Empa

Materials Science and Technology

20 years VERT Filter test

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9th VERT Forum: 20 years of VERT emission control certification
Empa, March 15, 2018

20 years VERT Filter test

Something to celebrate!

9th VERT Forum: 20 years of VERT emission control certification

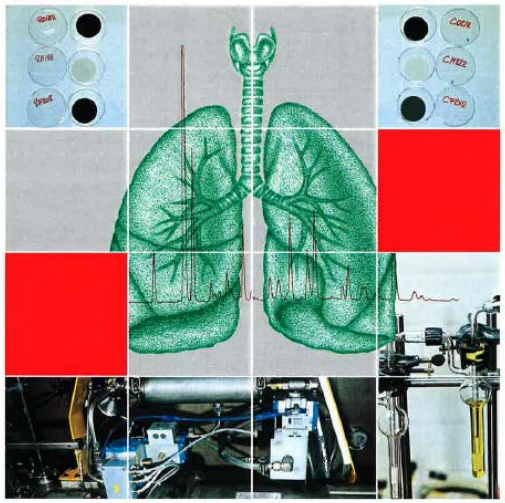
Empa, March 15, 2018

20 years VERT Filter test

The 1st, 2nd and with some delay the 3id DPF tested and reported

EMPA-Research report Nr. 167985

EMPA



Influence of particulate trap systems on the composition of Diesel engine exhaust gas emissions

(Includes tests on possible *de novo* synthesis of PCDD/F in particulate trap Systems)

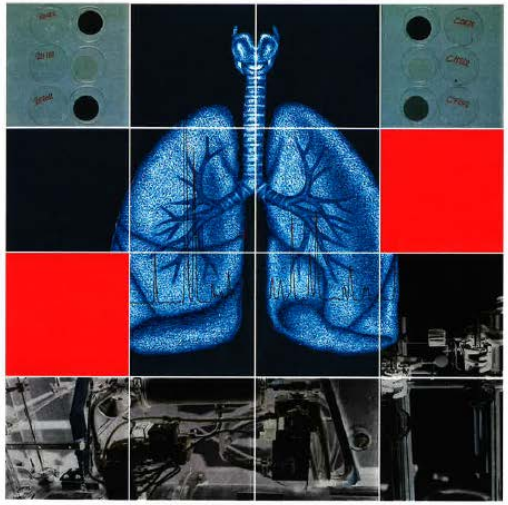
released January 11, 1998

Author:
N.V. Heeb

Ce, Fe

EMPA-Research report No. 172847
Includes tests with copper containing fuel additives
Extension of research report 167985

EMPA



Influence of particulate trap systems on the composition of Diesel engine exhaust gas emissions (Part II)

(Includes test on possible *de novo* synthesis of PCDD/F in particulate trap systems)

released July 17, 1998

Author:
N.V. Heeb

Cu

20 years VERT Filter test

- An urgent need for filters in NEAT tunnels
  (Why it all started)
- Highlights of the VSET
  (Hypotheses and facts)
- Filters needed more than ever
  (The near future still is combustion)

Something to celebrate!

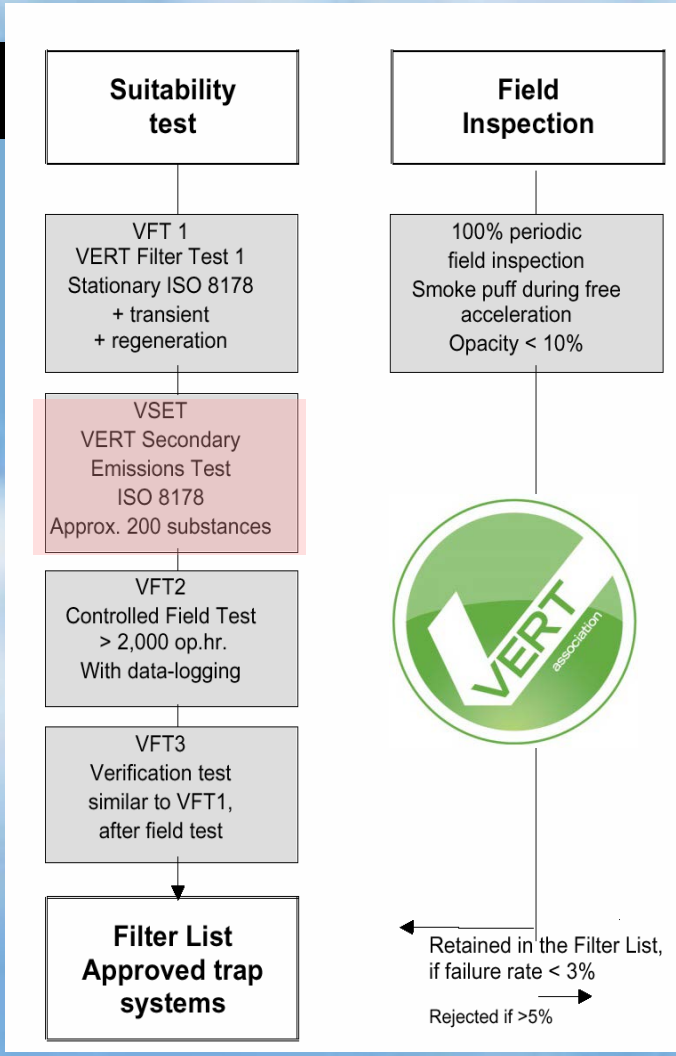
Our hypothesis: Any particle filter is a chemical reactor!

Are DPF safe to operate them in tunnels?

VERT secondary emissions test (VSET)

Approved filters should:

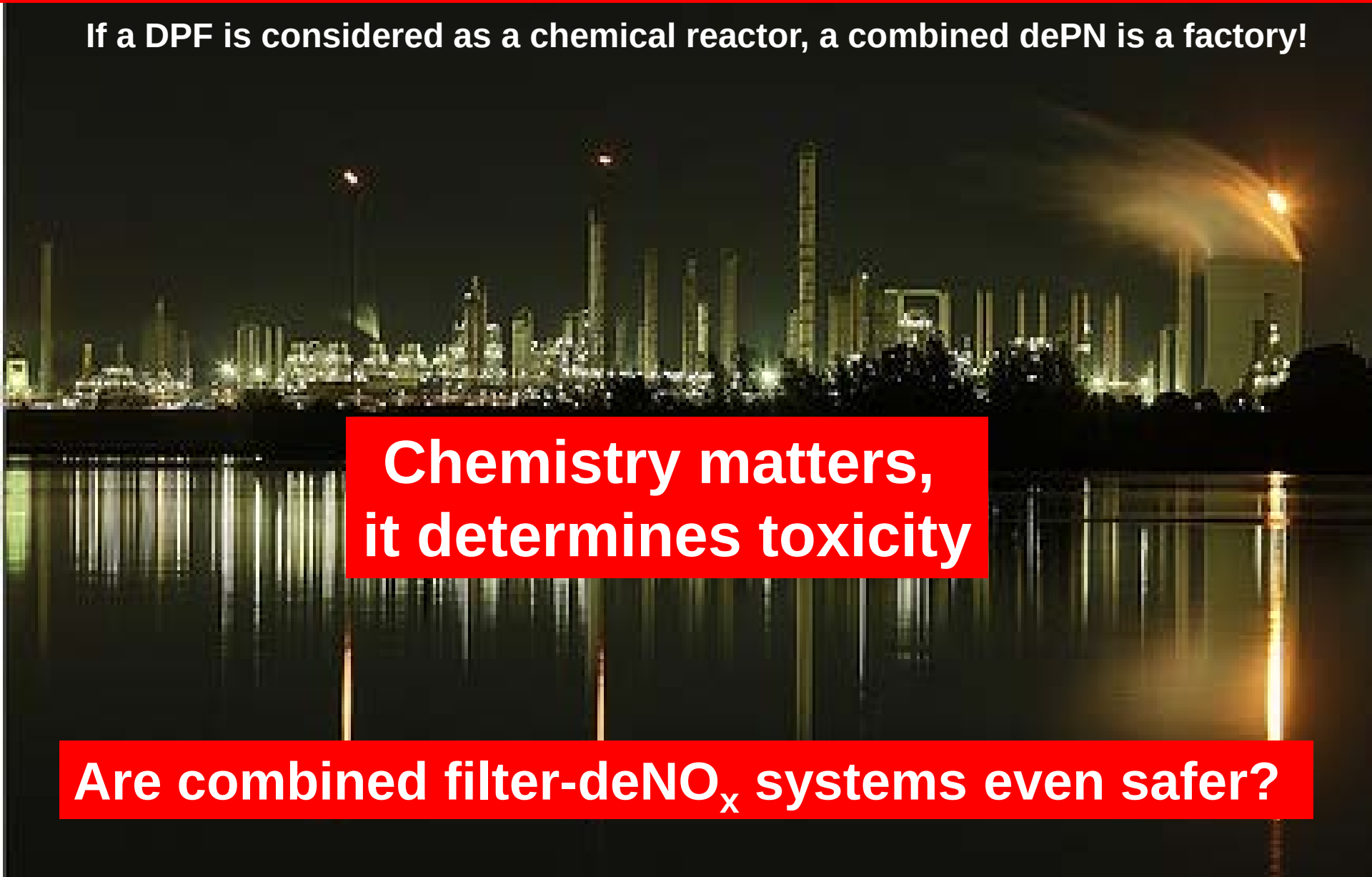
- **Reduce PM- & PN-emissions (>98%)**
- **Reduce toxic compounds a.m.a.p.**
- **Low risks for secondary emissions**



Are diesel particle filters safe?

Our hypothesis: Any combined deNO$_x$ and particle filter is a chemical factory!

If a DPF is considered as a chemical reactor, a combined dePN is a factory!



Chemistry matters, it determines toxicity

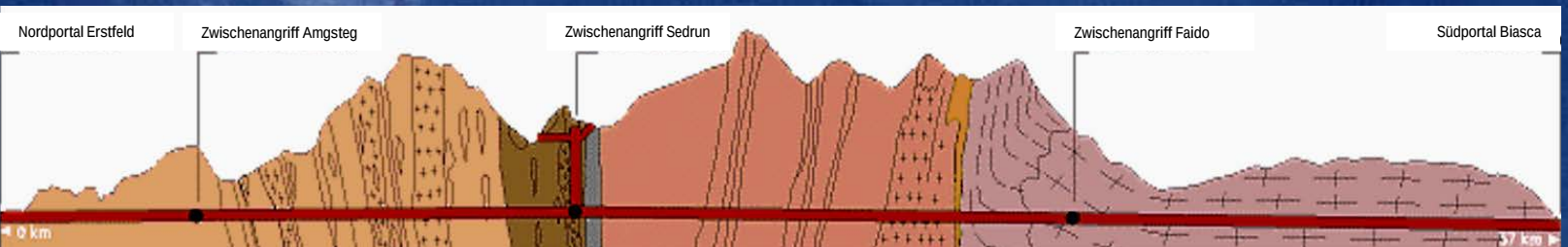
Are combined filter-deNO$_x$ systems even safer?

NEAT – the longest railway tunnel in the world

Visionary decisions of the Swiss people 26 years ago!

- 2 Swiss federal votes on:
  - Construction of a new railway link tunnelling the Swiss Alps, 21.9.92
  - Protection of the Alps, 20.2.94

- 2 tunnels at 57 km, 153 km shafts & tunnels
- costs >20 billion CHF
- build from 1993-2017
- hundreds of workers and diesel engines



NEAT – the longest railway tunnel of the world built with VERT-approved DPFs

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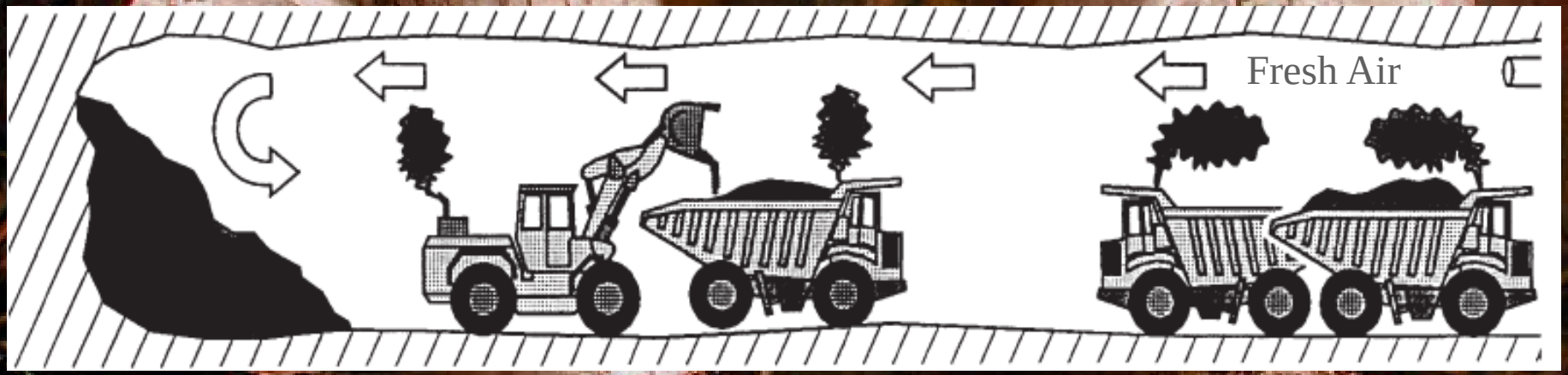
Is there enough fresh air to survive in these long tunnels?



NEAT – the longest railway tunnel of the world built with VERT-approved DPFs

Is there enough fresh air to survive in these long tunnels?

