

Nitration chemistry in non-catalyzed DPFs

A consequence of co-released NO_x , soot and soot adsorbates



22nd ETH Conference on Combustion Generated Nanoparticles

Zürich, June 18th – 21st, 2018

Nitration chemistry in non-catalyzed DPFs

What do we know about diesel exhaust after 130 years of application?



Empa

Materials Science and Technology

Non-treated diesel engine exhaust

What do we know about diesel exhaust after 130 years of application?

- consists of **billions** of soot nanoparticles
- EU limit for vehicles of **600 billion particles/km** is very high
- PN emissions are **not limited outside Europe** (US, Japan)
- soot nanoparticles are **persistent**, they hardly degrade in vivo
- soot particles are loaded with **genotoxic** compounds
- soot nanoparticles mainly **deposit in alveoli**
- sub100 nm particles may even **penetrate the alveolar membrane transporting adsorbates** in the body (**Trojan horse effect**)
- **class 1 carcinogen** causing **lung cancer** in humans



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Do not inhale it!



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World Health Organization, IARC Diesel engine exhaust: A group 1 carcinogen

engine exhausts cause lung cancer in humans

International Agency for Research on Cancer



PRESS RELEASE
N° 213

12 June 2012

June 12, 2012

IARC: DIESEL ENGINE EXHAUST CARCINOGENIC

Lyon, France, June 12, 2012 -- After a week-long meeting of international experts, the International Agency for Research on Cancer (IARC), which is part of the World Health Organization (WHO), today classified diesel engine exhaust as **carcinogenic to humans (Group 1)**, based on sufficient evidence that exposure is associated with an increased risk for lung cancer.

Group 1

Background

In 1988, IARC classified diesel exhaust as *probably carcinogenic to humans (Group 2A)*. An Advisory Group, which reviews and recommends future priorities for the IARC Monographs Program had recommended diesel exhaust as a high priority for re-evaluation since 1998.

There has been mounting concern about the cancer-causing potential of diesel exhaust, particularly based on findings in epidemiological studies of workers exposed in various settings. This was re-emphasized by the publication in March 2012 of the results of a large US National Cancer Institute/National Institute for Occupational Safety and Health study of occupational exposure to such emissions in underground miners, which showed an increased risk of death from lung cancer in exposed workers (1).

Lung cancer
in exposed workers

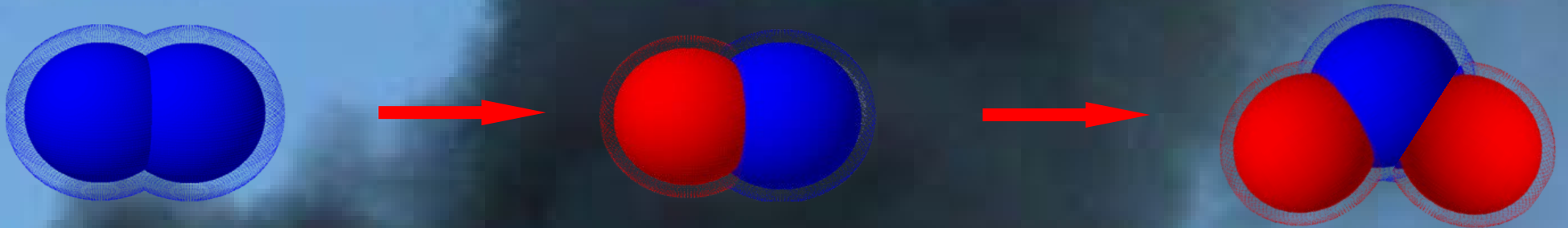
12'315 workers, 8 mines
198 lung cancer death

(16'000 in 1'000'000)

(1 in 1'000'000, target value LRV)

Nitration chemistry in non-catalyzed DPFs

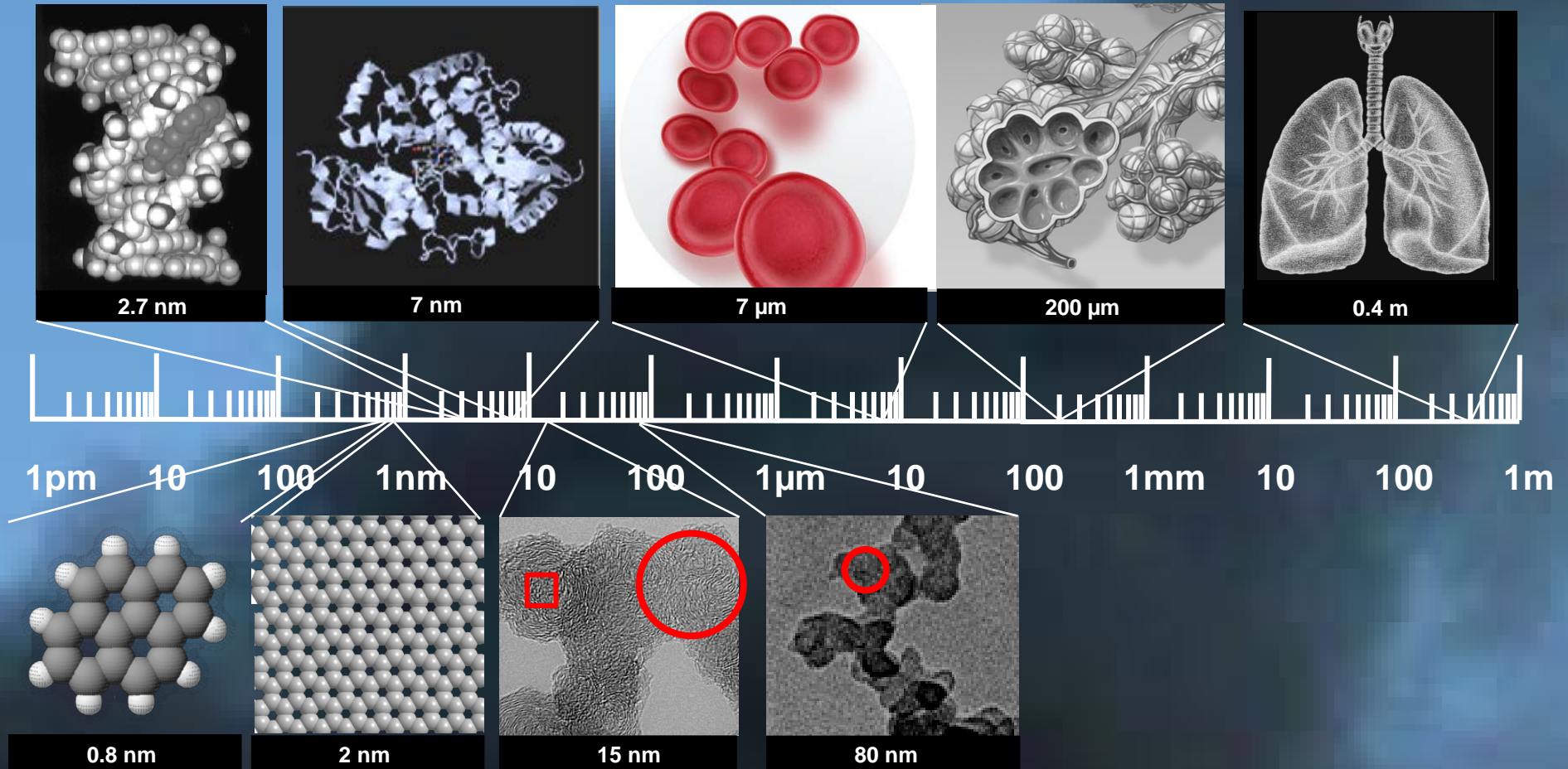
Does exposure of soot and adsorbates to NO_x alter exhaust toxicity?



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Particle dimensions and biological receptors



← PM 10 inhalable < 10 μ m
← PM 1 reaches alveoli < 1 μ m
← PM 0.1 can cross membranes < 0.1 μ m

Soot and soot adsorbates

Soot is, from a chemists perspective, an extended PAH

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

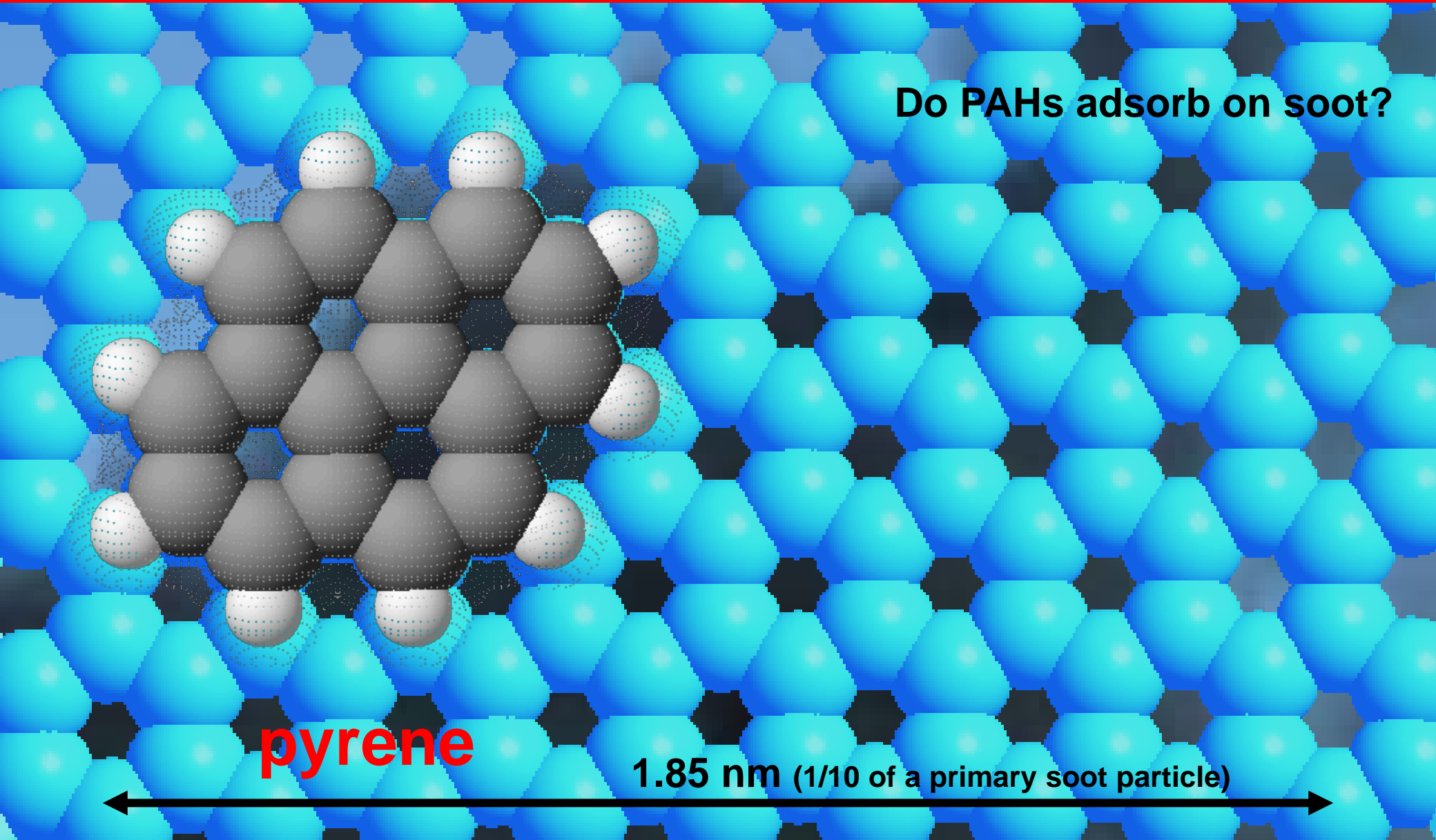


Soot and soot adsorbates

Do PAHs adsorb on soot?

pyrene

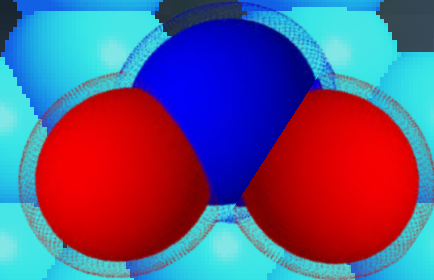
1.85 nm (1/10 of a primary soot particle)



Soot catalyzed nitration of PAHs

Can adsorbed PAHs be nitrated on soot?

+



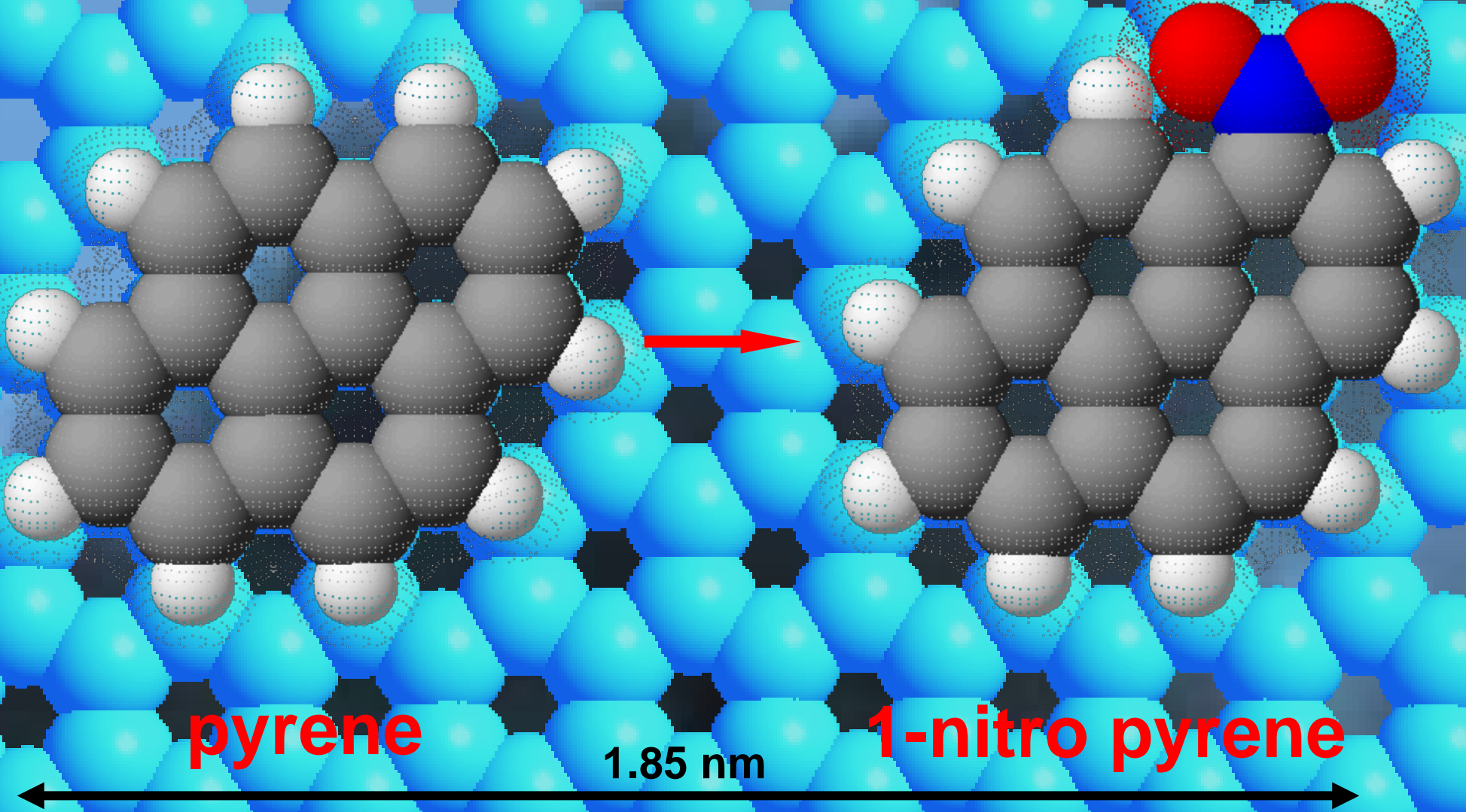
pyrene

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



Soot catalyzed nitration of PAHs

From harmless pyrene to mutagenic 1-nitro-pyrene?



