Secondary effects of catalytic diesel particulate filters: Conversion of PAHs versus formation of Nitro-PAHs

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Abstract: Ultra-fine particle emissions from diesel-fueled vehicles have a major impact on the respiratory air quality at work places. Diesel soot particles, with typical diameters of 10-200 nm, are small enough to pass the alveolar membrane, reaching the blood system. Diesel soot is rated as carcinogenic to humans and is acting as a carrier for several carcinogenic, mutagenic, and endocrine-disrupting compounds.

Diesel particulate filters (DPFs) are a promising technology to detoxify diesel exhaust. However, the post-combustion of trapped soot and adsorbed compounds may also induce the formation of new pollutants. The Swiss VERT procedures for DPF approval not only include a thorough evaluation of the filtration efficiency, they also require a comprehensive assessment of toxic compounds potentially formed in the catalytic converter (VERT secondary emission test, VSET). This includes an assessment of the *de novo* formation potential of polychlorinated dibenzodioxins/furans (PCDD/F), a detailed analysis of DPF-effects on known genotoxic compounds, and an analysis of metal penetration either from fuel additives or catalytic coatings [1]. Details on the currently applied VERT procedures are now documented in a Swiss national standard [2].

Herein we report effects of two cordierite-based, monolithic, wall-flow DPFs on the emissions of genotoxic polycyclic aromatic hydrocarbons (PAHs), assess the risks of a trap-induced nitro-PAH formation, and compare these findings with those of two reporter gene bioassays sensitive to aryl hydrocarbons (AHs) and to estrogenic compounds. Soot combustion was either catalyzed with an iron- or a copper/iron-based fuel additive (fuel-borne catalysts). A heavy duty diesel engine, operated according to the 8-stage ISO 8178/4 C1 cycle, was used as test platform.

Emissions of all investigated 4- to 6-ring PAHs were reduced by about 40-90%, including those rated as carcinogenic. Emissions of 1- and 2-nitronaphthalene increased by about 20-100%. Among the 3-ring nitro-PAHs, emissions of 3-nitrophenanthrene decreased by about 30%, whereas 9-nitrophenanthrene and 9-nitroanthracene were found only after DPFs. In case of 4-ring nitro-PAHs, emissions of 1-nitropyrene, 4-nitropyrene, and 3-nitrofluoranthene decreased by about 40-60% with DPFs [3].

Total AH-receptor (AHR) agonist concentrations of diesel exhaust were lowered by 80-90%, when using iron- and copper-based DPFs [4]. The tested PAHs accounted for <1% of the total AHR-mediated response, indicating that considerable amounts of other aryl hydrocarbons must be present in filtered and unfiltered diesel exhaust. We conclude that both DPFs substantially detoxified diesel exhaust with respect to total aryl hydrocarbons, including the investigated carcinogenic PAHs. But we also noticed a secondary formation of certain nitro-PAHs. Nitration reactions were found to be stereoselective with a preferential substitution of hydrogen atoms at peri-positions. The stereoisomers obtained are related to combustion chemistry, but differ from those formed upon atmospheric nitration of PAHs [3]. Similarly, the estrogenic activity of filtered and unfiltered exhaust were compared with an estrogen-receptor (ER)-based bioassay [5]. Both DPFs lowered the estrogenic activity by 55% and 66%, respectively, indicating that the majority of estrogen-like compounds are successfully removed in the filters [5].

The PCDD/F formation potential of both traps has been assessed as well and reported before [6]. As the major finding, we showed that the iron-catalyst DPF did not support a PCDD/F formation, even under worst case conditions, whereas the copper-based system clearly catalyzed a *de novo* formation of PCDD/Fs. Emissions increased by up to three orders of magnitude. This substantial increase of the PCDD/F emissions in case of the copper-catalyzed DPF was decided to be unacceptable [7]. Consequently, only the iron-system was recommended for approval, and the copper-catalyzed trap was excluded from the VERT-filter list [8].

Based on such findings, VERT-approved DPFs are now considered as best available technology to reduce both, soot particles and genotoxic PAHs such as benzo(a)pyrene from diesel exhaust. Consequently, several national occupational health authorities responsible for respiratory air quality at work places such as mining and tunneling, have decided that DPF use is mandatory for certain applications [9].

The presented data indicates that a comprehensive assessment of current and future exhaust gas treatment systems should also include investigations on a secondary formation of toxic pollutants (secondary poisoning).

Toxic secondary pollutants can also form in other exhaust gas treatment systems, e.g. an intense formation of ammonia in noble metal-based three-way catalysts has been reported [10,11]. Currently, several deNOx-technologies are developed for diesel vehicle applications. Especially the selective catalytic reduction system (SCR), relying on the thermal decomposition of urea to ammonia, the latter is used as the reducing agent for NOx reduction, has the potential for additional secondary pollutants not yet considered. Therefore, we strongly emphasize the need of a comprehensive risk assessment for such new catalytic DeNOx-systems as well, possibly prior to mass distribution [12].

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References:

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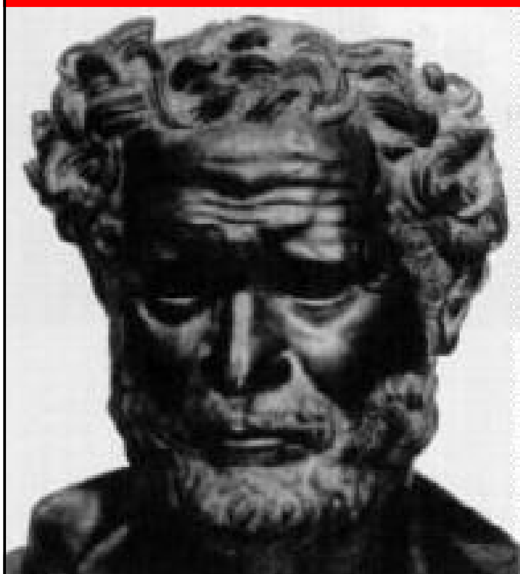
12th ETH Conference on Combustion Generated Nanoparticles
Zürich, June 23rd-25th, 2008

Relevance of secondary pollutants



Heraclitus (ca. 540 B.C. - 475 B.C.)

Heraclitus' philosophy in two words:

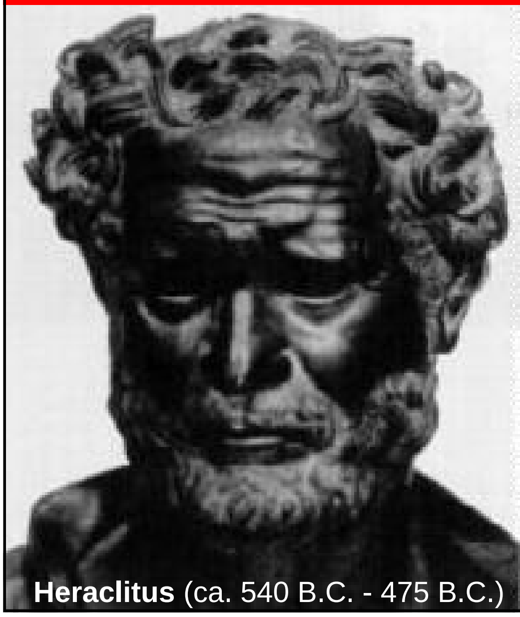
"panta rei"

Everything flows

or

There is nothing permanent except change

Relevance of secondary pollutants



Heraclitus (ca. 540 B.C. - 475 B.C.)

