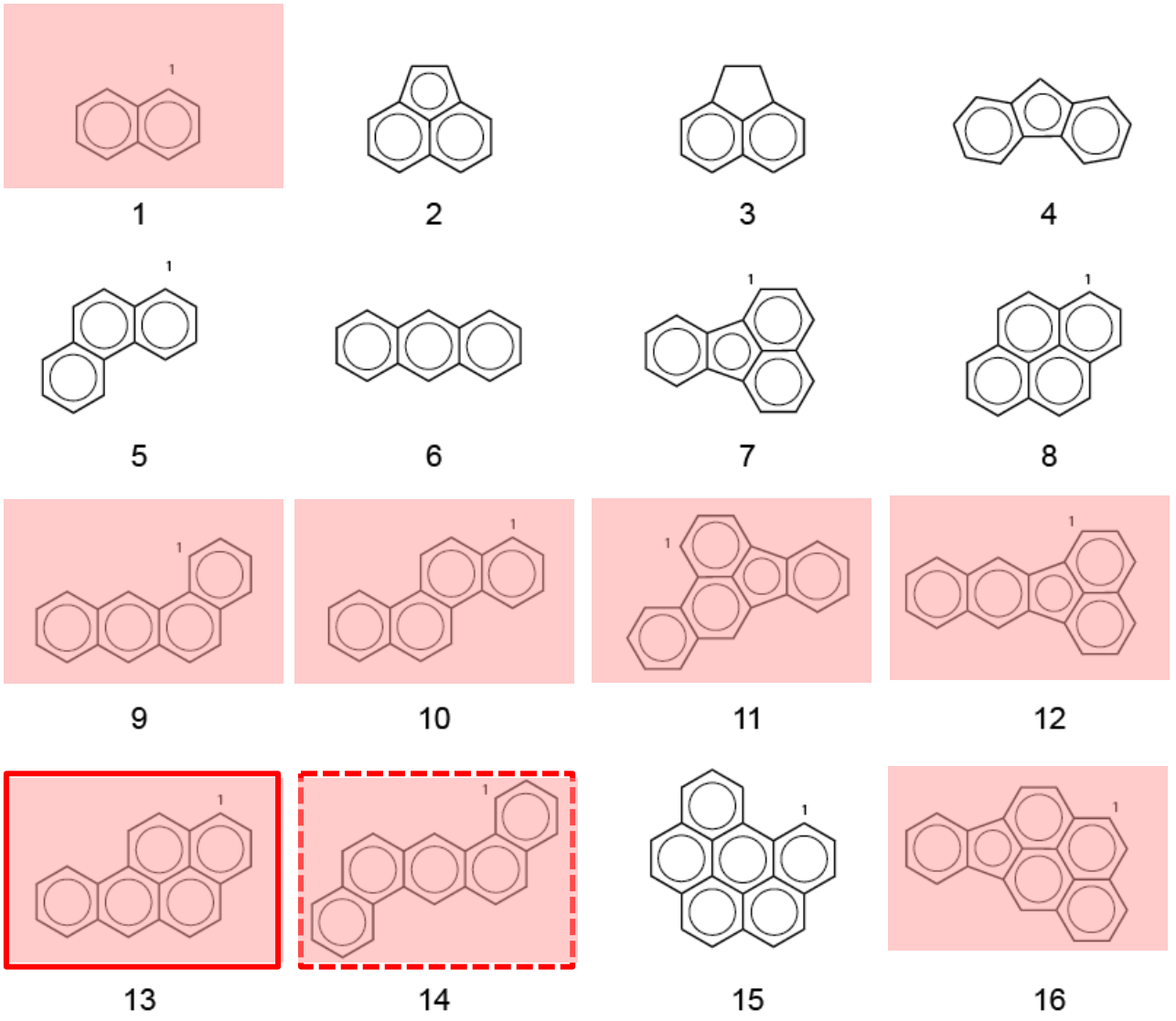


Polycyclic aromatic hydrocarbons

PAHs - a diverse class of compounds with variable physicochemical properties

2- to 6-ring PAHs

Luckily only some of the many PAHs are genotoxic!



Group 2B carcinogen

Group 2A carcinogen

Group 1 carcinogen

Polycyclic aromatic hydrocarbons

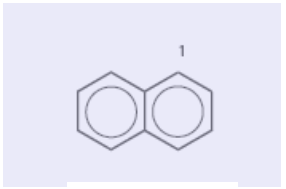
PAHs - a diverse class of compounds with variable physicochemical properties

2- to 6-ring PAHs

Volatile PAHs penetrate DPFs, both new and soot-loaded filters

Semi-volatile PAHs can be stored in new, but released from soot loaded DPFs

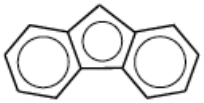
Thus, some PAHs can accumulate in filters for long periods of time (h, d, m, y)



218 °C

2

3



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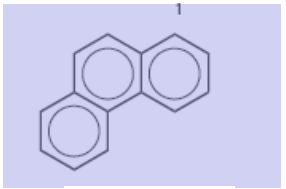
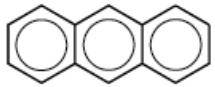


340 °C



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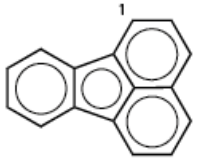

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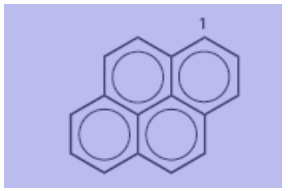
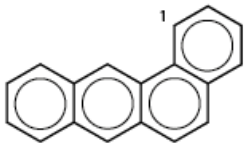


404 °C



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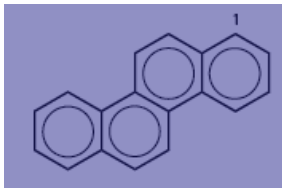
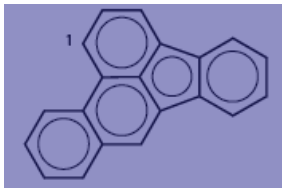
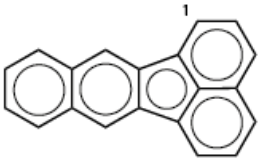


448 °C



481 °C



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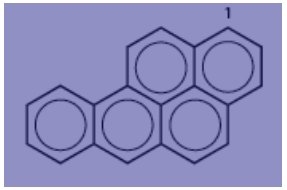
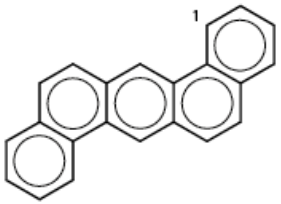


495 °C



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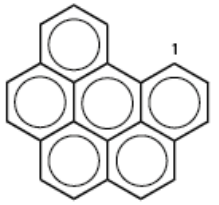

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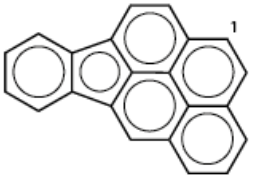
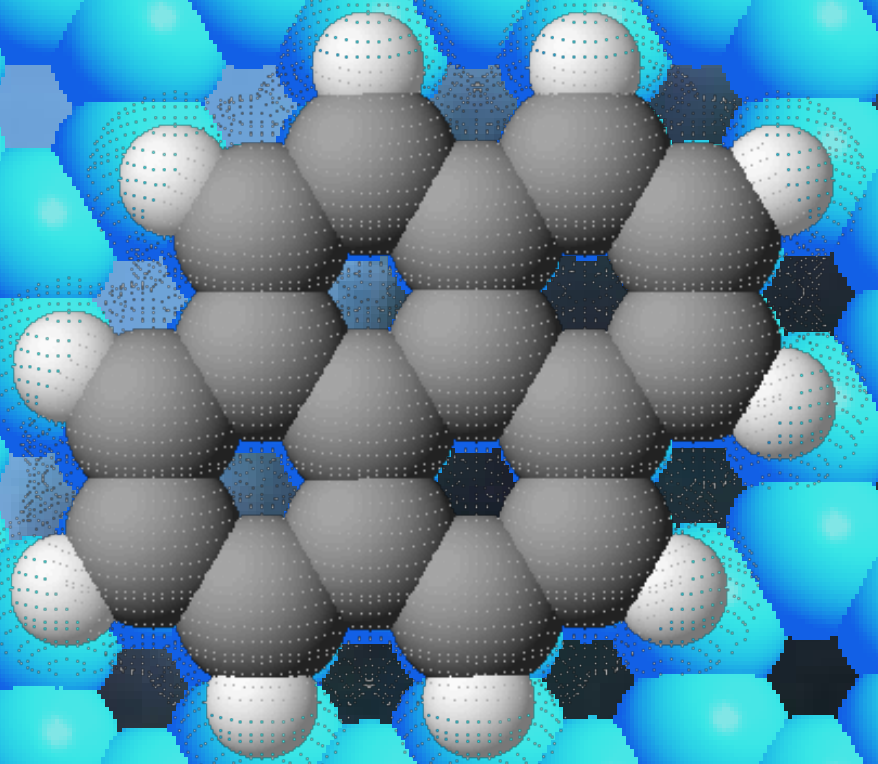


16

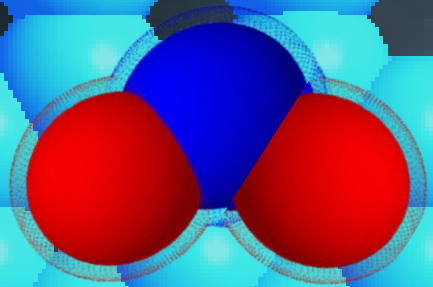
Soot catalyzed nitration of PAHs

Can adsorbed PAHs be nitrated on soot?



pyrene

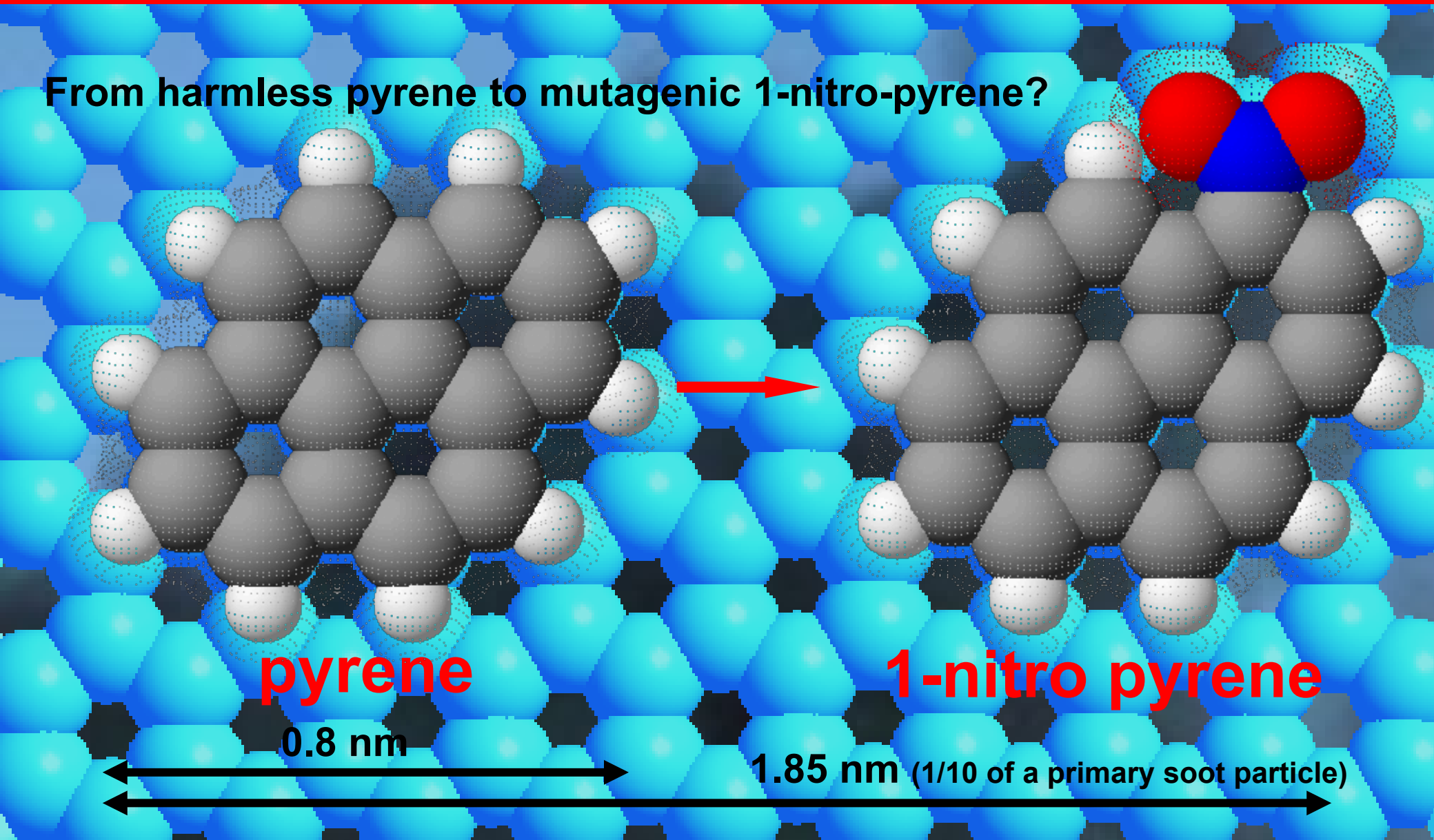
+



0.8 nm

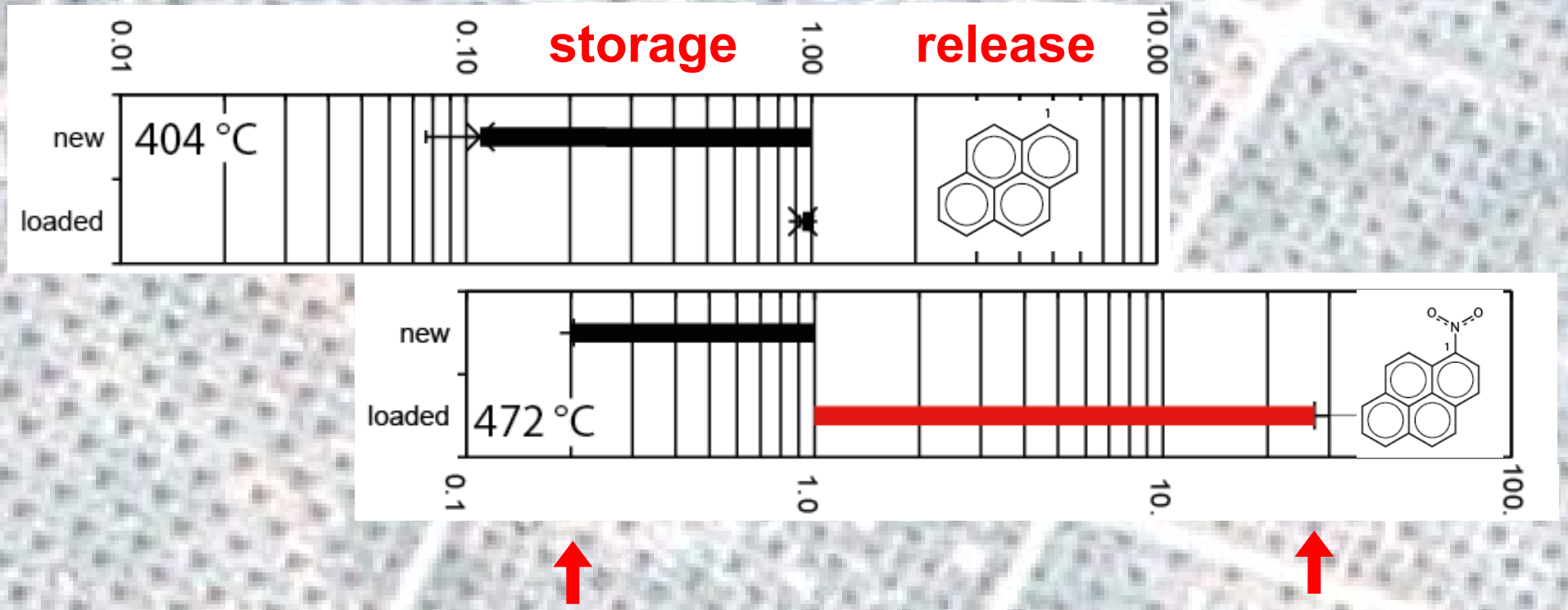
1.85 nm (1/10 of a primary soot particle)

Soot catalyzed nitration of PAHs



Nitro-PAH formation in a non-catalyzed DPF

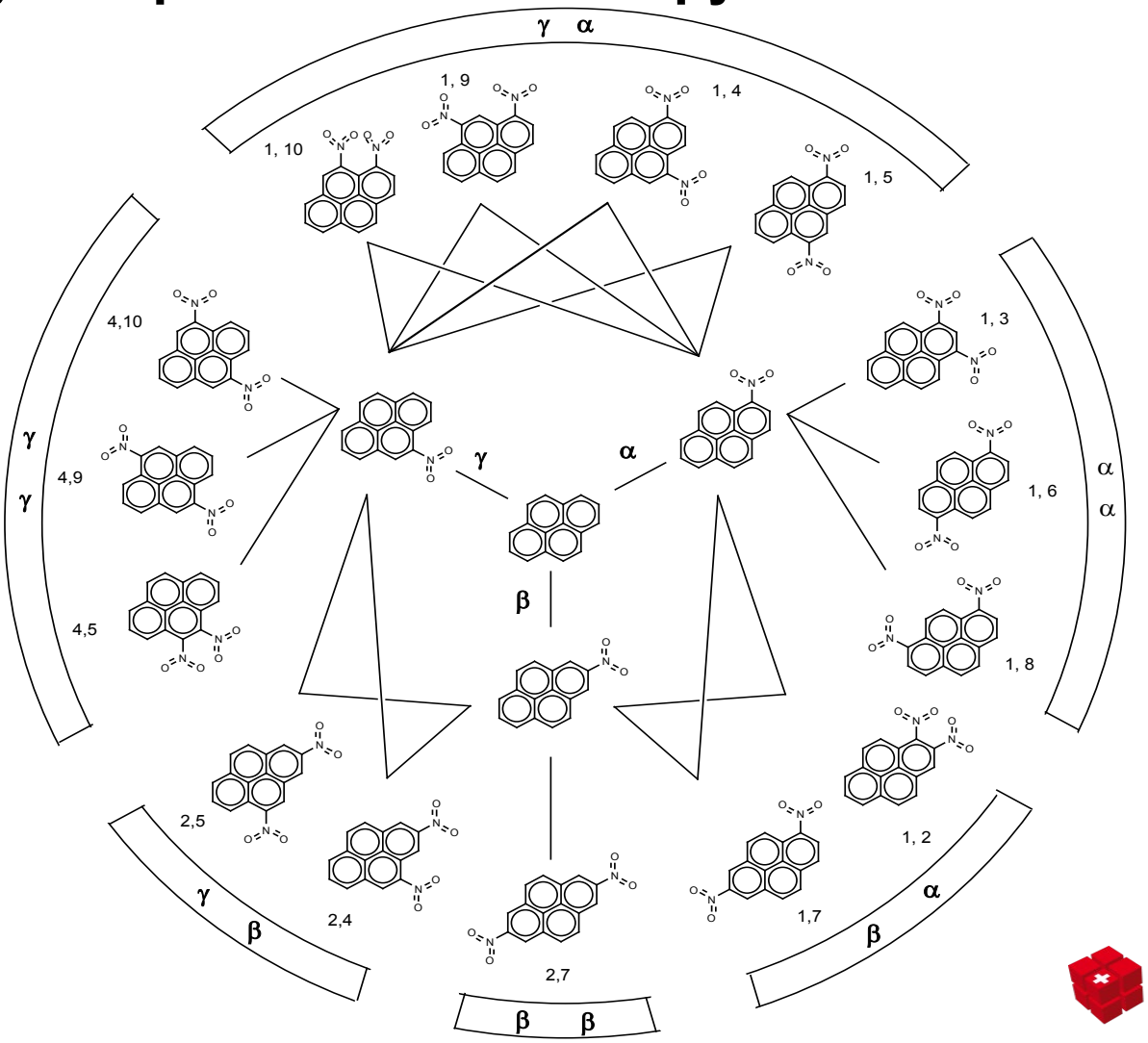
Non-catalyzed filter operated <200 °C accumulates soot and adsorbates



- 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)

The DPF - a chemical reactor

From one pyrene precursor to 3 nitropyrenes to 15 dinitropyrenes?