The visible effect of a DPF

7 m³ exhaust (2 minutes of an Euro-3 diesel engine (6.1 L, 105 kW))

450x10¹² particles

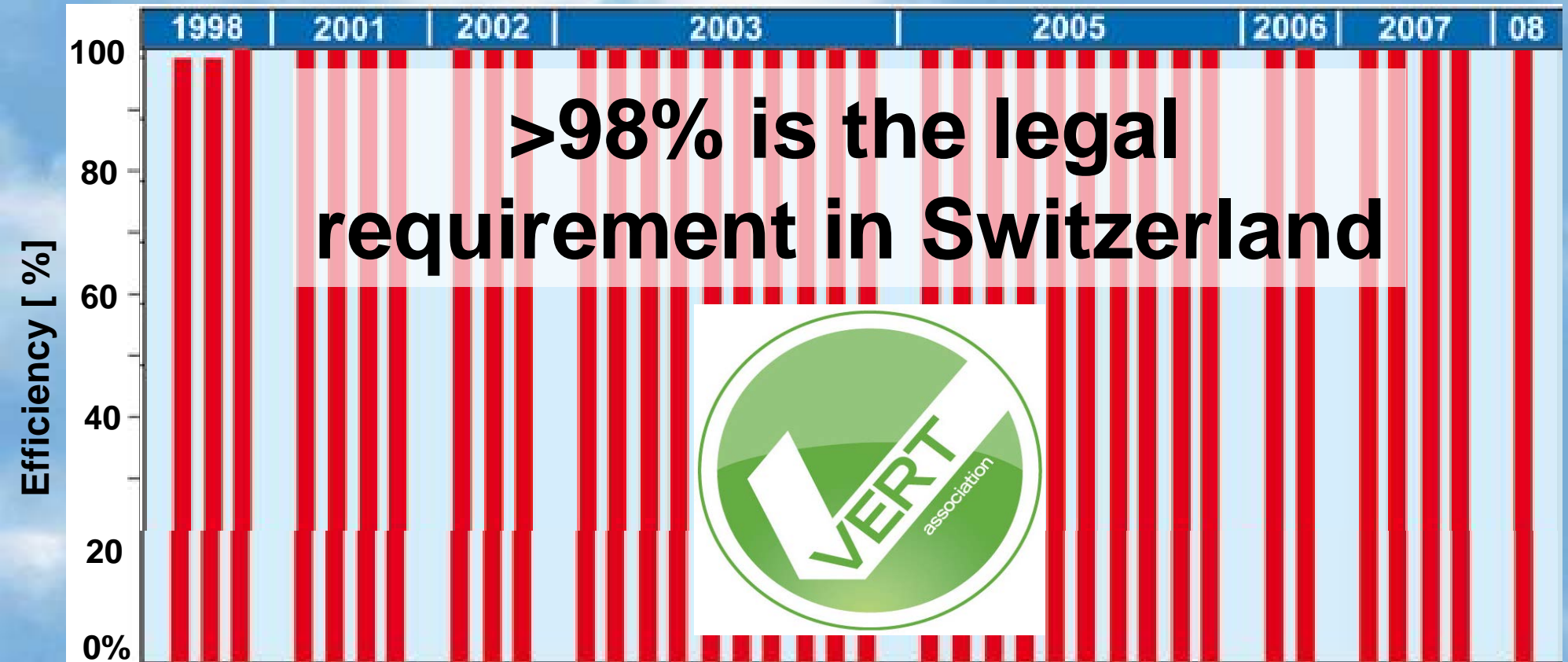


0.1x10¹² particles



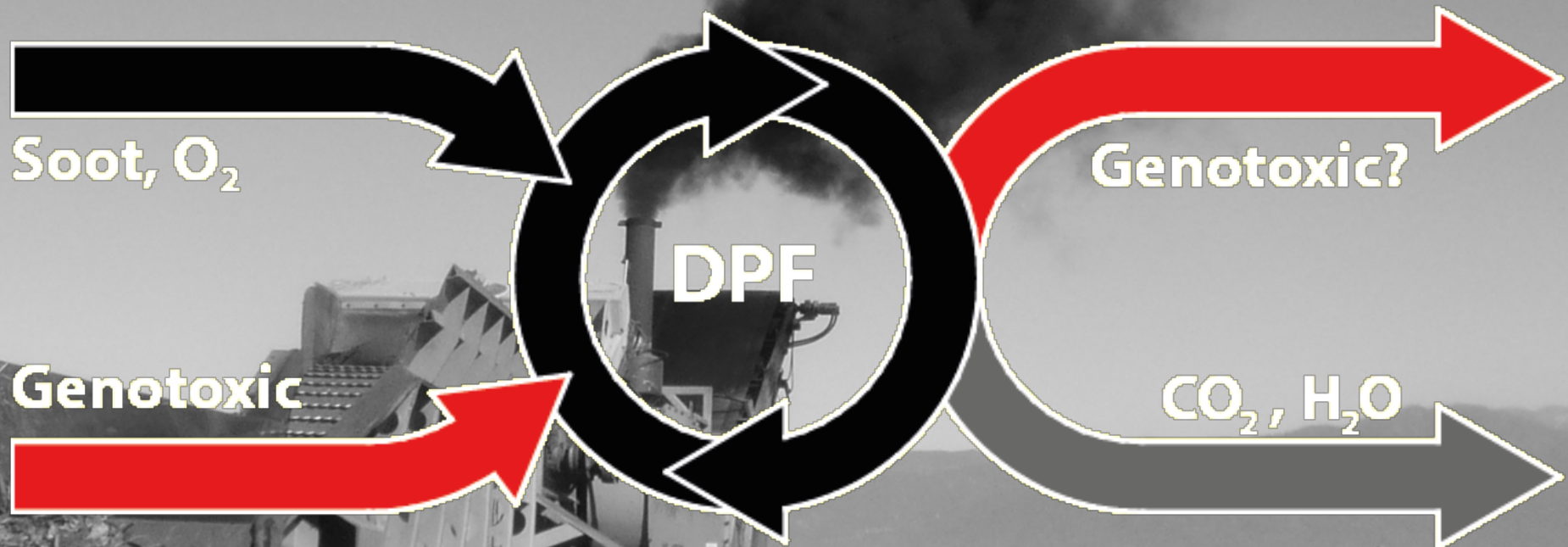
The visible effect of a DPF

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



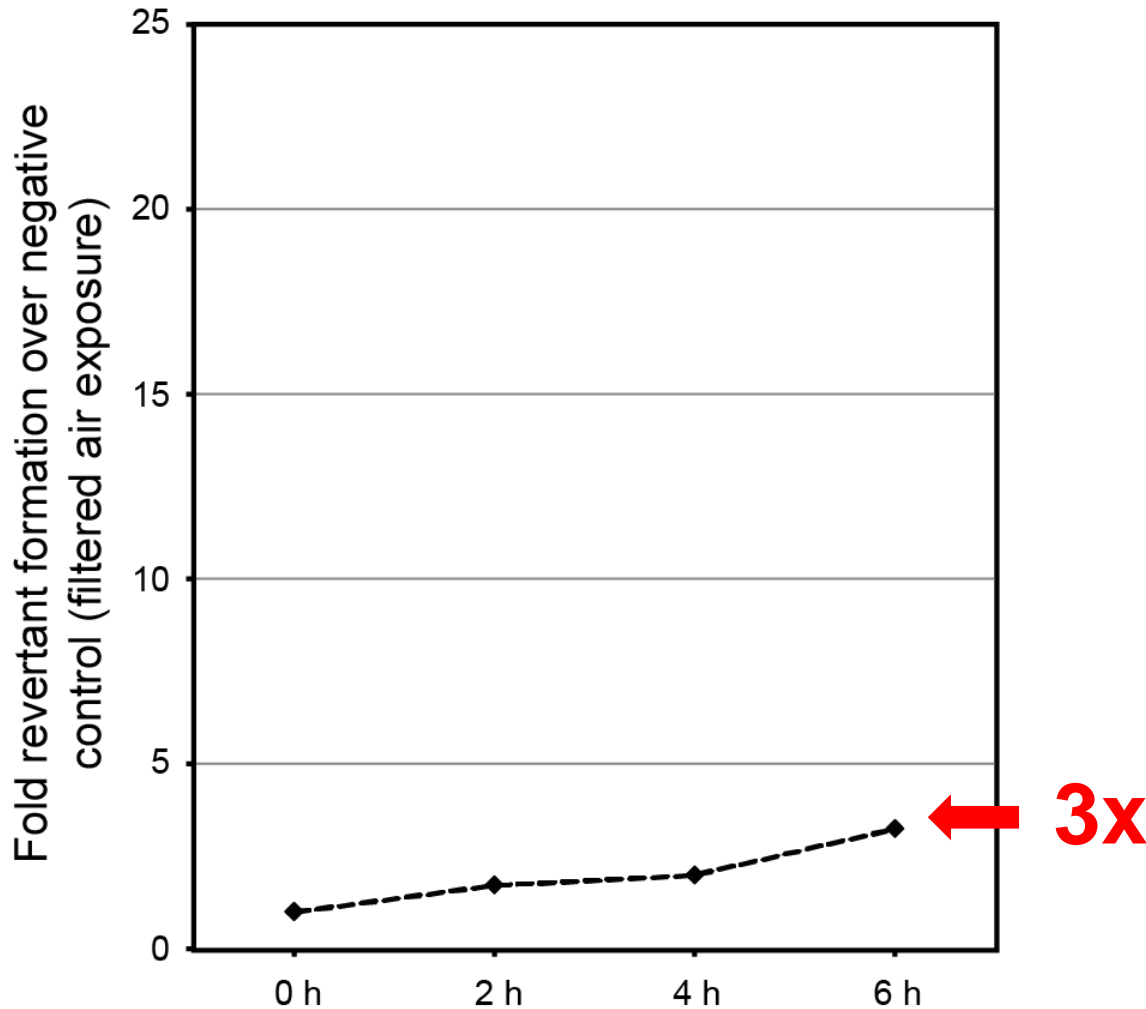
Impact of DPFs on genotoxicity

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

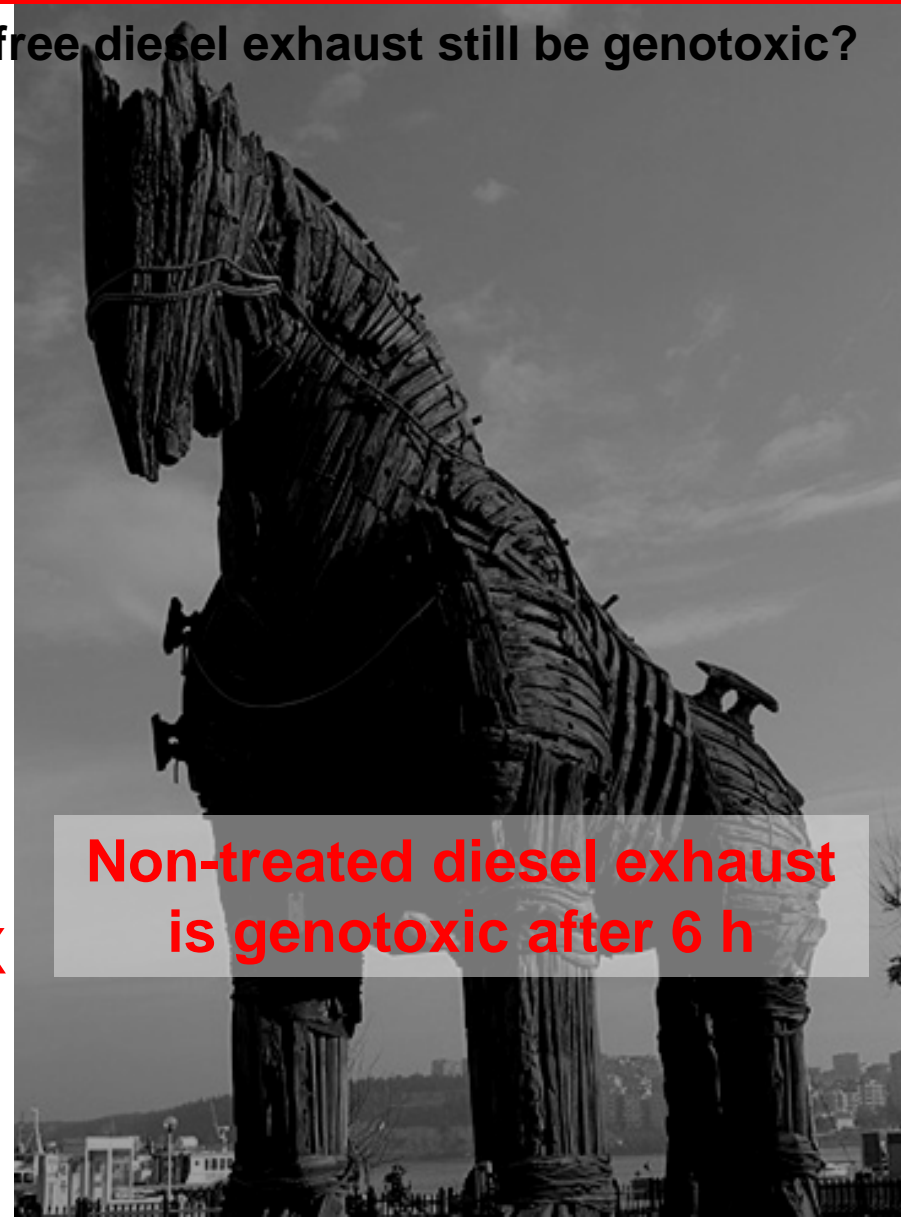


Impact of DPFs on genotoxicity

Why can filtered, particle-free diesel exhaust still be genotoxic?
Salmonella typhimurium TA100