Heraclitus' philosophy in two words:

"panta rei"

Everything flows

or

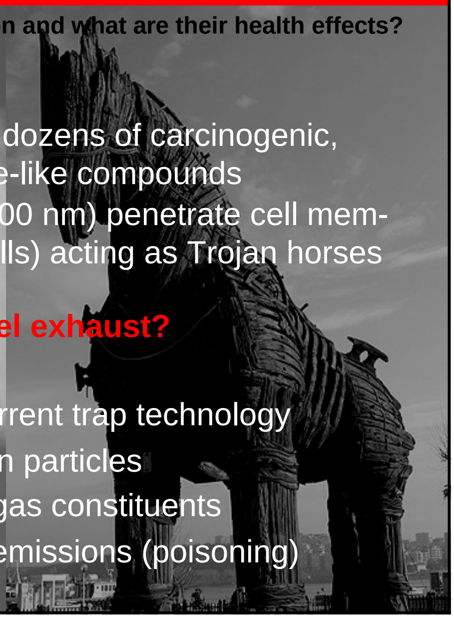
There is nothing permanent except change

or

from a chemist's perspective:

There must be a lot of chemistry involved to convert a black cloud of diesel exhaust into colorless CO_2 and H_2O

The particulate trap - a chemical reactor



What are the products of soot combustion and what are their health effects?

Problems:

- Diesel exhaust contains dozens of carcinogenic, mutagenic, and hormone-like compounds
- Diesel nanoparticles (<100 nm) penetrate cell mem-branes (alveoli, blood cells) acting as Trojan horses

Do DPFs detoxify diesel exhaust?

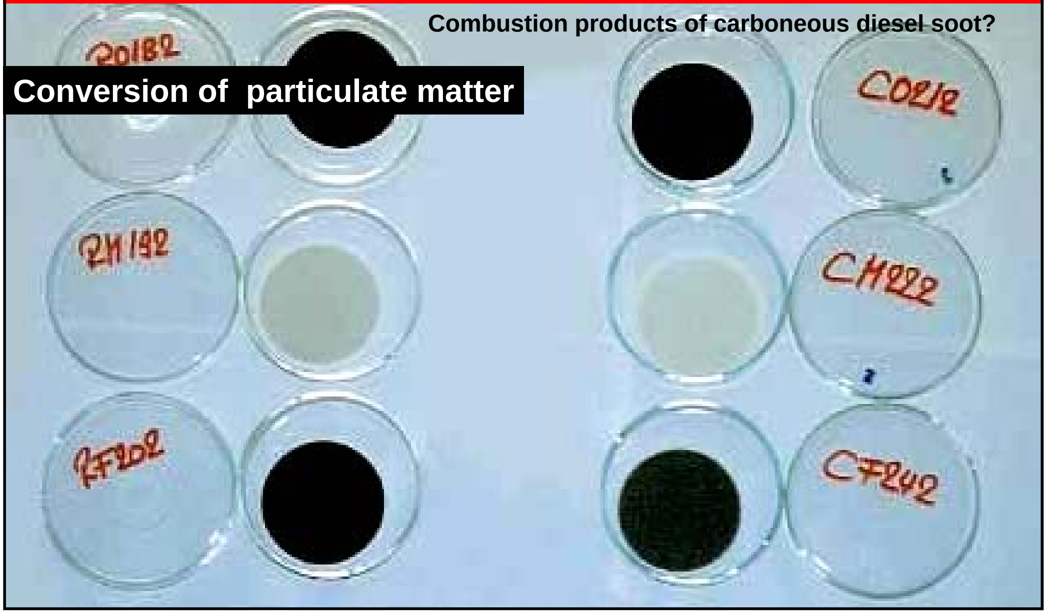
VERT-goals:

- Benefits and Risks of current trap technology
- Effectiveness of DPFs on particles
- Effects of toxic exhaust gas constituents
- Potential for secondary emissions (poisoning)

Catalytic decomposition of diesel soot

Combustion products of carboneous diesel soot?

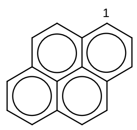
Conversion of particulate matter



Genotoxic polycyclic aromatic hydrocarbons

What about emissions of genotoxic PAHs?

Carcinogenic PAH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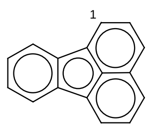
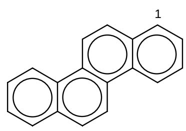
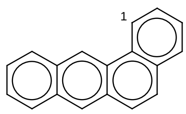
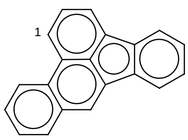
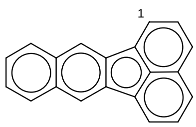

Fluoranthene


Chrysene


Benz(a)anthracene


Benzo[b]-
fluoranthene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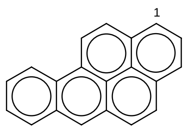
Benzo[a]-
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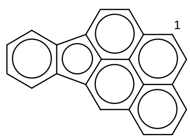
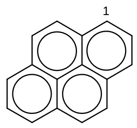
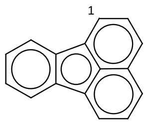

Indeno(1,2,3-cd)-
pyrene

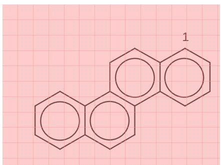
Genotoxic polycyclic aromatic hydrocarbons

Six PAHs are carcinogenic according to WHO

Carcinogenic PAH


Pyrene


Fluoranthene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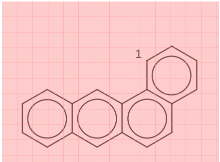
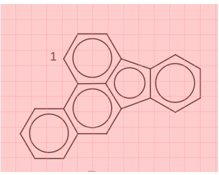
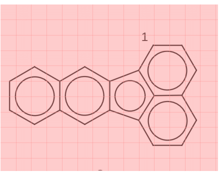

Benz(a)anthracene


Benzo[b]-
fluoranthene


Benzo[k]-
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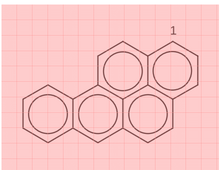
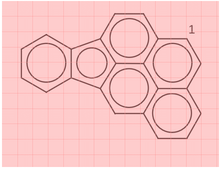
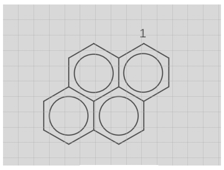

Benzo[a]-
pyrene

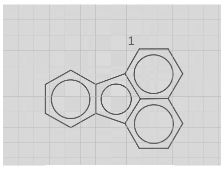

Indeno(1,2,3-cd)-
pyrene

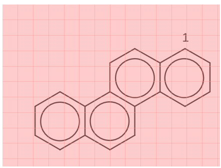
Genotoxic polycyclic aromatic hydrocarbons

