Parameters affecting the dioxin formation in diesel particle filters

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Catalytic diesel particle filters (DPFs) are currently the most promising technology to remove particles from diesel exhaust. DPFs also lower emissions of semi-volatile compounds including genotoxic polycyclic aromatic hydrocarbons (PAHs), nitro-PAHs and oxy-PAHs. At elevated temperatures, e.g. during filter regeneration, accumulated carbonaceous materials are combusted in catalytic DPFs. The respective reactions are typically supported by noble-, rare earth-, and transition-metal catalysts, which are either coated on various filter substrates or formed *in situ* via combustion of metal-containing precursors, so-called fuel-borne catalysts.

However, the combustion of diesel soot and adsorbed compounds may also induce the formation of new pollutants. The VERT secondary emission test is evaluating such risks. In principle, DPFs are ideal chemical reactors for a *de novo* synthesis of polychlorinated dibenzodioxins/furans (PCDD/Fs). Figure 1 displays the chemical structures of the investigated PCDD/Fs.

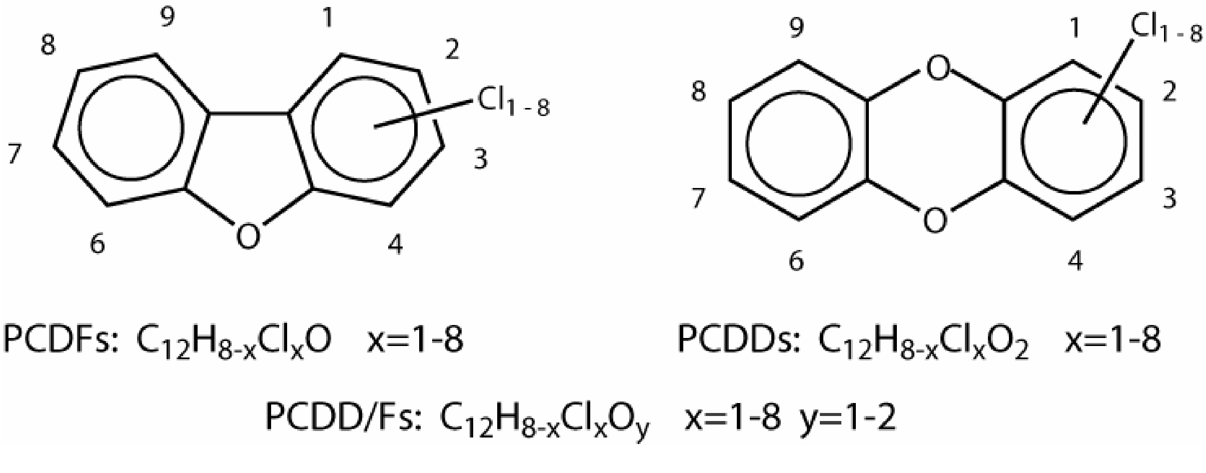


Fig. 1. Chemical structures of PCDFs (left) and PCDDs (right)

De novo PCDD/F formation has been observed in municipal waste incinerators during stack gas filtration. Filters are designed to accumulate solid particles, but they also offer large surface areas to accumulate dioxin precursors and potential catalysts. Certain transition metal oxides and halides e.g. from copper, have been identified as active dioxin catalysts in incinerator flue gas. Precursor and catalyst levels and with it their residence time in DPFs can increase considerably over time compared to open structures, offering only short contact times.

Up to now, the dioxin formation potential of 19 coated DPFs and 16 fuel-borne catalyst systems have been evaluated according to the Swiss norm SN 277205 and the Swiss ordinance on air quality control (LRV). Over the years, three heavy duty diesel engines (Liebherr, EURO-1, 6.1 L, EURO-2, 6.6 L, EURO-3, 6.4 L) have been used as test platforms, applying the 8-stage ISO 8178/4 C1 cycle. Temperatures in this cycle are ideal to support a PCDD/F formation. About 75% of the cycle time, DPFs are operated in a critical temperature range of 260-440 °C, in which PCDD/Fs can be formed, but are not combusted yet. The dioxin formation potential is evaluated under best-case conditions, with new filters and commercial, low sulfur diesel fuels as well as under worst-case conditions with chlorine-doped fuels.

So far, only three catalytic DPFs showed increased PCDD/F emissions, whereas the dioxin formation potentials of all other systems were judged to be low. Figure 2 displays emission levels of the most toxic of the PCDD/F isomers, the 2,3,7,8-TCDD or the so-called Seveso dioxin.

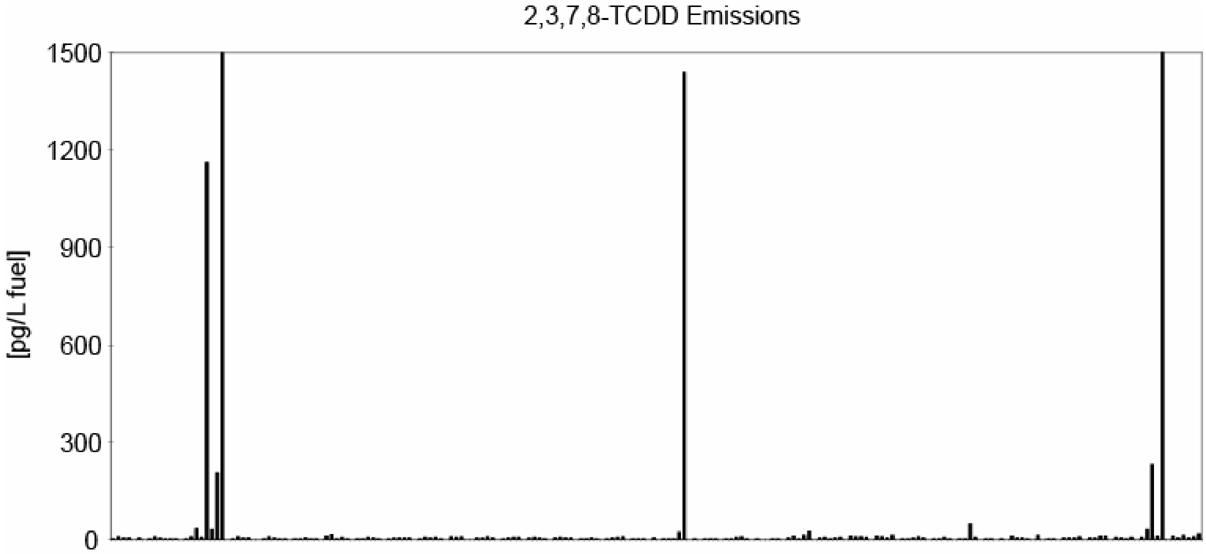


Fig. 2. Emissions of 2,3,7,8-TCDD (pg/L fuel) of various DPFs under best and worst case conditions.

Not only PCDD/F emissions levels but also the PCDD/F patterns of those DPFs with increased dioxin formation differ considerably when compared with data of similar technologies without a secondary PCDD/F formation. These pattern changes can be used as indicators for an increased *de novo* formation potential.

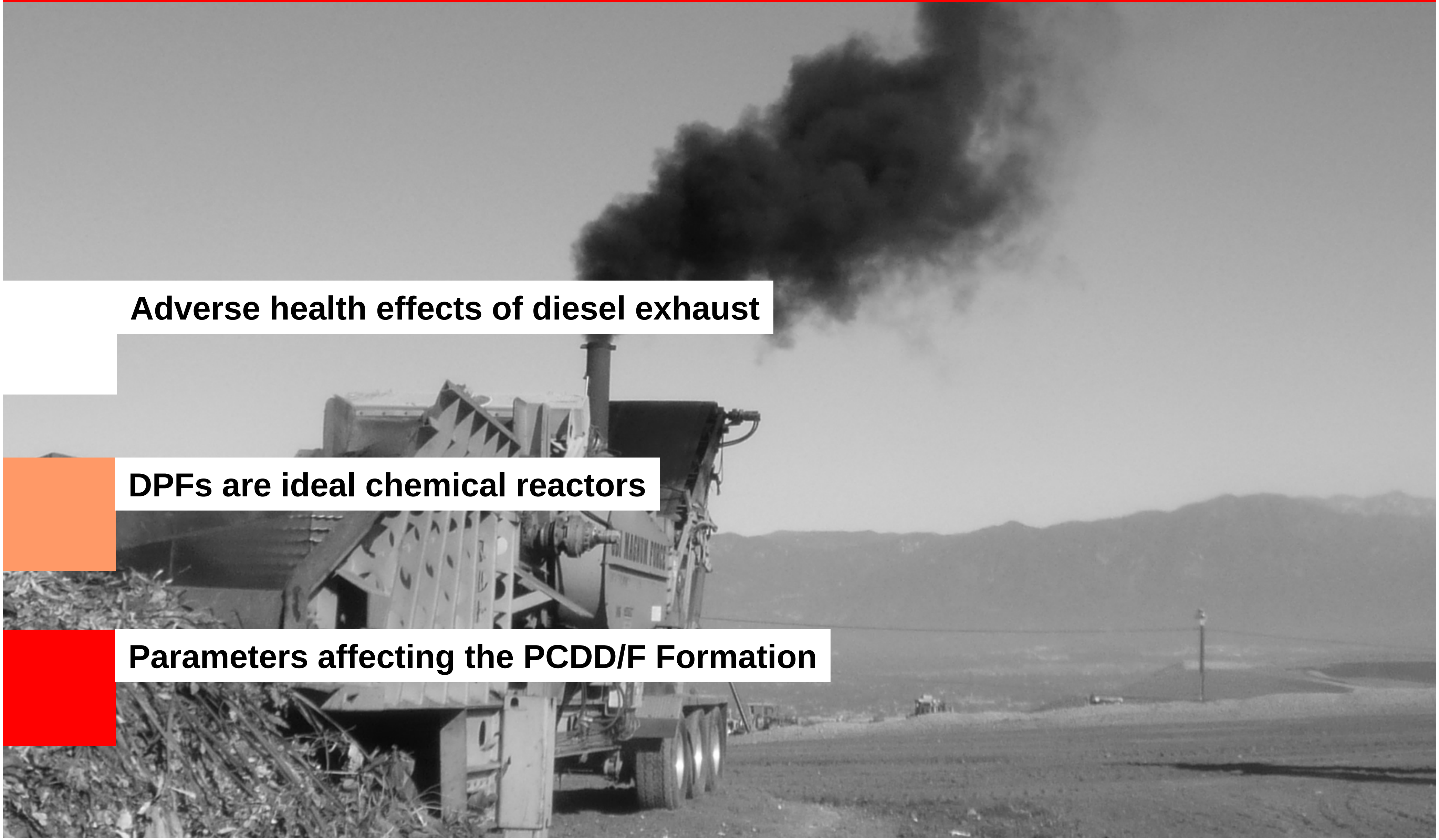
In summary, an assessment of the PCDD/F formation potential of any new catalytic DPF has become an integral part of the VERT filter testing. With now well-established procedures, those DPFs with high risks can be identified at an early stage of product development. Similar test are currently performed for deNO$_x$- and combined DPF-deNO$_x$-systems.

