



# Effects of low- and high-oxidation DPFs on genotoxic exhaust constituents



13<sup>th</sup> ETH-Conference on Combustion Generated Nanoparticles

Zürich, June 22. - 24. 2009

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# Effects of low- and high-oxidation DPFs on genotoxic exhaust constituents

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



Trojan horse, Harbour of Canakkale, Turkey



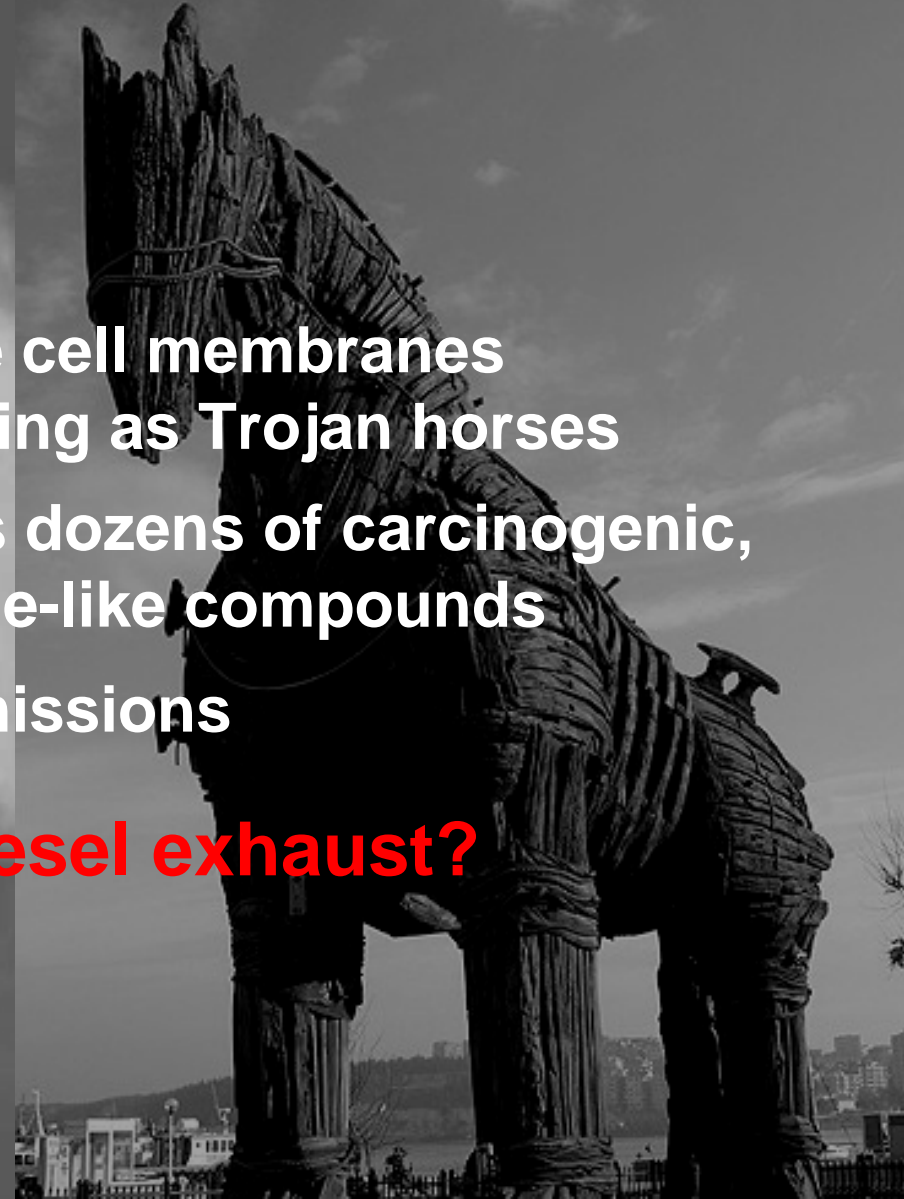
# Diesel nanoparticles –Trojan horses for genotoxic compounds

## Problems:

- Nanoparticles penetrate cell membranes (alveoli, blood cells) acting as Trojan horses
- Diesel exhaust contains dozens of carcinogenic, mutagenic, and hormone-like compounds
- Toxic nitrogen oxide emissions

**Do DPFs detoxify diesel exhaust?**

Trojan horse, Harbour of Canakkale, Turkey



# Secondary pollutants of catalytic converter systems

What else can a converter produce besides  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$ ?

**Toxic secondary pollutants - relevant examples**



# Secondary pollutants of catalytic converter systems

What else can a converter produce besides  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$ ?

## Toxic secondary pollutants - relevant examples

- **TWC-induced formation of ammonia**  
TWCs – the most efficient DeNOx systems on road
- **Formation of  $\text{NO}_2$  in diesel oxidation catalysts**  
From a reducing to an oxidizing exhaust
- **Formation of PAHs in diesel particulate filters?**  
Carcinogenic PAHs from soot combustion?
- **Nitration of PAHs in particulate traps?**  
From harmless precursors to mutagenic Nitro-PAHs?
- **Formation of PCDD/Fs in particulate traps?**  
The DPF- an ideal reactor

# The VERT approach

One engine, one test cycle, 14 DPFs, 4 years of work

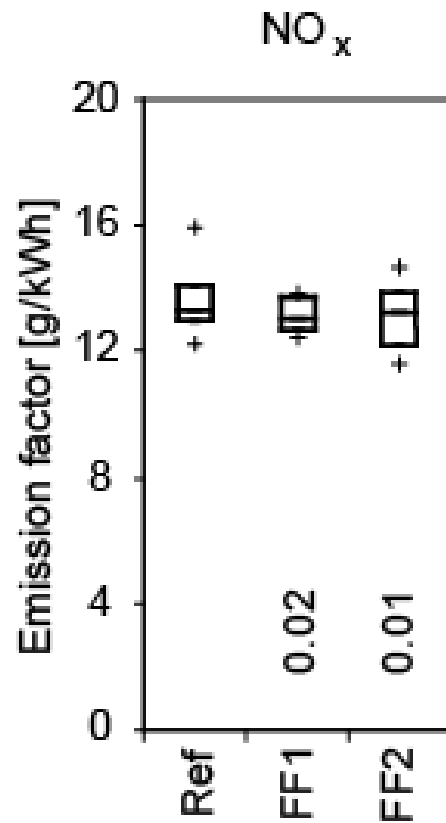




# The NO<sub>x</sub> problem

Do DPFs affect nitrogen oxide emissions?

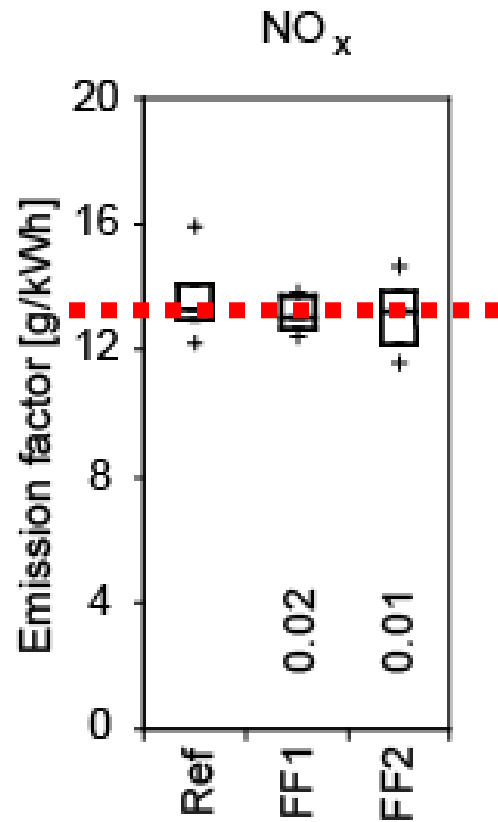
**Nitrogen oxides (NO<sub>x</sub>, NO, NO<sub>2</sub>)**



# The NO<sub>x</sub> problem

No effects with respect to engine and vehicle legislation!

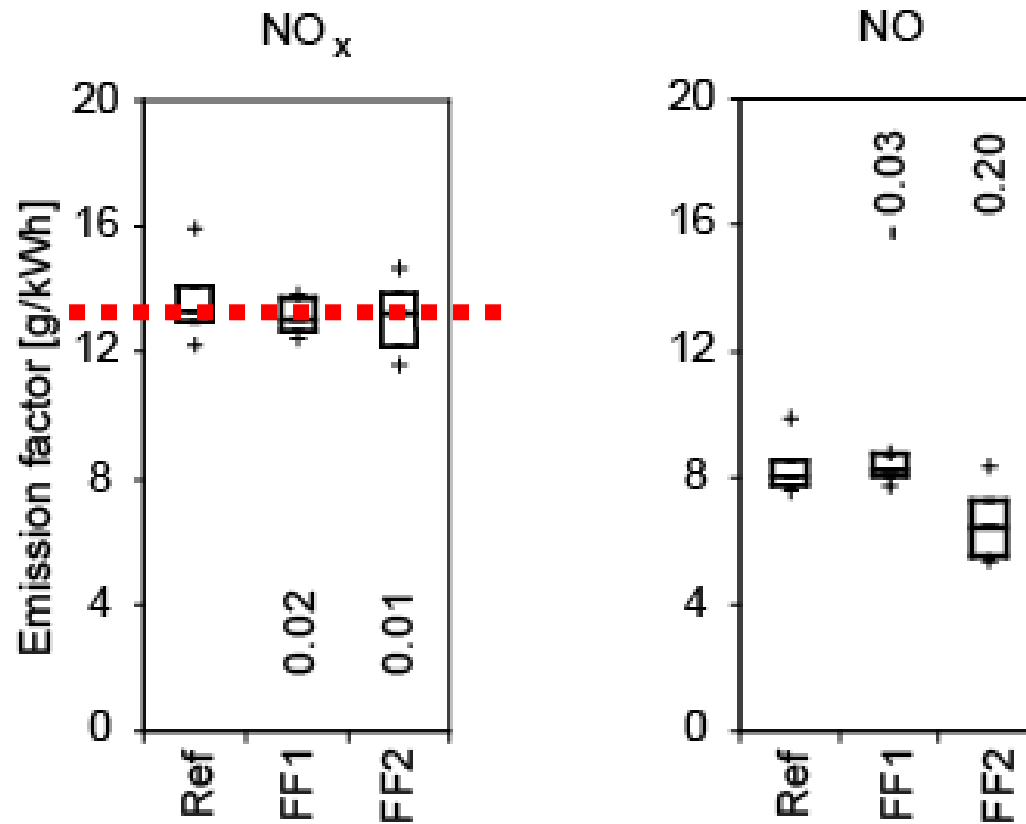
## Nitrogen oxides (NO<sub>x</sub>, NO, NO<sub>2</sub>)



# The NO<sub>x</sub> problem

With respect to nitric oxide?

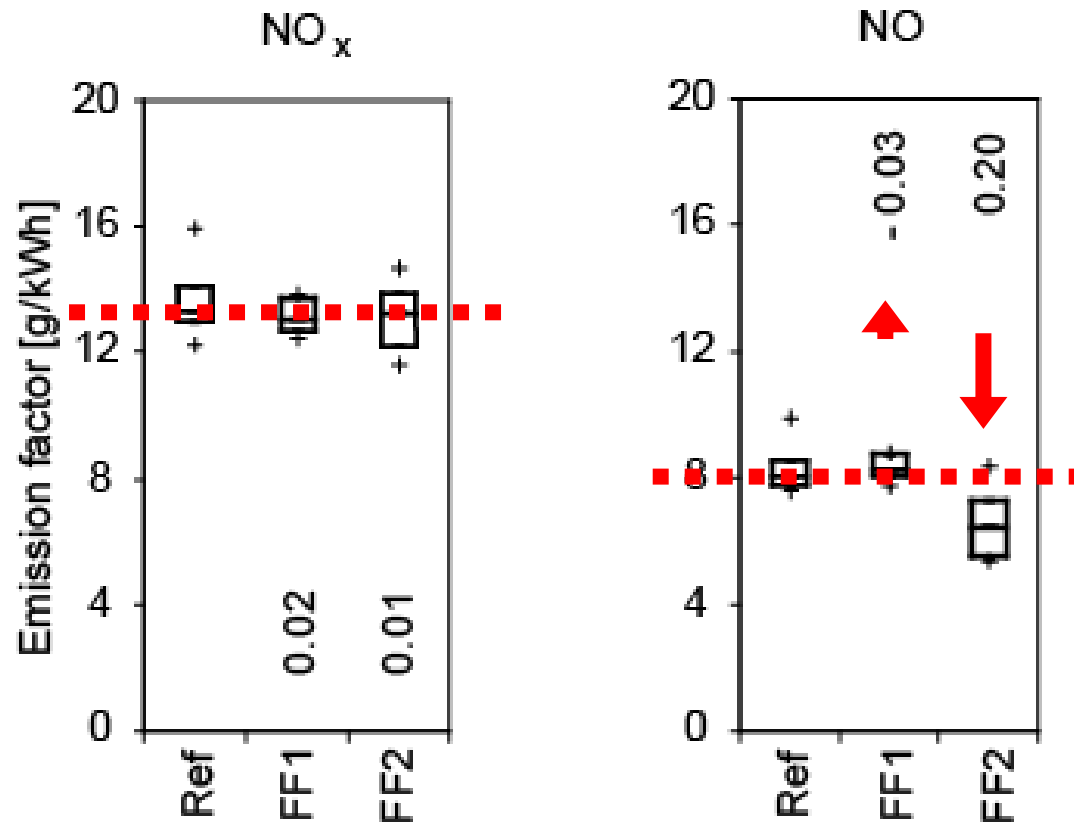
## Nitrogen oxides (NO<sub>x</sub>, NO, NO<sub>2</sub>)



# The NO<sub>x</sub> problem

With respect to nitric oxide?