Two are precursors for mutagenic nitro-PAHs

Carcinogenic PAH


Pyrene


Fluoranthene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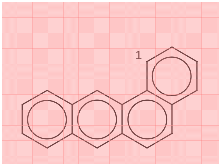
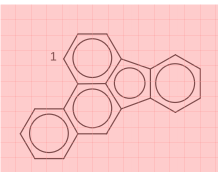
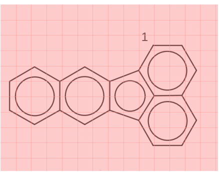
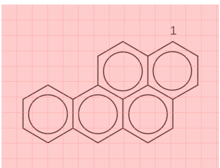
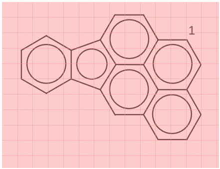

Benz(a)anthracene


Benzo[b]-
fluoranthene

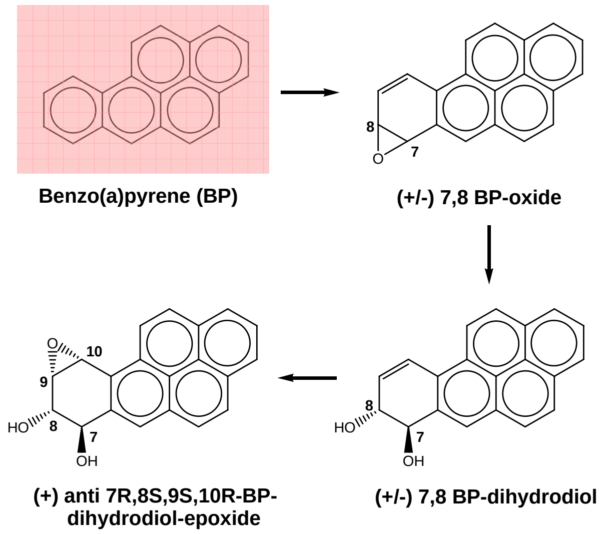

Benzo[k]-
fluoranthene


Benzo[a]-
pyrene


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

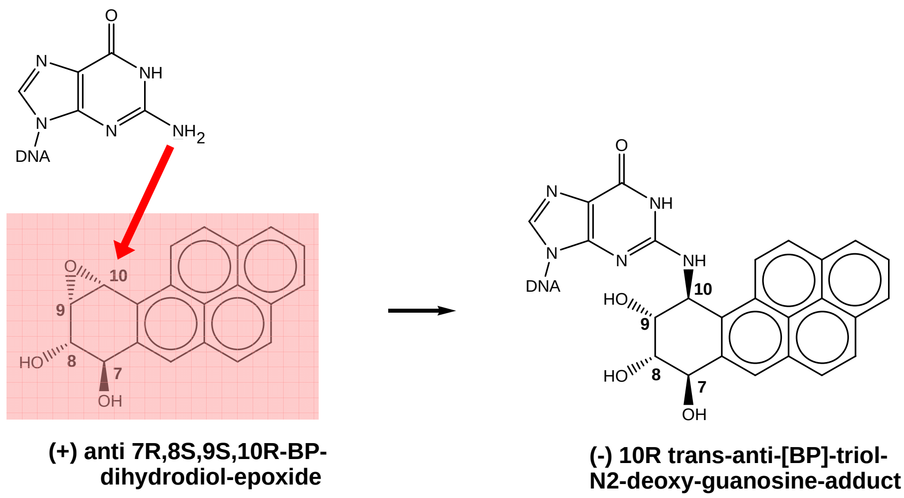
Carcinogenesis from benzo(a)pyrene

Oxidative metabolic activation of benzo(a)pyrene

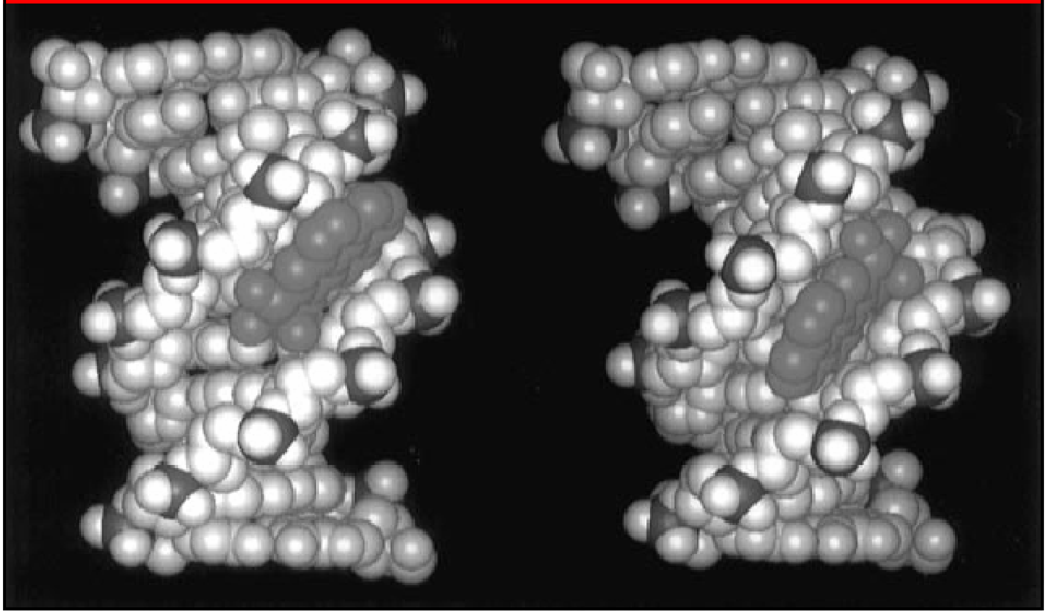


Carcinogenesis from benzo(a)pyrene

Stereoselective formation of benzo(a)pyrene-DNA adducts



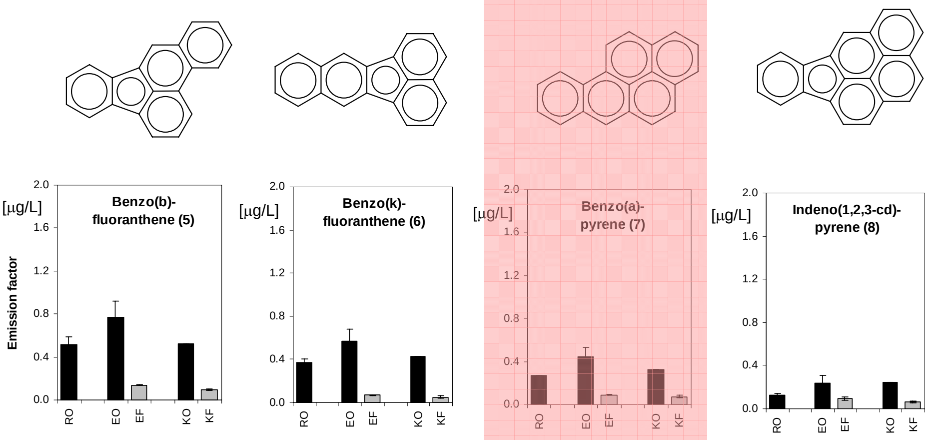
Carcinogenesis from benzo(a)pyrene



Catalytic decomposition of diesel soot

What about benzo(a)pyrene with an ambient air threshold level of 1 ng/m³?