Diesel soot working place limit: 0.1 mg/m³ (>1000x dilution)

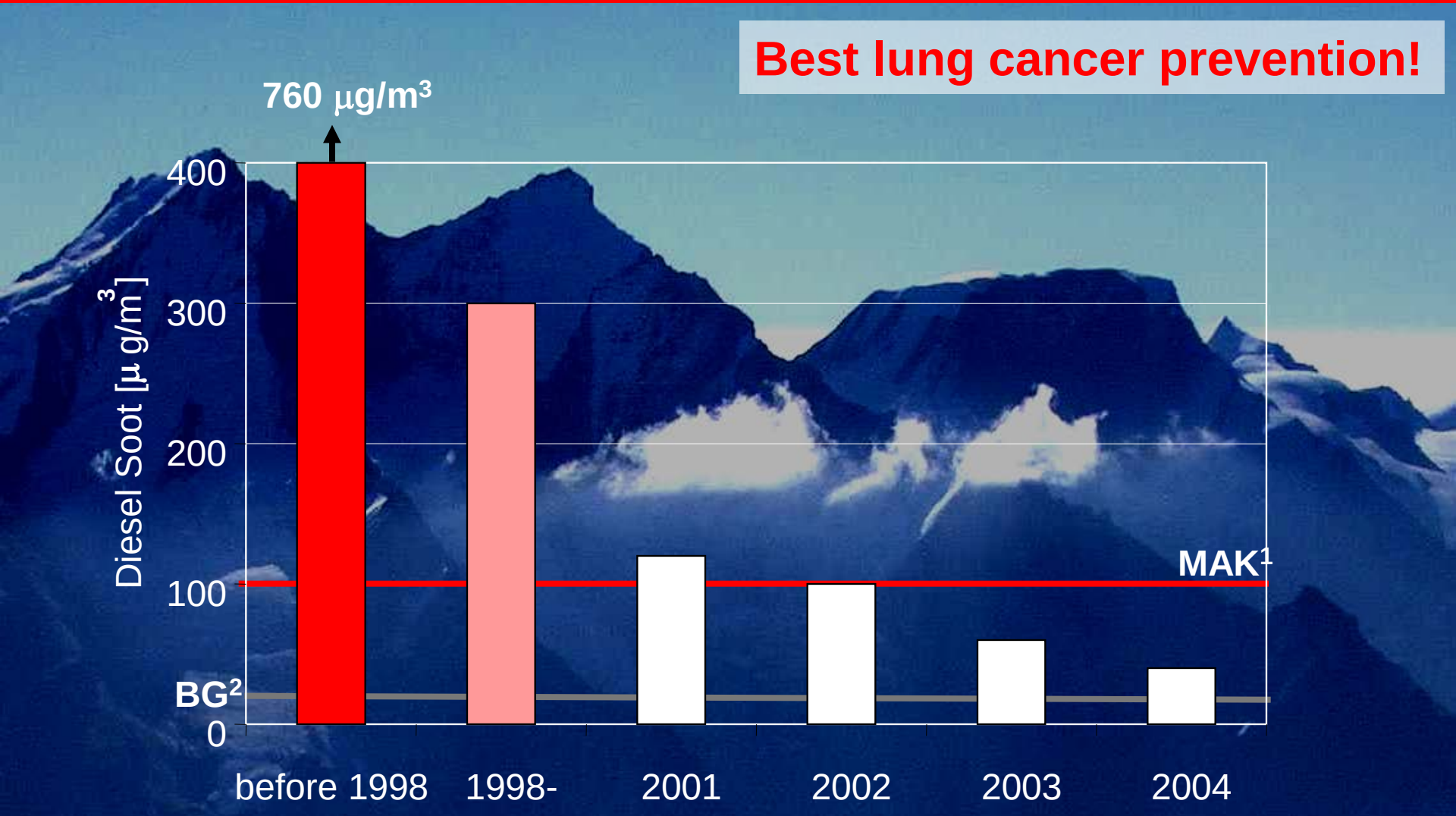
VERT: Verminderung der Emissionen von Realmaschinen im Tunnelbau

	Gases				Aerosols	
[mg/Nm³]	CO	NO	NO_2	SO_2	PM / DME	H_2SO_4
Emisisons of construction heavy duty engines	1000	2700	300	100	250	25
Exposition limits						
Switzerland MAK (max. working place conc.)	35	30	6	5	0.2 (EC +OC)	1
Germany TRGS (limits for working places)	35	30	6	5	0.1 (EC)	1
Required dilution	>26	>90	>50	>20	>1000	>25

NEAT – the longest railway tunnel of the world built with VERT-approved DPFs

DPFs in the NEAT - a success story

Best lung cancer prevention!



[2] Back ground concentration

[1] **Maximum working place concentration**

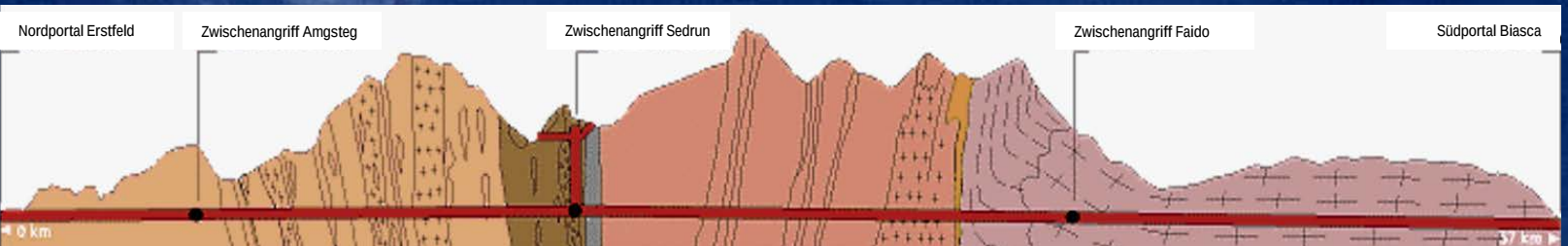
SUVA 2004

The VERT project

With impact on local, cantonal, national and international level

Environmental technology and politics at work

- DPF obligation on NEAT-construction sites, proven soot reduction in tunnel air
- VERT®-approved filters – a accepted label for good filter quality
- Extention of filter obligation on large construction sites (Obligation to retro-fit engines >37 kWh with VERT approved filters)
- Swiss norm on filter testing (SNR 277206)
- Revision of the LRV for construction machinery, ban of copper catalyzed filters, first particle number limit of $1x10^{12}$ particles/kWh
- Several attempts in the Swiss parliament for or against filter obligations for on-road HDV, busses, farming machinery



20 years VERT Filter test

An urgent need for filters in NEAT tunnels

(Why it all started)

Highlights of the VSET

(Hypotheses and facts)

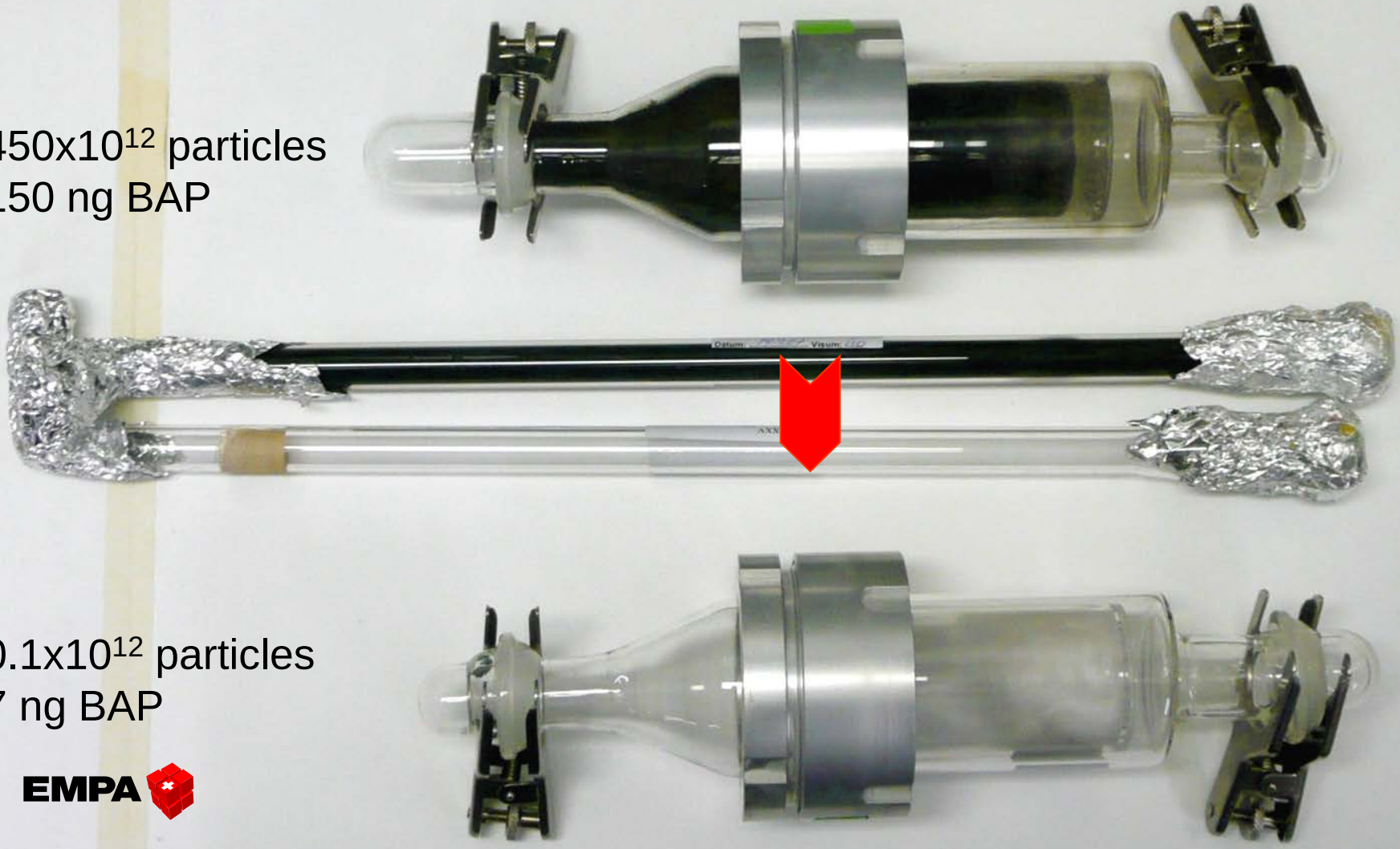
Filters needed more than ever

(The near future still is combustion)

Something to celebrate!

The visible effect of a high quality diesel particle filter

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



$450x10^{12}$ particles
150 ng BAP

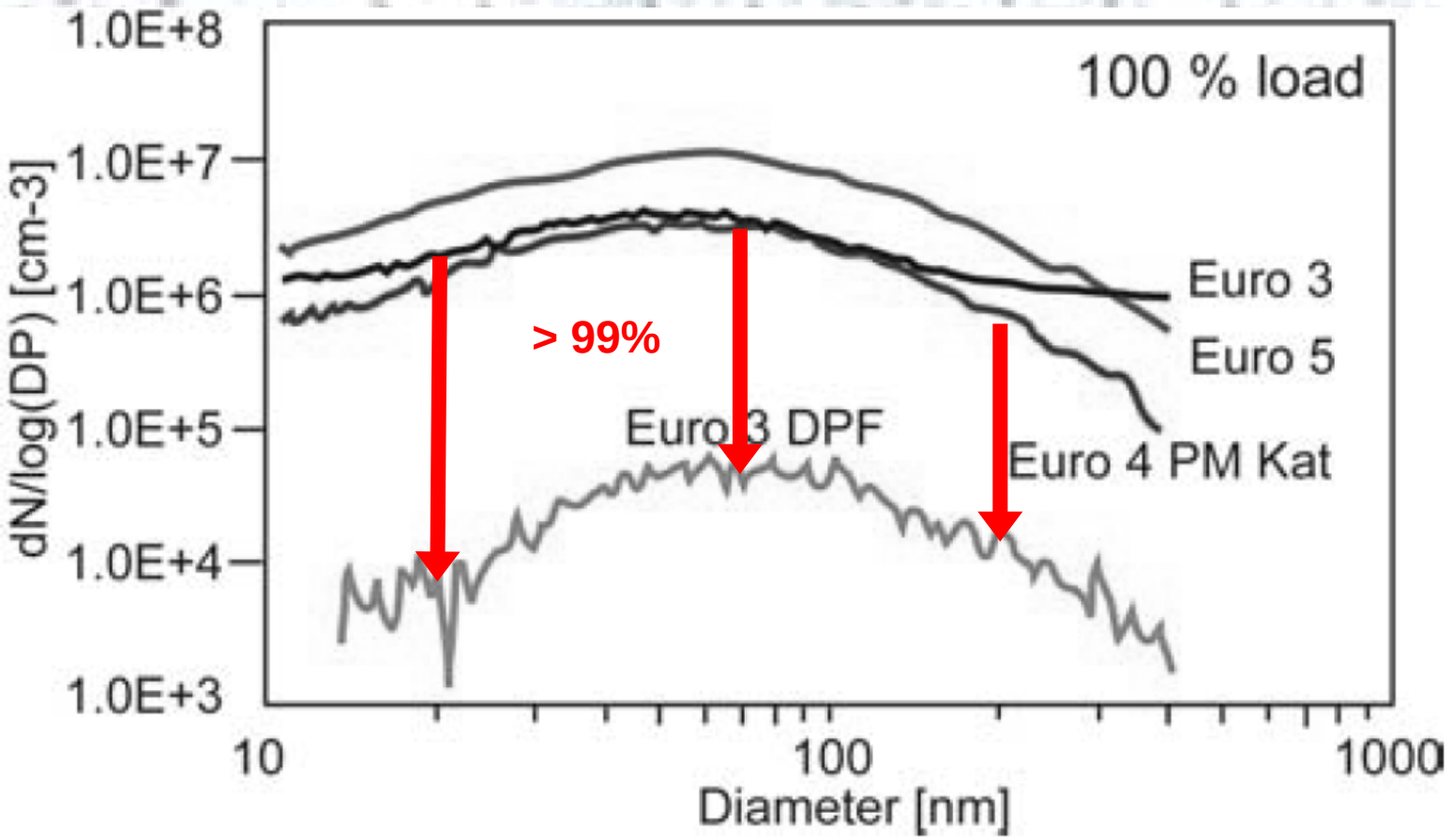
$0.1x10^{12}$ particles
7 ng BAP

EMPA

The invisible effect of a high quality diesel particle filter

Why we have to count particles and not weight them!

Why we need a particle number based legislation!