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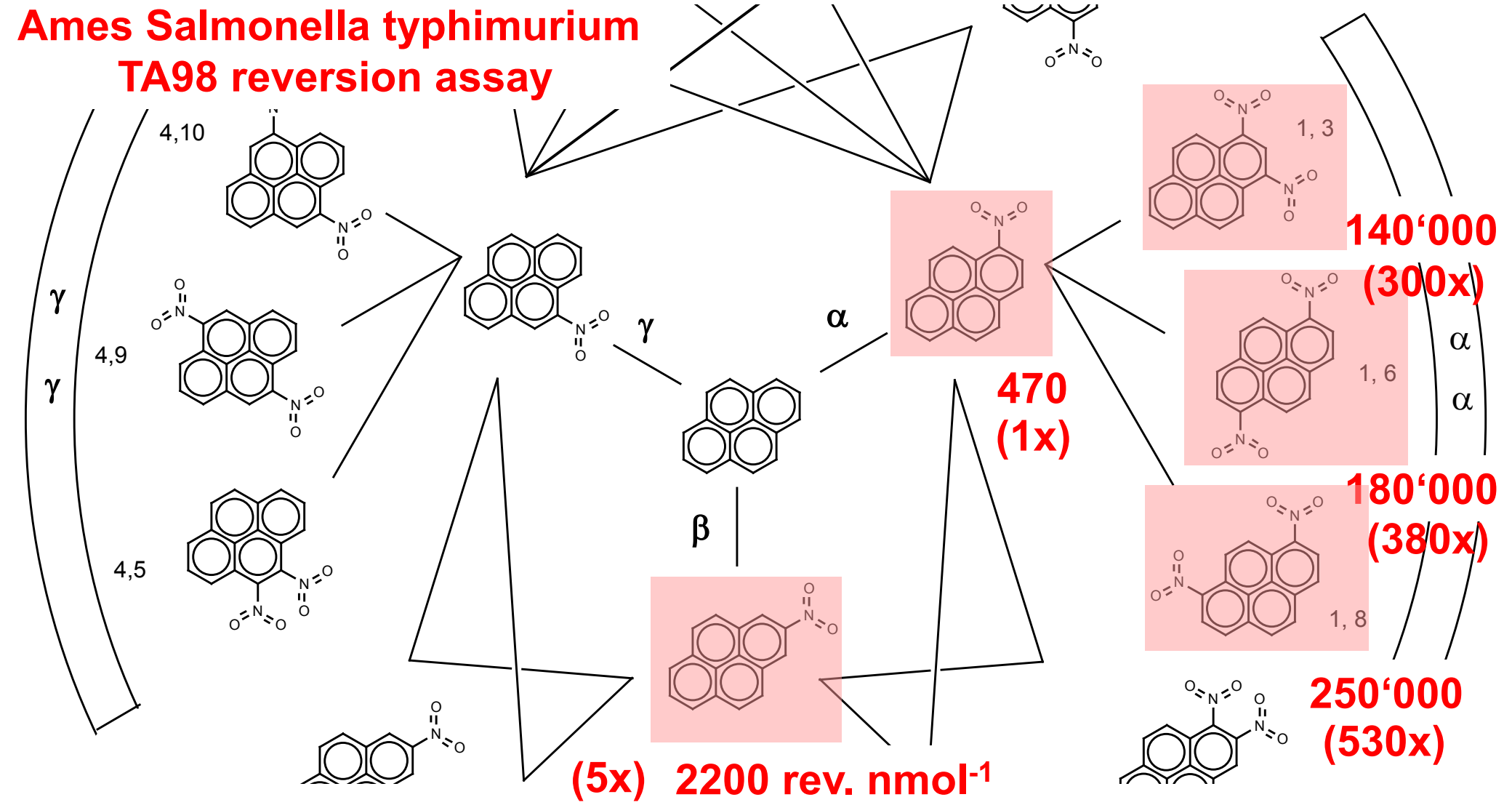
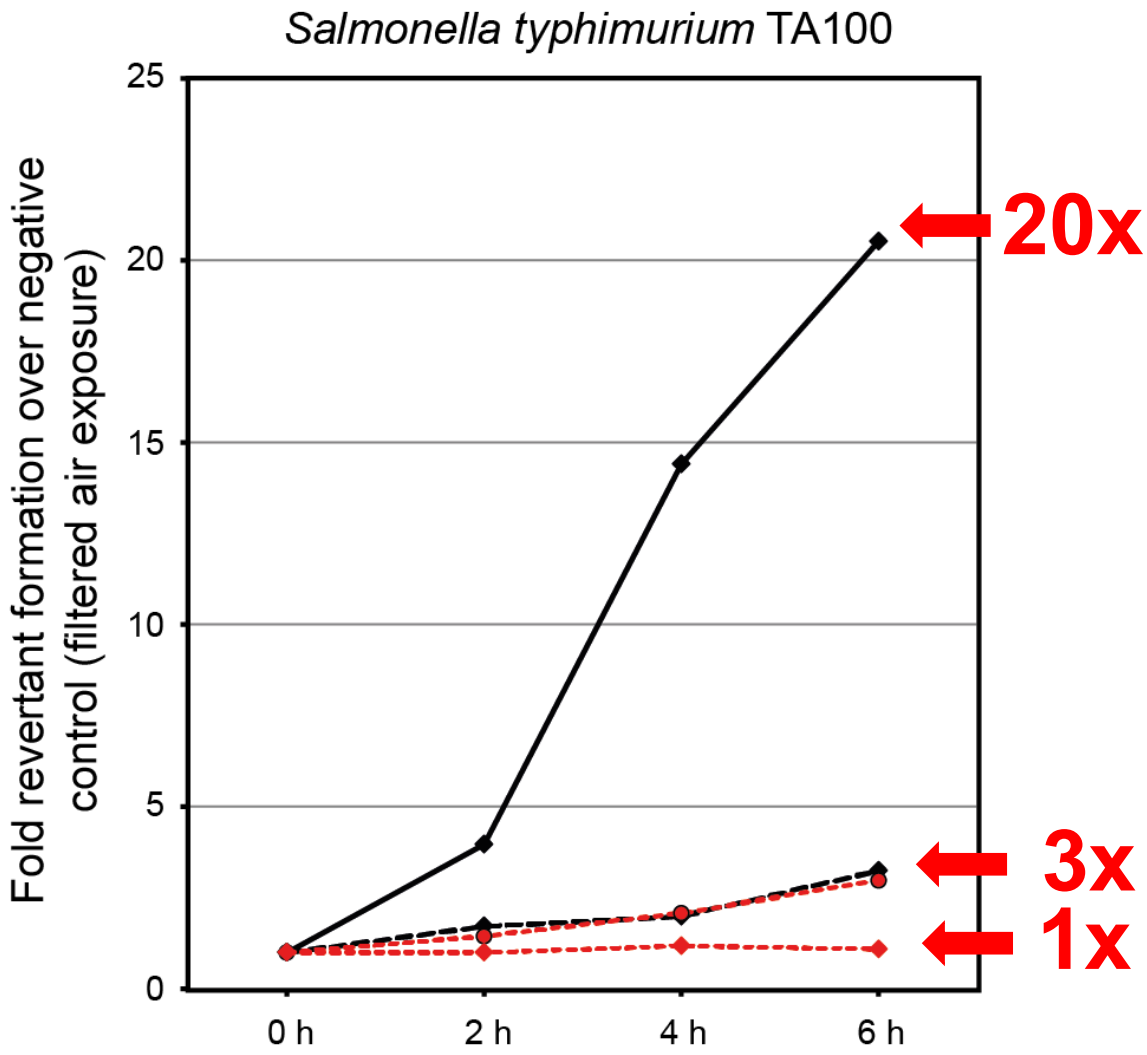
The DPF - a chemical reactor

The most potent direct-acting mutagens known are dinitropyrenes



Impact of DPFs on genotoxicity

Why can filtered, particle-free diesel exhaust still be genotoxic?



Steiner et al., Anal. Bioanal. Chem **2015**, 407, 5977-5986

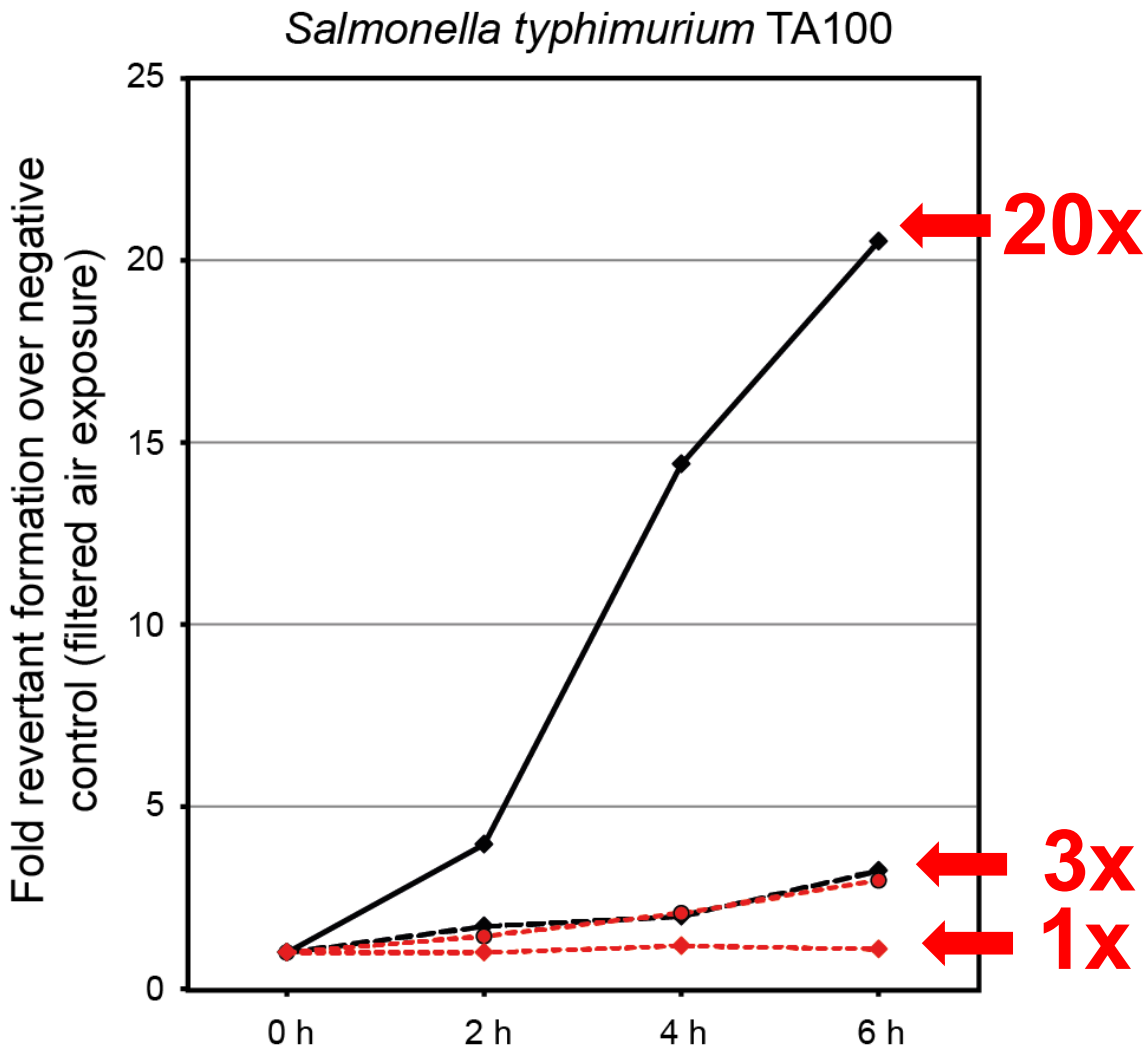
Filtered diesel exhaust of a non-catalyzed filter can even be more genotoxic!

Non-treated diesel exhaust is genotoxic after 6 h, also with iron catalyst (Satacen)

Catalytic DPF lowered genotoxicity

Impact of DPFs on genotoxicity

Why can filtered, particle-free diesel exhaust still be genotoxic?



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Filtered diesel exhaust of a non-catalyzed filter can even be more genotoxic!

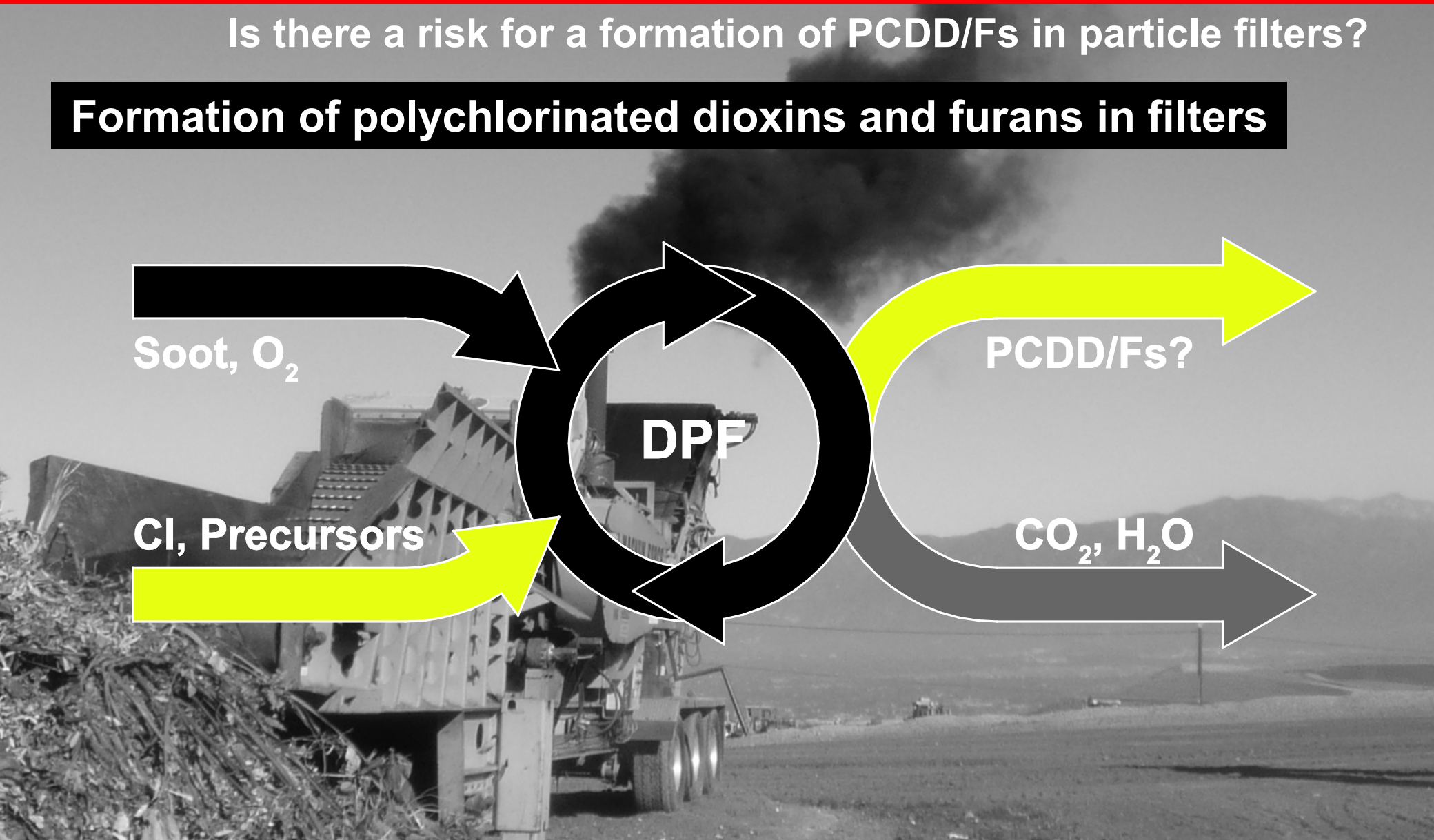
Filteration is not enough! We need catalysts converting genotoxic compounds not baking new ones!

Catalytic DPF lowered genotoxicity

Assessment of the PCDD/F formation potential

Is there a risk for a formation of PCDD/Fs in particle filters?

Formation of polychlorinated dioxins and furans in filters



Dioxin formation in Seveso

The dioxin problem

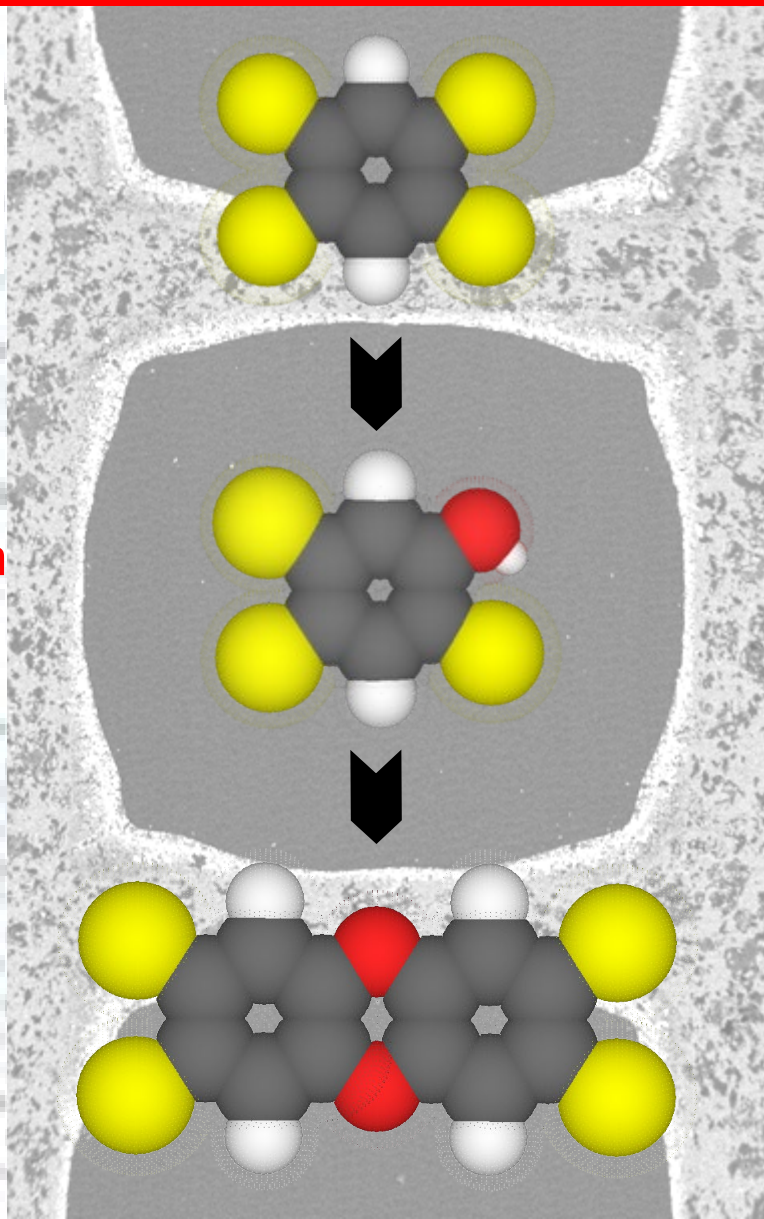
Stockholm Convention on persistent organic pollutants (POPs)

- Toxic
- Persistent, ubiquitous, bioaccumulating
- Side products of various combustion processes

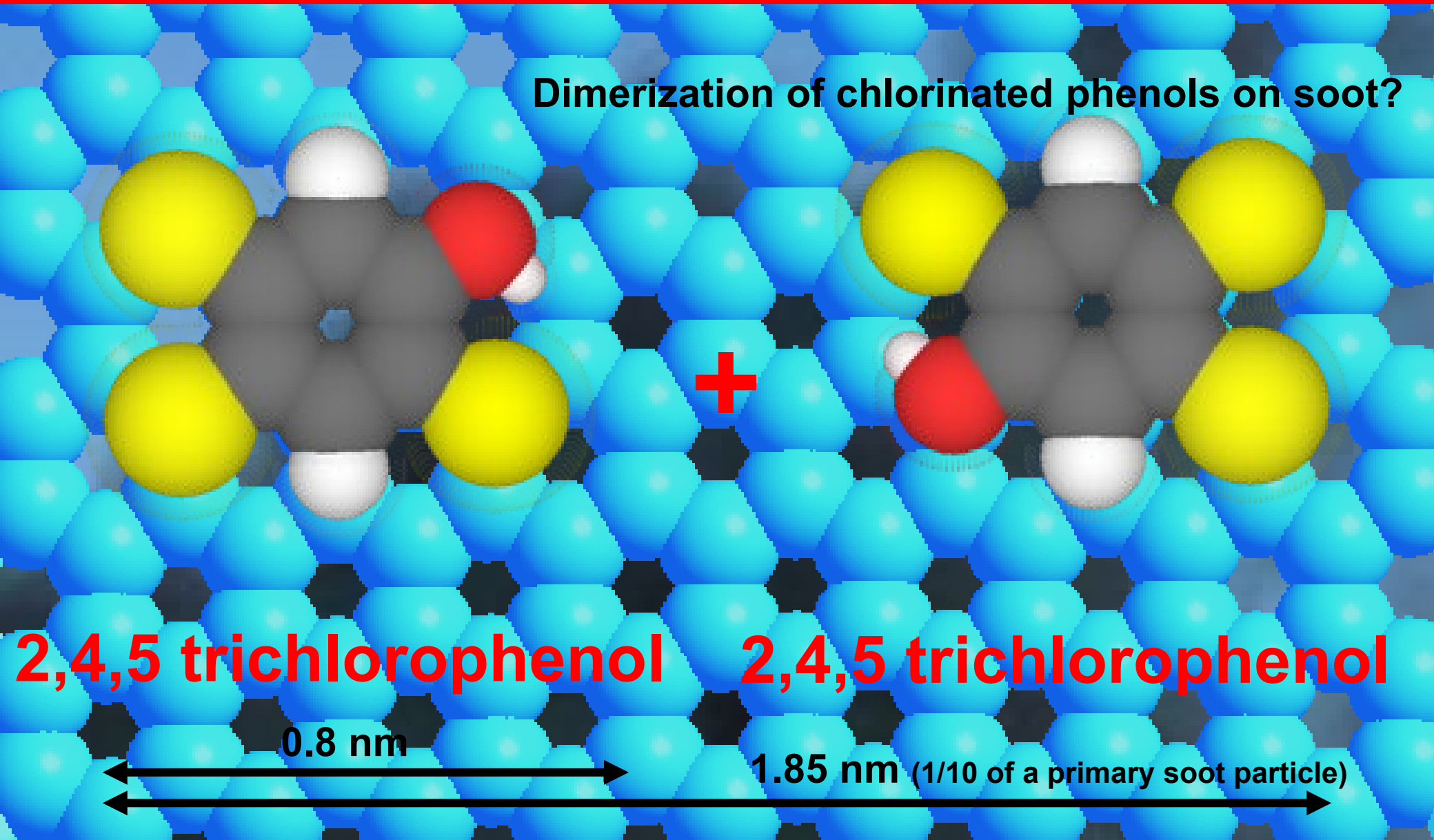
banned under the UN Stockholm Convention

Properties:

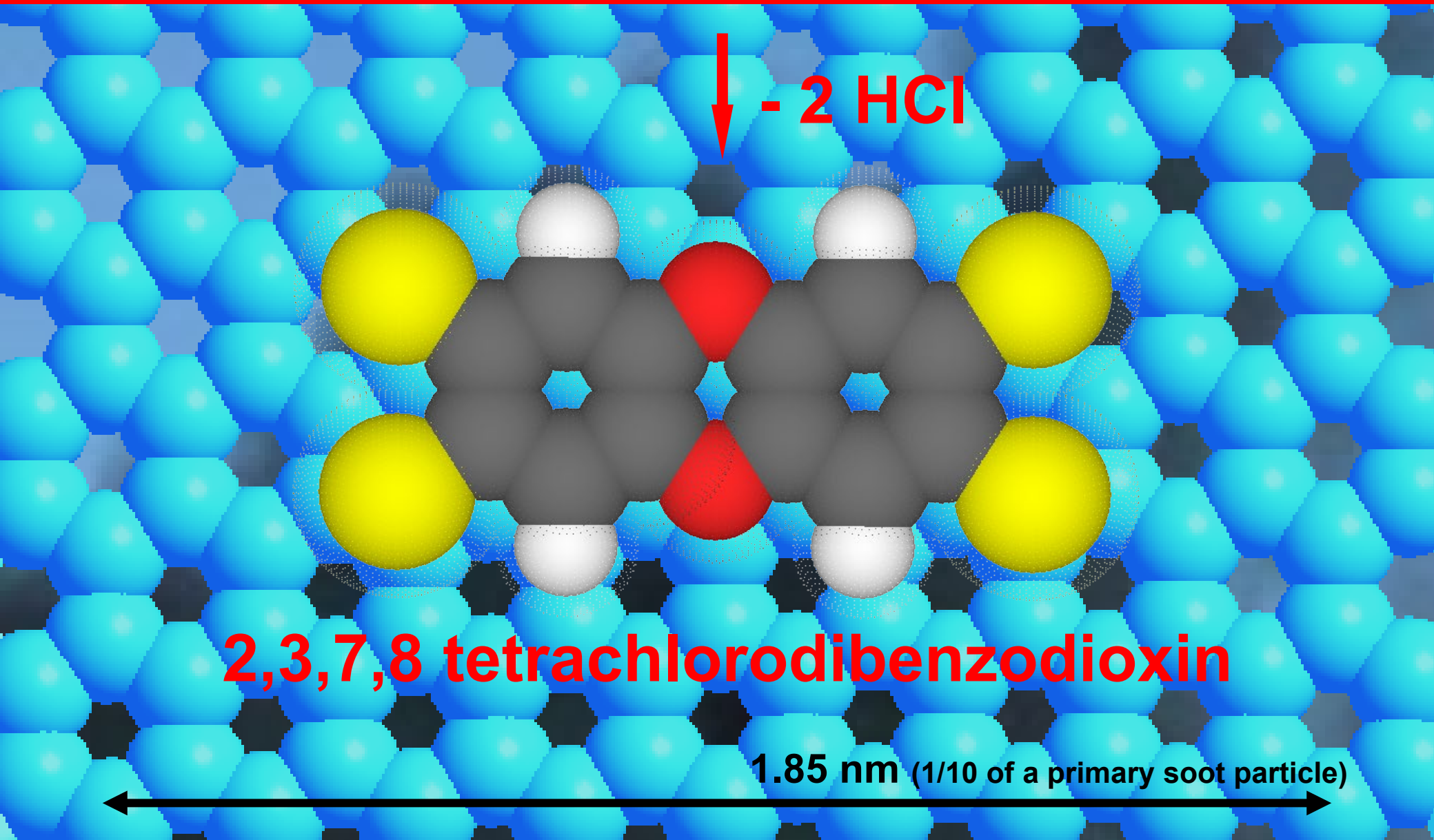
- Thermally stable up to 440°C
- Solid, semi-voaltile, bound to particles
- Should be removed in a DPF if not formed, *de novo*



Dioxin formation in particle filters

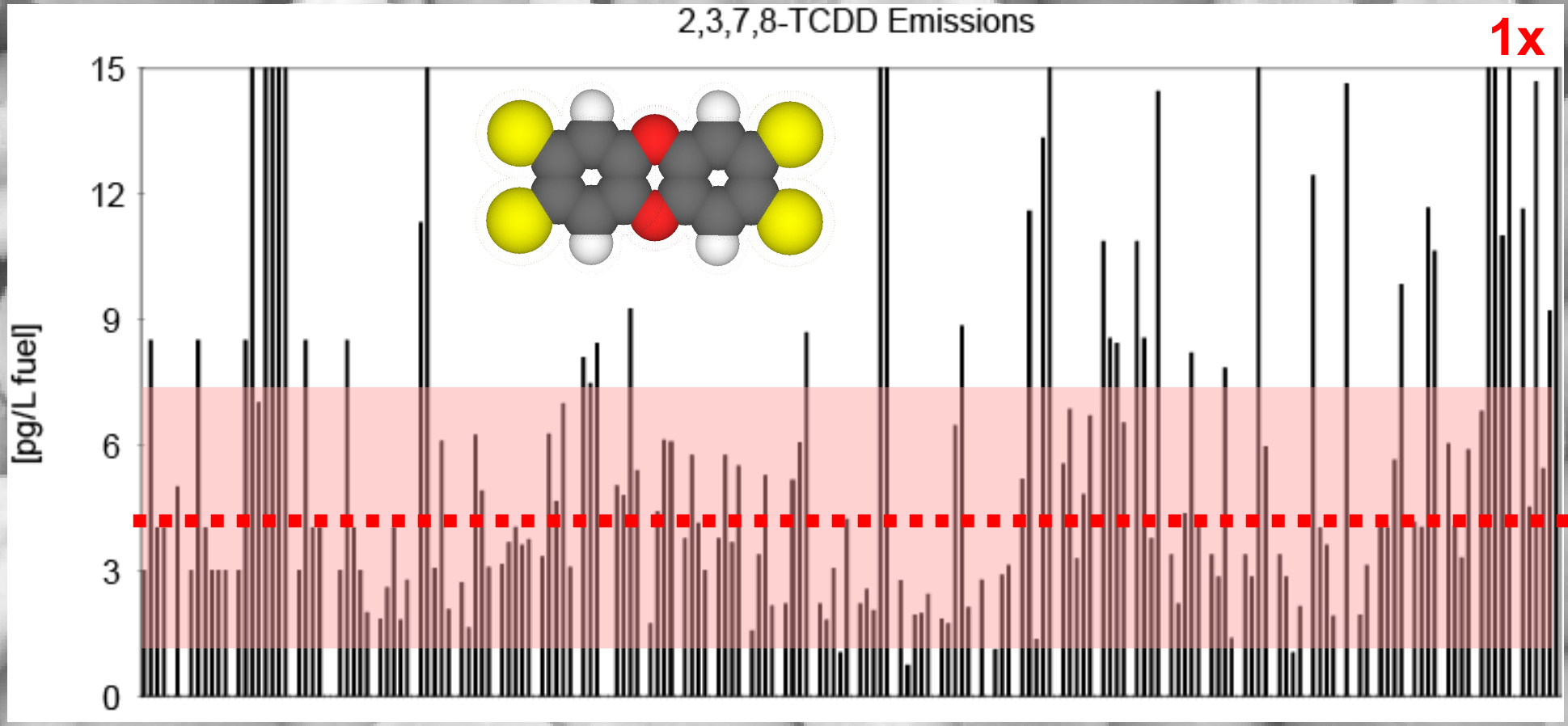


Dioxin formation in particle filters



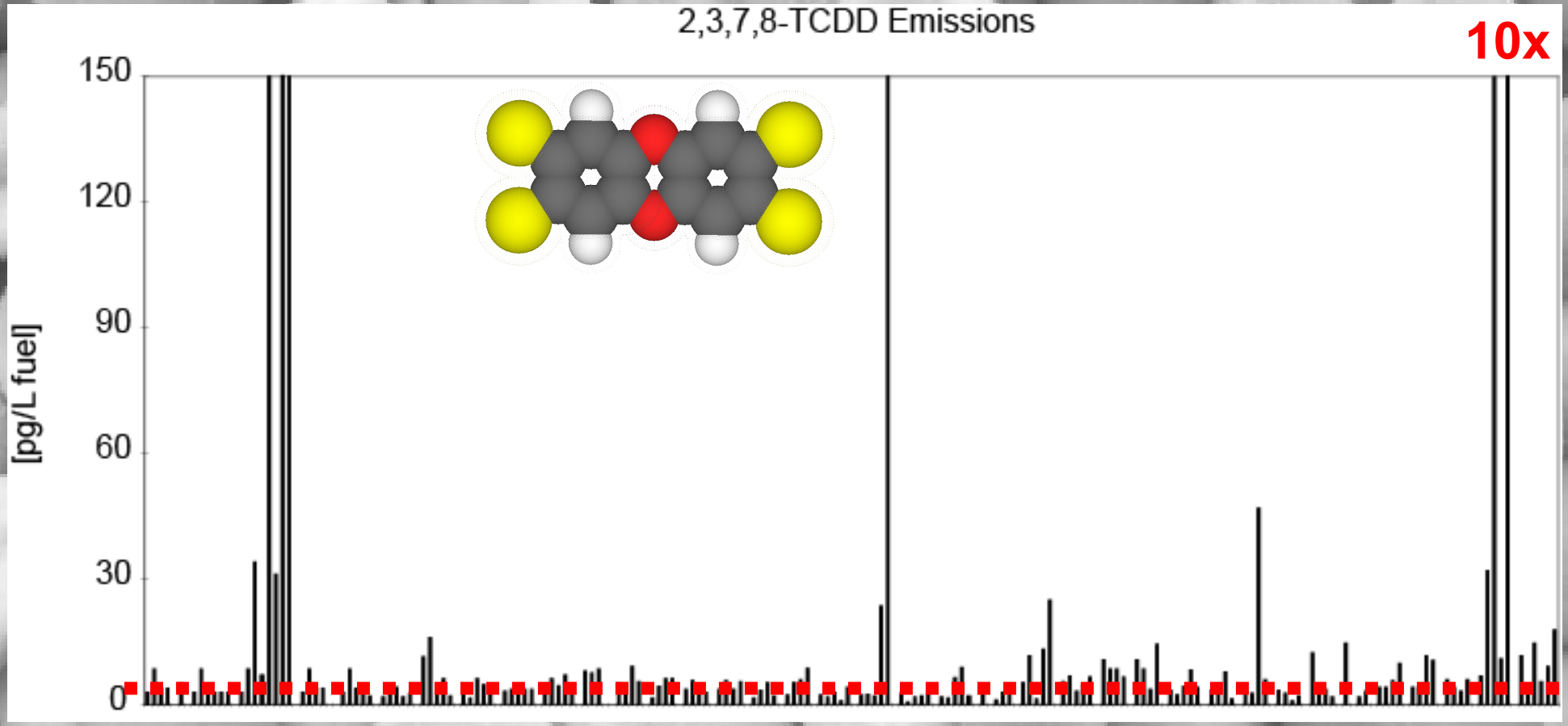
Assessment of the PCDD/F-formation potential of DPFs

We just have to pick the right ones



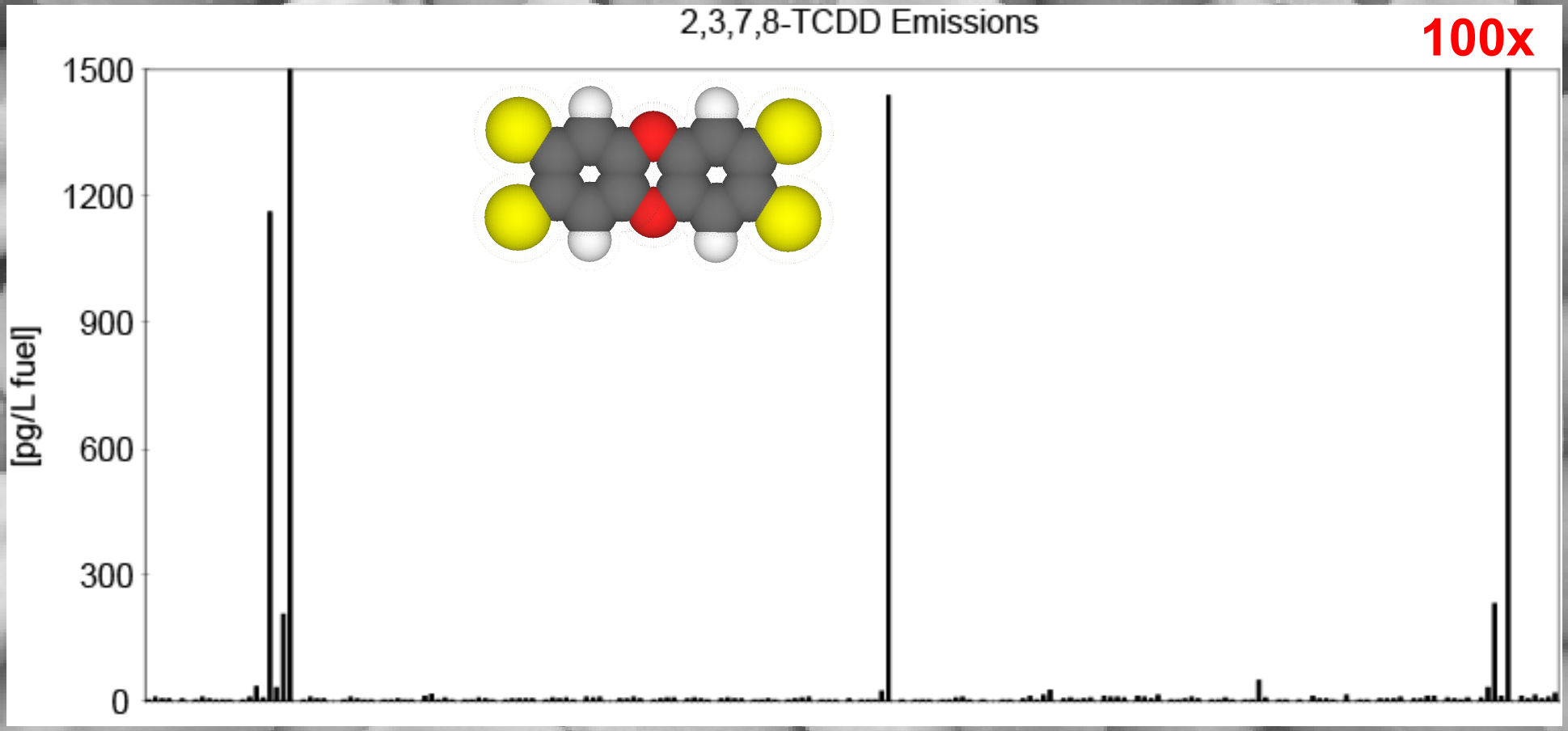
Assessment of the PCDD/F-formation potential of DPFs

The dioxin formation potential of the respective DPFs?



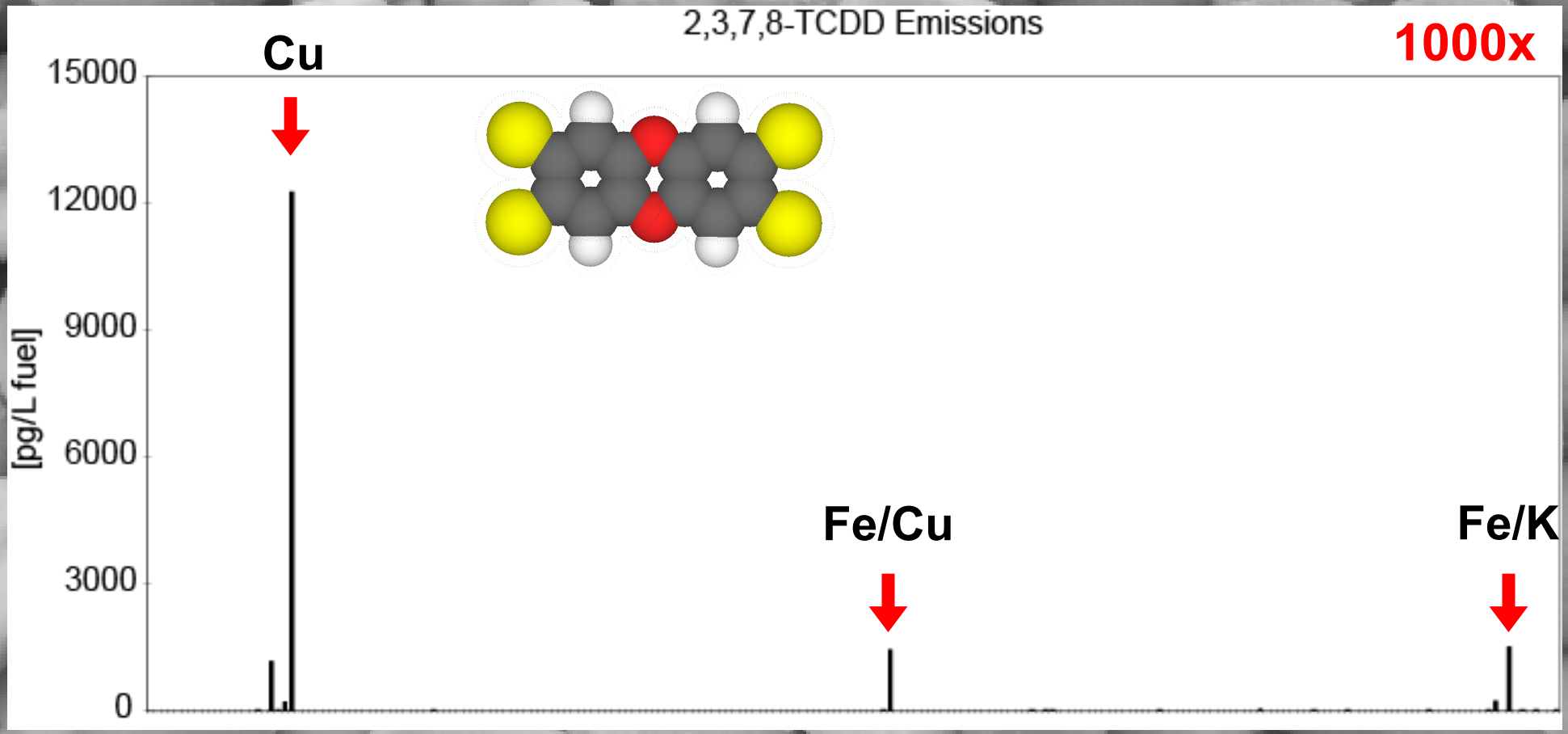
Assessment of the PCDD/F-formation potential of DPFs

Only 3 of the 37 tested DPFs until 2010 induced a PCDD/F formation?



Assessment of the PCDD/F-formation potential of DPFs

Exhausts of these 3 DPFs exceed the MWI emission limit of 100 pg/m³



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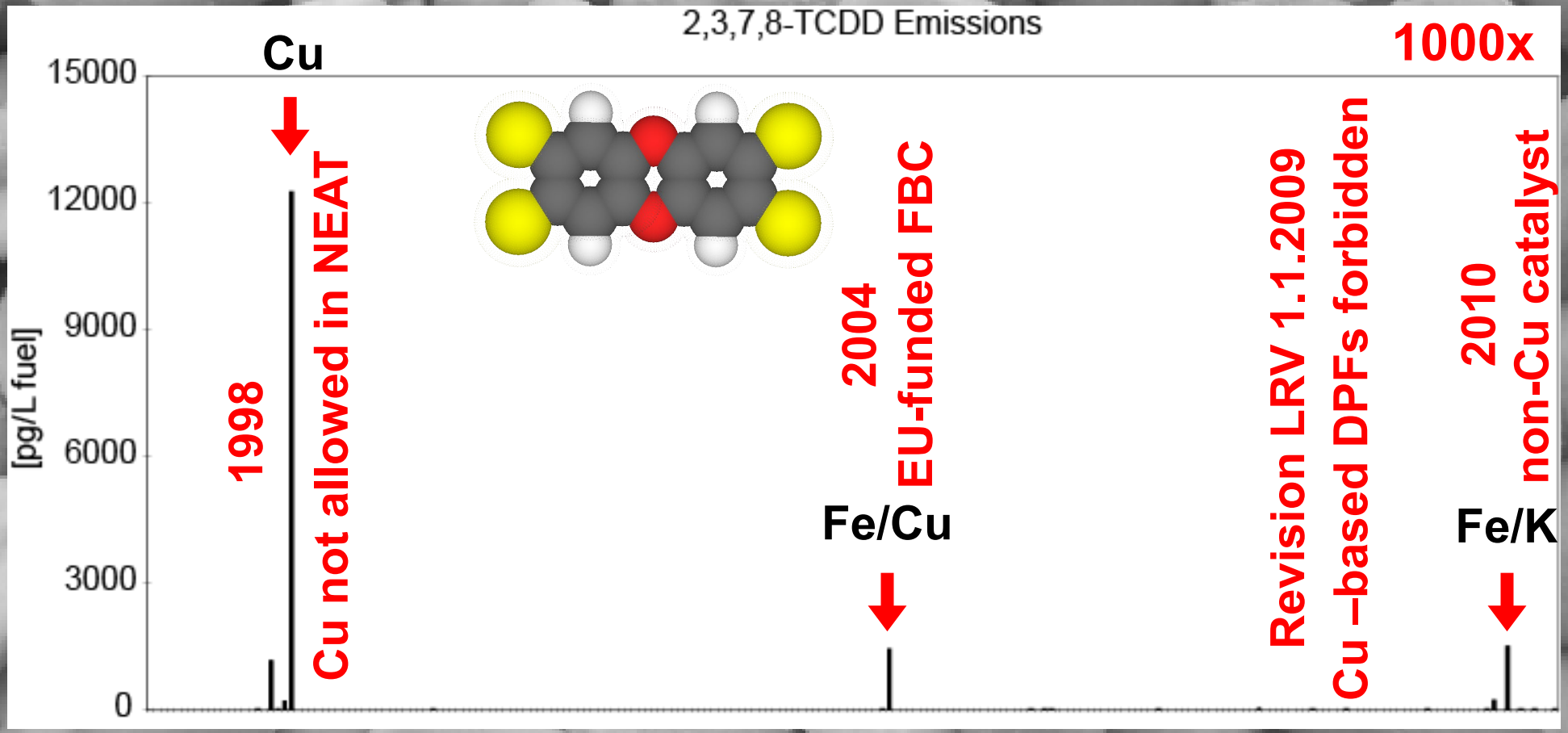


