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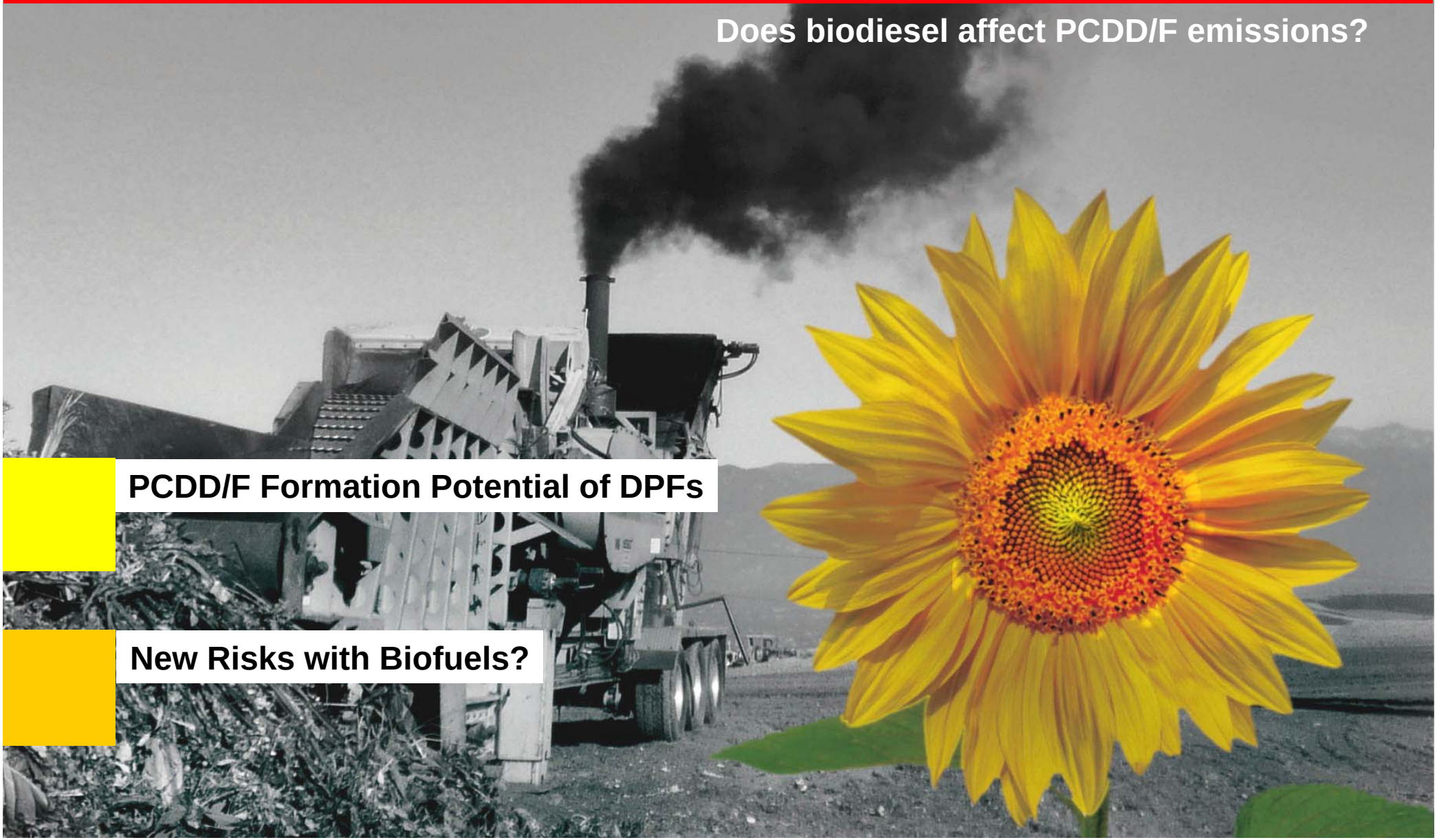
PCDD/F formation in catalytic DPFs: New risks with biofuels?