Parameters affecting the PCDD/F Formation: in Diesel Particle Filters

15th ETH-Conference on Combustion Generated Nanoparticles

Zürich, June 26. - 29. 2011

Parameters affecting PCDD/F Formation: in Diesel Particle Filters

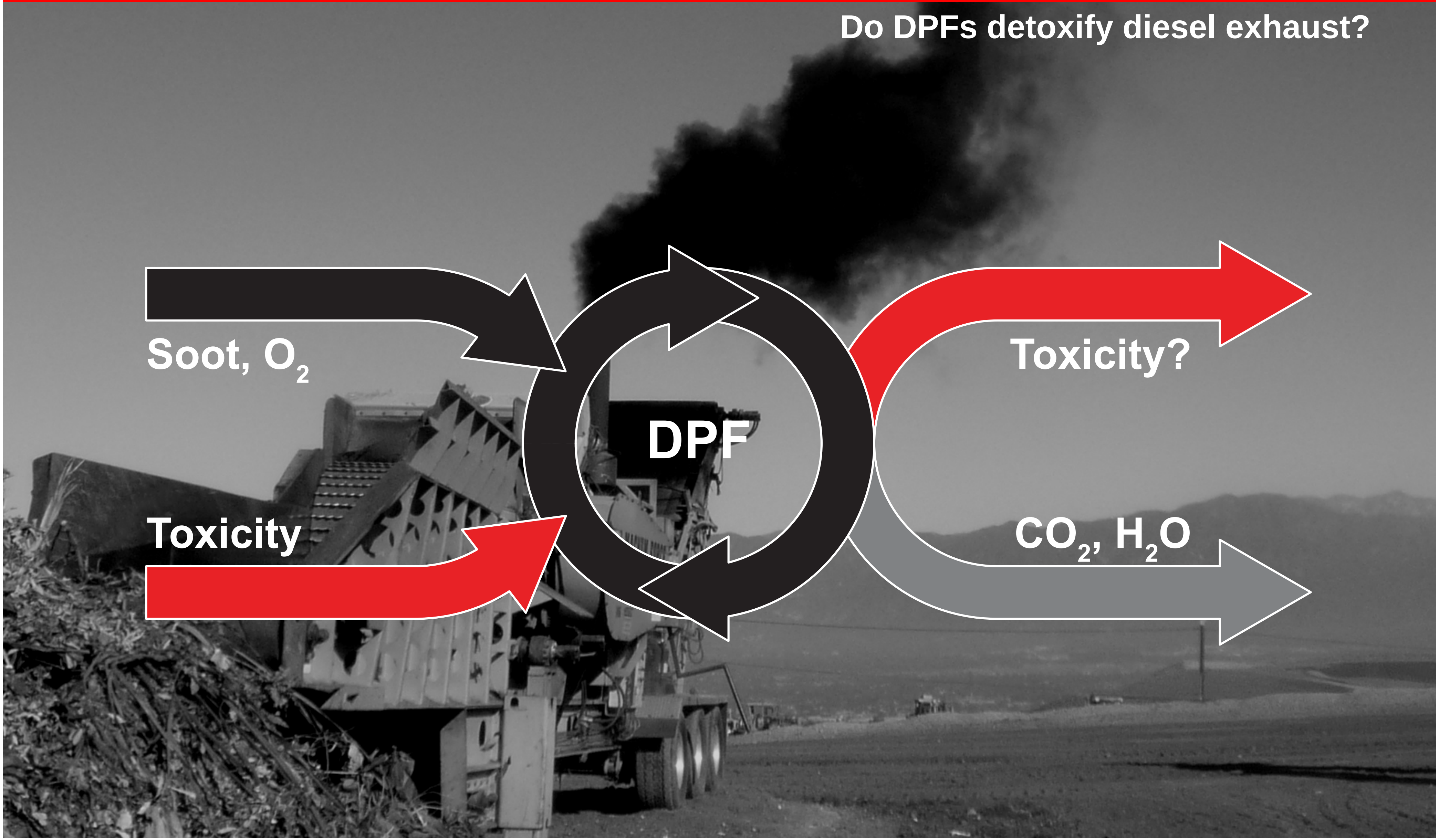


Adverse health effects of diesel exhaust

DPFs are ideal chemical reactors

Parameters affecting the PCDD/F Formation

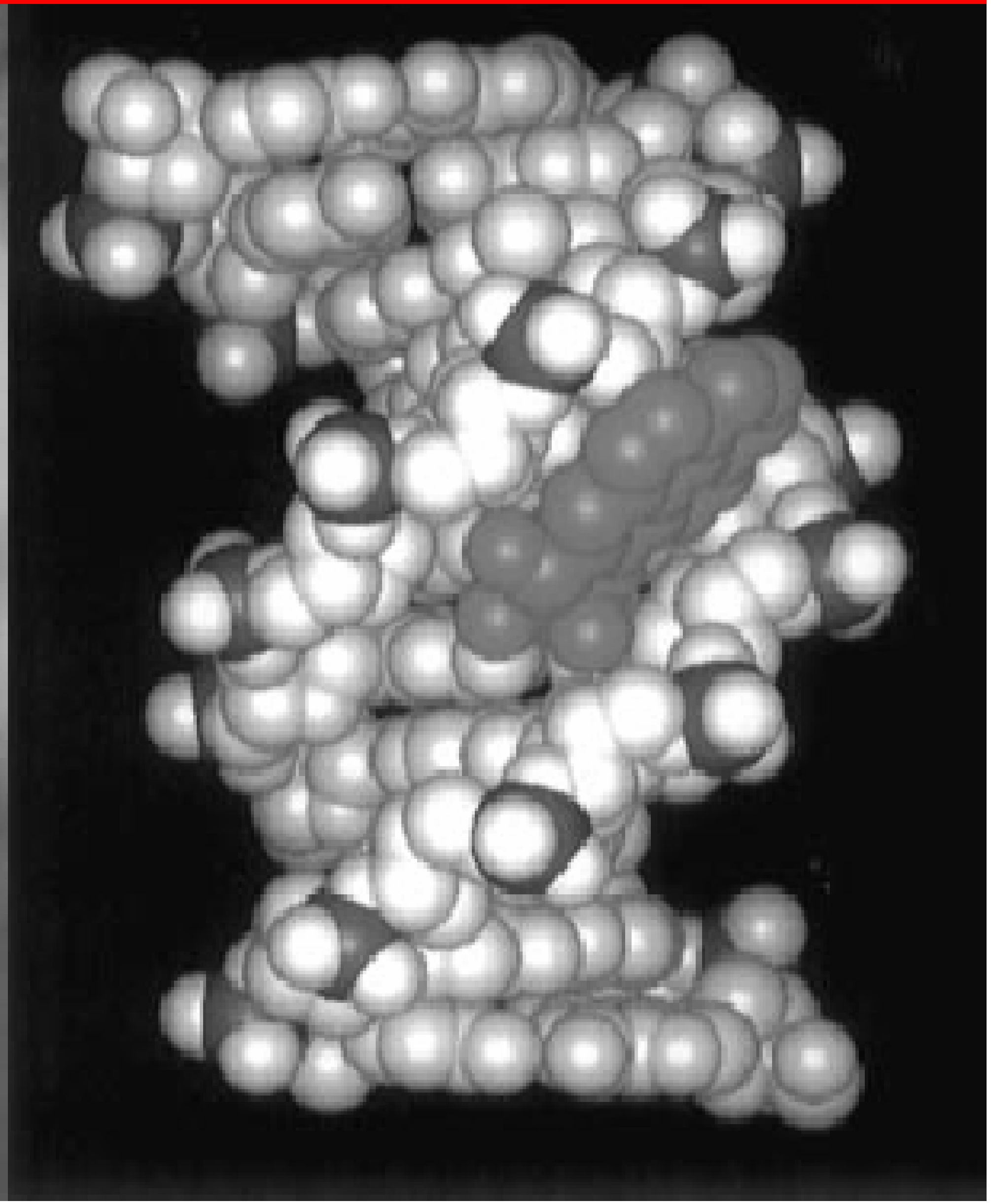
Adverse health effects of diesel exhaust



Adverse health effects of diesel exhaust

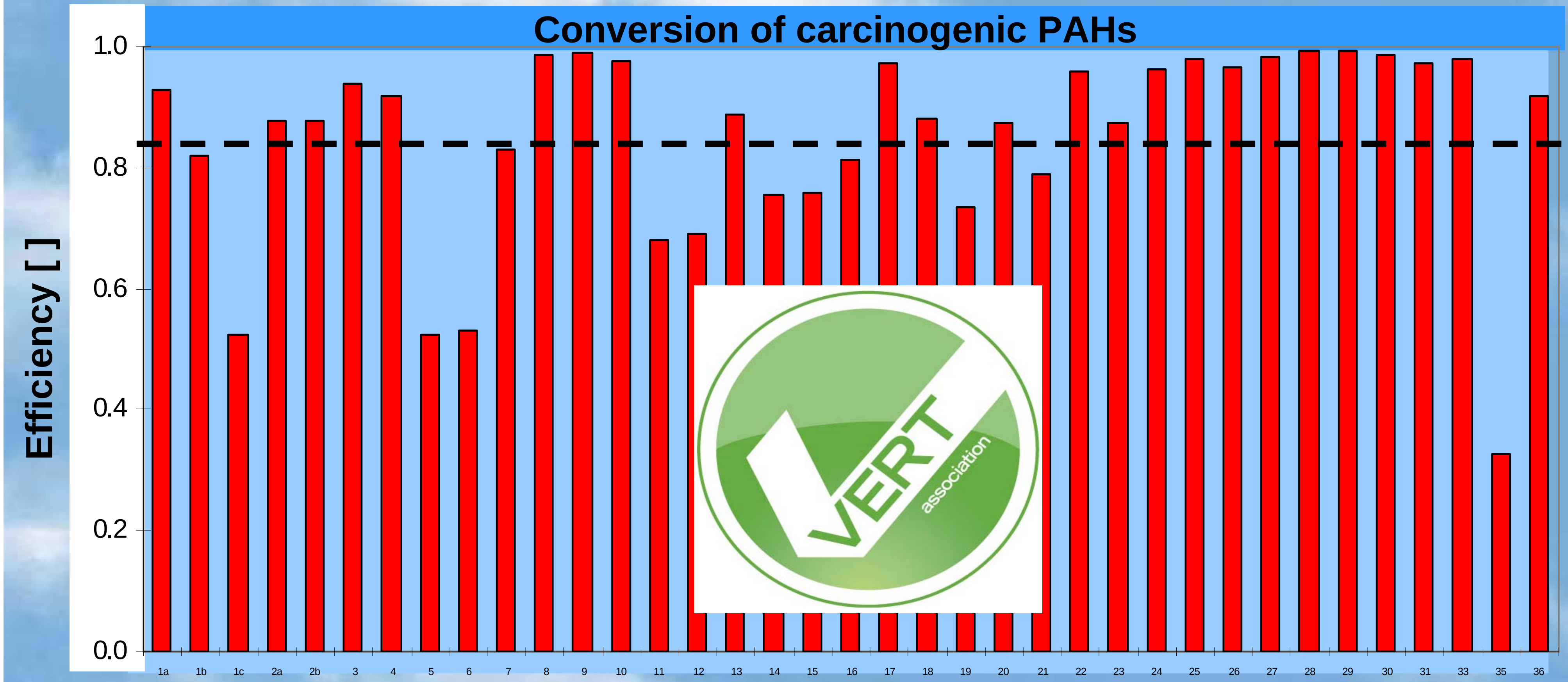
Problem: Genotoxicity

- Diesel exhaust is genotoxic (mutagenic and carcinogenic compounds)



Adverse health effects of diesel exhaust

All VERT-tested DPFs convert carcinogenic PAHs

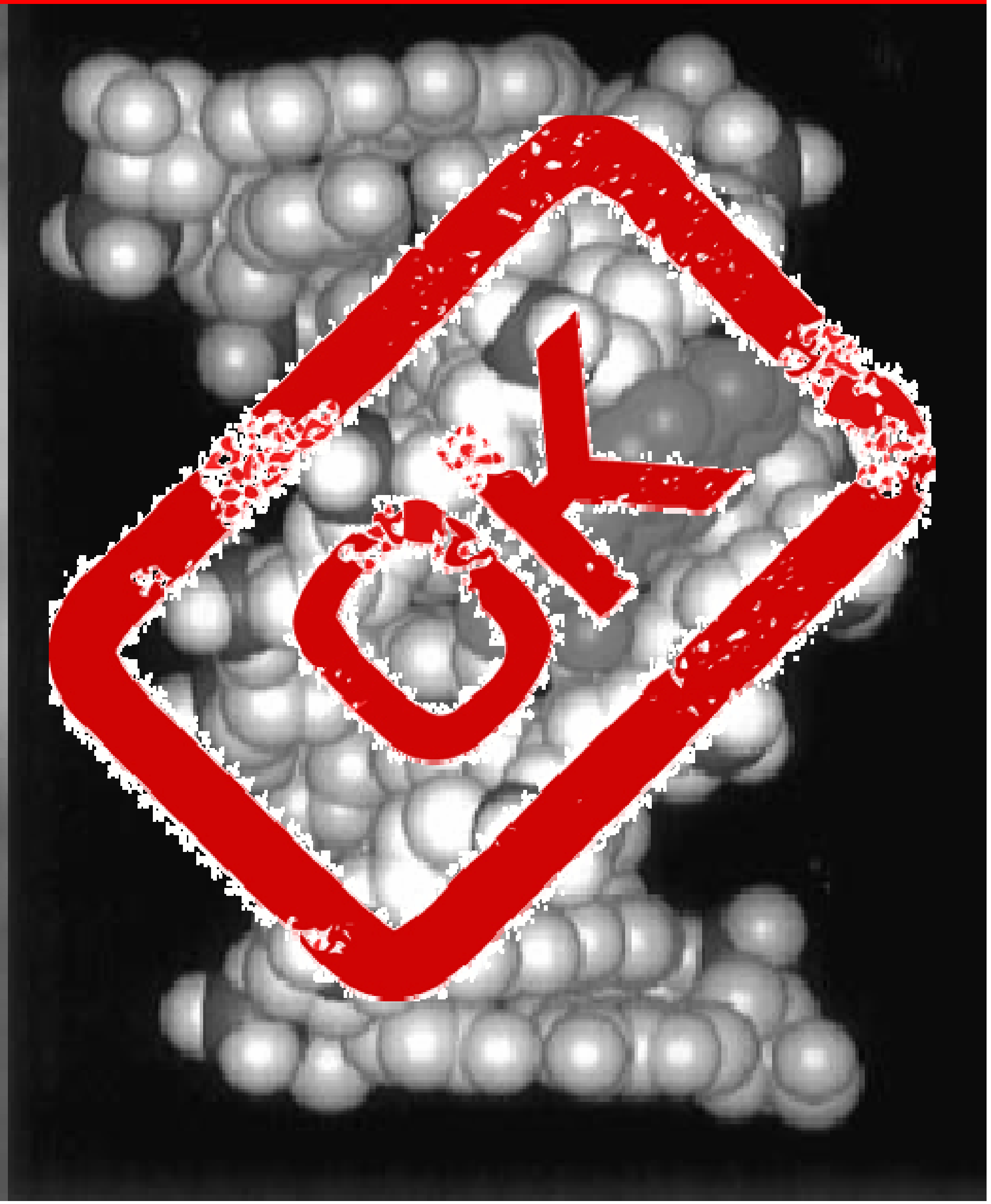


Adverse health effects of diesel exhaust

Problem: Genotoxicity

- **Diesel exhaust is genotoxic (mutagenic and carcinogenic compounds)**
- **DPF remove genotoxic compounds, 85% on average**