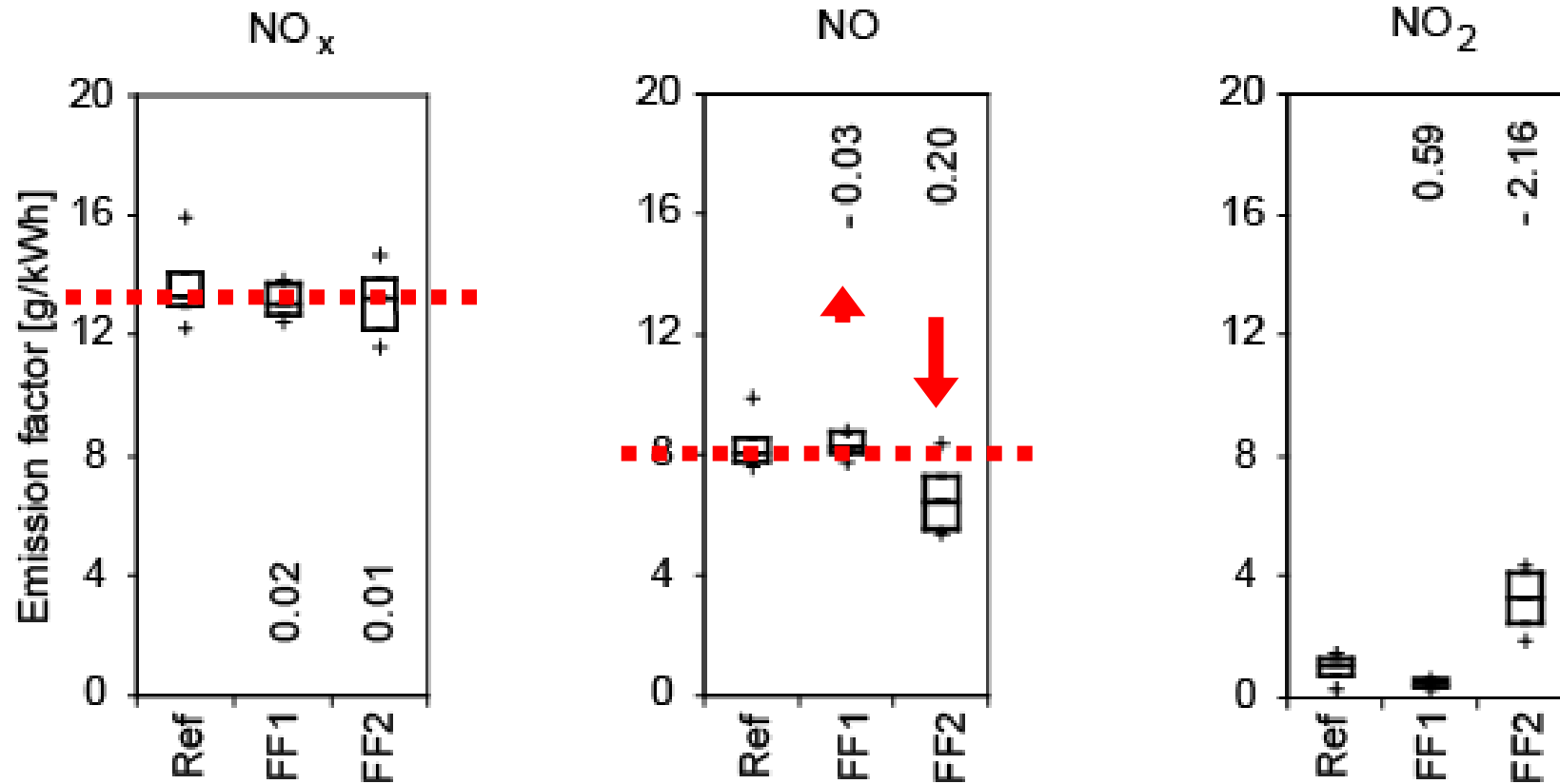
## Nitrogen oxides (NO<sub>x</sub>, NO, NO<sub>2</sub>)



# The NO<sub>x</sub> problem

With respect to nitrogen dioxide?

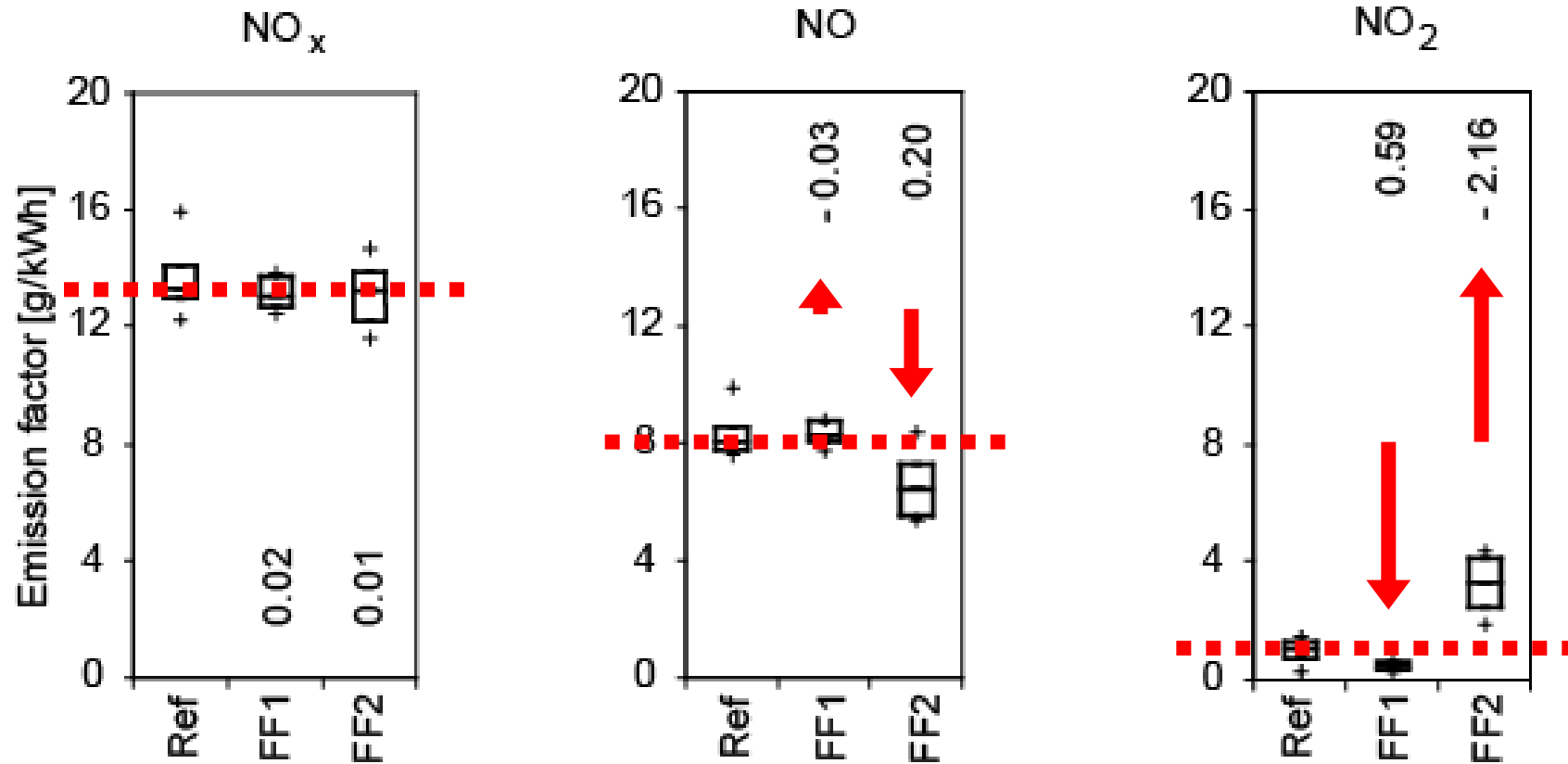
## Nitrogen oxides (NO<sub>x</sub>, NO, NO<sub>2</sub>)



# The NO<sub>x</sub> problem

We have 2 filter families, one converts NO<sub>2</sub> the other forms NO<sub>2</sub>!

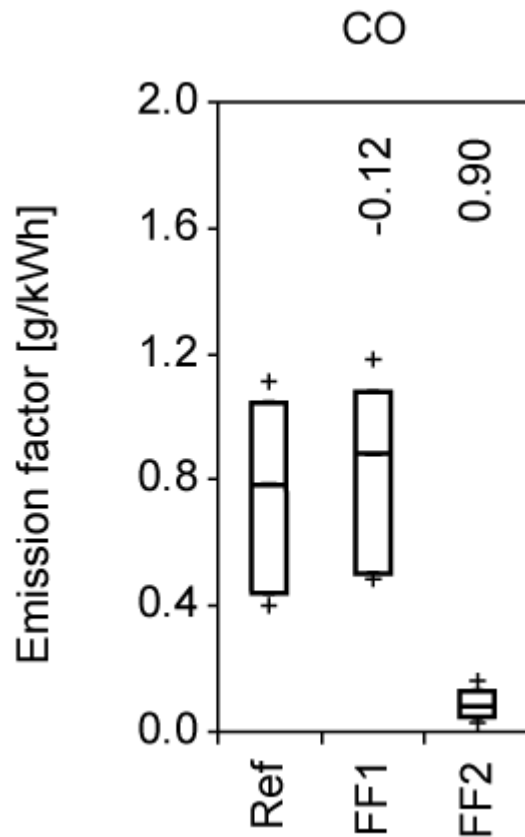
## Nitrogen oxides (NO<sub>x</sub>, NO, NO<sub>2</sub>)



# Low- / high-oxidation potential DPFs

We have 2 filter families, one converts CO the other doesn't!

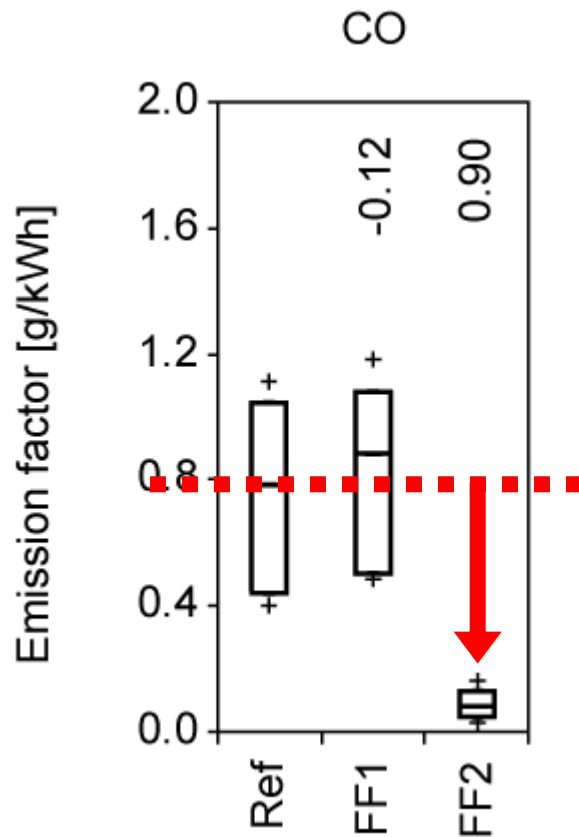
Carbon monoxide, hydrocarbons, fuel



# Low- / high-oxidation potential DPFs

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Carbon monoxide, hydrocarbons, fuel