Carcinogenic PAHs



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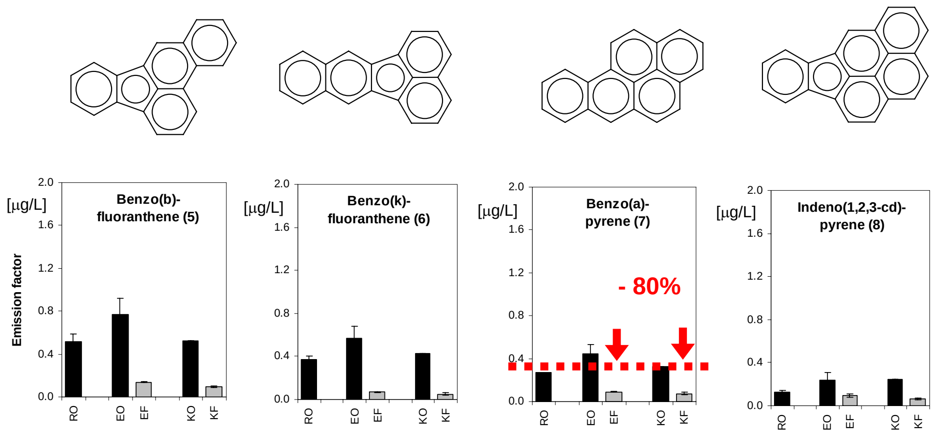
Genotoxic polycyclic aromatic hydrocarbons

Efficient filtration of benzo(a)pyrene from 18 to 4 ng/m3

Carcinogenic PAHs



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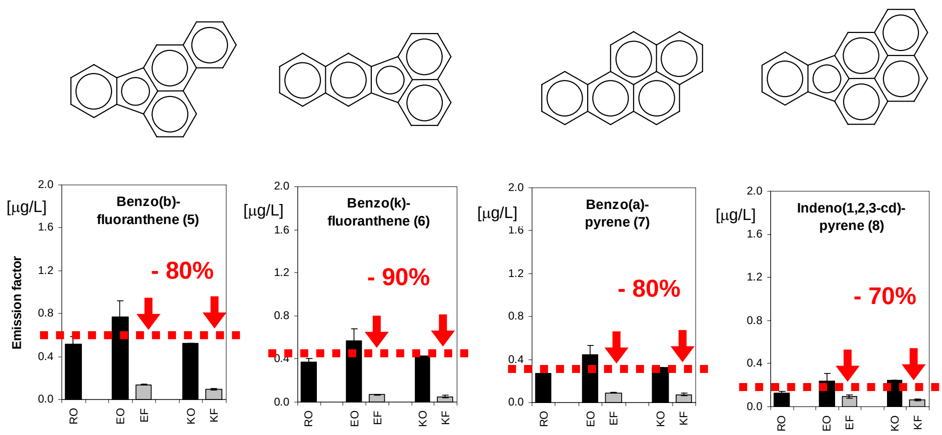
Genotoxic polycyclic aromatic hydrocarbons

Efficient removal of all examined carcinogenic PAHs

Carcinogenic PAHs



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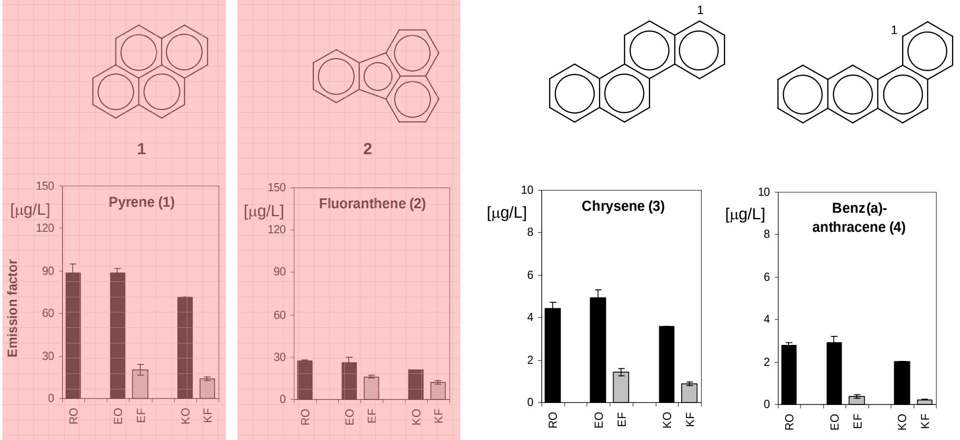
Genotoxic polycyclic aromatic hydrocarbons

Compound-specific conversion efficiencies?

Carcinogenic PAHs



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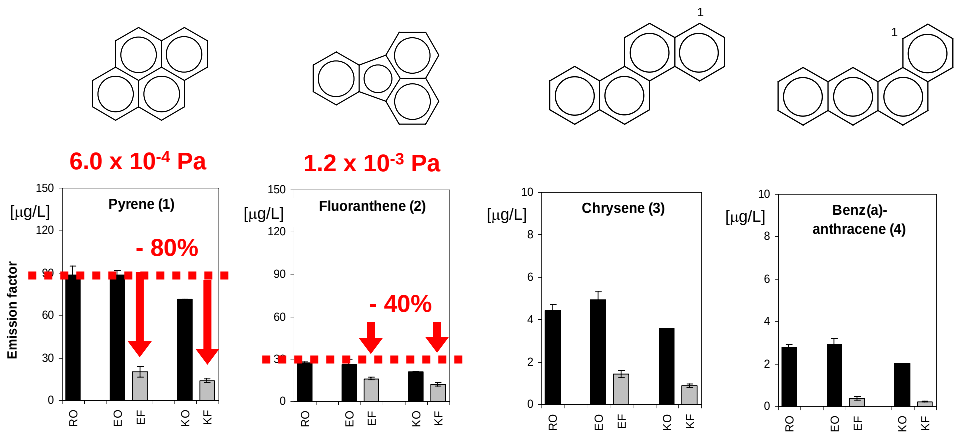
Genotoxic polycyclic aromatic hydrocarbons

Volatility affects conversion efficiency

Carcinogenic PAHs



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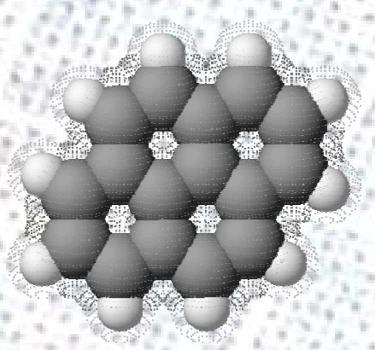
The particulate trap - a chemical reactor

What about nitration of PAHs in NOx-rich diesel exhaust?