Heeb et al., ES&T **2007**, 41, 5789-5794

Heeb et al., ES&T **2015**, 49, 9273-9279

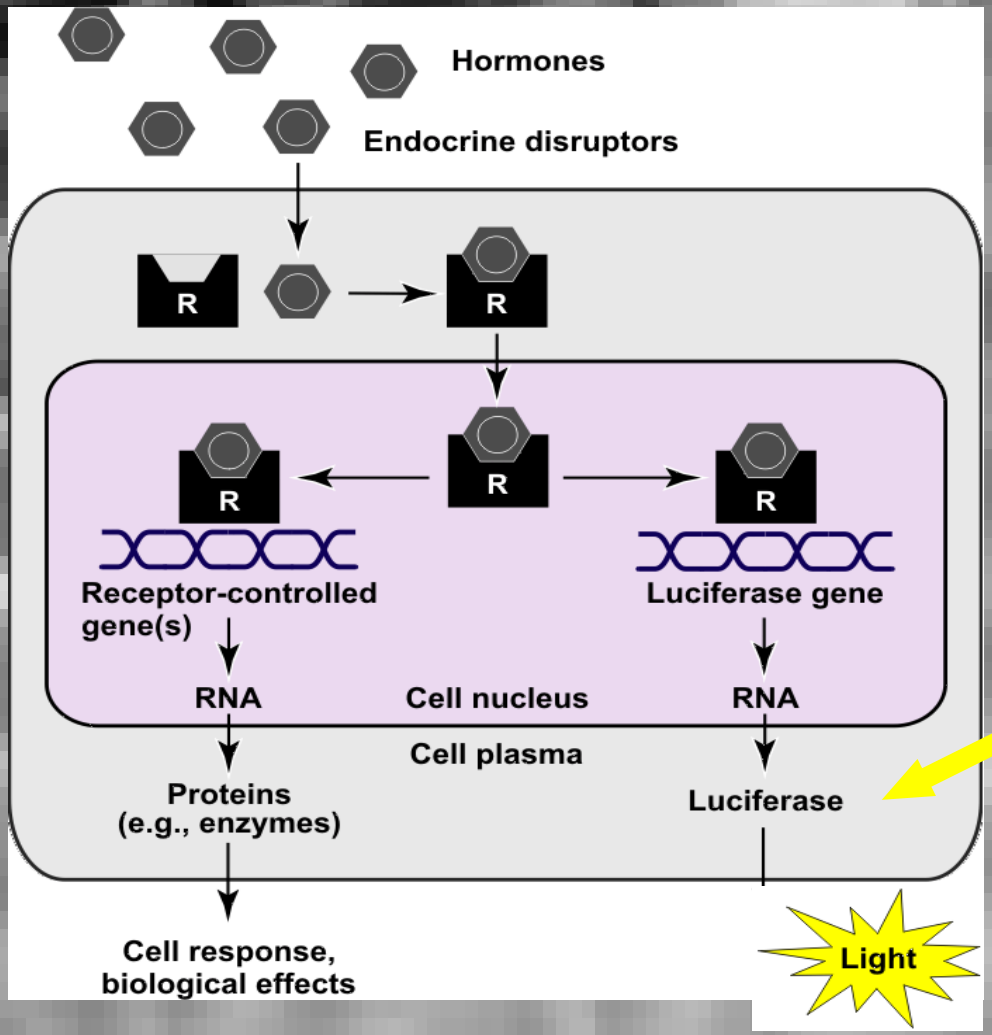
Cell assays – alternative ways for benefit/risk assessments

- **CALUX**: Chemically activated Luciferase Gene Expression
- CALUX Assays are **Reporter Gene Assays**
- **Cumulated activity of all compounds following the same mode of action**

➔ Detection of known and unknown compounds

CALUX cell assays

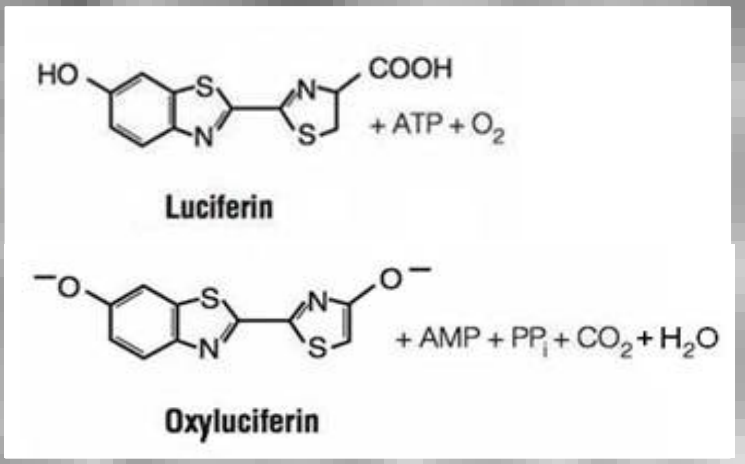
A sensor for aromatic compounds



Rat hepatoma cells (H4IIE)

R — Aryl hydrocarbon receptor (**AhR**)

„Dioxin-like“ compounds

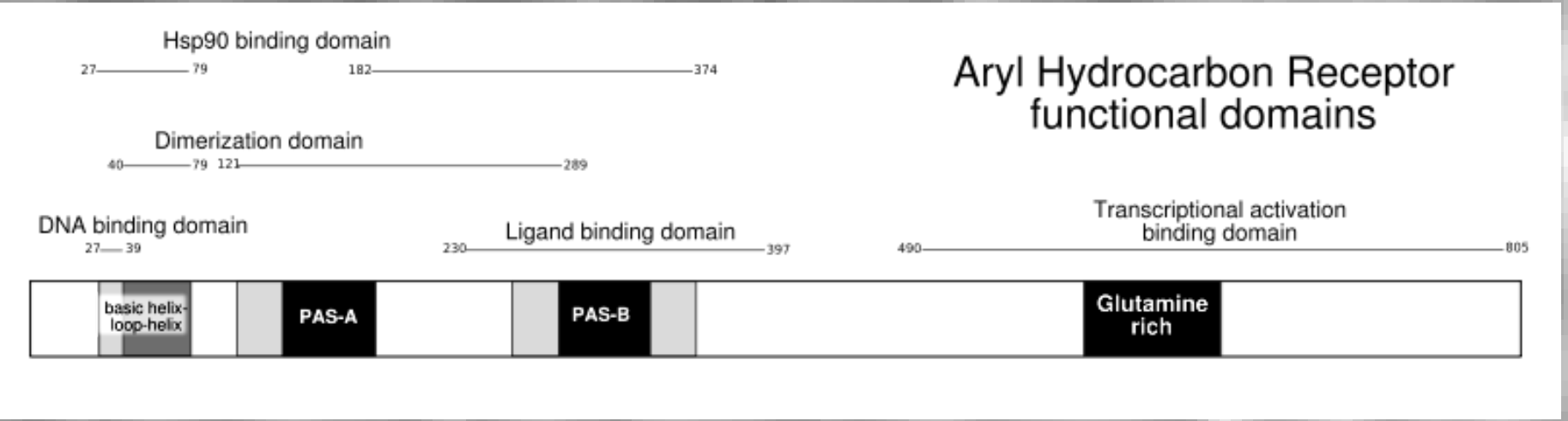


The aryl hydrocarbon-receptor

A sensor for aromatic hydrocarbons

DNA-binding transcription factor:

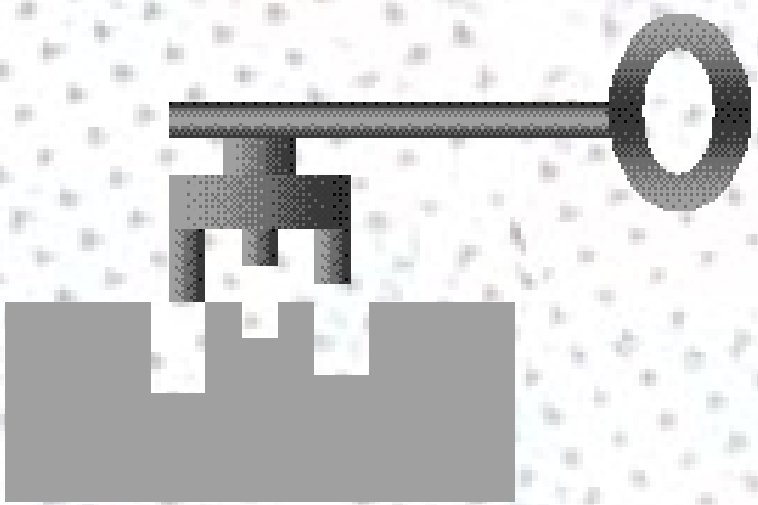
- Cyctosolic transcription factor (DNA-binding protein, 805 AS, ~90’000 amu, basic helix-turn-helix motive)
- Ligand-binding domain (PAS-B, AS230-397)
- Ligand-AHR complex migrates to nucleus and binds DNA



Specific recognition at molecular level

We know a few keys to the aryl hydrocarbon receptor!

The key and lock principle:



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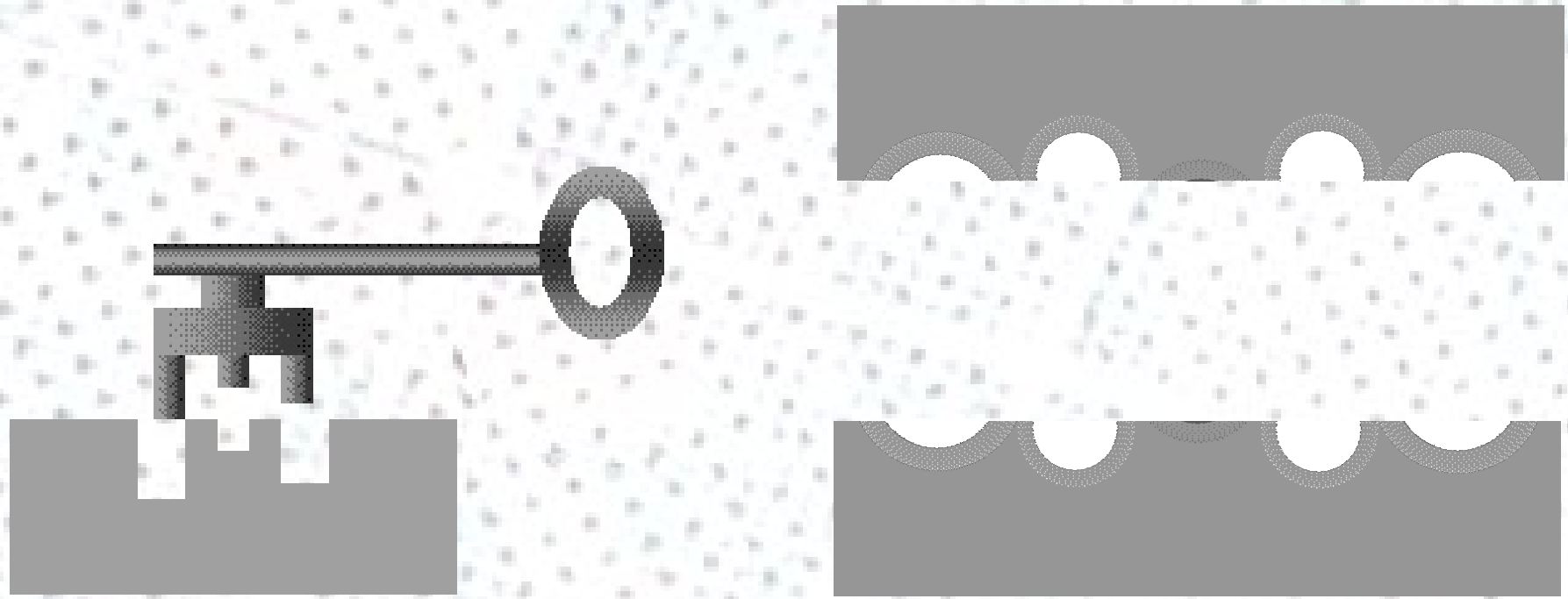
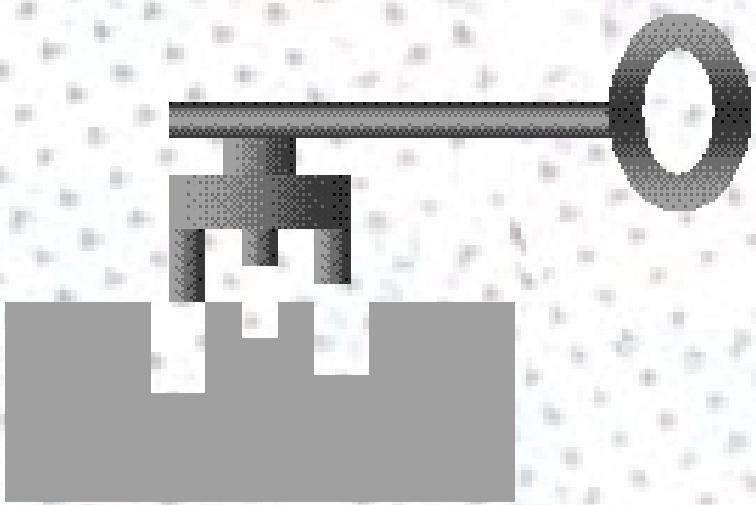
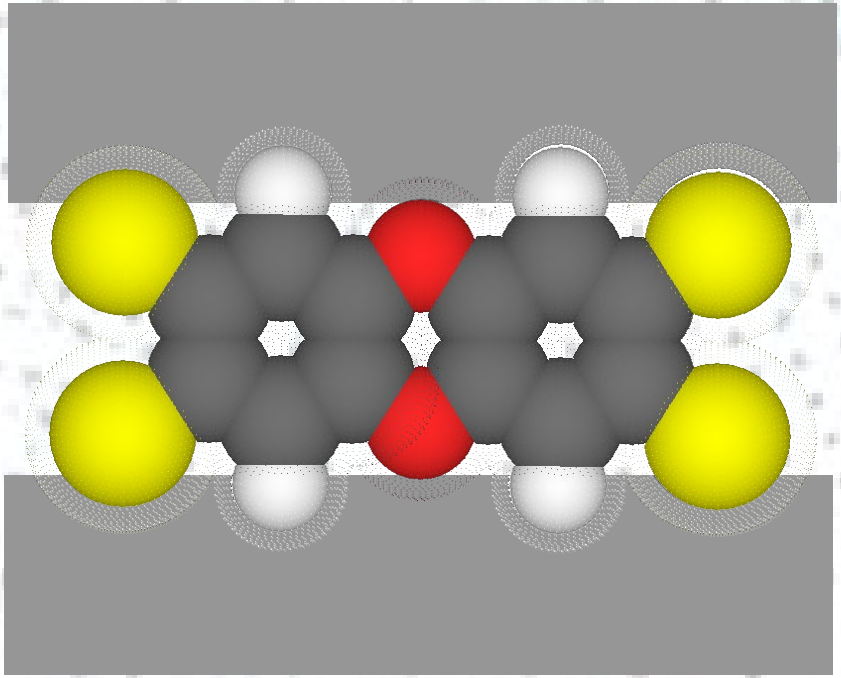


Specific recognition at molecular level

2,3,7,8-TCDD, the Seveso dioxin, is the ligand with the highest AhR affinity

The key and lock principle:

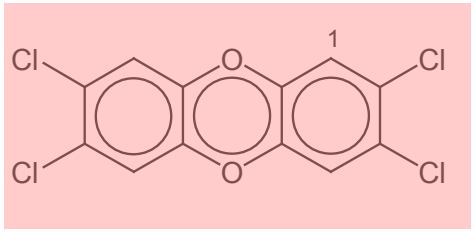




Specific recognition at molecular level

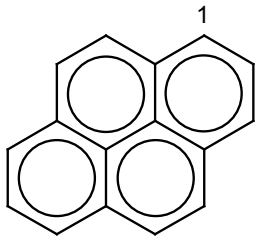
We know a few keys to the aryl hydrocarbon receptor. They all are PAH like!

Relative affinities of some aryl hydrocarbons:



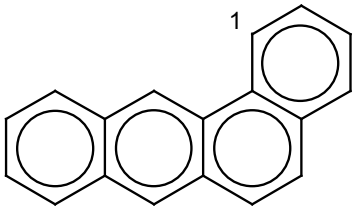
1.00

1 / 1



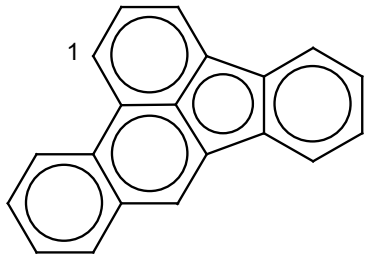
0.000014

1 / 71’400



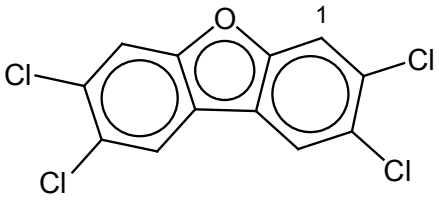
0.00017

1 / 5’880



0.0042

1 / 240



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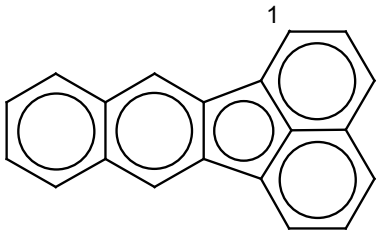
1 / 2



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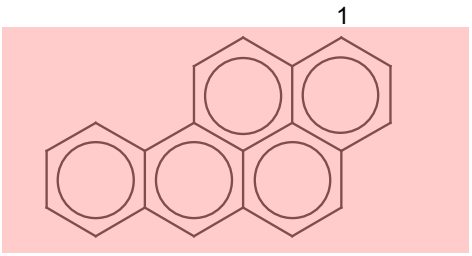
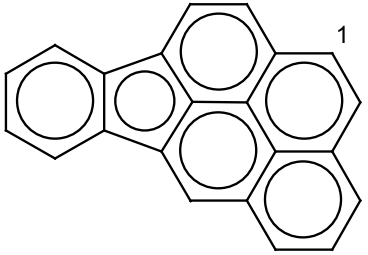
1 / 240



0.00058

1 / 1’720



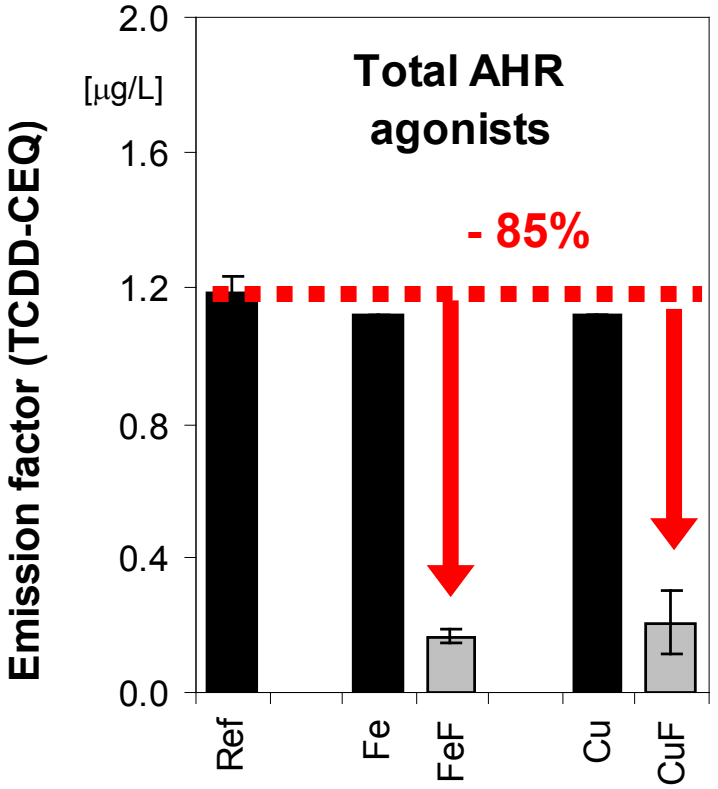
0.0041

1 / 240

Specific recognition at molecular level

Cell assays can support a benefit/risk analysis of PFs

AHR-Reporter gene assay:



Heeb et al. ES&T, **2008**, 42, 3773-3779

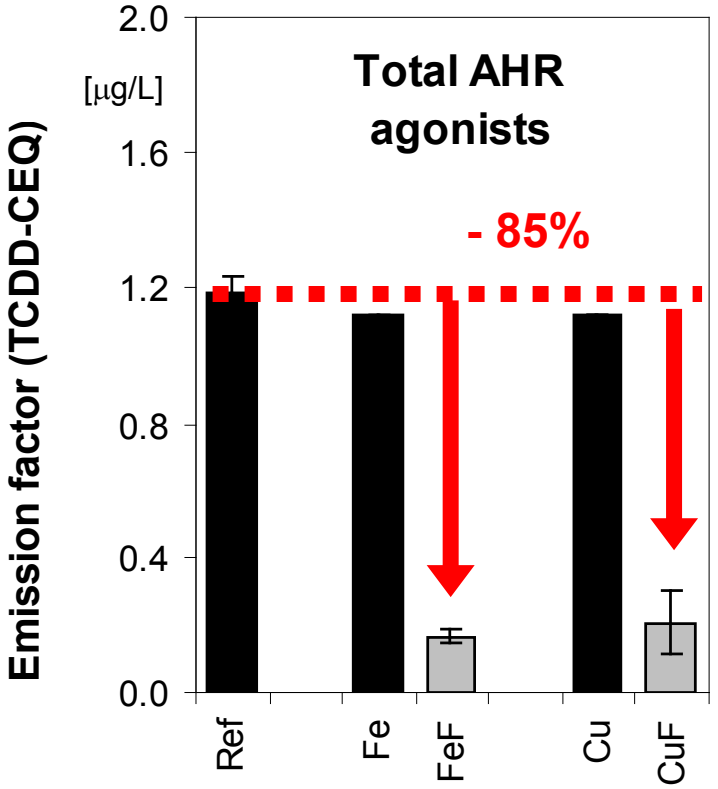
Wenger et al. ES&T, **2008**, 42, 2992-2993