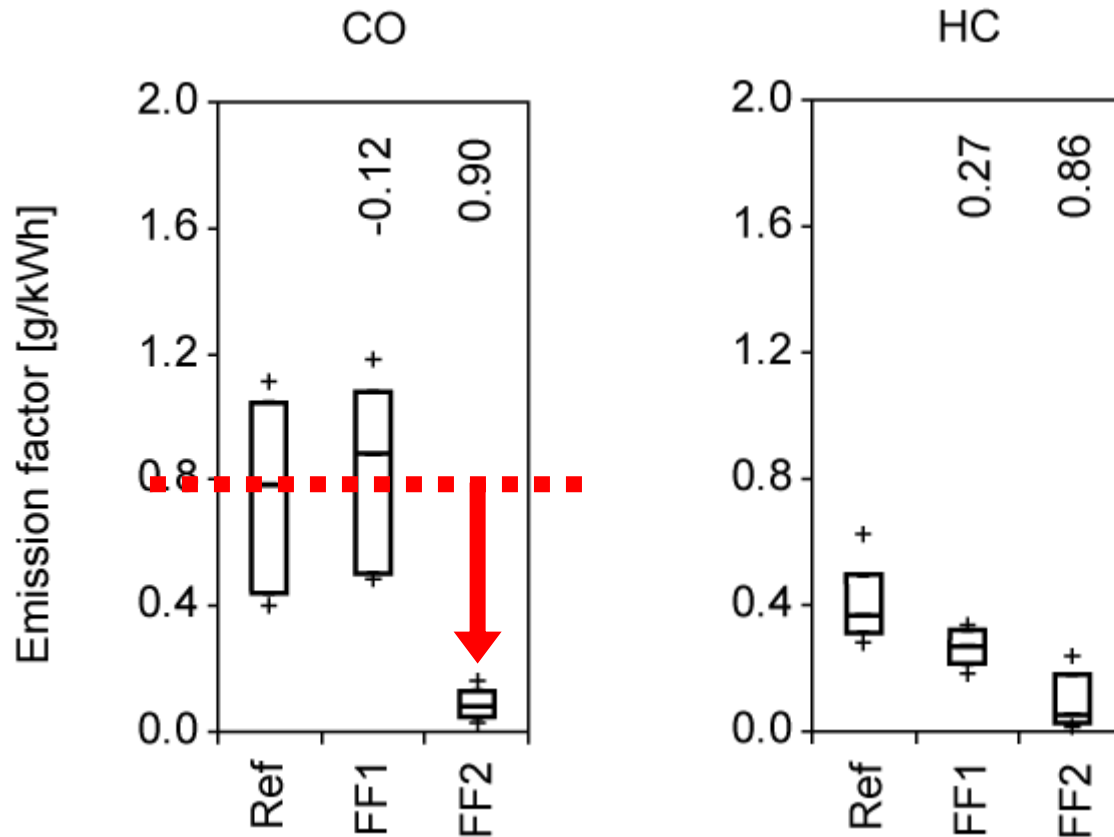




# Low- / high-oxidation potential DPFs

Both filter families convert HCs

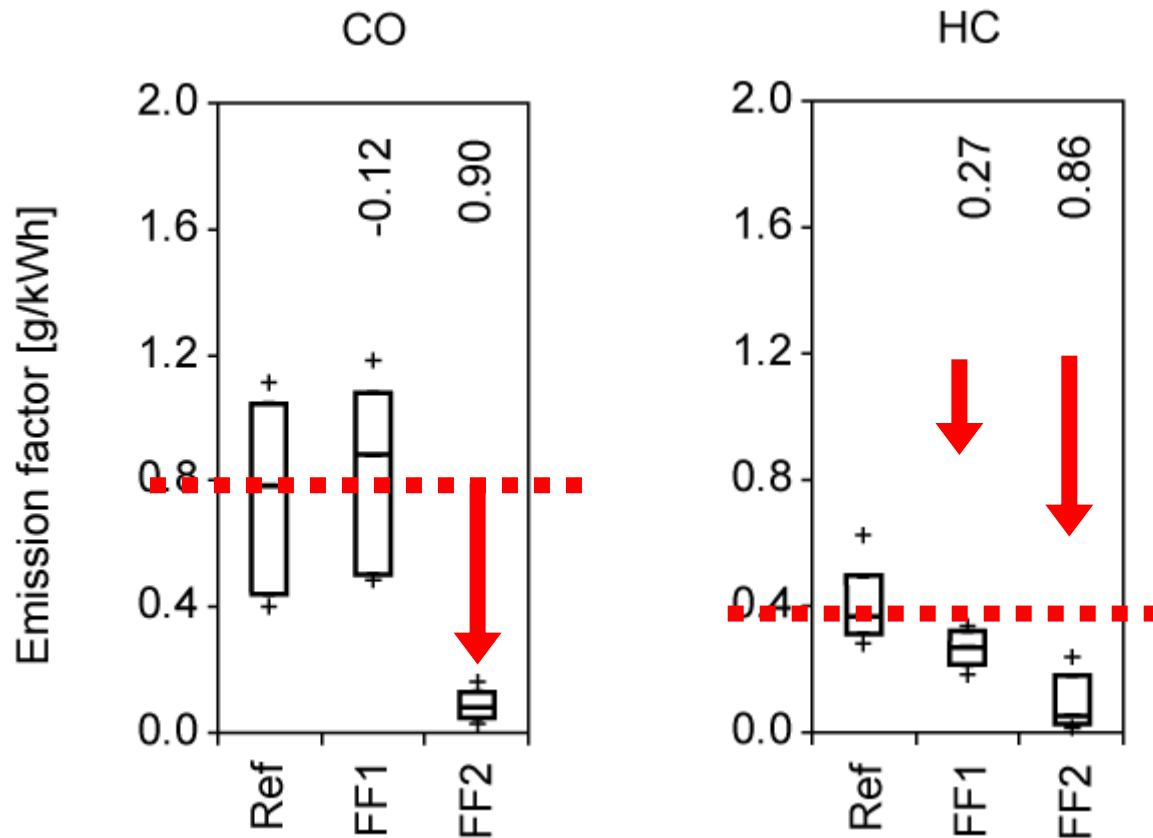
Carbon monoxide, hydrocarbons, fuel



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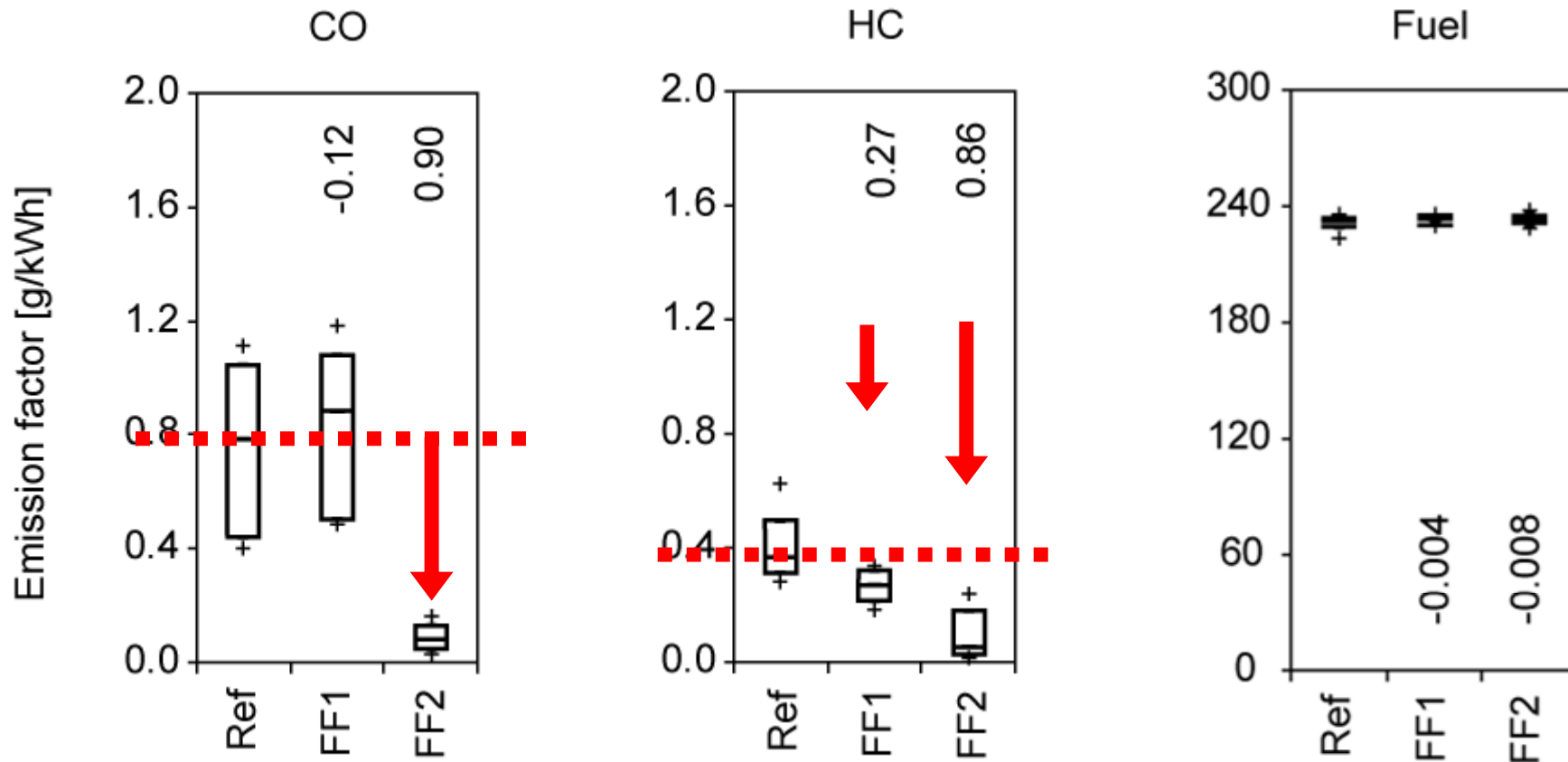
Carbon monoxide, hydrocarbons, fuel



# Low- / high-oxidation potential DPFs

No significant effects on fuel consumption

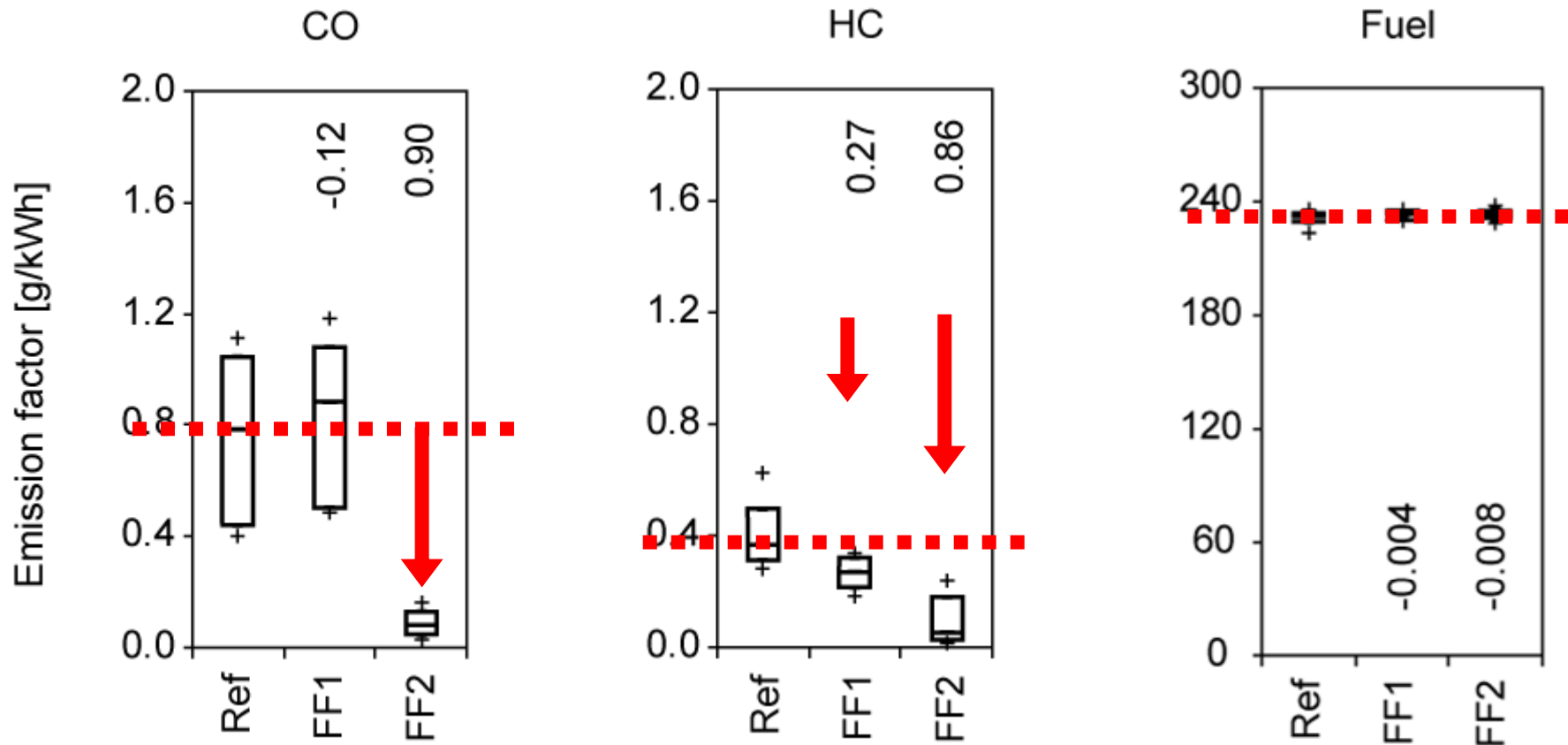
Carbon monoxide, hydrocarbons, fuel



# Low- / high-oxidation potential DPFs

High-ox filters, convert CO and NO forming NO<sub>2</sub>, lox-DPFs don't!

## Carbon monoxide, hydrocarbons, fuel



# Secondary pollutants of catalytic converter systems

What else can a converter produce besides  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$ ?

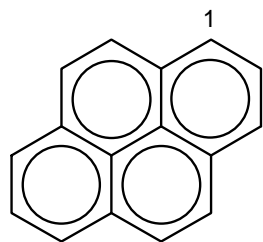
## Toxic secondary pollutants - relevant examples

- **TWC-induced formation of ammonia**  
TWCs – the most efficient DeNO<sub>x</sub> systems on road
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The DPF- an ideal reactor

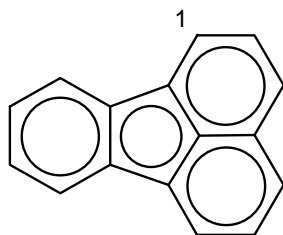
# Genotoxic polycyclic aromatic hydrocarbons

## Genotoxic PAHs in diesel exhaust

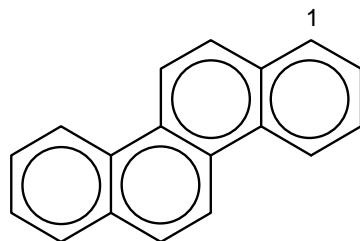
### Carcinogenic PAH



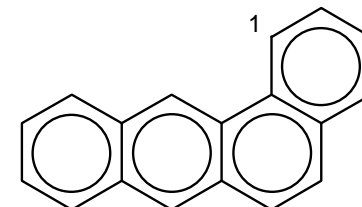
Pyrene



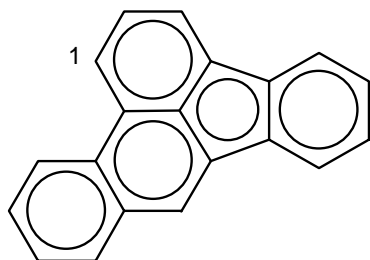
Fluoranthene



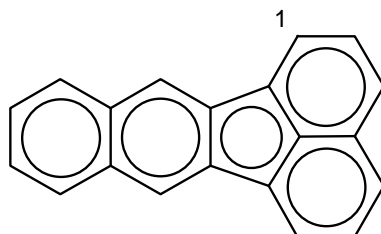
Chrysene



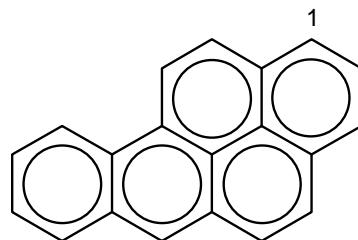
Benz(a)anthracene



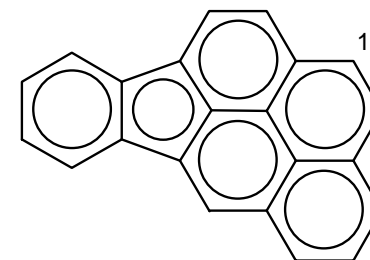
Benzo[b]-  
fluoranthene



Benzo[k]-  
fluoranthene



Benzo[a]-  
pyrene

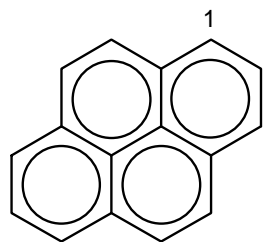


Indeno(1,2,3-cd)-  
pyrene

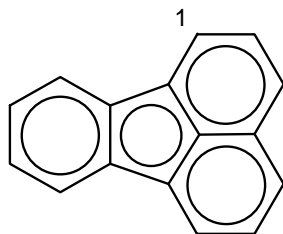
# Genotoxic polycyclic aromatic hydrocarbons