Nitration of PAHs

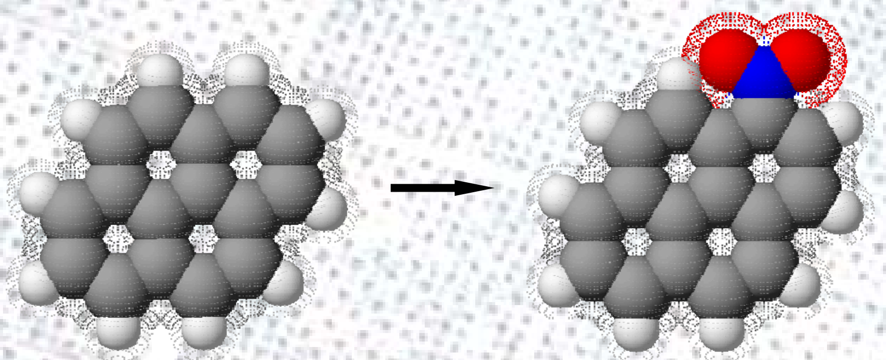


pyrene

The particulate trap - a chemical reactor

In one step from a harmless precursor to a mutagen?

Nitration of PAHs

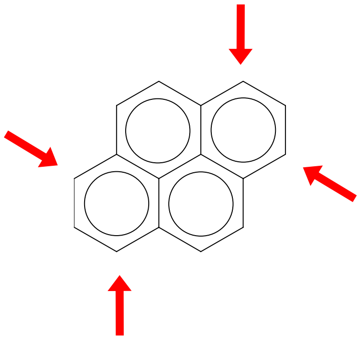


pyrene 1-nitropyrene

The particulate trap - a chemical reactor

Nitration in alpha-position?

Regioselective nitration of pyrene



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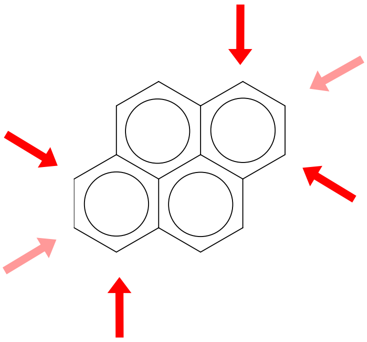
The particulate trap - a chemical reactor

or in beta-position?

Regioselective nitration of pyrene



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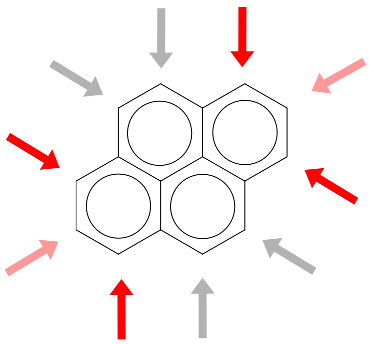
Forschung die begeistert 125 Jahre Empa

The particulate trap - a chemical reactor

or in gamma-position?

Regioselective nitration of pyrene



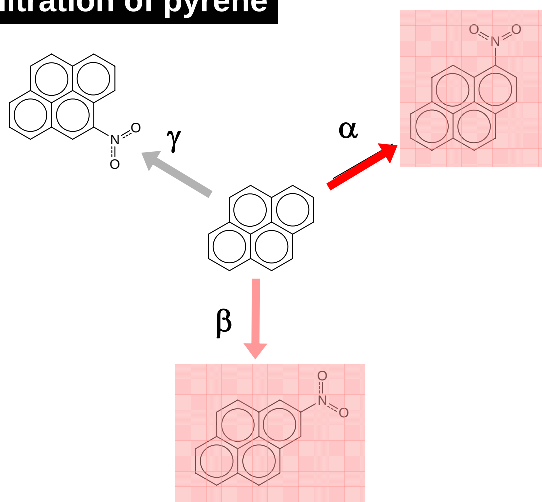
EMPA

125 Jahre Empa

The particulate trap - a chemical reactor

Two of the three isomers are mutagenic.

Regioselective nitration of pyrene



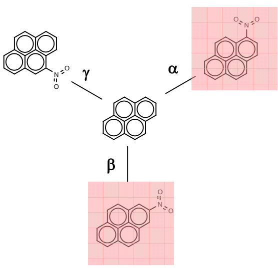
EMPA

125 Jahre Empa

The particulate trap - a chemical reactor

If nitration is possible ones, why not twice?

Nitration of nitropyrenes

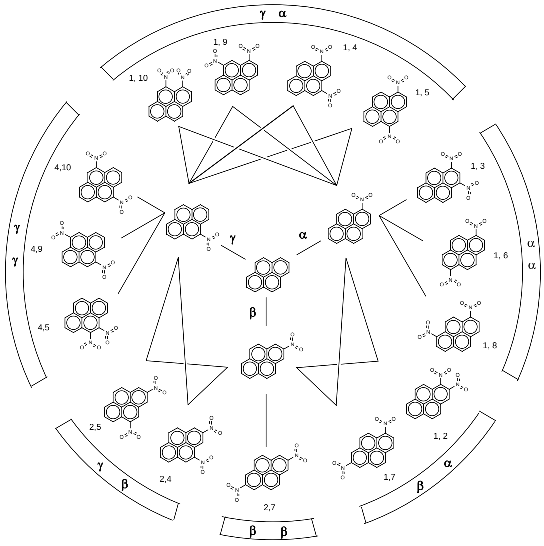


EMPA

Forschung die begeistert 125 Jahre Empa

The particulate trap - a chemical reactor

From one precursor molecule to 3 nitropyrenes to 15 dinitropyrenes?