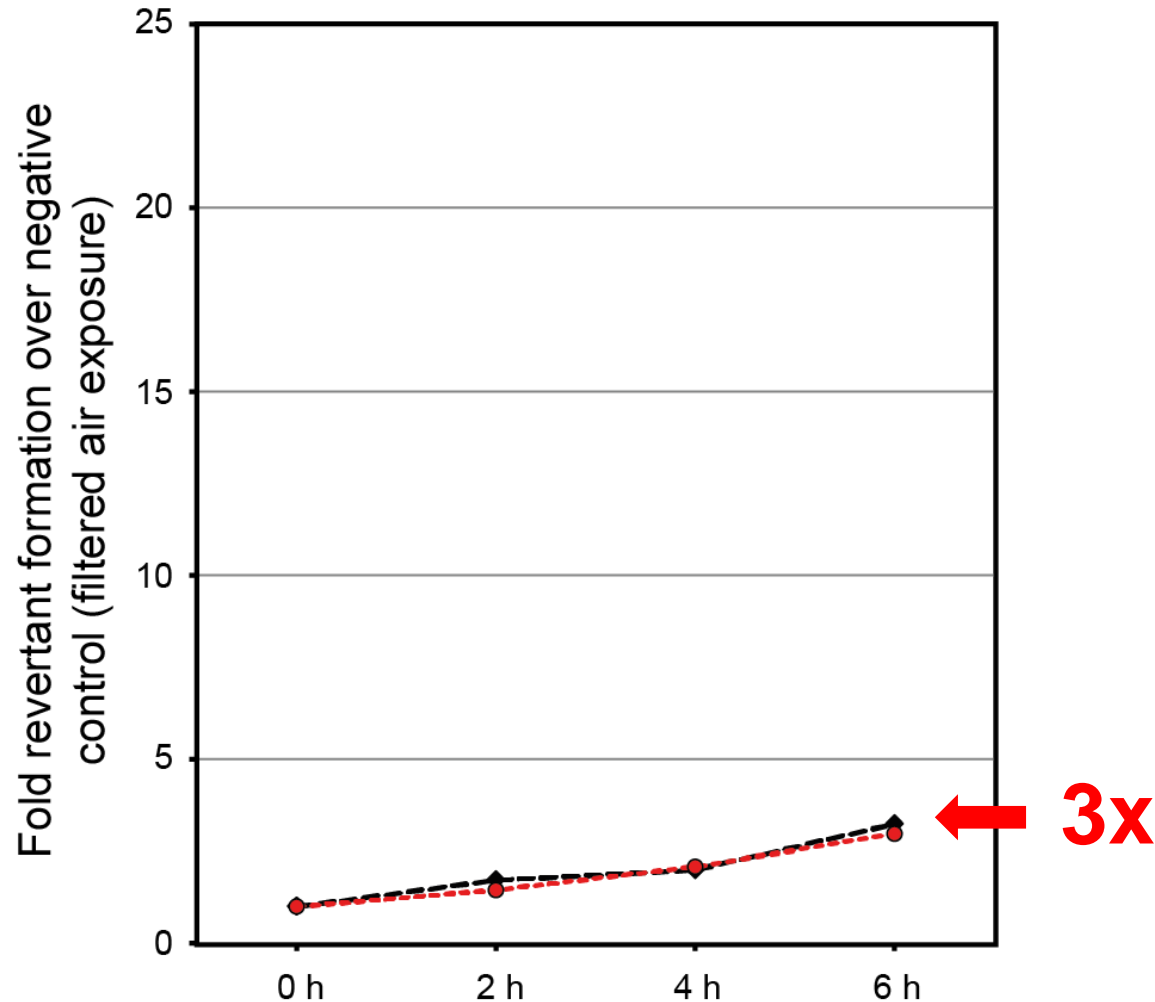


Steiner et al., Anal. Bioanal. Chem 2015, 407, 5977-5986

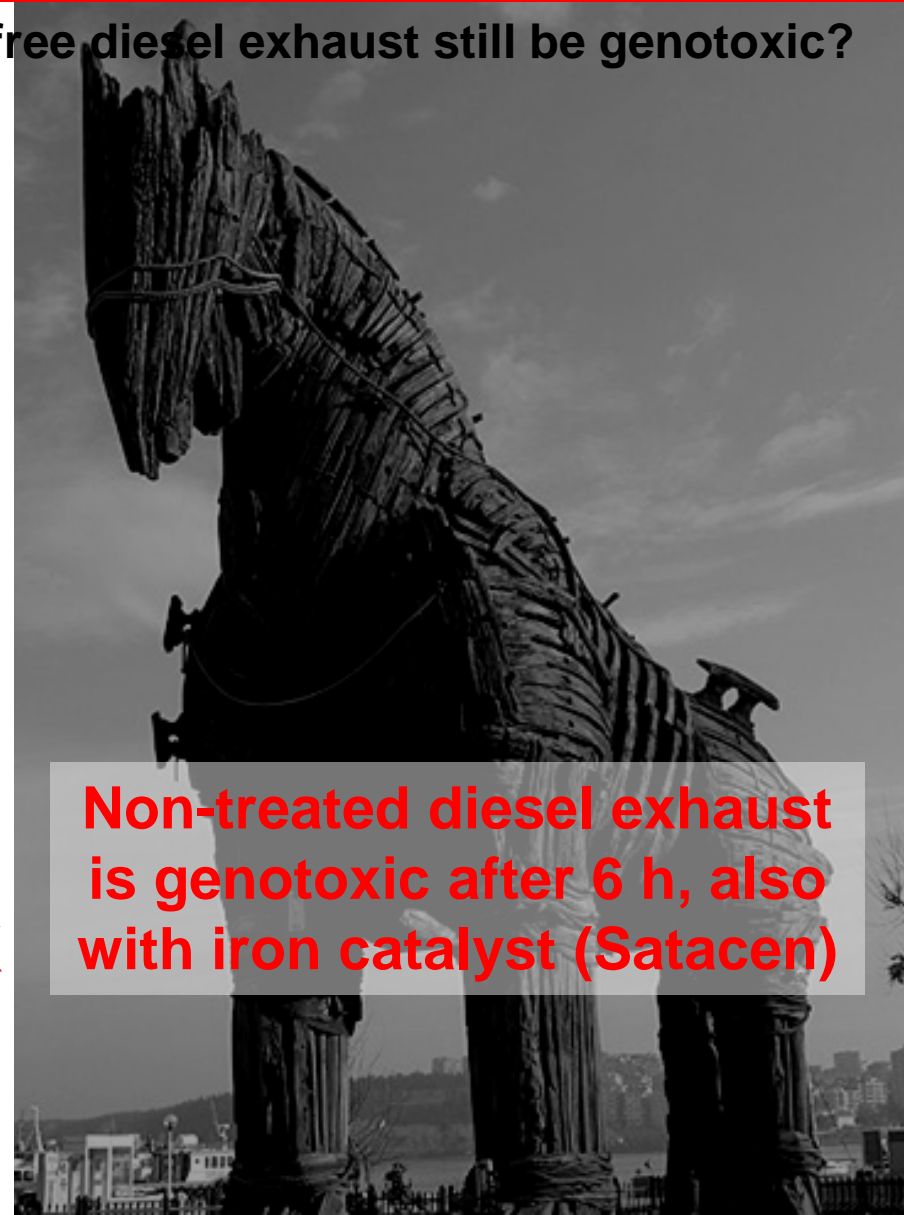


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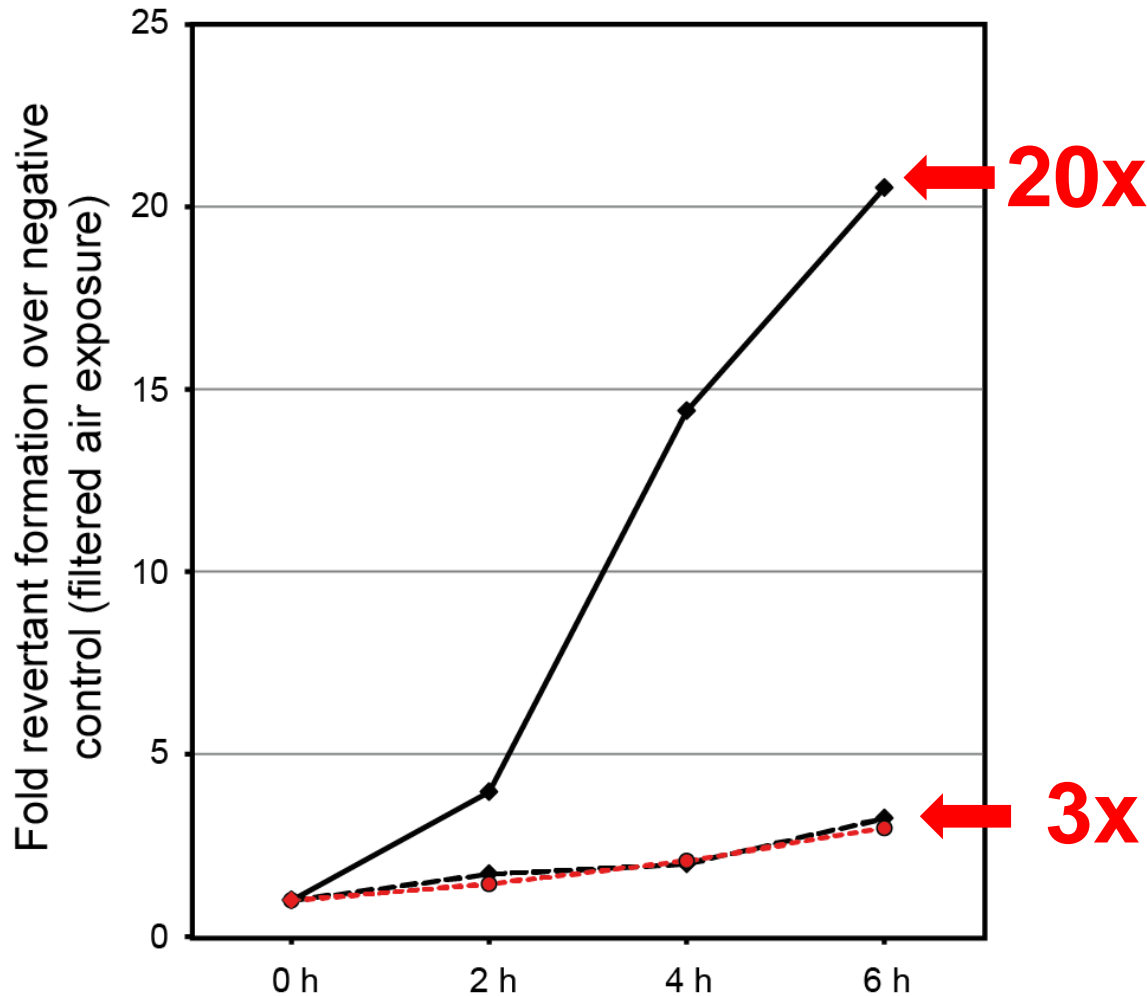


Non-treated diesel exhaust is genotoxic after 6 h, also with iron catalyst (Satacen)

Impact of DPFs on genotoxicity

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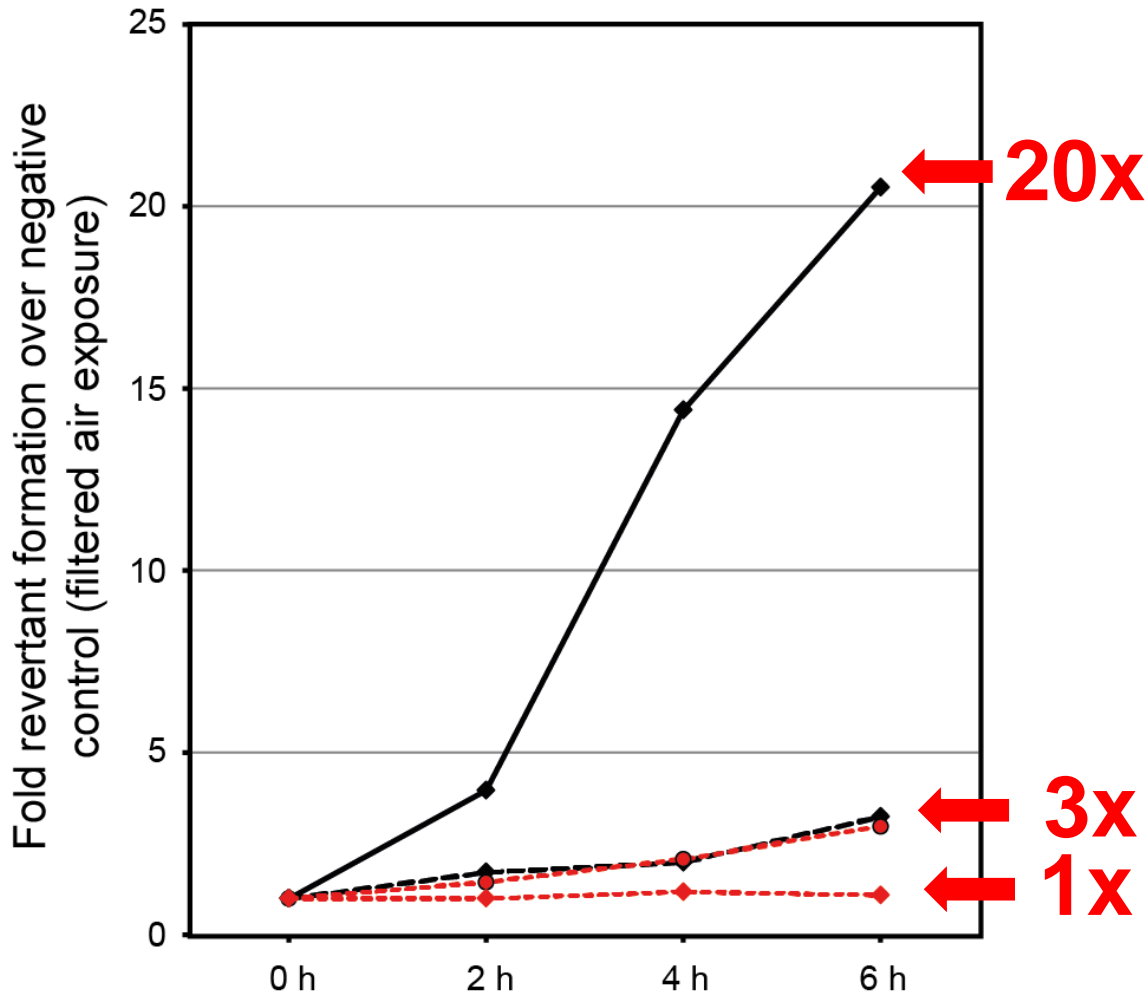
Filtered diesel exhaust can even be more genotoxic!

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Filtered diesel exhaust can even be more genotoxic!

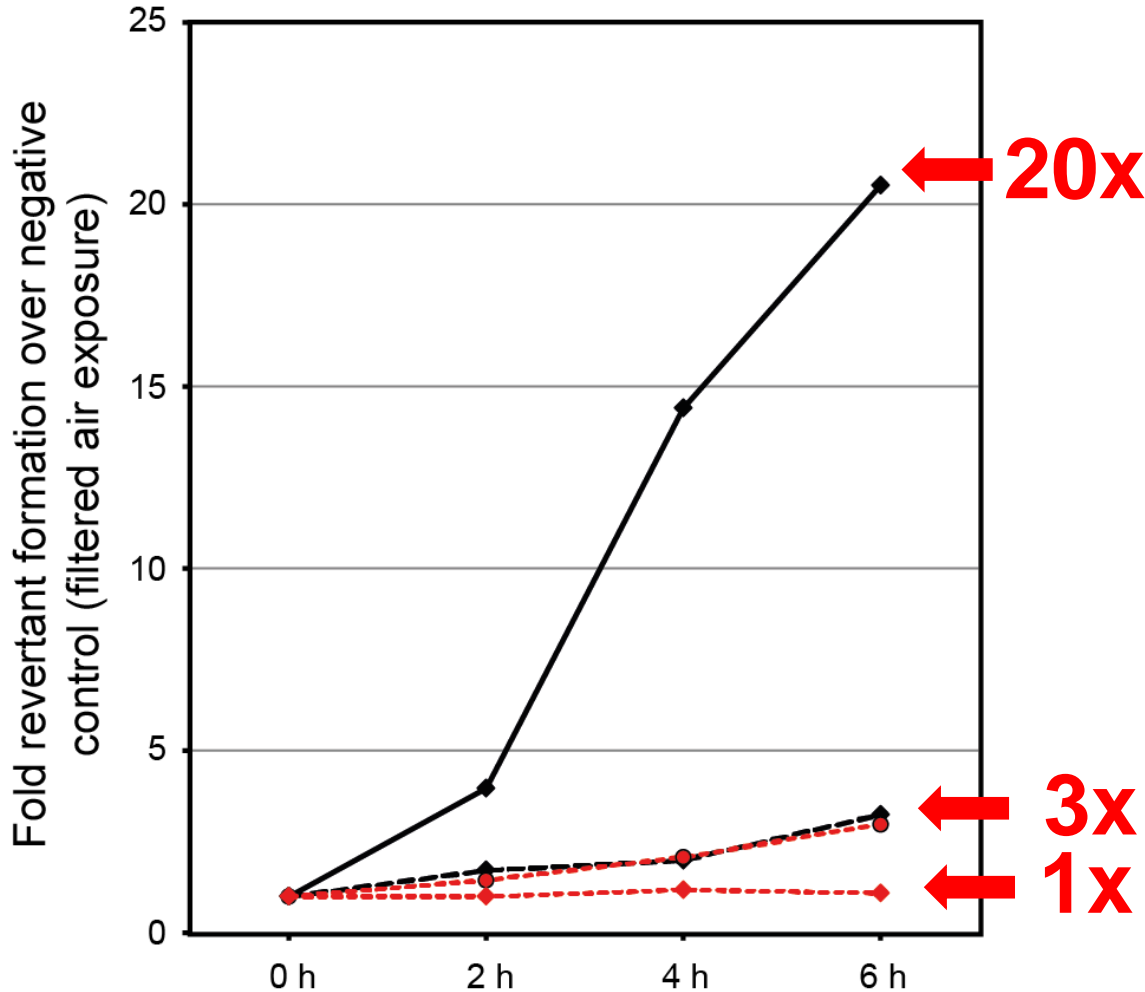
Non-treated diesel exhaust is genotoxic after 6 h, also with iron catalyst (Satacen)

Catalytic DPF lowered genotoxicity

Impact of DPFs on genotoxicity

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

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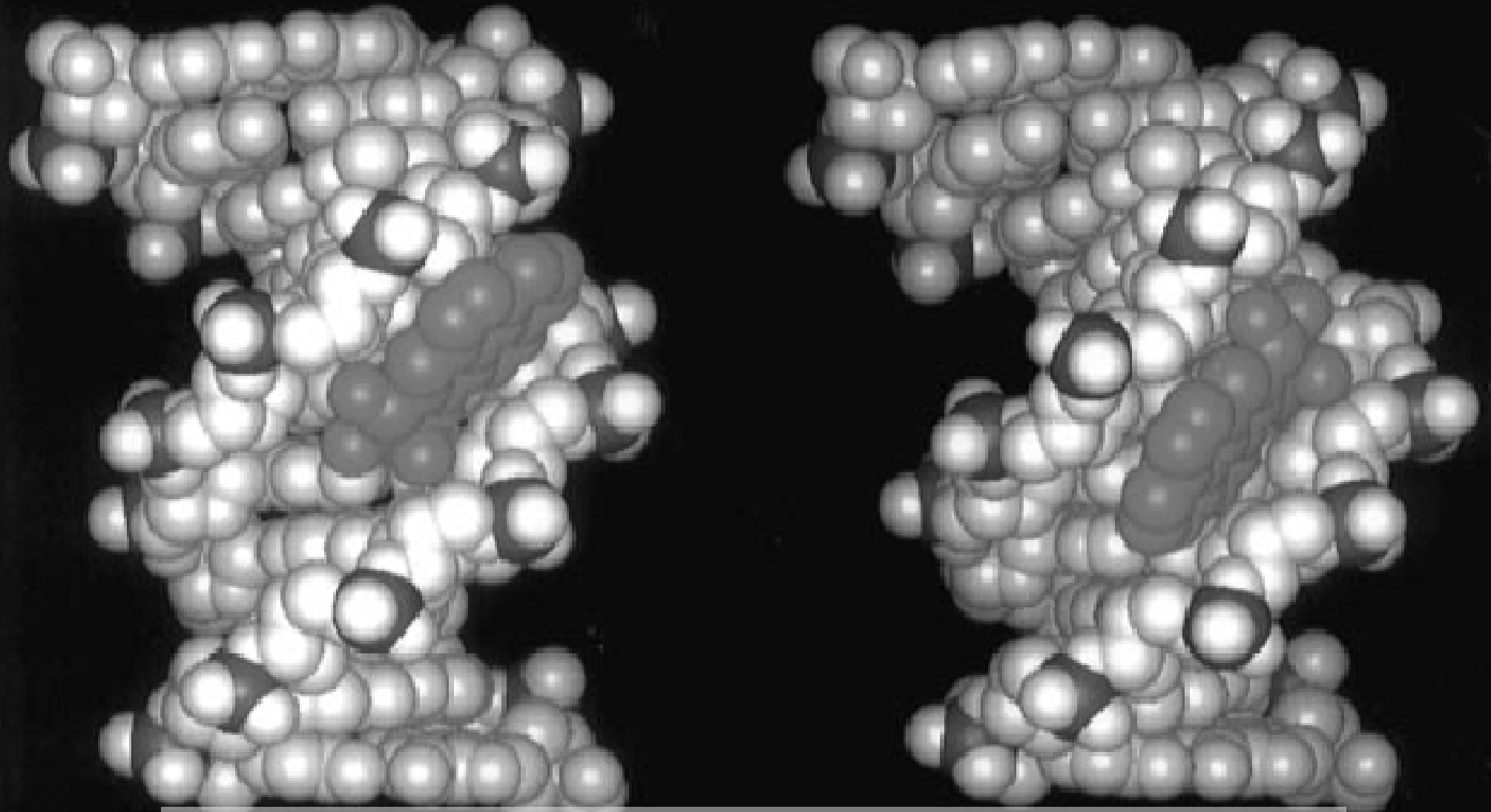


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Filtered diesel exhaust is
Filteration is not
enough! We need
catalytic filters
converting
genotoxic
compounds not
baking new ones!