Heeb et al. ES&T, **2010**, 42, 3773-3779



Adverse health effects of diesel exhaust

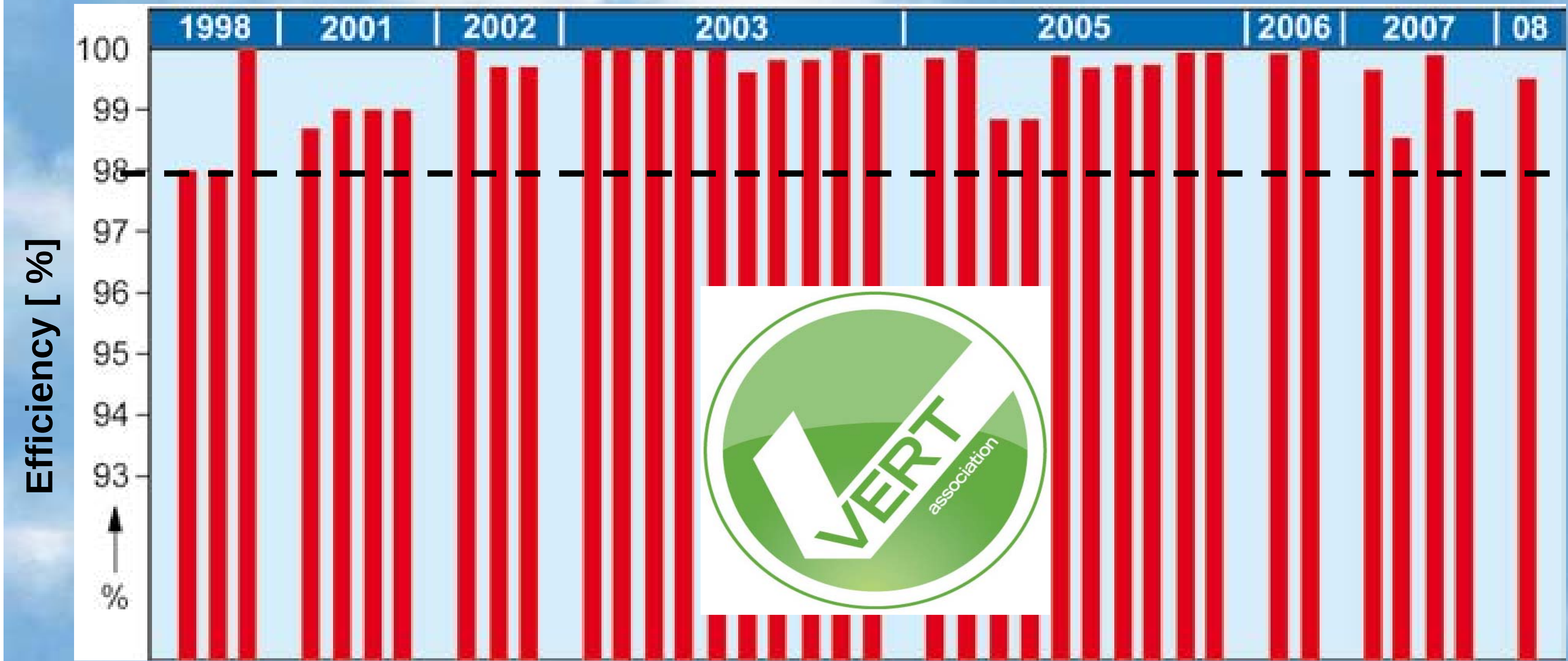
Problem: Trojan horse effect

- **Nanoparticles penetrate cell membranes (alveoli, placenta, blood cells) acting like a Trojan horse**

Trojan horse, Harbour of Canakkale, Turkey

Adverse health effects of diesel exhaust

more than 40 VERT-tested DPFs are on the market (to be used).



Mayer et al. MTZ, **2009**, 70, 72-79

Adverse health effects of diesel exhaust

Problem: Trojan horse effect

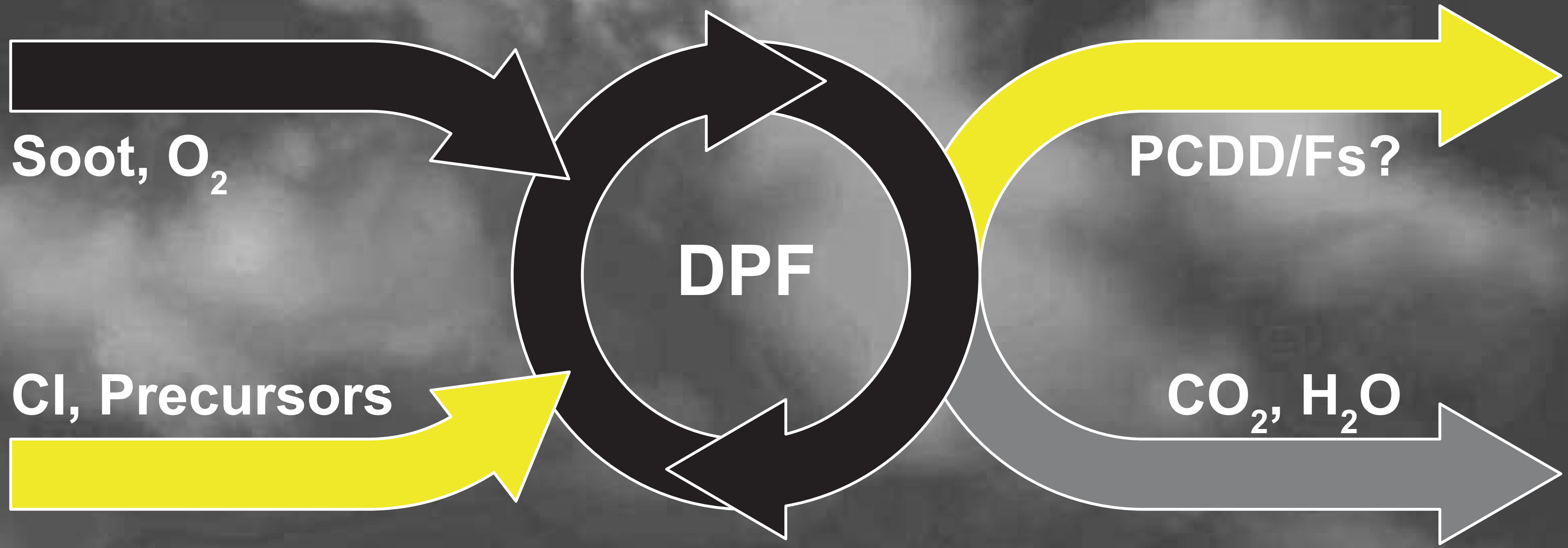
- **Nanoparticles penetrate cell membranes (alveoli, placenta, blood cells) acting like a Trojan horse**
- **DPF remove > 98% of nanoparticles**

Trojan horse, Harbour of Canakkale, Turkey

VERT Secondary emissions test

Is there a risk for a trap-induced formation of PCDD/Fs?

Problem: Secondary emissions



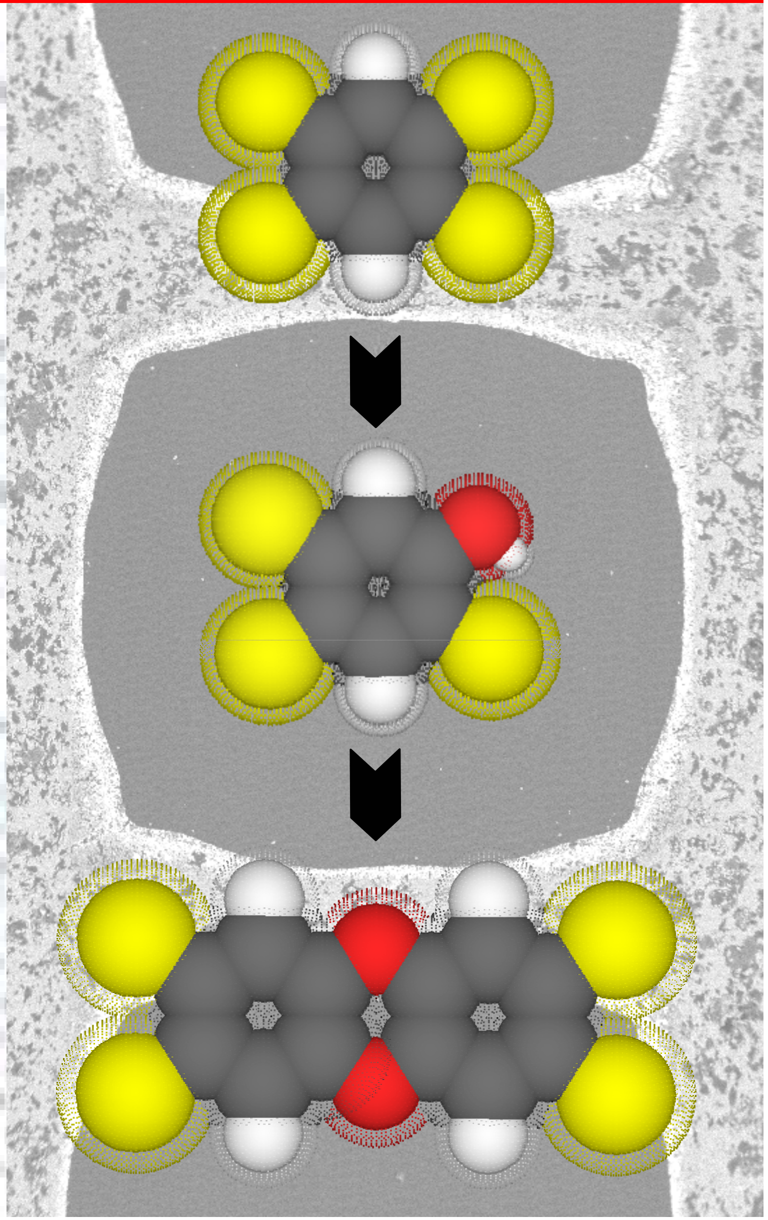
Dioxin formation in Seveso

The dioxin problem

- Highly toxic
- Persistent, bioaccumulative, ubiquitous
- Unwanted side product of combustion processes
- Regulated under the Stockholm convention

PCDD&F Properties:

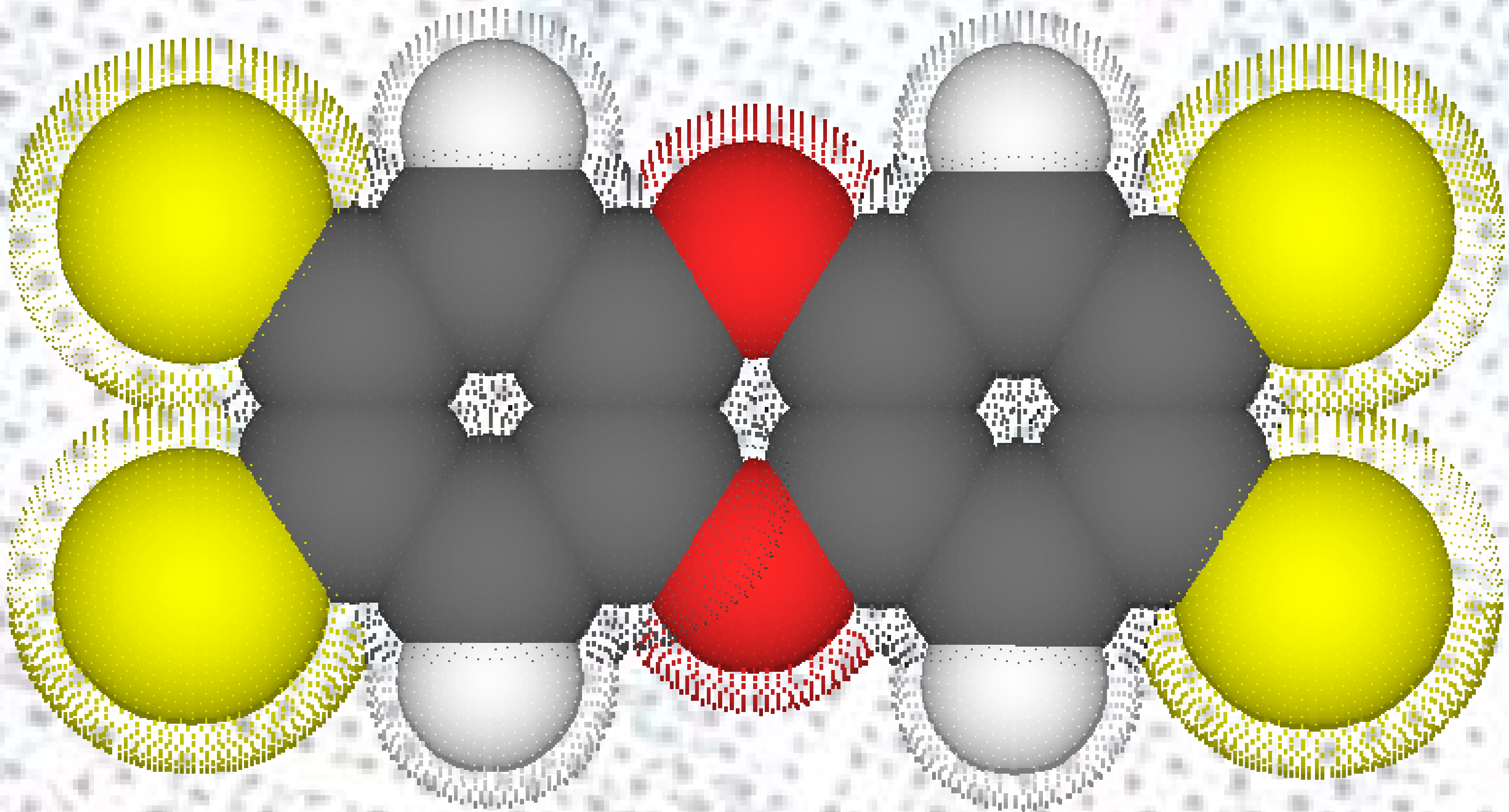
- Thermally stable up to 440°C
- Solid, non-volatile, particle-bound
- Should be trapped in DPFs unless they are formed *de novo*



PCDD/Fs: toxic at pg-quantities

What are PCDD/Fs?