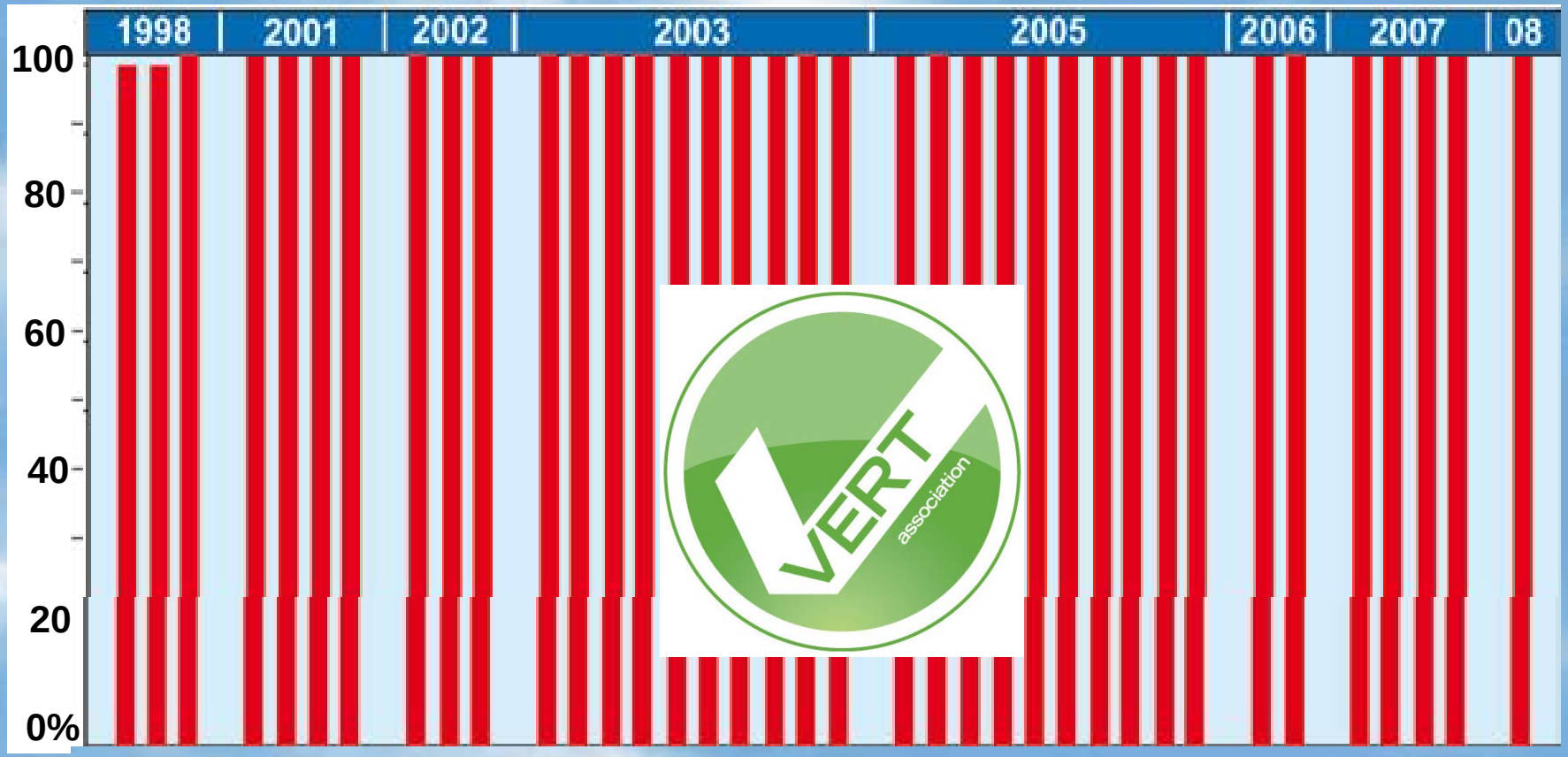


A. Mayer et al., SAE 2007-01-1112

The VERT label for approved particle filter

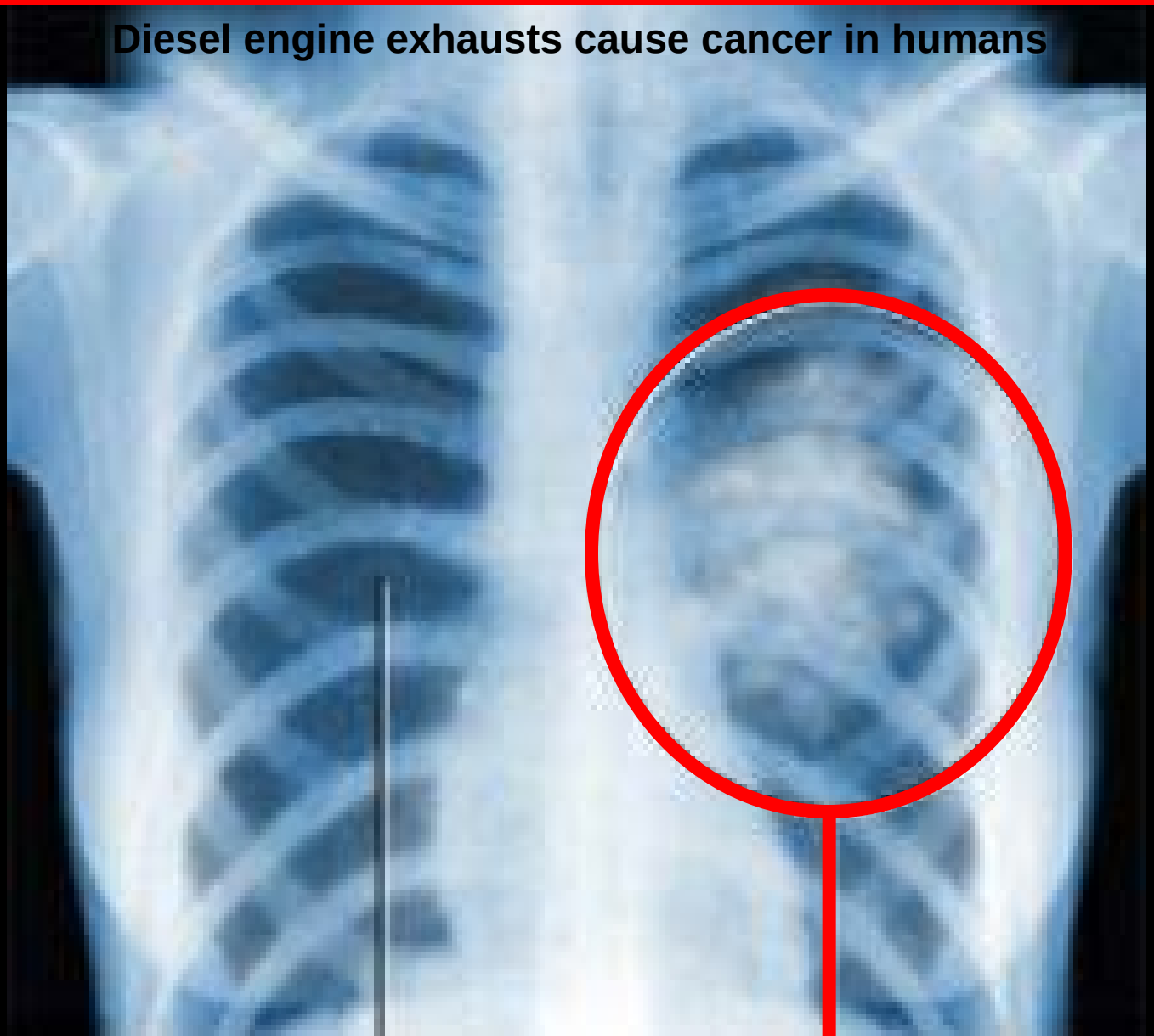
>60 VERT-approved DPFs available (to use them)

PN filtration efficiencies >98% for all particles (23 – 400 nm)



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

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



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

Diesel engine exhausts cause lung cancer in humans

International Agency for Research on Cancer

World Health Organization

PRESS RELEASE
N° 213

12 June 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.

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-enforced 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).

only 125 years after Rudolf Diesels patent!

Group 1

Lung cancer in exposed workers

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

Diesel engine exhaust cause cancer in humans

The Diesel Exhaust in Miners Study: A Nested Case–Control Study of Lung Cancer and Diesel Exhaust

Debra T. Silverman, Claudine M. Samanic, Jay H. Lubin, Aaron E. Blair, Patricia A. Stewart, Roel Vermeulen, Joseph B. Coble, Nathaniel Rothman, Patricia L. Schleiff, William D. Travis, Regina G. Ziegler, Sholom Wacholder, Michael D. Attfield

Manuscript received February 16, 2011; revised June 3, 2011; accepted October 21, 2011.

Correspondence to: Debra T. Silverman, ScD, Occupational and Environmental Epidemiology Branch, Division of Cancer Epidemiology and Genetics, National Cancer Institute, Rm 8108, 6120 Executive Blvd, Bethesda, MD 20816 (e-mail: silvermd@mail.nih.gov).

Background Most studies of the association between diesel exhaust exposure and lung cancer suggest a modest, but consistent, increased risk. However, to our knowledge, no study to date has had quantitative data on historical diesel exposure coupled with adequate sample size to evaluate the exposure–response relationship between diesel exhaust and lung cancer. Our purpose was to evaluate the relationship between quantitative estimates of exposure to diesel exhaust and lung cancer mortality after adjustment for smoking and other potential confounders.

Methods We conducted a nested case–control study in a cohort of 12315 workers in eight nonmetal mining facilities which included 198 lung cancer deaths and 562 incidence density–sampled control subjects. For each case subject, we selected up to four control subjects, individually matched on mining facility, gender, ethnicity, and birth year (within 5 years), from all workers who were alive before the day the case subject died. We estimated diesel exhaust exposure, represented by respirable elemental carbon (REC), by job and year, for each subject, based on an extensive retrospective exposure assessment at each mining facility. We conducted both categorical and continuous regression analyses adjusted for cigarette smoking and other potential confounding variables (eg, history of employment in high-risk occupations for lung cancer and a history of respiratory disease) to estimate odds ratios (ORs) and 95% confidence intervals (CIs). Analyses were both unlagged and lagged to exclude recent exposure such as that occurring in the 15 years directly before the date of death (case subjects)/reference date (control subjects). All statistical tests were two-sided.

Results We observed statistically significant increasing trends in lung cancer risk with increasing cumulative REC and average REC intensity. Cumulative REC, lagged 15 years, yielded a statistically significant positive gradient in lung cancer risk overall (P_{trend} = .001); among heavily exposed workers (ie, above the median of the top quartile [REC ≥ 1005 μg/m³-y]), risk was approximately three times greater (OR = 3.20, 95% CI = 1.33 to 7.69) than that among workers in the lowest quartile of exposure. Among never smokers, odd ratios were 1.0, 1.47 (95% CI = 0.29 to 7.50), and 7.30 (95% CI = 1.46 to 36.57) for workers with 15-year lagged cumulative REC tertiles of less than 8, 8 to less than 304, and 304 μg/m³-y or more, respectively. We also observed an interaction between smoking and 15-year lagged cumulative REC ($P_{interaction}$ = .086) such that the effect of each of these exposures was attenuated in the presence of high levels of the other.

Conclusion Our findings provide further evidence that diesel exhaust exposure may cause lung cancer in humans and may represent a potential public health burden.

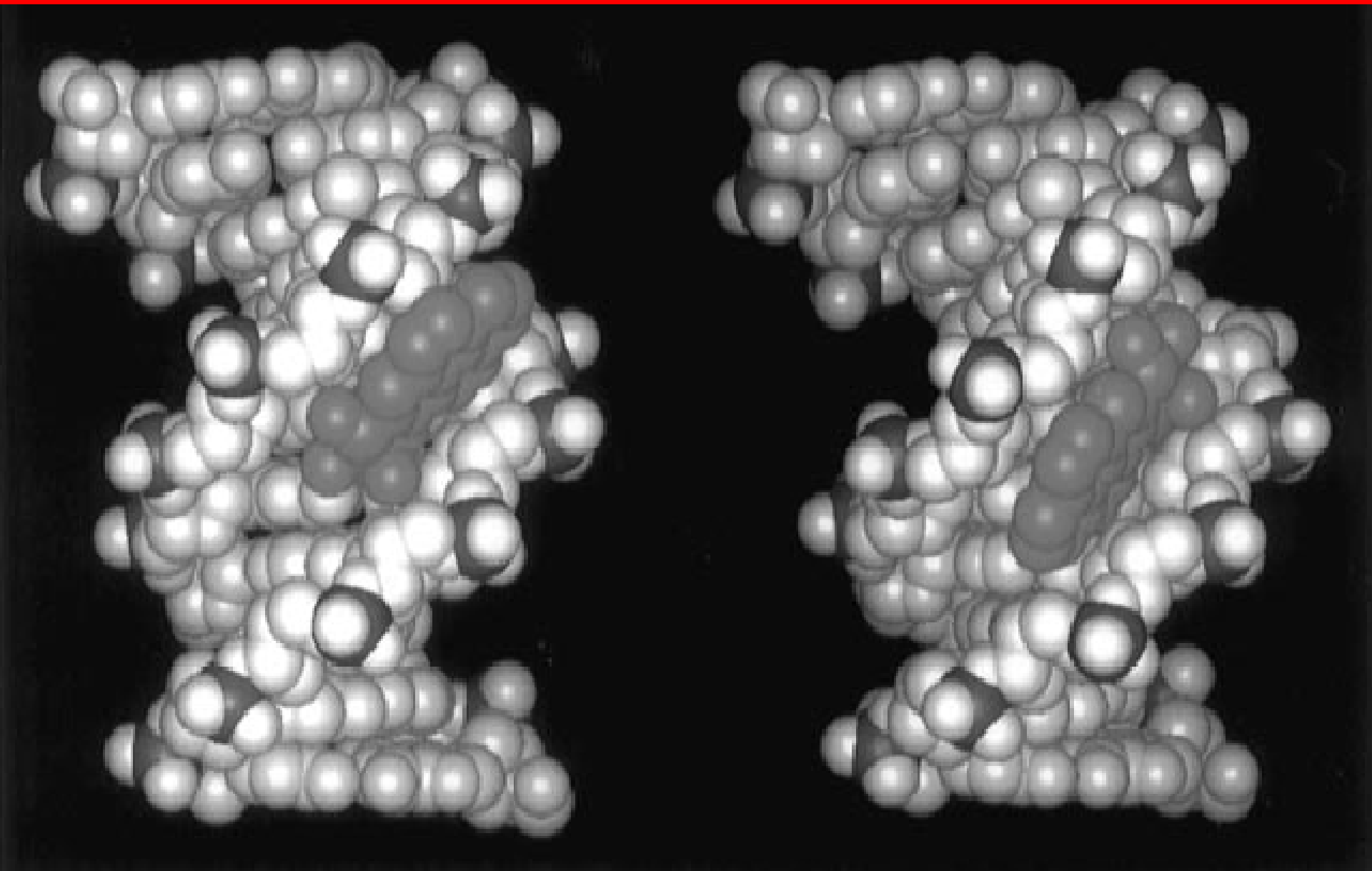
J Natl Cancer Inst 2012;104:1–14

In 2012, the NEAT tunnel was drilled and workers exposed for 14 years

12315 workers, 198 lung cancer death (16 in 1000)

diesel exhaust exposure: a potential public health burden

Carcinogenesis of benzo(a)pyrene



Swiss workplace legislation

Grenzwerte am Arbeitsplatz 2009

suvapro
Sicher arbeiten

Stoff [CAS-Nummer]	MAK-Wert ml/m³ (ppm)	MAK-Wert mg/m³	Kurzzeitgrenzwerte ml/m³ (ppm)	Kurzzeitgrenzwerte mg/m³	Kurzzeitgrenzwerte Zeitl. Begrenzung (Häufigkeit x Dauer in min./Schicht)	HSB	C	M	R_F	R_E	SS	Messmethoden/ besondere Bemerkungen
1,3-Dichlorpropen (cis und trans) [542-75-6]	0,11	0,5				HS	2	3				
2,2-Dichlorpropionsäure [75-99-0] und ihr Natriumsalz [127-20-8]	1	6	1	6	15 min							
1,2-Dichlor-1,1,2,2-tetrafluorethan (R 114) [76-14-2]	1000	7000										DFG, NIOSH
Dicyclopentadienyleisen [102-54-5]		10 e										
Dieldrin (HEOD) [60-57-1]		0,25 e				H	3					NIOSH
Dieselmotor-Emissionen (gemessen als elementarer Kohlenstoff)		0,1 a					2					BG

