Norbert Heeb
Empa, Überlandstrasse 129
Advanced Analytical Technologies
CH-8600 Dübendorf
Phone +41-58-765 42 57
e-mail norbert.heeb@empa.ch
Internet http://www.empa.ch

Empa
Materials Science and Technology

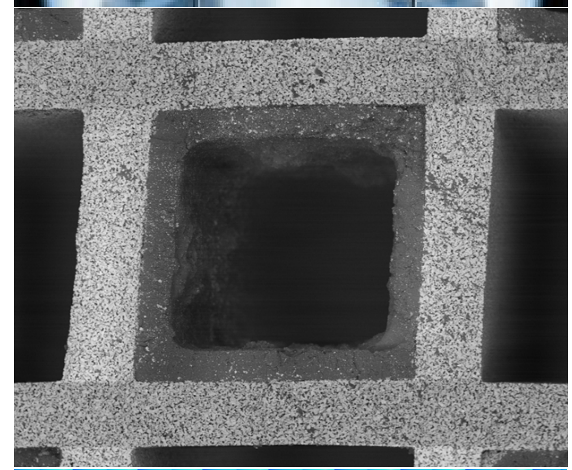
Secondary emissions from emission control devices and their impact on occupational health and safety

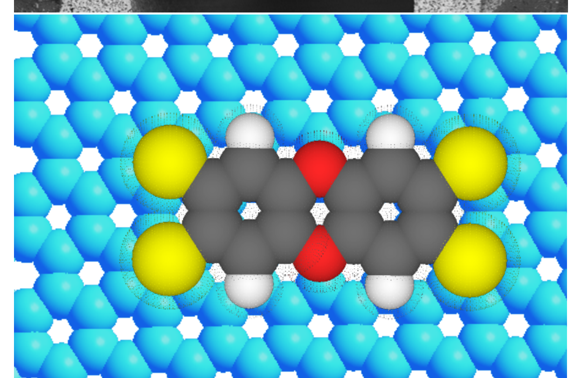
12th VERT-Forum – Moving targets in nanoparticle abatement

On line, March 24th, 2022

Secondary emissions from emission control devices and their impact on occupational health and safety

Moving targets in nanoparticle abatement





Outline

- **Risks and health impact of exhausts containing combustion-generated nanoparticles**
  - What should you know about it?
- **Catalytic particle filters**
  - Do cPFs detoxify combustion engine exhausts?
- **Secondary emissions of emission control devices**
  - How to avoid or manage them?

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Risks and health impact of diesel exhausts

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

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

Diesel engine exhausts cause cancer in humans

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

Diesel engine exhausts cause cancer in humans

International Agency for Research on Cancer

World Health Organization

PRESS RELEASE
N° 213

12 June 2012

June 12, 2012

IARC: DIESEL ENGINE EXHAUST CARCINOGENIC

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

Group 1

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

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

Lung cancer
in exposed workers

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 non-metal mining facilities, which included 198 lung cancer deaths and 562 incidence density–sampled control subjects. For each case subject, we selected up to [illegible] control subjects, individually matched on mining facility, sex, race/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

Lung cancer in exposed workers

12'315 workers, 8 mines
198 lung cancer death
(16'000 in 1'000'000)
(1 in 1'000'000, target value Swiss LRV)

diesel exhaust exposure: a potential public health burden

Occupational health regulation in Switzerland

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

„Diesel engine emissions, measured as elemental carbon, should not exceed 100 µg/m³"

The **precusionnary principle**: Because diesel engine emissions are **carcinogenic (WHO)** inducing lung cancer in humans, general measures have to be applied to lower exposure to diesel exhausts with best available technology (**BAT**).

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

Soot nanoparticles – Trojan horses for genotoxic compounds

Non-treated exhausts of combustion engines, containing nanoparticles, are toxic cocktails

This includes exhausts of:
- diesel engines,
- GDI-vehicles,
- jet engines,
- non-road machinery,
- ships,

etc.

Do not inhale them!

Secondary emissions from emission control devices and their impact on occupational health and safety

Moving targets in nanoparticle abatement

Outline

- **Risks and health impact of exhausts containing combustion-generated nanoparticles**
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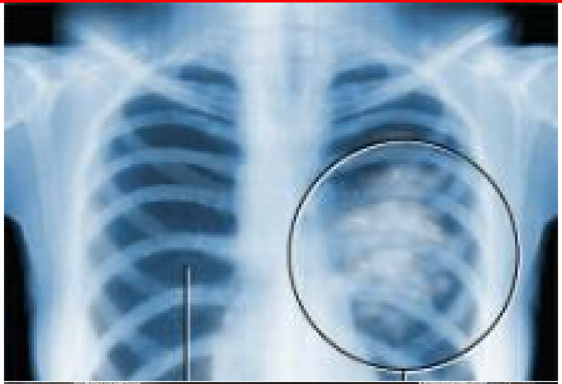
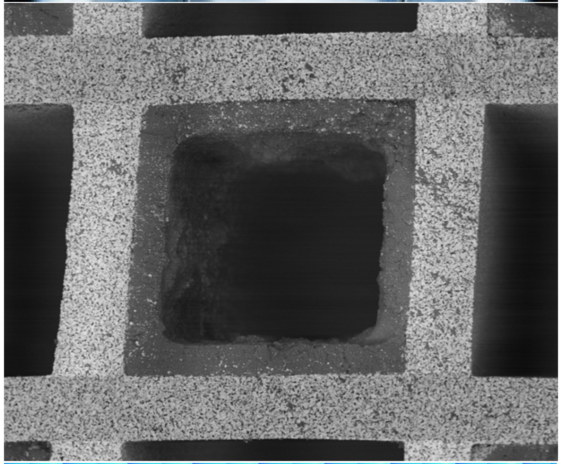
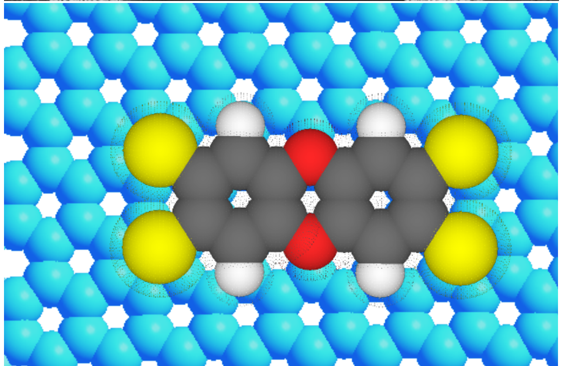
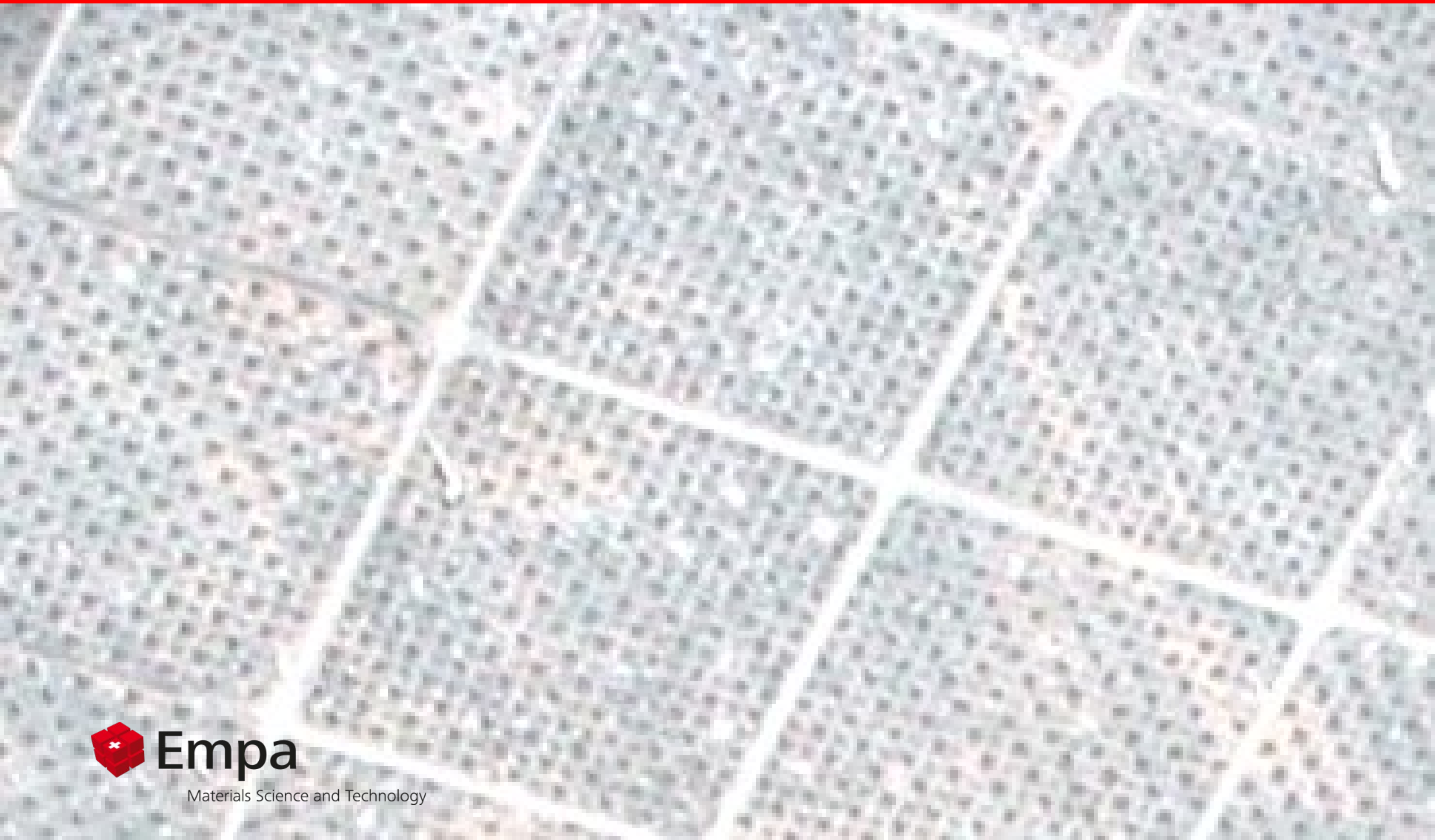






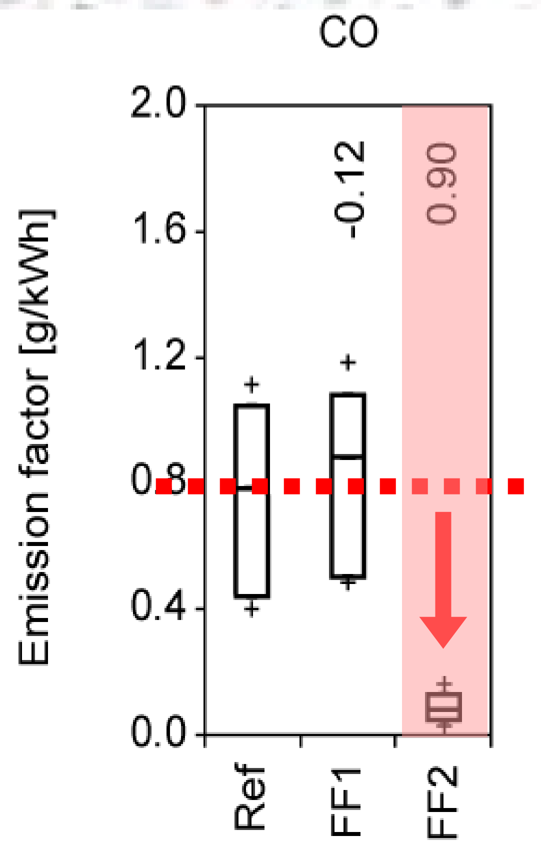
Catalytic particle filters
Do cPFs detoxify combustion engine exhausts?



Low- & high-oxidation potential DPFs

Two filter families (FF), one converts CO, the other doesn't!