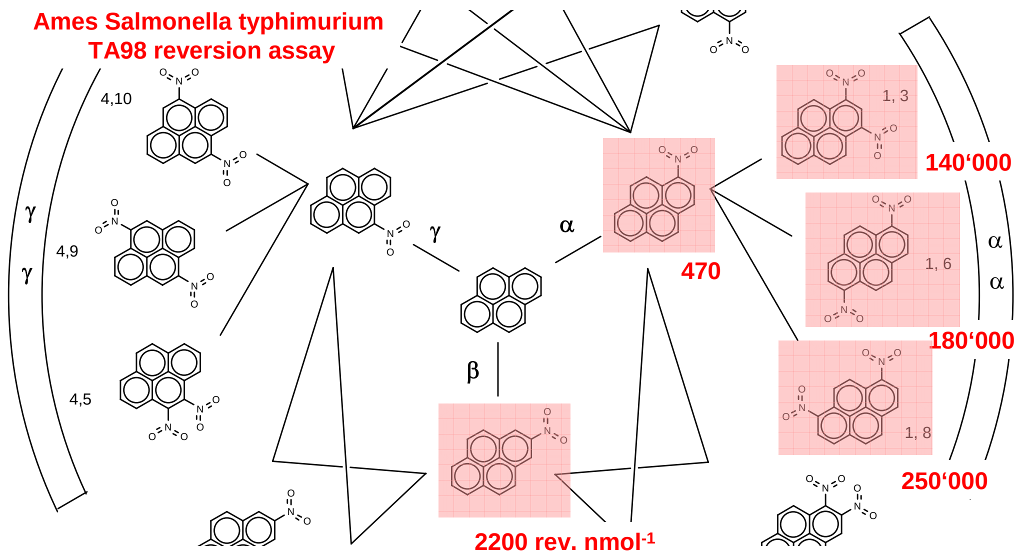


EMPA

Forschung die begeistert 125 Jahre Empa

The particulate trap - a chemical reactor

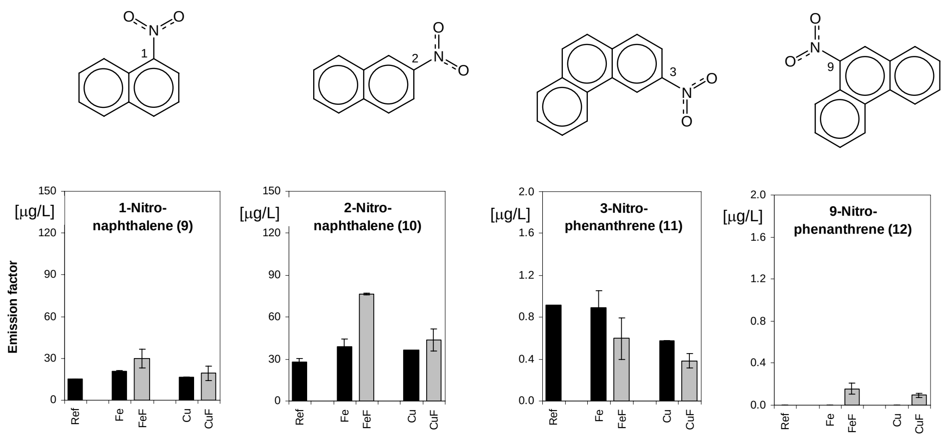
The most potent direct-acting mutagens known are dinitropyrenes



Genotoxic nitro-PAHs

No substantial reduction of 1- and 2-nitronaphthalenes

DPF-induced nitration of PAHs

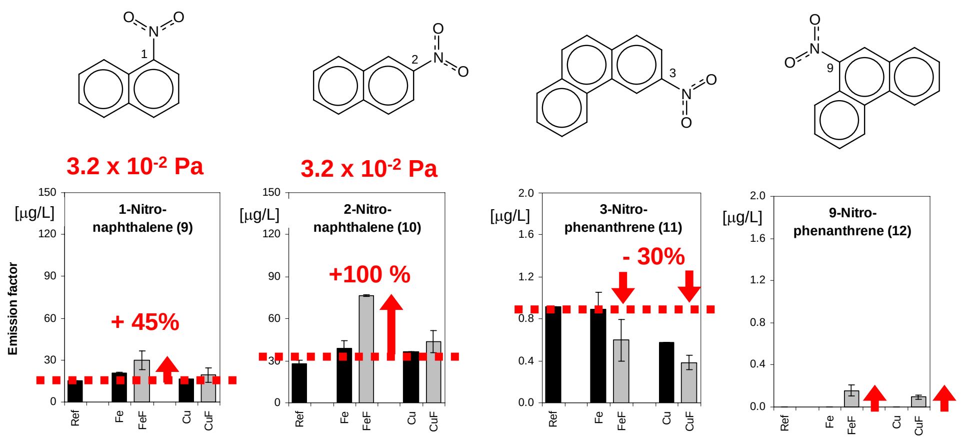


Heeb et al. ES&T, **2008**, 42, 3773-3779

Genotoxic nitro-PAHs

One would expect conversion efficiencies of 40% like for fluoranthene (1.2 x 10^{-3} Pa)

DPF-induced nitration of PAHs

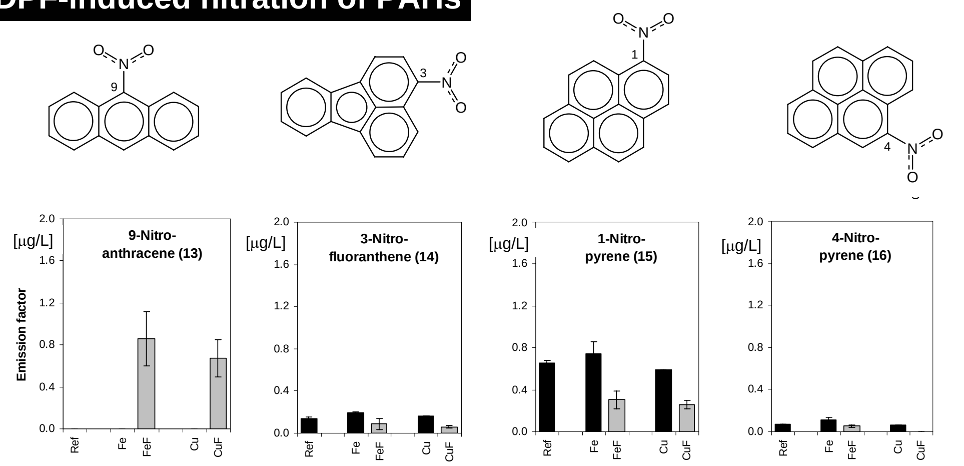


Heeb et al. ES&T, **2008**, 42, 3773-3779

Genotoxic nitro-PAHs

Some are formed, some are converted

DPF-induced nitration of PAHs

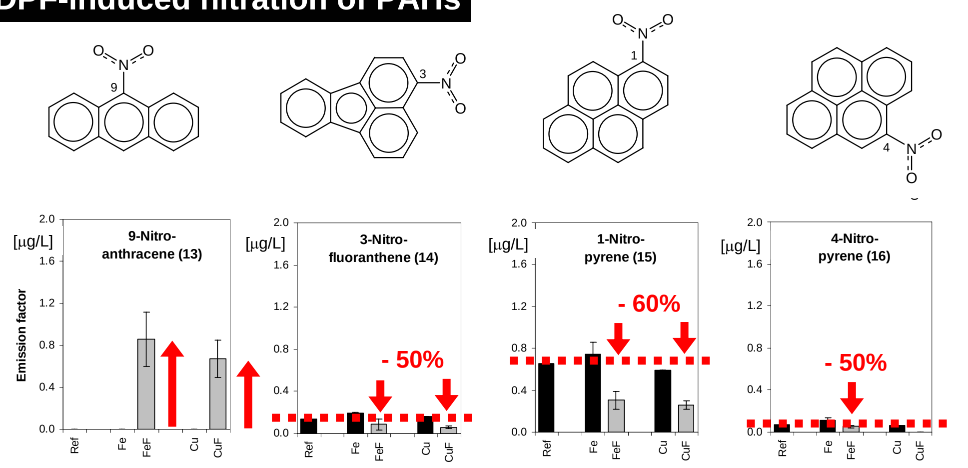


Heeb et al. ES&T, **2008**, 42, 3773-3779

Genotoxic nitro-PAHs

Out of 8 nitro-PAHs 4 are formed and 4 are reduced in both DPFs

DPF-induced nitration of PAHs



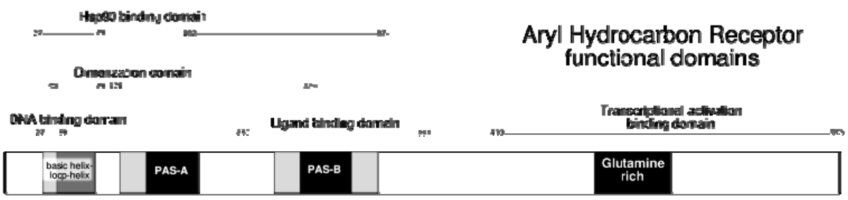
Heeb et al. ES&T, **2008**, 42, 3773-3779