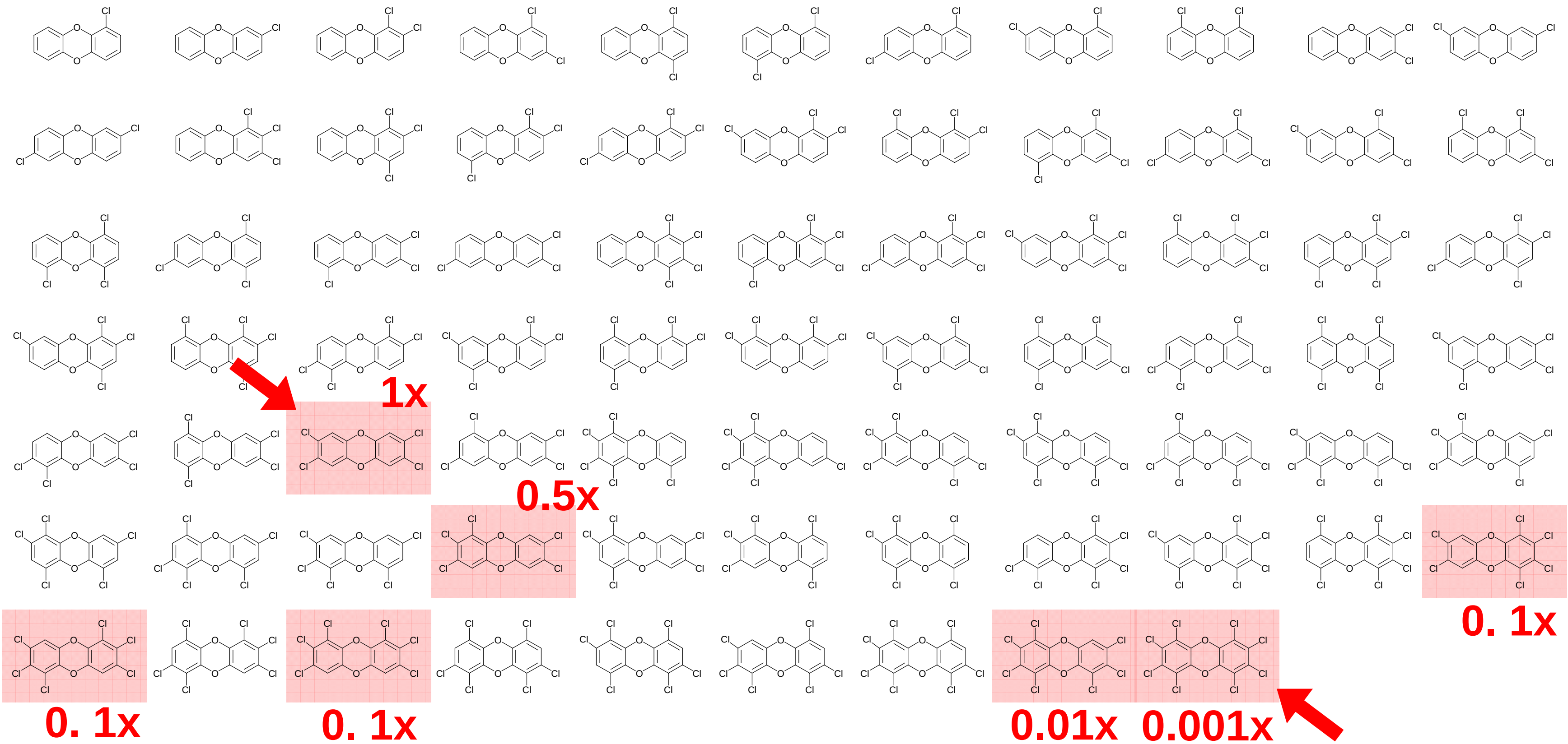
2,3,7,8-Tetrachlorodibenzodioxin - the so-called Seveso-dioxin



Analysis of dibenzodioxins at ultratrace level

Which are the 7 toxic PCDD?

Chemical structures of polychlorinated dibenzodioxins



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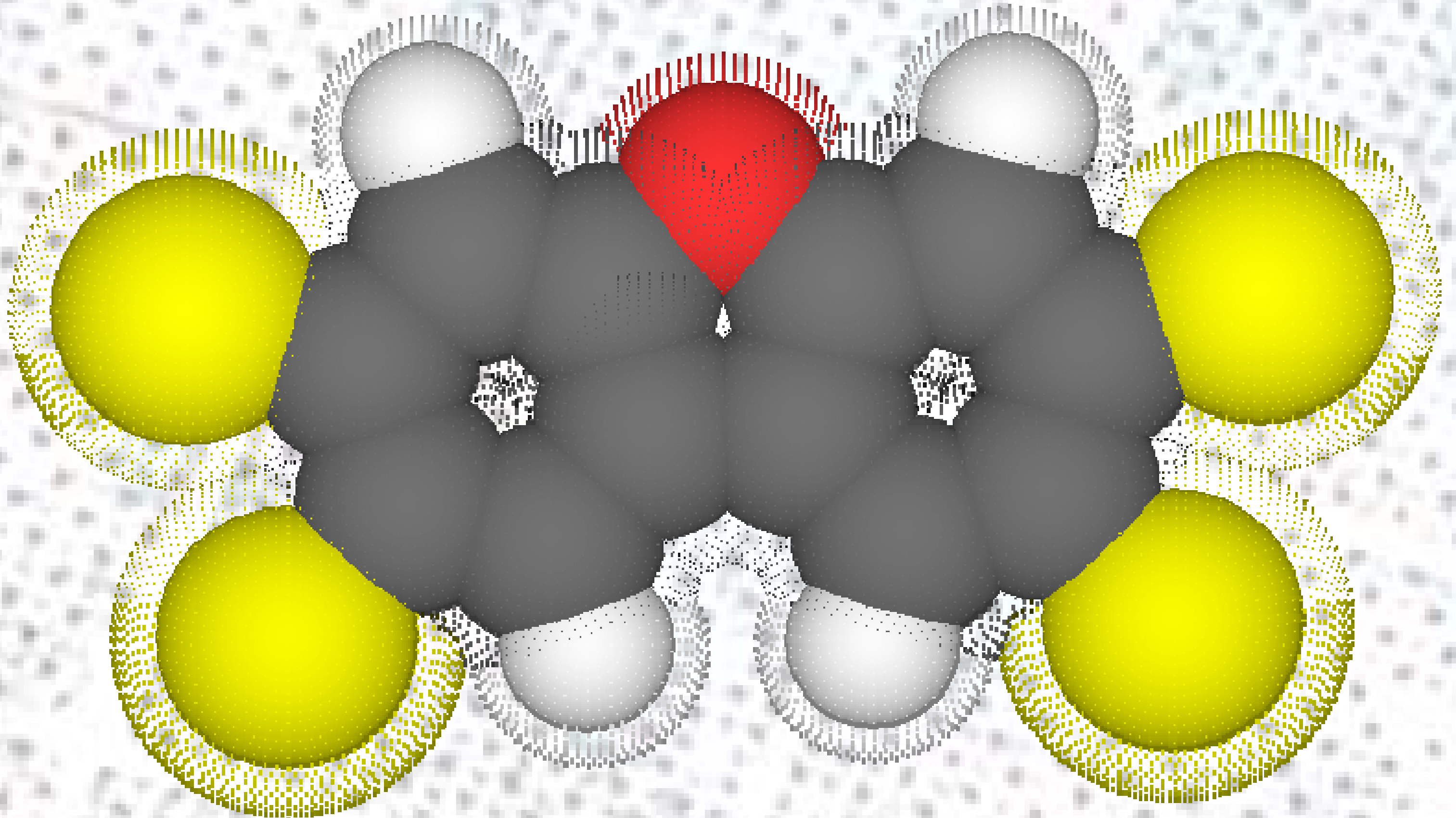
PCDD/Fs: toxic at pg-quantities

What are PCDD/Fs?

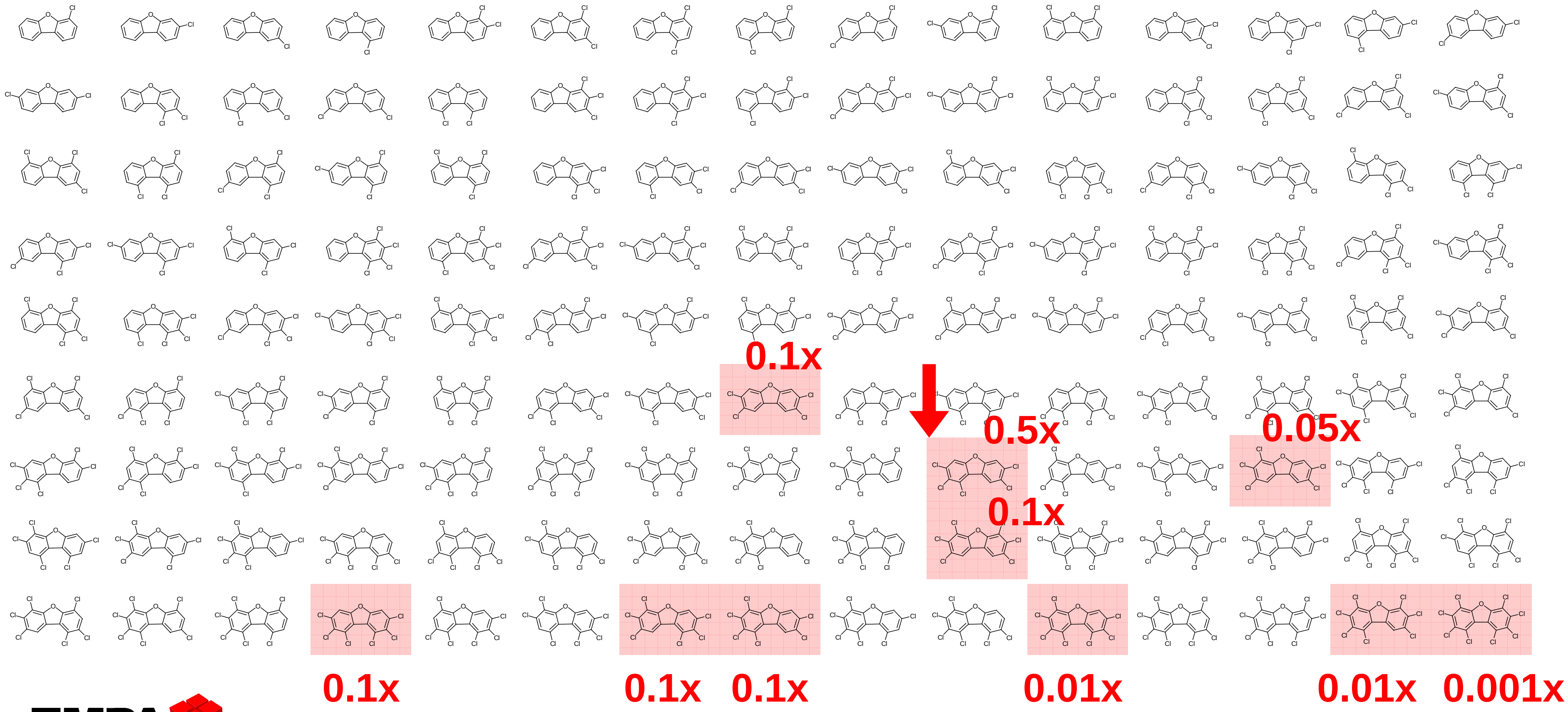
2,3,7,8-Tetrachlorodibenzofuran



Analysis of dibenzofurans at ultratrace level

Which are the 10 toxic PCDF?