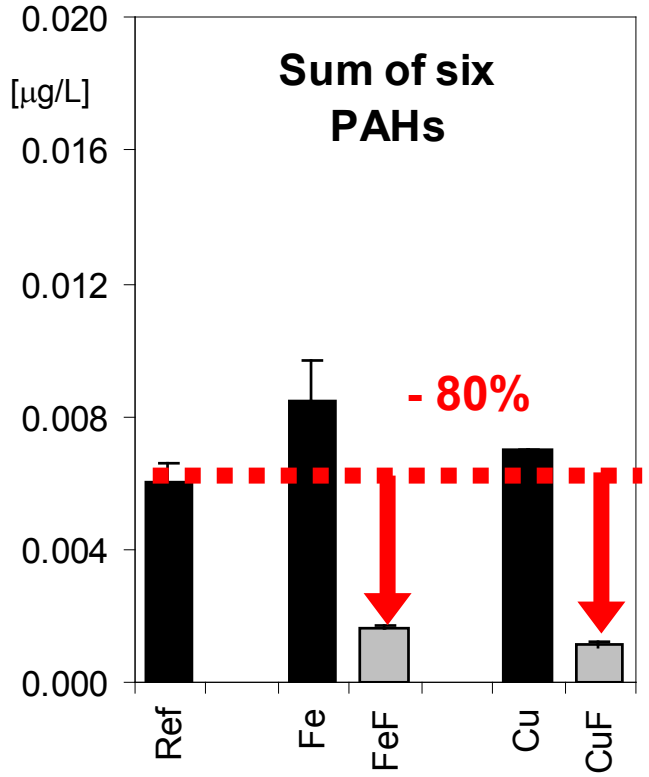
Specific recognition at molecular level

Cell assays can support a benefit/risk analysis of PFs

AHR-Reporter gene assay:

1/100

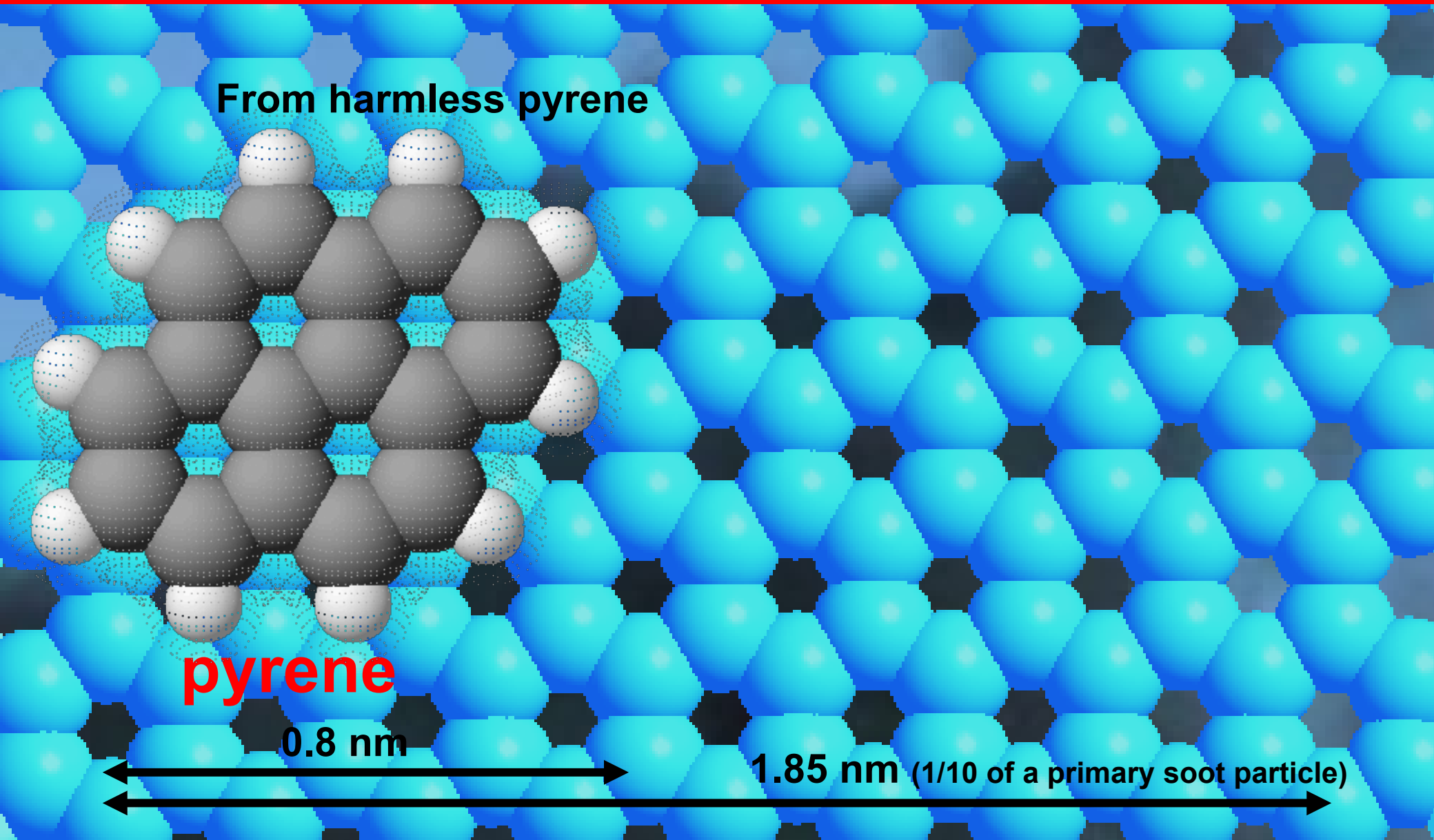




Heeb et al. ES&T, **2008**, 42, 3773-3779

Wenger et al. ES&T, **2008**, 42, 2992-2993

Oxidation of PAHs on soot



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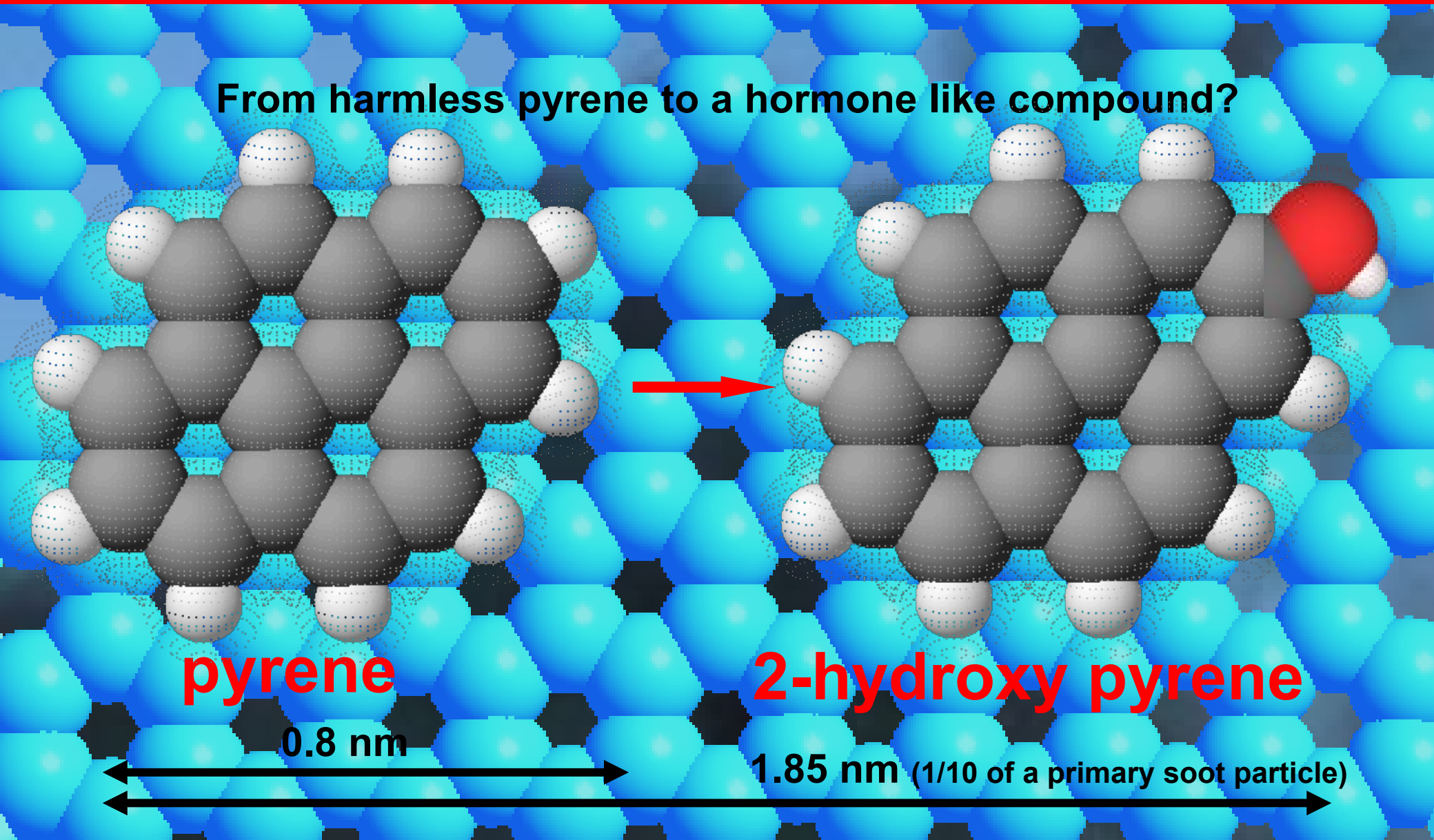
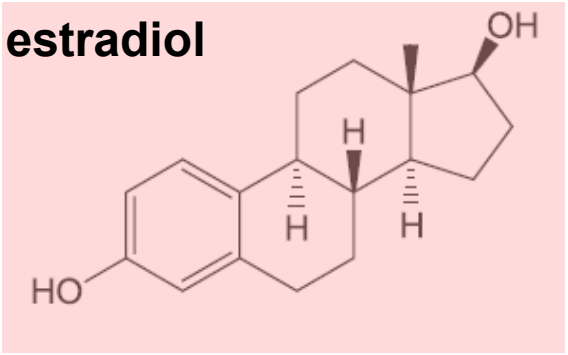


Specific recognition at molecular level

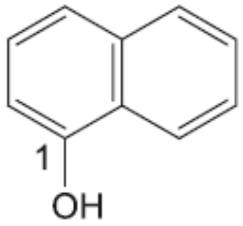
Cell assays can support a benefit/risk analysis of PFs

ER-CALUX reporter gene assay:

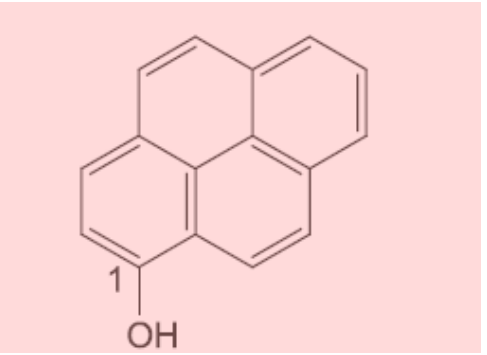
17-beta estradiol



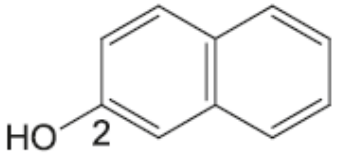
1
1.0



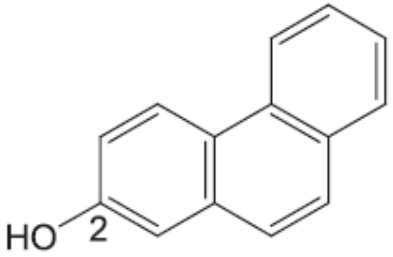
2
6.5×10^{-8}



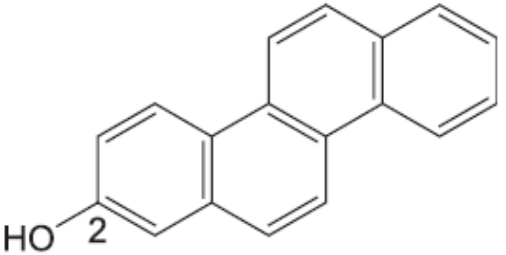
6
3.7×10^{-7}



3
1.5×10^{-7}



4
1.1×10^{-6}



5
1.0×10^{-5}

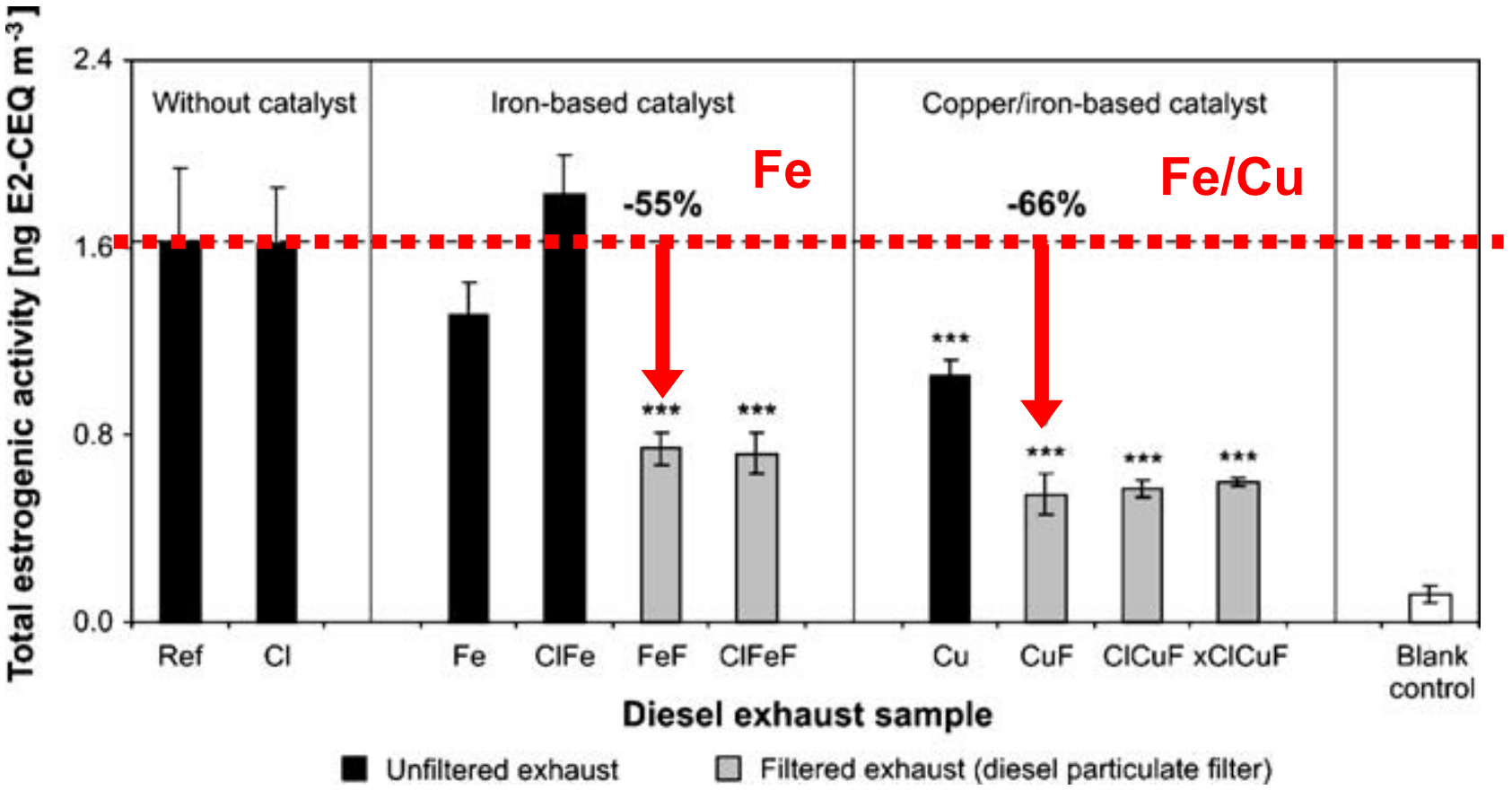
Wenger et al. J.Appl.Toxicol, **2009**, 29, 223-232

Wenger et al. ABC, **2008**, 390, 2021-2029

Specific recognition at molecular level

Hormone-like compounds in non-filtered and filtered diesel exhausts!

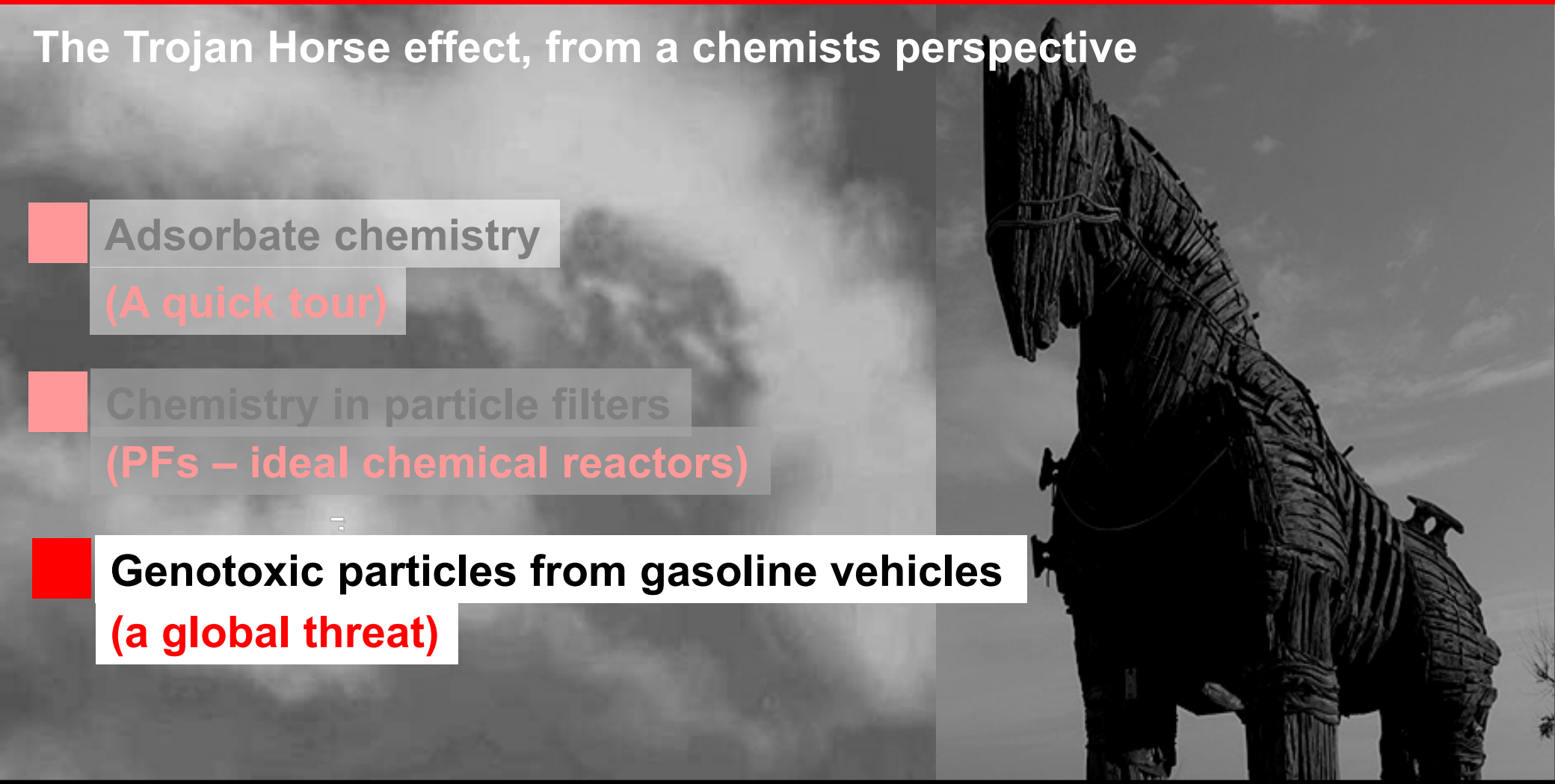
ER-CALUX reporter gene assay:



Heeb et al. ES&T, **2008**, 42, 3773-3779

Wenger et al. ABC, **2008**, 390, 2021-2029

The chemistry of nanoparticle adsorbates from diesel and gasoline combustion engines



The Trojan Horse effect, from a chemists perspective

- Adsorbate chemistry
  (A quick tour)
- Chemistry in particle filters
  (PFs – ideal chemical reactors)
- **Genotoxic particles from gasoline vehicles**
  (a global threat)

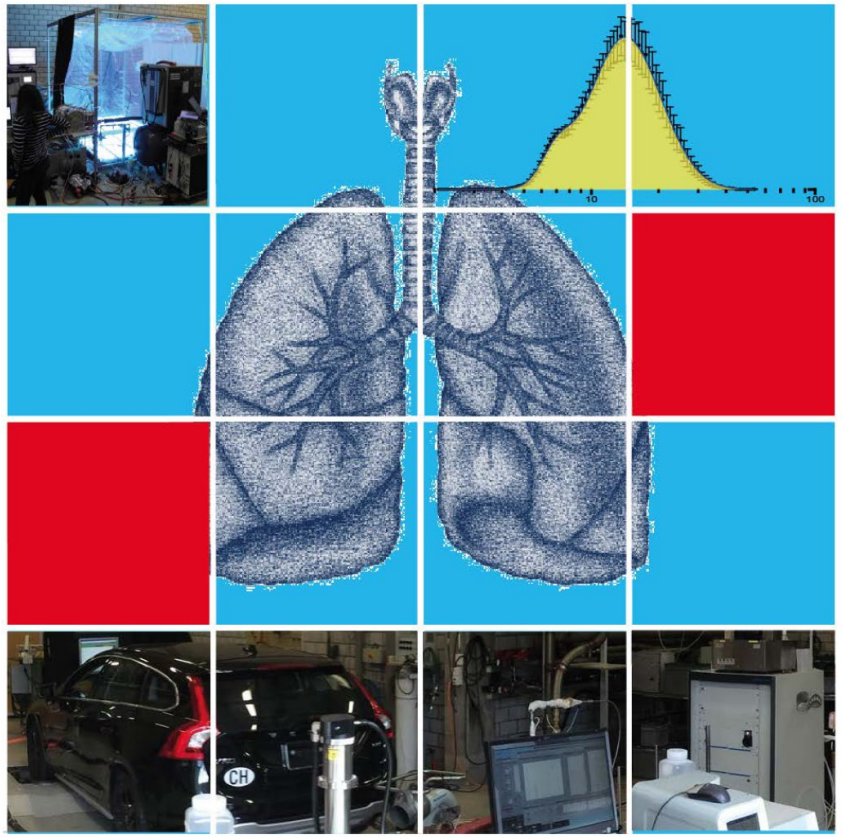
23id ETH Conference on Combustion Generated Nanoparticles

Zürich, June 17th – 20th, 2019

Properties of non-filtered exhaust of gasoline-direct injection vehicles (GDI)

What do we know on the properties and toxicity of GDI exhausts?