Minimization principle for exposure to carcinogens

With best available technology

Swiss clean air act (LRV): List of carcinogenic compounds

Luftreinhalte-Verordnung
(LRV)

814.318.142.1

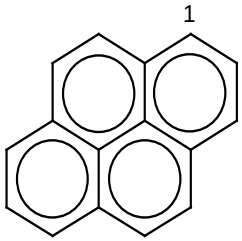
83 Tabelle von krebserzeugenden Stoffen

Stoff	Summenformel	Klasse
Benzo(a)pyren	$C_{20}H_{12}$	1
Benzol	C_6H_6	3
Dibenz(a, h)anthracen	$C_{22}H_{14}$	1
1,2-Dibromethan	$C_2H_4Br_2$	3
1,4 Dichlorbenzol	$C_6H_4Cl_2$	3
1,2-Dichlorethan	$C_2H_4Cl_2$	3
Dieselruss		3
Diethylsulfat	$C_4H_{10}O_4S$	2

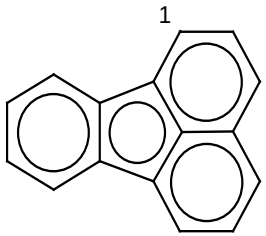
Genotoxic PAHs

Some PAHs are carcinogenic according to the WHO

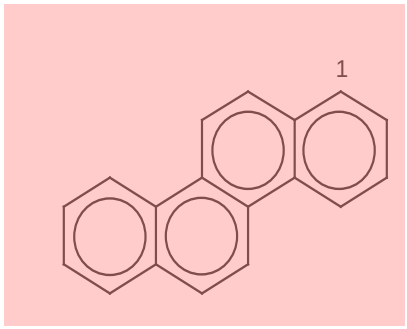
Carcinogenic PAHs



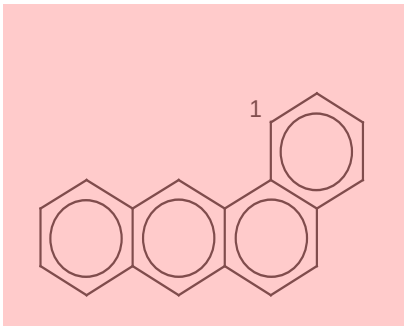
Pyrene



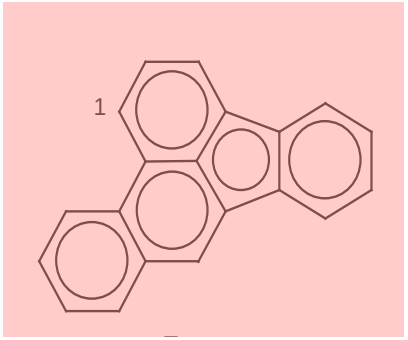
Fluoranthene



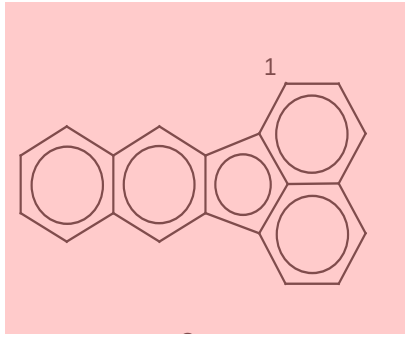
Chrysene



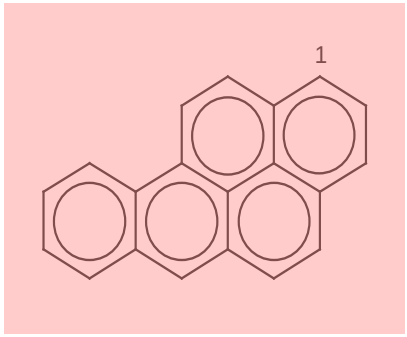
Benz(a)anthracene



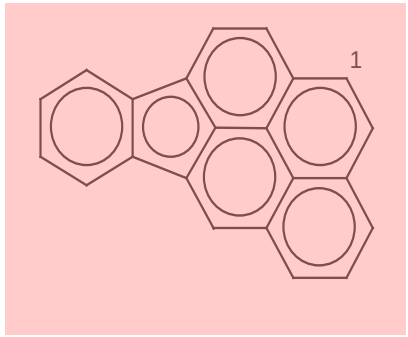
Benzo[b]-
fluoranthene



Benzo[k]-
fluoranthene



Benzo[a]-
pyrene



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

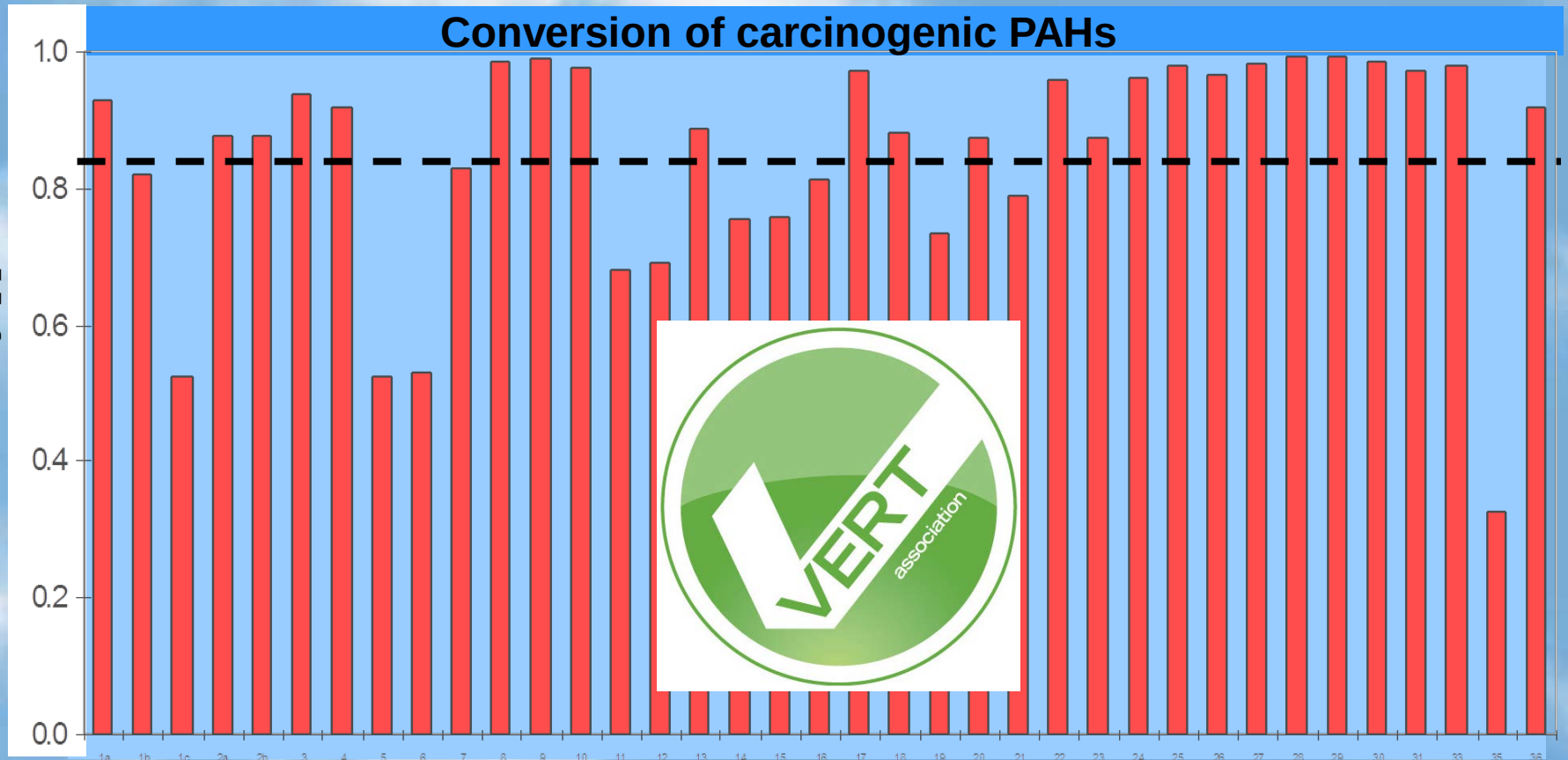
More PAHs in diesel and GDI exhausts tomorrow

Focus event 12:00 Maria Munoz

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

VERT approved DPF convert genotoxic PAHs

All VERT approved DPFs convert PAHs, many rather efficient



Soot nanoparticles act as Trojan horses for genotoxic compounds

Problem: Trojan horse effect

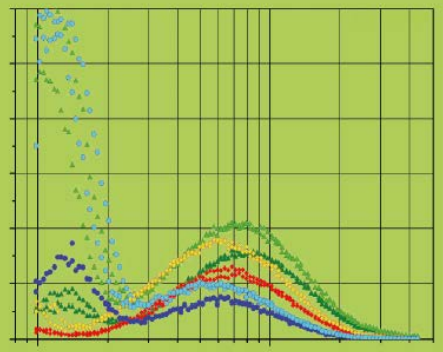
- Nanoparticles penetrate cell membranes (alveoli, placenta, blood cells) acting like a Trojan horse

Win the Trojan horse prize at this years ETH conference! deadline March 23, 2018

Invitation and call for papers to the

22nd ETH-Conference on Combustion Generated Nanoparticles

Focus Event:
Emissions of in-use vehicles:
Quality and control



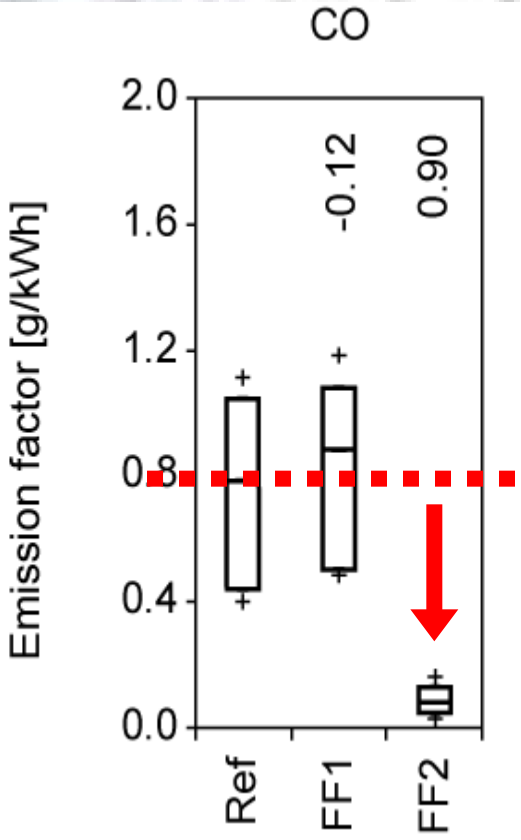
June 18th – 21st, 2018
ETH Zurich, Switzerland
www.nanoparticles.ch

Trojan horse, Harbour of Canakkale, Turkey

Low- / high-oxidation potential DPFs

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

Carbon monoxide



- **Ref: Engine-out**
- **FF1: Low oxidation potential (n=6)**
- **FF2: High oxidation potential (n=8)**

