Secondary effects of catalytic DPF: Assessment of the PCDD/F formation potential

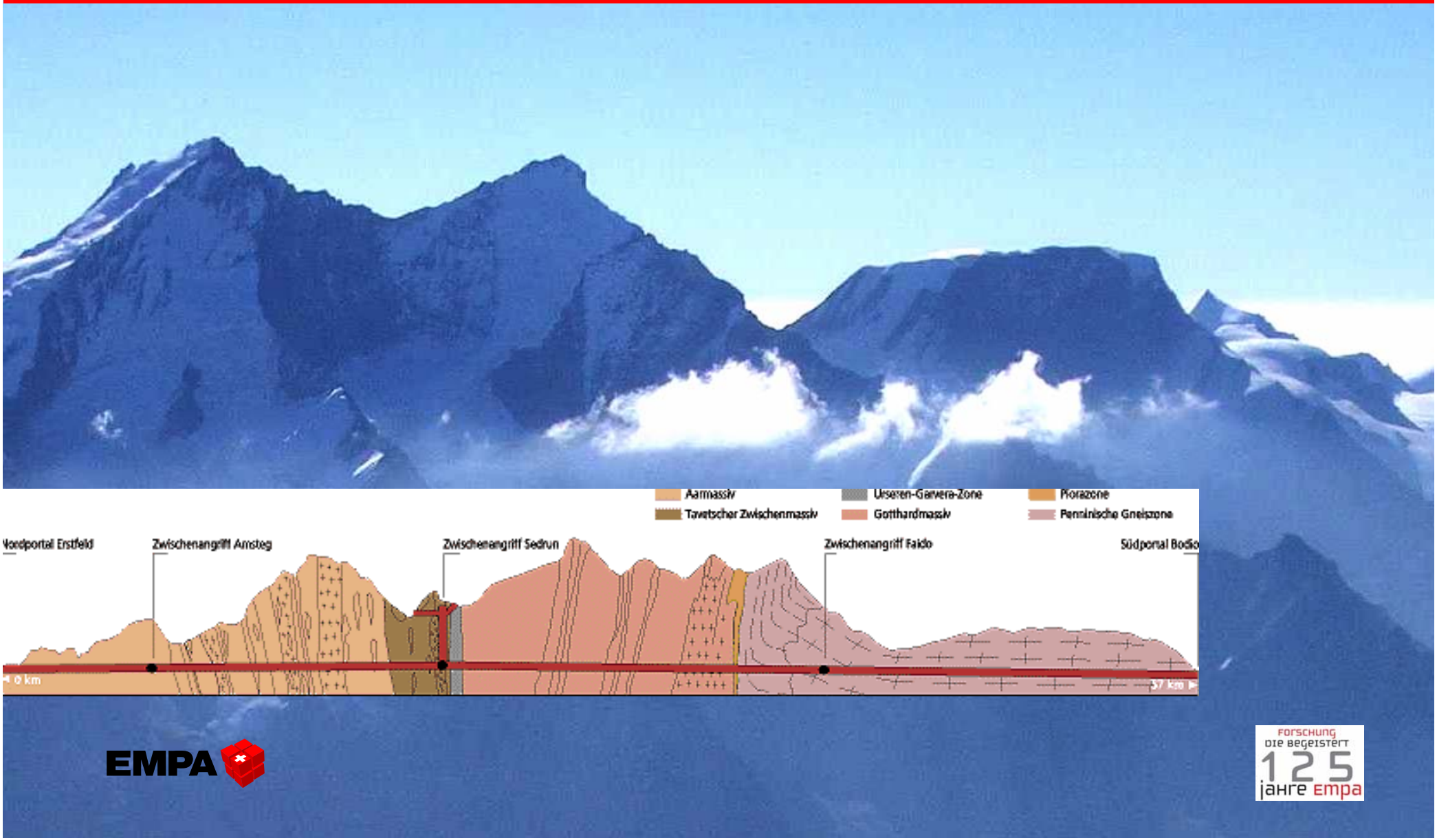
Dr. Norbert Heeb
Empa, Überlandstrasse 129
Laboratory of Solid State Chemistry & Catalysis
CH-8600 Dübendorf
Phone +41-44-823 42 57
Fax +41-44-823 40 41
e-mail norbert.heeb@empa.ch
Internet http://www.empa.ch

11th ETH-Conference on Combustion generated Nanoparticles
Zurich, August 13th-15th, 2007

Secondary effects of catalytic DPF: Assessment of the PCDD/F formation potential

- Background of the VERT procedures
- Relevance of secondary pollutants
- Secondary pollutants of catalytic exhaust gas treatment systems
- Outlook

Background of the VERT procedure



EMPA

Forschung die begeistert 125 Jahre Empa

Background of the VERT procedure

VERT – assessement of benefits and risks of catalytic DPFs

NEAT – a multibillion project

- World longest tunnel, 2 bores of 57 km, 153 km shafts & tunnels
- at costs of 16 billion US$
- construction from 1993-2015 with hundreds of diesel engines

Goals of the VERT Project

- Curtail diesel soot emissions of construction machinery with DPFs
- Fullfill EC limit of <100 ug/m3 for respiratory air in the tunnel
- High filtration efficiencies for all particle sizes (20-600 nm)
- **Assess risks of secondary formation of pollutants**
- Evaluate durable, effective DPFs with low failure rates (<5%)

EMPA

Forschung die begeistert 125 Jahre Empa

Relevance of secondary pollutants

Why should we care on secondary emissions? No problem in Europe!

Legal Aspects

US Clean Air Act (Section 220):

- "Effective with respect to vehicles and engines manufactured after model year 1978, no emission control device, system or element of design shall be used if such a devise will cause or contribute to an unreasonable risk to public health, welfare, or safety. The administrator shall consider, among other factors, whether and to what extent the use of any device, system, or element of design, causes, increases, reduces, or eliminates emissions of any unregulated pollutants".

CH EJPD 8/1990:

- " In Verkehr stehende und neue, ohne Partikelfilter typengeprüfte Fahrzeuge, können nachträglich mit Partikelfiltern ausgerüstet werden.... .beim Einsatz von additiv- oder katalytischunterstützte Regenerationsverfahren ist nachzuweisen, dass eine Gefährdung von Gesundheit und Umwelt durch die zusätzlichen entstehenden Reaktionsprodukte ausgeschlossen ist"

Relevance of secondary pollutants

What are relevant secondary pollutants?

Definition

- **Relevant secondary pollutants are:**

  Toxic and harmful compounds formed from precursor molecules via chemical transformation reactions.

Problems with secondary pollutants

- **How to reduce secondary pollutants?**

  - Knowledge of formation reactions, precursors, co-reagents and critical formation conditions.