The 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/

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

GDI fleet

In 2018, about 927'000 GDI vehicles without filters on Swiss roads (>20%)!

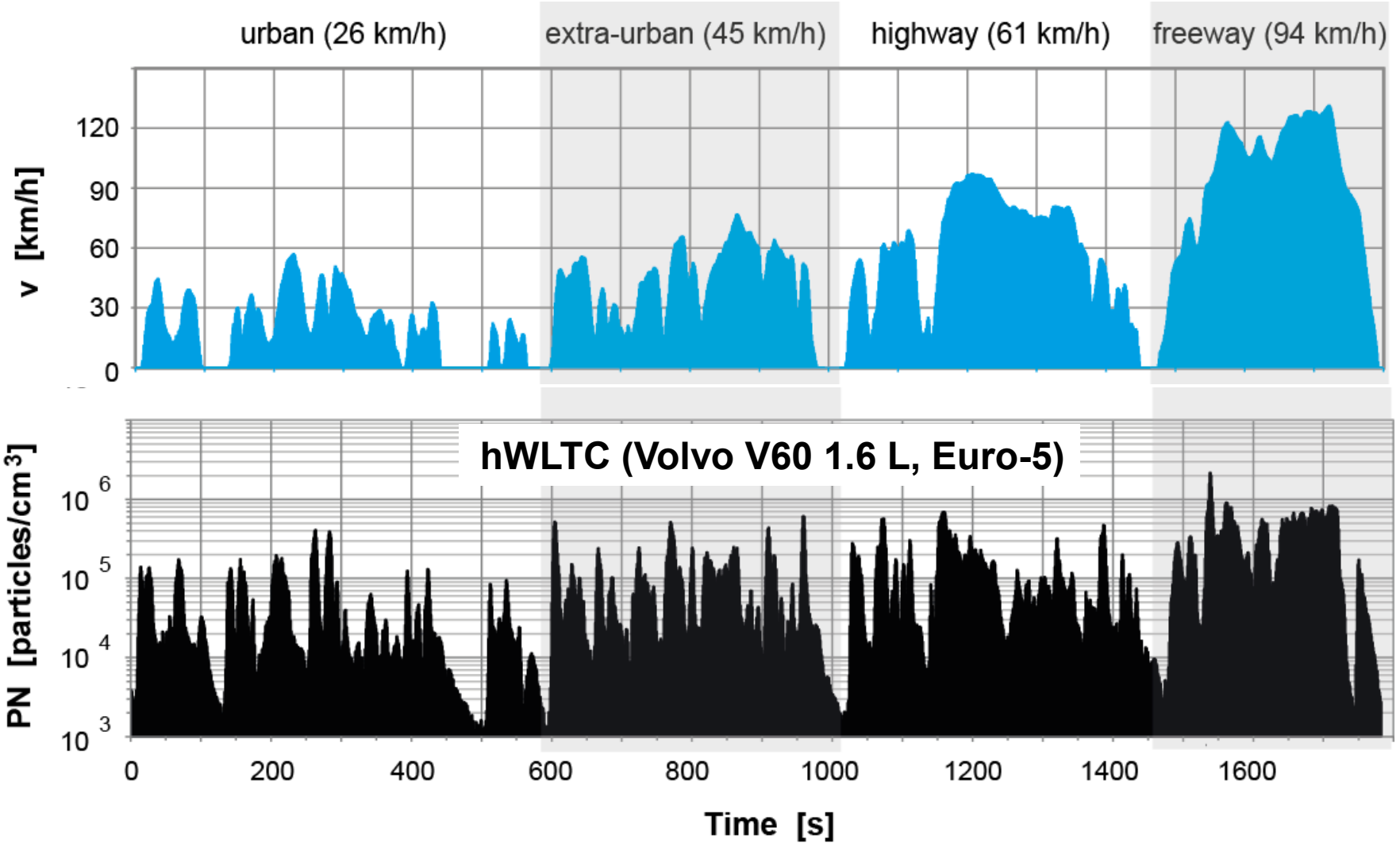
The GASOMEP fleet (n=7)

GDI-1:	Mitsubishi Carisma (1.8 L)	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)	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 generation vehicle technology

Nanoparticle emissions of GDI vehicles

Substantial release of nanoparticles, where ever you drive!



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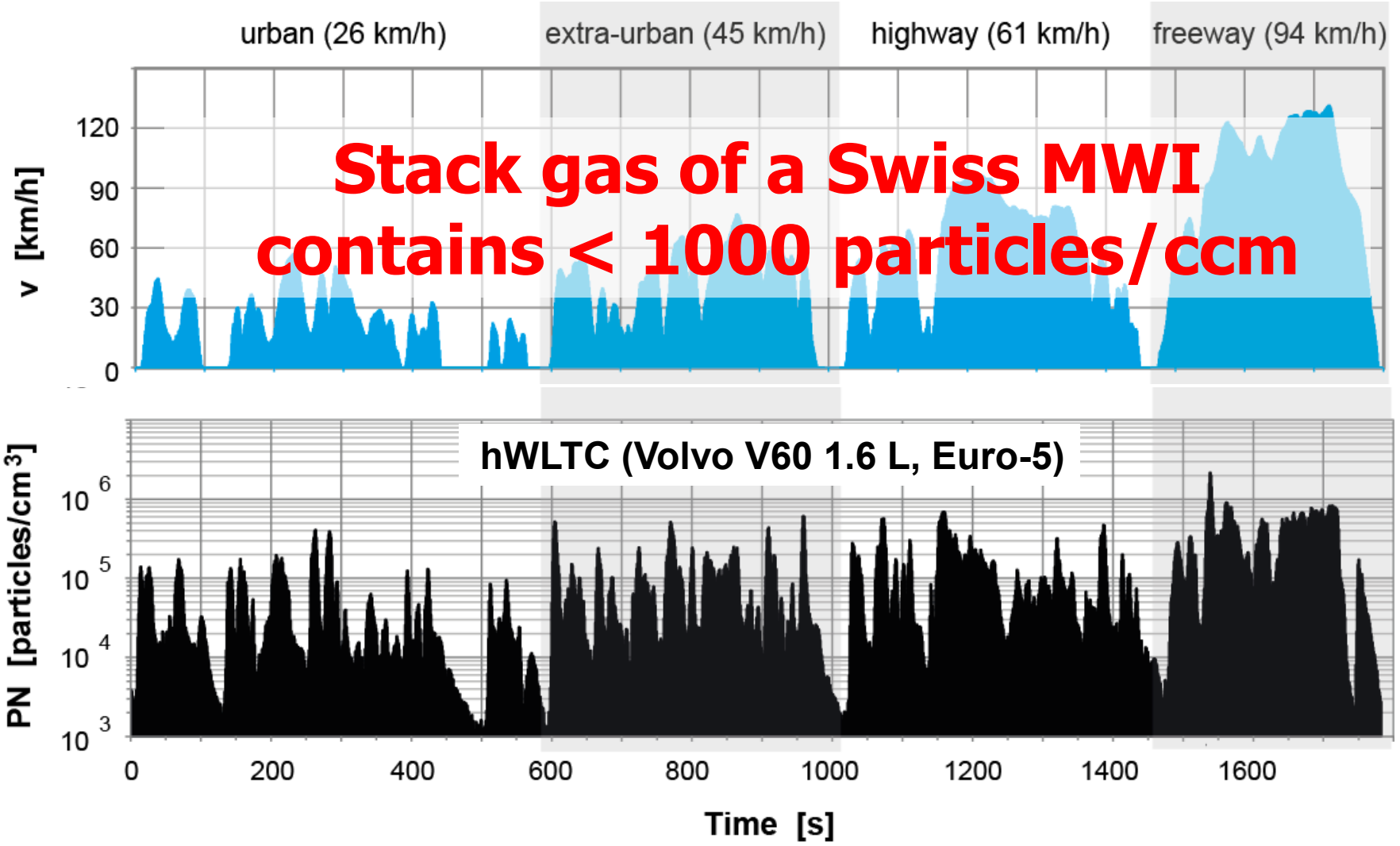
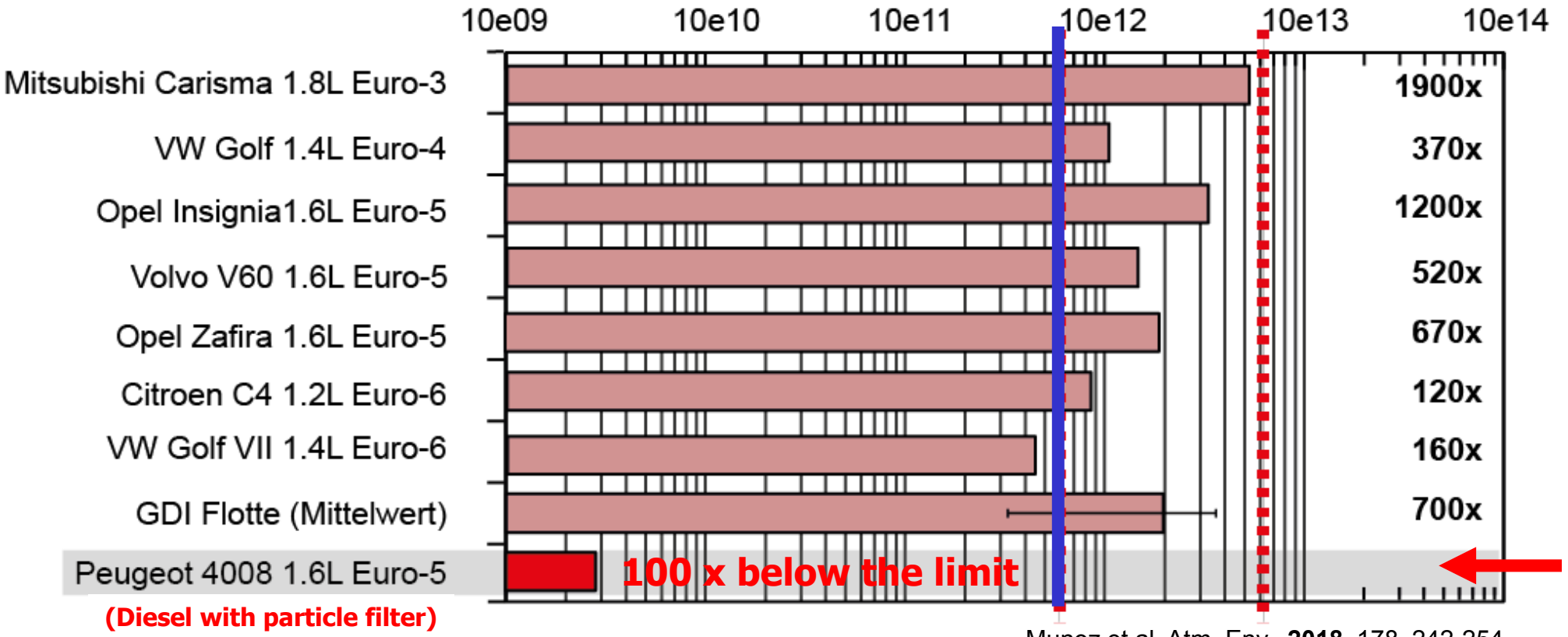


Nanoparticle emissions of GDI vehicles

GDI vehicles release 120 -1900x more particles 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

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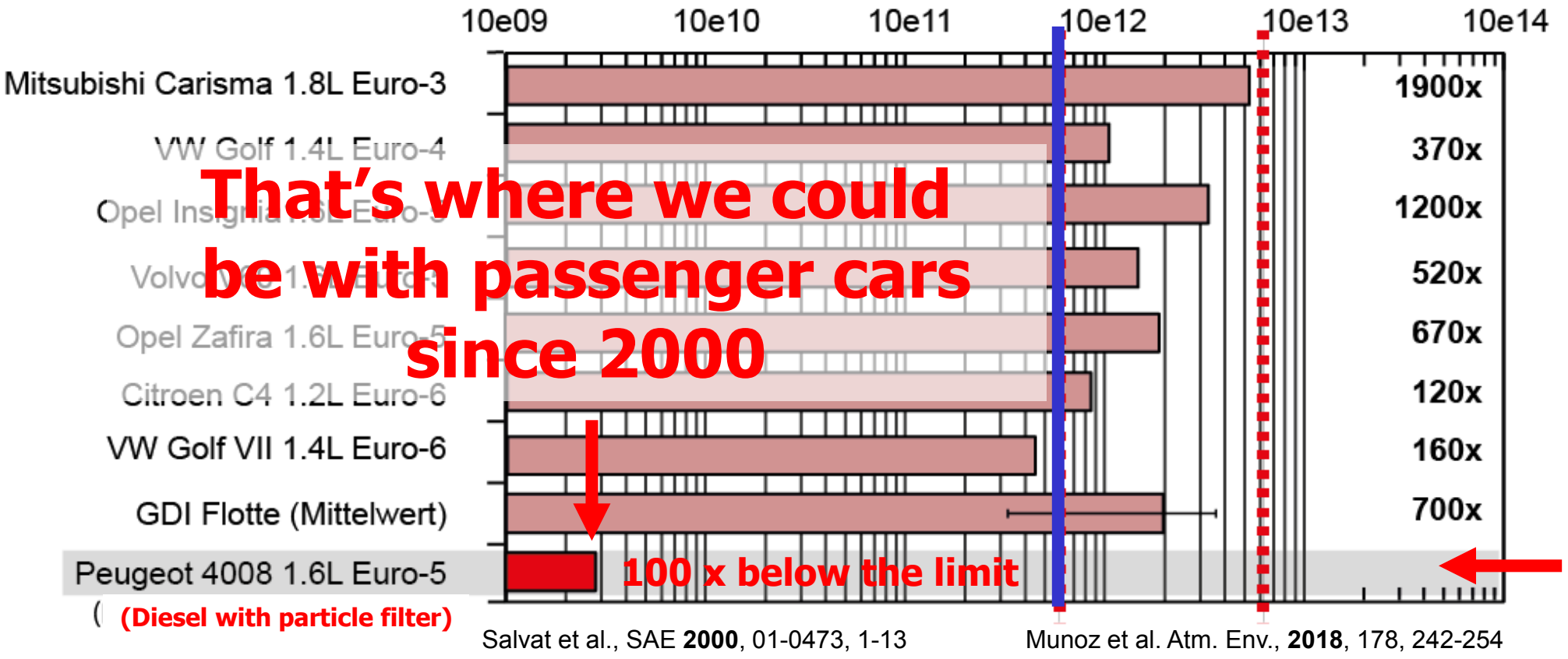
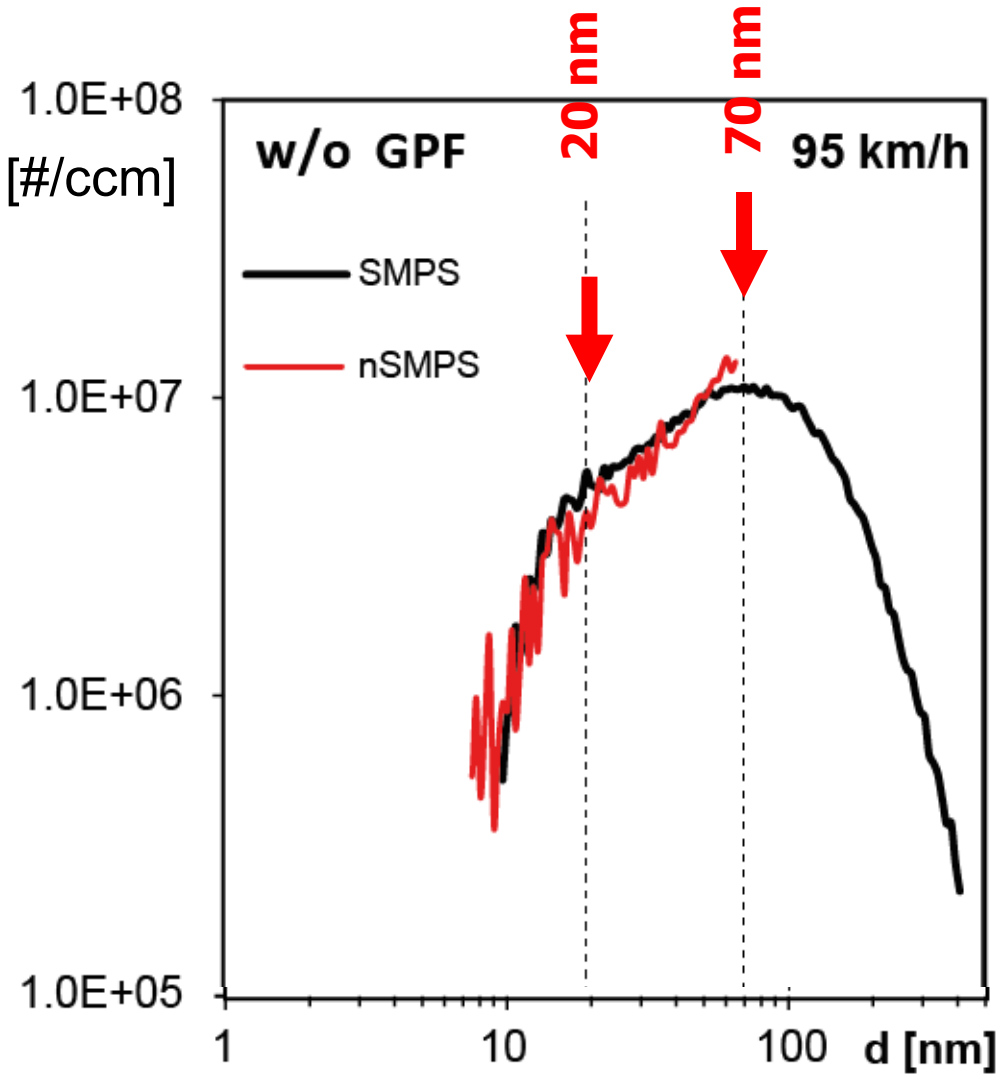


Salvat et al., SAE **2000**, 01-0473, 1-13

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

Nanoparticle emissions of GDI vehicles

Two modes of GDI particles, one at 20 nm the other at 70 nm.

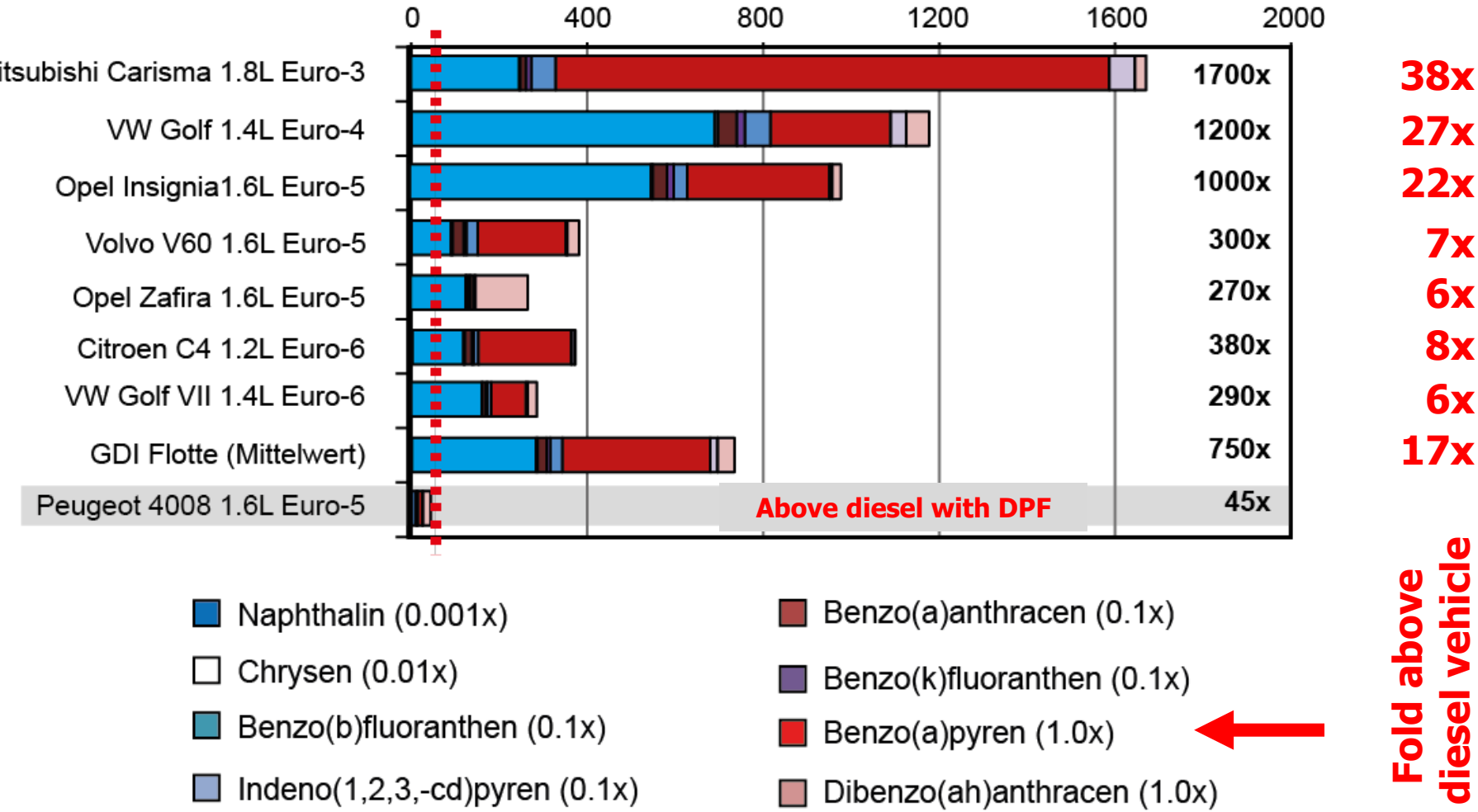


GDI particles are nanoparticles!