Chemical structures of polychlorinated dibenzofurans



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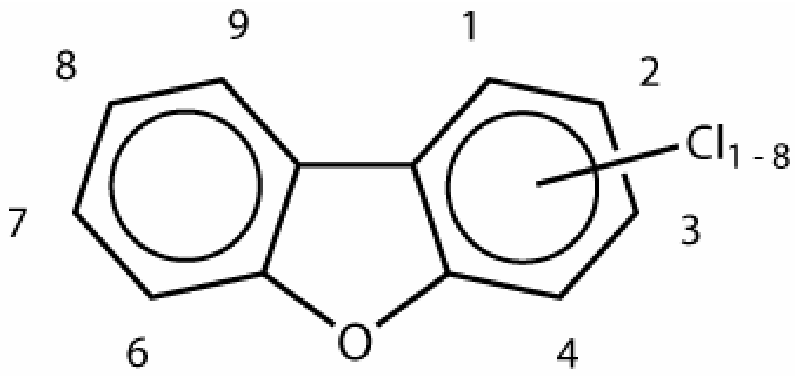
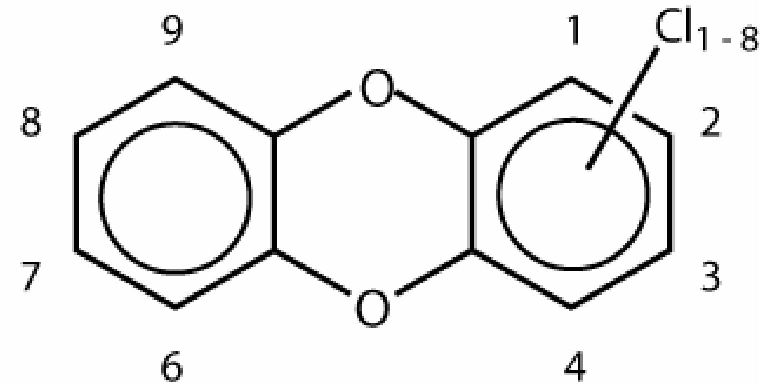
PCDD/Fs: Two classes of compounds

What are PCDD/F?

Polychlorinated dibenzodioxins/furans (PCDD/Fs)





PCDFs: $C_{12}H_{8-x}Cl_xO$ x=1-8

PCDDs: $C_{12}H_{8-x}Cl_xO_2$ x=1-8

PCDD/Fs: $C_{12}H_{8-x}Cl_xO_y$ x=1-8 y=1-2

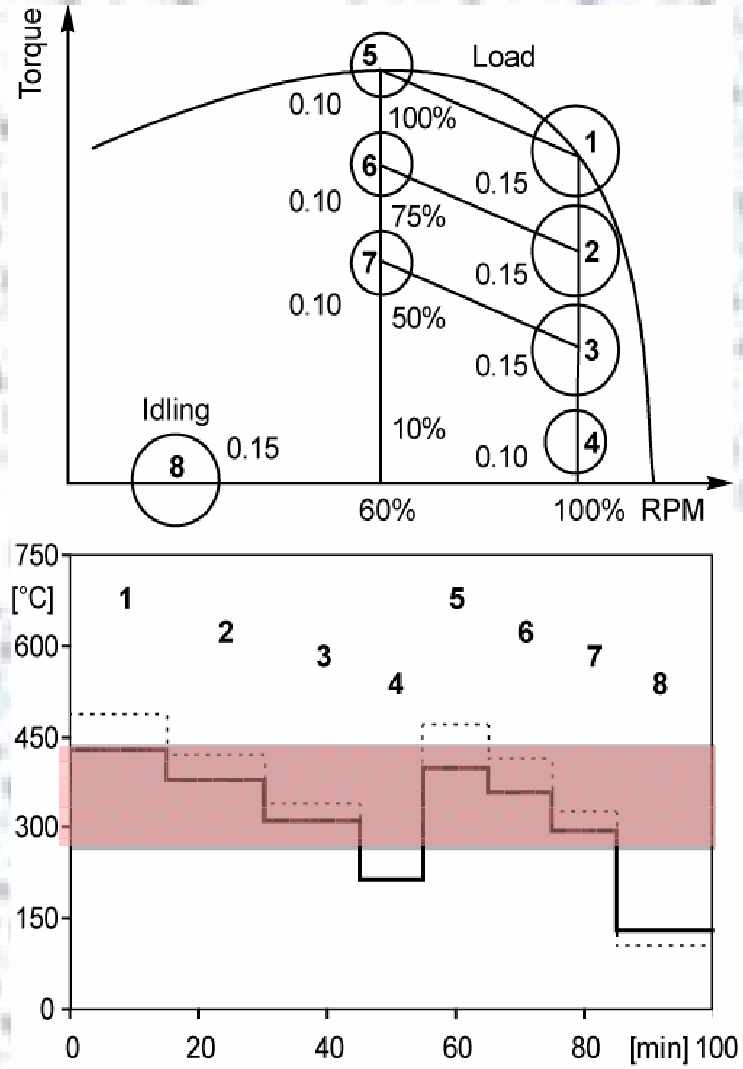
Secondary PCDD/F Formation in DPFs?

There are some reasons to worry about PCDD/F formation in DPFs

The DPF: a perfect chemical reactor

- Elongated residence times
- Accumulation of precursors
- Ideal temperature range (260-440 °C)
- Large surface areas, heterogeneous catalysis
- Active catalyst coatings or fuel-borne catalysts

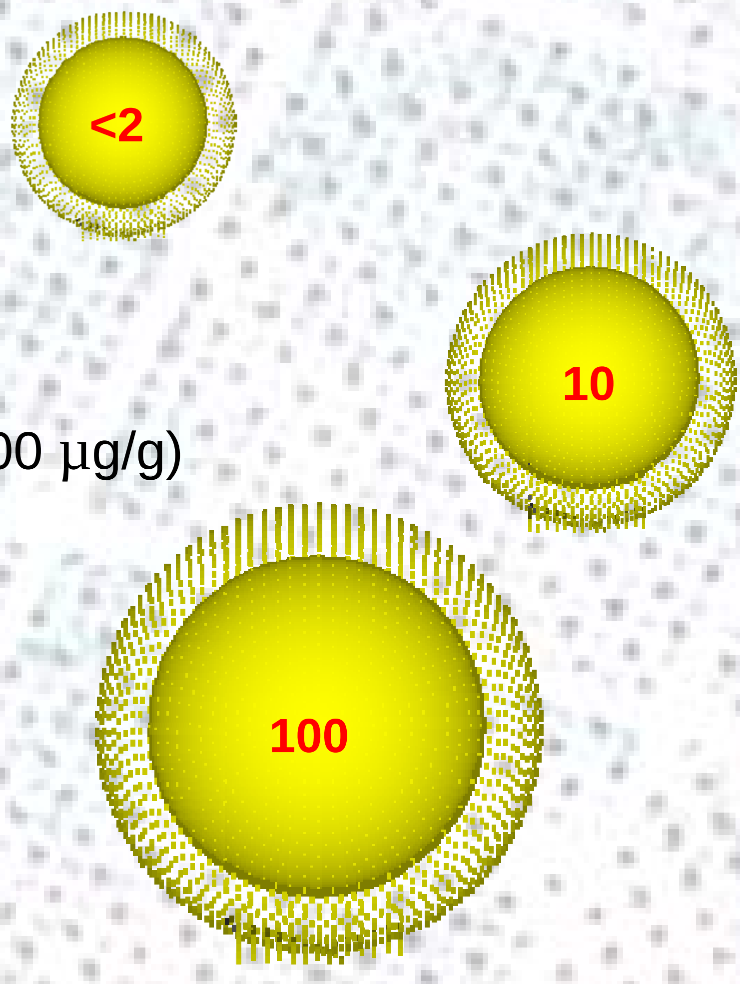
***De novo* formation is possible during 75-80% of operation time in the ISO8178/4 cycle**



Secondary PCDD/F Formation in DPFs?

µg-quantites of chlorine are more than enough to produce pg-amounts!

Potential chlorine sources



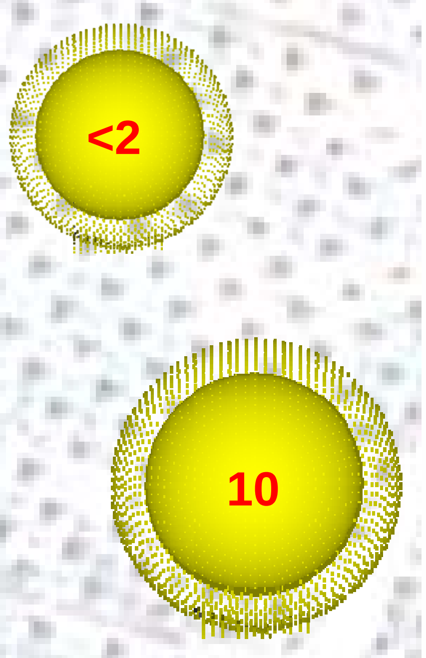
- Commercial diesel (<2 µg/g)
- Intake air contains µg quantities of chlorinated hydrocarbons (several $\mu g/m^3$ in Zürich)
- Lubricants contain Cl-containing additives (>100 µg/g)
- Street dust & urban aerosols (deicing agents)
- Marine aerosols

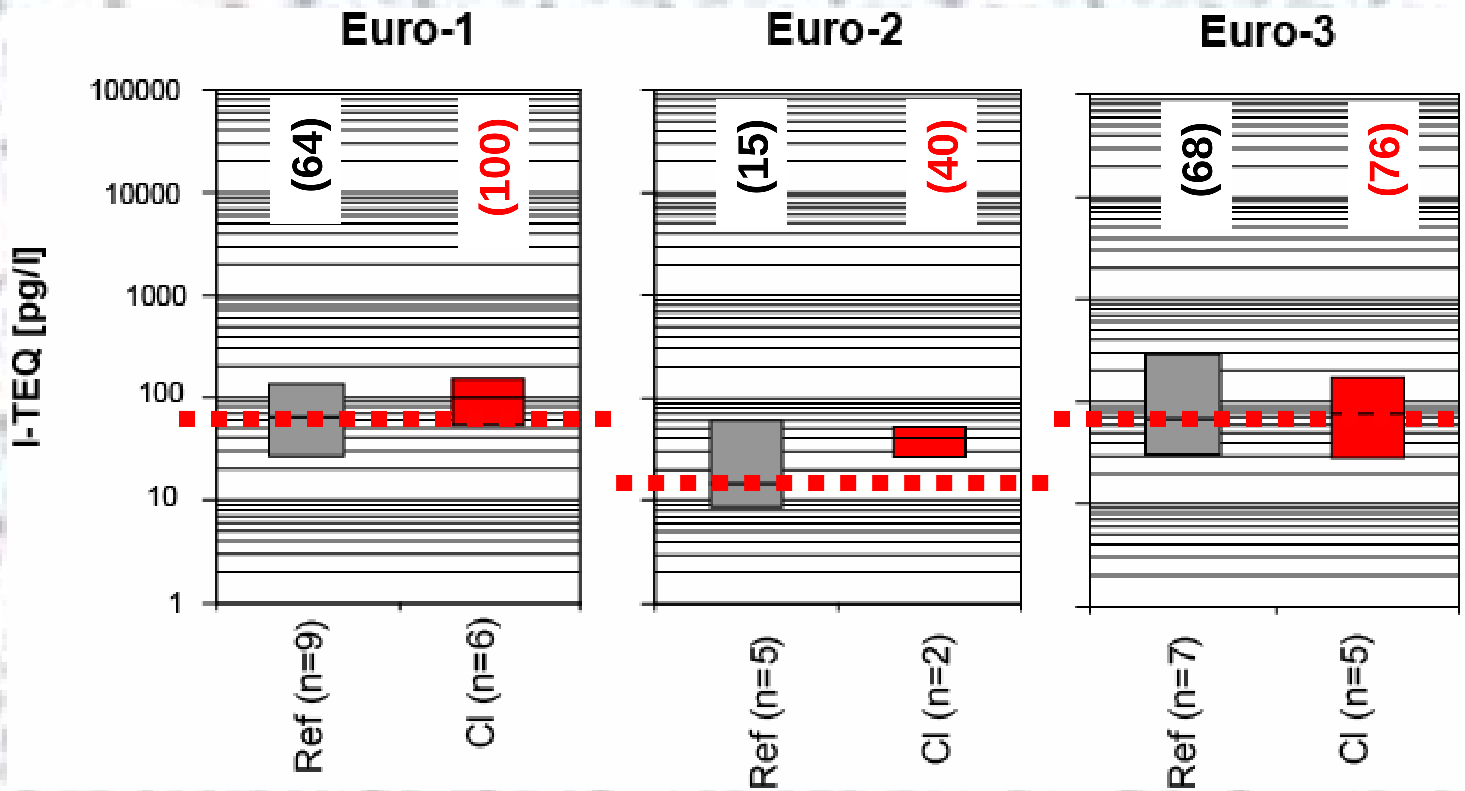
Worst case scenarios with 10 and 100 ug/g fuel

Secondary PCDD/F Formation in DPFs?