    If known one can:
  - Reduce emissions of precursor and co-reagents
  - Avoid critical formation conditions

Secondary pollutants of catalytic exhaust gas treatment systems

What else can a catalyst produce except CO_2, H_2O and N_2?

Toxic secondary pollutants - relevant examples

- **Benzene formation in a 3-way-catalyst**
  Benzene is also a secondary pollutant of the TWC
- **TWC-induced formation of ammonia**
  TWC - an efficient DeNOx system - What about SCR, NOx-Traps?
- **Nitration of PAH in the particulate trap**
  Carcinogenic PAH versus mutagenic Nitro-PAH
- **Formation of PCDD/F in particulate traps**
  The ideal reactor (precursors, temperature, residence time)
- **Emissions of catalyst metals**
  Pd, Rh, Pt, Ce from TWC or Ce, Fe, Sr, V, from traps

The particulate trap - a chemical reactor

What are the main products and trace compounds of soot combustion?

Problems:

- Diesel exhaust is rated as carcinogenic to humans
- Nanoparticles can penetrate the alveolar membrane
- Carcinogenic, mutagenic compounds are bound to soot
- Diesel vehicles without effective exhaust gas treatment

Are catalytic particulate traps an alternative?

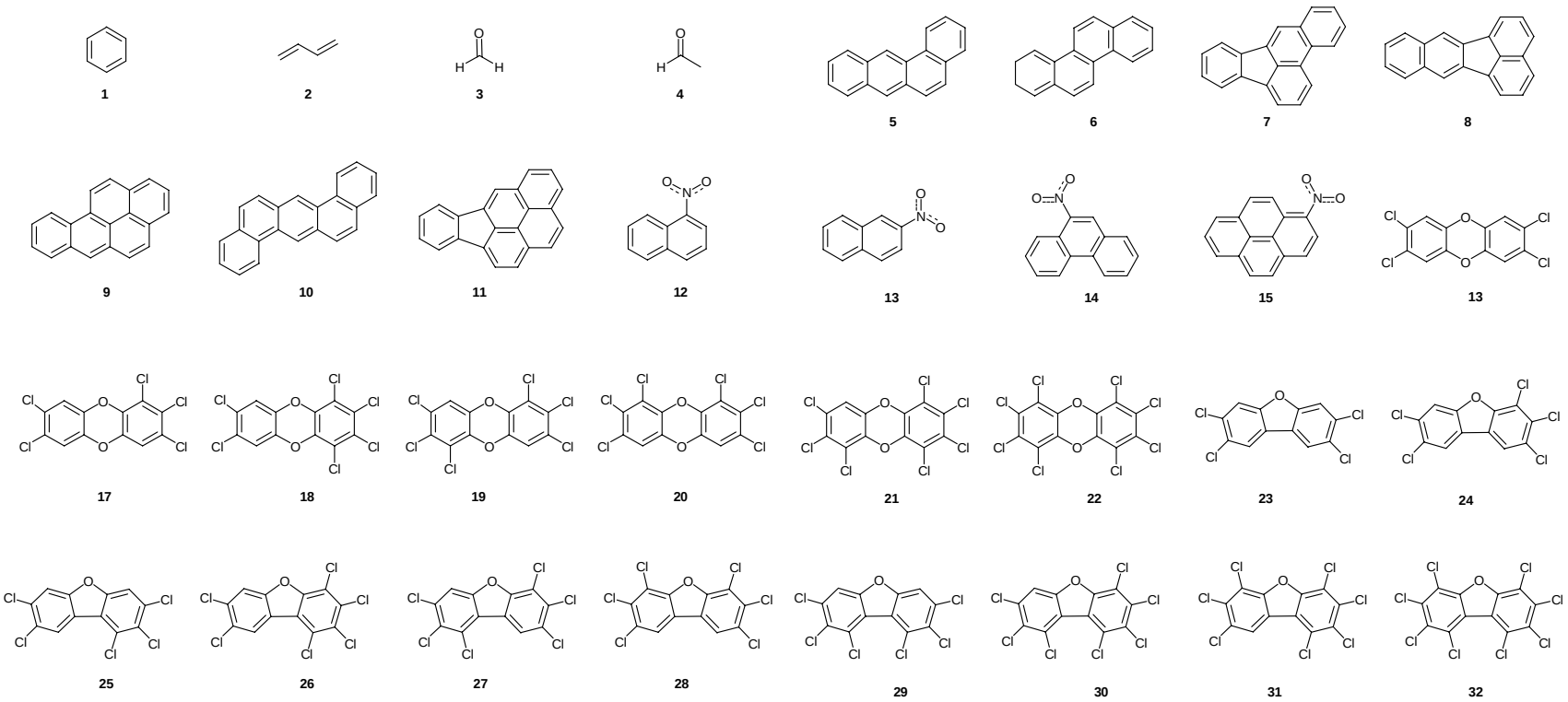
Questions:

- Benefits/Risks of the trap technology
- Effectiveness of particulate traps
- Effects of traps on exhaust gas composition
- Secondary formation of toxic compounds
- Additive metal penetration, release of catalyst coatings

Diesel exhaust - a molecular zoo

Which compounds in this zoo are of relevance?