They will, like diesel particles, reach the alveoli of the lung possibly even penetrating alveolar membranes.

Genotoxic emissions of GDI vehicles

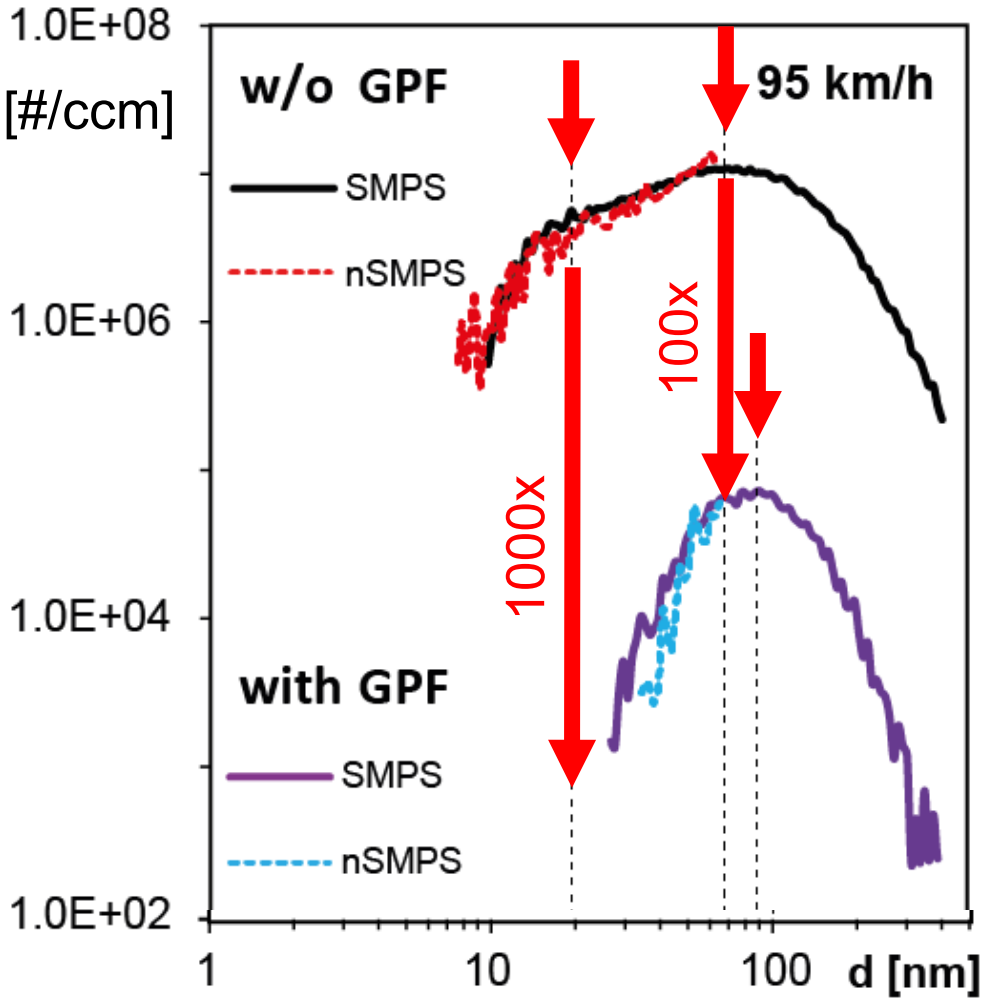
Genotoxic potential of GDI vehicle exhausts (ngTEQ/m³, cWLTC)
(EU ambient air limit: 1 ng benzo(a)pyrene/m³, yearly mean)



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

Particle filters for GDI vehicles (GPFs)

One mode left at 90 nm after the GPF

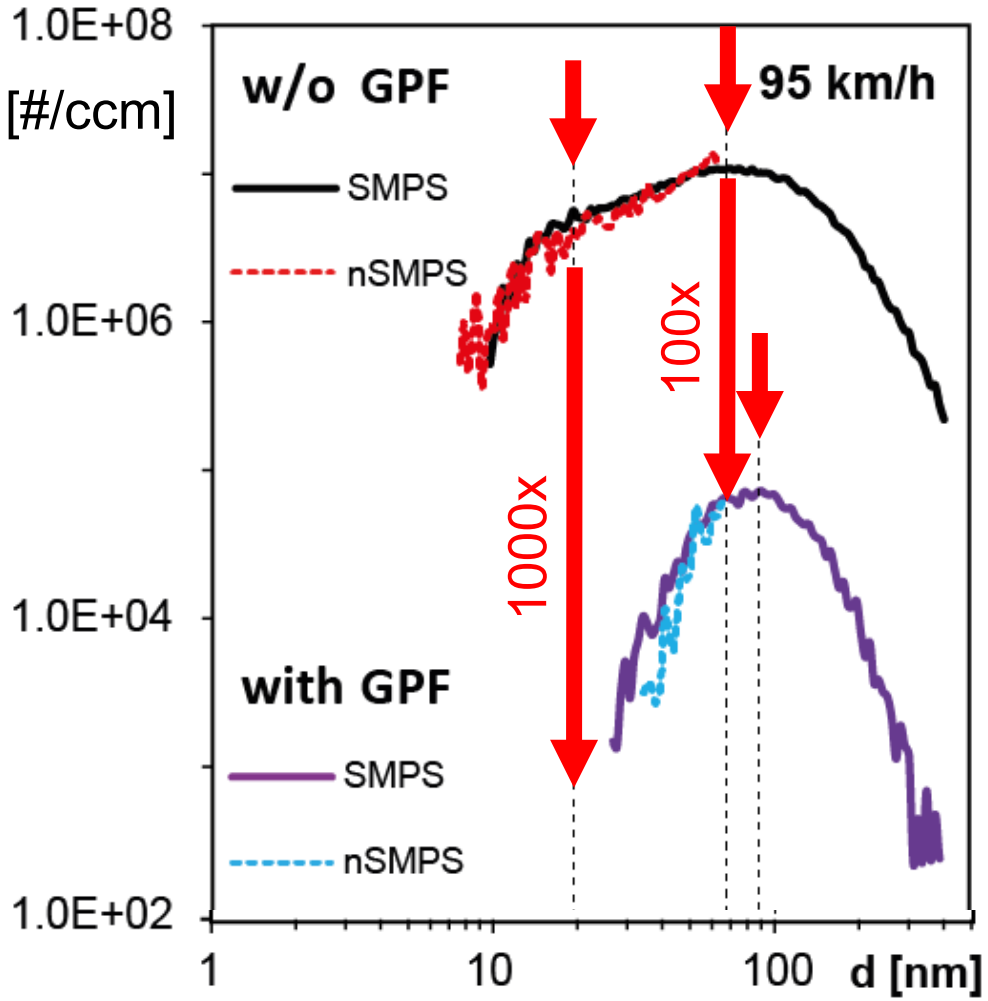


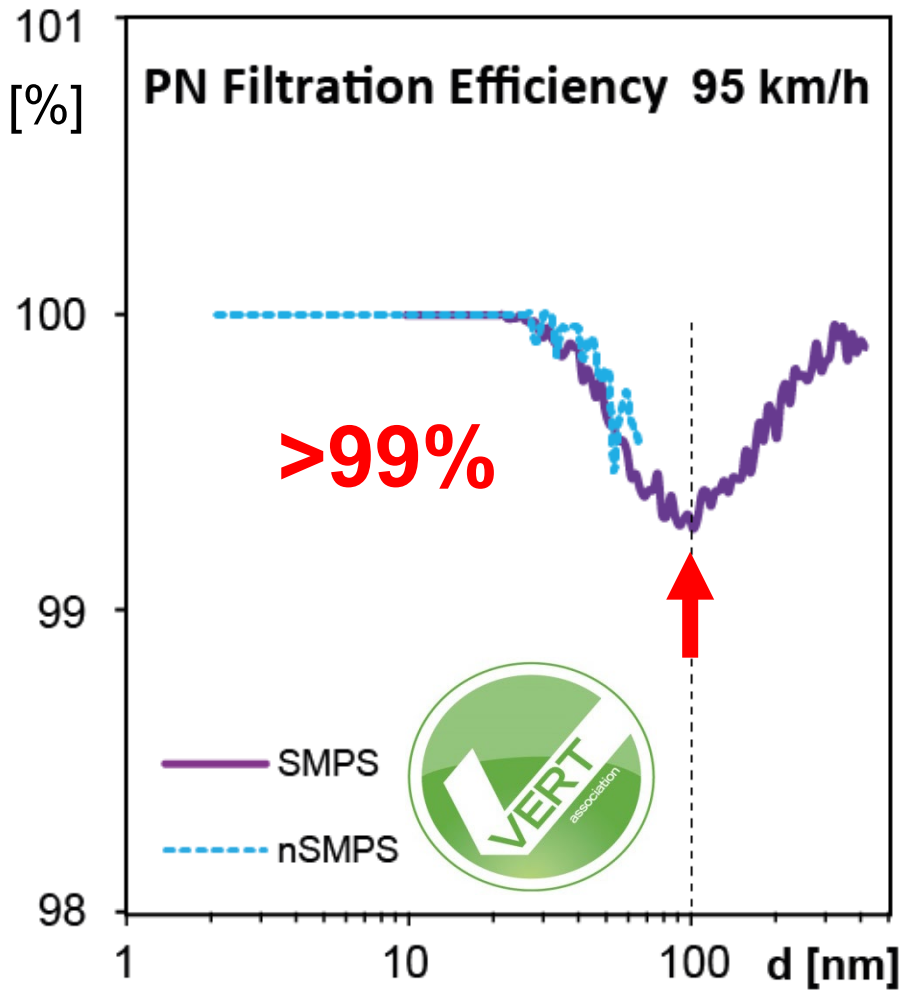
Prototype GPF can remove nanoparticles by 2-3 orders of magnitude, even the 20 nm particles

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

Particle filters for GDI vehicles (GPFs)

GPFs can be as efficient as DPFs and should become BAT





Properties of non-filtered exhausts of a gasoline multi-point-injection vehicle (GMPI)

What do we know on the exhaust properties of all other gasoline vehicles?

GMPI vehicle (Fiat Panda Twinair, Euro 6b, 0.9 L)

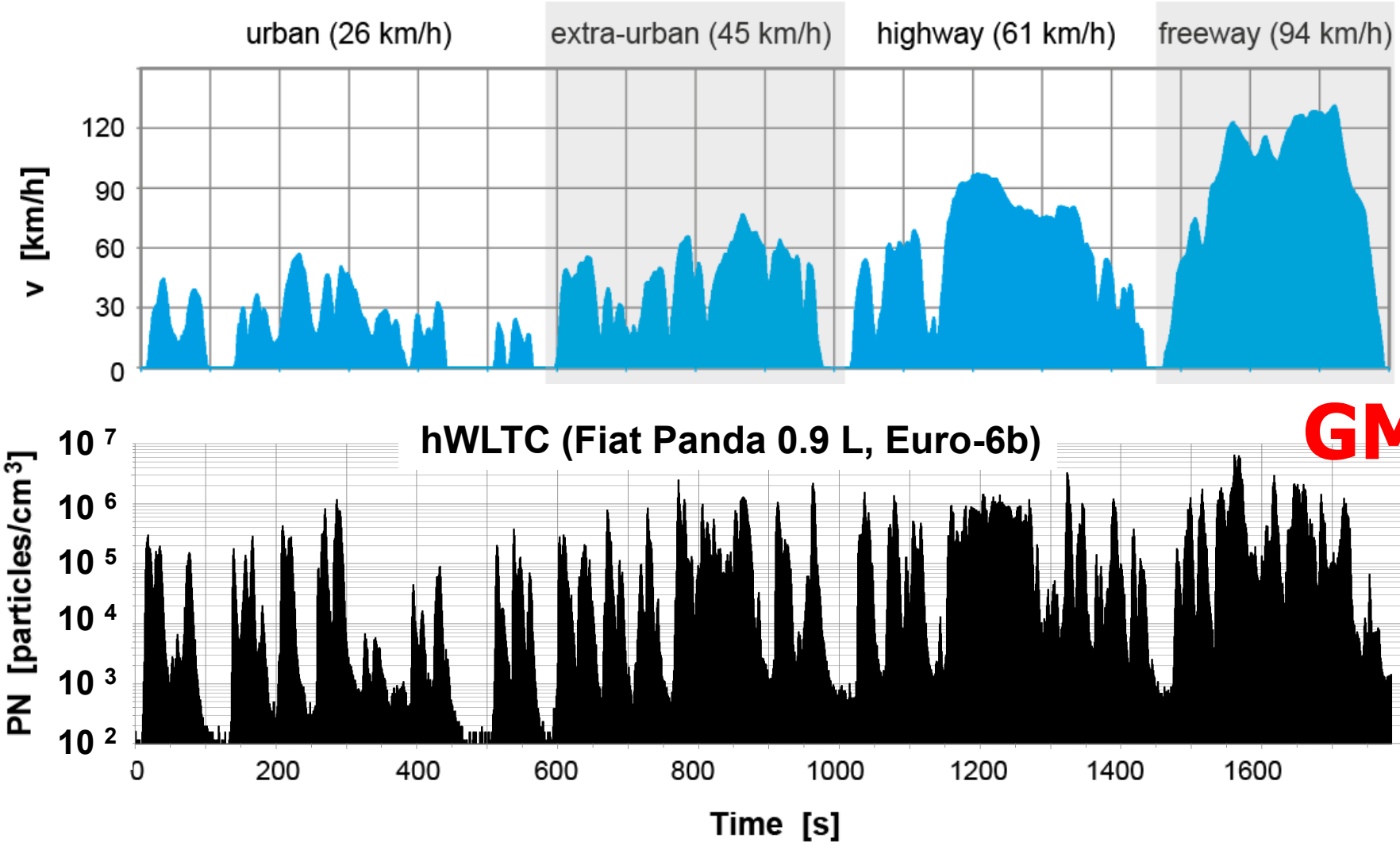
No PN-limit for these vehicles!

Even a two-cylinder 0.9 L engine can drink as much as 6.7 L fuel/100 km (155 g CO_2/km)!

But at much lower tax!

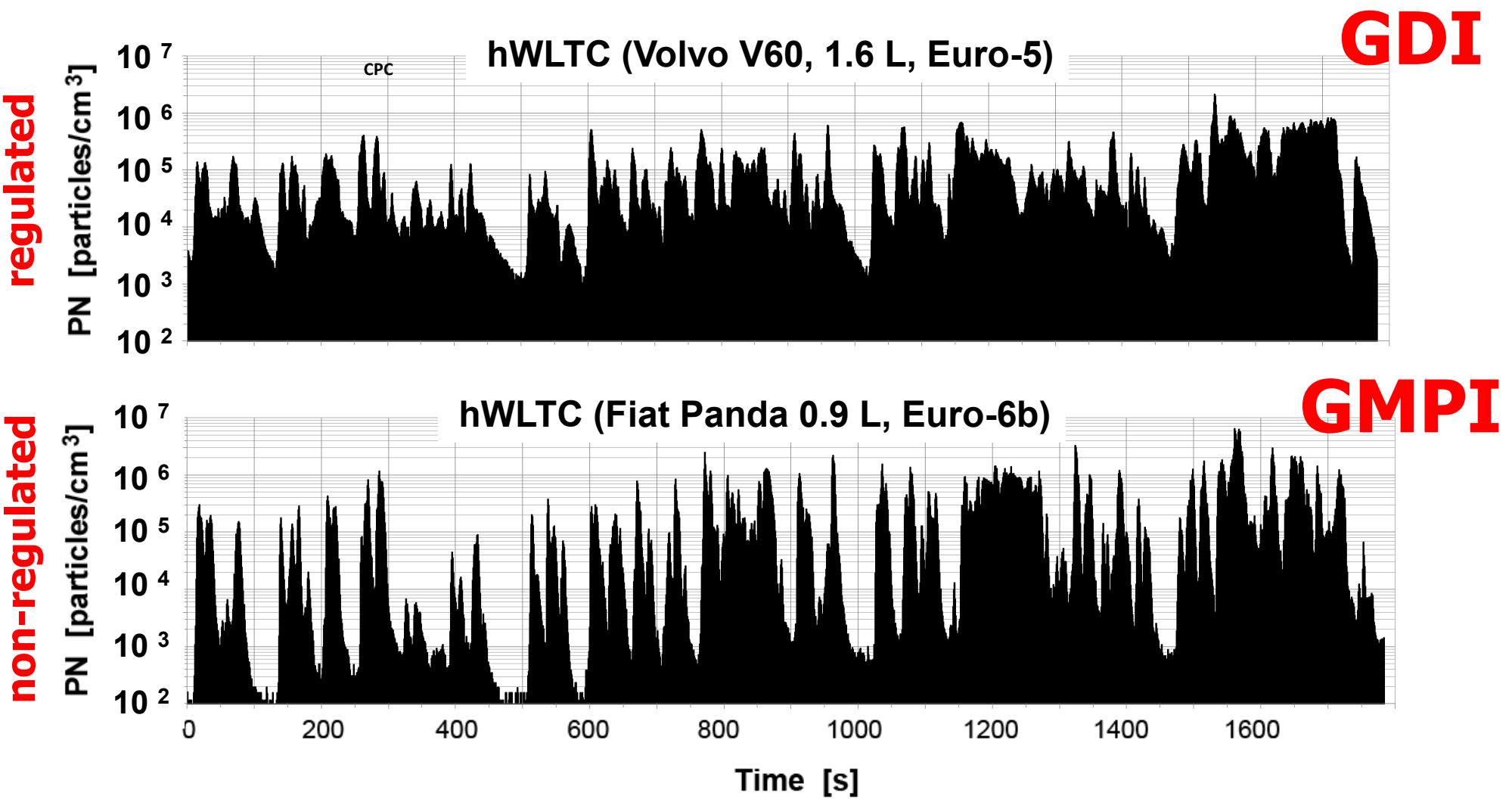
Nanoparticle emissions of a non-regulated gasoline multi-point-injection vehicle

Billions of nanoparticles released, where ever you drive!



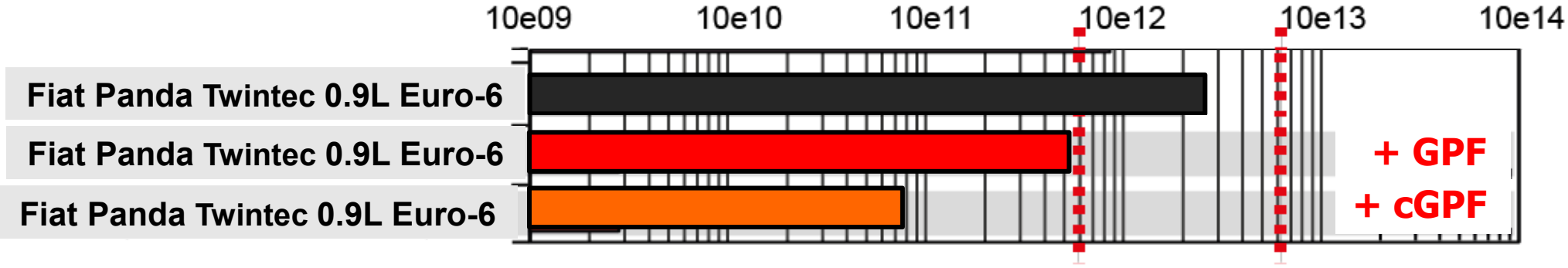
Nanoparticle emissions of a non-regulated gasoline multi-point-injection vehicle

The PN-regulated GDI- and the non-regulated GMPI vehicles are in the same league!



Comparison of nanoparticle emissions of a non-regulated GMPI- and regulated GDI-vehicles

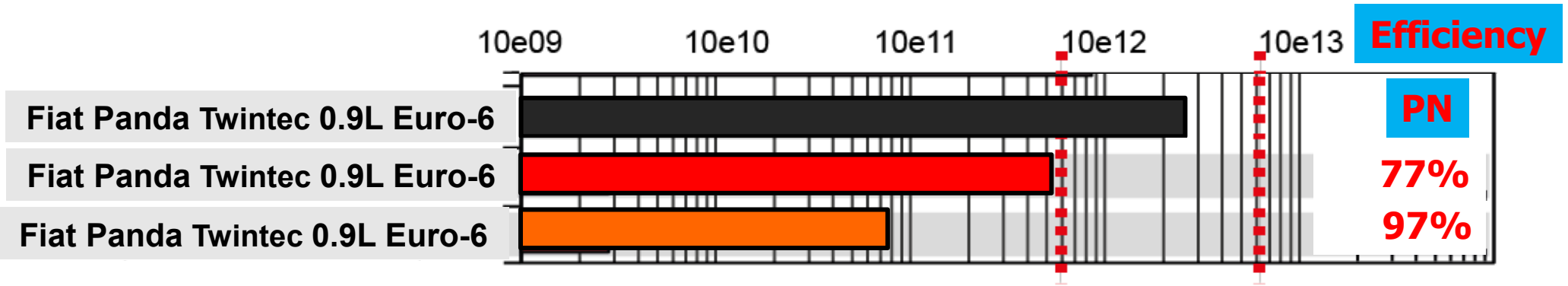
The GMPI vehicle exceeds the PN limit of 600 billion particles/km, even in the hWLTC!



Comparison of nanoparticle emissions of a non-regulated GMPI- and regulated GDI-vehicles

Both filters lowered PN emissions, the catalyzed filter is close to the VERT standard.