The aryl hydrocarbon receptor

Effect-based risk assessment with bioassays: A alternatives to chemical analyses

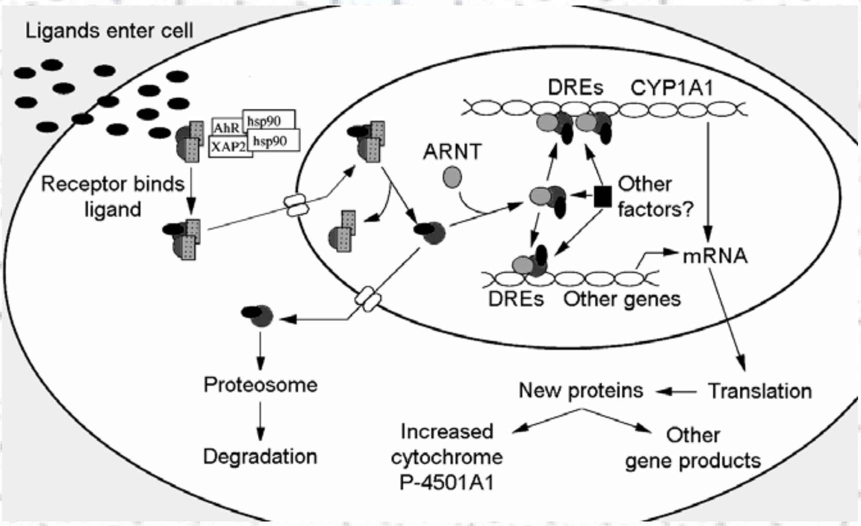
DNA-binding transcription factor:

- 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



The AHR mode of action

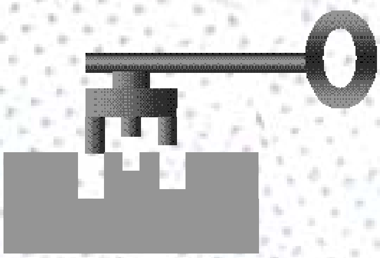
Ligand binding to the AHR triggers a cascade of fundamental reactions



Specific molecular recognition

We do not know the protein structure yet but we know some of the keys that bind to it

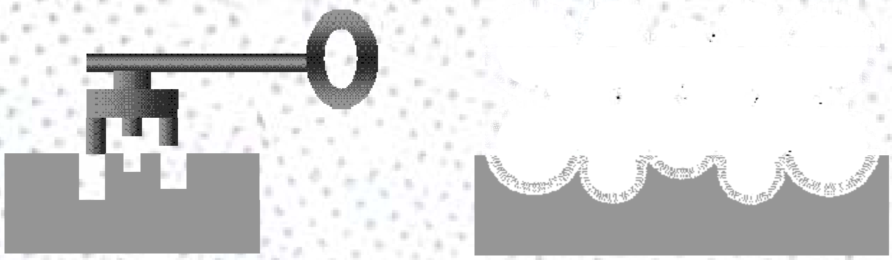
The key-lock principle:



Specific molecular recognition

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

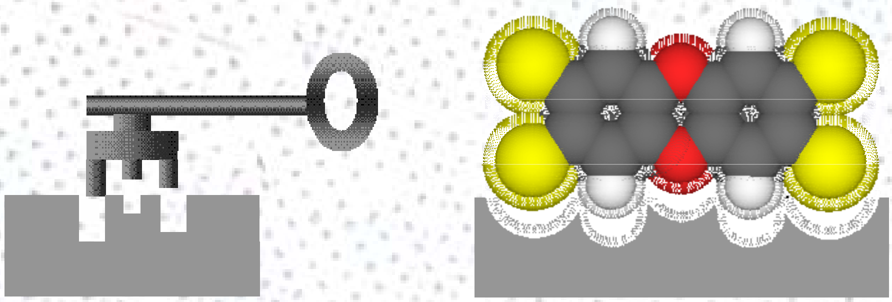
The key-lock principle:



Specific molecular recognition

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

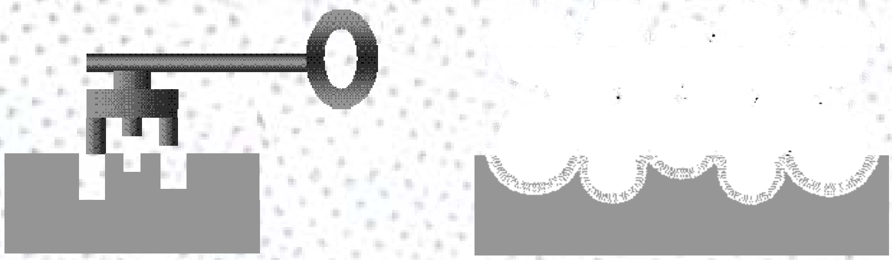
The key-lock principle:



Specific molecular recognition

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

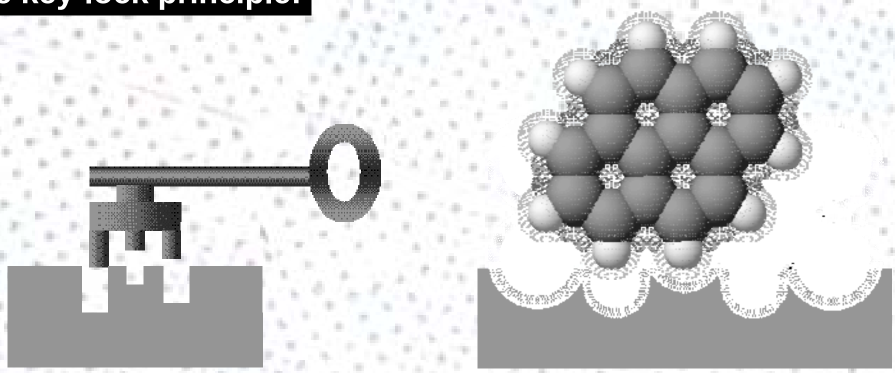
The key-lock principle:



Specific molecular recognition

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

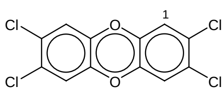
The key-lock principle:



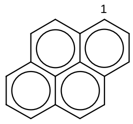
Specific molecular recognition

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

Affinity of some aryl hydrocarbons:



1.00



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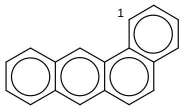

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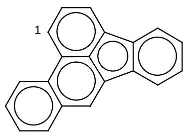

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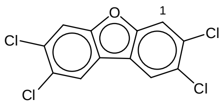

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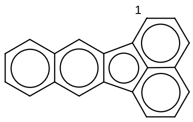

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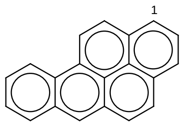

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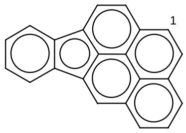

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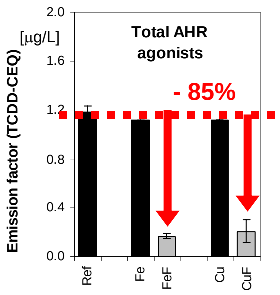
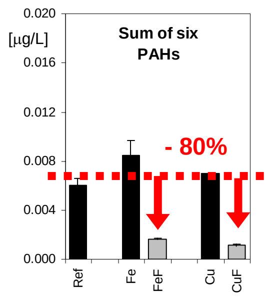
Specific molecular recognition