Chemical structures of some toxic trace compounds



EMPA

Forschung die begeistert 125 Jahre Empa

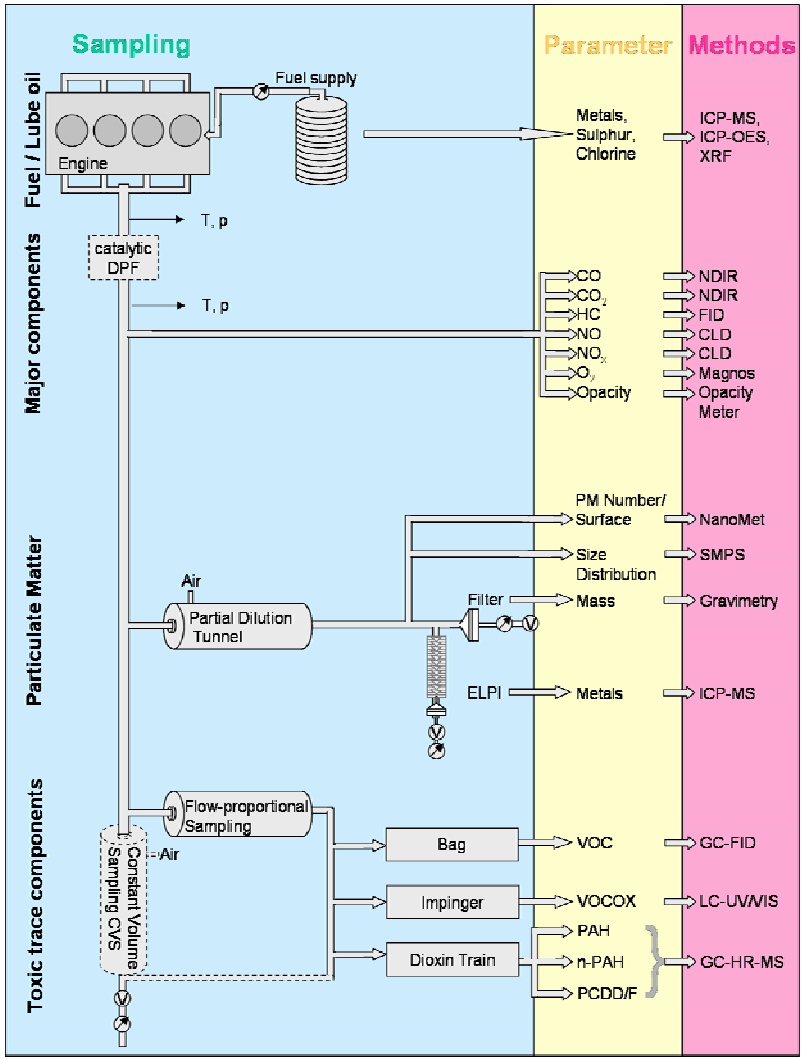
Exhaust gas analysis - ambitious team work

From kg to pg level - analysis over 15 orders of magnitude

Experimental set-up

1. Test series (EMPA):
Liebherr 924TI, 6.6 Liters engine,
143 kW rated power, 2000 RPM
Turbocharger
Sinter metal filters in combination
with Fe-, Ce-, & Cu-fuel additives

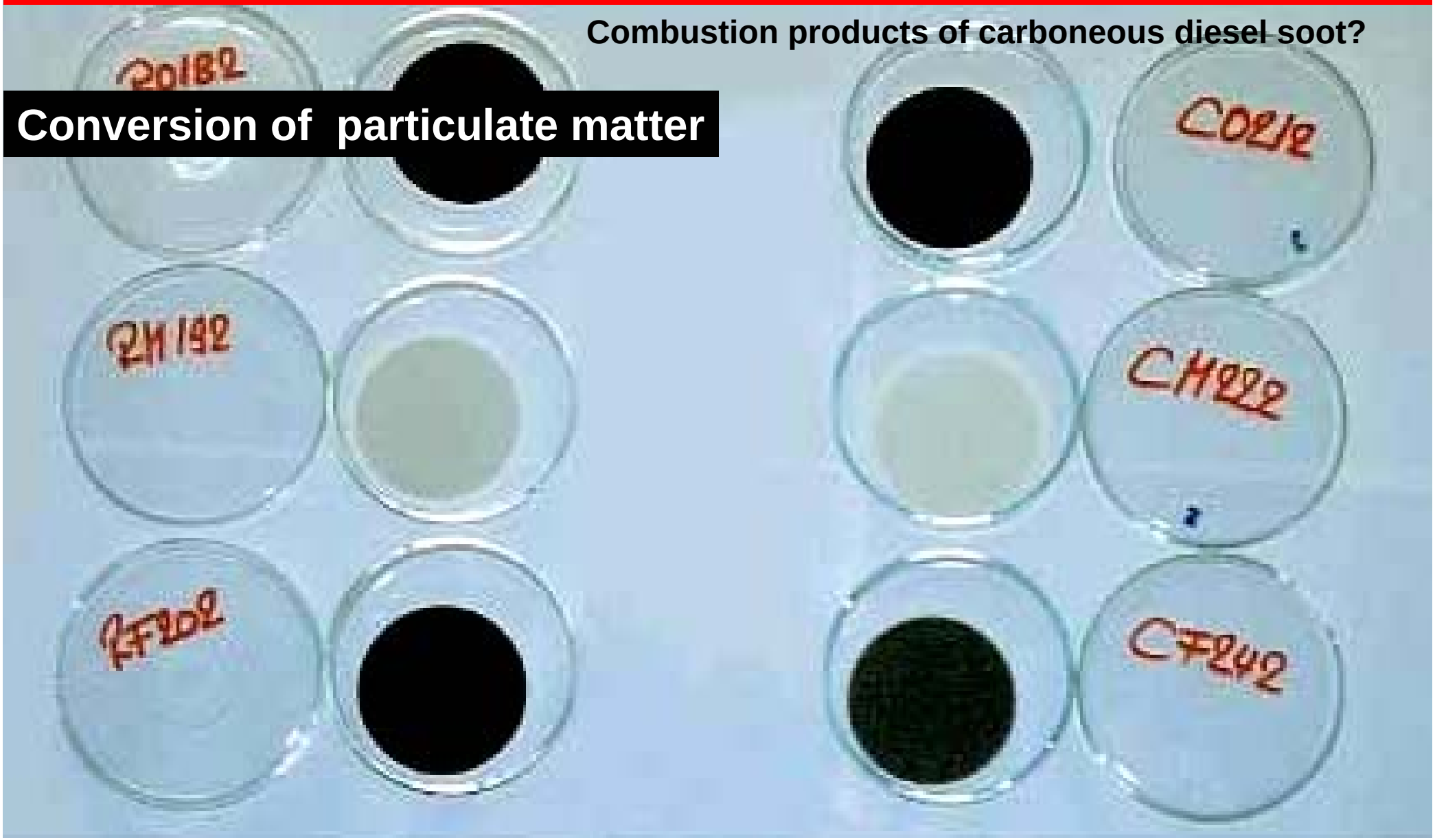
2. Test series (UASB):
Liebherr 914T, 6.1 Liters engine,
105 kW rated power, 2000 RPM
Turbocharger
Ceramic filters in combination
with Fe and Cu/Fe-fuel additives



Catalytic decomposition of diesel soot

Combustion products of carboneous diesel soot?