Carbon monoxide



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

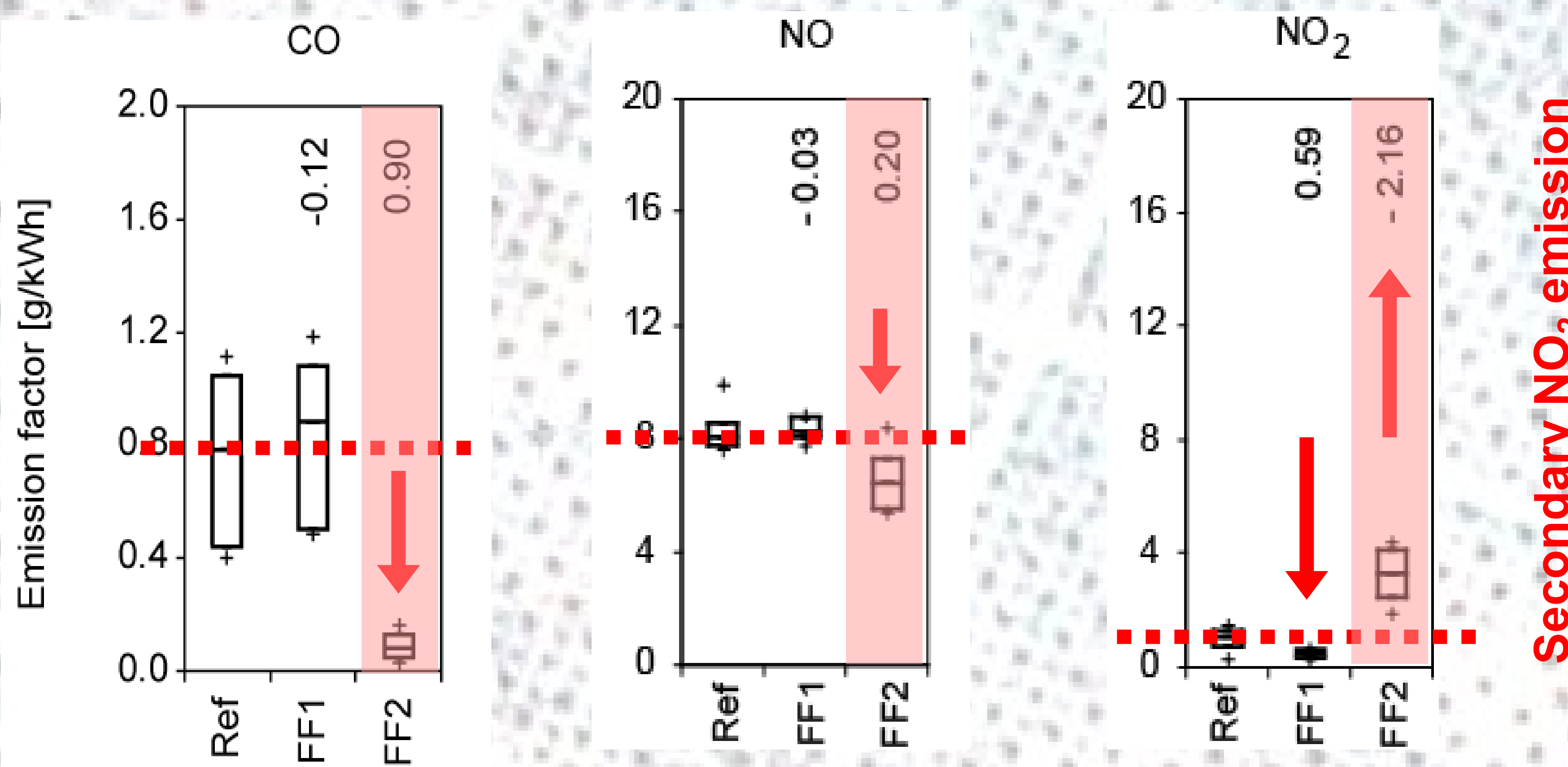
Heeb et al. ES&T, **2008**, 42, 3773-3779

Heeb et al. ES&T, **2010**, 44, 1078-1084

Low- & high-oxidation potential DPFs

Two FFs, one converts CO and NO, and forms NO_2, the other doesn't!

Carbon monoxide, nitric oxide, nitrogen dioxide

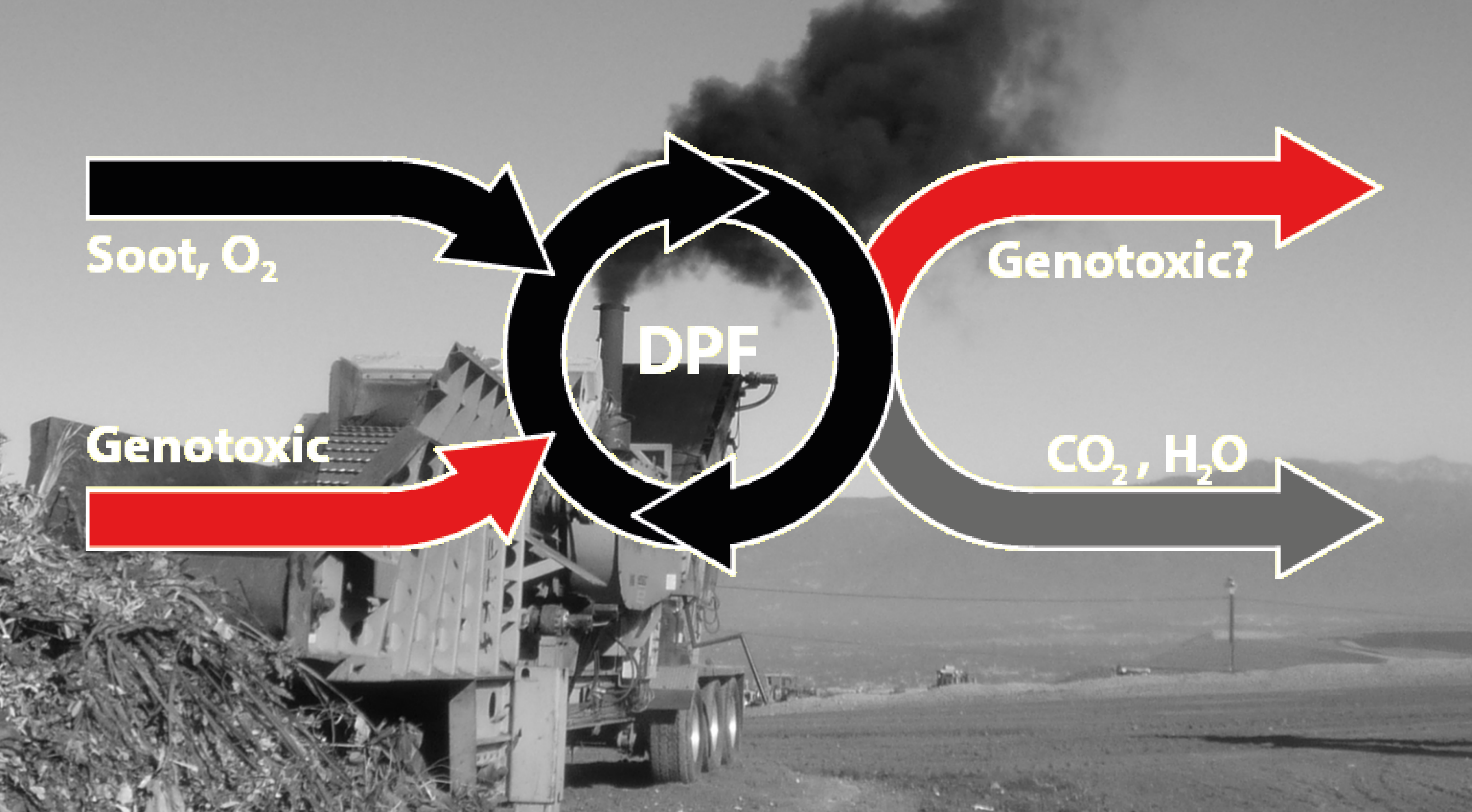


Heeb et al. ES&T, **2008**, 42, 3773-3779

Heeb et al. ES&T, **2010**, 44, 1078-1084

Impact of PFs on genotoxicity

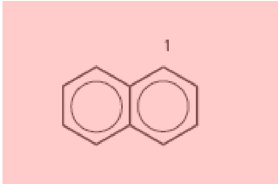
Is filtration of soot sufficient to lower the genotoxicity of combustion engine exhaust?



Polycyclic aromatic hydrocarbons

PAHs - a diverse class of compounds with variable physicochemical properties

2- to 6-ring PAHs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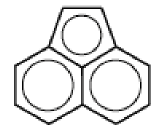
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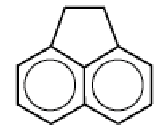
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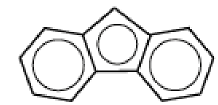
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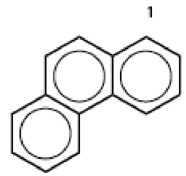
some PAHs are genotoxic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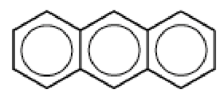
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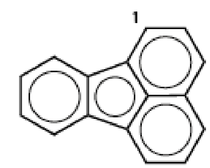
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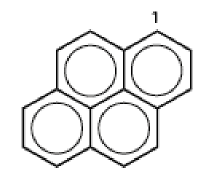
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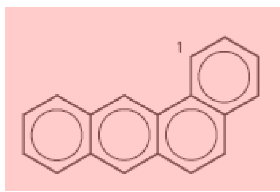
all PAHs are nitro-PAH precursors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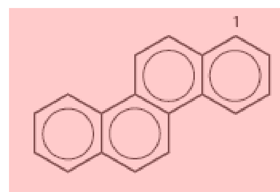
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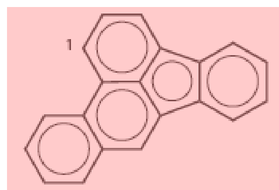
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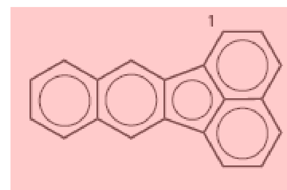
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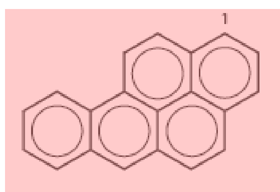
several nitro-PAHs are strong mutagens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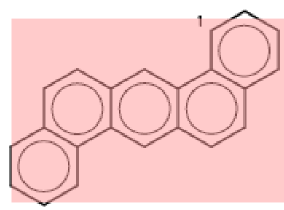
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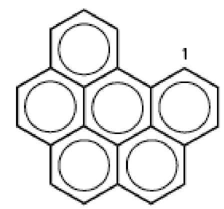
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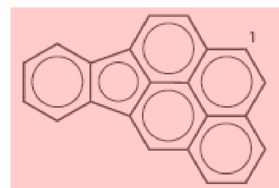
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PAH penetration of a non-catalyzed DPF

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

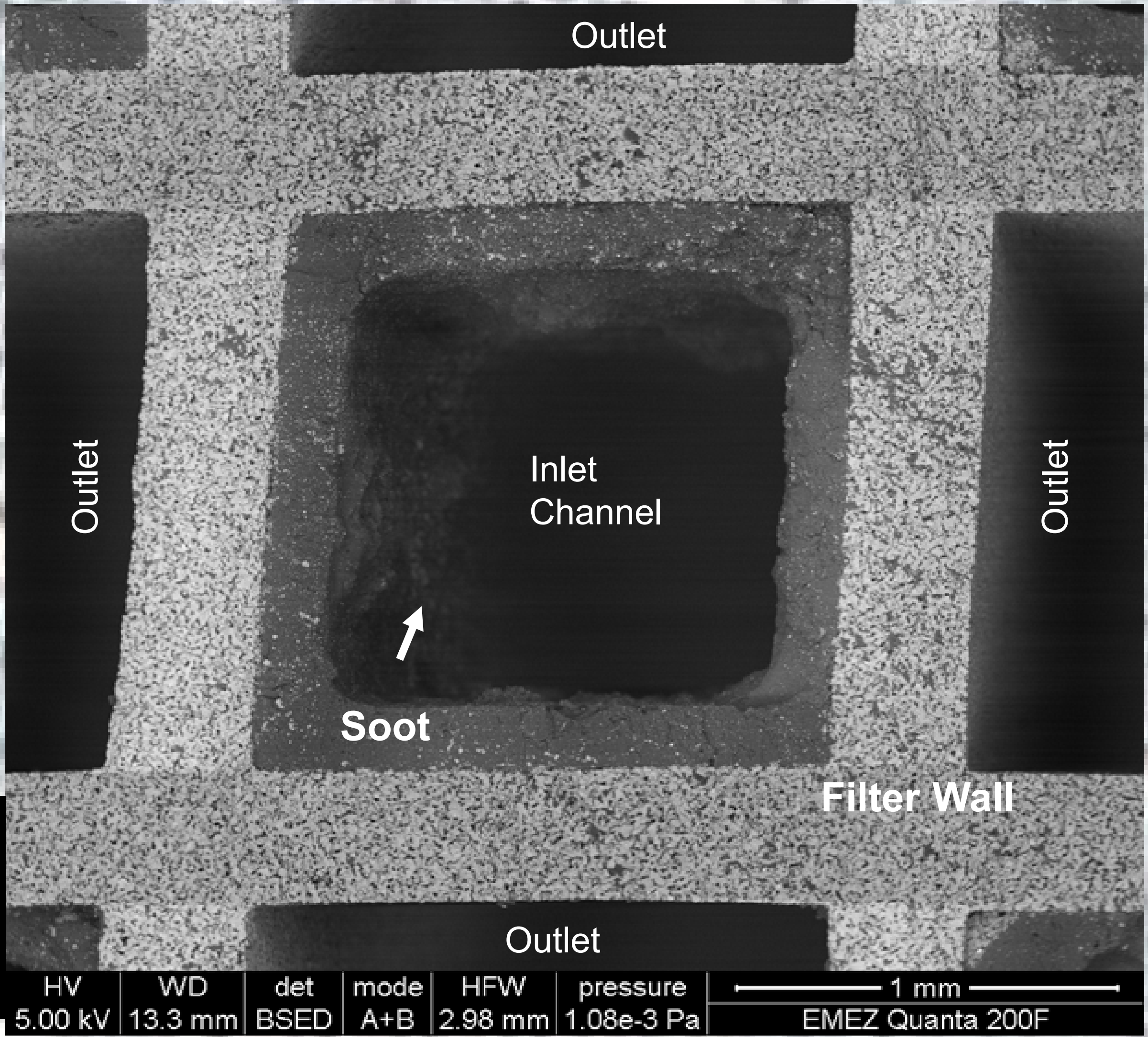
Non-catalyzed DPFs:

Accumulate soot (>98%)

Can PAHs penetrate soot loaded DPFs?

Do DPFs remove Genotoxic compounds?

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



PAH penetration of a non-catalyzed DPF

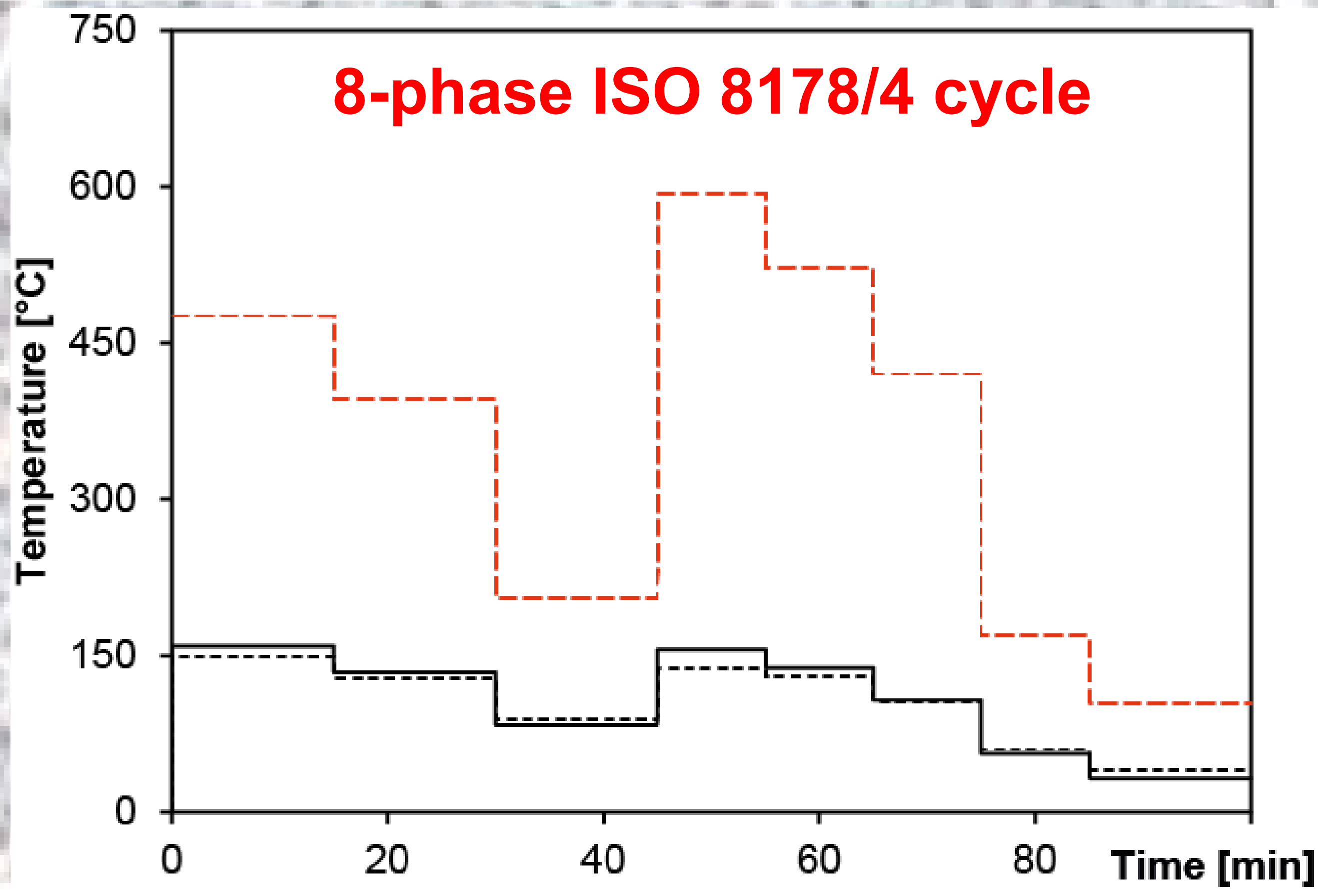
Can PAHs penetrate non-catalyzed filters if operated <200 °C?

Two cellulose-based filters studied, a new and a soot-loaded filter (>2000 h road application)

engine-out

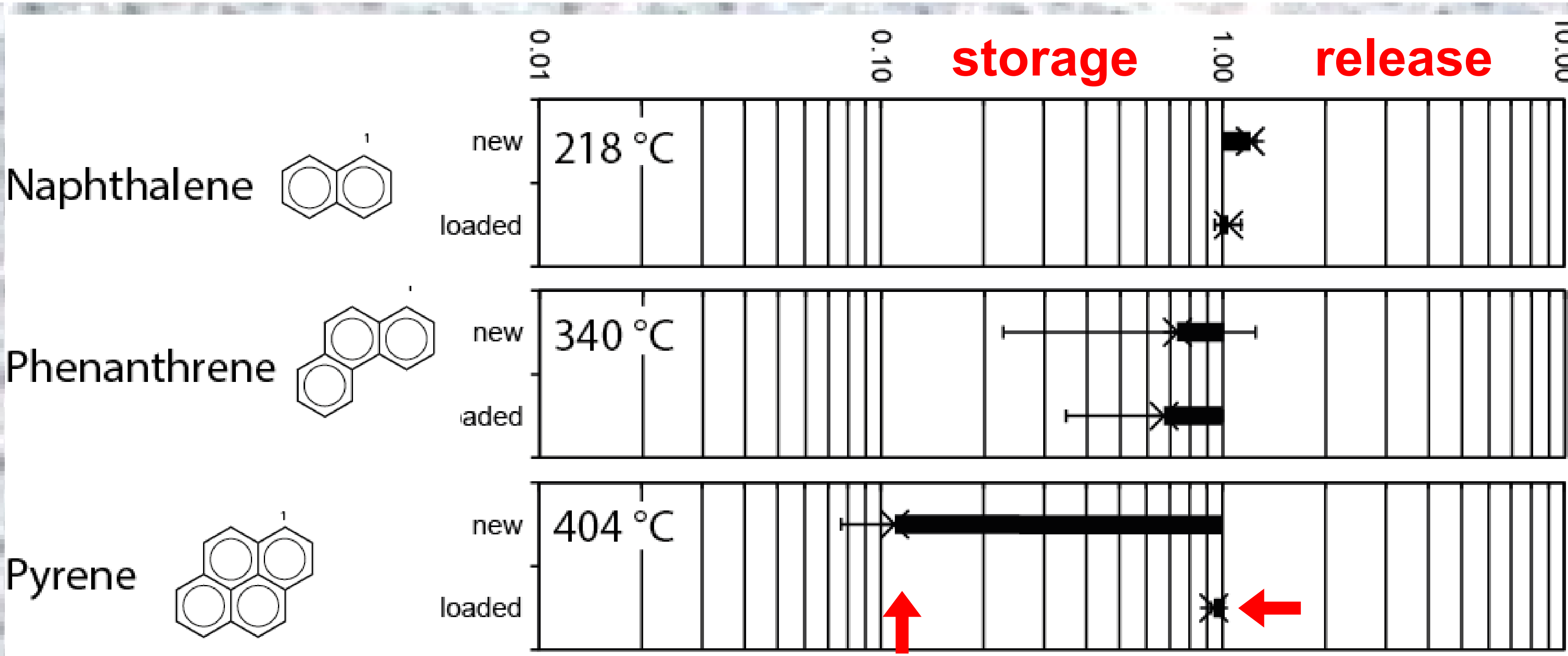
before DPF

after DPF



PAH penetration of a non-catalyzed DPF

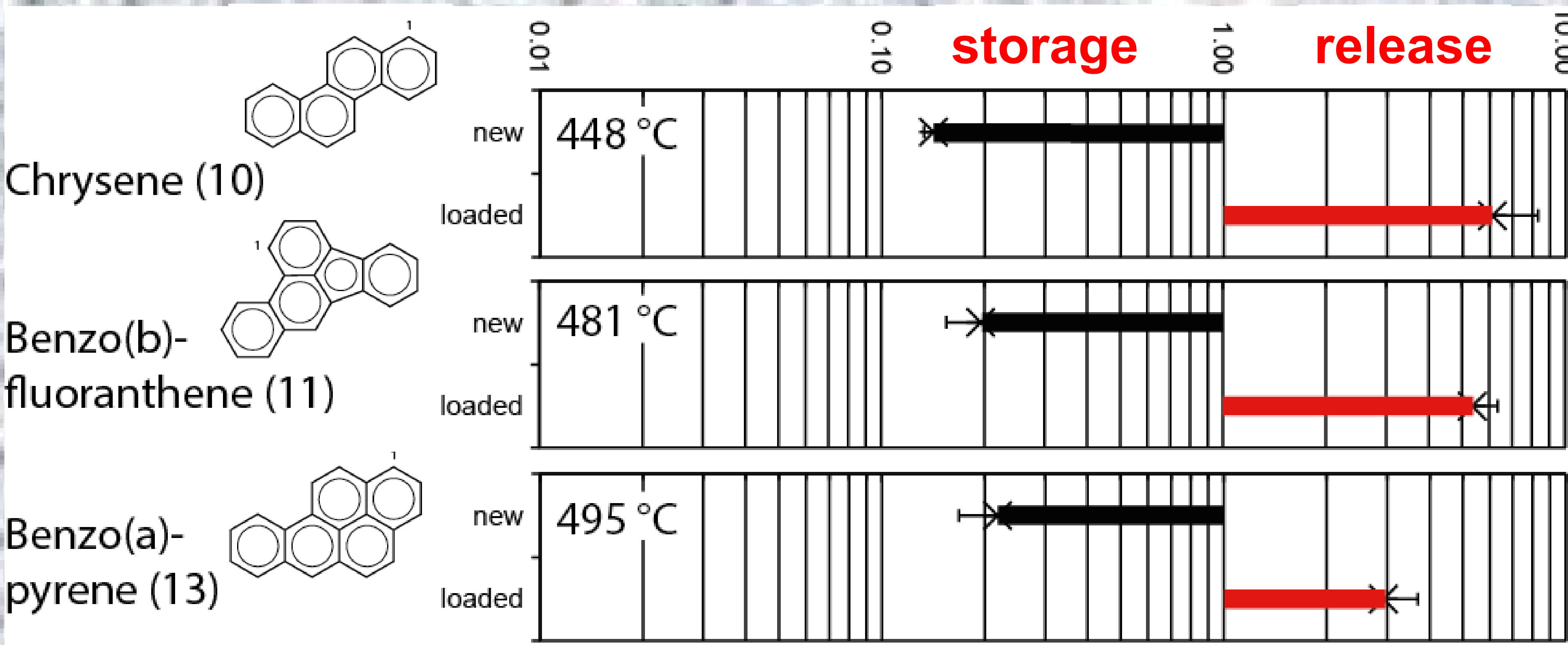
Non-catalyzed filters operated <200 °C do accumulate soot and some hydrocarbons