Six PAHs are carcinogenic according to the WHO

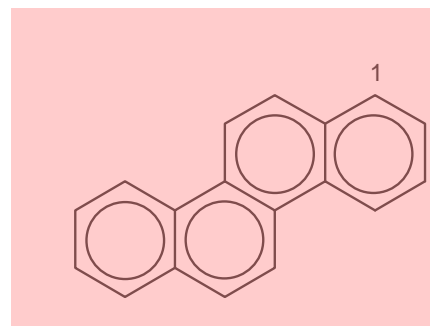
## Carcinogenic PAH



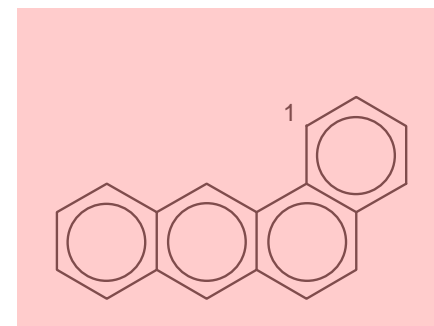
Pyrene



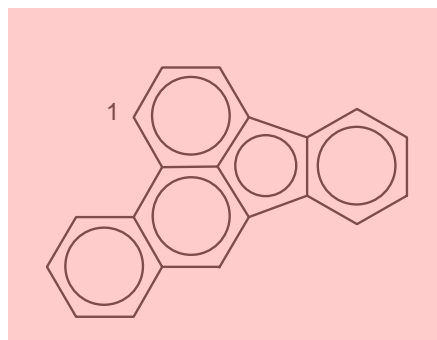
Fluoranthene



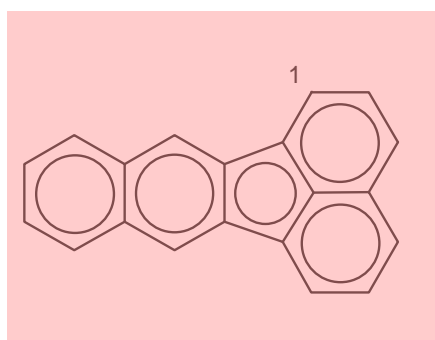
Chrysene



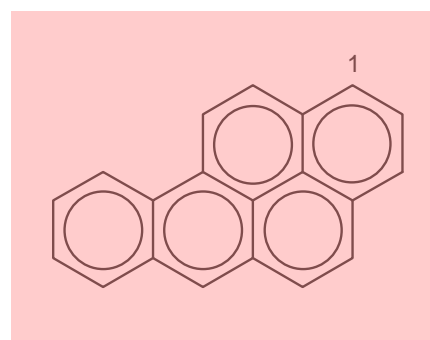
Benz(a)anthracene



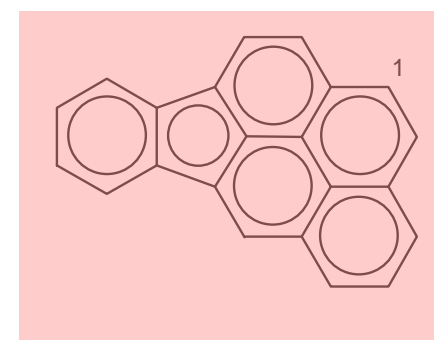
Benzo[b]-  
fluoranthene



Benzo[k]-  
fluoranthene



Benzo[a]-  
pyrene

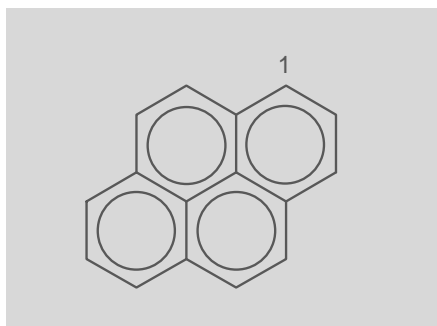


Indeno(1,2,3-cd)-  
pyrene

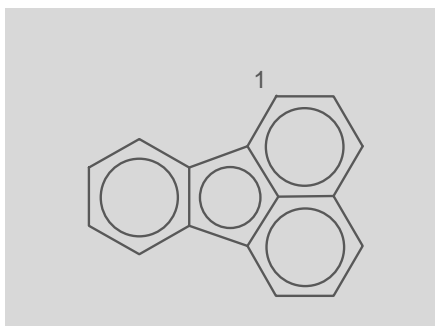
# Genotoxic polycyclic aromatic hydrocarbons

Two are precursors for mutagenic nitro-PAHs

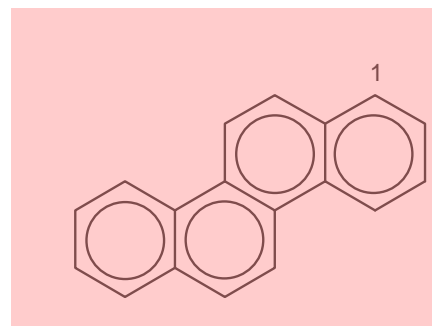
## Carcinogenic PAH



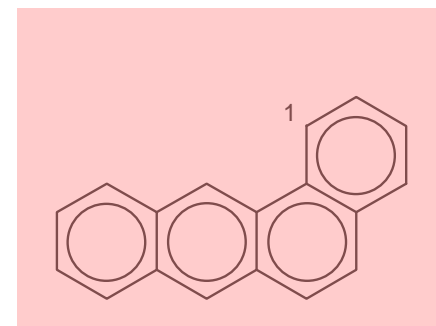
Pyrene



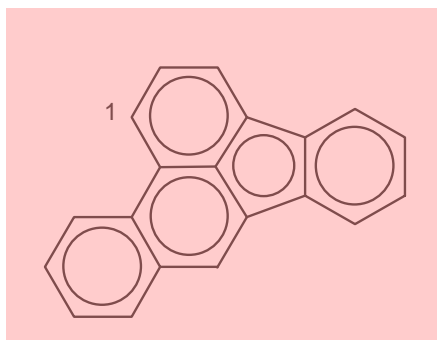
Fluoranthene



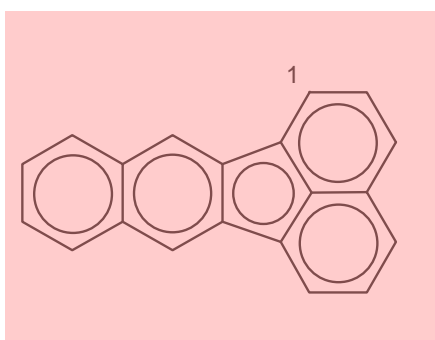
Chrysene



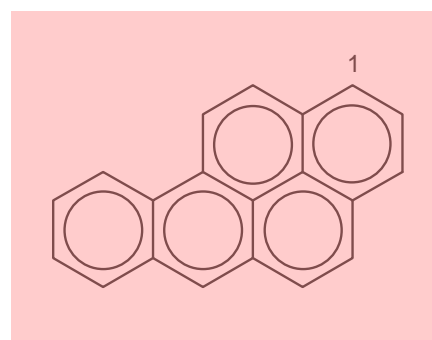
Benz(a)anthracene



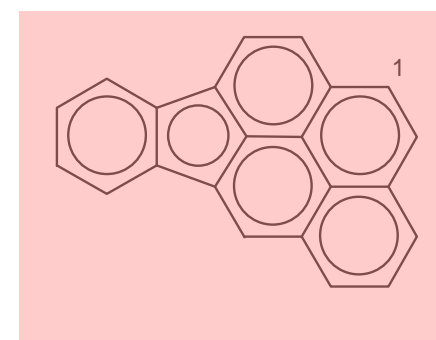
Benzo[b]-  
fluoranthene



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fluoranthene



Benzo[a]-  
pyrene

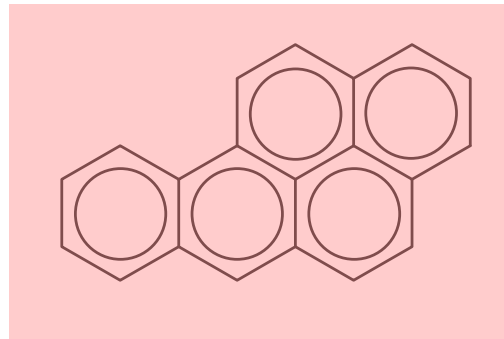


Indeno(1,2,3-cd)-  
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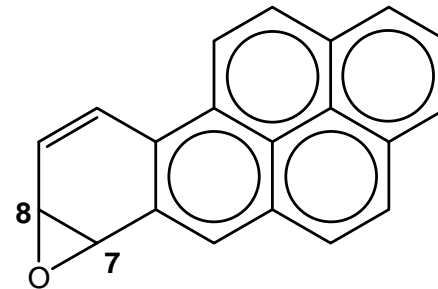


# Carcinogenesis from benzo(a)pyrene

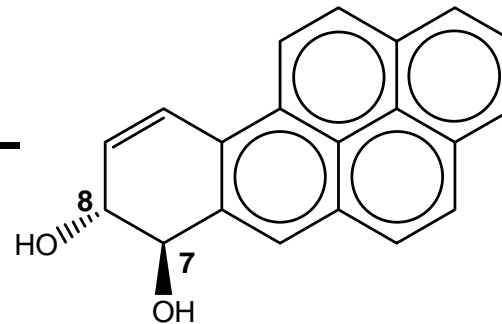
Oxidative metabolic activation of benzo(a)pyrene by cytochrome P450 enzymes



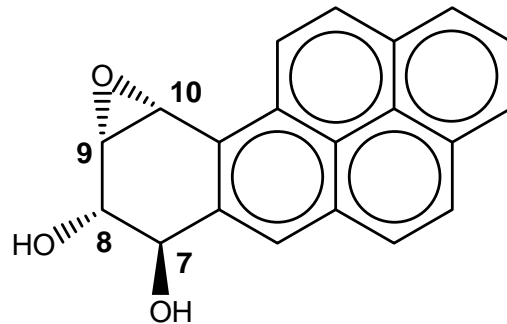
**Benzo(a)pyrene (BP)**



**(+/-) 7,8 BP-oxide**



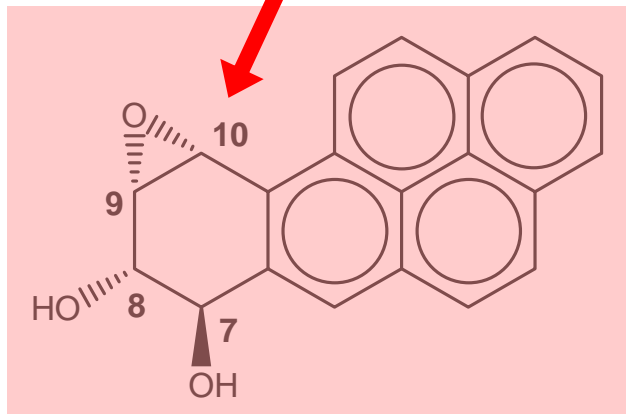
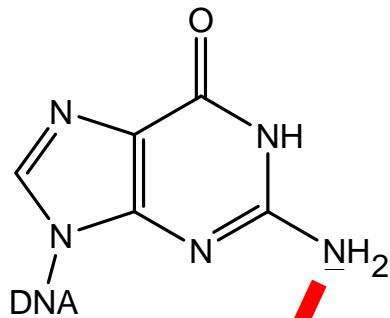
**(+/-) 7,8 BP-dihydrodiol**



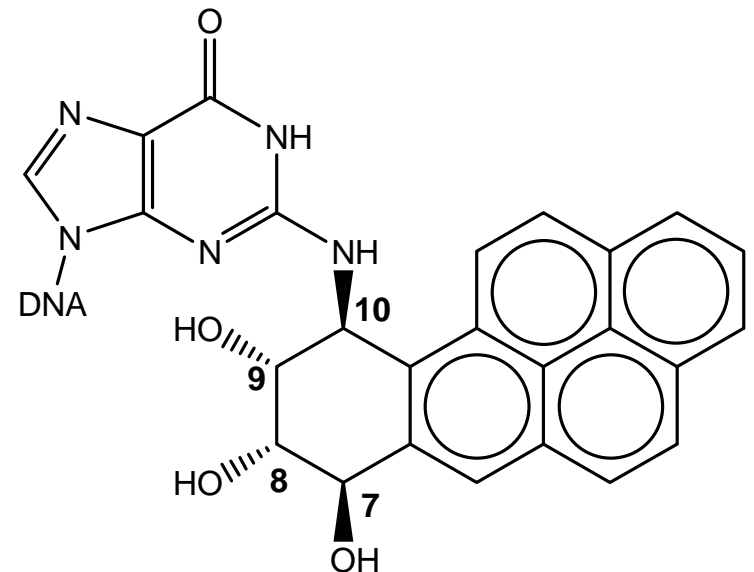
**(+) anti 7R,8S,9S,10R-BP-dihydrodiol-epoxide**

# Carcinogenesis from benzo(a)pyrene

## Stereoselective formation of benzo(a)pyrene-DNA-adducts

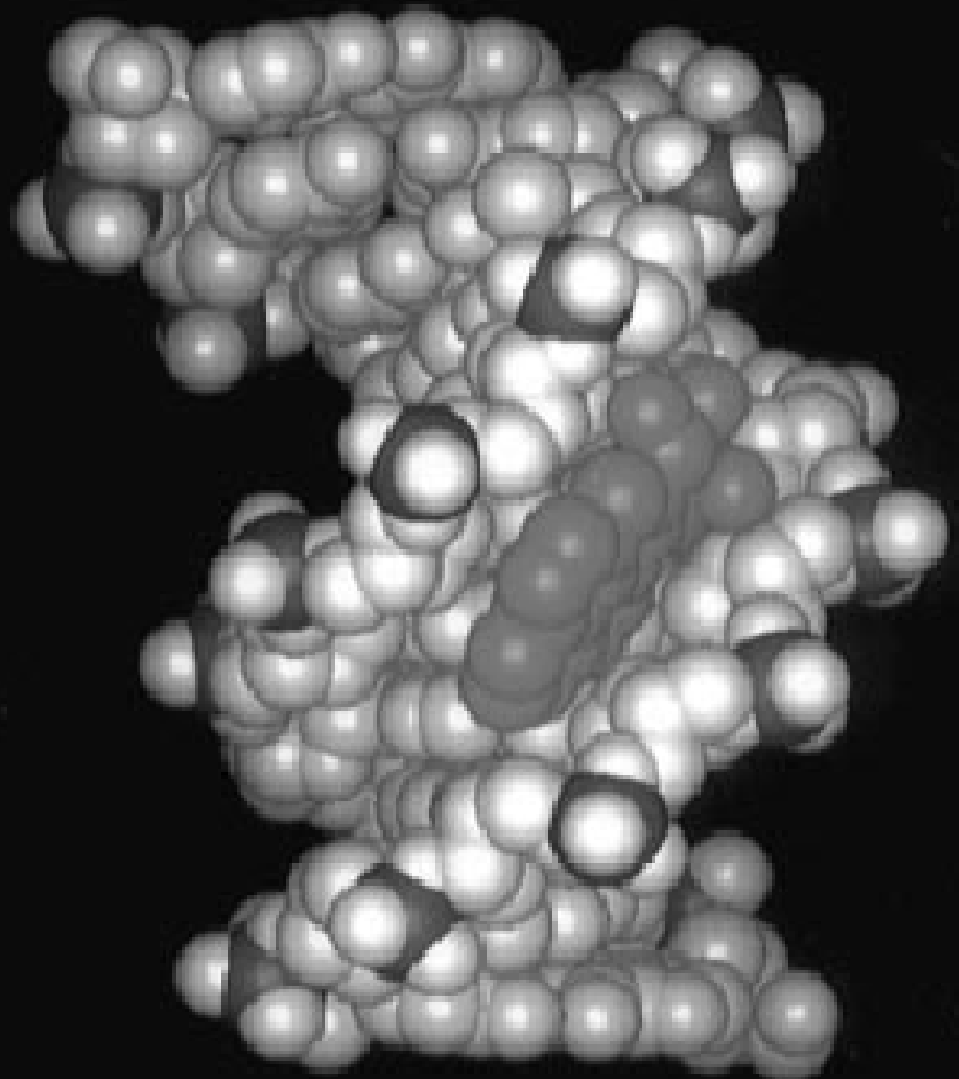
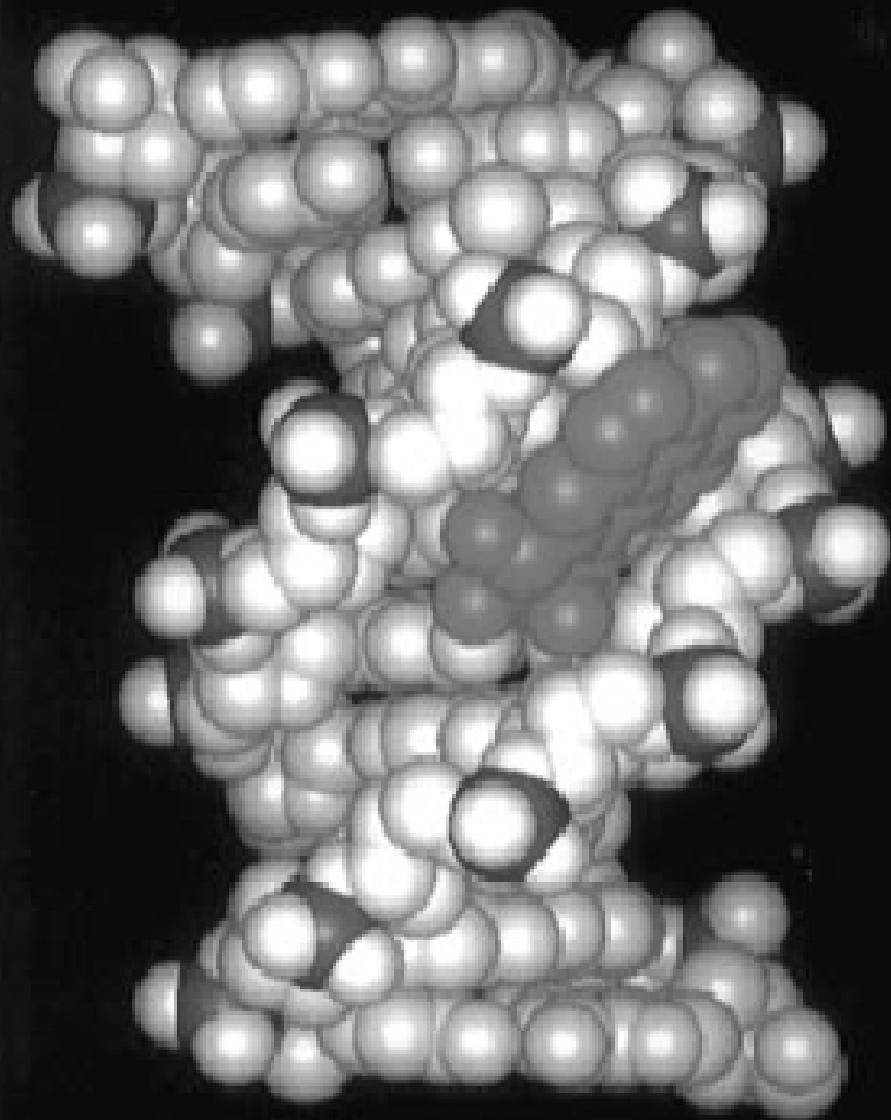