Conversion of particulate matter



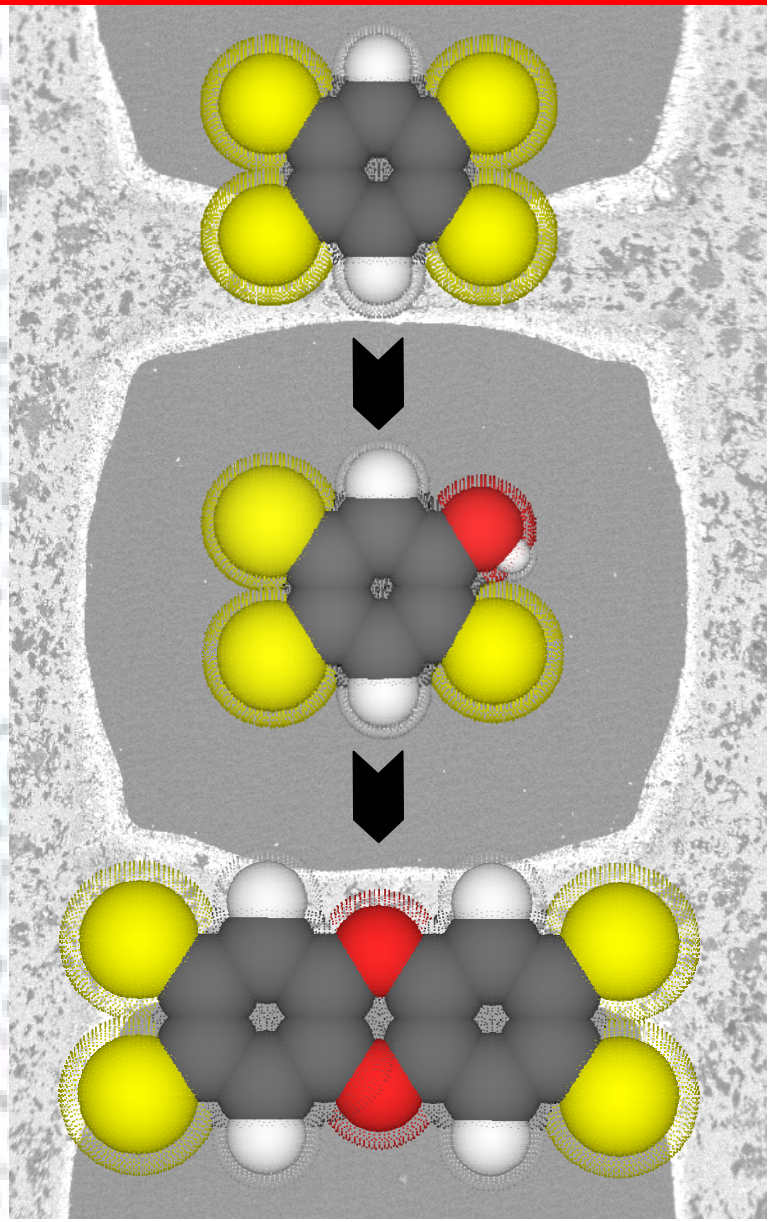
Dioxin formation in Seveso

The dioxin problem

- Highly toxic
- Persistant, ubiquitous
- Bioaccumulating
- Unwanted side product of combustion processes

Properties:

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

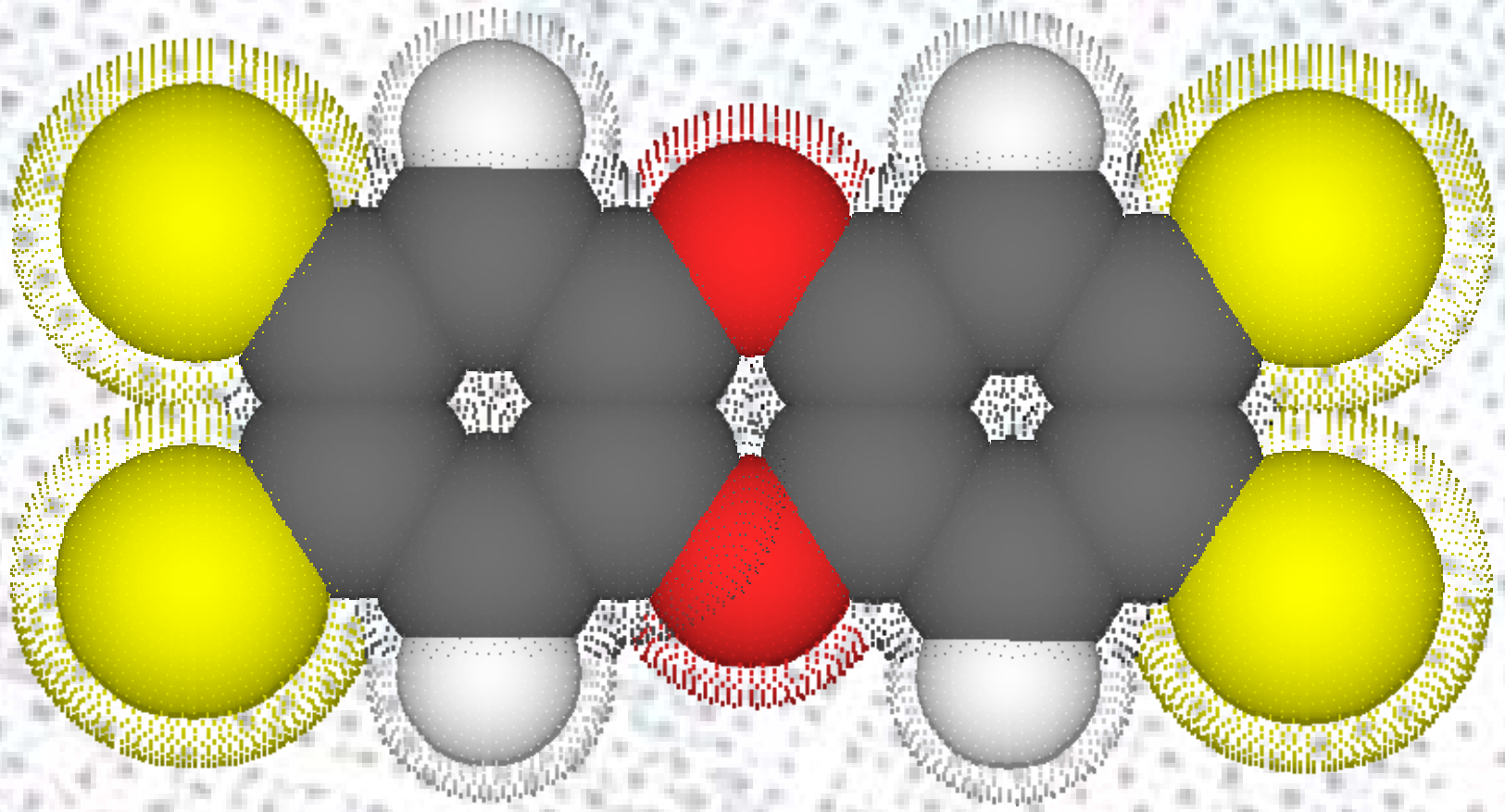


Heeb et al. SAE. 2005-24-014 (2005) 329
Heeb et al. ES&T. in press (2007)

PCDD/Fs: toxic at pg-quantities

What are PCDD/Fs?