Catalytic DPF lowered
genotoxicity

Carcinogenesis from benzo(a)pyrene

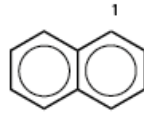


learn more on this in Maria Muñoz' talk in the health session

Polycyclic aromatic hydrocarbons

PAHs - a diverse class of compounds with variable physicochemical properties

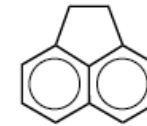
2- to 6-ring PAHs



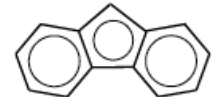
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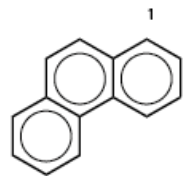
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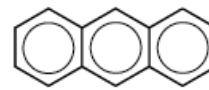
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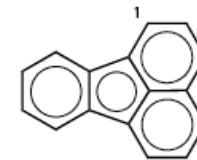
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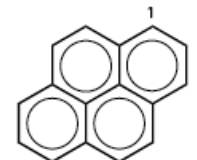
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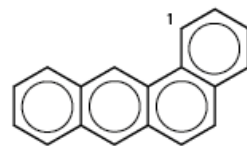
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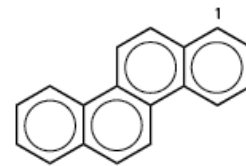
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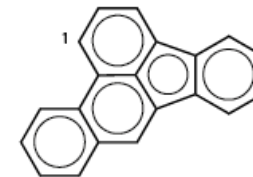
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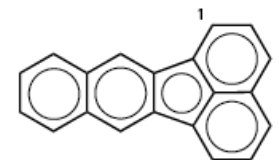
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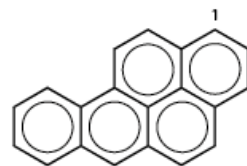
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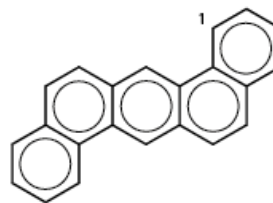
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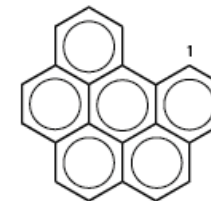
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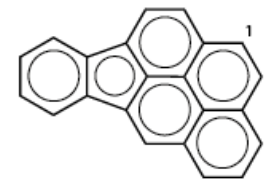
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15



16

Polycyclic aromatic hydrocarbons

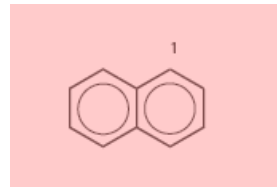
PAHs - a diverse class of compounds with variable physicochemical properties

2- to 6-ring PAHs

some PAHs are genotoxic

all PAHs are potential nitro-PAH precursors

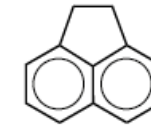
several nitro-PAHs are strong mutagens



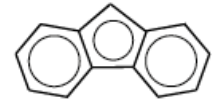
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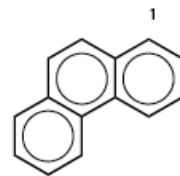
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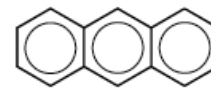
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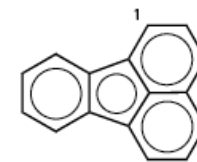
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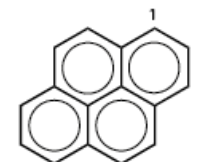
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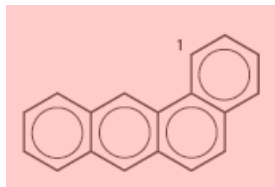
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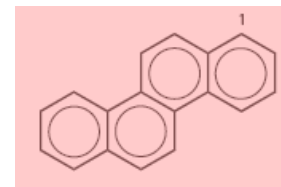
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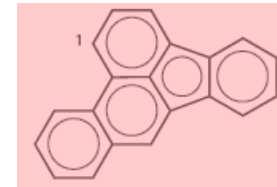
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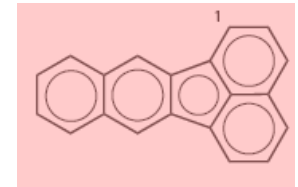
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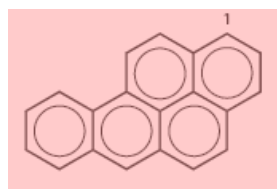
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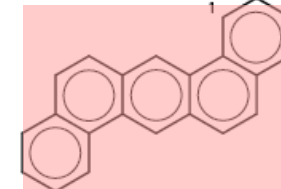
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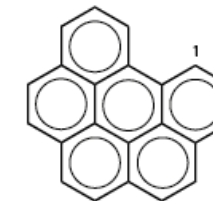
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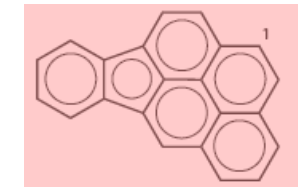
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PAH Penetration of a non-catalyzed DPF

Non-catalyzed filters are as efficient for soot. How about genotoxic compounds?

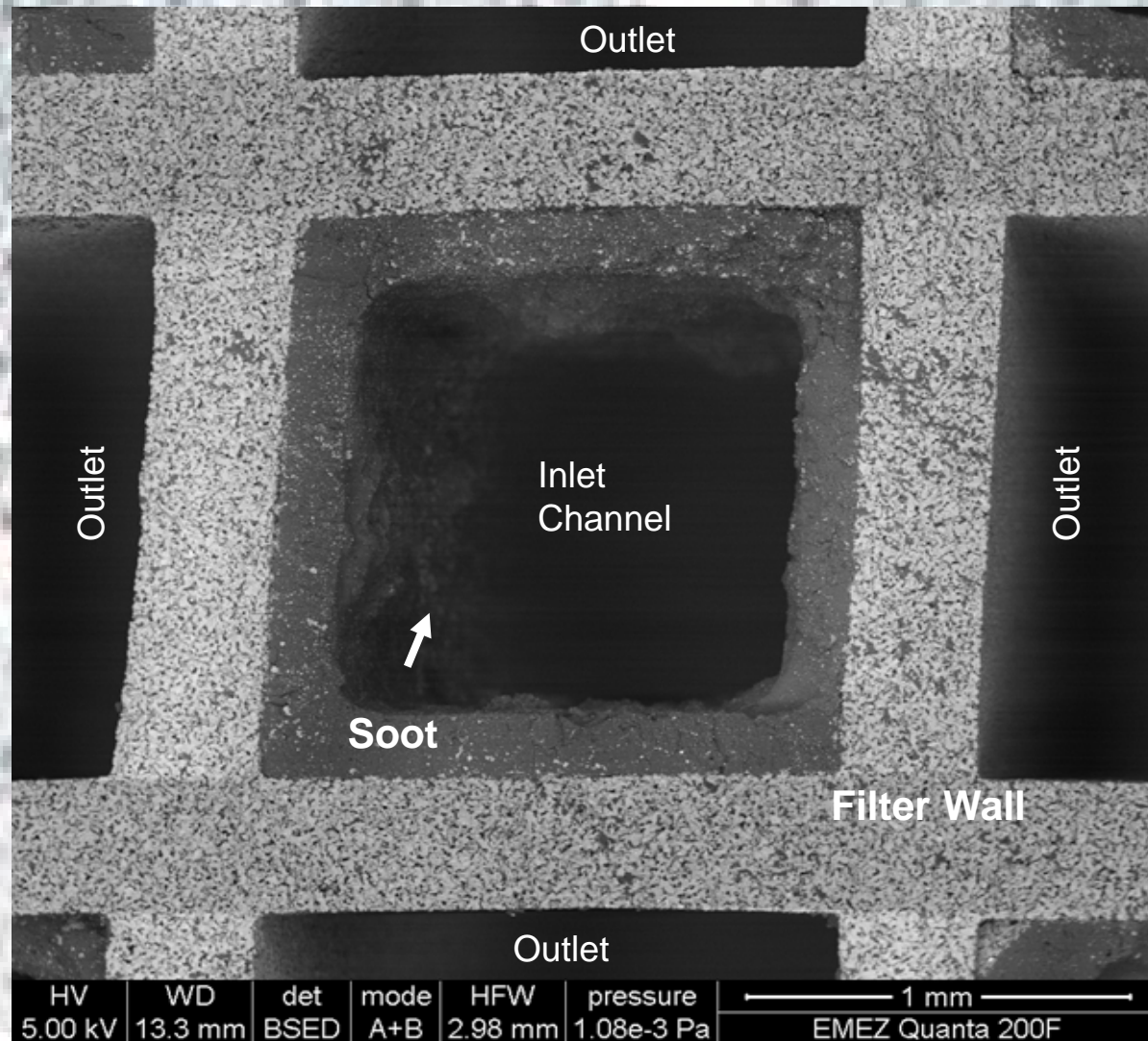
Non-catalyzed DPFs:

Accumulate soot (>98%)

Can PAHs penetrate soot loaded DPFs?

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

Do DPFs support a formation of toxic secondary pollutants like nitro-PAHs?



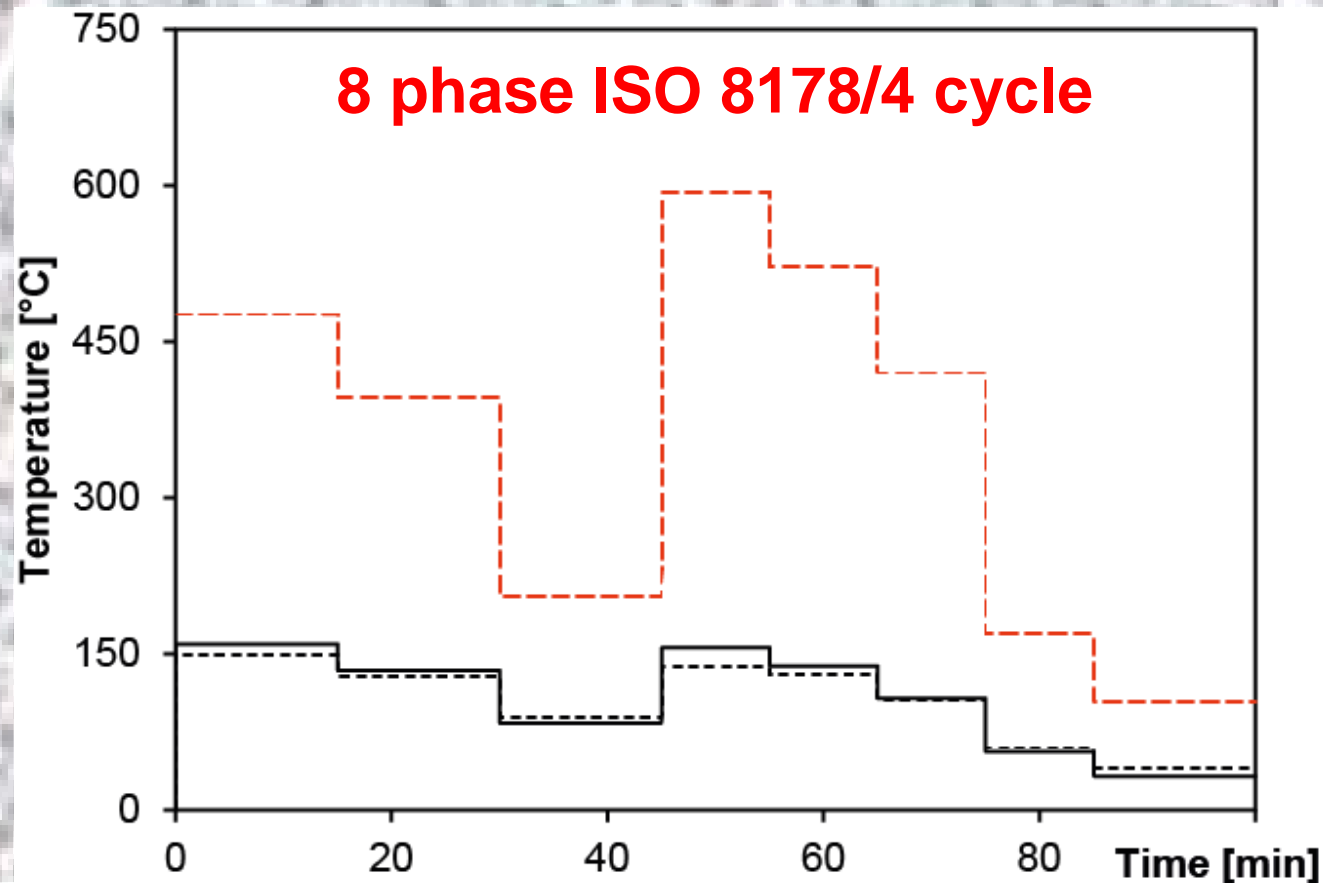
PAH penetration of a non-catalyzed DPF

Can PAHs penetrate non-catalyzed filters if operated $<200\text{ }^{\circ}\text{C}$?