PCDD/F emissions of Euro-1, -2, and -3 engines

Chlorine effects





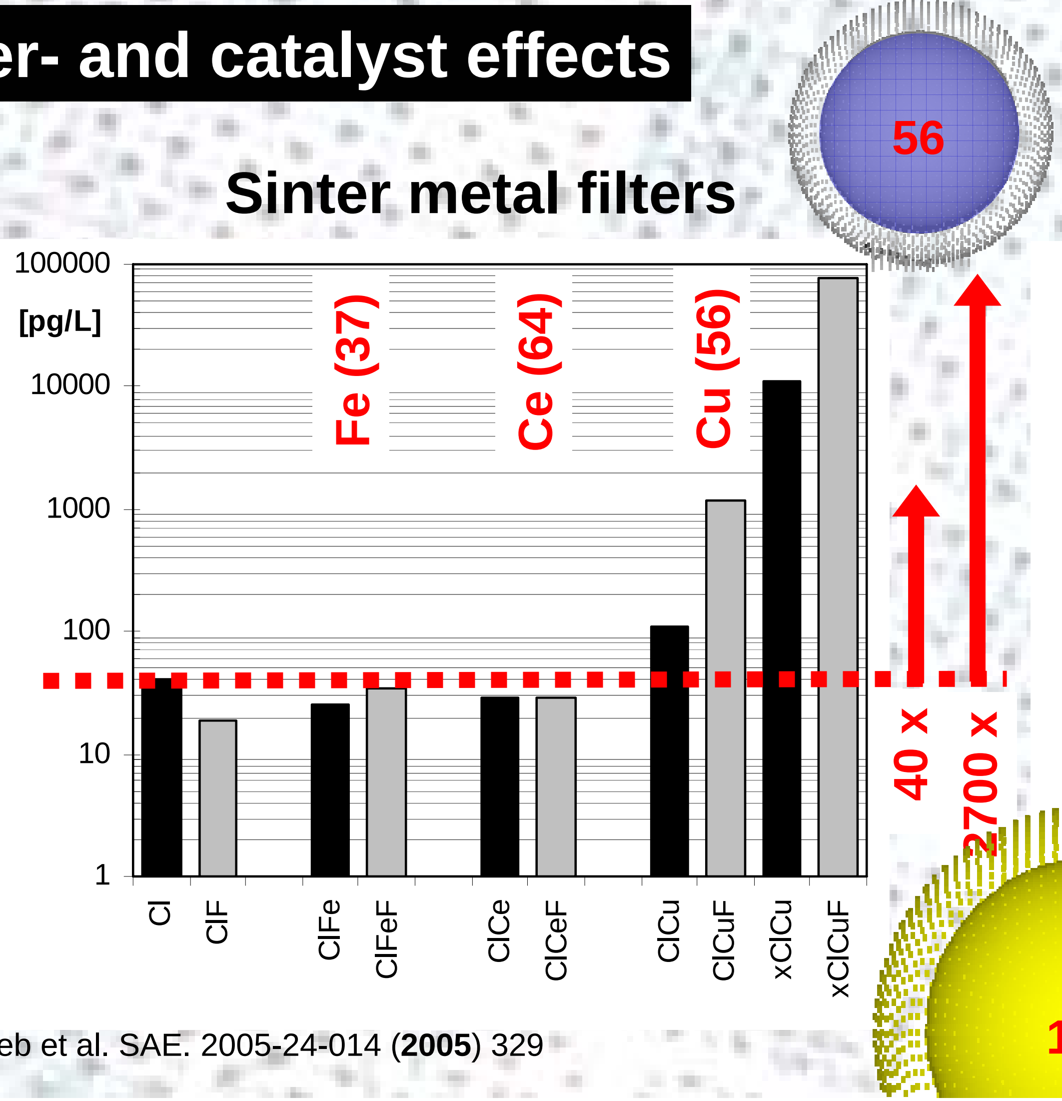
No significant increase of PCDD/F emissions with 10 ug Cl/g fuel

Copper-induced *de novo* PCDD/F-formation

PCDD/F emissions of catalytic DPF in presence of chlorine?

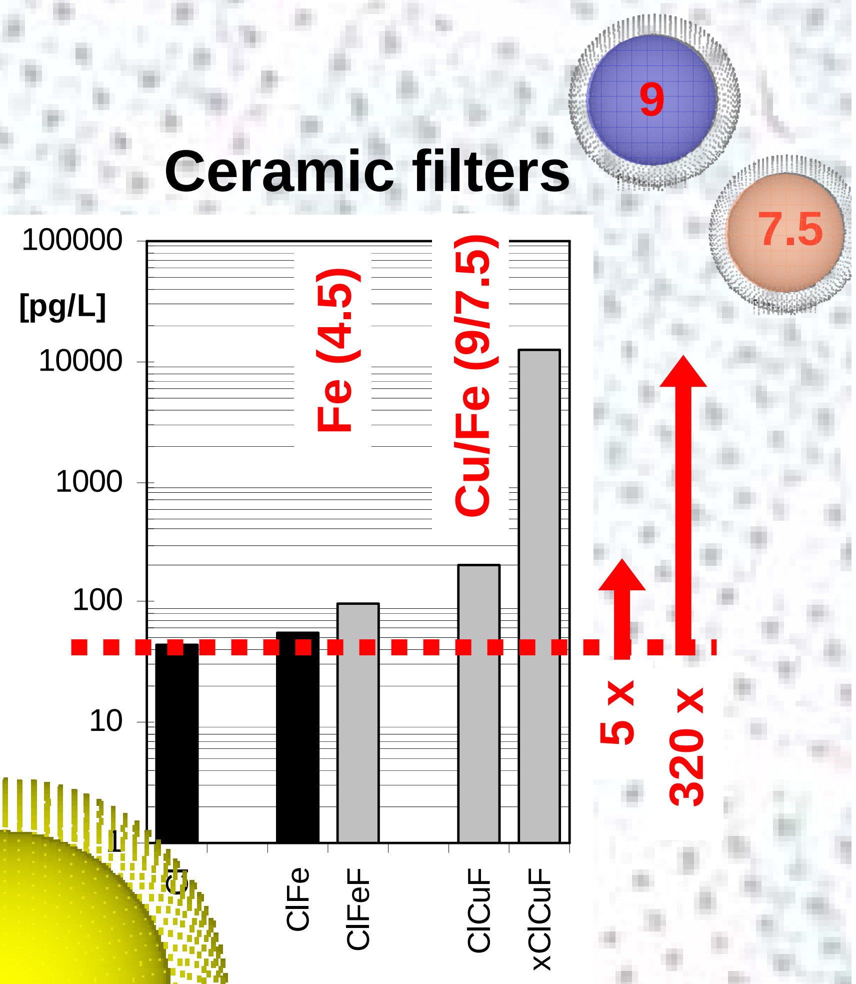
Filter- and catalyst effects

Sinter metal filters



Heeb et al. SAE. 2005-24-014 (**2005**) 329

Ceramic filters

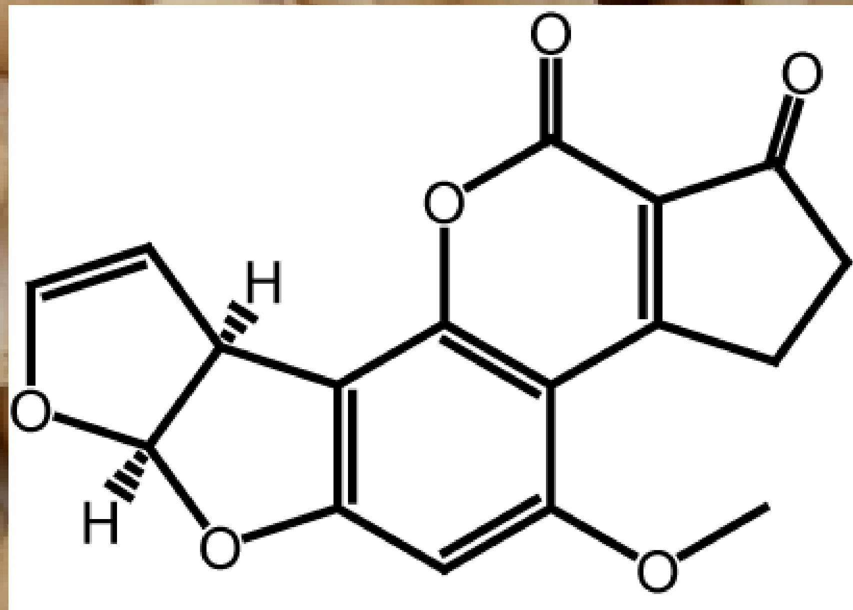


Heeb et al. ES&T, **2007**, 42, 3773-3779

de novo PCDD/F-formation in DPFs

de novo PCDD/F-formation in DPFs

It is like eating peanuts, some peanuts contain aflatoxins, some do not



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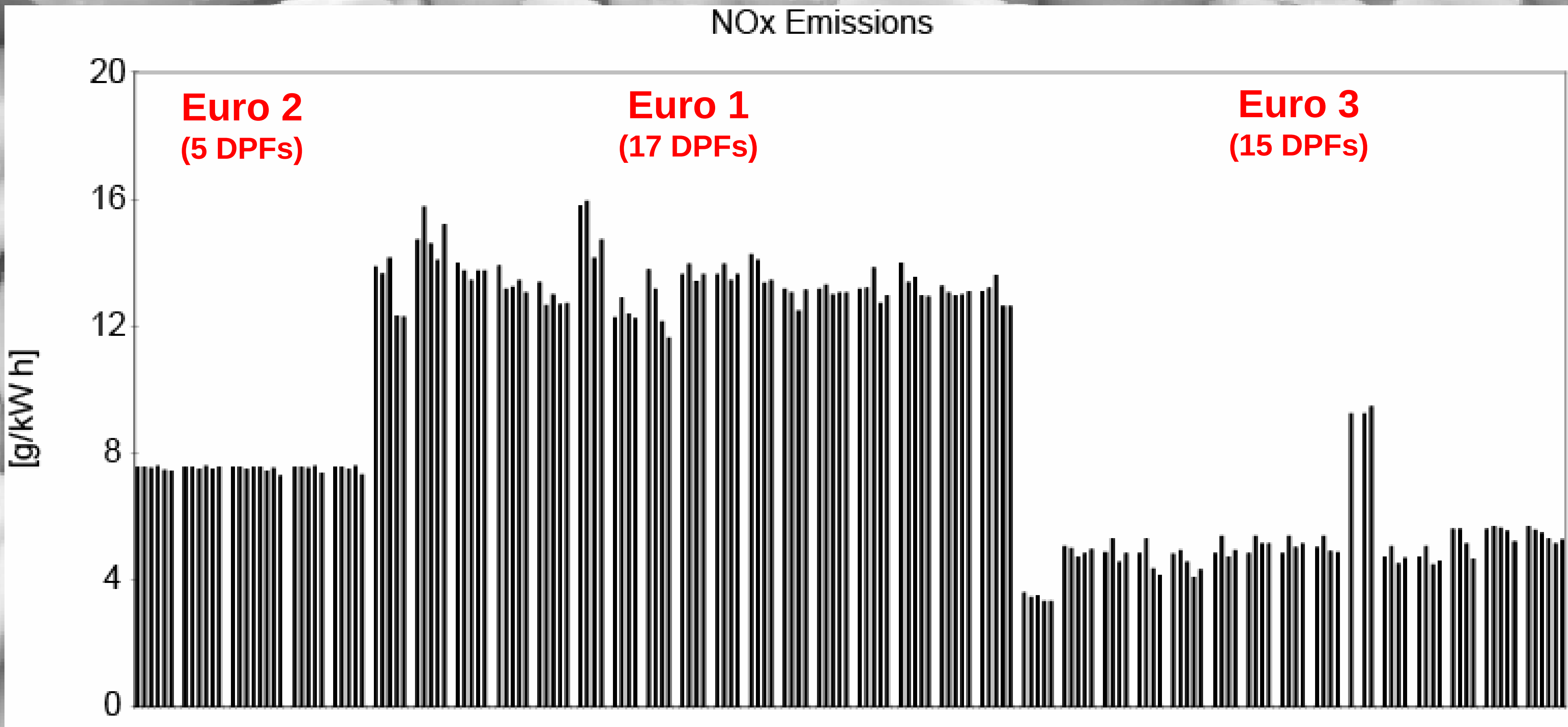
de novo PCDD/F-formation in DPFs