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

Store-and-release of PAHs in a non-catalyzed DPF

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

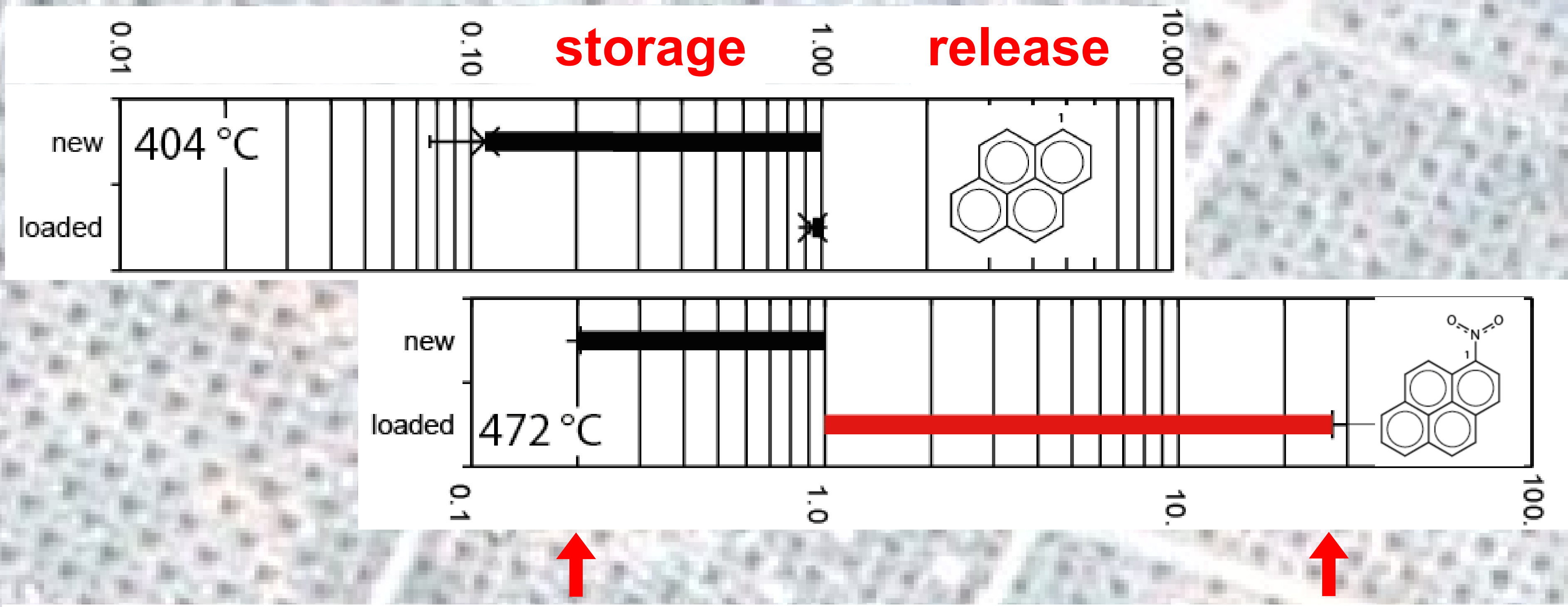


- **80% retention of benzo(a)pyrene in the new DPF**
- **3x higher emissions from the soot-loaded DPF**

What about secondary formation on nitro-PAHs?

Nitro-PAH formation in non-catalyzed DPF

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



- pyrene is stored in a new, but released from a soot-loaded DPF

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

That's why we require catalyzed particle filters

Store-and-release of PAHs in a non-catalyzed DPF

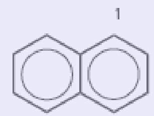
PAHs - a diverse class of compounds with variable physicochemical properties

2- to 6-ring PAHs

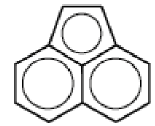
Volatile PAHs can penetrate DPFs both, new and soot-loaded onces

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

Also true for gasoline particle filters, GPFs



218 °C



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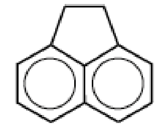

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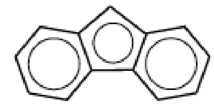

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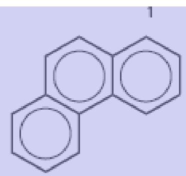
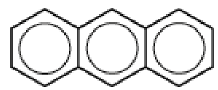


340 °C



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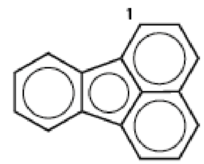

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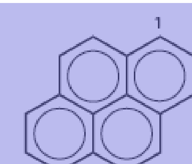
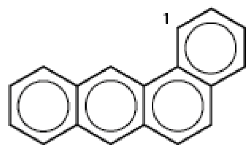


404 °C



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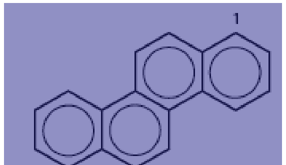
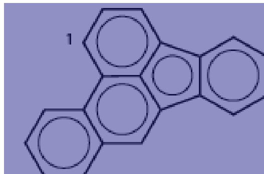
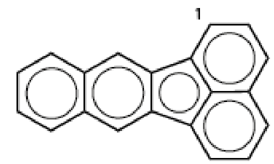


448 °C



481 °C



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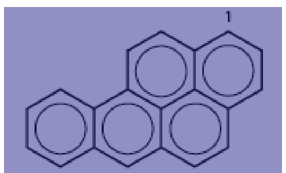
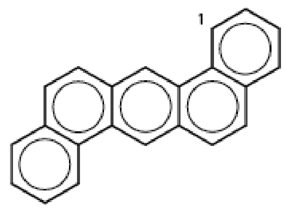


495 °C



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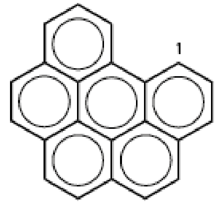

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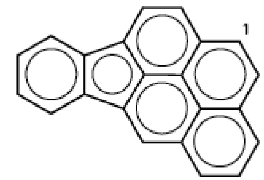

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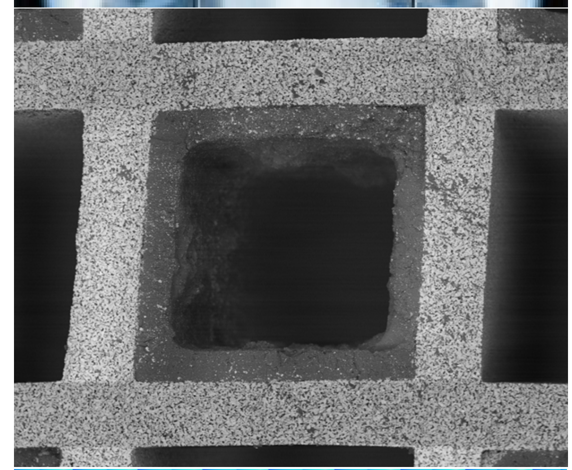
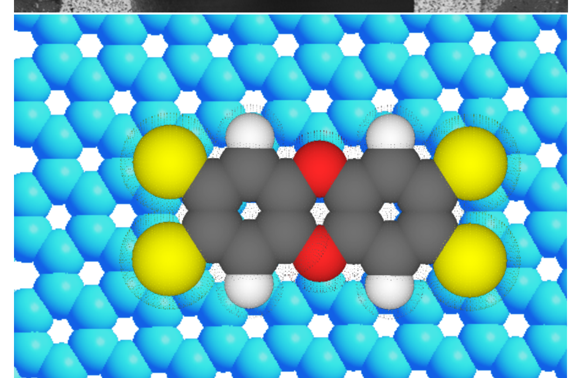
Secondary emissions from emission control devices and their impact on occupational health and safety

Moving targets in nanoparticle abatement





Outline

- **Risks and health impact of exhausts containing combustion-generated nanoparticle**
  - What should you know about it?
- **Catalytic particle filters**
  - Do cPFs detoxify combustion engine exhausts?
- **Secondary emissions of emission control devices**
  - How to avoid or manage them?

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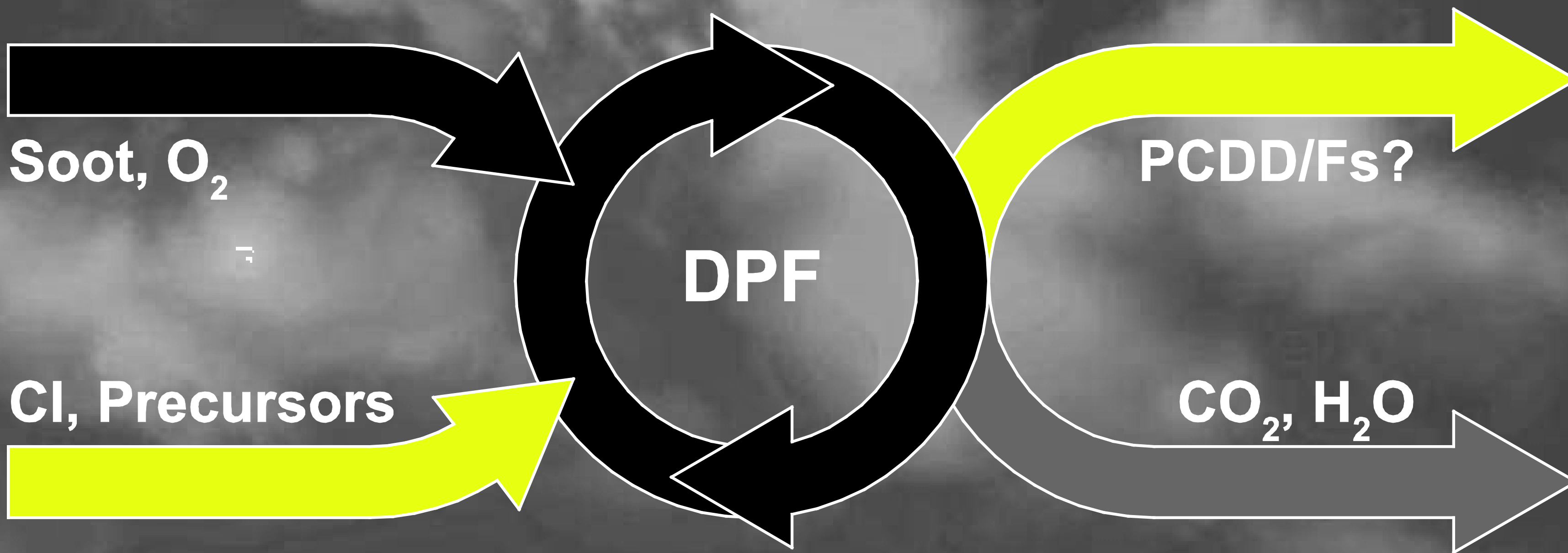
de novo PCDD/F-formation in DPFs

Is there a risk for a catalytic formation of PCDD/Fs in particle filters?