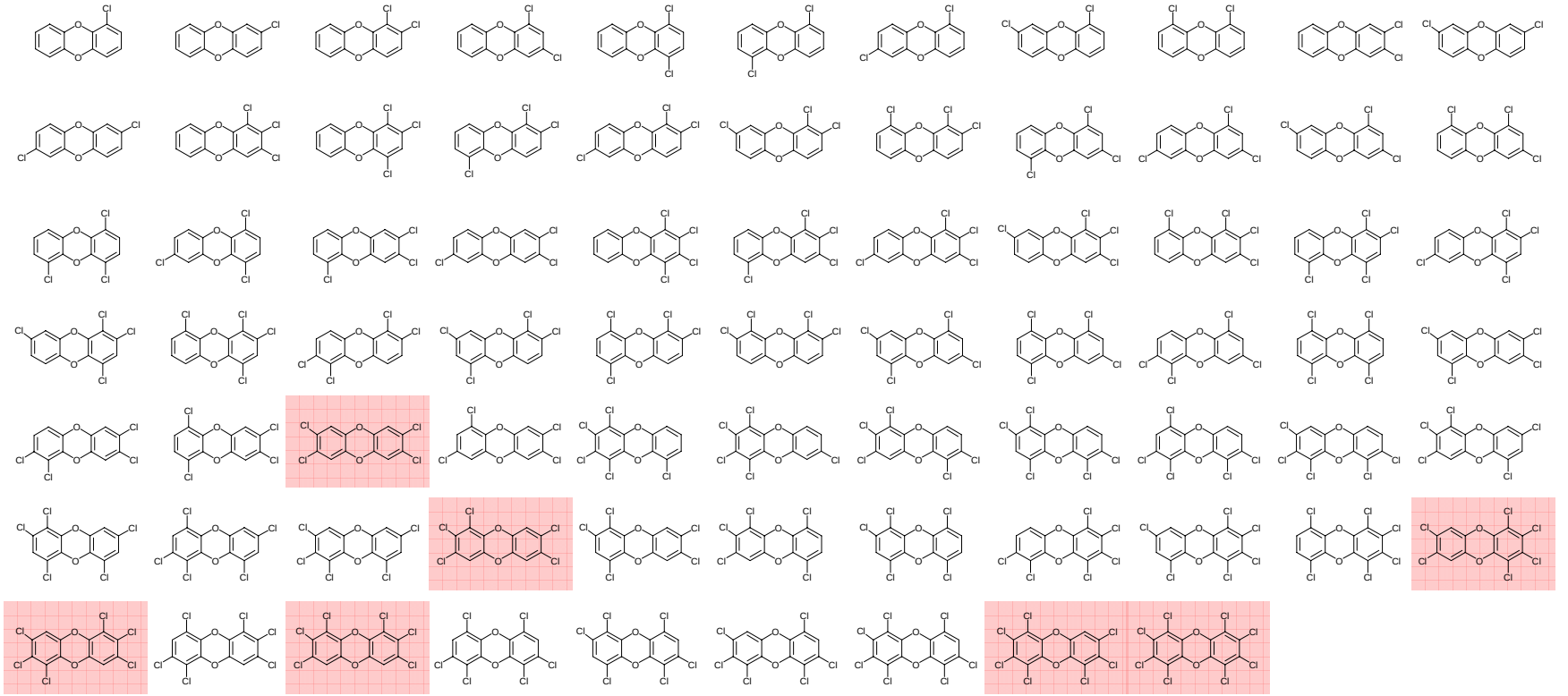
2,3,7,8-Tetrachlordibenzodioxin - the so-called Seveso-dioxin



Analysis of dioxins at ultratrace level

Which are the 7 toxic PCDD?