We studied 2 cellulose-based filters, a new and a soot-loaded filter ($>2000\text{ h}$ road application)

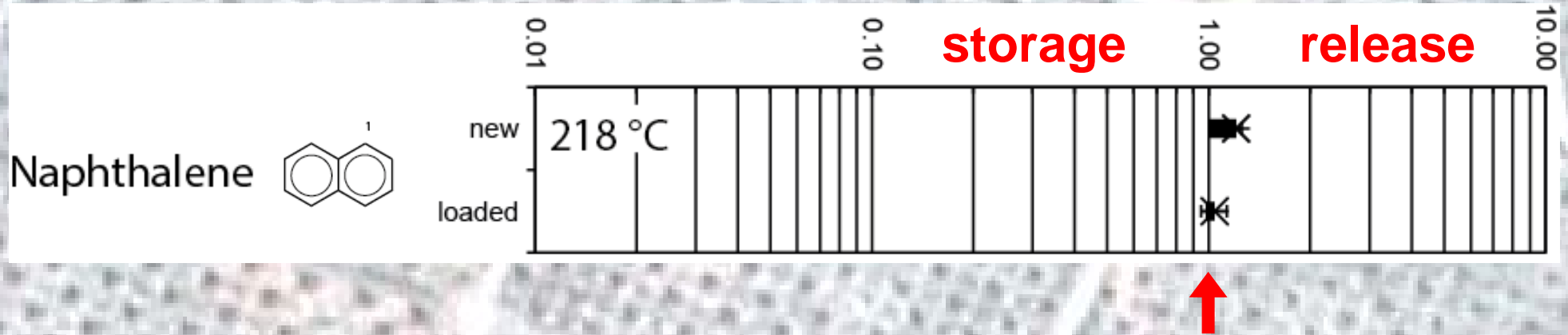
engine-out →

before DPF →
after DPF →



PAH penetration of a non-catalyzed DPF

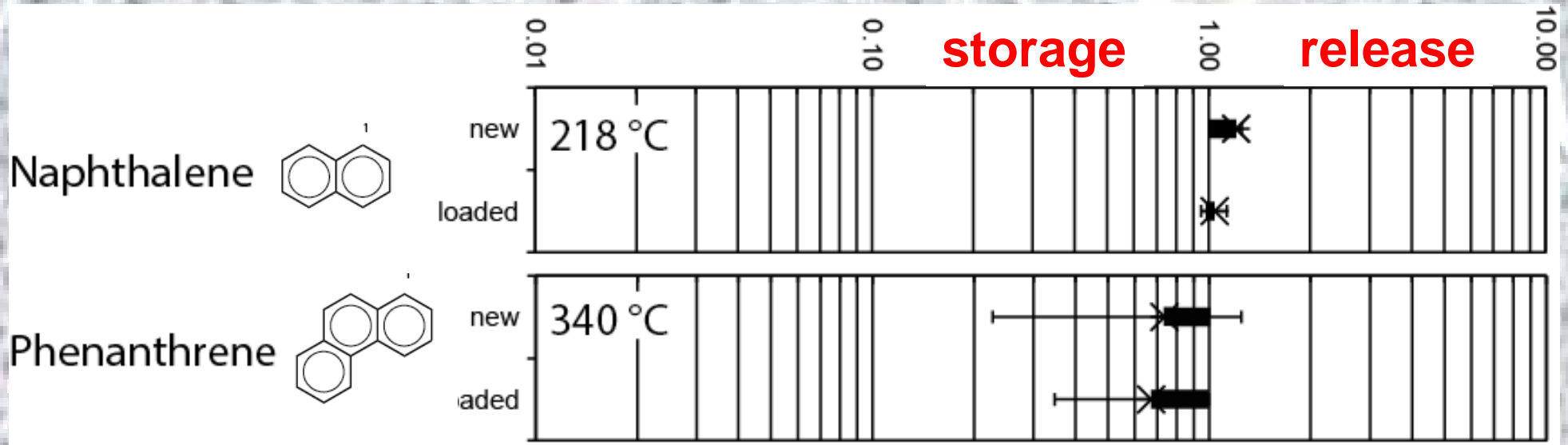
Non-catalyzed filter operated $<200\text{ }^{\circ}\text{C}$ do accumulate soot



- no retention of naphthalene in a new and a soot-loaded DPF
- naphthalene is too volatile, it escapes even from a cold filter ($<200\text{ }^{\circ}\text{C}$)

PAH penetration of a non-catalyzed DPF

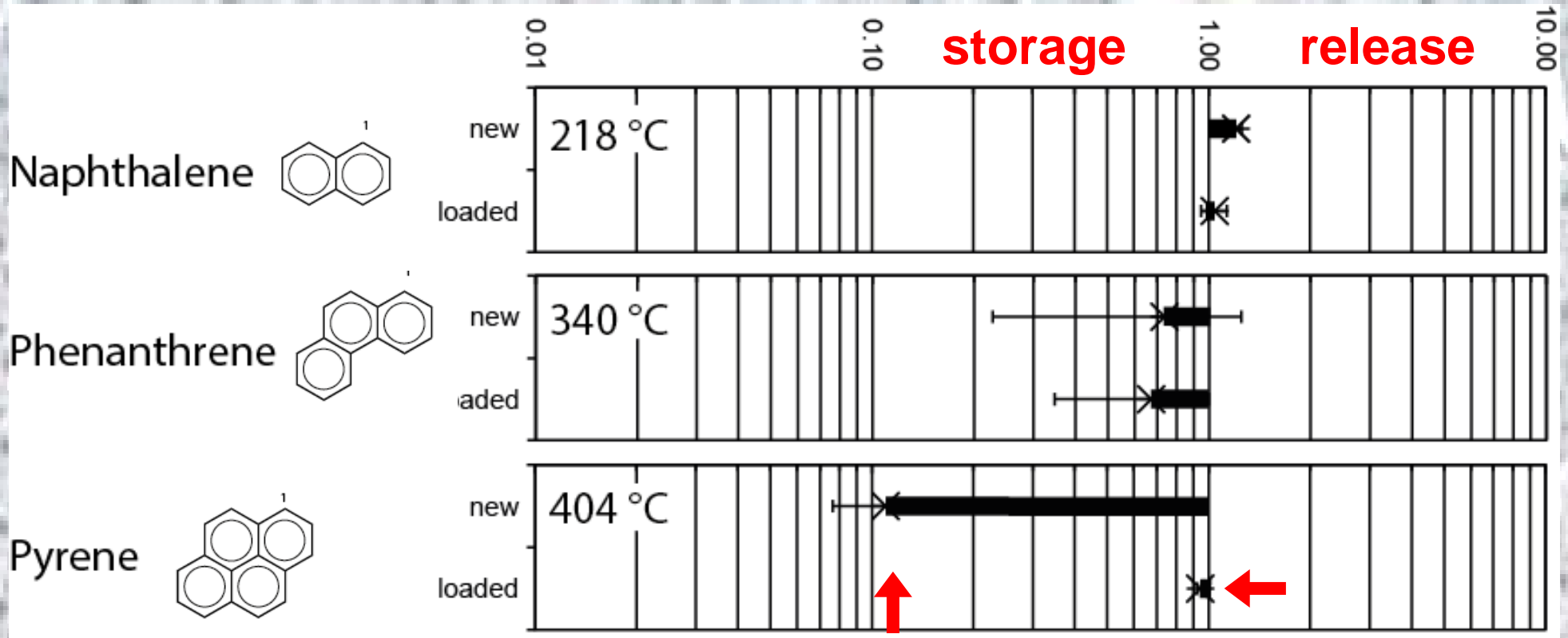
Non-catalyzed filter operated <200 °C do accumulate soot and some hydrocarbons



- about 30% retention, both in a new and a soot-loaded DPF
- Phenanthrene is partly stored in both filters (<200 °C).

PAH penetration of a non-catalyzed DPF

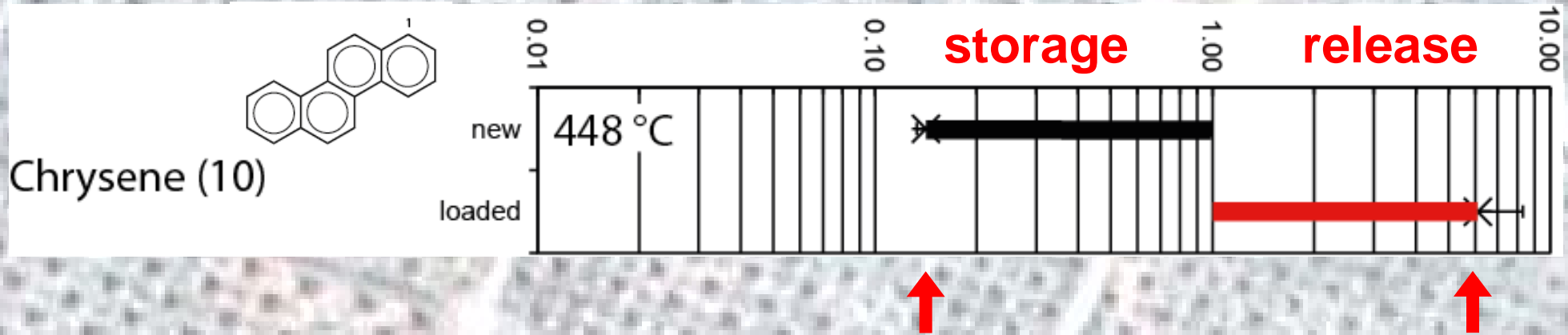
Non-catalyzed filter operated <200 °C do accumulate soot and some hydrocarbons



- 90% pyrene is retained in a new, only 5% in a soot-loaded DPF

PAH store-and-release in a non-catalyzed DPF

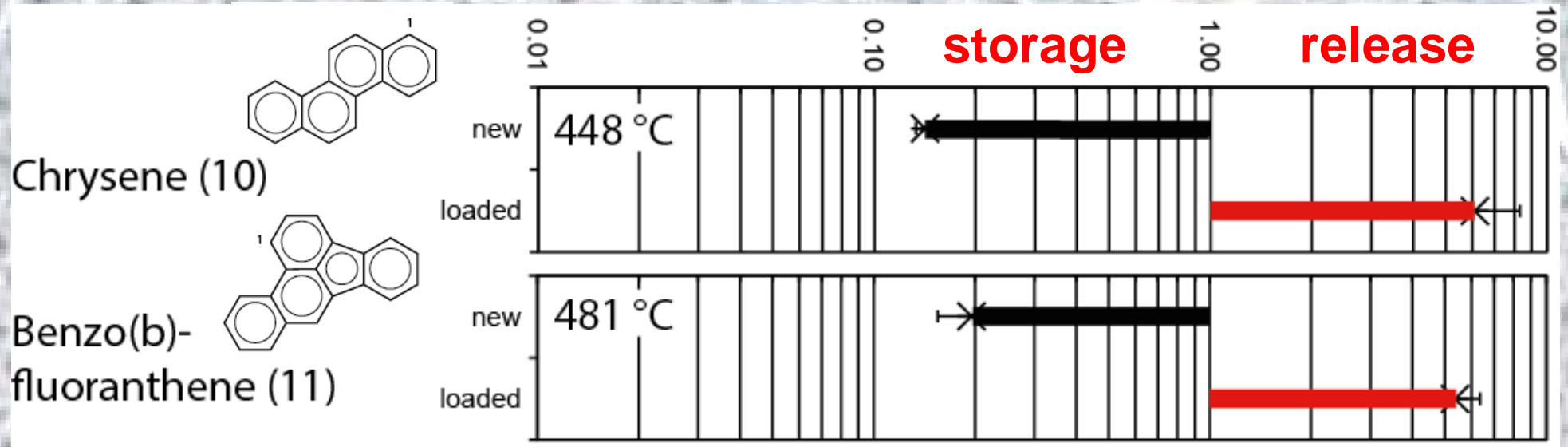
Non-catalyzed filter operated $<200\text{ }^{\circ}\text{C}$ do accumulate soot and some hydrocarbons



- 85% retention in the new DPF
- 6x higher emissions from the soot-loaded DPF

PAH store-and-release in a non-catalyzed DPF

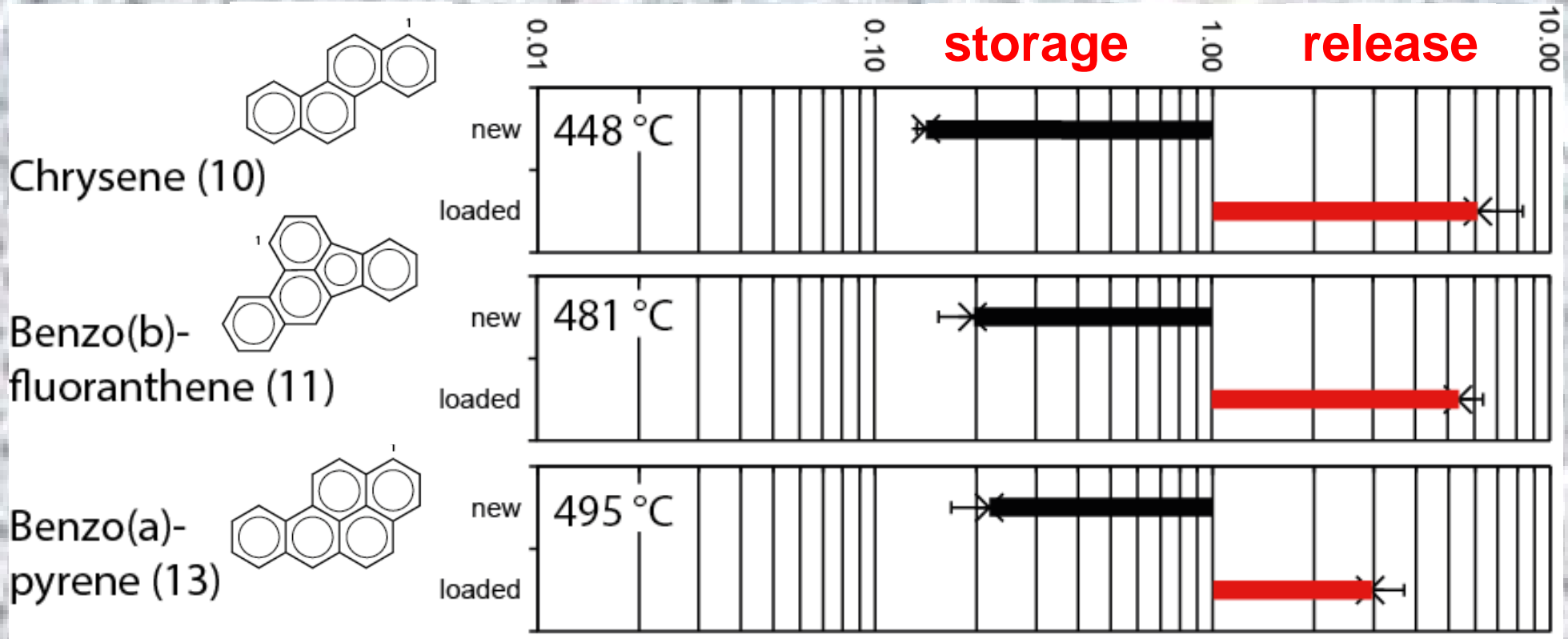
Non-catalyzed filter operated <200 °C do accumulate soot and hydrocarbons



- 80% benzo(b)fluoranthene is retained in the new DPF
- 5x higher emissions from the soot-loaded DPF

PAH store-and-release in a non-catalyzed DPF

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



- 80% retention of benzo(a)pyrene in the new DPF

- 3x higher emissions from the soot-loaded DPF

→ We can store and release PAHs from a non-catalyzed DPF

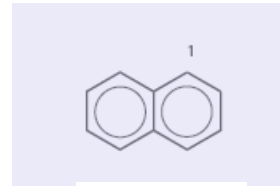
Polycyclic aromatic hydrocarbons

PAHs - a diverse class of compounds with variable physicochemical properties

2- to 6-ring PAHs

- **Volatile PAHs**
penetrate DPFs,
both new and soot
loaded once

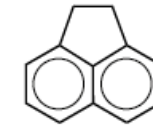
- **Semi-volatile PAHs**
are stored in new,
but can be released
again from soot
loaded DPFs



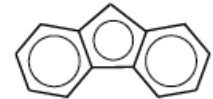
218 °C



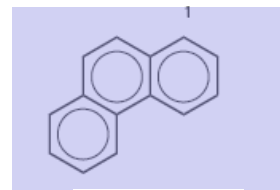
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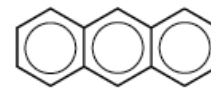
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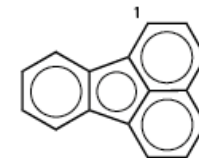
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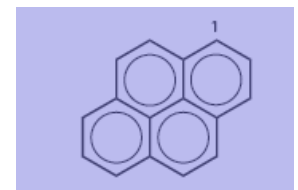
340 °C



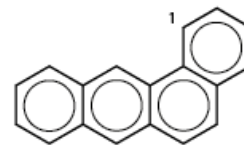
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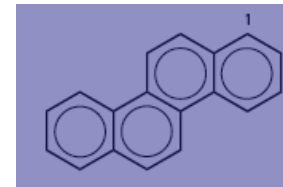
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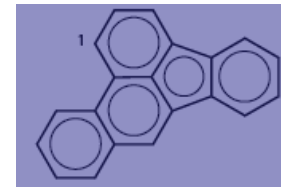
404 °C



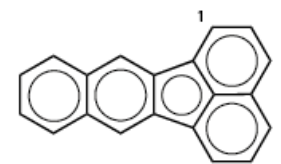
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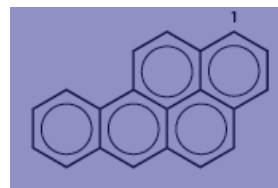
448 °C