Problem: Secondary emissions



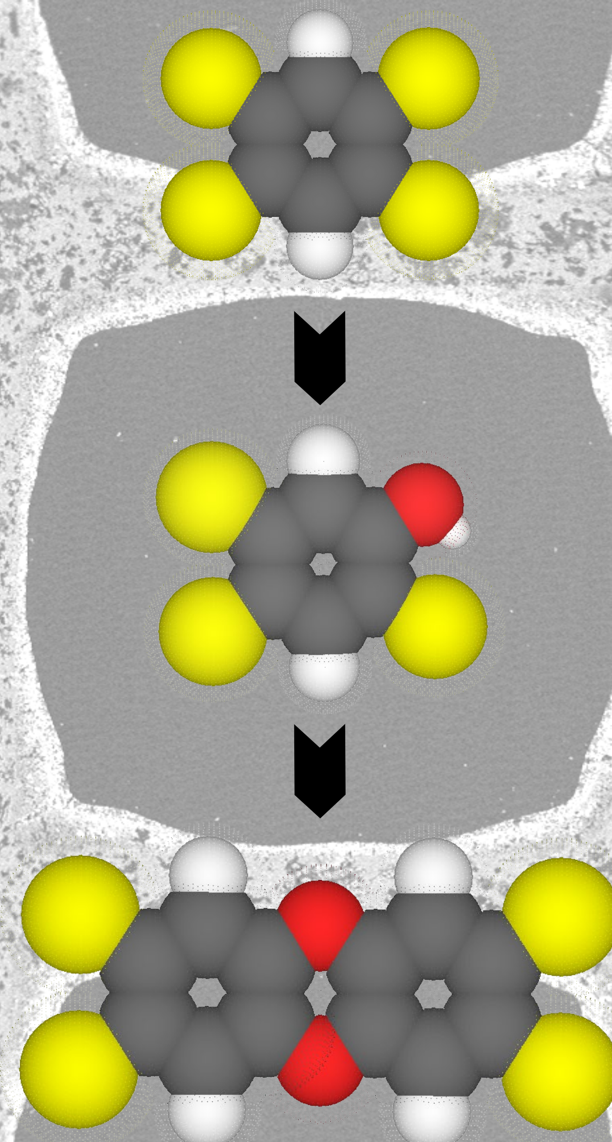
Dioxin formation in Seveso (1976)

The dioxin problem

- Highly toxic, bind to aryl hydrocarbon receptor
- Persistent, bioaccumulative, ubiquitous
- Regulated under Stockholm convention on POPs
- Contaminants in pesticides, e.g. trichlorophenols for herbicides, Agent orange (defoliation agent applied in the Vietnam war by U.S. troops)
- Unwanted combustion products

PCDD/F properties:

- Thermally stable up to 440°C
- Solid, semi-volatile, particle-bound
- Should be stored in PFs unless formed *de novo*



Attempted assassination of Viktor Yushchenko, former President of the Ukraine

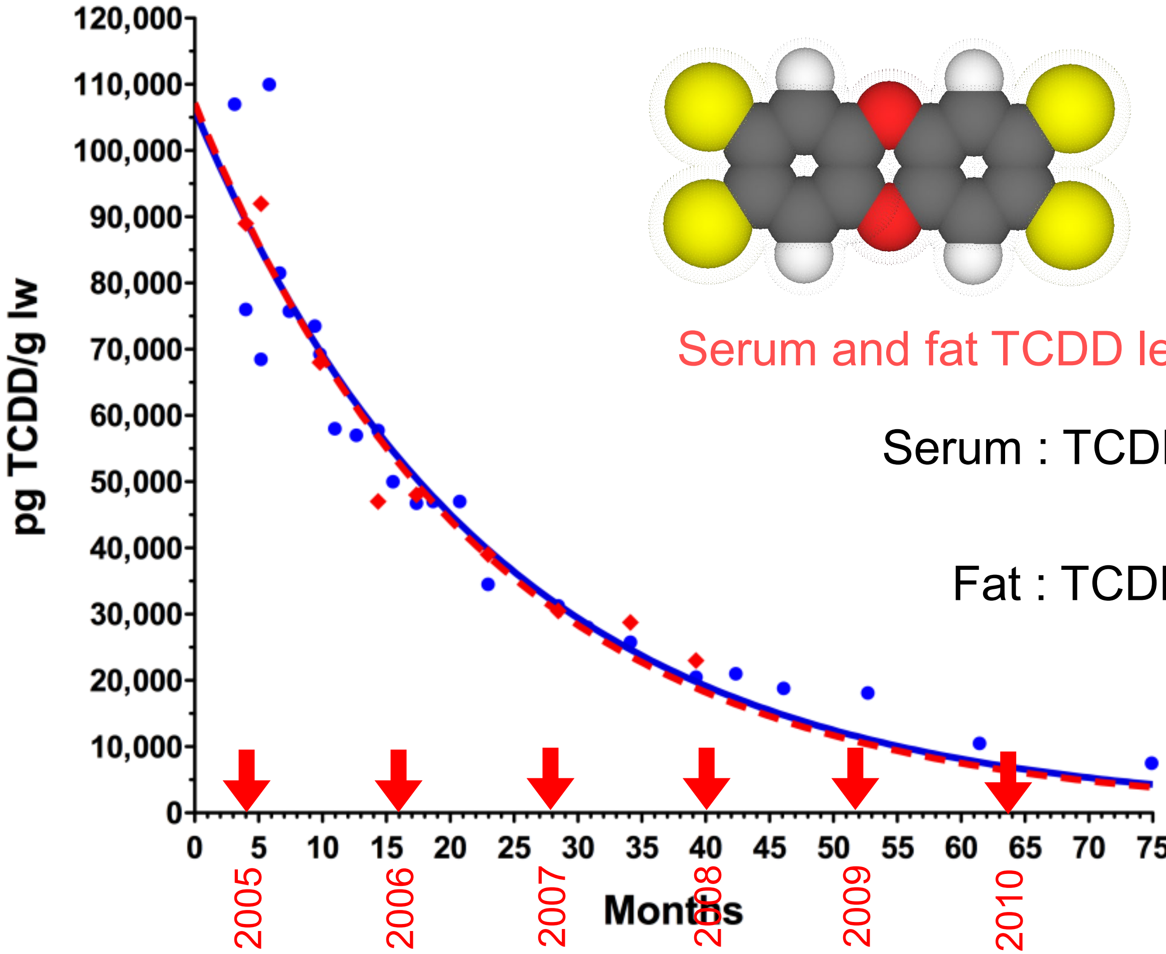
What happened during the 2004 presidential election campain in the Ukraine?

Before and after the severe dioxin poisoning

Attempted assassination of Viktor Yushchenko, former President of the Ukraine

1st order decrease of 2,3,7,8-TCDD levels in the months and years after the poisoning

2,3,7,8-TCDD, the only congener found



Serum and fat TCDD levels (based on lipid weight)

Serum : TCDD (t) = 106'000 (pg/g lw) $e^{-0.04276\ t}$

$t_{1/2}$ = 16.2 months

Fat : TCDD (t) = 107'000 (pg/g lw) $e^{-0.04429\ t}$

$t_{1/2}$ = 15.7 months

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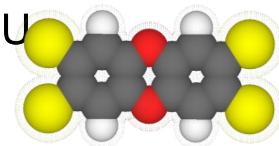
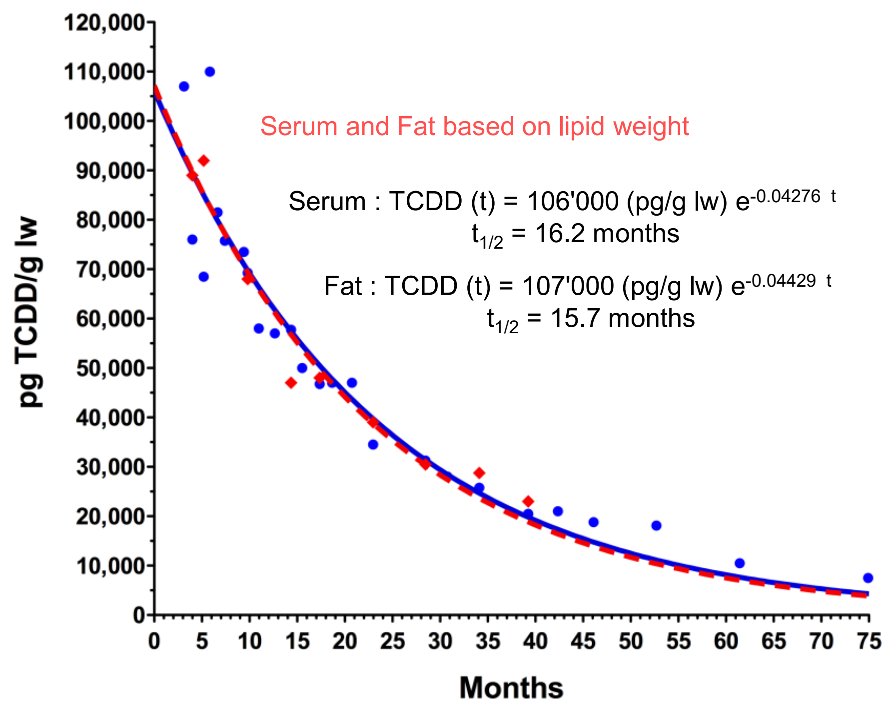
Attempted assassination of Viktor Yushchenko, former President of the Ukraine

What happened during the 2004 presidential election campaign in the Ukraine?

2,3,7,8-TCDD, the only congener found

- Poisoned Sunday, Sept 5, 2004 at dinner with SBU (Ukrainian National Security)
- Uptake of approximately 1-2 mg 2,3,7,8-TCDD!
- Second highest TCDD serum level in a human body ever measured
- 50‘000 x more than the normal population (2 pg/g lipid)
- Nov. 23, J. Henry, St. Mary‘s Hospital, London suggests dioxin poisoning
- Dec. 17, two independent laboratories confirmed that exclusively 2,3,7,8-TCDD was found in the blood (108’000 and 109‘000 ng/kg lipid)





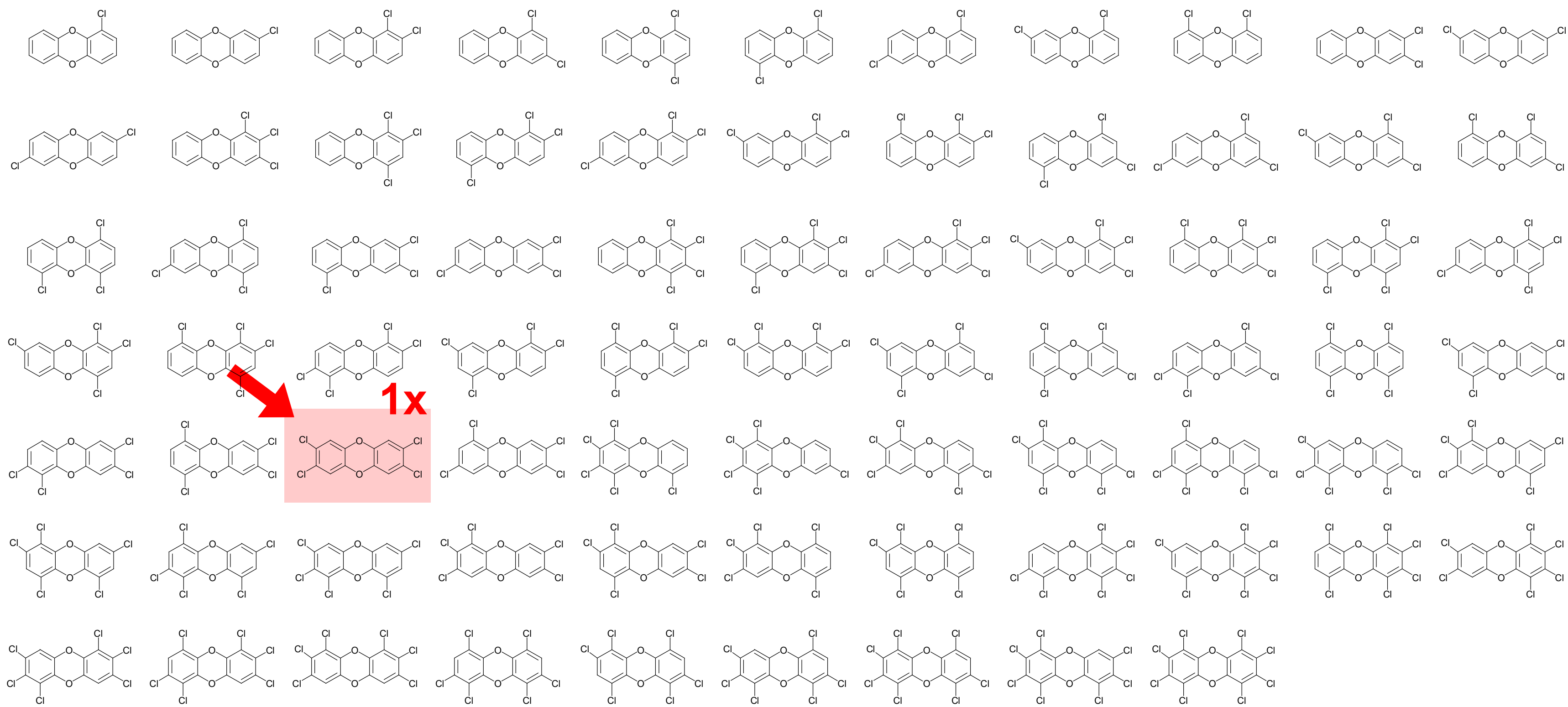
Viktor Yushchenko was poisoned with synthesized material, PCDD/Fs formed in combustion reactions, e.g. in certain active DPFs produce very different pattern!