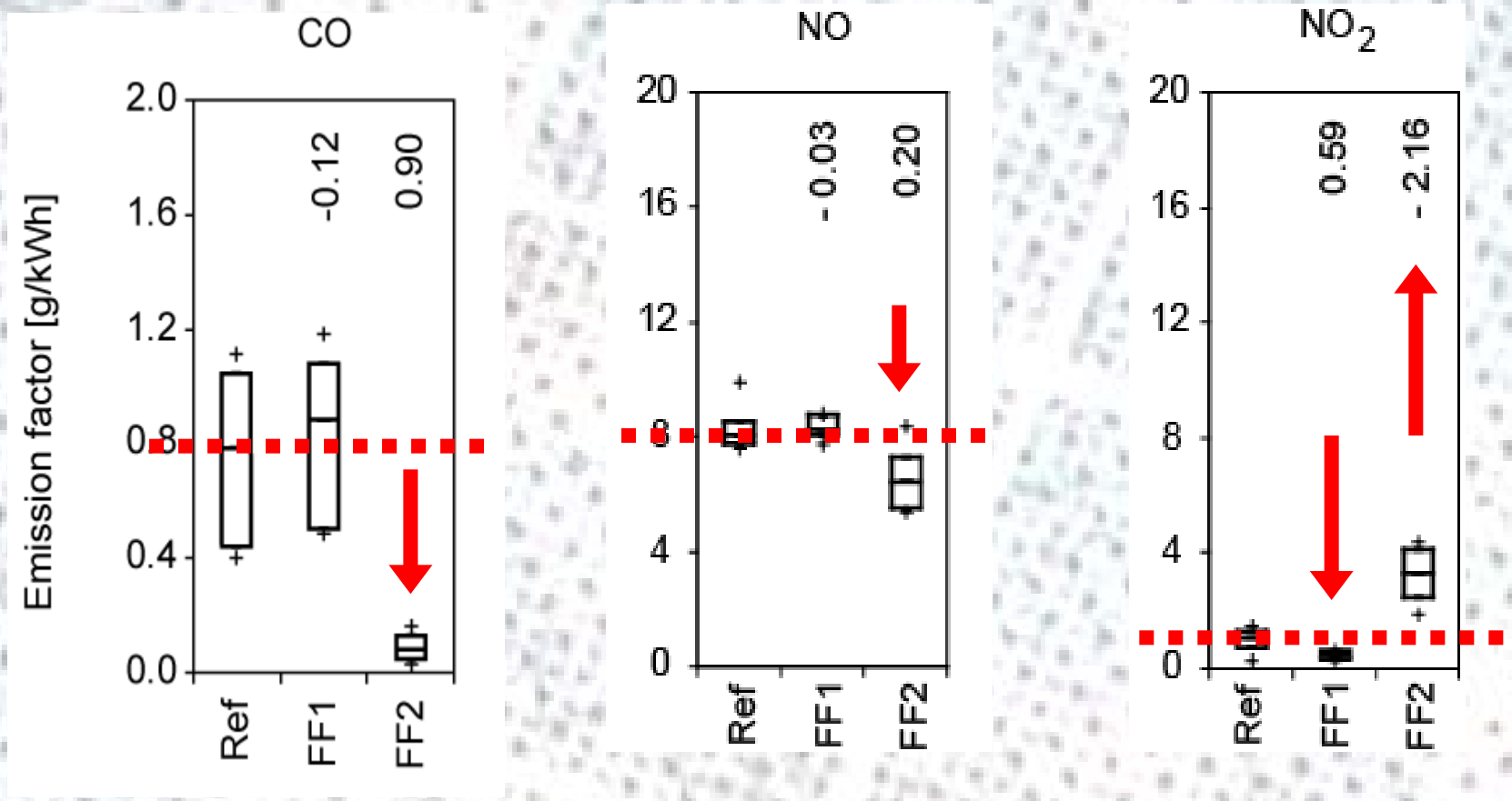
Heeb et al. ES&T, **2008**, 42, 3773-3779

Heeb et al. ES&T, **2010**, 442, 1078-1084

Low- / high-oxidation potential DPFs

We have 2 filter families, one forms NO_2, the converts it!

CO, NO, NO_2



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

Heeb et al. ES&T, **2010**, 442, 1078-1084

Store and release phenomena in non-catalyzed DPF

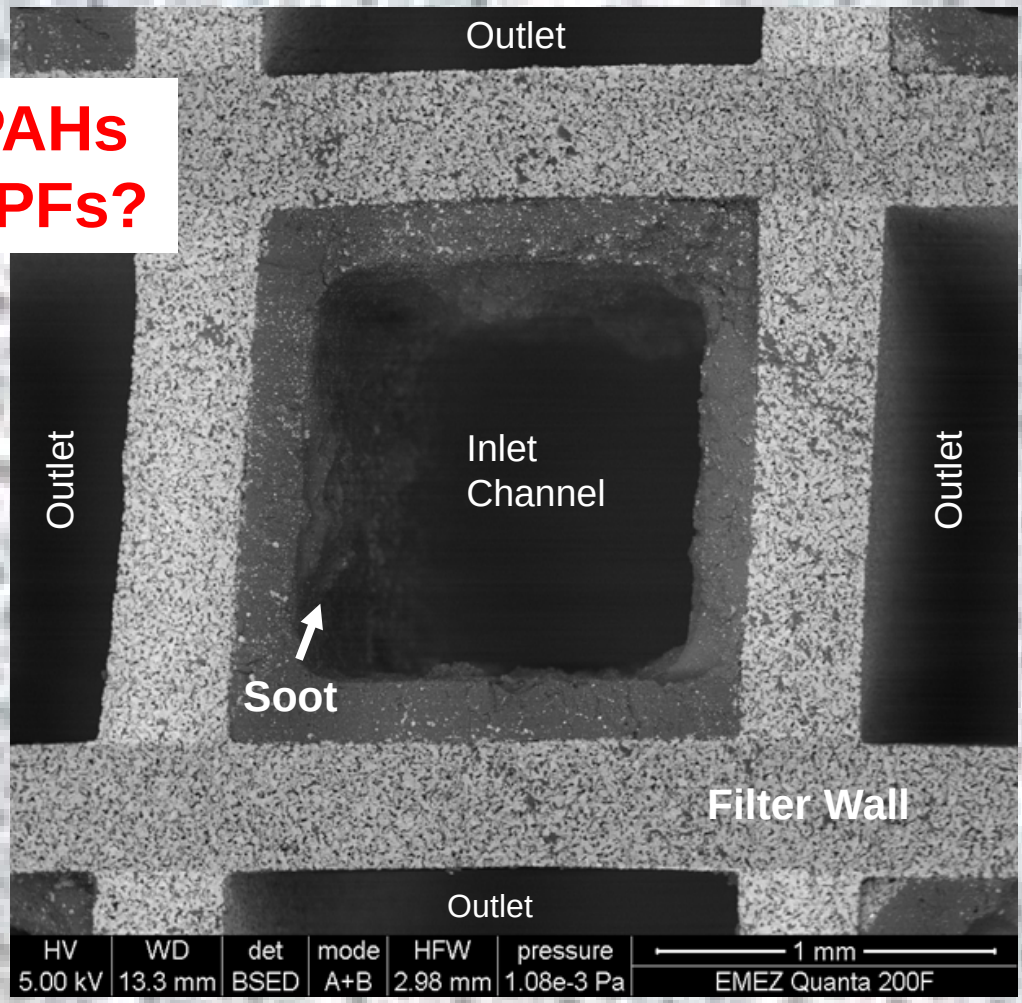
Non-catalyzed filters are efficient for soot. How about semi-volatile compounds?

What do you expect, can PAHs penetrate non-catalyzed DPFs?

Non-catalyzed DPFs:

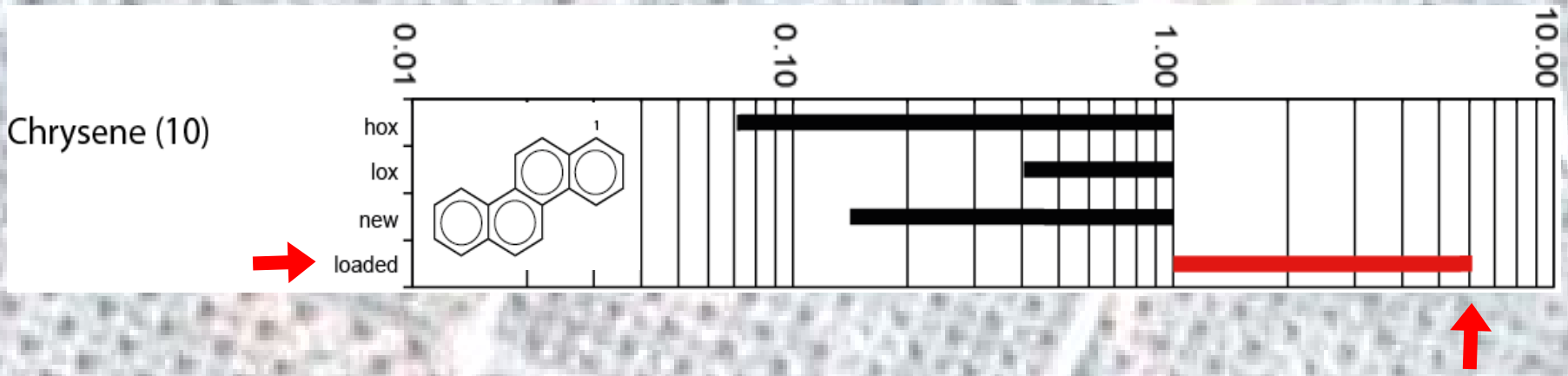
Accumulate soot (>98%)

- **Do they reduce genotoxic compounds a.m.a.p?**
- **Do they have toxic secondary emissions?**



Catalyzed DPFs convert PAHs, non-catalyzed accumulate and release them

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



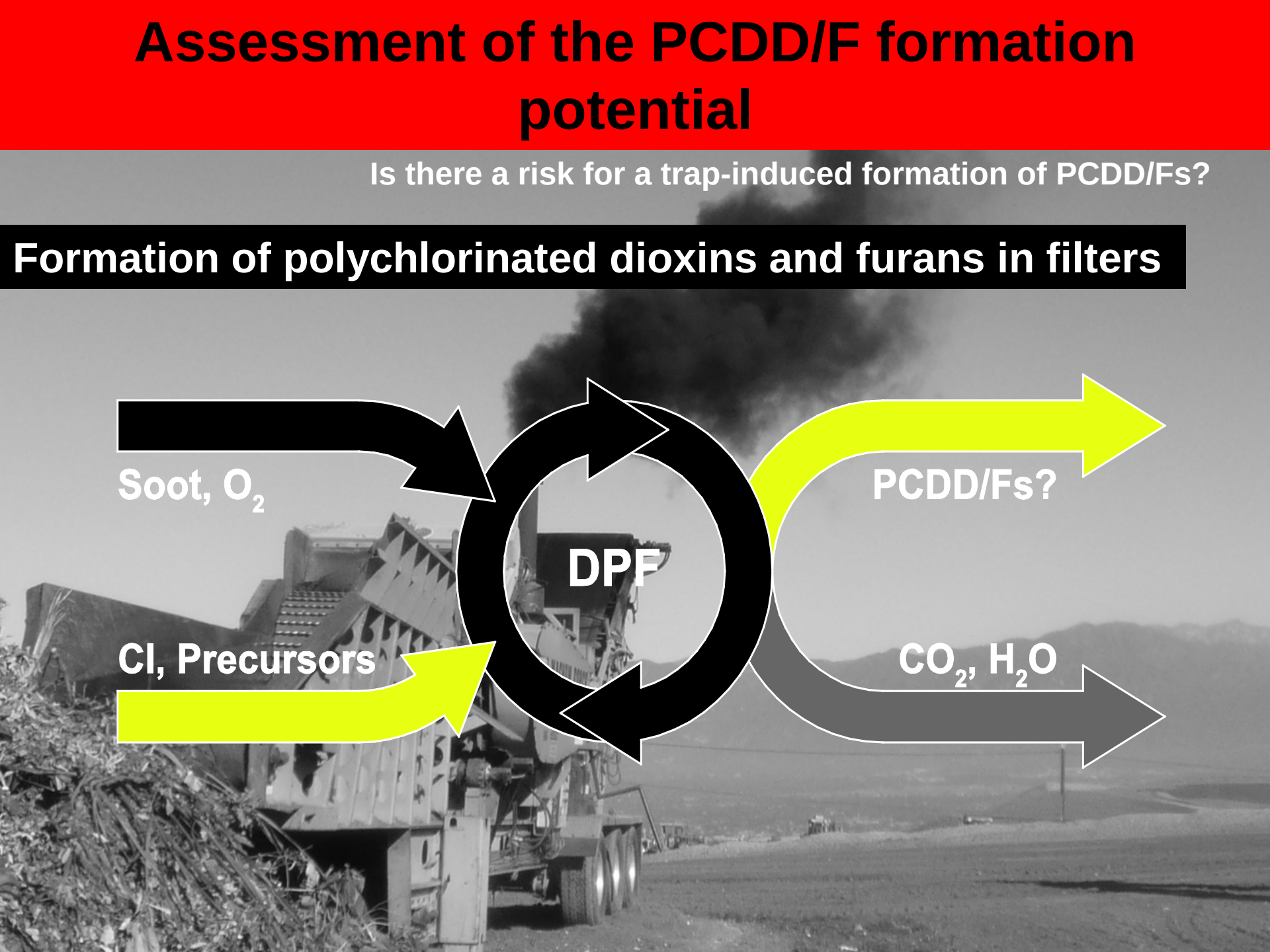
- **Hox-DPF convert >94% chrysene**
- **Lox-DPF convert >60% chrysene**
- **A new non-catalyzed DPF can store chrysene**
  (at cold conditions even better than a lox-DPF)
- **A loaded non-catalyzed DPF can release chrysene**

Store and release phenomena in open & non-cat. DPF!