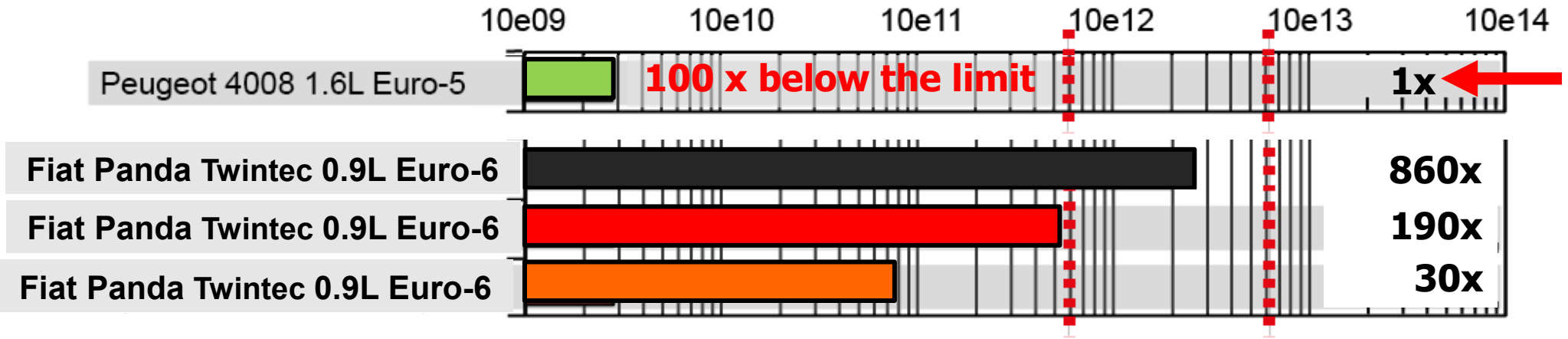
VERT
BAT >98%



Comparison of nanoparticle emissions of a non-regulated GMPI- and regulated GDI-vehicles

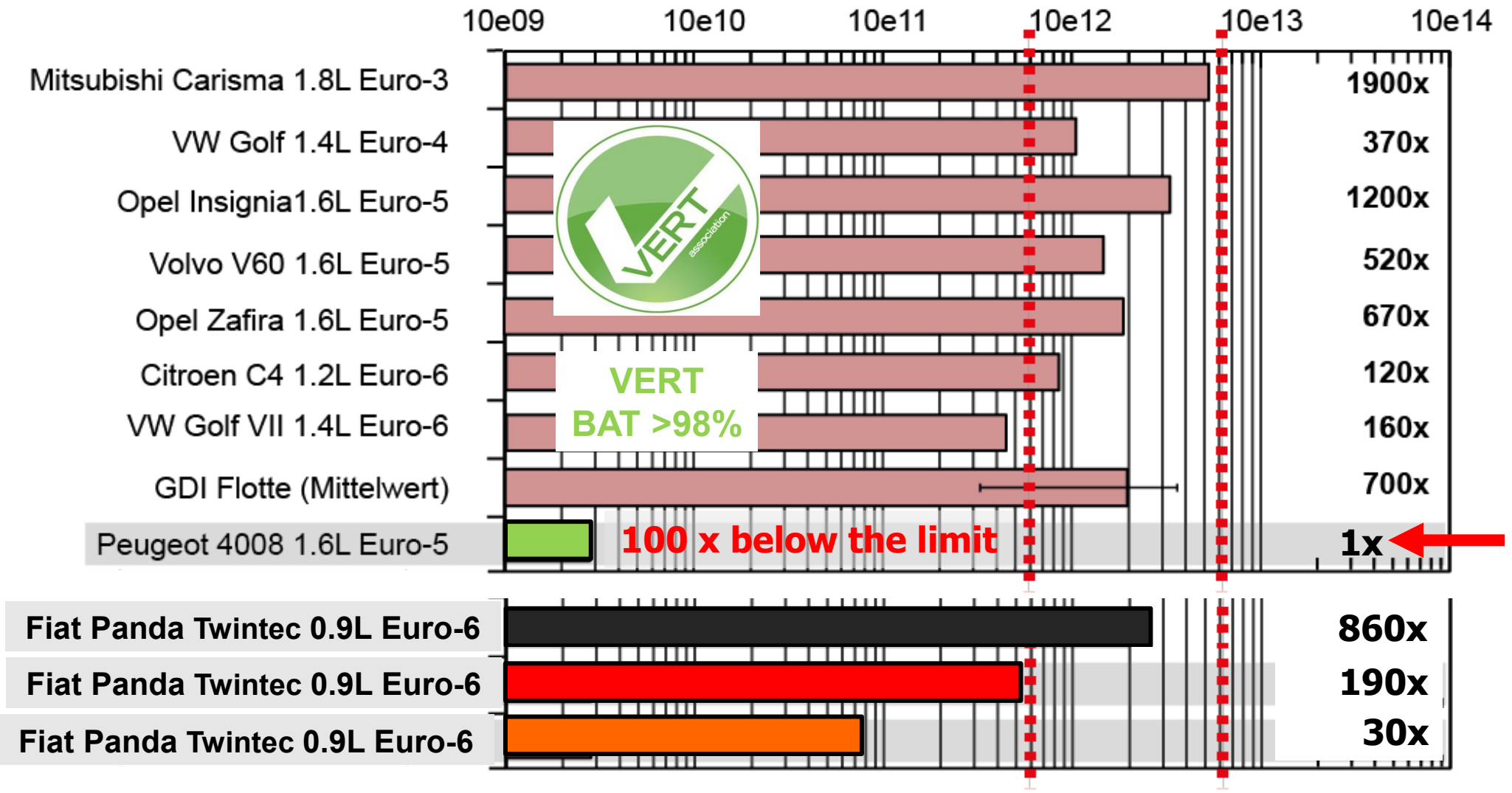
However, a high quality DPF can lower PN emissions 100x below the current limit!

VERT
BAT >98%



Comparison of nanoparticle emissions of a non-regulated GMPI- and regulated GDI-vehicles

PN emissions of GMPI- and GDI-vehicles are 120 – 1900x above diesel vehicle with DPF

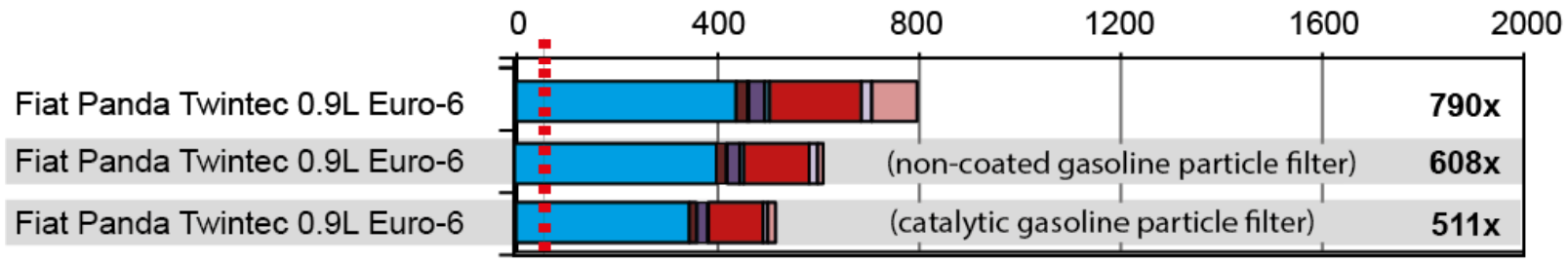


Genotoxic emissions of regulated GDI- and non-regulated GMPI-vehicles

Genotoxic potential of GDI-, GMPI- and Diesel exhausts (ngTEQ/m³, cWLTC)
(EU air quality limit: 1 ng benzo(a)pyrene/m³)

Filter effects on genotoxic potentials are moderate only!

Lower than for PN!



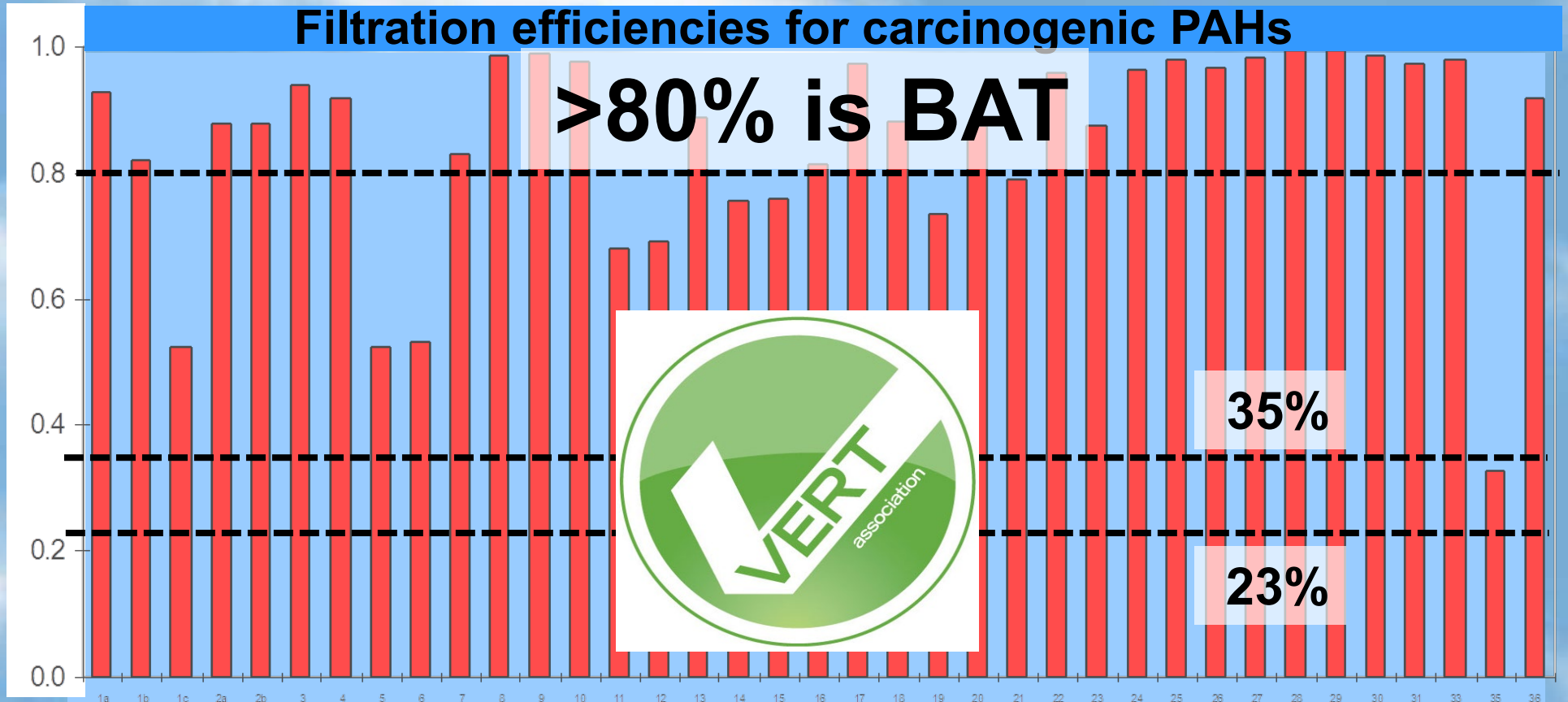
Naphthalene(0.001x)
Benzo(k)fluoranthene (0.1x)
Indeno(1,2,3,-cd)pyrene (0.1x)
Benzo(a)anthracene (0.1x)
Benzo(b)fluoranthene (0.1x)
Dibenzo(ah)anthracene (1.0x)
Chrysene (0.01x)
Benzo(a)pyrene (1.0x)

VERT-BAT
PN >98%
PAHs >80%
(a.m.a.p)

Efficiency	
TEQ	PN
23%	81%
35%	92%

Filtration efficiencies of VERT-certified DPFs for genotoxic PAHs

More than 60 VERT-tested DPFs. All approved systems are excellent particle filters



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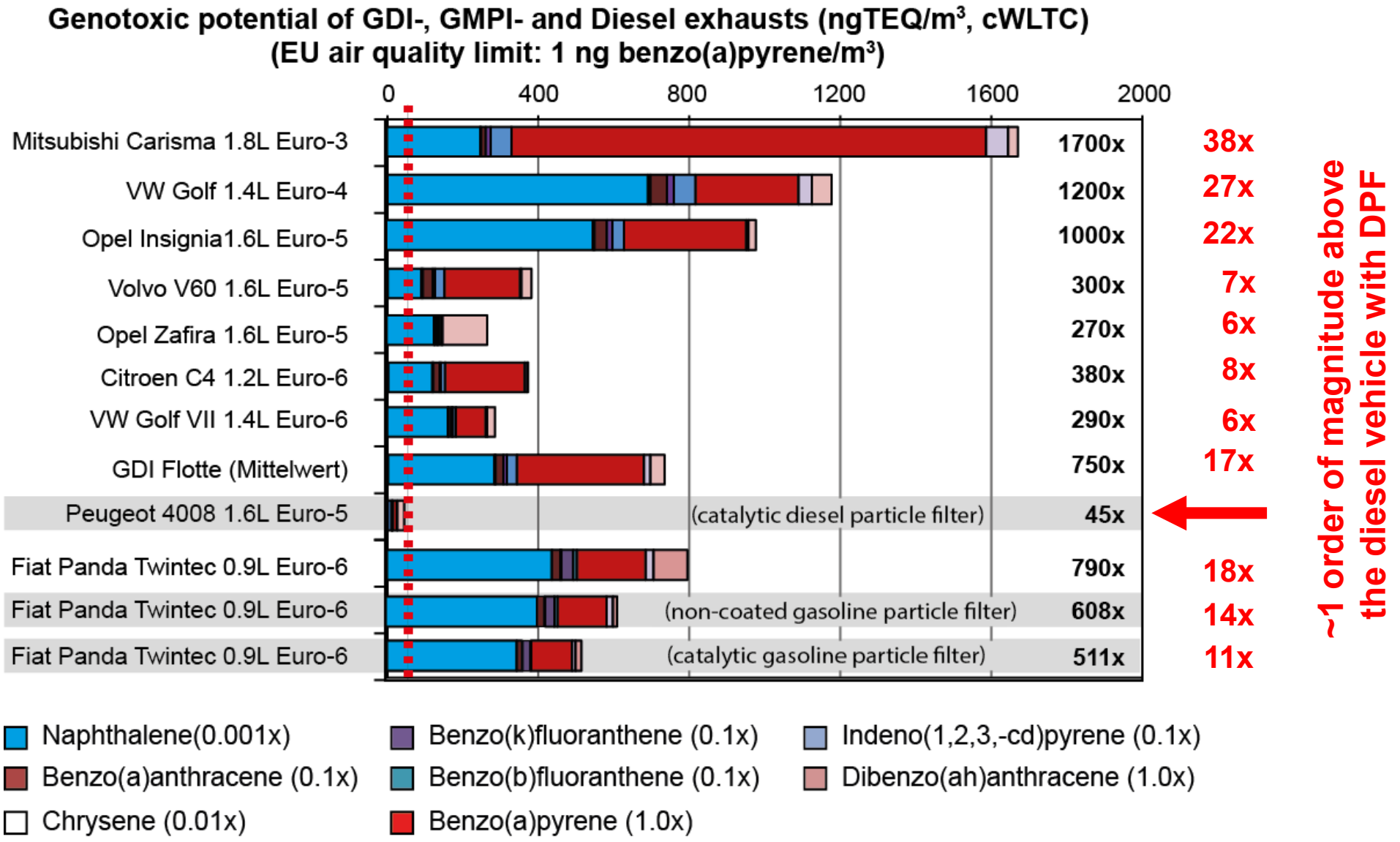
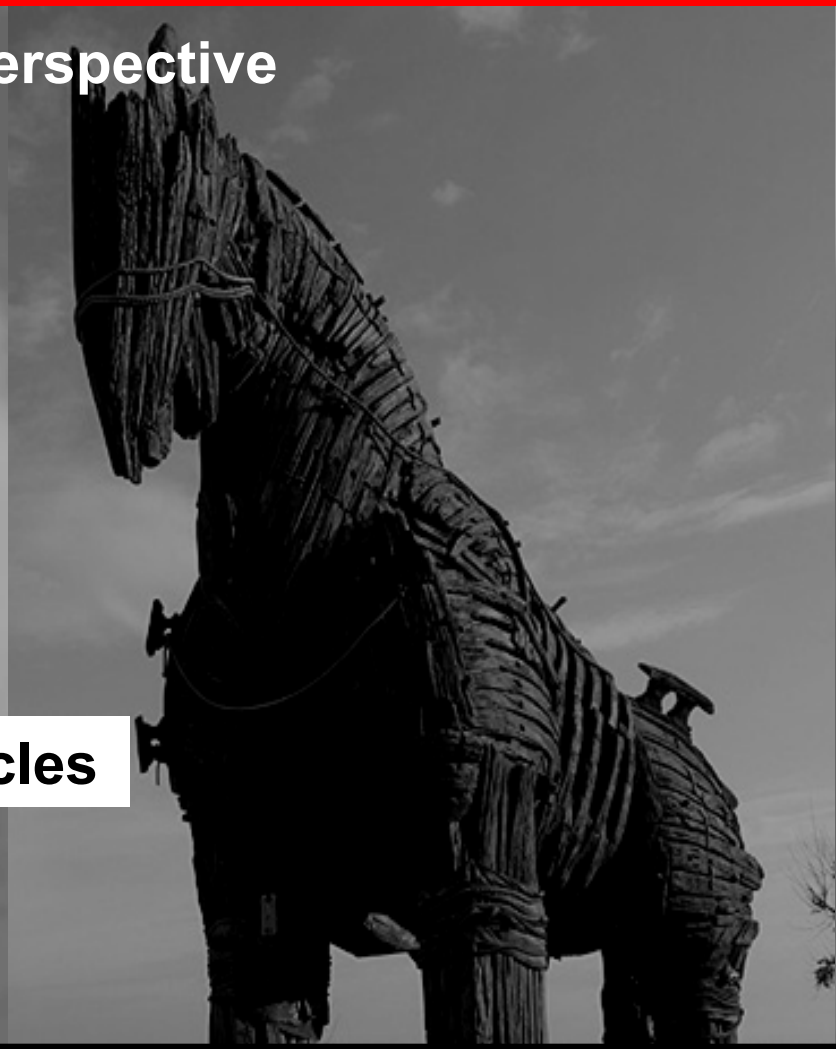
Genotoxic emissions of regulated GDI- and non-regulated GMPI-vehicles



The chemistry of nanoparticle adsorbates from diesel and gasoline combustion engines

The Trojan Horse effect, from a chemists perspective



- **Adsorbate chemistry**
  (A quick tour)
- **Chemistry in particle filters**
  (PFs – ideal chemical reactors)
- **Genotoxic particles from gasoline vehicles**
  (a global threat)

23id ETH Conference on Combustion Generated Nanoparticles

Zürich, June 17th – 20th, 2019

20 years VERT filter tests – 20 years of excellent team work

A combined effort with many important contributions

Thanks:

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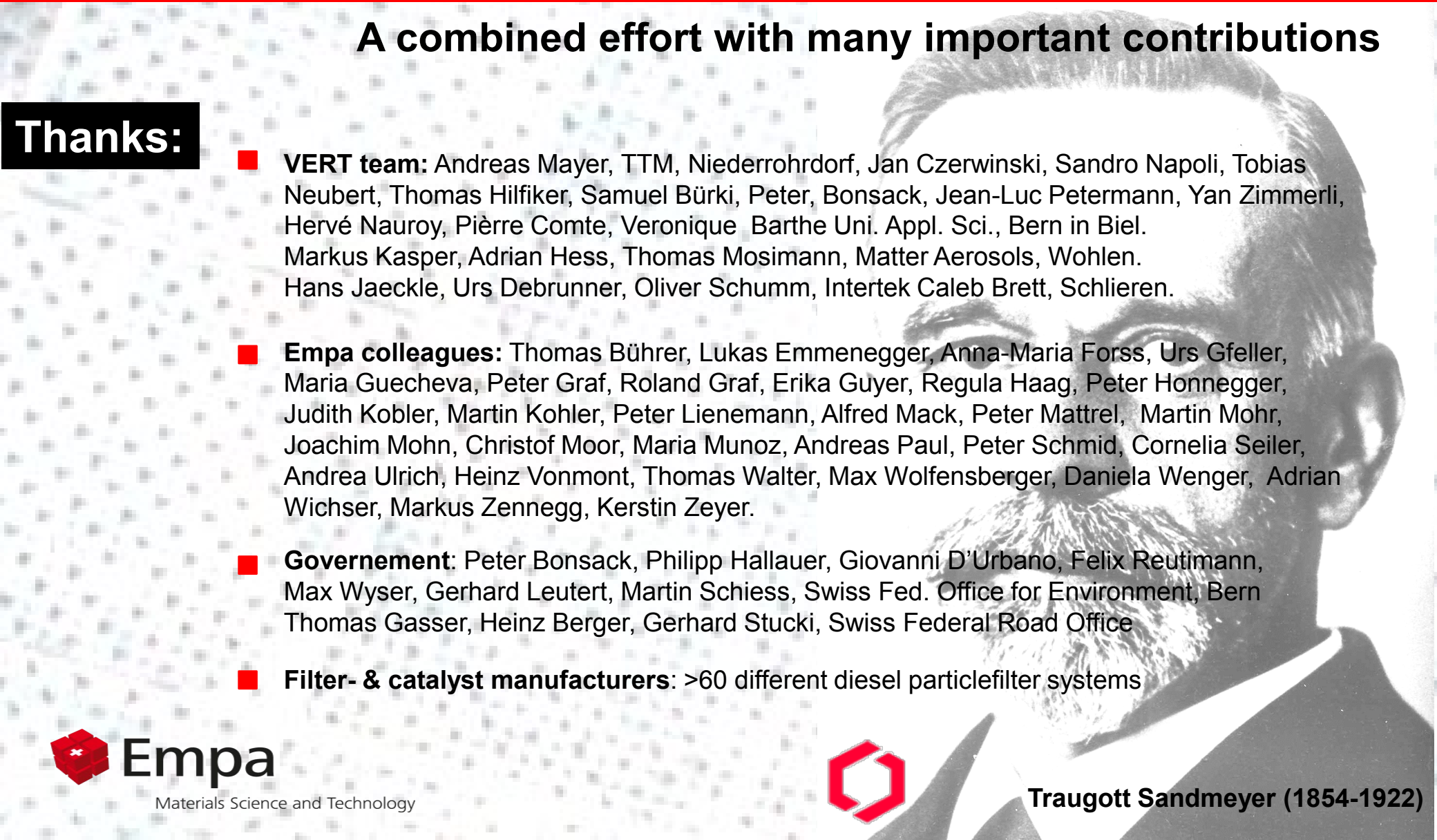
  Thomas Gasser, Heinz Berger, Gerhard Stucki, Swiss Federal Road Office

- **Filter- & catalyst manufacturers**: >60 different diesel particlefilter systems



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Traugott Sandmeyer (1854-1922)

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