Sorg, O., Zennegg, M. Schmid, P. et al. The Lancet, **2009**, 9696, 1179-85

The dibenzodioxin class of compounds (PCDDs)

We surely assess 2,3,7,8-TCDD, but should have an eye on other congeners as well?

Chemical structures of polychlorinated dibenzodioxins

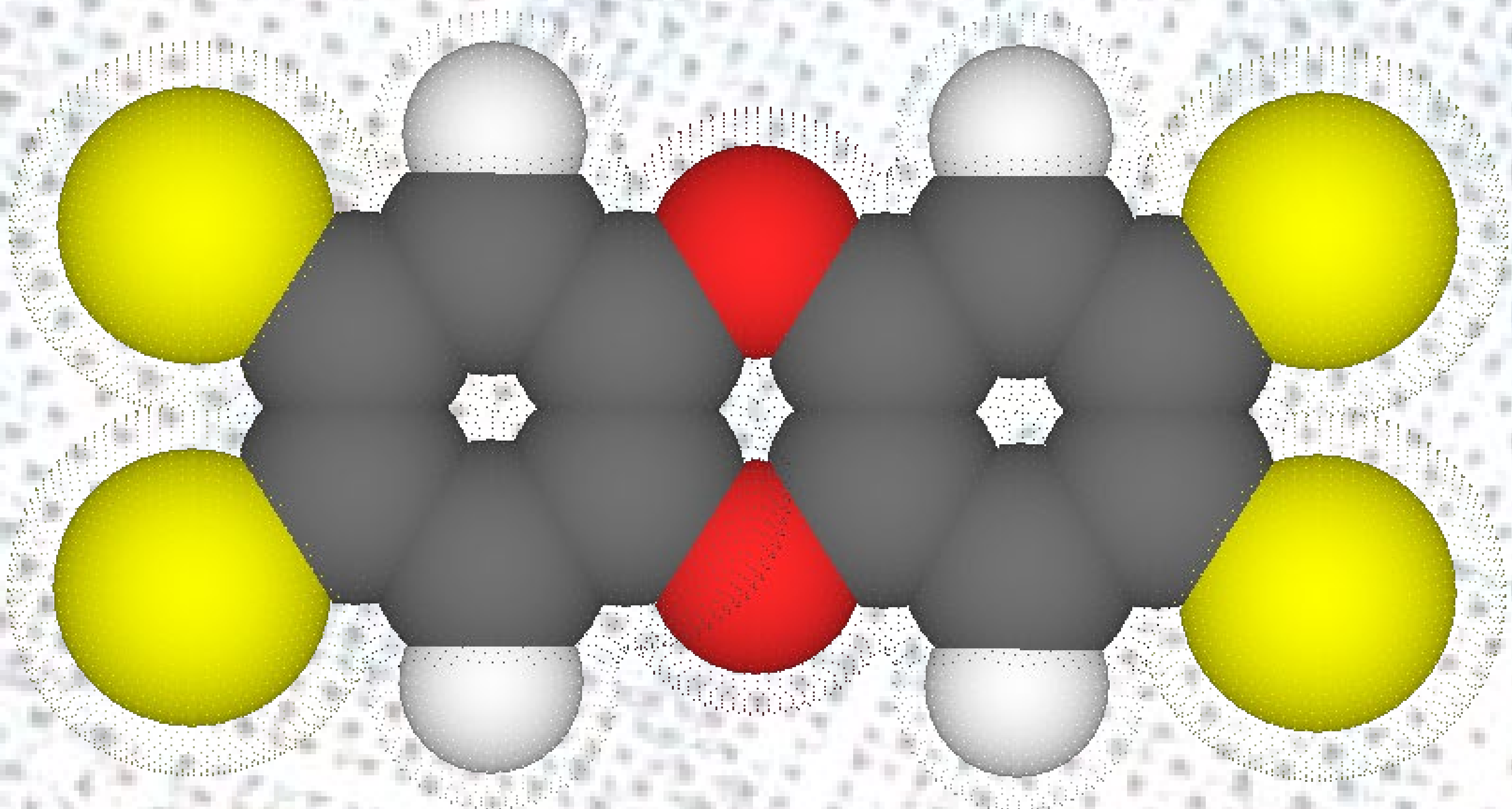


Poisened with pure synthetic 2,3,7,8-TCDD material

PCDD/Fs: toxic at pg-quantities

What are PCDD/Fs?

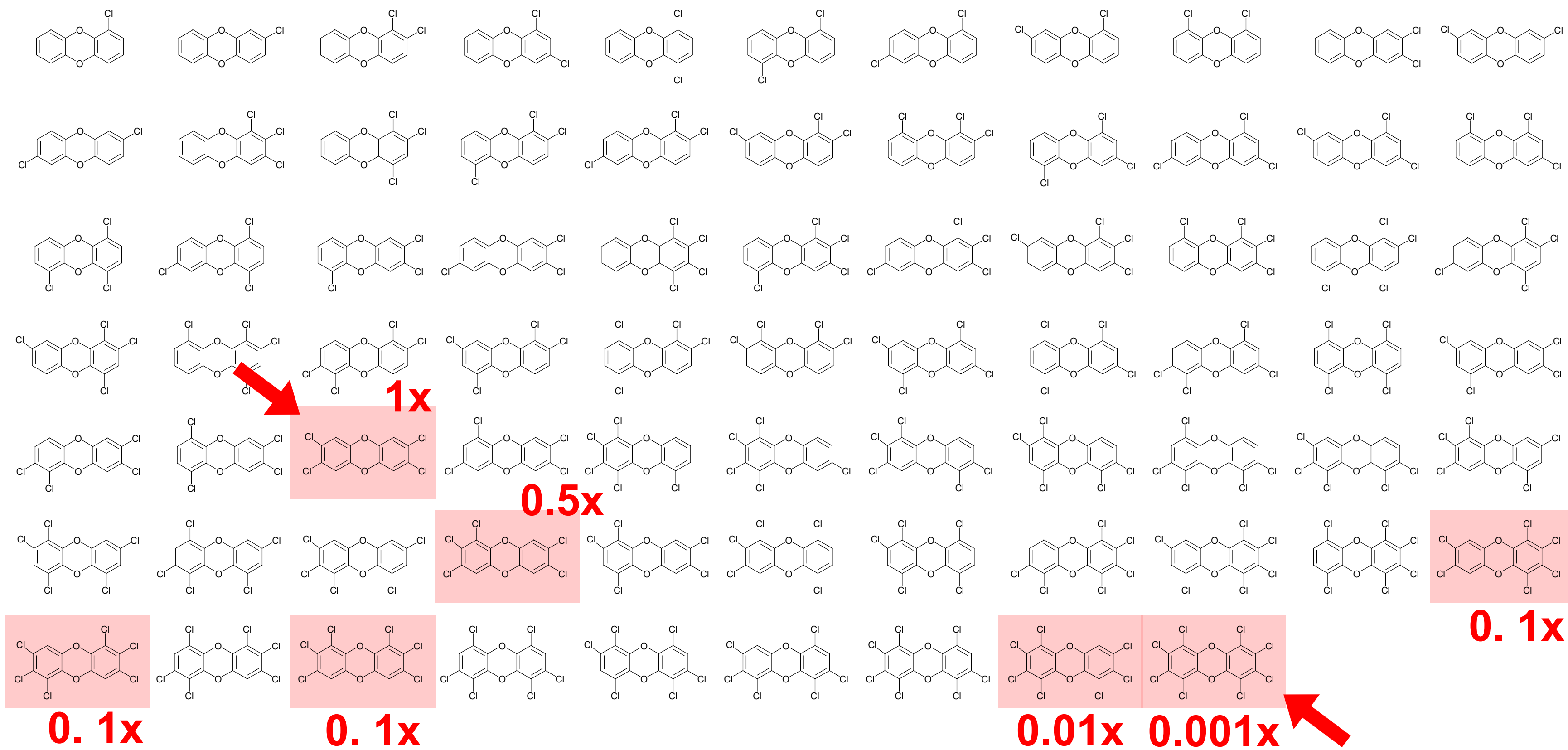
2,3,7,8-Tetrachlorodibenzodioxin - the most toxic dioxin



The dibenzodioxin class of compounds (PCDDs)

Which are the 7 toxic PCDD?

Chemical structures of polychlorinated dibenzodioxins

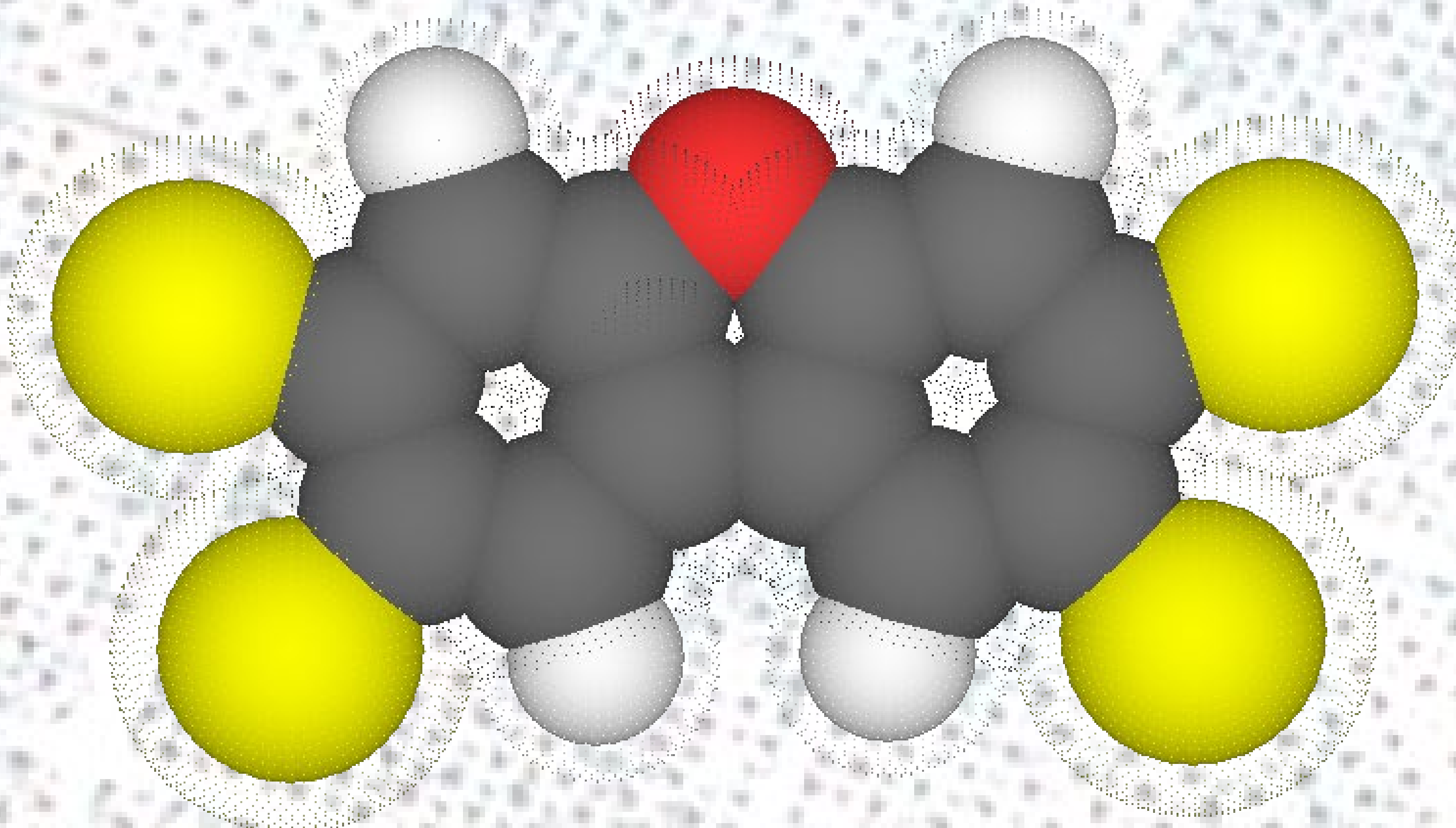


PCDD/Fs formed in combustion processes are complex mixtures

PCDD/Fs: toxic at pg-quantities

What are PCDD/Fs?