Assessment of the PCDD/F formation potential

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

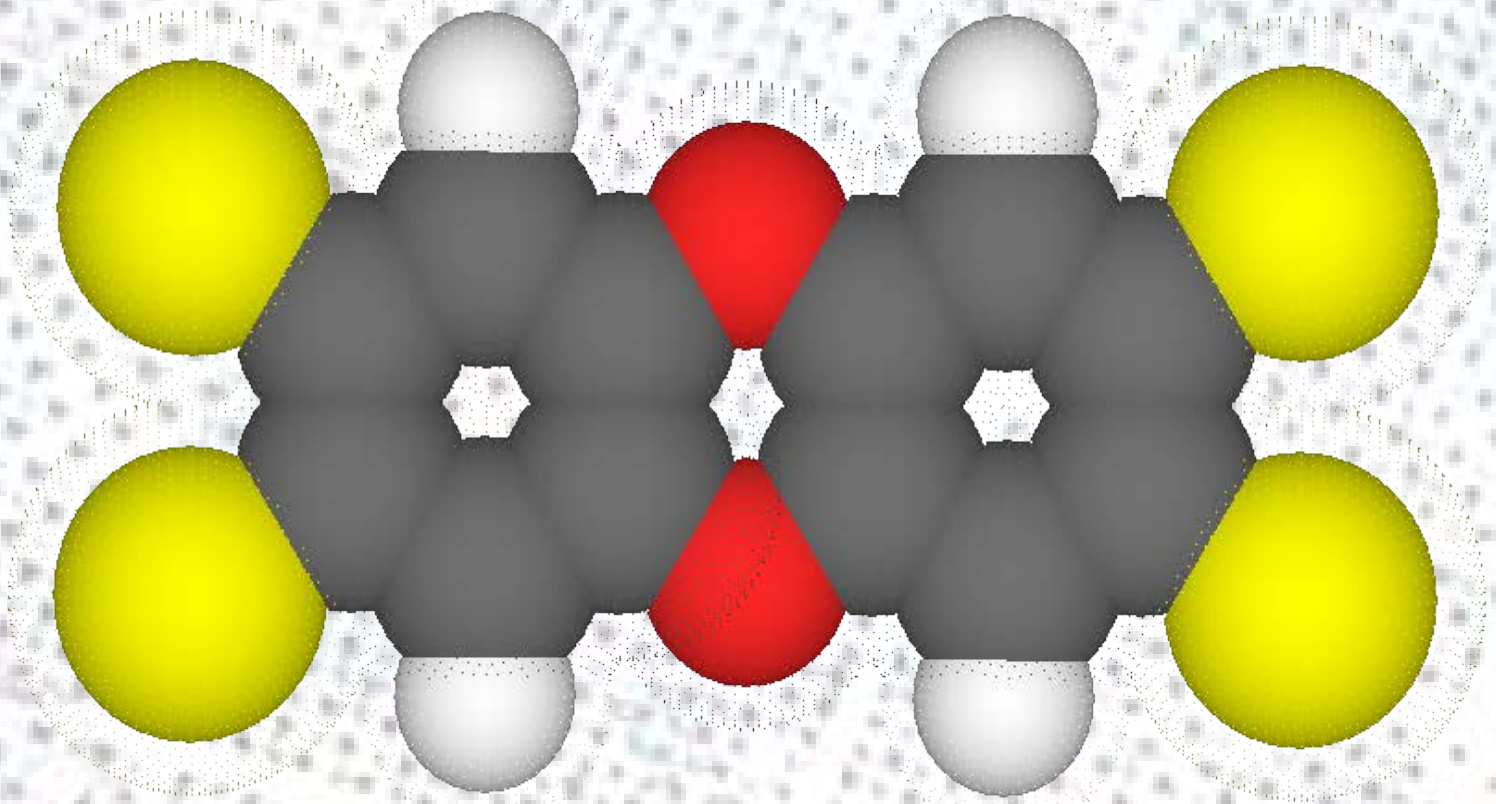
Formation of polychlorinated dioxins and furans in filters



PCDD/Fs: toxic at pg-quantities

What are PCDD/Fs?

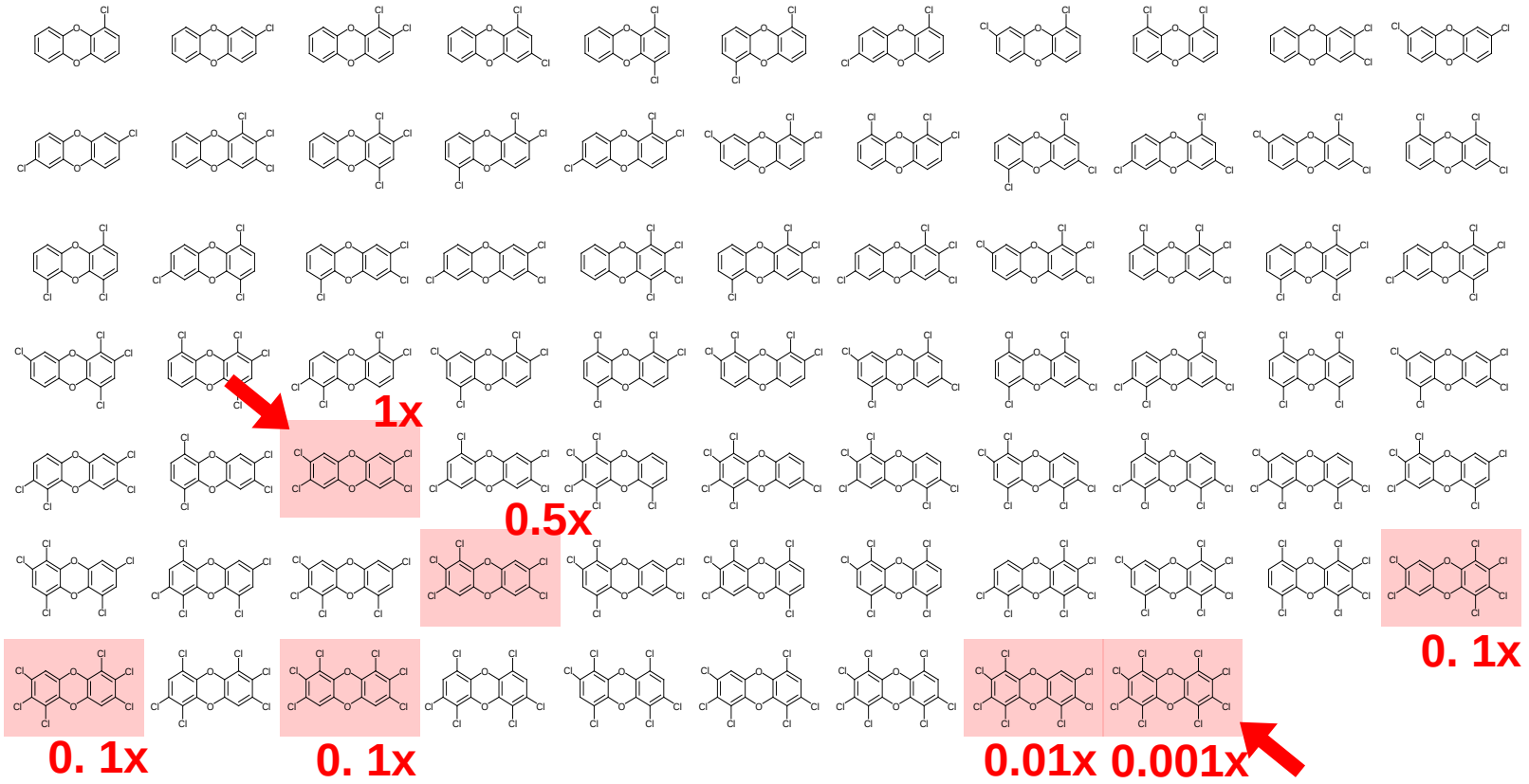
2,3,7,8-Tetrachlorodibenzodioxin - the so-called Seveso-dioxin



Analysis of dioxins at ultratrace level

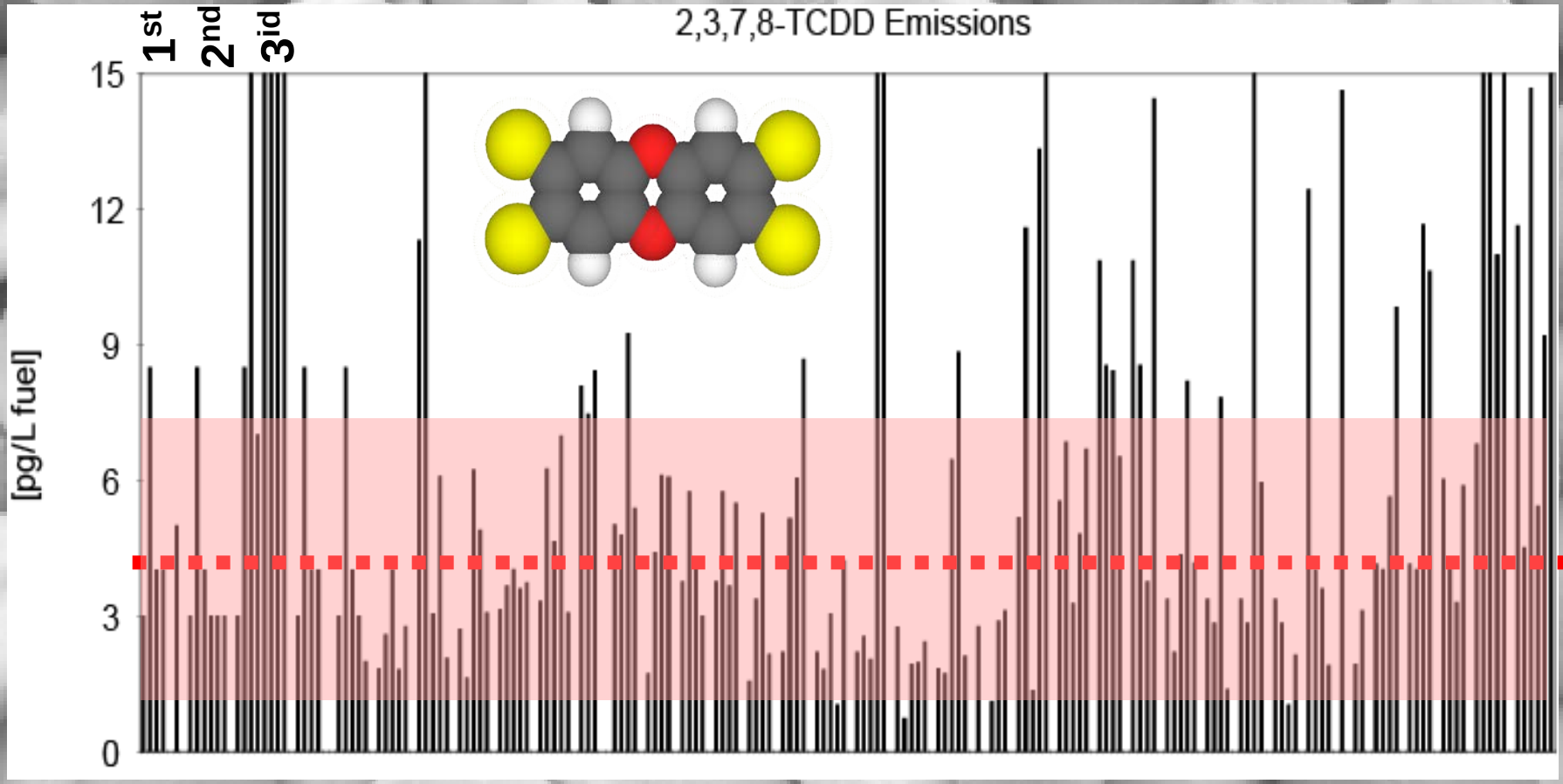
Which are the 7 toxic PCDD?