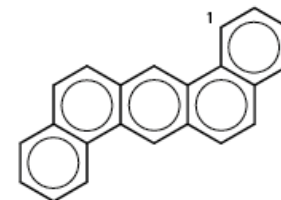
481 °C



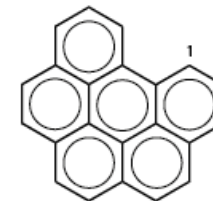
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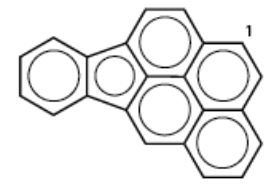
495 °C



14



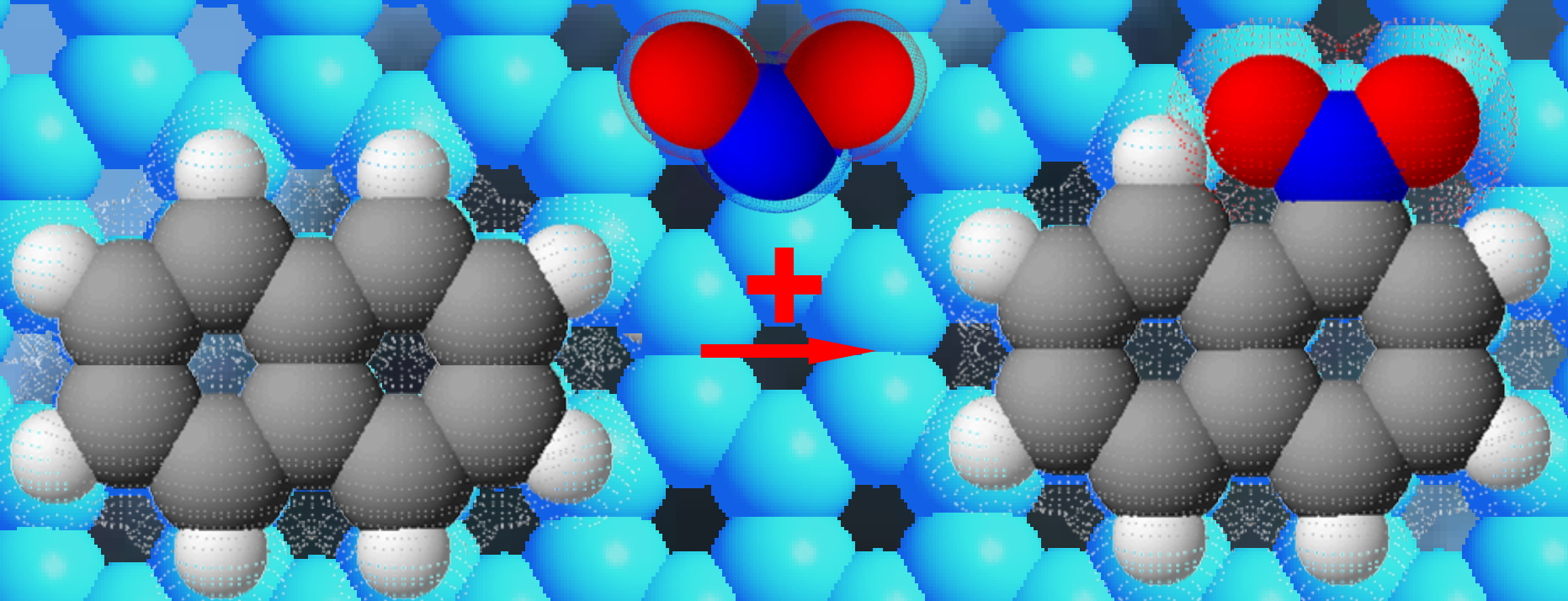
15



16

Soot catalyzed nitration of PAHs

From naphthalene to nitro-naphthalenes?

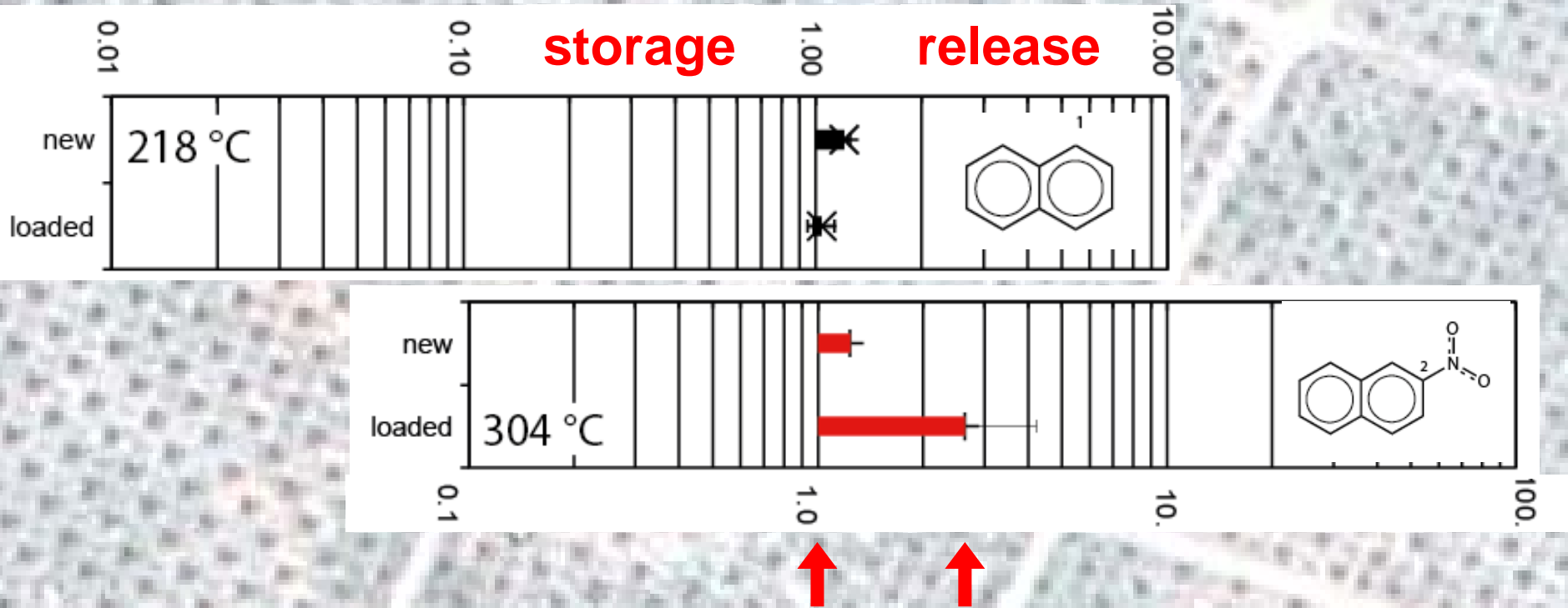


naphthalene

nitro-naphthalenes

Nitro-PAH formation in non-catalyzed DPF

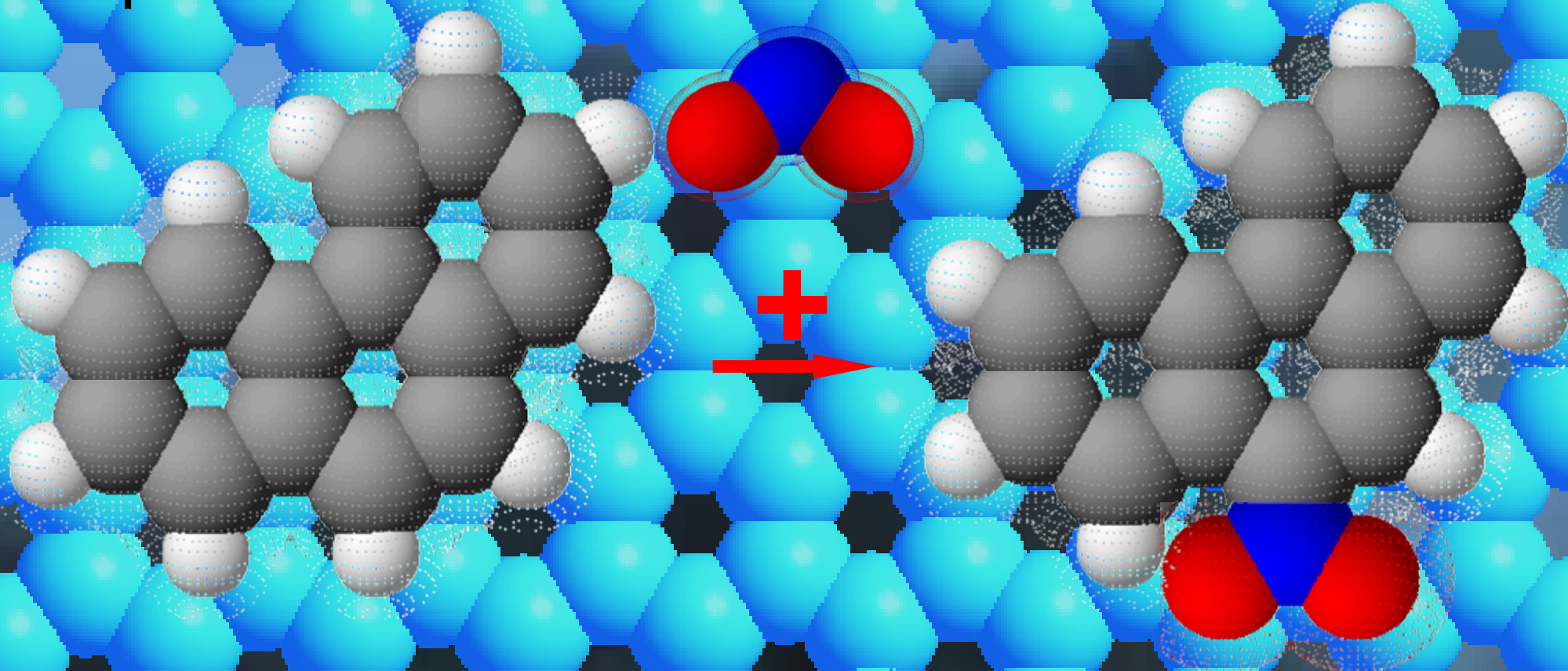
Non-catalyzed filter operated <200 °C to accumulate soot and hydrocarbons



- Naphthalene is not stored, neither in new nor soot-loaded DPFs
- However, some nitro-naphthalenes are stored and released again from a soot-loaded DPF (2x)

Soot catalyzed nitration of PAHs

Can phenanthrene adsorb on soot to be nitrated?

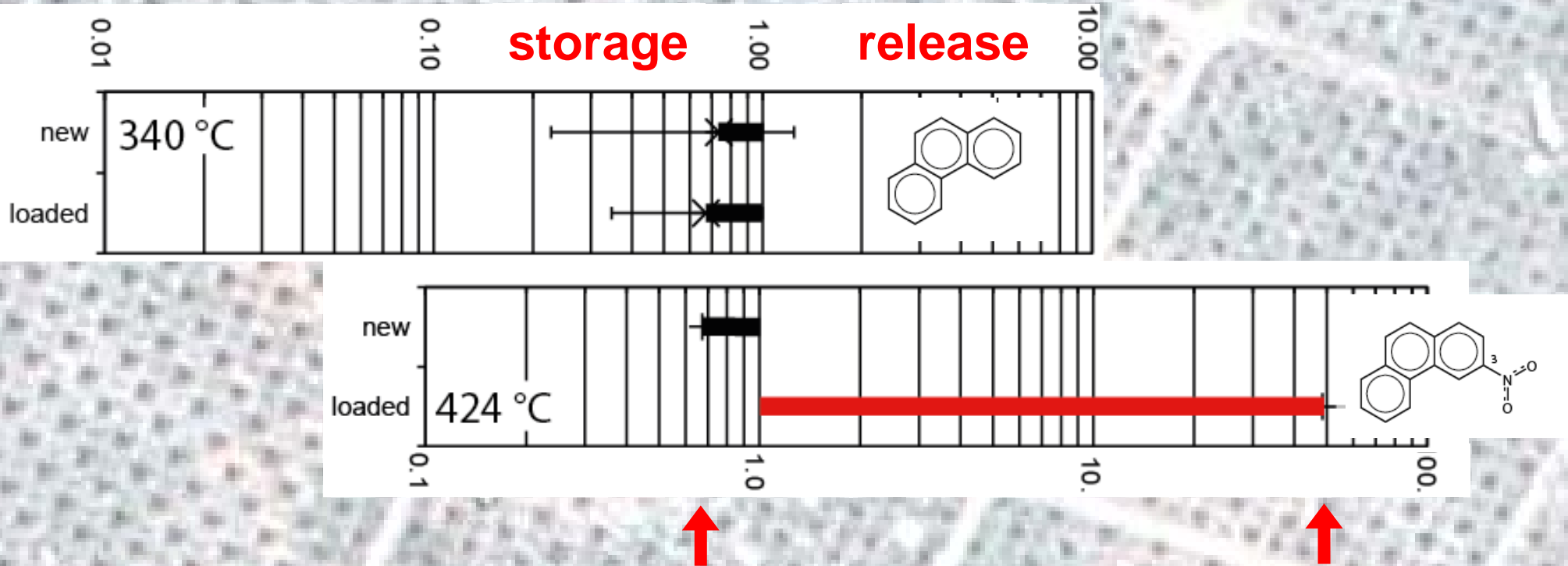


phenanthrene

nitro-phenanthrenes

Nitro-PAH formation in non-catalyzed DPF

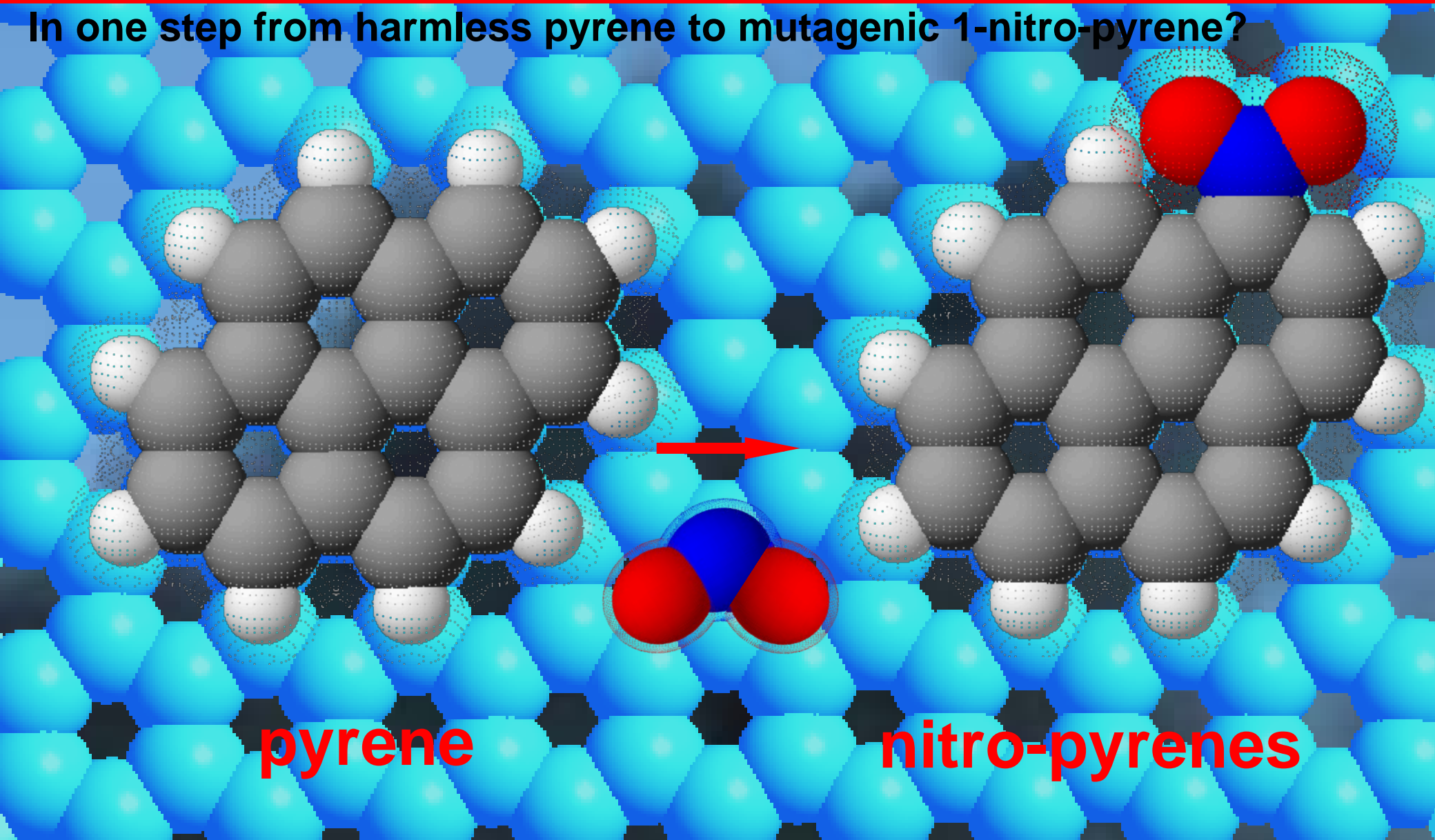
Non-catalyzed filter operated <200 °C to accumulate soot and hydrocarbons