Bioassay-supported benefit/risk assessment of DPFs

AHR-Reporter gene assay:

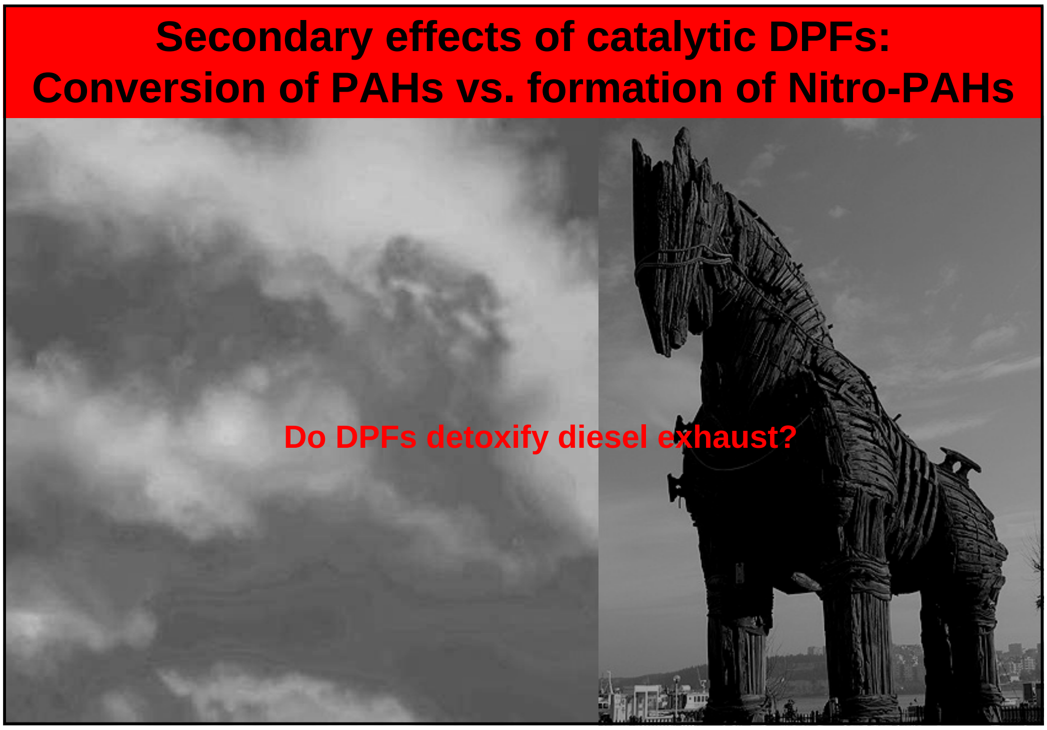
1/100

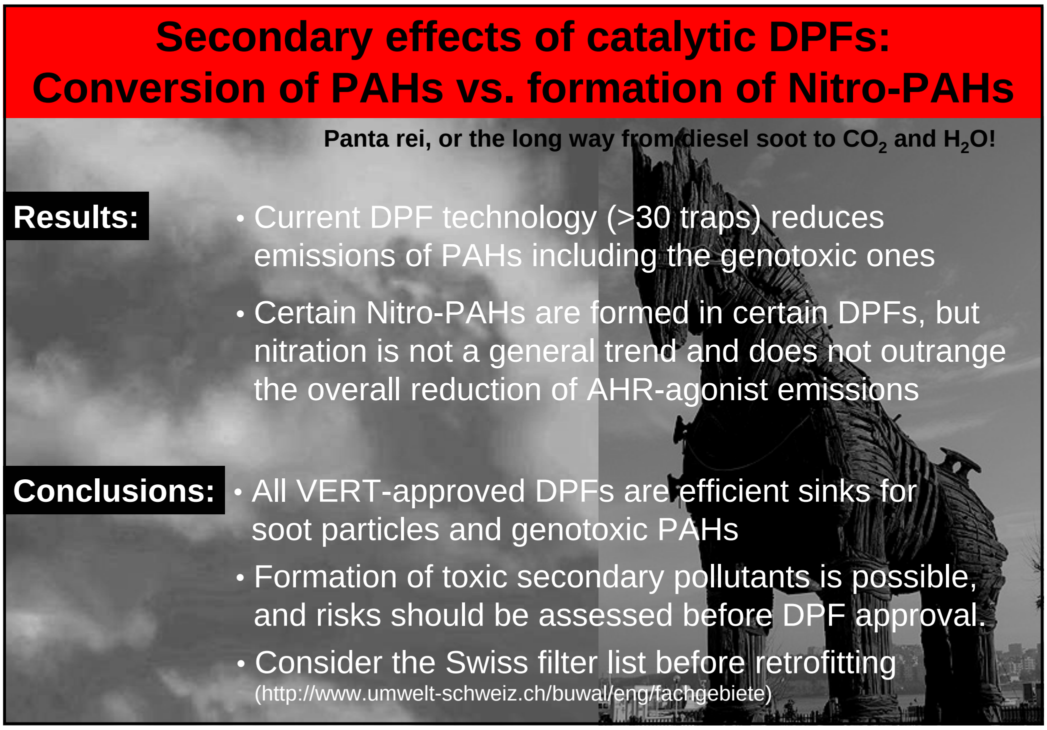




Heeb et al. ES&T, **2008**, 42, 3773-3779

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


Secondary effects of catalytic DPFs:
Conversion of PAHs vs. formation of Nitro-PAHs
Do DPFs detoxify diesel exhaust?


Secondary effects of catalytic DPFs:
Conversion of PAHs vs. formation of Nitro-PAHs
Panta rei, or the long way from diesel soot to CO_2 and H_2O!
Results:
• Current DPF technology (>30 traps) reduces emissions of PAHs including the genotoxic ones
• Certain Nitro-PAHs are formed in certain DPFs, but nitration is not a general trend and does not outrange the overall reduction of AHR-agonist emissions
Conclusions:
• All VERT-approved DPFs are efficient sinks for soot particles and genotoxic PAHs
• Formation of toxic secondary pollutants is possible, and risks should be assessed before DPF approval.
• Consider the Swiss filter list before retrofitting
(http://www.umwelt-schweiz.ch/buwal/eng/fachgebiete)

Secondary effects of catalytic DPFs: Conversion of PAHs vs. formation of Nitro-PAHs

Was there a question not answered yet?

Thanks:

- to the VERT team: A. Mayer, TTM, Niederrohrdorf
  Prof. J. Czerwinski, L. Petermann, Uni. Appl. Sci., Biel
  G. Durbano, M. Wyser, Swiss Fed. Office for Envir. (BafU), Bern
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- for your attention

EMPA

The importance of secondary pollutants

How to deal with risks of a secondary formation of pollutants?

Outlook

Lessons to learn from VERT:

- Toxic secondary emissions are of relevance
- Benefits and risks of a new technology have to be assessed before its wide application, in case of retrofitting, Swiss legislation requires VERT approved technology
- Combined DeNOx- and trap-technolgies have to be assessed as well.