Chemical structures of polychlorinated dibenzodioxins



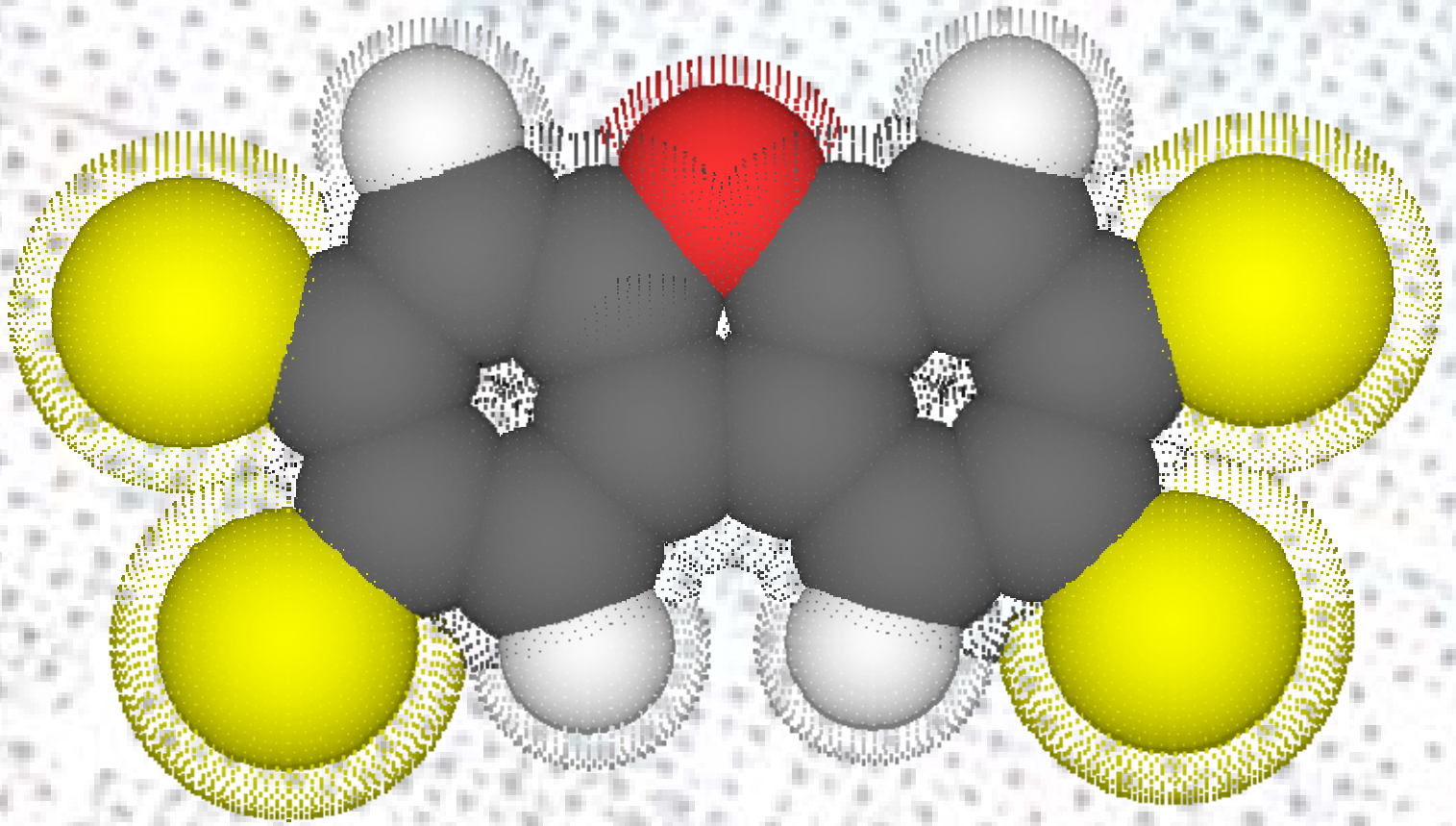
EMPA

Forschung die begeistert 125 Jahre Empa

PCDD/Fs: toxic at pg-quantities

What are PCDD/Fs?

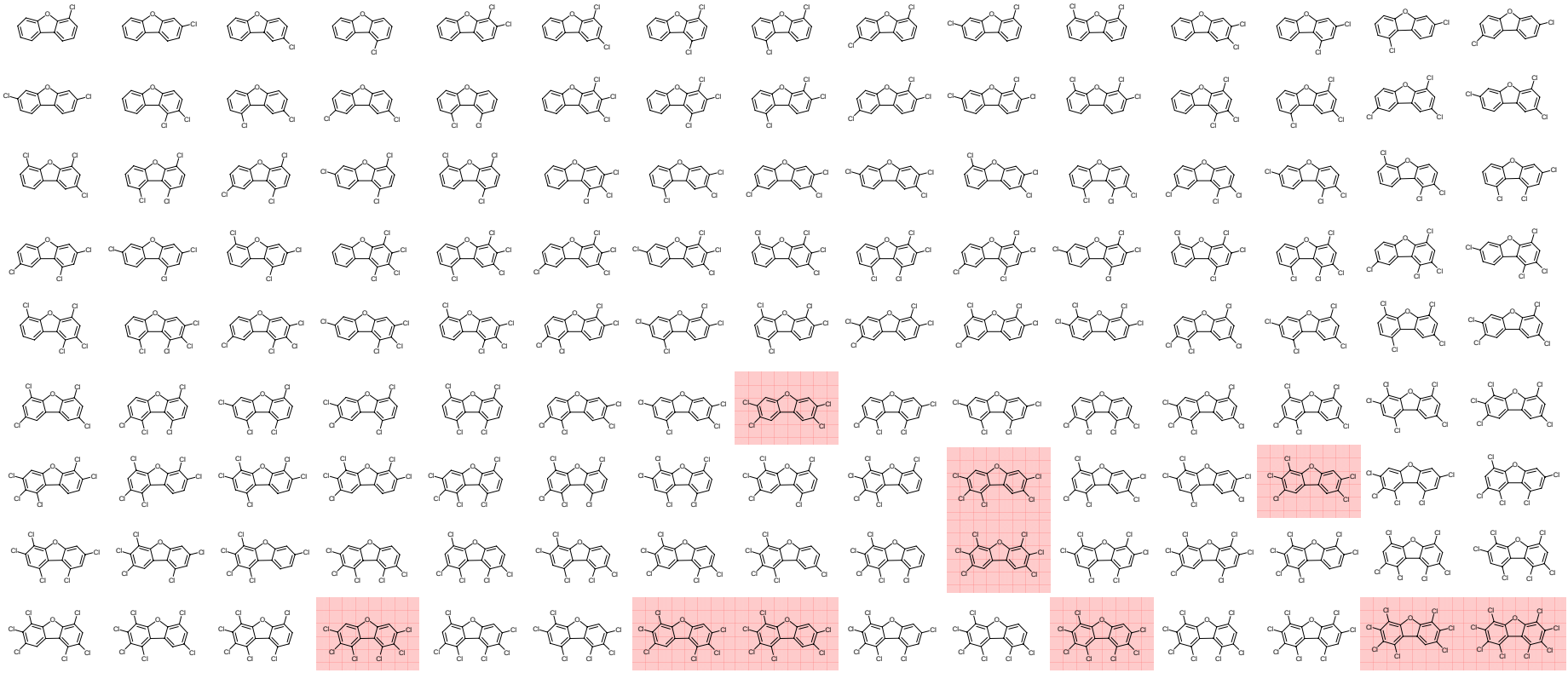
2,3,7,8-Tetrachlordibenzofuran



Analysis of furans at ultratrace level

Which are the 10 toxic PCDF?

Chemical structures of polychlorinated dibenzofurans



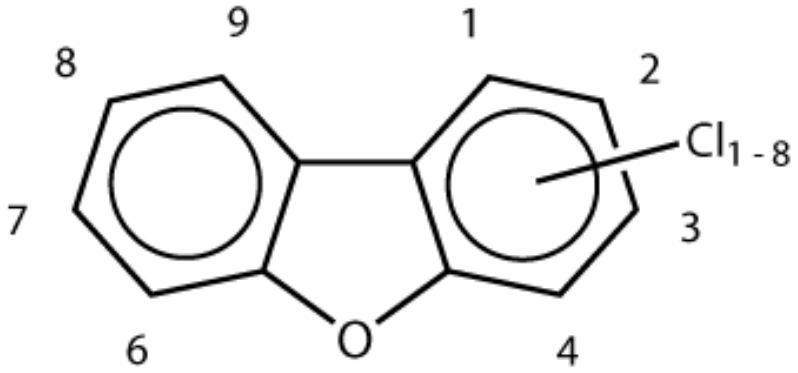
EMPA

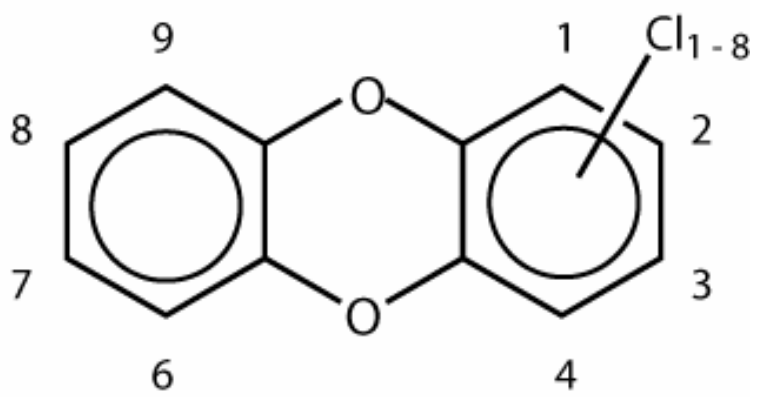
Forschung die begeistert 125 Jahre Empa

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

EMPA

Forschung die begeistert 125 Jahre Empa

Risks of trap-induced dioxin formation

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

The DPF: a perfect chemical reactor

- Elongates residence time of non- or semi-volatile compounds
- Can accumulate potential precursors such as phenols
- Ideal temperature range (260-440 °C), plenty of time
- Surface-rich structure supporting heterogeneous catalysis
- Catalytic metals from additives, coatings, lubrication oil