Chemical structures of polychlorinated dibenzodioxins



Assessment of the PCDD/F-formation potential of DPFs

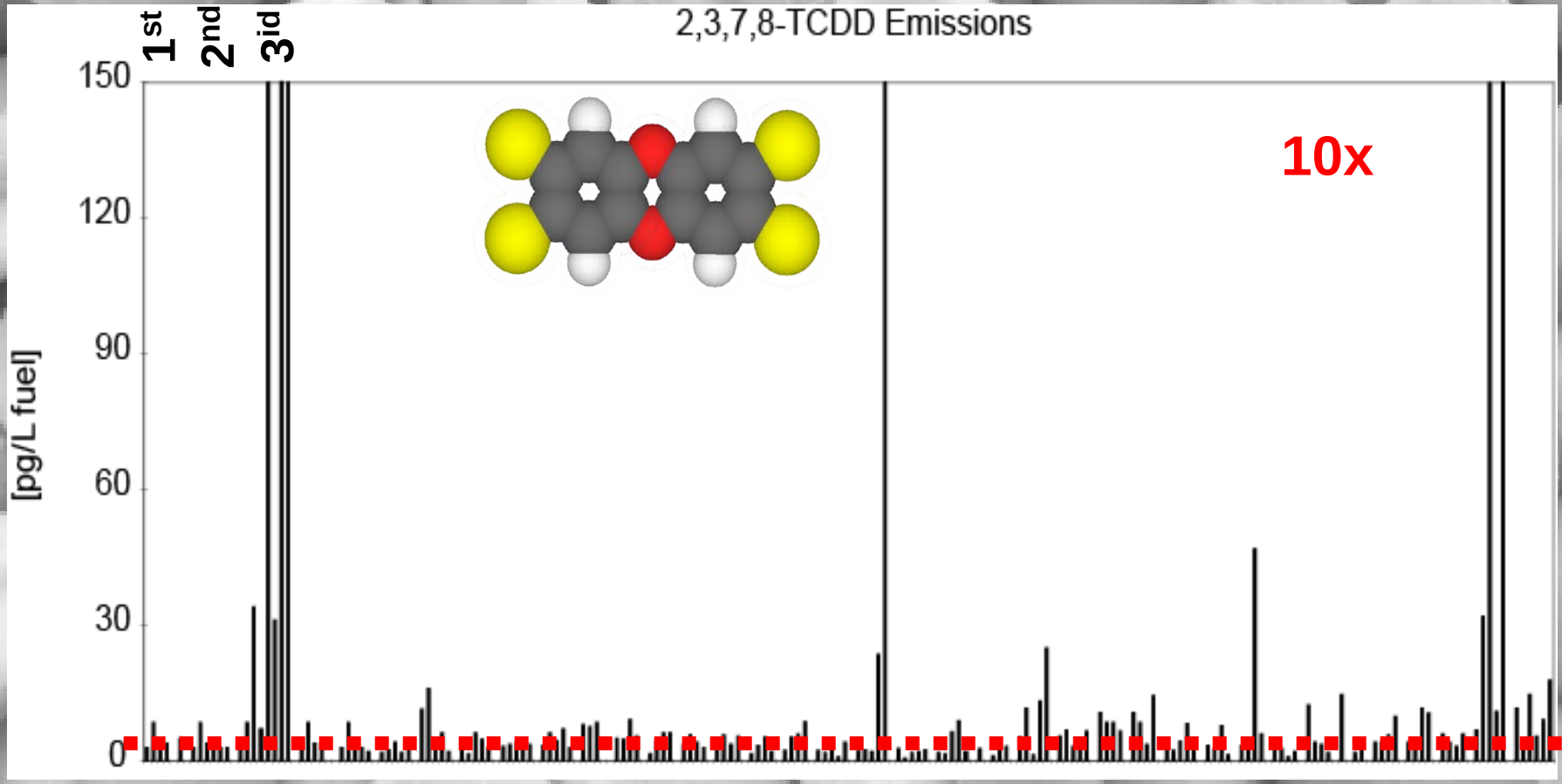
We just have to pick the right ones



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

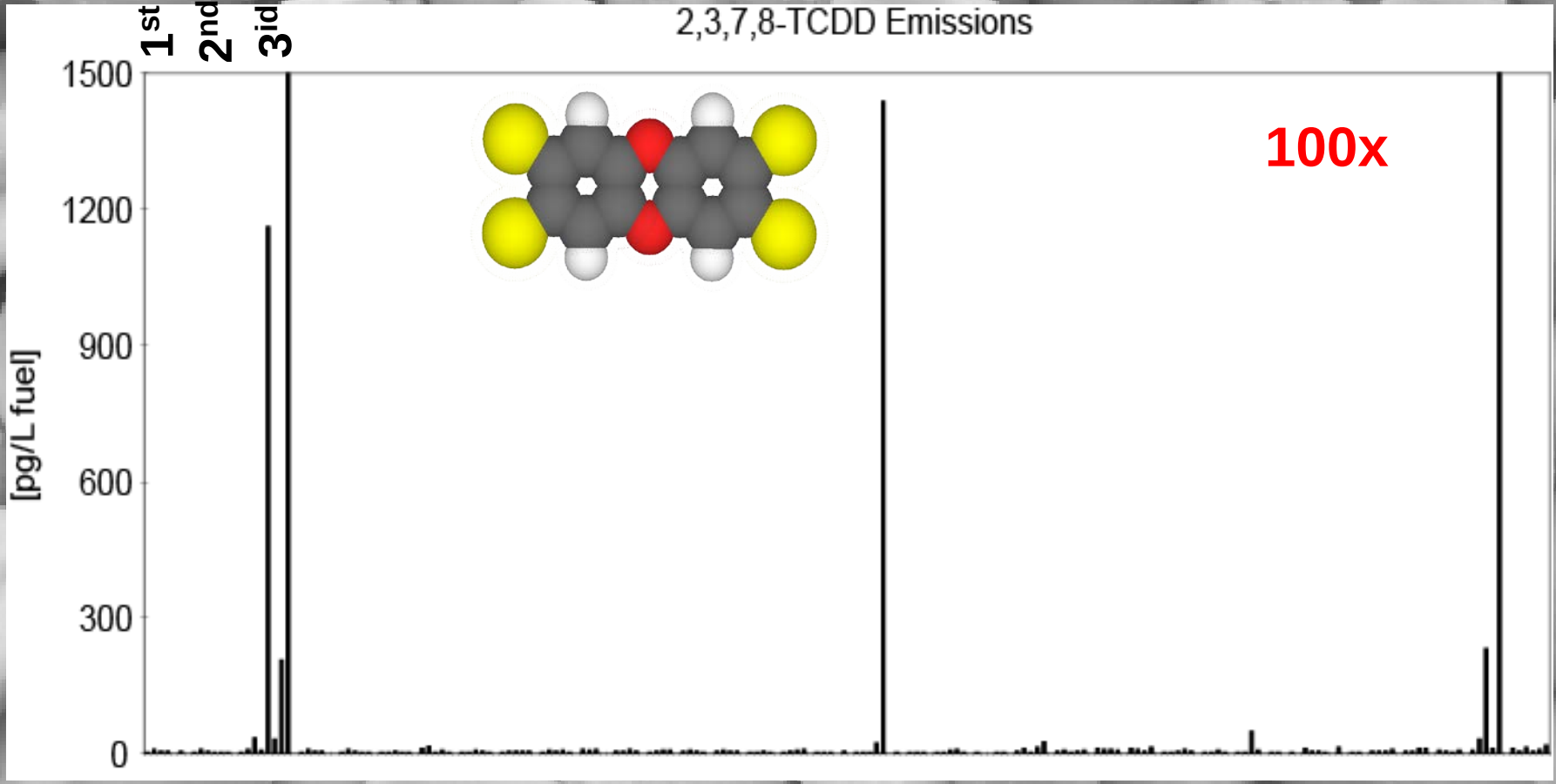
Assessment of the PCDD/F-formation potential of DPFs

The dioxin formation potential of the respective DPFs?



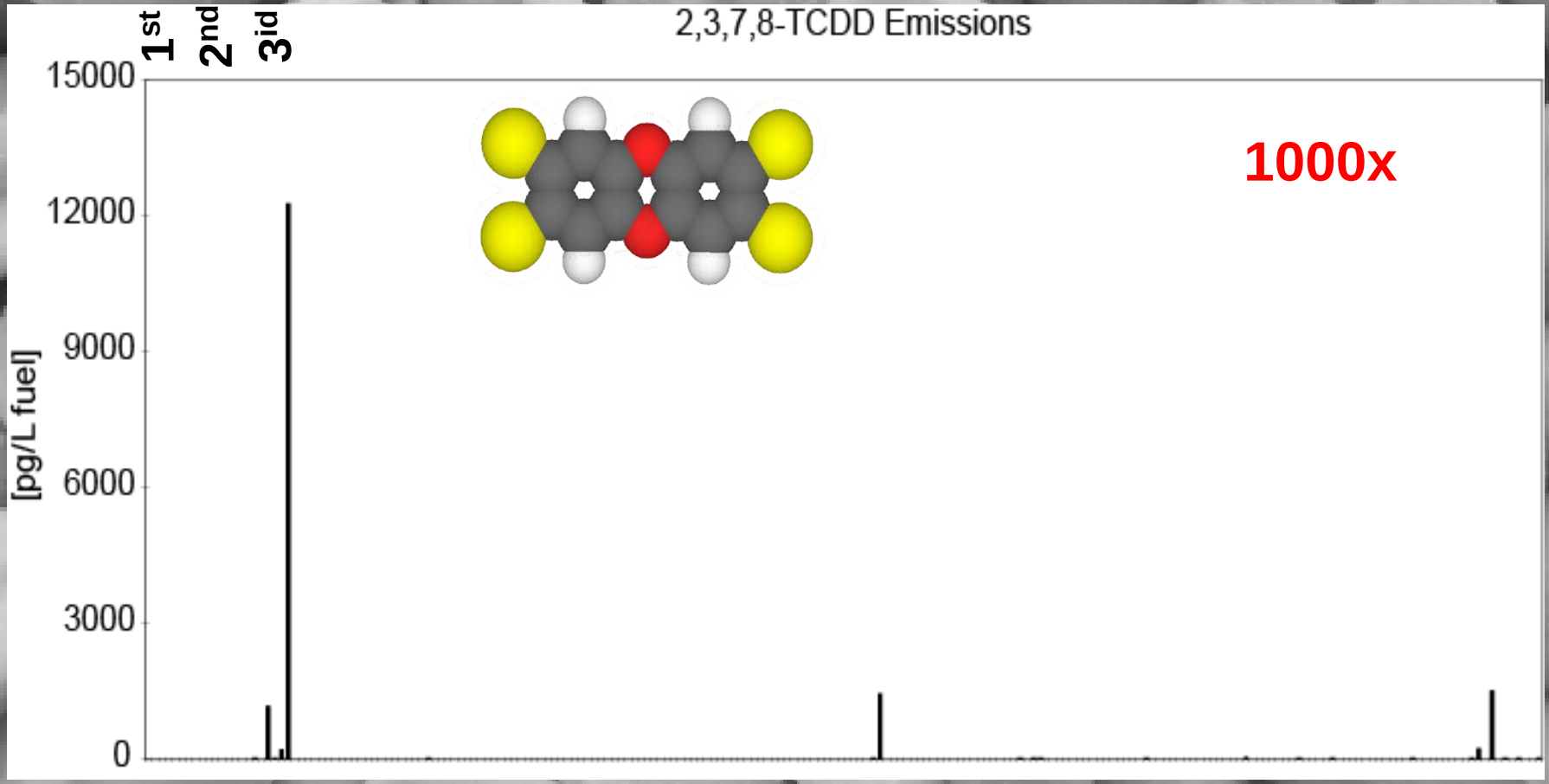
Assessment of the PCDD/F-formation potential of DPFs

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



Assessment of the PCDD/F-formation potential of DPFs

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



Assessment of the PCDD/F-formation potential of DPFs

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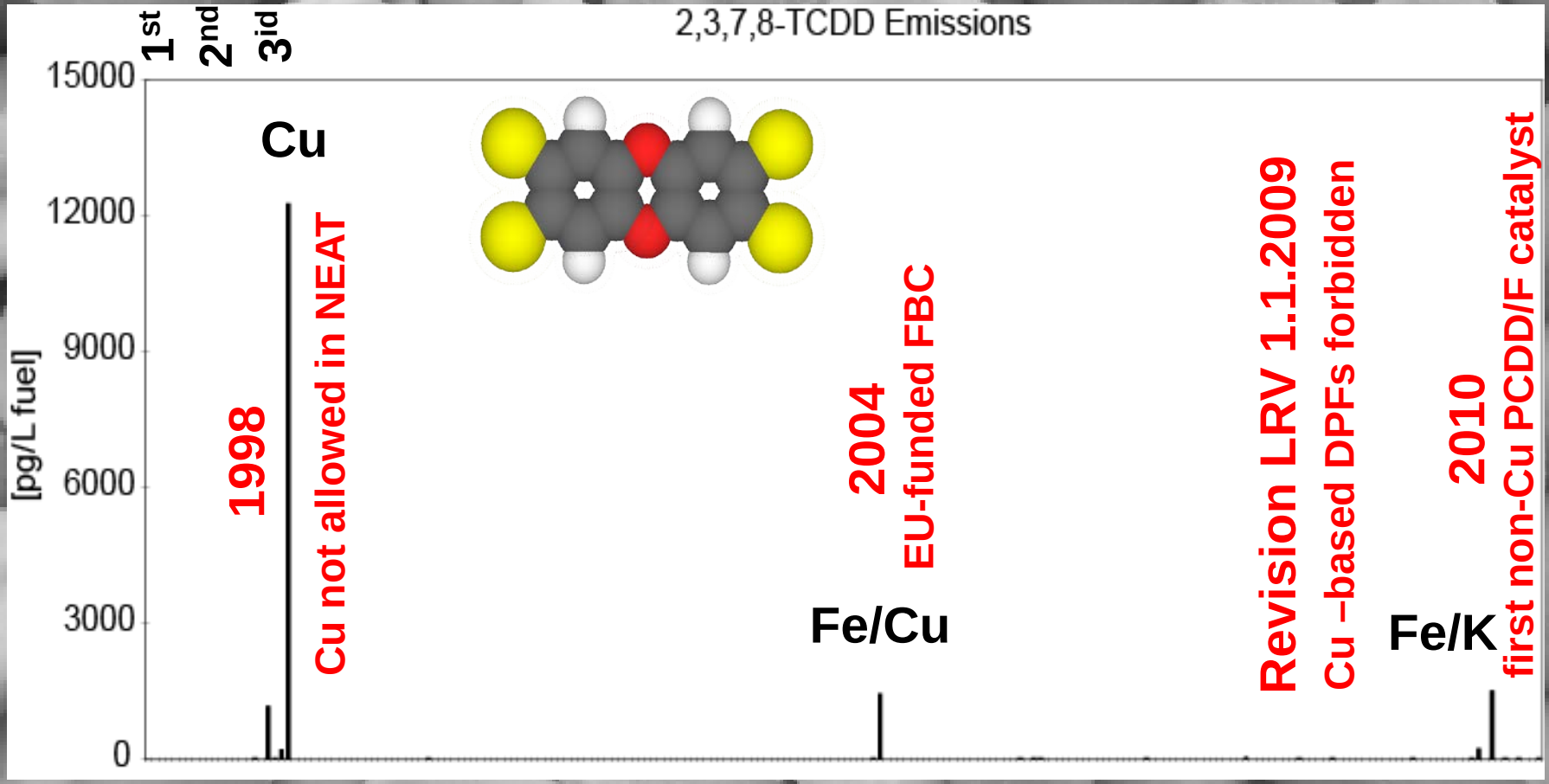


PCDD/F Formation Potential of DPFs: New Risks with Biofuels?

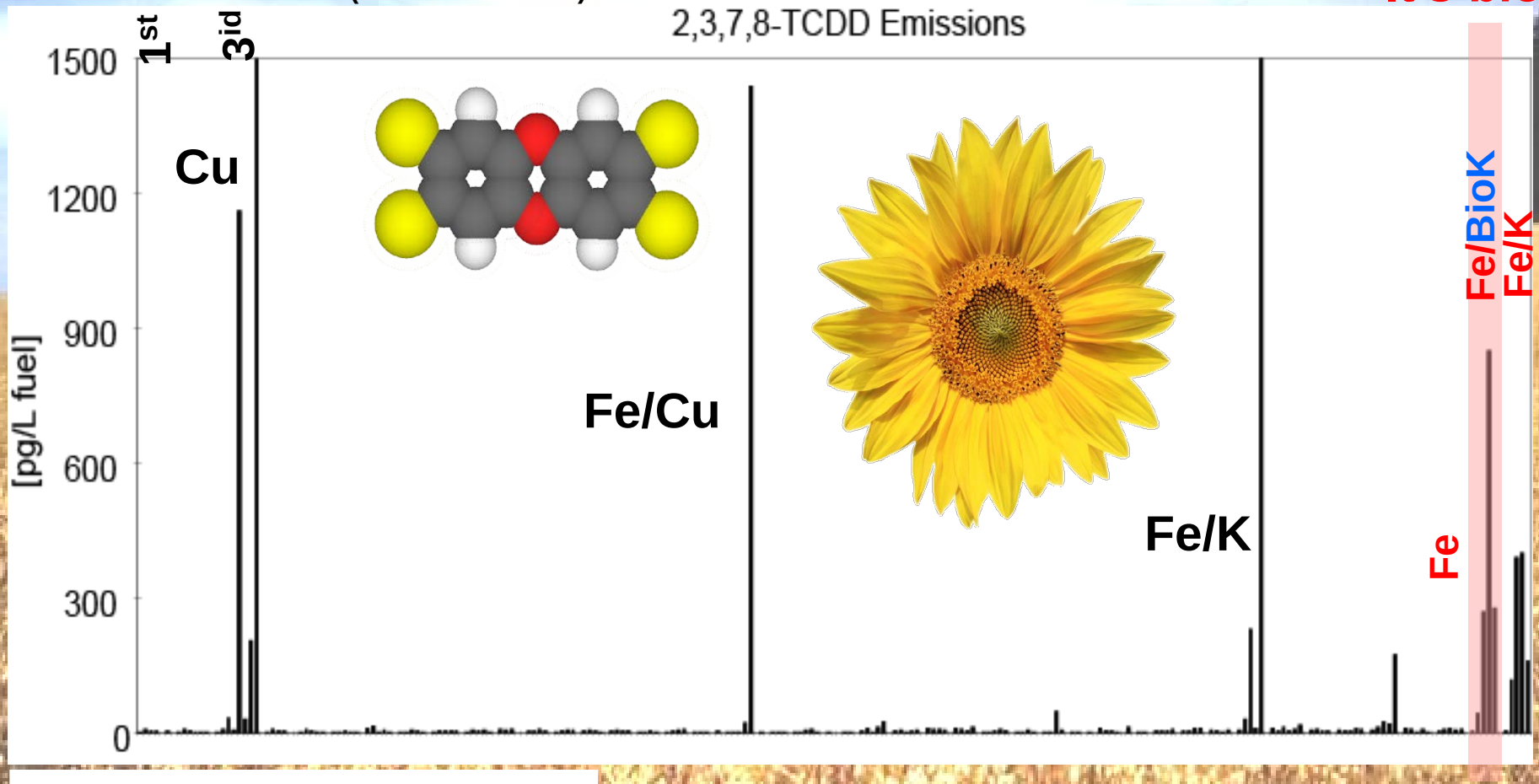
K, bio or not, can promote a PCDD/F formation in certain Fe-catalyzed DPFs

PCDD/F Formation Potential of DPFs: New Risks with Biofuels?