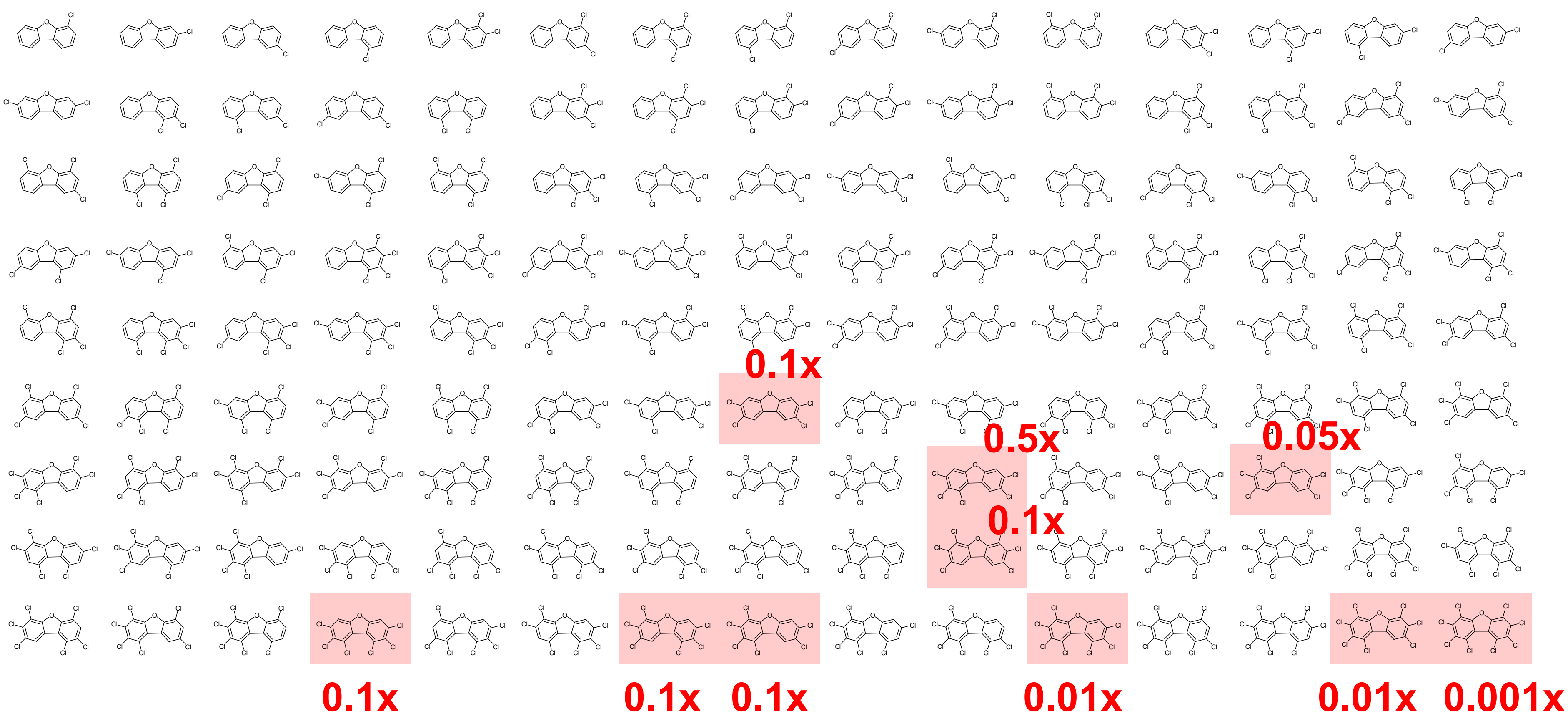
2,3,7,8-Tetrachlorodibenzofuran



The dibenzofuran class of compounds (PCDFs)

Which are the 10 toxic PCDF?

Chemical structures of polychlorinated dibenzofurans

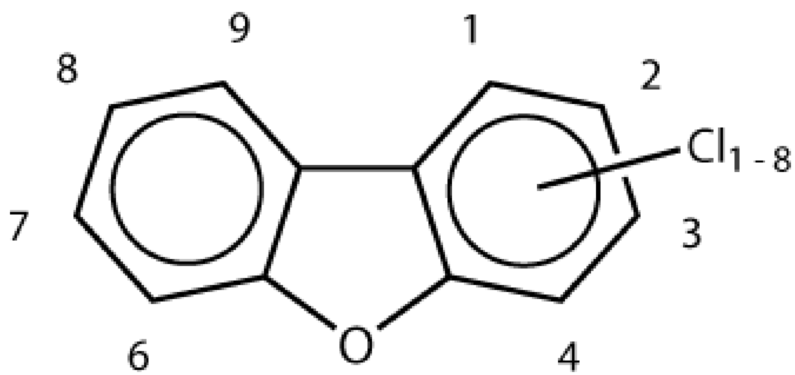


PCDD/Fs formed in combustion processes are complex mixtures

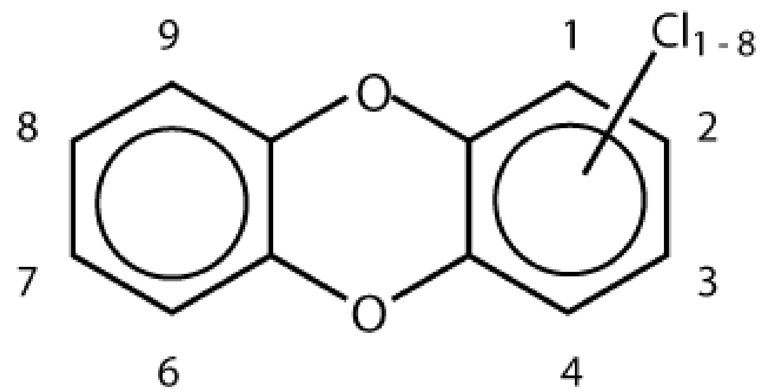
PCDD/Fs: Two classes of compounds

What are PCDD/F?

Polychlorinated dibenzodioxins/furans (PCDD/Fs)



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



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

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

Overall, 75 PCDDs and 135 PCDFs formed in combustion processes

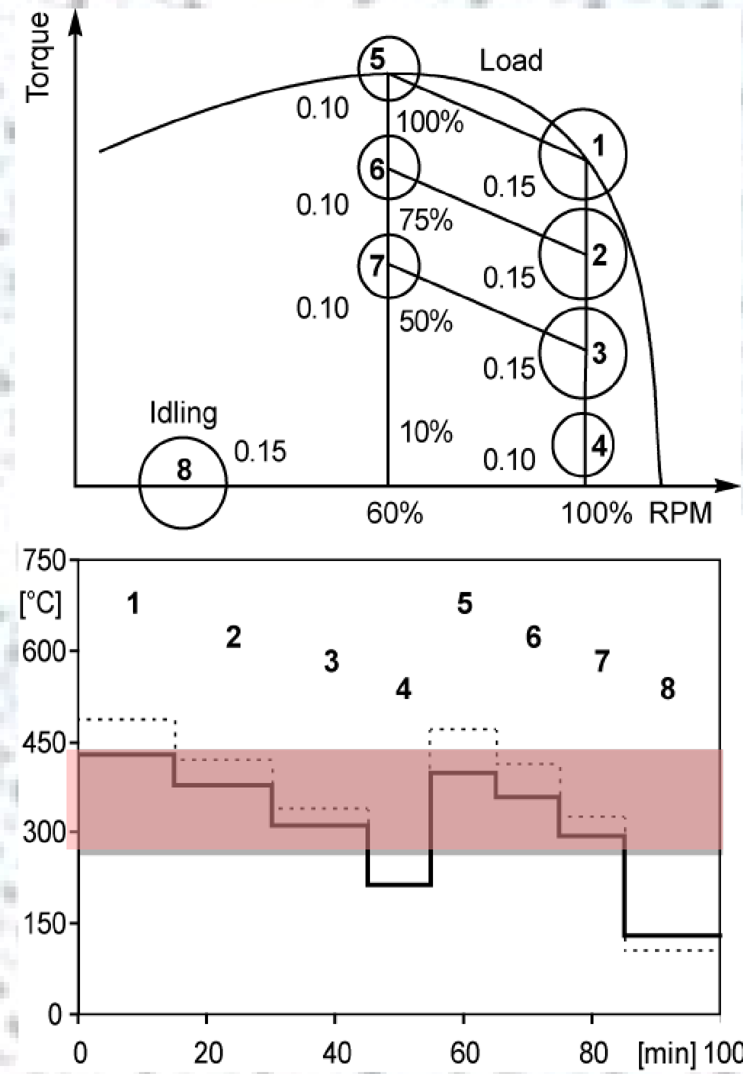
Secondary PCDD/F formation in DPFs?

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

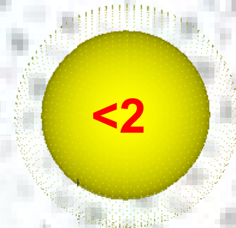
***De novo* formation is possible during 75-80% of operation time in the ISO8178/4 cycle**



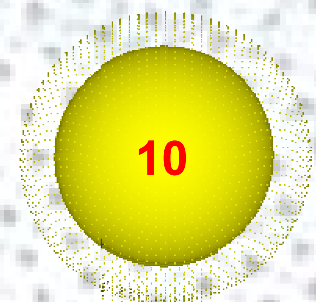
Secondary PCDD/F formation in DPFs?

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

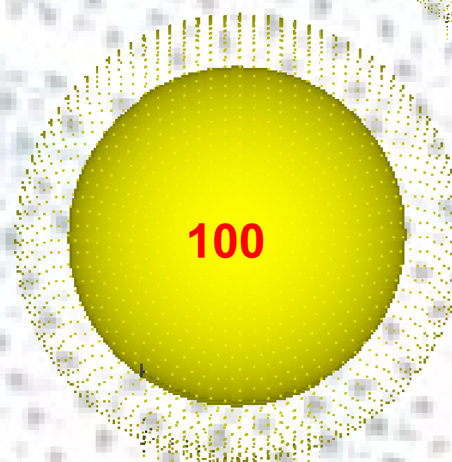
Potential chlorine sources



- 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



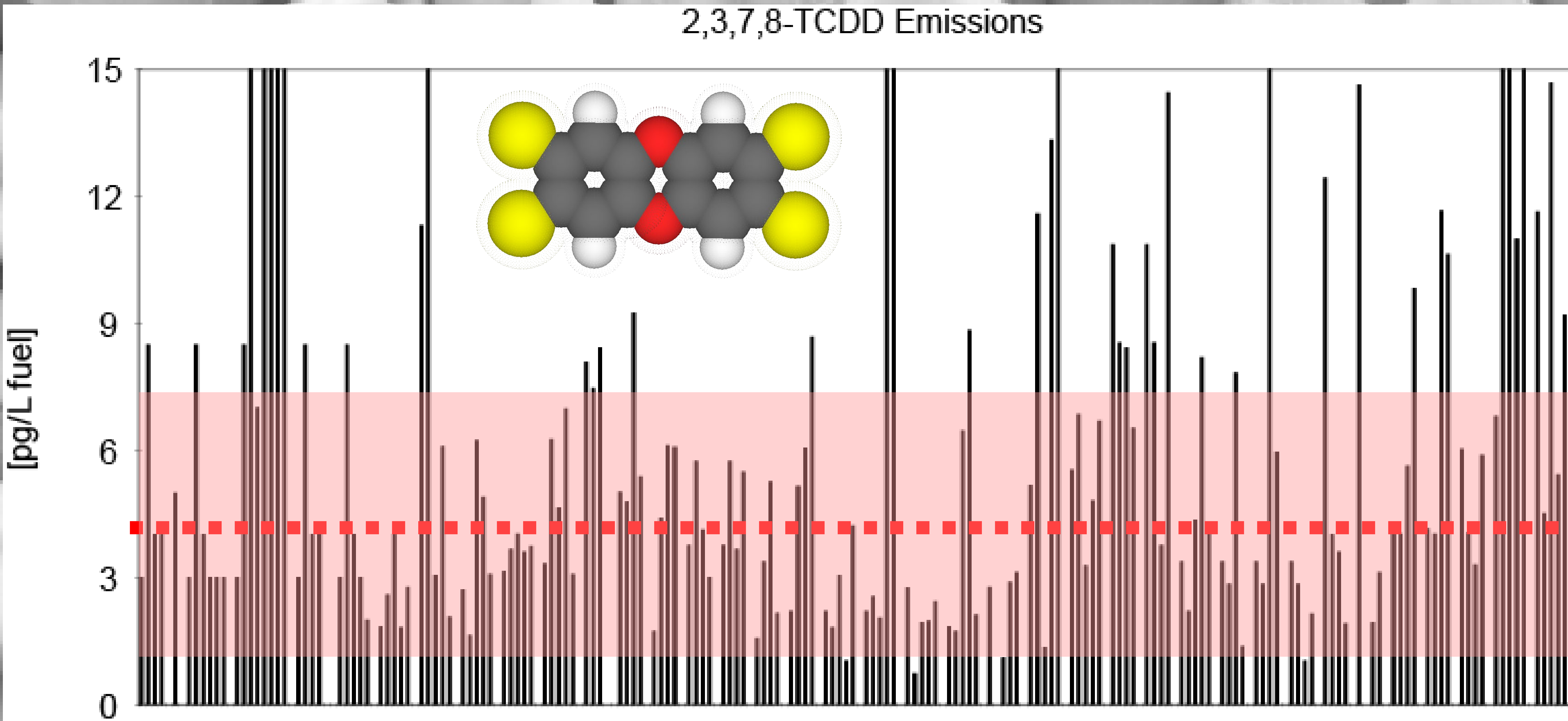
Worst case scenarios with 10 and 100 ug/g fuel

Secondary PCDD/F formation in DPFs?