- Some phenanthrene is stored in new and soot-loaded DPFs
- 3-nitro phenanthrene is stored in a new, but **formed** and **released** from a soot-loaded DPF (**50x**)

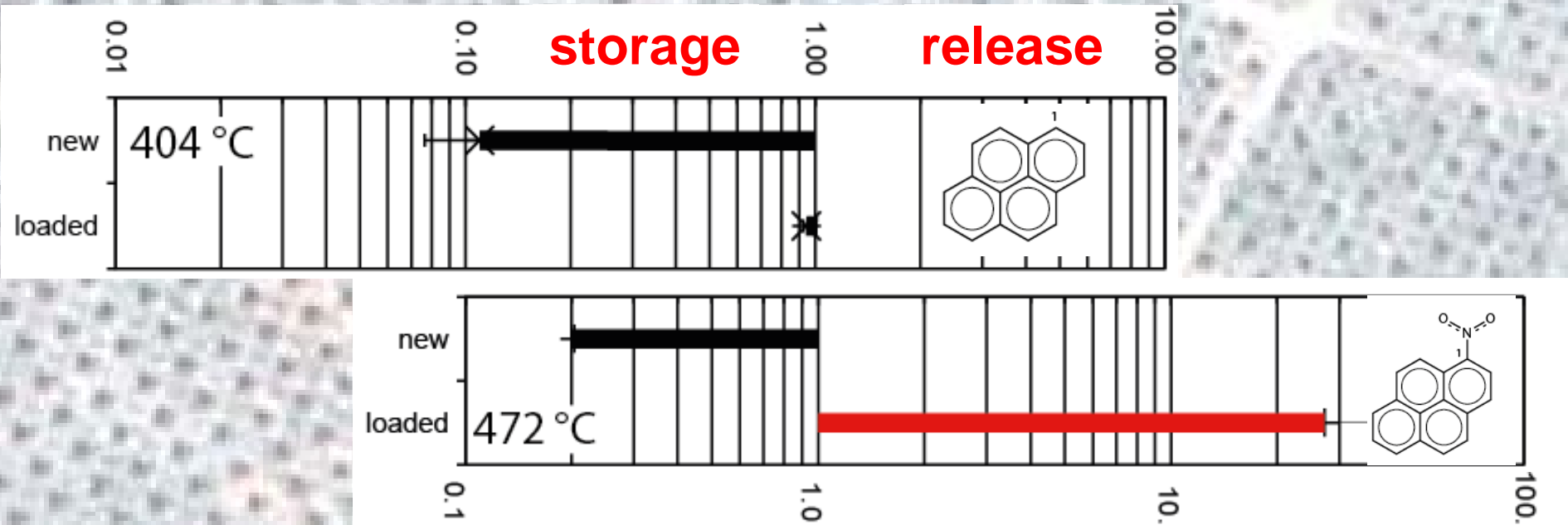
Soot catalyzed nitration of PAHs

In one step from harmless pyrene to mutagenic 1-nitro-pyrene?



Nitro-PAH formation in non-catalyzed DPF

Non-catalyzed filter operated $<200\text{ }^{\circ}\text{C}$ to accumulate soot and hydrocarbons

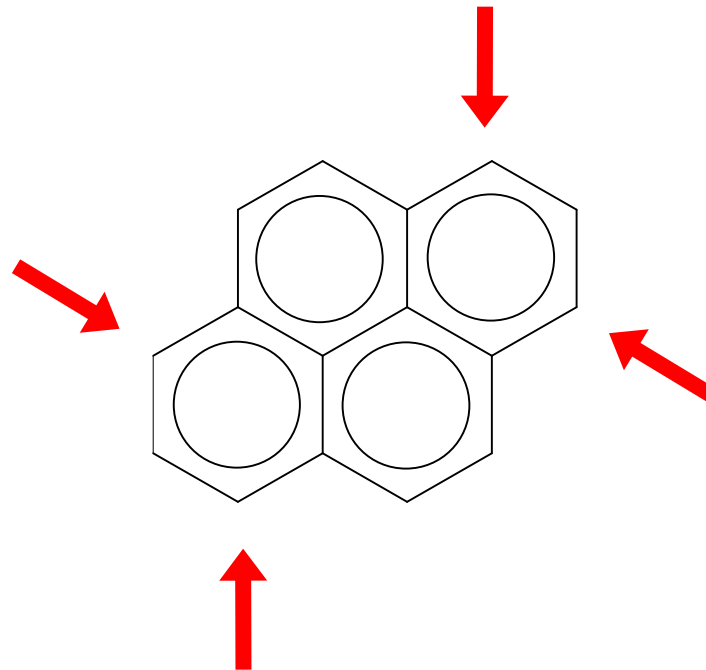


- pyrene is stored in a new, but released from a soot-loaded DPF
- 1-nitro pyrene is stored in a new, but **formed** and **released** from a soot-loaded DPF (**30x**)

The DPF – a chemical reactor

Nitration in alpha-position?

Regioselective nitration of pyrene



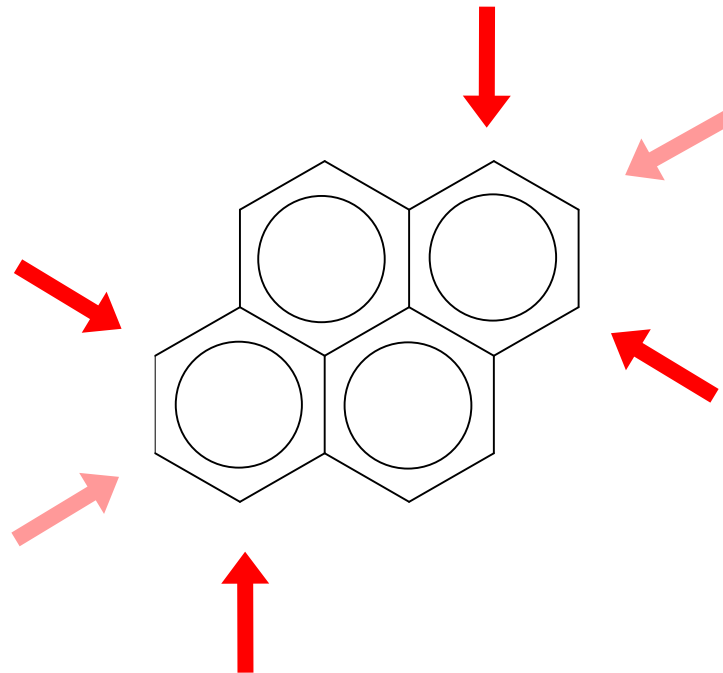
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The DPF - a chemical reactor

or in beta-position?

Regioselective nitration of pyrene



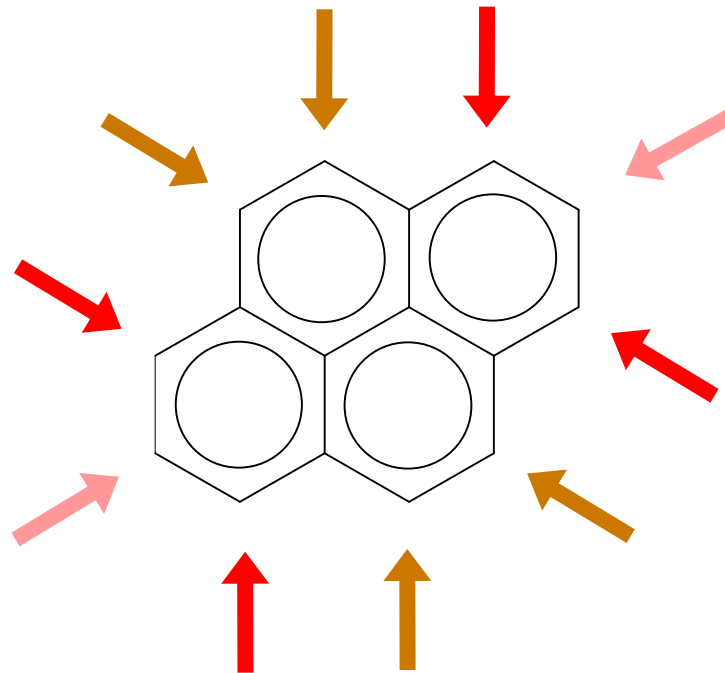
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The DPF - a chemical reactor

or in gamma-position?

Regioselective nitration of pyrene



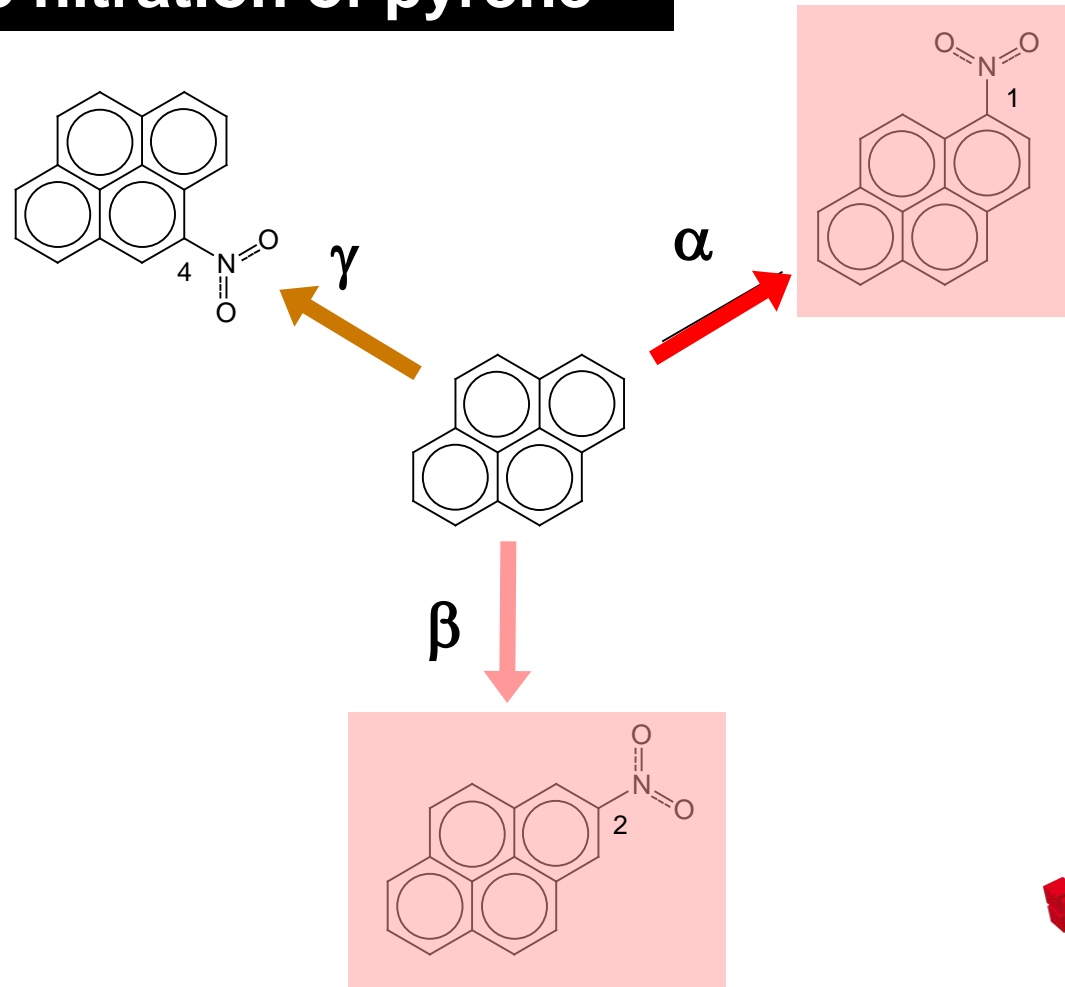
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The DPF - a chemical reactor

Two of the three isomers are mutagenic.

Regioselective nitration of pyrene



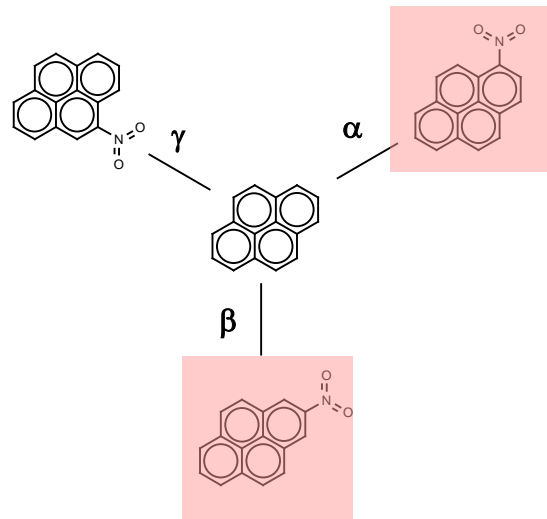
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The DPF - a chemical reactor

If nitration is possible ones, why not twice?

Nitration of nitropyrenes

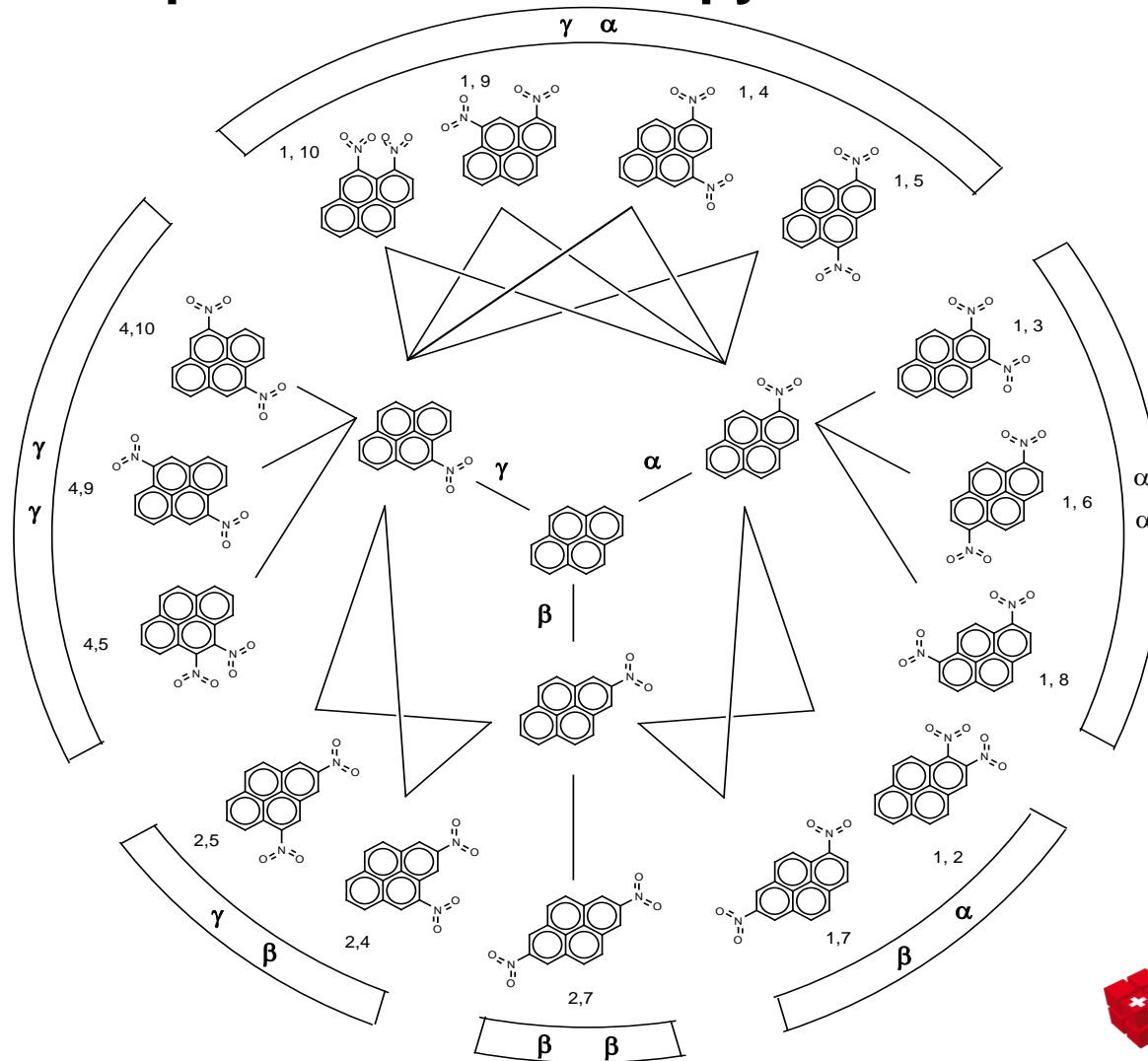


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The DPF - a chemical reactor

From one precursor to 3 nitropyrenes to 15 dinitropyrenes?