The only scientific reason to not investigate PCDD/F emissions is the low chlorine content of diesel exhaust. However,

Risks of trap-induced dioxin formation

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

Potential chlorine sources

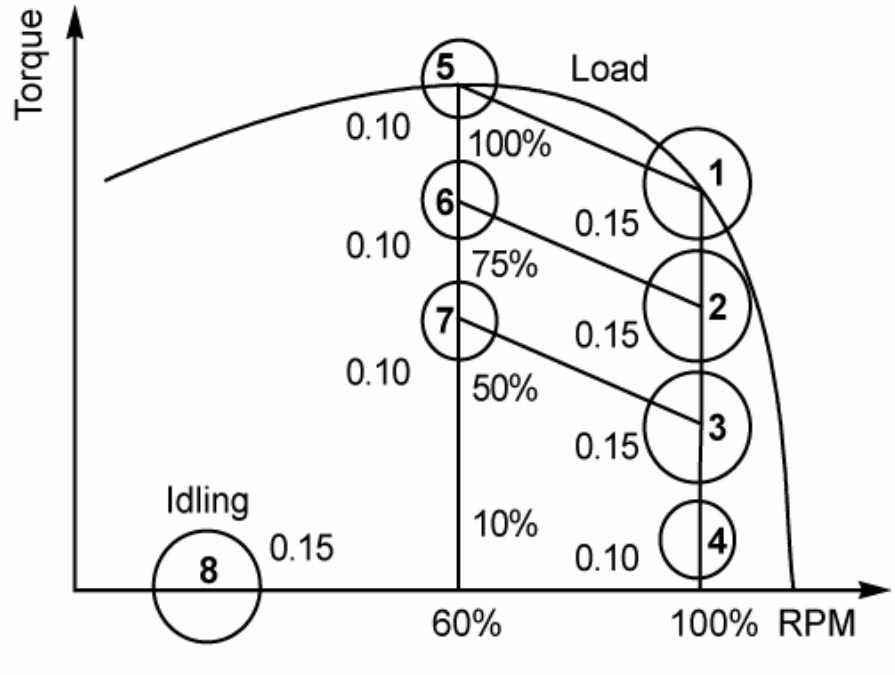
- Commercial diesel should not contain chlorine (LOD: 2 µg/g)
- Worldwide, intake air contains halogenated compounds such as solvents, e.g. urban air of Zürich several µg/m^3
- Lubrication oil (high pressure additives, 120 µg/g in this case)
- Marine aerosols contain salt
- Dust from streets (deicing agents), geological salt layers

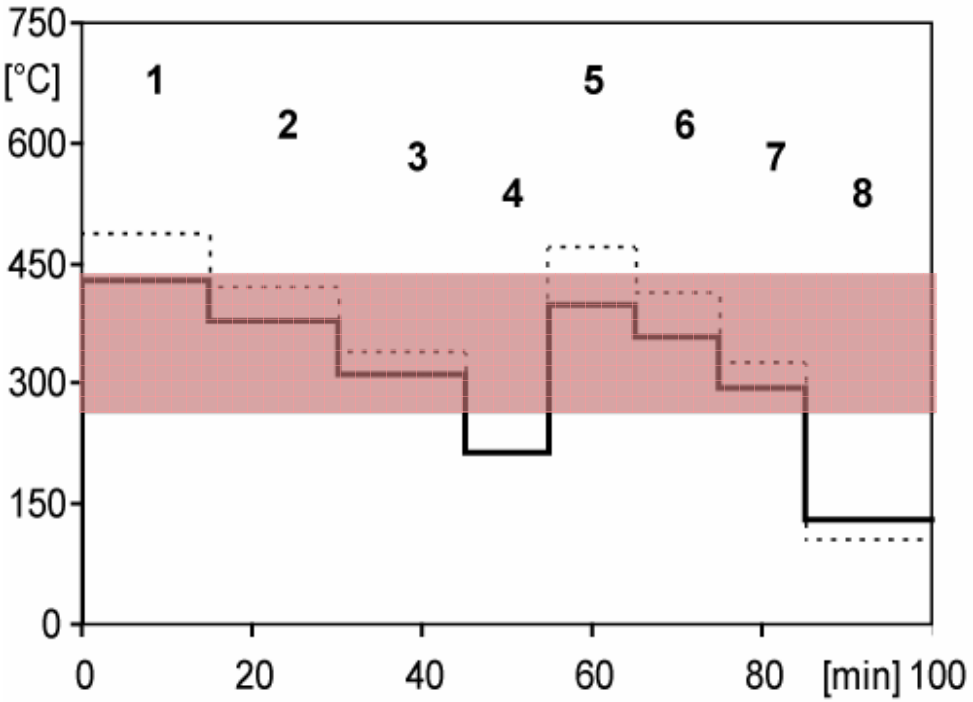
A worst case scenario with a forced chlorine uptake is included