**(+) anti 7R,8S,9S,10R-BP-dihydrodiol-epoxide**



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

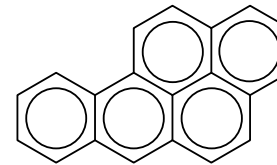
# Carcinogenesis from benzo(a)pyrene



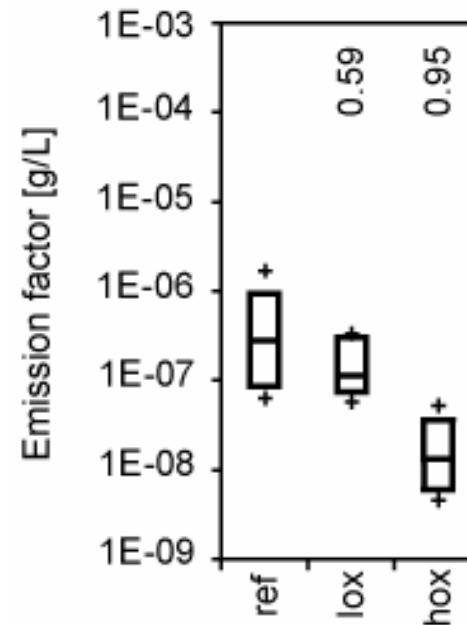
# Genotoxic PAHs

For example benzo(a)pyrene?

## Carcinogenic PAHs



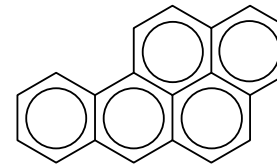
Benzo(a)-  
pyrene (7)



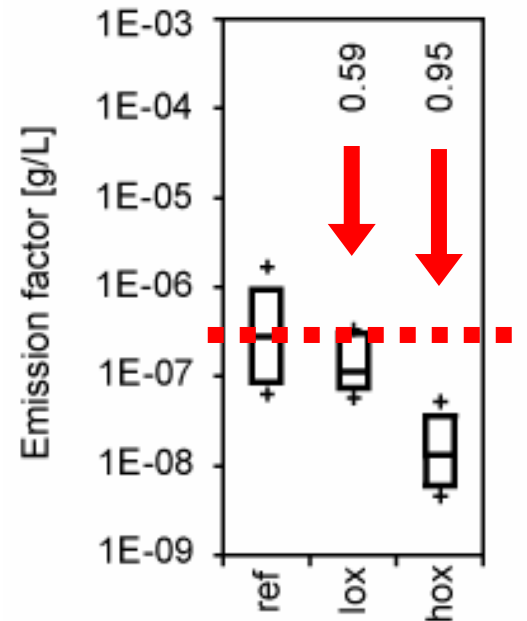
# Genotoxic PAHs

Efficient conversion of benzo(a)pyrene

Carcinogenic PAHs



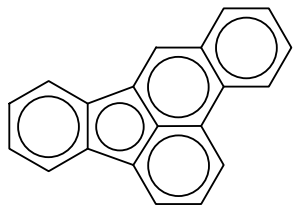
Benzo(a)-pyrene (7)



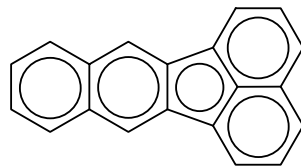
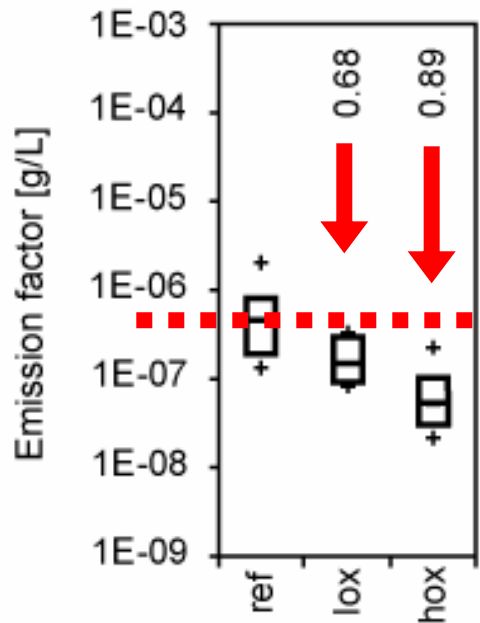
# Genotoxic PAHs

Conversion of all carcinogenic PAHs!

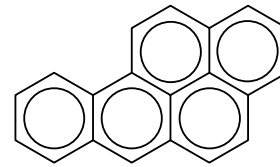
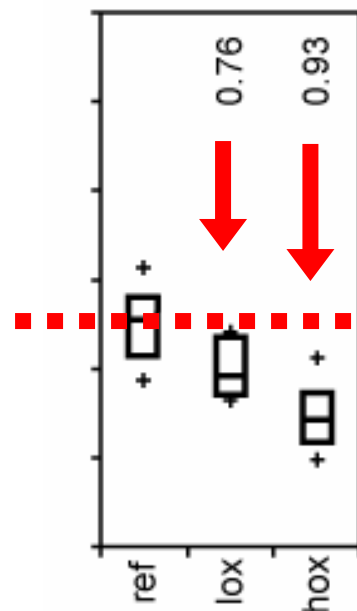
## Carcinogenic PAHs



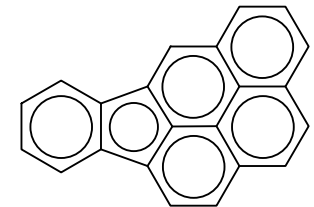
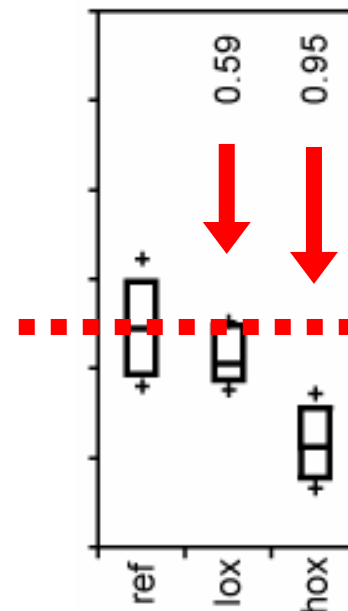
Benzo(b)-  
fluoranthene (5)



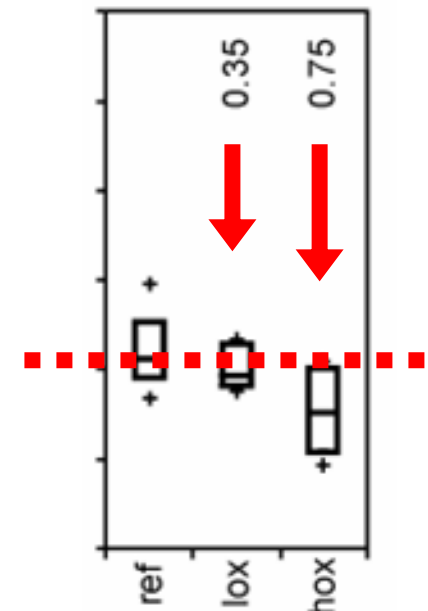
Benzo(k)-  
fluoranthene (6)



Benzo(a)-  
pyrene (7)



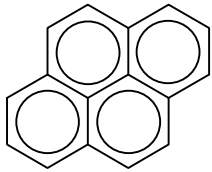
Indeno(1,2,3-cd)-  
pyrene (8)



# Genotoxic PAHs

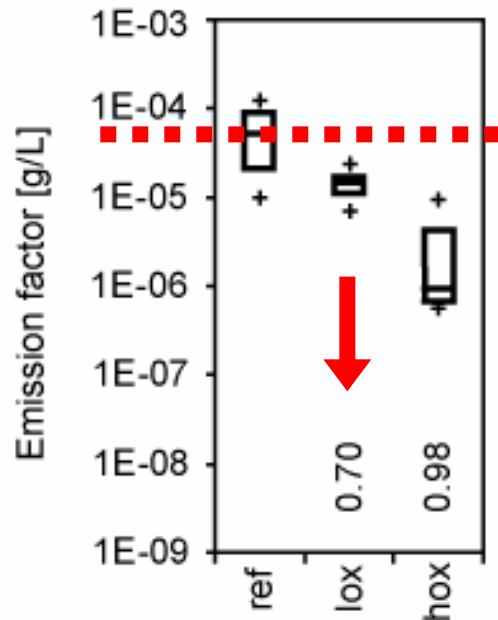
Compound specific conversion?

## Carcinogenic PAHs



Pyrene (1)

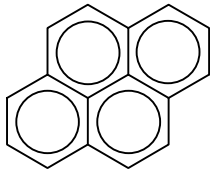
$6.0 \times 10^{-4}$  Pa



# Genotoxic PAHs

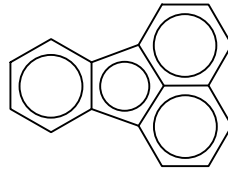
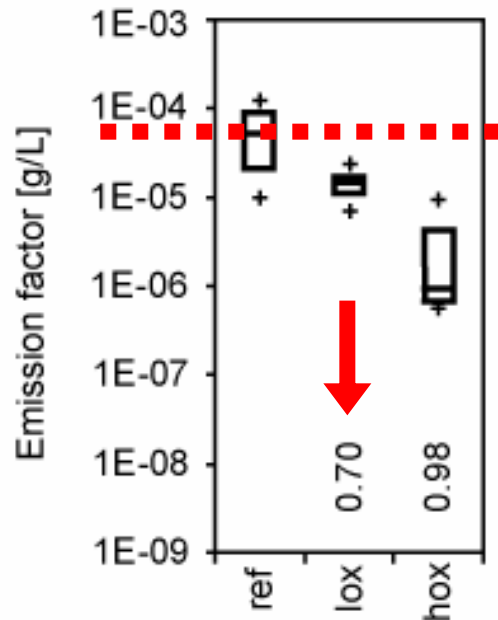
Compound specific conversion?

## Carcinogenic PAHs



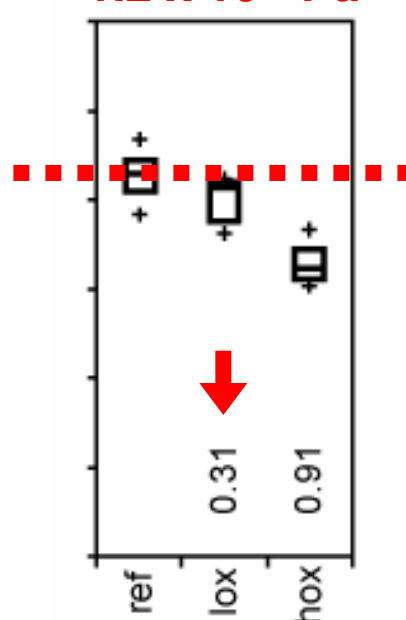
Pyrene (1)

$6.0 \times 10^{-4}$  Pa



Fluoranthene (2)

$1.2 \times 10^{-3}$  Pa

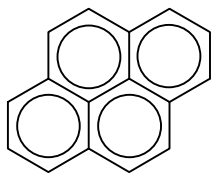




# Genotoxic PAHs

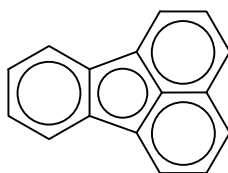
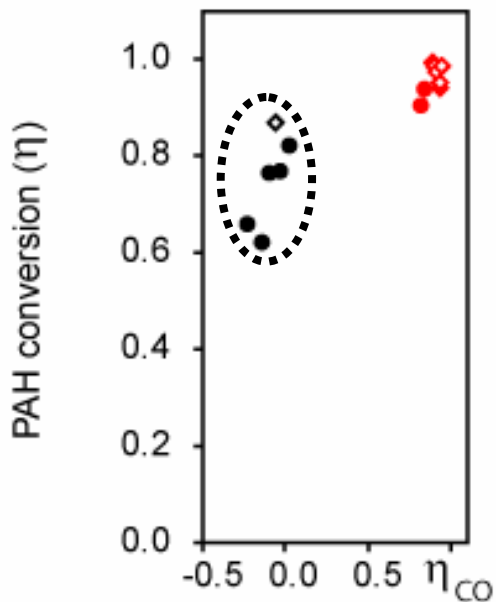
Volatility and reactivity affect filtration efficiency!