Secondary PCDD/F formation in DPFs?

Assessment of the PCDD/F-formation potential

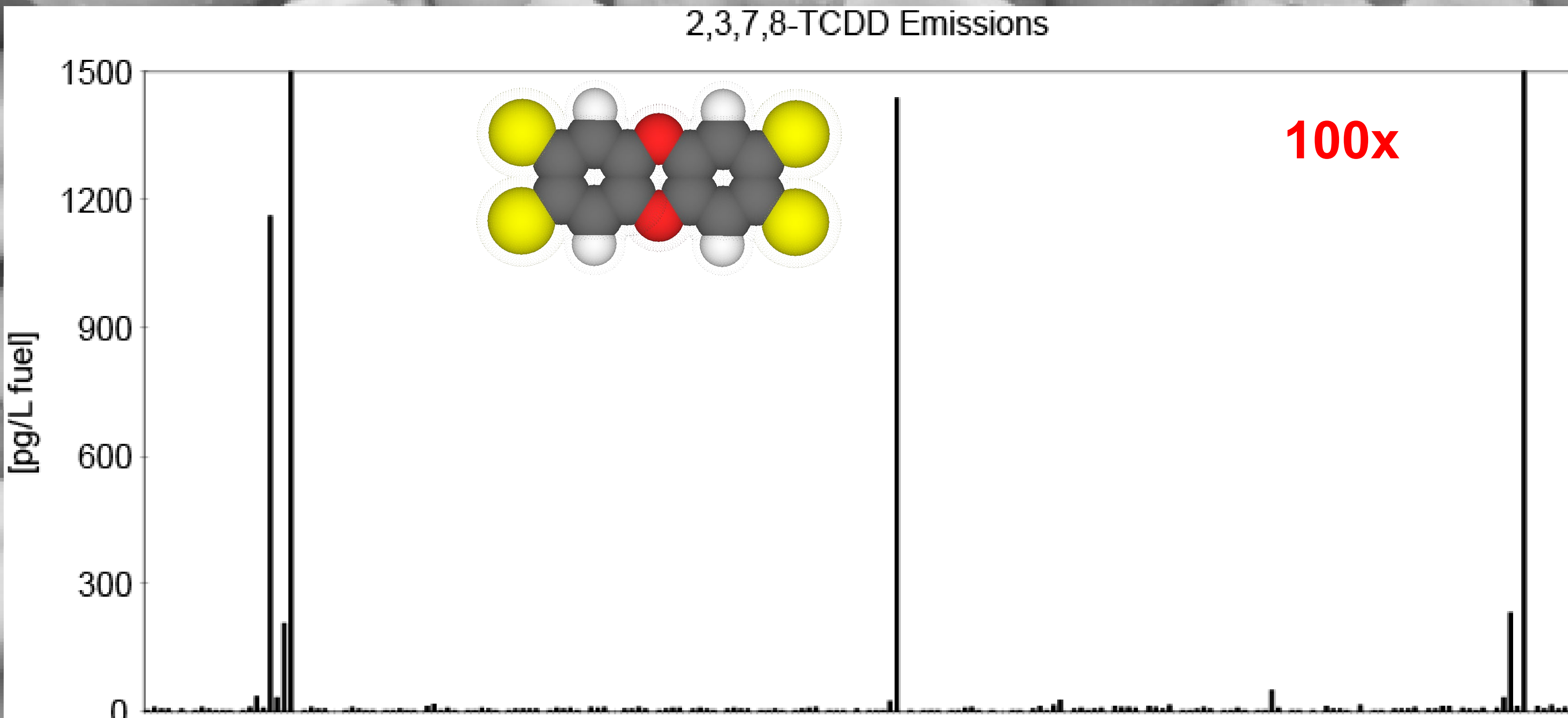
Engine out emissions or emissions of inactive DPFs are on average 4 +/- 3 pg/L



37 DPFs tested, most do not increase dioxin levels above 10 pg / L fuel

Assessment of the PCDD/F-formation potential

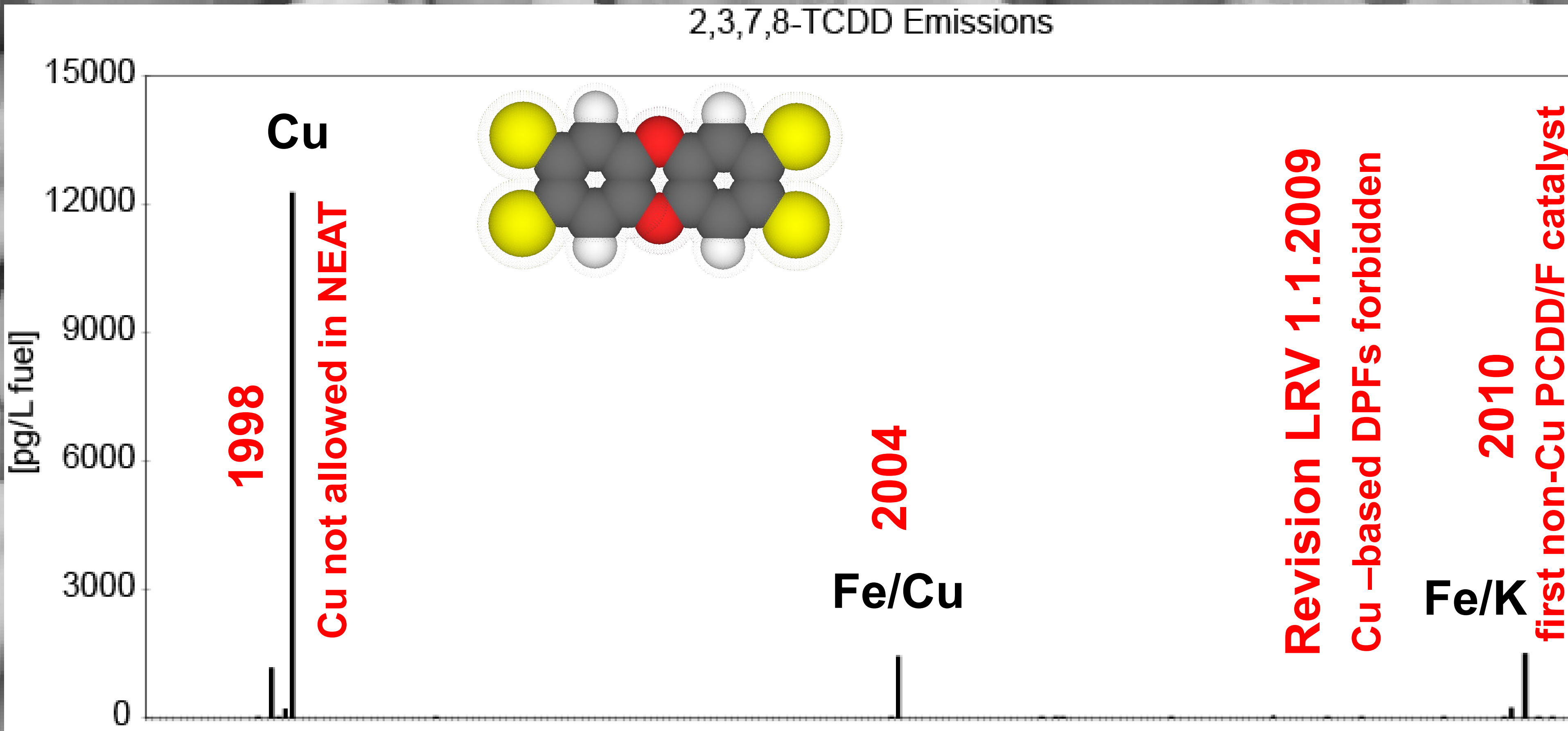
So far, only 3 of the 37 tested DPFs induced a PCDD/F formation?



37 DPFs tested, 3 catalyzed DPFs increase dioxin levels above 1000 pg / L fuel

Assessment of the PCDD/F-formation potential

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



Heeb. et al. Env. Sci. Techn., **2013**, 47, 6510-6517

Heeb. et al. Env. Sci. Techn., **2015**, 49, 9273-9279

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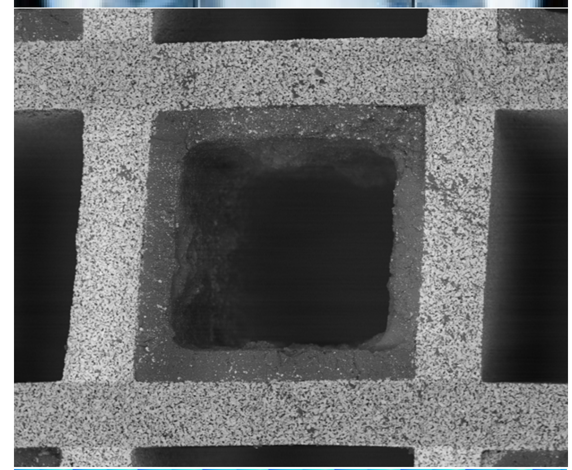

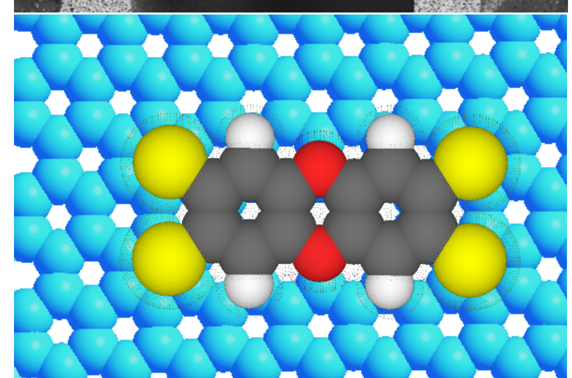

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Consider VERT-approved filters

VERT association

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Online Conference

Organized by the NPC-association
Under the auspices of the FOEN, SCS and ETH

Invitation and call for e-papers to the

25th ETH-Conference on Combustion Generated Nanoparticles

Focus Event:
New legislation to guide the world

June 21 - 23, 2022, online

www.nanoparticles.ch

ETH zürich

Scope

The conference serves as an interdisciplinary platform for expert discussions on all aspects of nanoparticles, freshly emitted from various sources, aged in ambient air, technical mitigation aspects, impact of particles on health, environment and climate, and particle legislation.
The international conference brings together representatives from research, industry and legislation.

SCS Swiss Chemical Society

Deadlines

Abstract submission for oral and video poster presentations and exhibition applications: April 22, 2022
Information on acceptance by May 20, 2022

Registration and Conference Fee

Online registration opening February 25, 2022
under www.nanoparticles.ch/registration.
No conference fee, sponsors welcome.

by Empa

e-Exhibition

The virtual exhibition on particle measurement instrumentation (PMI) and emission control devices (ECDs) is an important part of the conference.

For further information and registration contact:
Prof. Dr. H. Burtscher (PMI)
E-mail: heinz.burtscher@fhnw.ch

Dr. A. Mayer (ECDs)
E-mail: ttm.a.mayer@bluewin.ch

Important Dates and Deadlines

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- e-Exhibition application: April 22, 2022
- Information on paper/poster acceptance by May 20, 2022
- Video upload for virtual posters: June 16, 2022

www.nanoparticle.ch/registration

Secondary emissions from emission control devices and their impact on occupational health and safety

A combined effort with many important contributions

Thanks:

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  Thomas Gasser, Heinz Berger, Gerhard Stucki, Swiss Federal Road Office

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

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Traugott Sandmeyer (1854-1922)