Certain DPFs are not compatible with certain biofuels!

It's fossil fuel! (fossilized biofuel)

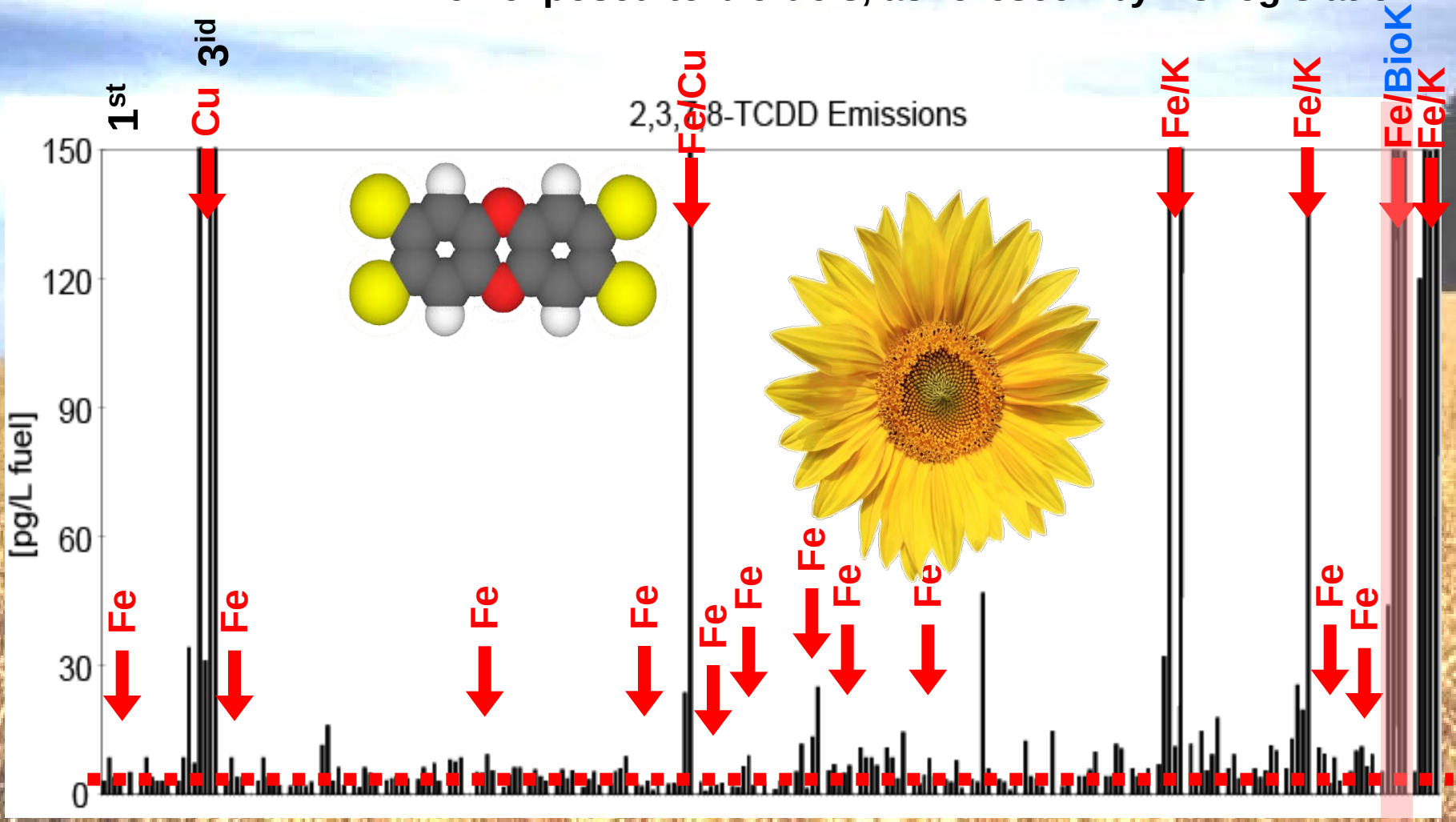
It's bio!



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

PCDD/F Formation Potential of DPFs: New Risks with Biofuels?

Possibly thousands of vehicles with Fe-catalyzed DPFs might become active, when exposed to biofuels, as foreseen by EU legislation!



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

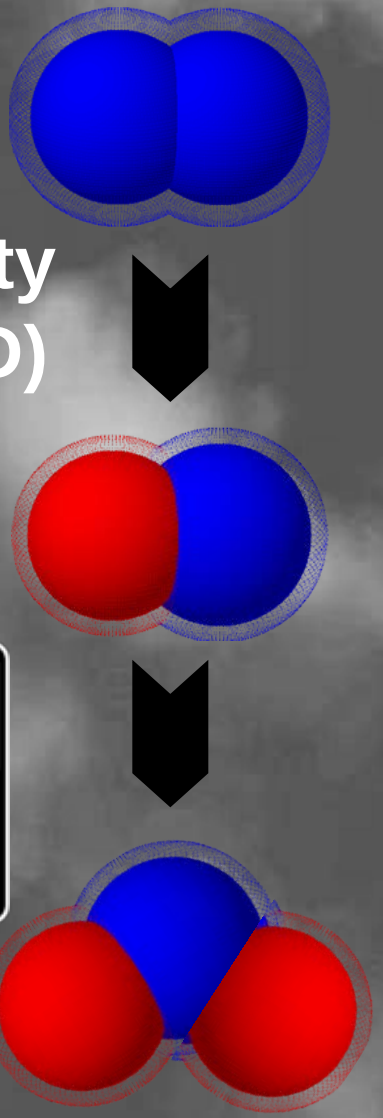
The NO_2 problem of high oxidation potential DPFs

Nitrogen dioxide problem:

NO_2 induces acute and chronic toxicity (oxidative stress, inflammation, COPD)

Diesel-gate, too high NO_2 levels in many European cities, Diesel ban in German cities!

We urgently need efficient deNOx technologies!

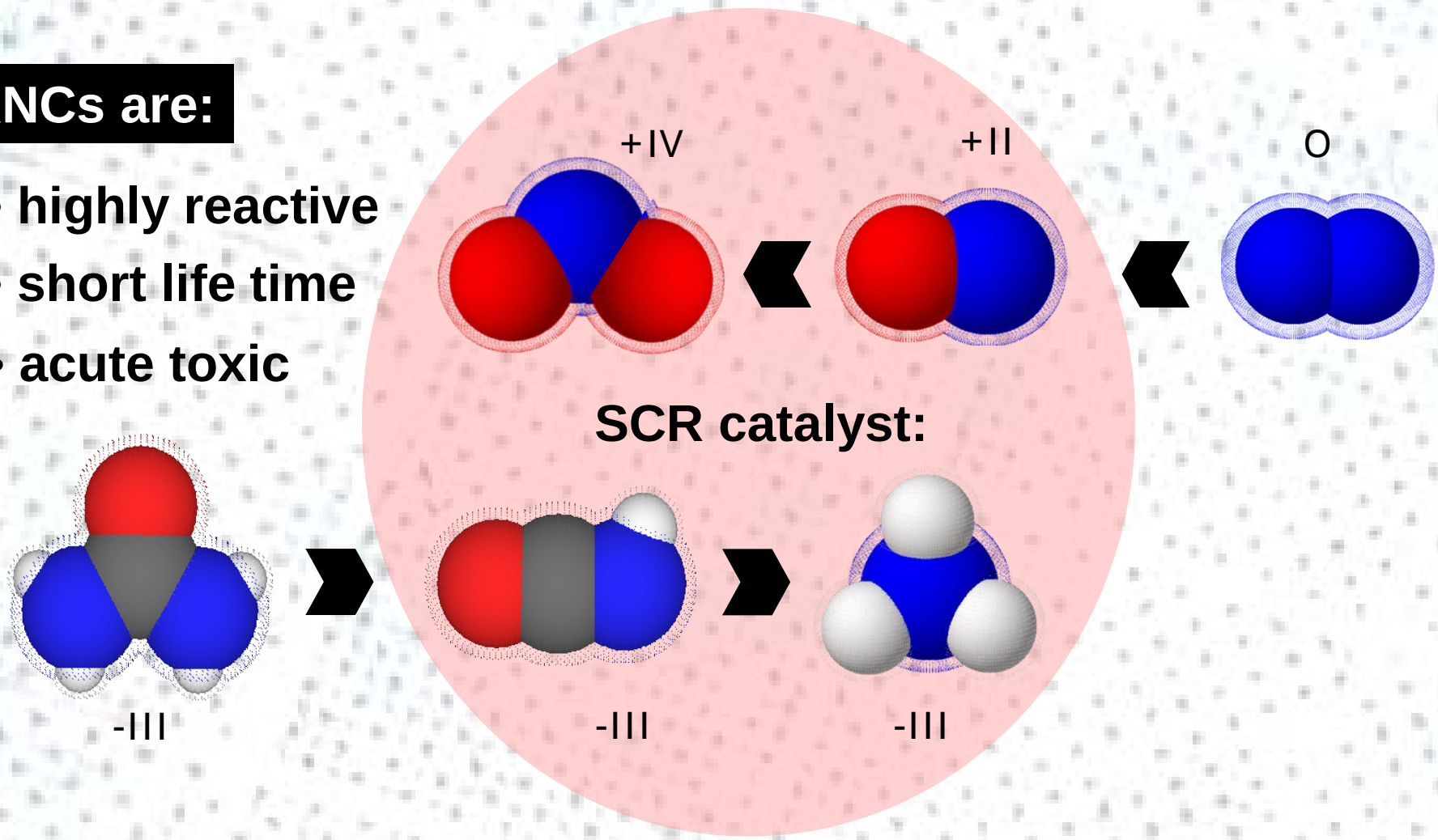


Urea-based SCR

Some key molecules of the selective catalytic reduction with urea

RNCs are:

- highly reactive
- short life time
- acute toxic



Heeb et al., ES&T 2012, 46, 13317-13325

The visible effect of a SCR system

Why were Euro-III, -IV, -V HDVs not equipped with DPFs?

EU commission fines HDV producers for antitrust law violations

Europäische Kommission - Pressemitteilung

Kartellrecht: Kommission verhängt Geldbuße in Höhe von 2.93 Mrd. EUR gegen Lkw-Hersteller*

Brüssel, 19. Juli 2016

Die Europäische Kommission hat festgestellt, dass MAN, Volvo/Renault, Daimler, Iveco und DAF gegen die EU-Kartellvorschriften verstoßen haben. Die LKW-Hersteller hatten über 14 Jahre hinweg Verkaufspreise für Lastkraftwagen abgesprochen und die mit der Einhaltung der strengeren Emissionsvorschriften verbundenen Kosten in abgestimmter Form weitergegeben. Wegen dieser Verstöße verhängte die Kommission eine Rekordgeldbuße in Höhe von 2 926 499 000 EUR.

MAN wurde die Geldbuße erlassen, weil das Unternehmen als Kronzeuge die Kommission von dem Kartell in Kenntnis gesetzt hatte. Alle Unternehmen räumten ihre Kartellbeteiligung ein und stimmten einem Vergleich zu.

EC Press release IP-16-2582-DE

Why were Euro-III, -IV, -V HDVs not equipped with DPFs?

EU commission fines HDV producers for antitrust law violations

Europäische Kommission - Pressemitteilung

Brussels, July 19, 2016

9 out of 10 HDVs in Europa are involved

illegal trust was active for 14 years (1997-2011, Euro-III to Euro-V)

illegal agreement on price and convertor technology

3.8 billions Euro fine (MAN was the whistle blower, fine of 1 billion Euro was canceled)

Volvo/Renault	0.7 Mia,	Daimler	1.0 Mia,
Iveco	0.5 Mia,	DAF	0.8 Mia,
Scania	0.9 Mia		

EC Press release IP-16-2582-DE

20 years VERT Filter test

Chemistry matters, it determines toxicity

- An urgent need for filters in NEAT tunnels
  (Why it all started)
- Highlights of the VSET
  (Hypotheses and facts)
- Filters needed more than ever
  (The near future still is combustion)

Something to celebrate!

Secondary emissions of current and future converter technologies

A combined effort with many important contributions

Thanks:

- **VERT team:** Andreas Mayer, TTM, Niederrohrdorf
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  Thomas Gasser, Heinz Berger, Gerhard Stucki, Swiss Federal Road Office

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

Empa
Materials Science and Technology

SCHWEIZ. CHEMISCHE GESELLSCHAFT SCG
SOCIETE SUISSE DE CHIMIE SSC
SWISS CHEMICAL SOCIETY SCS

Traugott Sandmeyer (1854-1922)