## Carcinogenic PAHs



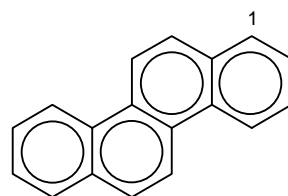
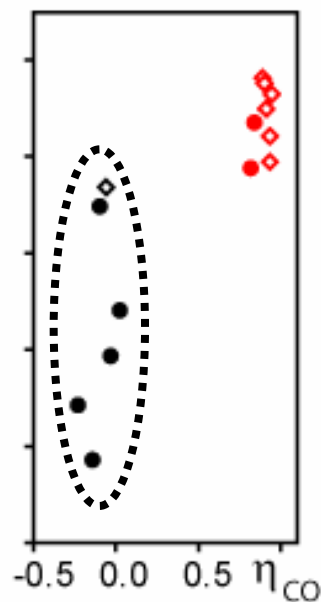
Pyrene (1)

$6.0 \times 10^{-4}$  Pa



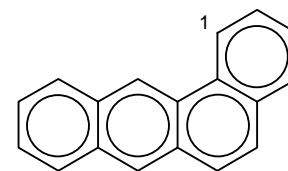
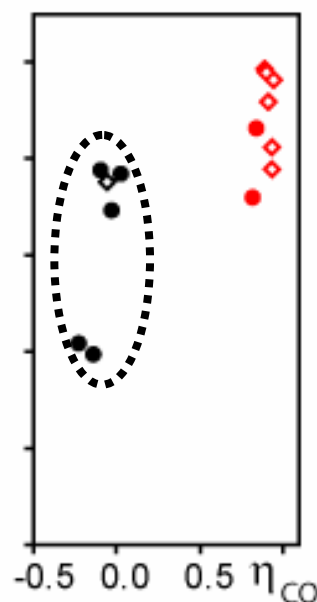
Fluoranthene (2)

$1.2 \times 10^{-3}$  Pa



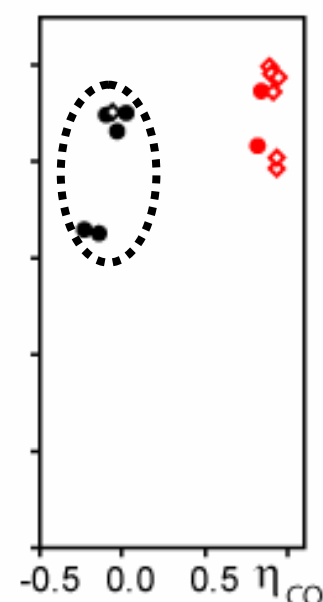
Chrysene (3)

$8.5 \times 10^{-7}$  Pa



Benz(a)anthracene (4)

$2.8 \times 10^{-5}$  Pa



# Secondary pollutants of catalytic converter systems

What else can a converter produce besides  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$ ?

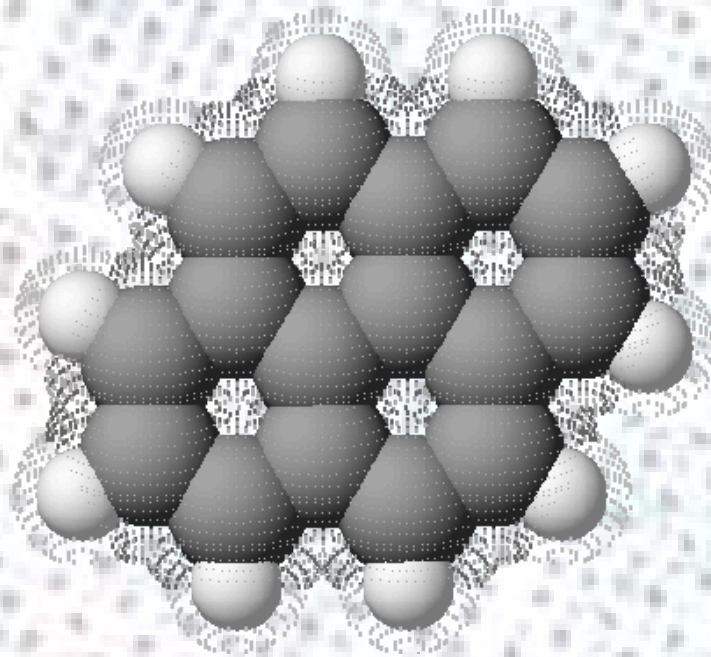
## Toxic secondary pollutants - relevant examples

- **TWC-induced formation of ammonia**  
TWCs – the most efficient DeNOx systems on road
- **Formation of  $\text{NO}_2$  in diesel oxidation catalysts**  
From a reducing exhaust to an oxidizing exhaust
- **Formation of PAHs in diesel particulate filters?**  
Carcinogenic PAHs from soot combustion?
- **Nitration of PAHs in particulate traps?**  
From harmless precursors to mutagenic Nitro-PAHs?
- **Formation of PCDD/Fs in particulate traps?**  
The DPF- an ideal reactor

# The DPF – a chemical reactor

Is nitration of PAHs in NO<sub>x</sub>-rich diesel exhaust an issue?

Nitration of PAHs

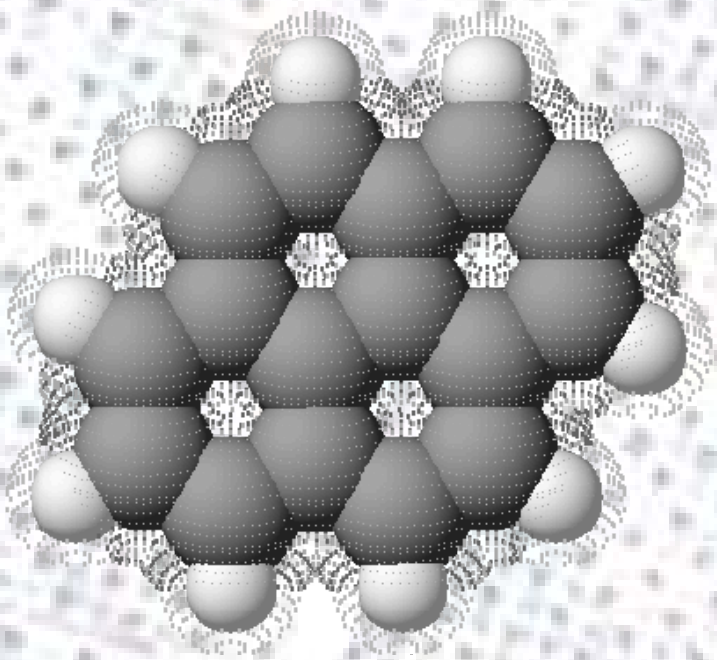


pyrene

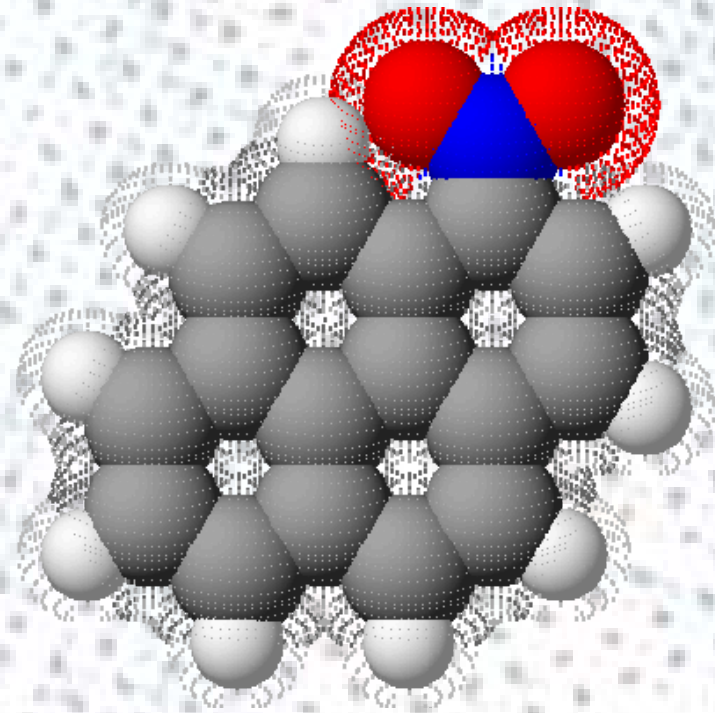
# The DPF – a chemical reactor

In one step from a harmless precursor to a mutagen?

## Nitration of PAHs



pyrene

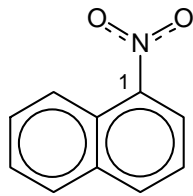


1-nitropyrene

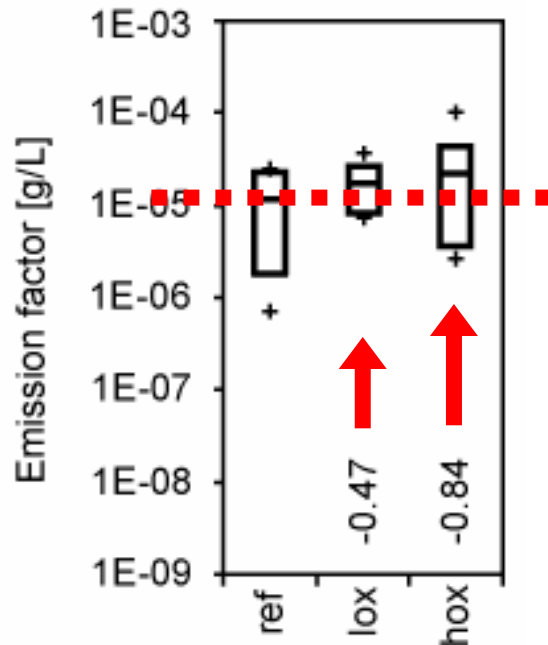
# Genotoxic Nitro-PAHs

## Formation of 1-nitronaphthalene

### DPF-induced nitration of PAHs



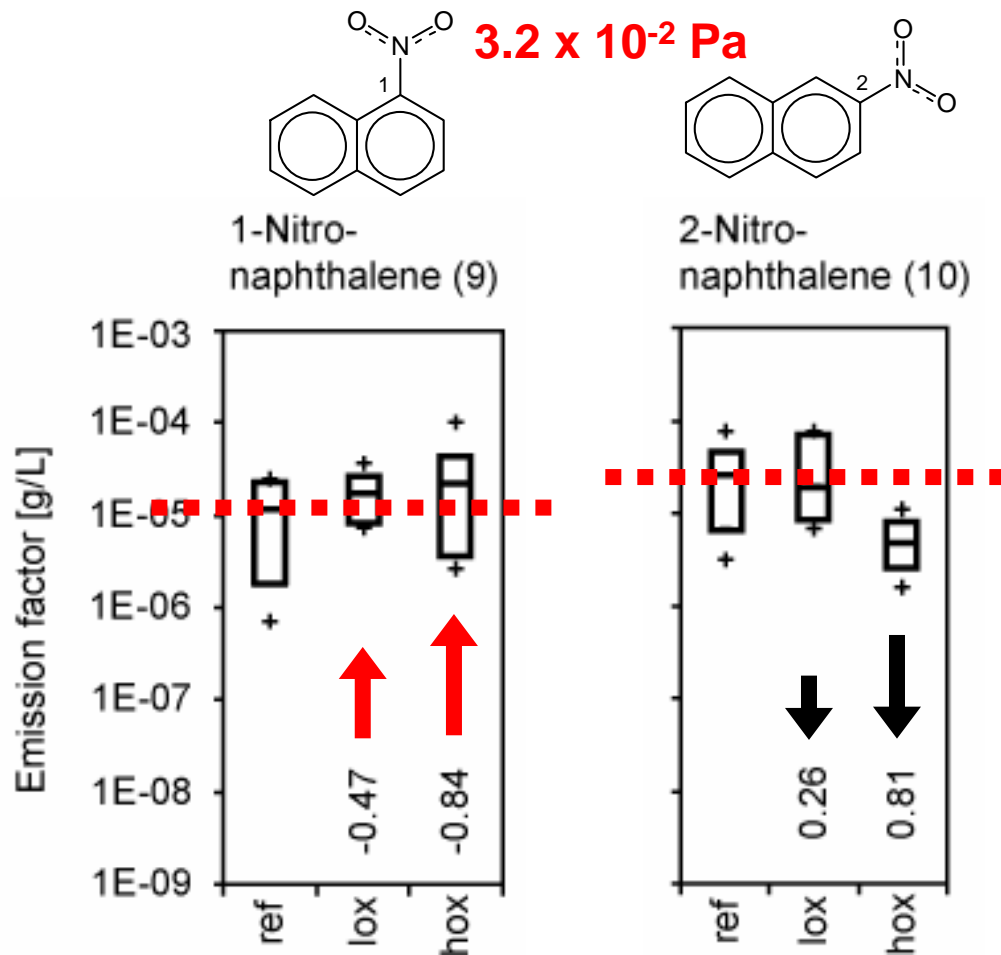
1-Nitro-naphthalene (9)



# Genotoxic Nitro-PAHs

Formation of 1-nitronaphthalene but conversion of 2-nitronaphthalene

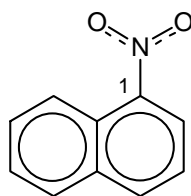
## DPF-induced nitration of PAHs



# Genotoxic Nitro-PAHs

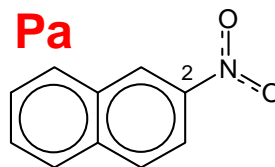
Formation of 1-nitronaphthalene but conversion of 2-nitronaphthalene

## DPF-induced nitration of PAHs



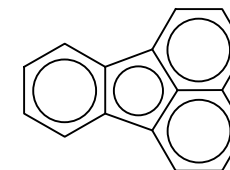
$3.2 \times 10^{-2}$  Pa

1-Nitro-naphthalene (9)