Assessment of the PCDD/F-formation potential

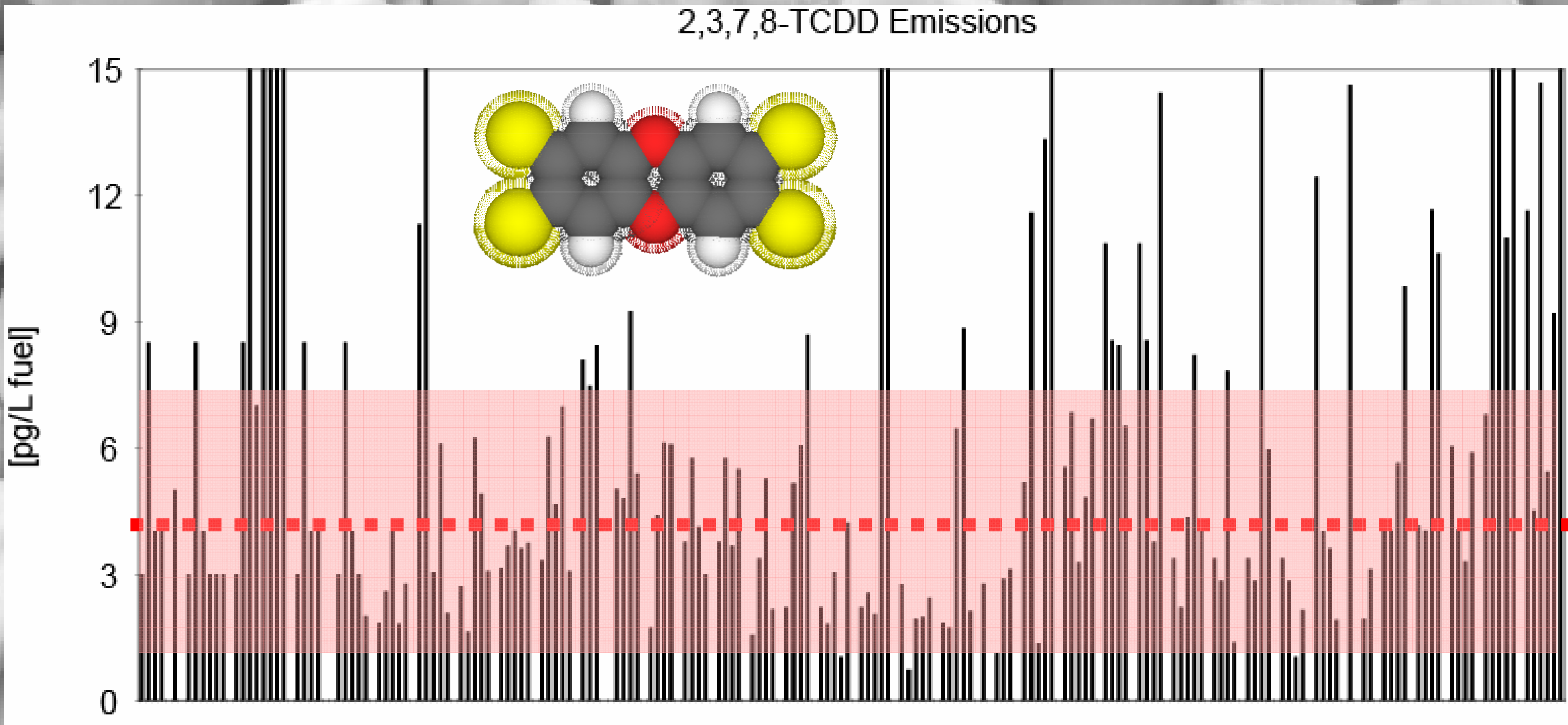
Are DPFs deNOx active?



37 DPFs tested, none is deNOx active, the engine technology is more important

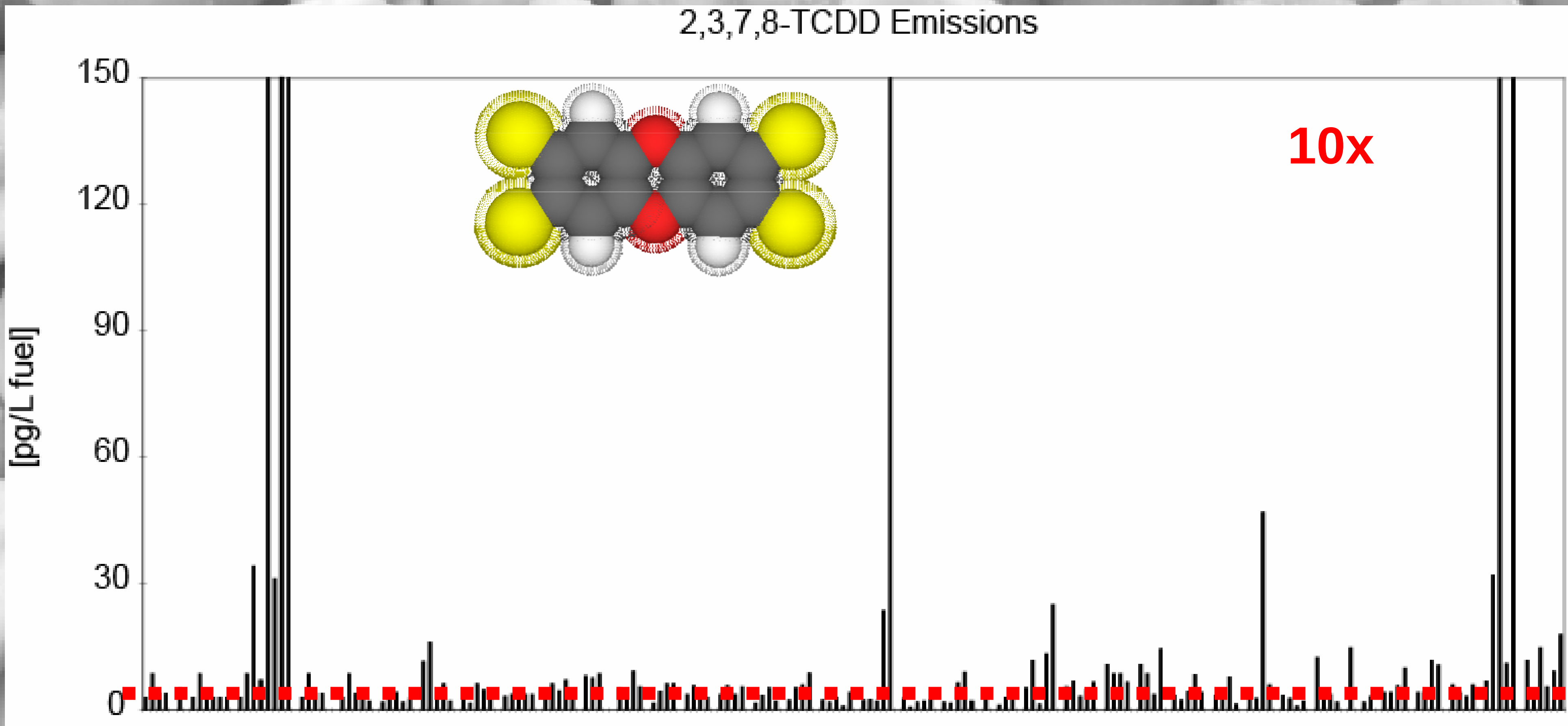
Assessment of the PCDD/F-formation potential

The dioxin formation potential of the respective DPFs?



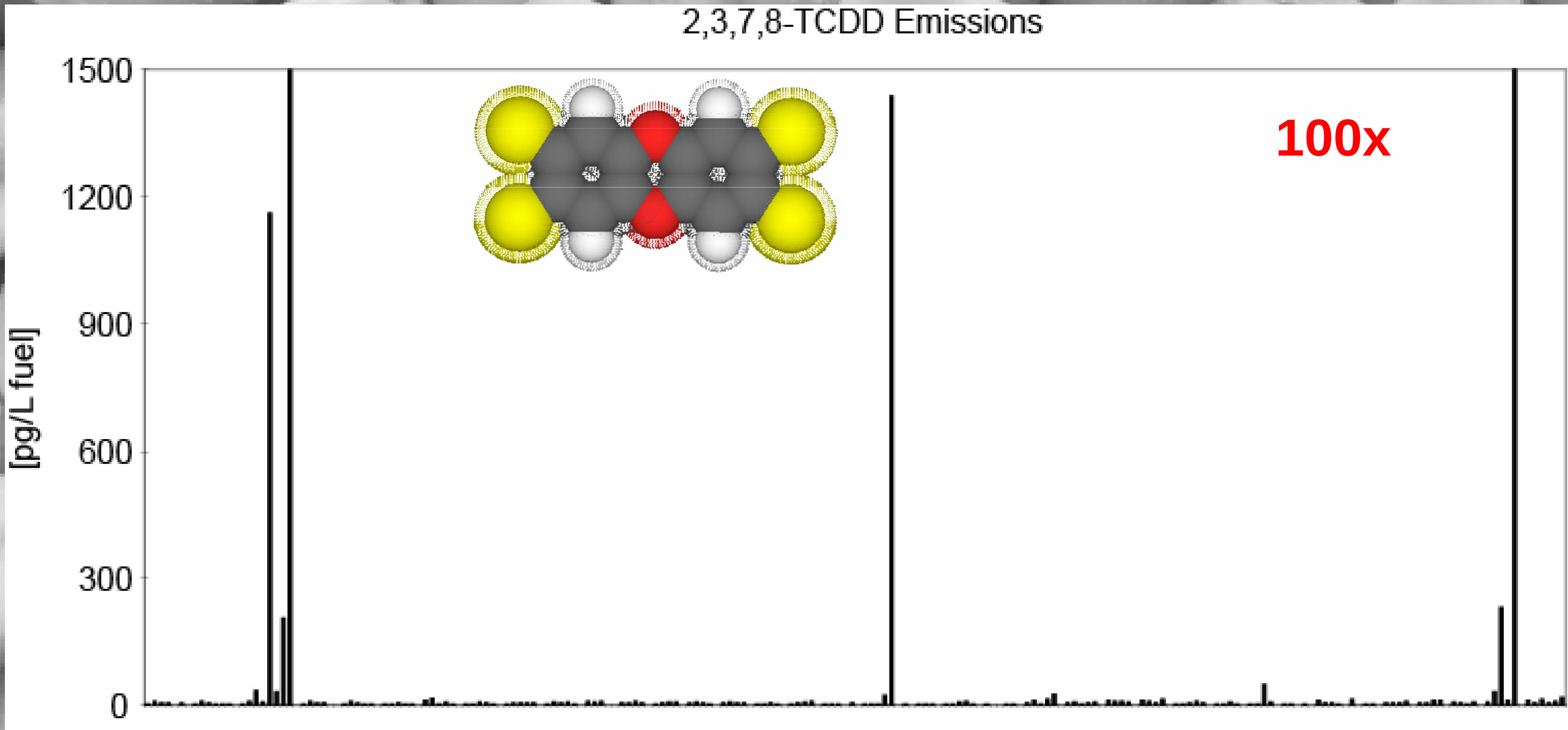
Assessment of the PCDD/F-formation potential

The dioxin formation potential of the respective DPFs?



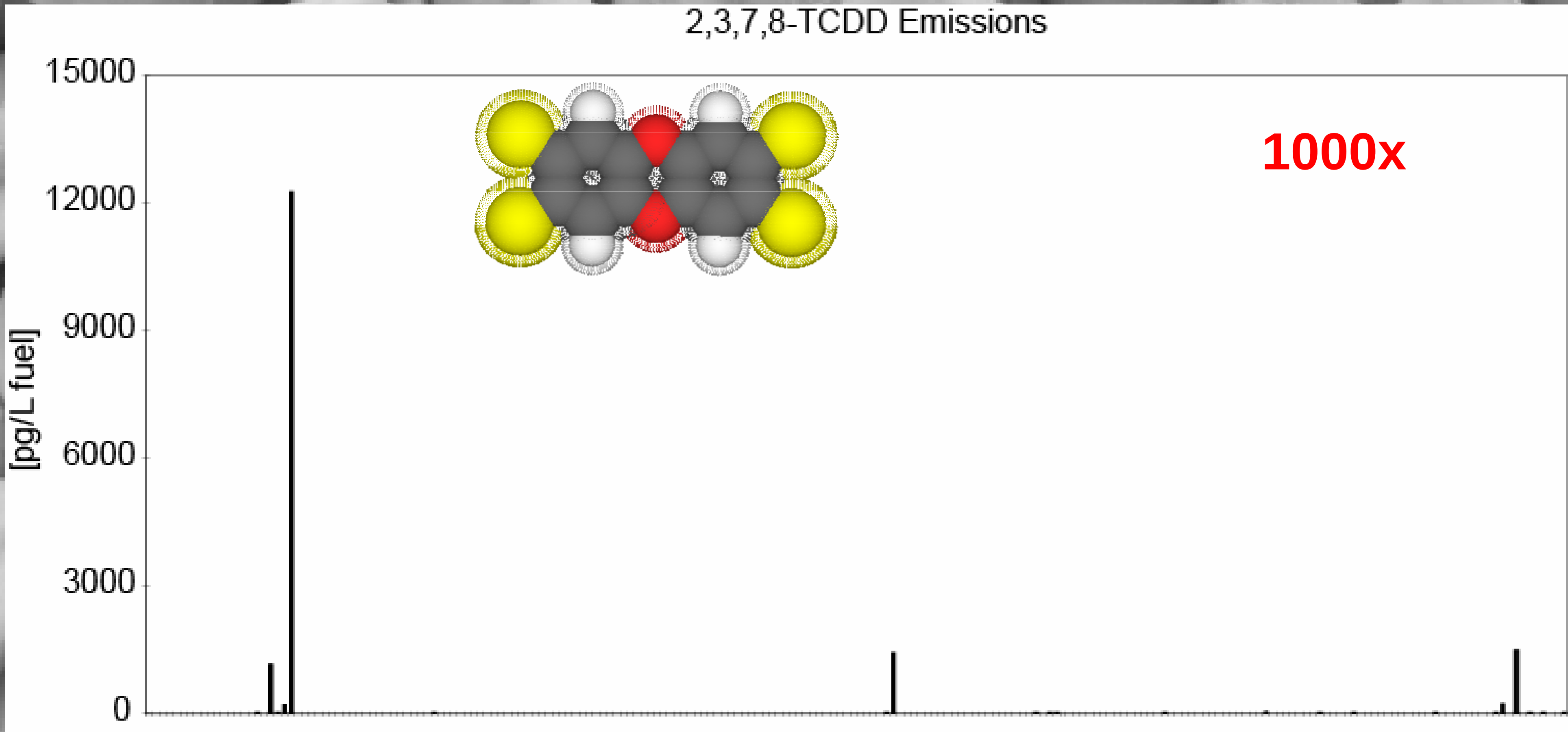
Assessment of the PCDD/F-formation potential

So far only 3 of the 37 tested DPFs induced a PCDD/F formation?