Risks of trap-induced dioxin formation

De novo formation is possible during 75-80% of operating time

Temperature range for *de-novo* PCDD/F-formation





EMPA

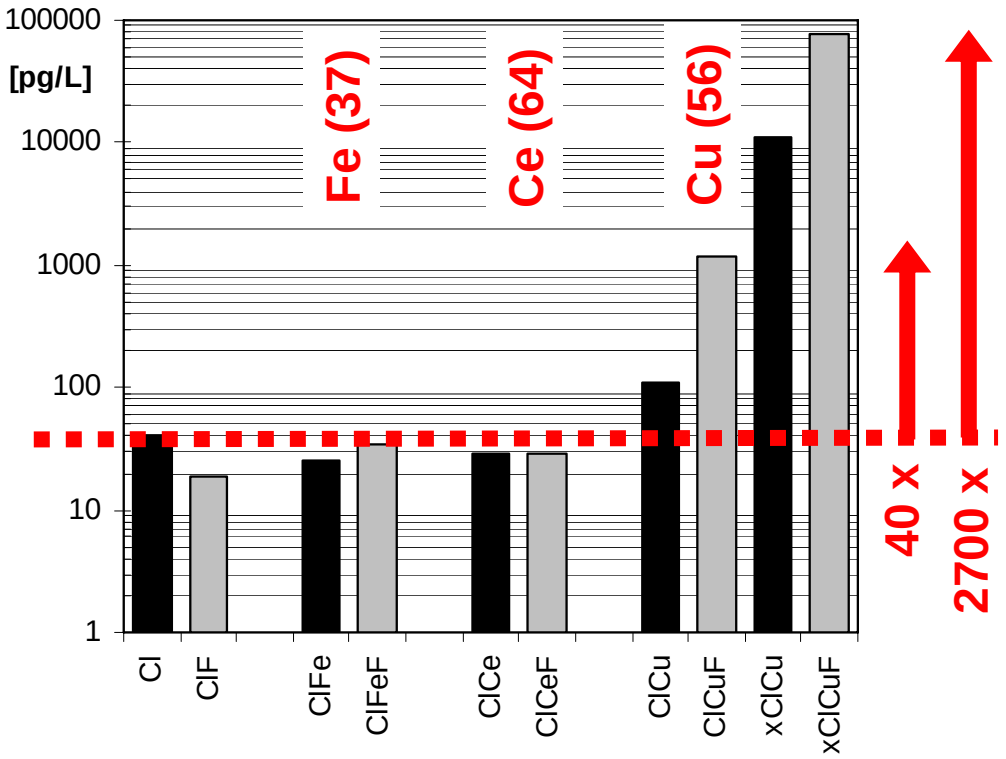
Forschung die begeistert 125 Jahre Empa

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

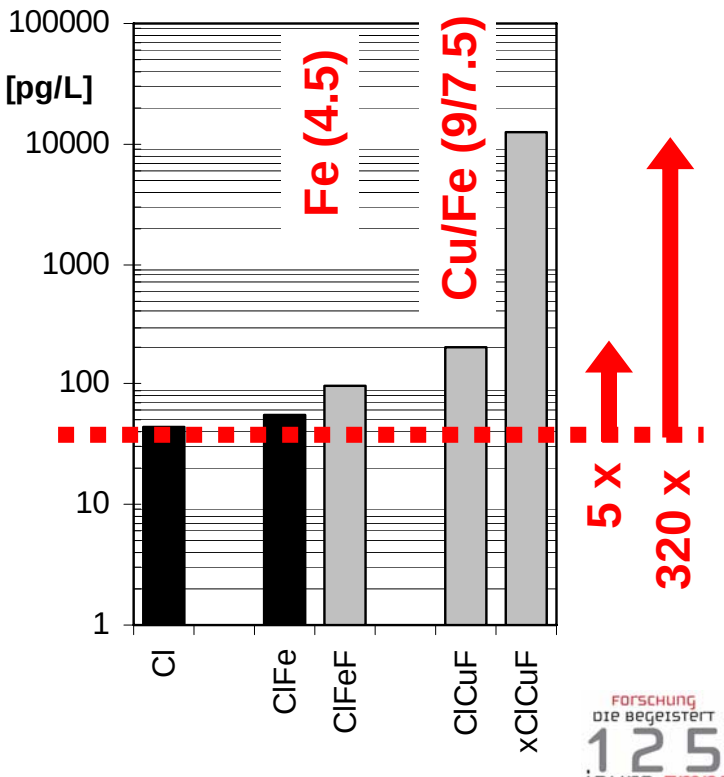
What happens if traces of chlorine enter the system?

2,3,7,8-chlorinated PCDD/F (TEQ-Sum)

Sinter metal filters



Ceramic filters



FORSCHUNG DIE BEGEISTERT
125 JAHRE EMPA

The particulate trap - a chemical reactor

What are reaction products of soot combustion?

Results:

- Current trap technology (20 systems) reduce emissions of PM, PAH, THC, CO (in some cases)
- Trap-induced PCDD/F-formation in 2 of 20 cases (10^4-fold increase of PCDD/F for Cu-regenerated traps)
- Combustion of soot can induce formation of Nitro-PAH, benzene, 1,3-butadiene, formaldehyde, acetaldehyde

Conclusions:

- All investigated traps are efficient sinks for soot particles and particle-bound pollutants
- Formation of toxic secondary pollutants is possible, but their are traps with low risks on lots of benefits
- Consider the Swiss filter list before trap application (http://www.umwelt-schweiz.ch/buwal/eng/fachgebiete)

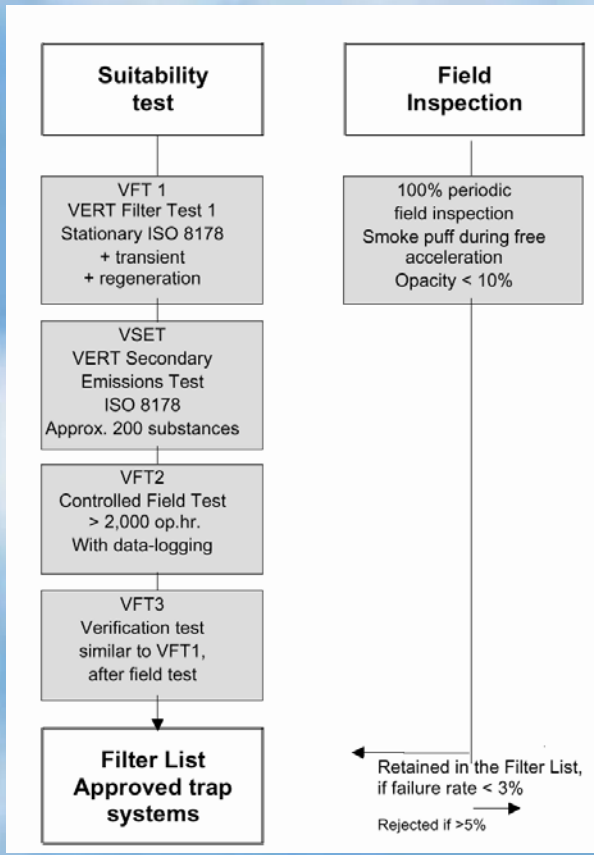
Secondary pollutants of catalytic exhaust gas treatment systems

How to deal with risks of secondary pollutant formation?

Outlook

Lessons to learn from VERT:

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



Secondary effects of catalytic DPF: Assessment of the PCDD/F formation potential

Was there a question not answered yet?

Thanks:

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

- to my Empa colleagues: L. Emmenegger, E. Guyer, U. Gfeller, R. Graf, R. Haag, P. Honnegger, M. Kohler, P. Mattrel, P. Schmid, A. Ulrich, D. Wenger, A. Wichser, M. Zennegg,

- for your attention

EMPA

Forschung die begeistert 125 Jahre Empa