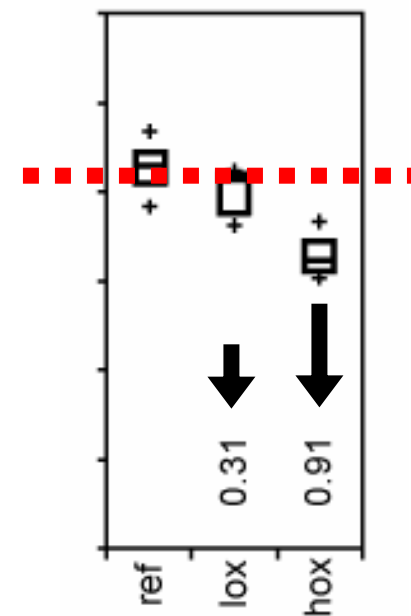
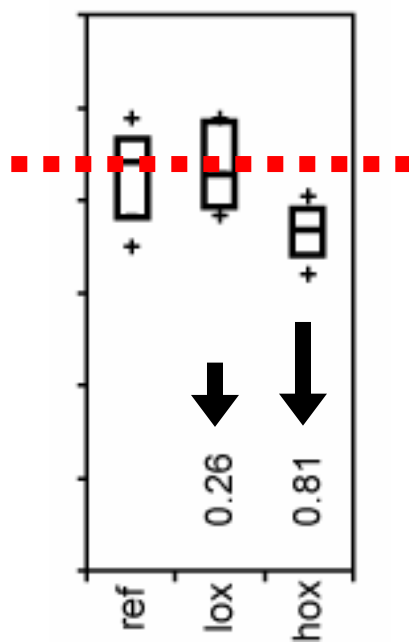
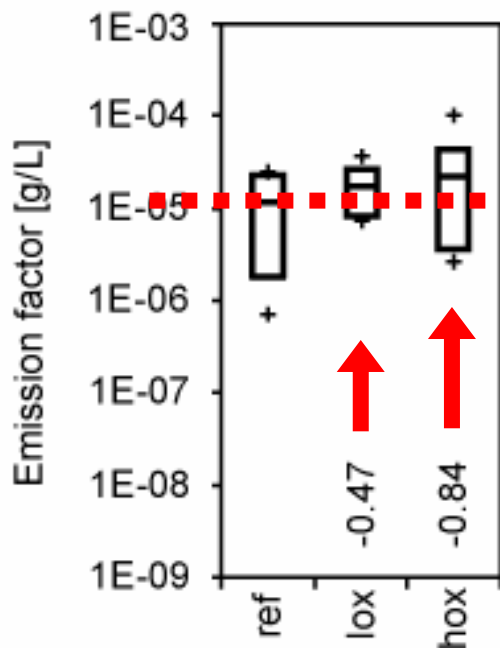
$1.2 \times 10^{-3}$  Pa

2-Nitro-naphthalene (10)



For comparison

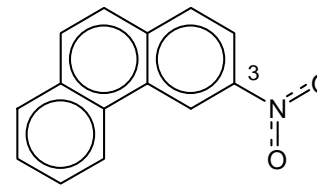
Fluoranthene (2)



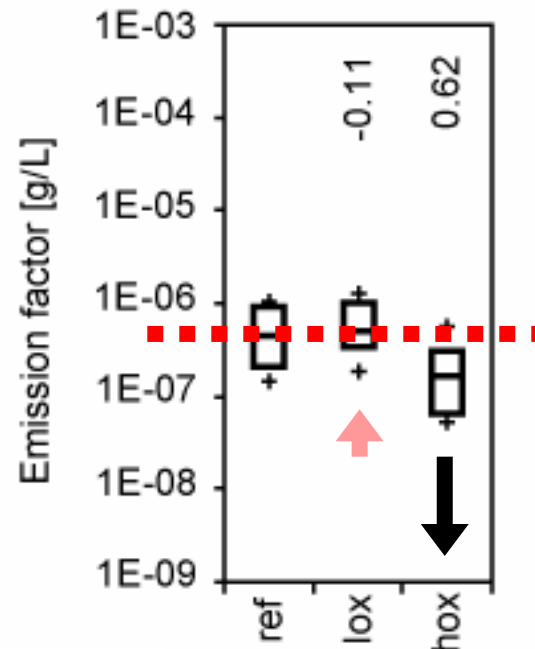
# Genotoxic Nitro-PAHs

What about 3-ring Nitro-PAHs?

## DPF-induced nitration of PAHs



3-Nitro-phenanthrene (11)

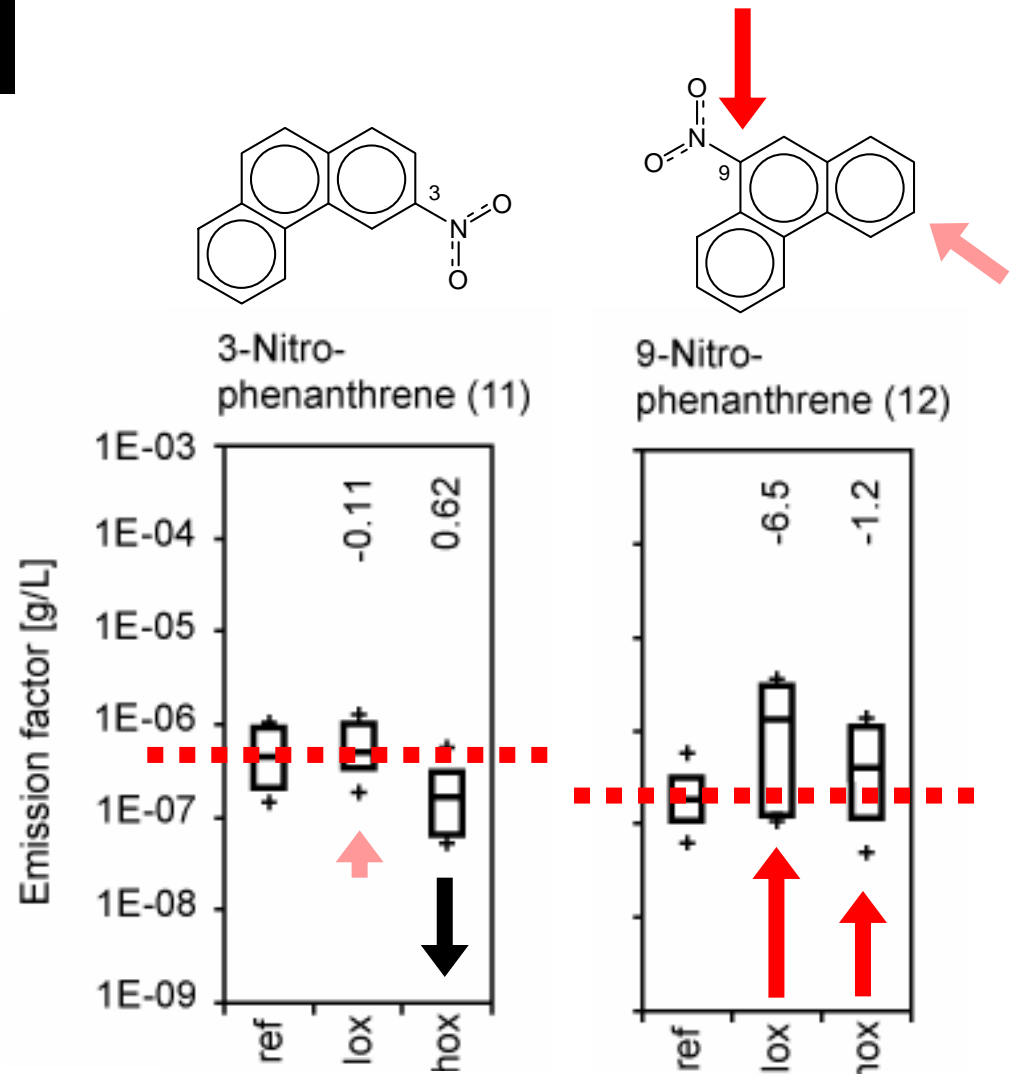




# Genotoxic Nitro-PAHs

Formation of 9-nitrophenanthrene but some conversion of 3-nitrophenanthrene

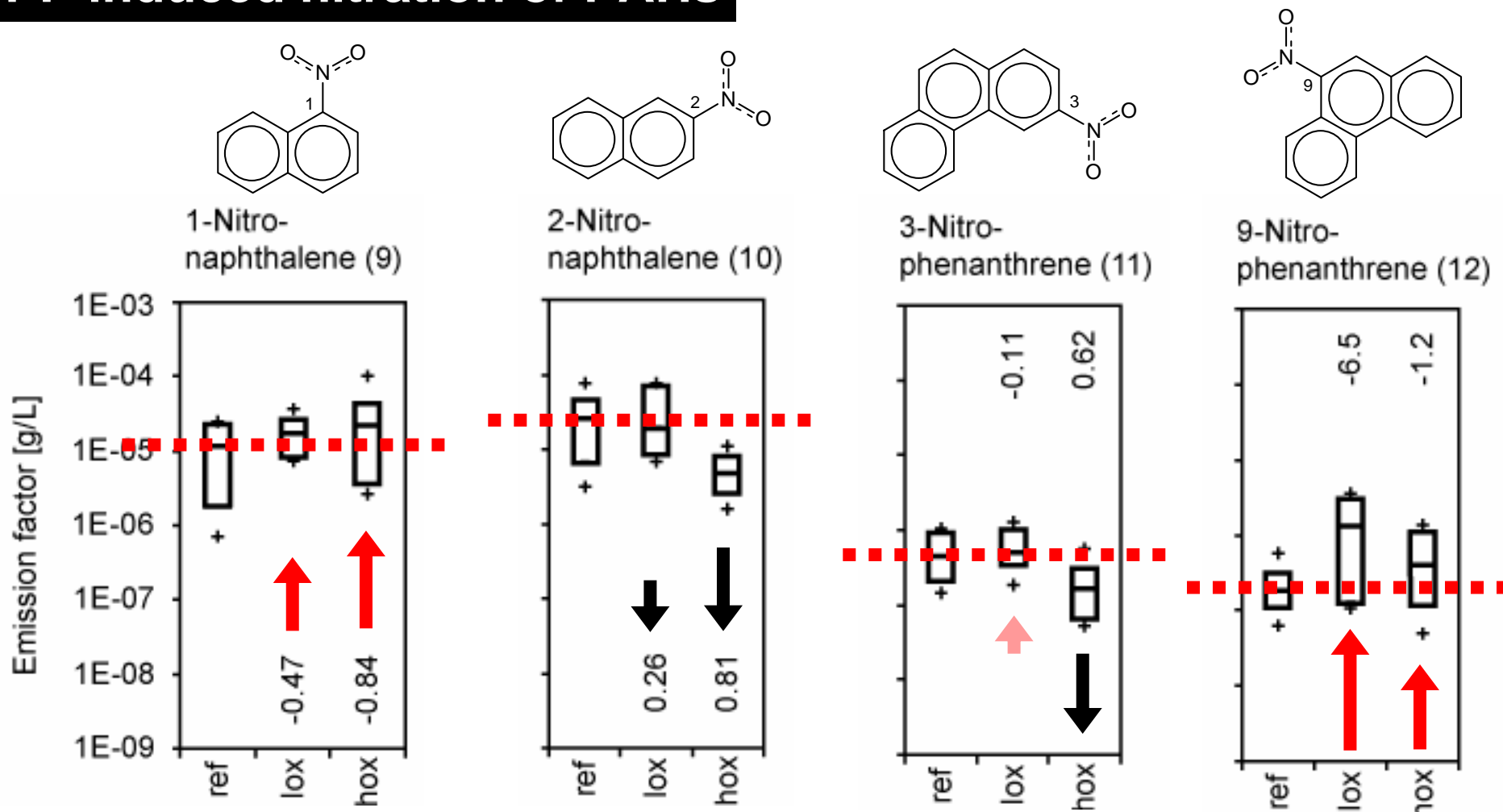
## DPF-induced nitration of PAHs



# Genotoxic Nitro-PAHs

Nitration is regioselective – peri-positions are more reactive.

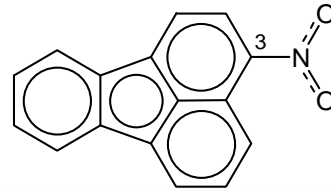
## DPF-induced nitration of PAHs



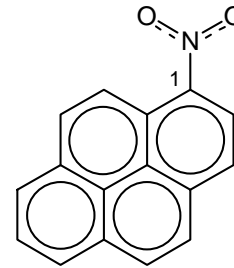
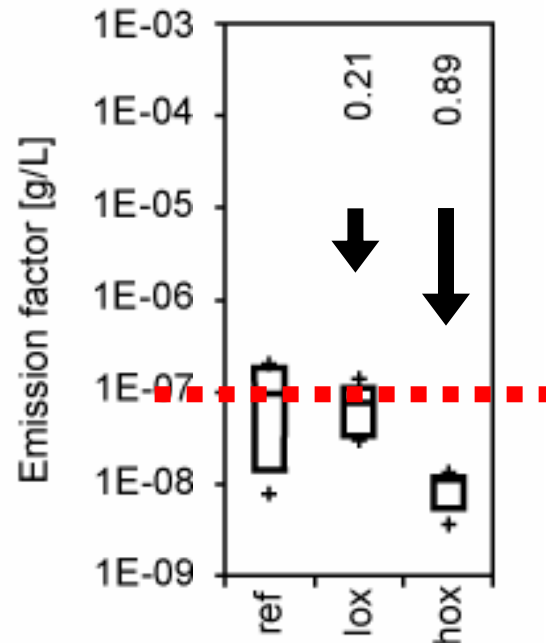
# Genotoxic Nitro-PAHs

What about mutagenic Nitro-PAHs?

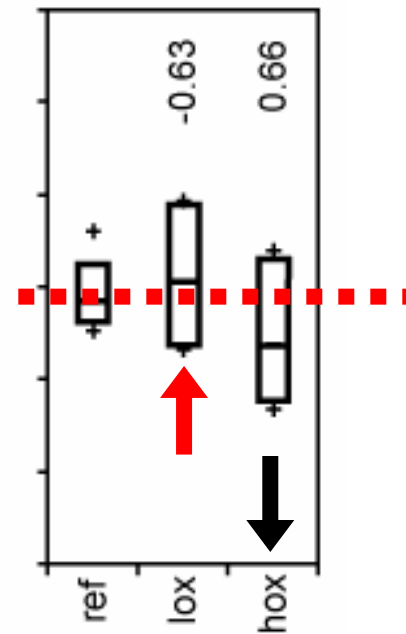
## DPF-induced nitration of PAHs



3-Nitrofluoranthene (14)



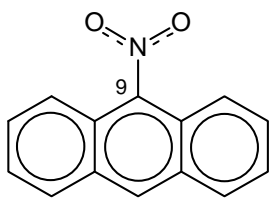
1-Nitropyrene (15)



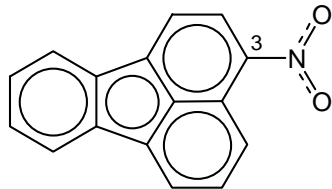
# Genotoxic Nitro-PAHs

What about less volatile Nitro-PAHs?