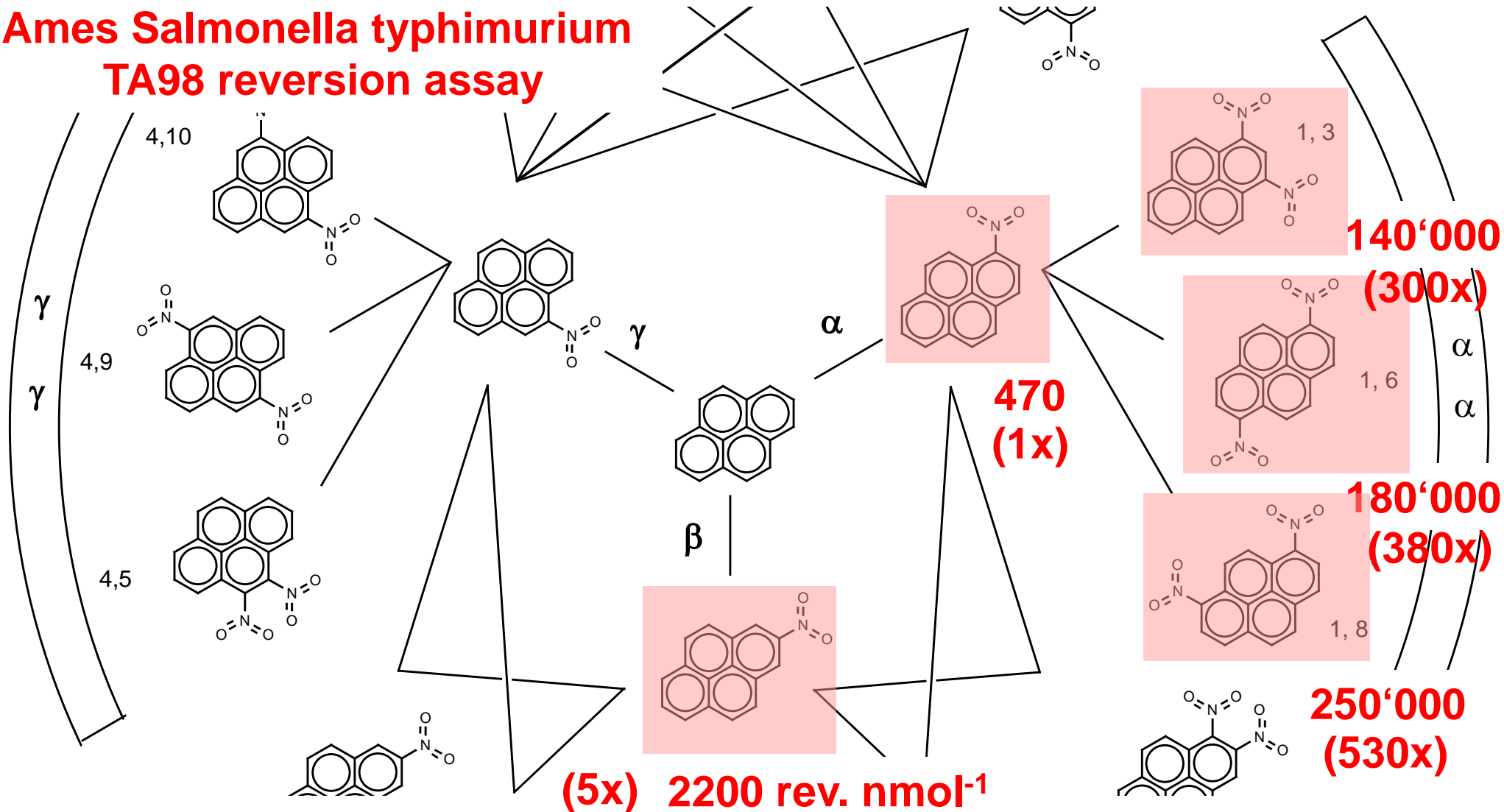
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The DPF - a chemical reactor

The most potent direct-acting mutagens known are dinitropyrenes

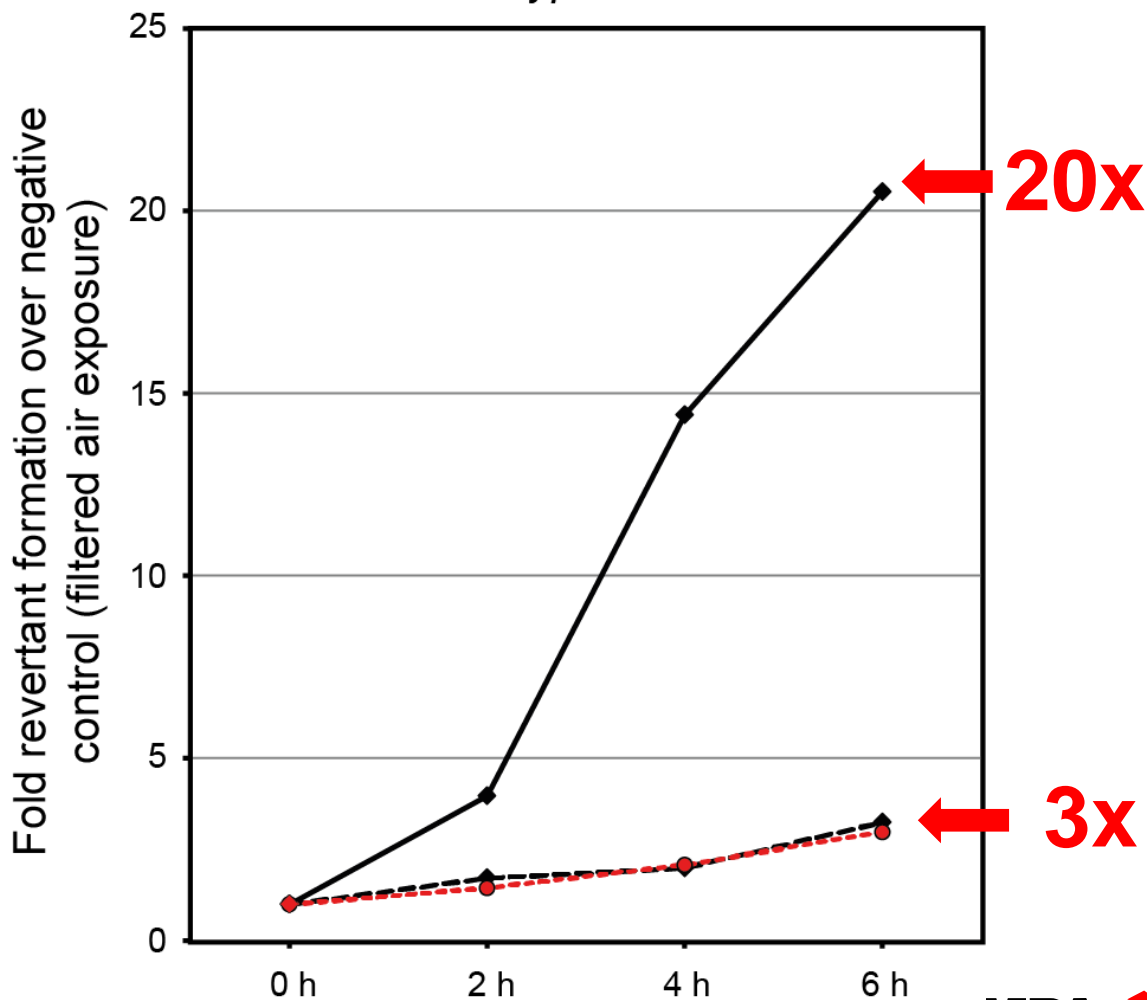
**Ames Salmonella typhimurium
TA98 reversion assay**



Impact of DPFs on genotoxicity

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

Salmonella typhimurium TA100



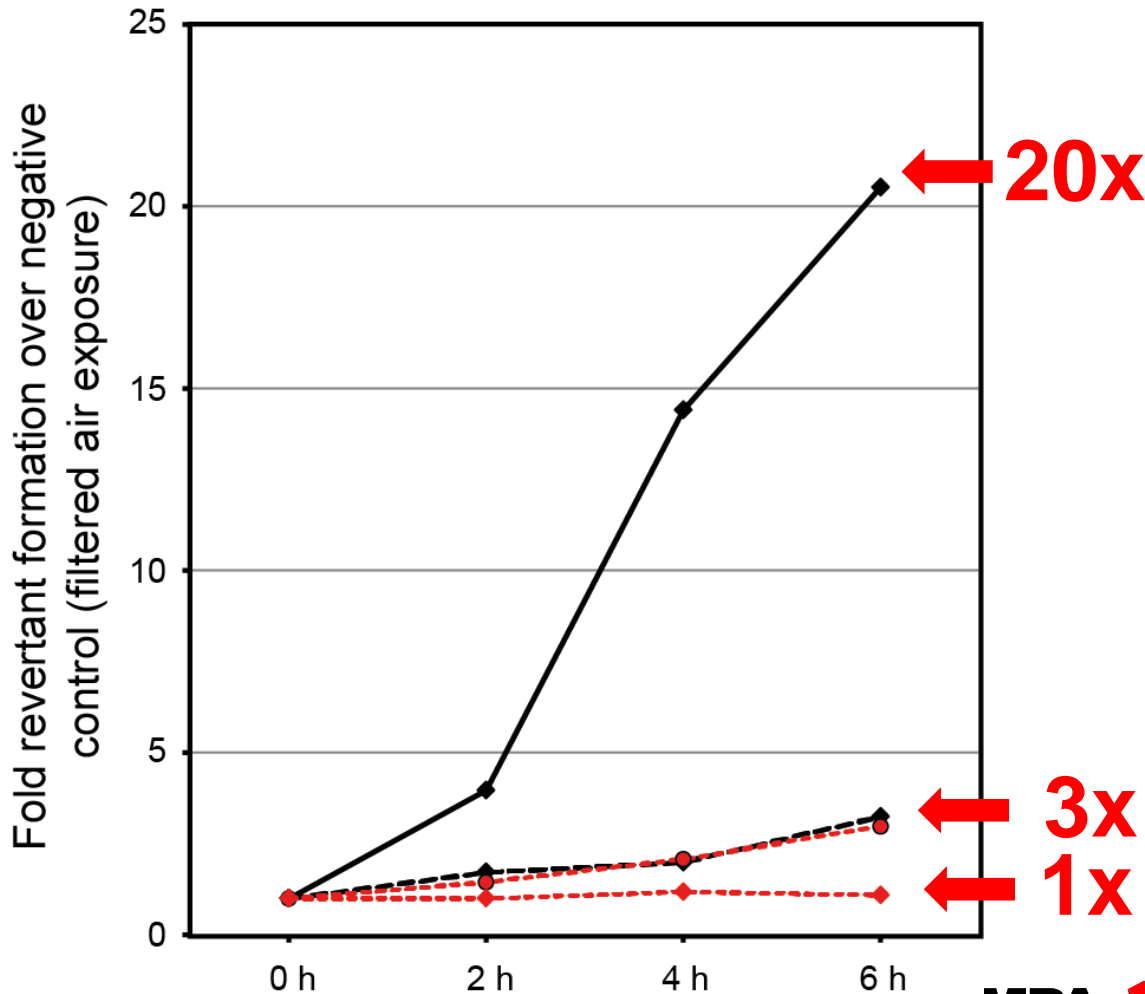
Filtered diesel exhaust can even be more genotoxic!

Non-treated diesel exhaust is genotoxic after 6 h

Impact of DPFs on genotoxicity

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

Salmonella typhimurium TA100



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

Filtered diesel exhaust is
Filteration is not
enough! We need
catalyzed filters
converting
genotoxic
compounds not
baking new ones!

Catalytic DPF lowered
genotoxicity

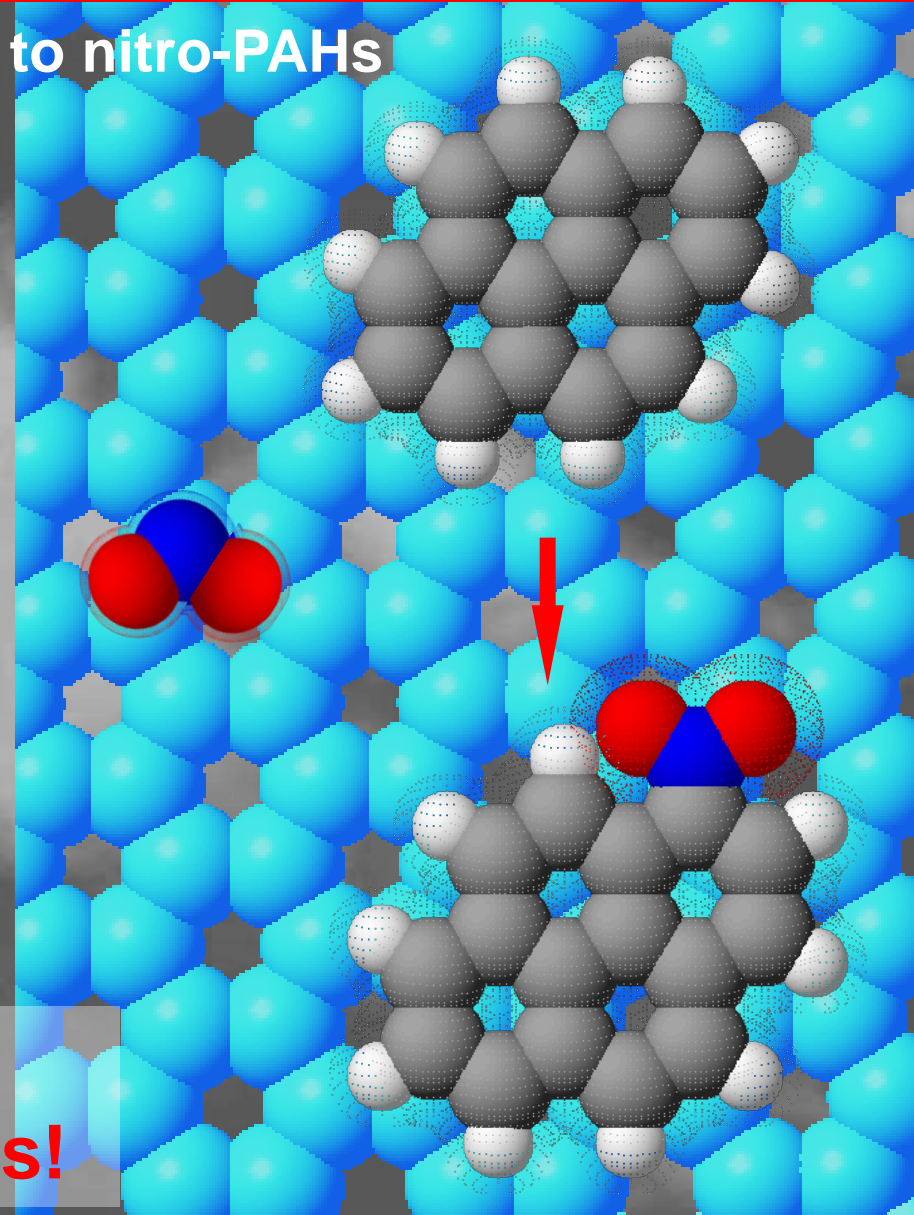
Non-catalyzed DPFs are chemical reactors

Co-release of NO_x , soot and PAHs leads to nitro-PAHs

Problem: Genotoxicity

- **Non-filtered** diesel exhaust is **genotoxic**
- Filtration of soot is not enough to remove all genotoxic compounds
- **Nitration reactions** in DPFs can produce **mutagenic nitro-PAHs**

We need catalytic converters that remove NO_x , soot and PAHs!



Catalysis, a key property of particle filters to lower genotoxicity of diesel exhaust

A combined effort with many important contributions

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- **Filter- & catalyst manufacturers:** >40 different diesel particulate filter systems



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SOCIÉTÉ SUISSE DE CHIMIE SSC
SWISS CHEMICAL SOCIETY SCS

Traugott Sandmeyer (1854-1922)