Assessment of the PCDD/F-formation potential

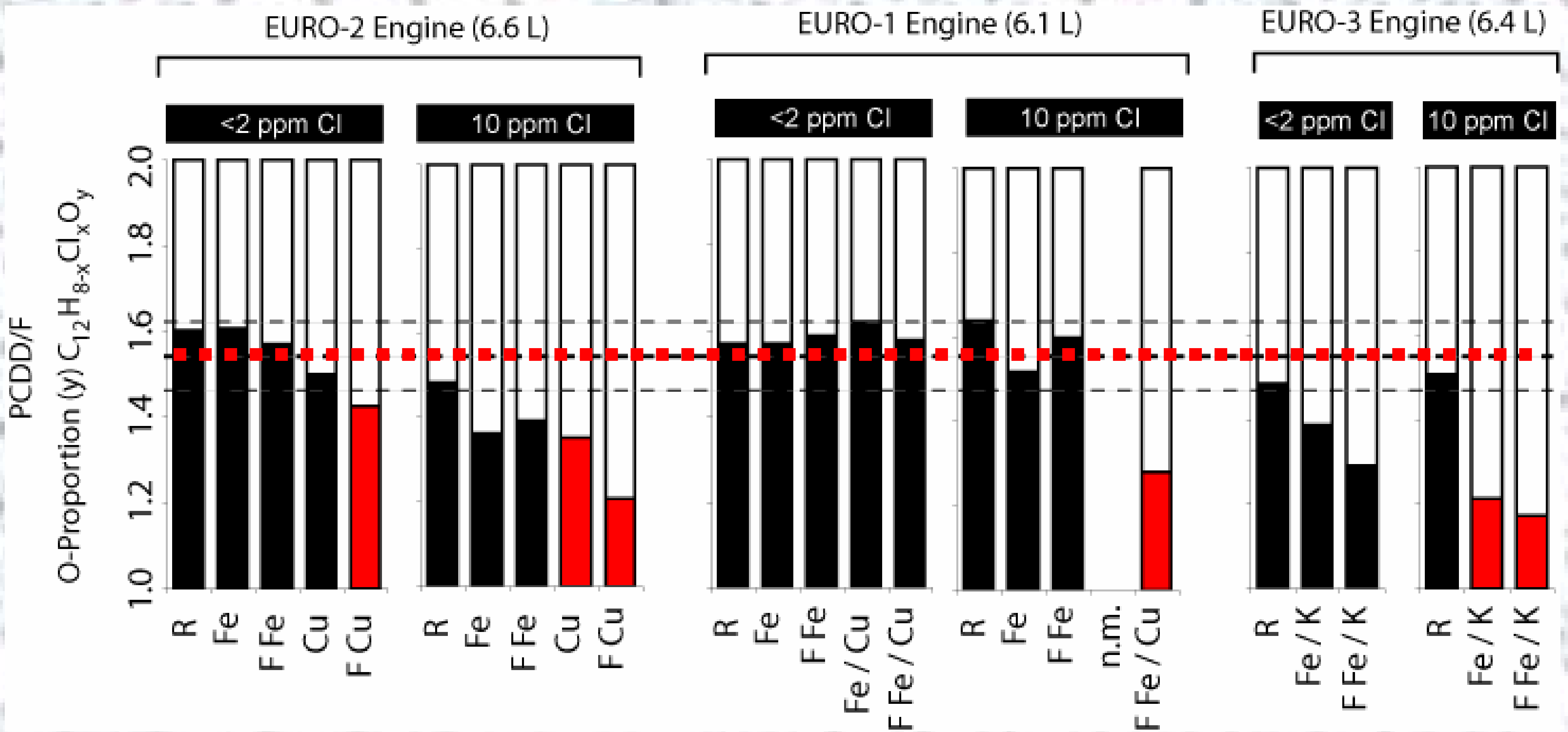
These 3 DPFs exceed the MWI emission limit of 100 pg/m3 exhaust



Pattern changes during PCDD/F Formation

More of a formation of PCDFs than PCDDs

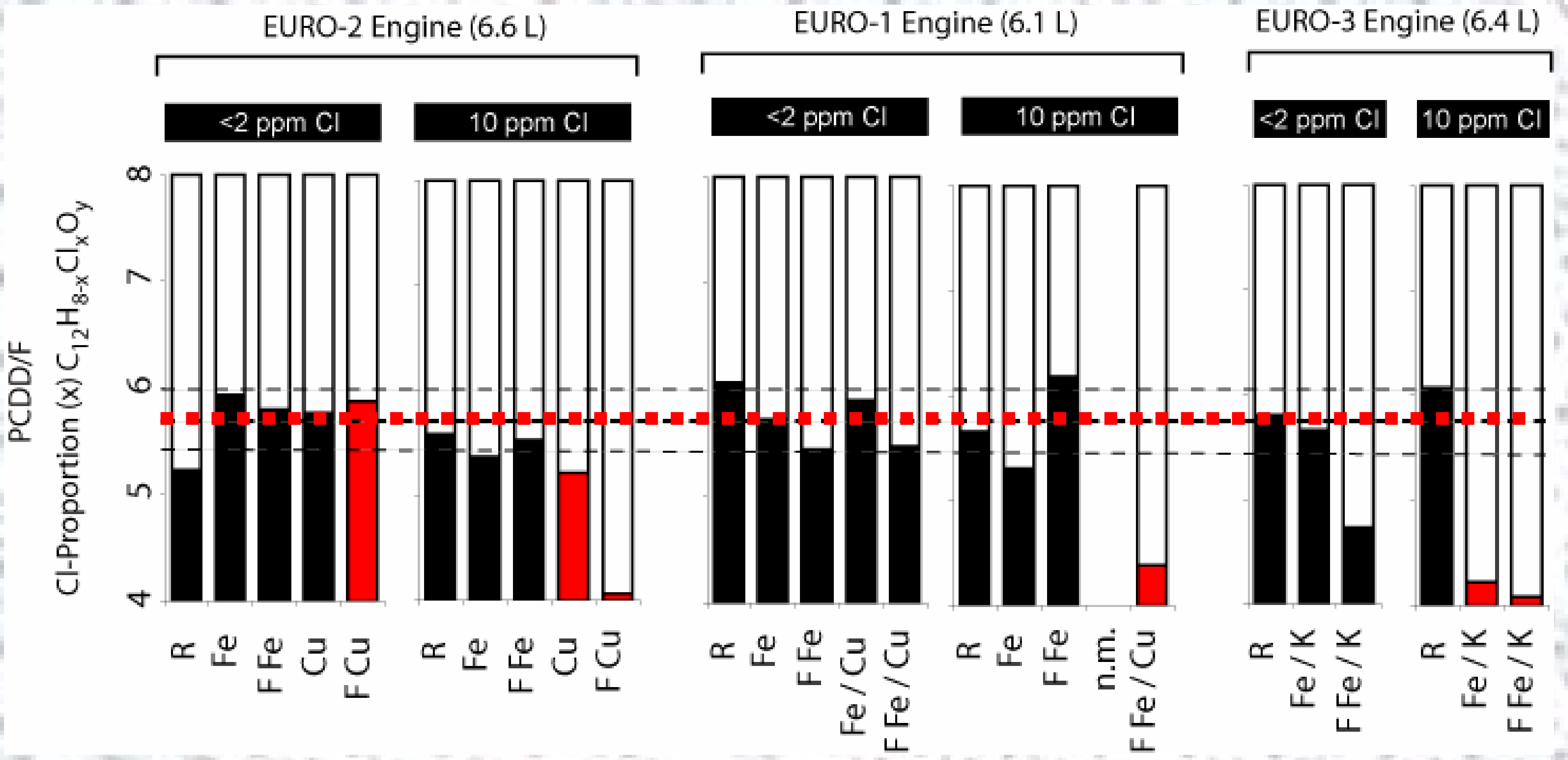
PCDD/PCDF ratios



Pattern changes during PCDD/F Formation

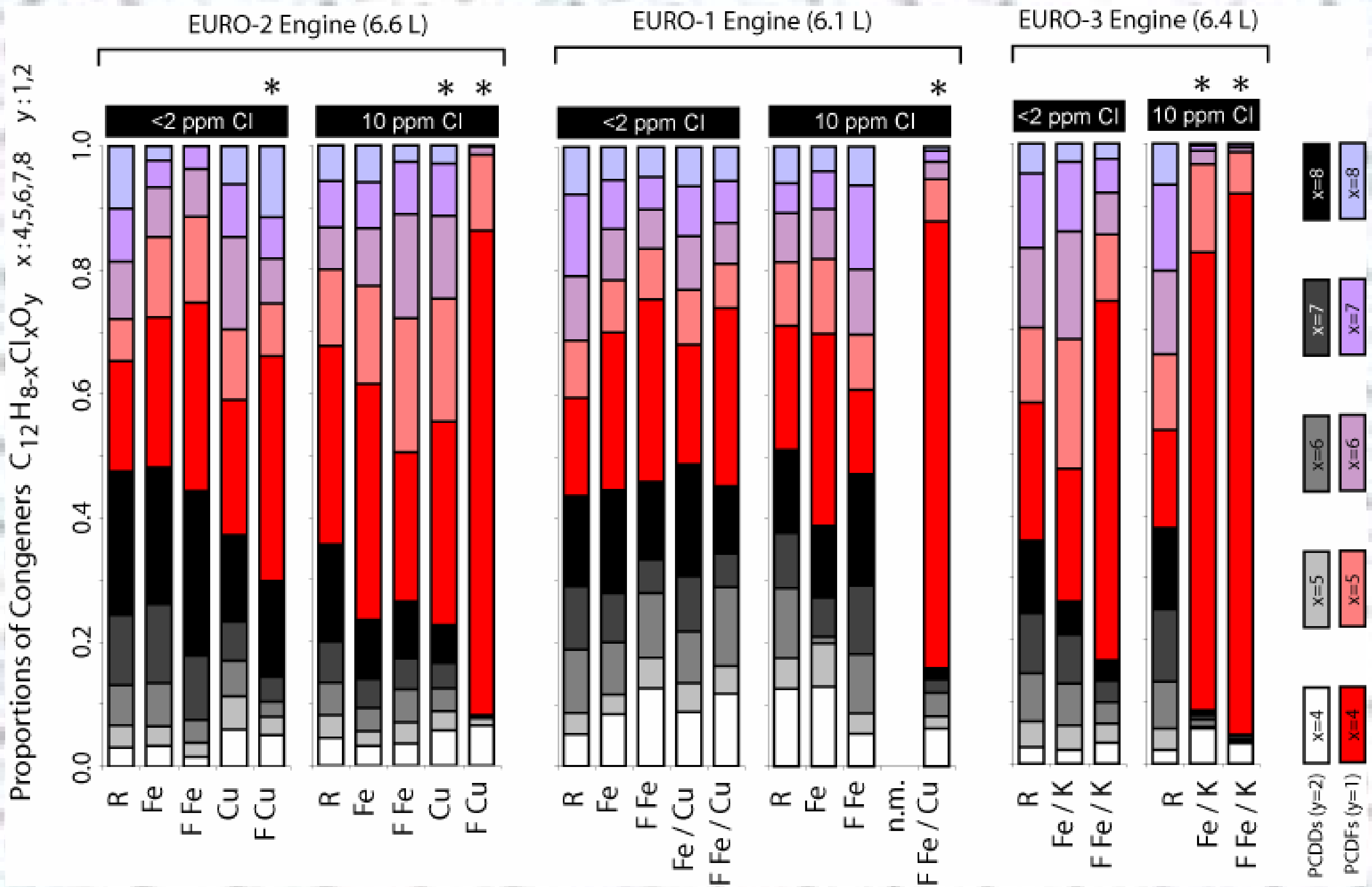
More of the lower chlorinated PCDD/Fs are formed

Chlorine proportion in PCDD/Fs



Pattern changes during PCDD/F Formation

TCDFs clearly dominate among the different congener classes



Parameters affecting PCDD/F formation: in diesel particle filters

The PCDD/F formation potential in DPFs is not peanuts, but today we have a choice

- **There are some risks for a DPF-induced PCDD/F formation**
- **Higher chlorine levels are not sufficient**
- **The chemical nature of the catalyst is most important**

- **PCDD/F potential of DPFs has to be tested in advance**

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Parameters affecting PCDD/F formation: in diesel particle filters

The PCDD/F formation potential of DPFs is not peanuts

Thanks:

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  Thomas Gasser, Swiss Federal Roads Office, Bern

- **Filter- & catalyst manufacturers**: >40 different industrial partners

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