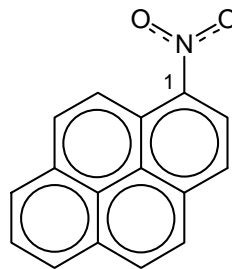
## DPF-induced nitration of PAHs



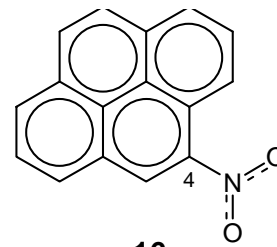
9-Nitro-anthracene (13)



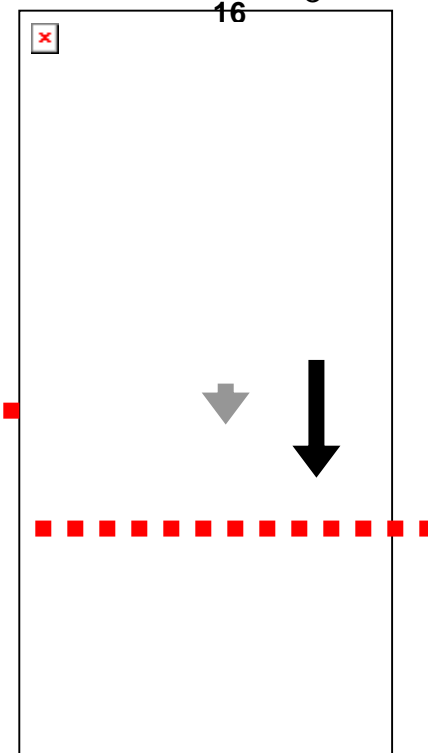
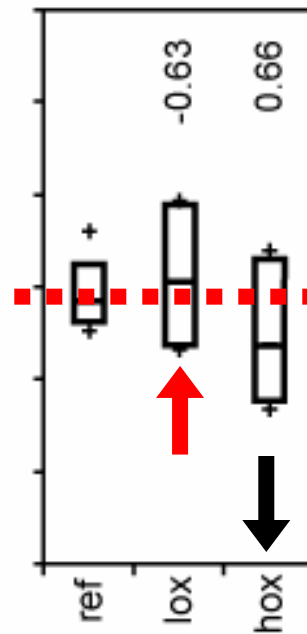
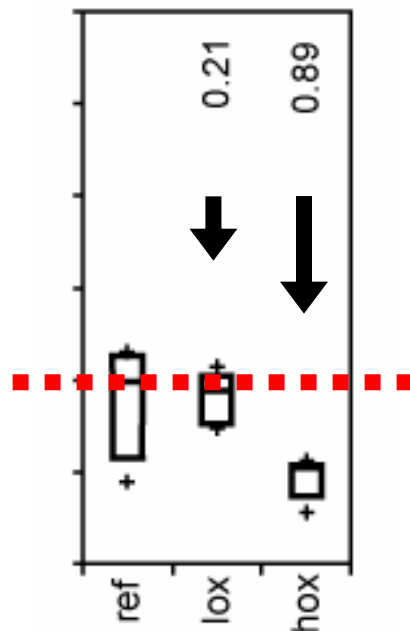
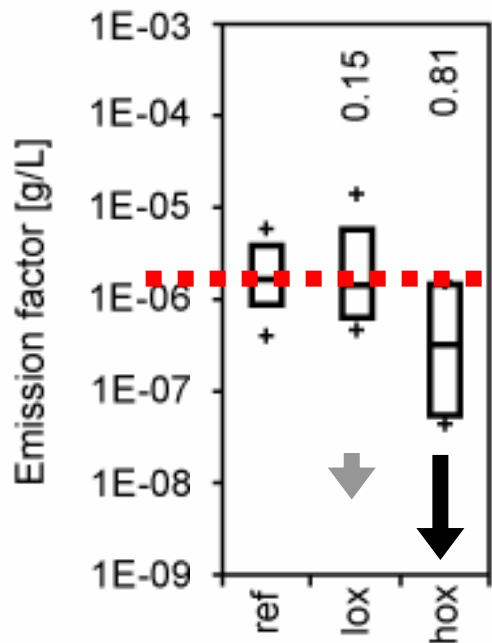
3-Nitro-fluoranthene (14)



1-Nitro-pyrene (15)



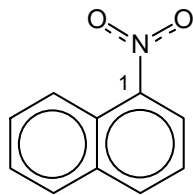
16



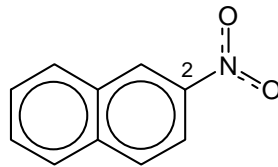
# Genotoxic Nitro-PAHs

Substantial variation among DPFs, but similar nitration chemistry

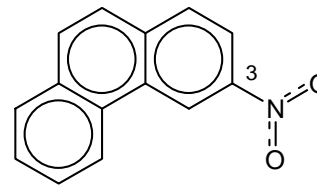
## DPF-induced nitration of PAHs



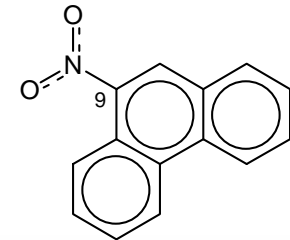
1-Nitro-naphthalene (9)



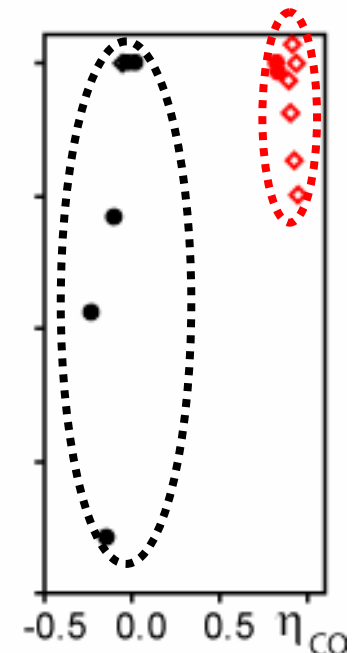
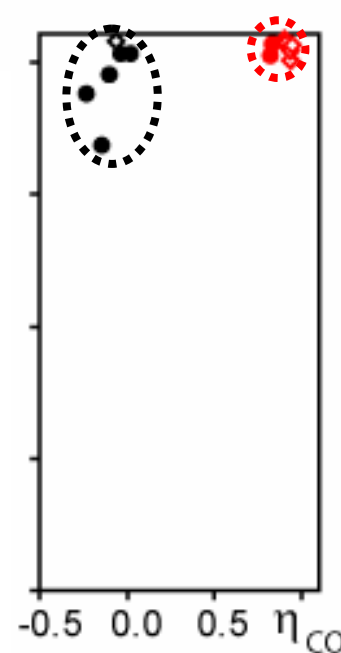
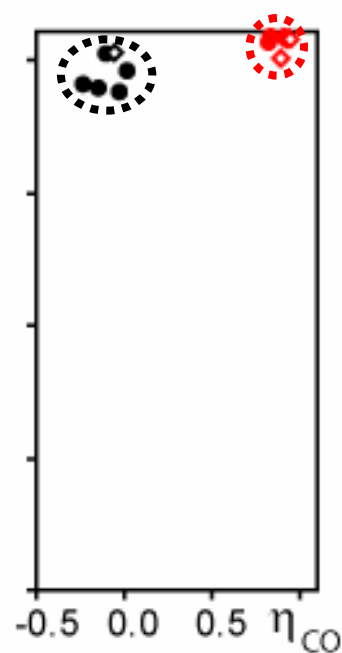
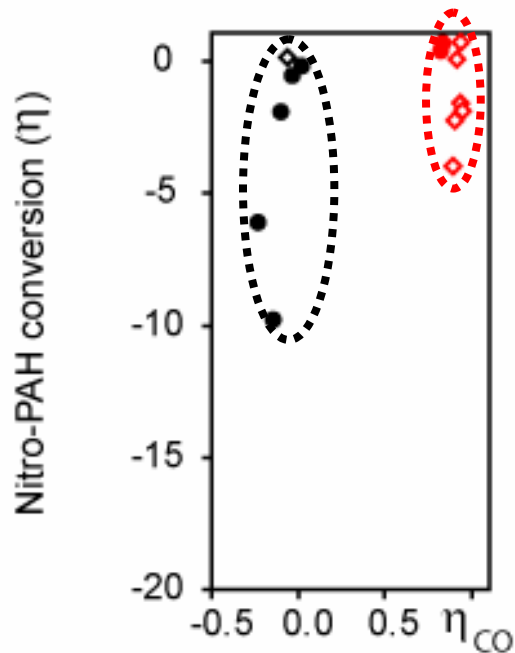
2-Nitro-naphthalene (10)



3-Nitro-phenanthrene (11)



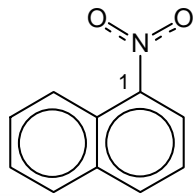
9-Nitro-phenanthrene (12)



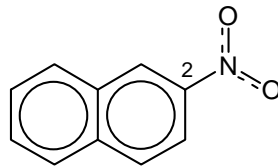
# Genotoxic Nitro-PAHs

Formation and release of 1-nitronaphthalene and 9-nitrophenanthrene is frequent

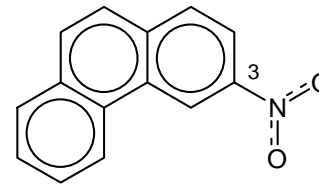
## DPF-induced nitration of PAHs



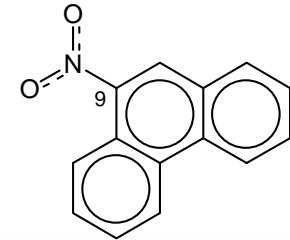
1-Nitro-naphthalene (9)



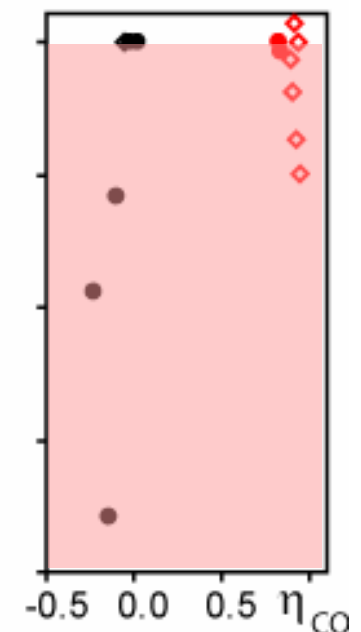
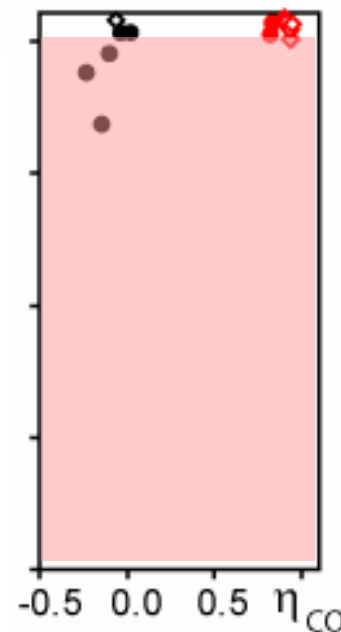
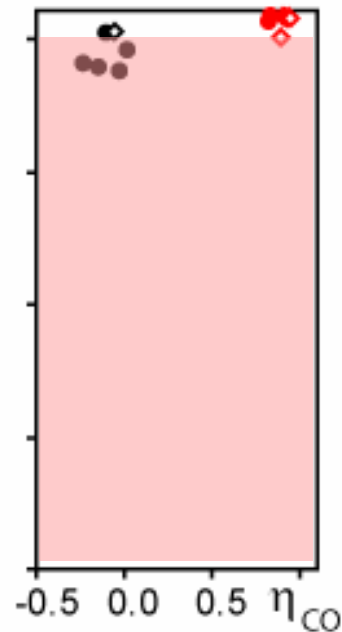
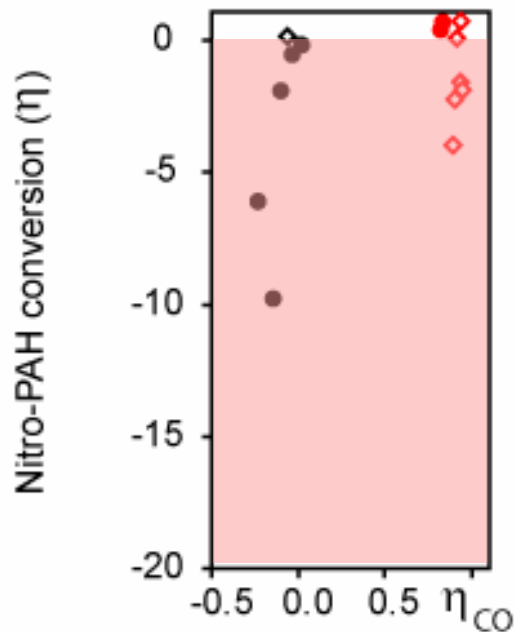
2-Nitro-naphthalene (10)



3-Nitro-phenanthrene (11)



9-Nitro-phenanthrene (12)



# Effects of low- and high-oxidation DPFs on genotoxic exhaust constituents

**Do DPFs detoxify diesel exhaust?**

Trojan horse, Harbour of Canakkale, Turkey



# Effects of low- and high-oxidation DPFs on genotoxic exhaust constituents

Its a long way from diesel soot to CO<sub>2</sub> and H<sub>2</sub>O!

## Results:

- Wall-flow DPFs eliminate solid nanoparticles
- Some DPFs form NO<sub>2</sub>, others convert it
- Current DPF technology lowers emissions of genotoxic compounds
- Some nitro-PAHs are formed *de novo*, others are converted

## Conclusion:

- **VERT<sup>®</sup>-approved DPF are efficient sinks for soot nanoparticles and genotoxic compounds with moderate risks for secondary poisoning**
- **DPFs to not abate the NO<sub>x</sub> problem, some even enhance it!**



# Effects of low- and high-oxidation DPFs on genotoxic exhaust constituents

About 7 m<sup>3</sup> exhaust (3 min operation of a 3.0 L Euro-3 engine (100 kW))



# Effects of low- and high-oxidation DPFs on genotoxic exhaust constituents



Today, wall-flow DPFs are best available technology to detoxify diesel exhaust. Are combined DPF-DeNO<sub>x</sub> systems the future?

# Effects of low- and high-oxidation DPFs on genotoxic exhaust constituents

## Thanks:

- **VERT team:** Andreas Mayer, TTM, Niederrohrdorf  
Jan Czerwinski, Sandro Napoli, Tobias Neubert, Thomas Hilfiker,  
Jean-Luc Petermann, Yan Zimmerli, Uni. Appl. Sci., Biel.  
Markus Kasper, Adrian Hess, Thomas Mosimann, Matter Engineering, Wohlen  
Hans Jaeckle, Urs Debrunner, Oliver Schumm, Intertek Caleb Brett, Schlieren.
- **Empa colleagues:** Brigitte Buchmann, Thomas Bühler, Anna-Maria Forss, Urs Gfeller,  
Maria Guecheva, Peter Graf, Roland Graf, Erika Guyer, Regula Haag, Peter Honnegger,  
Judith Kobler, Martin Kohler, Peter Lienemann, Alfred Mack, Peter Mattrel, Martin Mohr,  
Joachim Mohn, Christof Moor, Peter Schmid, Cornelia Seiler, Andreas Paul, Heinz  
Vonmont, Thomas Walter, Max Wolfensberger, Daniela Wenger, Adrian Wichser,  
Markus Zennegg, Kerstin Zeyer.
- **Gouvernement:** Giovanni D'Urbano, Max Wyser, Gerhard Leutert, Martin Schiess,  
Swiss Fed. Office for Environment, Bern
- **Filter- & catalyst manufacturers:** >30 different diesel particulate filter systems



Materials Science & Technology



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Traugott Sandmeyer (1854-1922)