17th ETH Conference on Combustion Generated Nanoparticles

Zürich, June 23-26, 2013

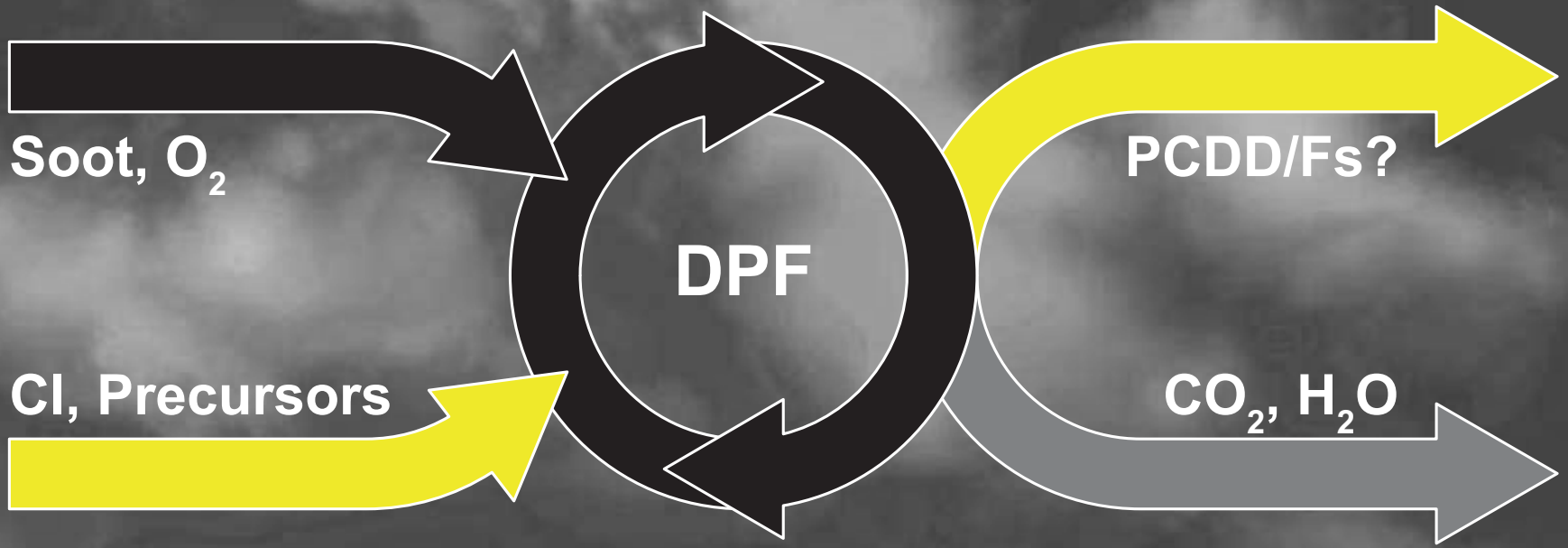
PCDD/F formation in catalytic DPFs: New risks with biofuels?



VERT Secondary emissions test: A must for catalytic DPFs

Is there a risk for a PCDD/F formation in catalytic DPFs?

PCDD/F Formation Potential



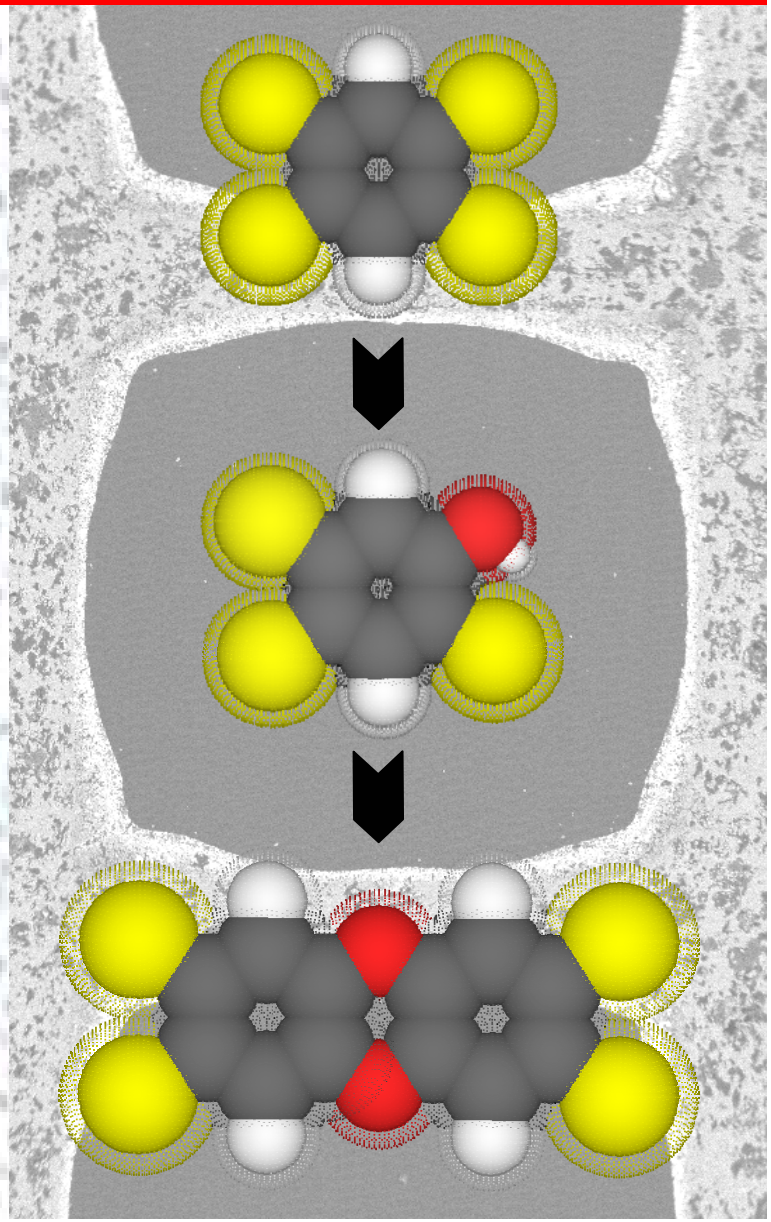
Dioxin formation in Seveso (1976)

The dioxin problem

- Highly toxic, bind to Ah receptor
- Persistent, bioaccumulative, ubiquitous
- Unwanted side products of combustion
- Regulated under the Stockholm convention on POPs, since 2001, 152 signatory states

PCDD/F Properties:

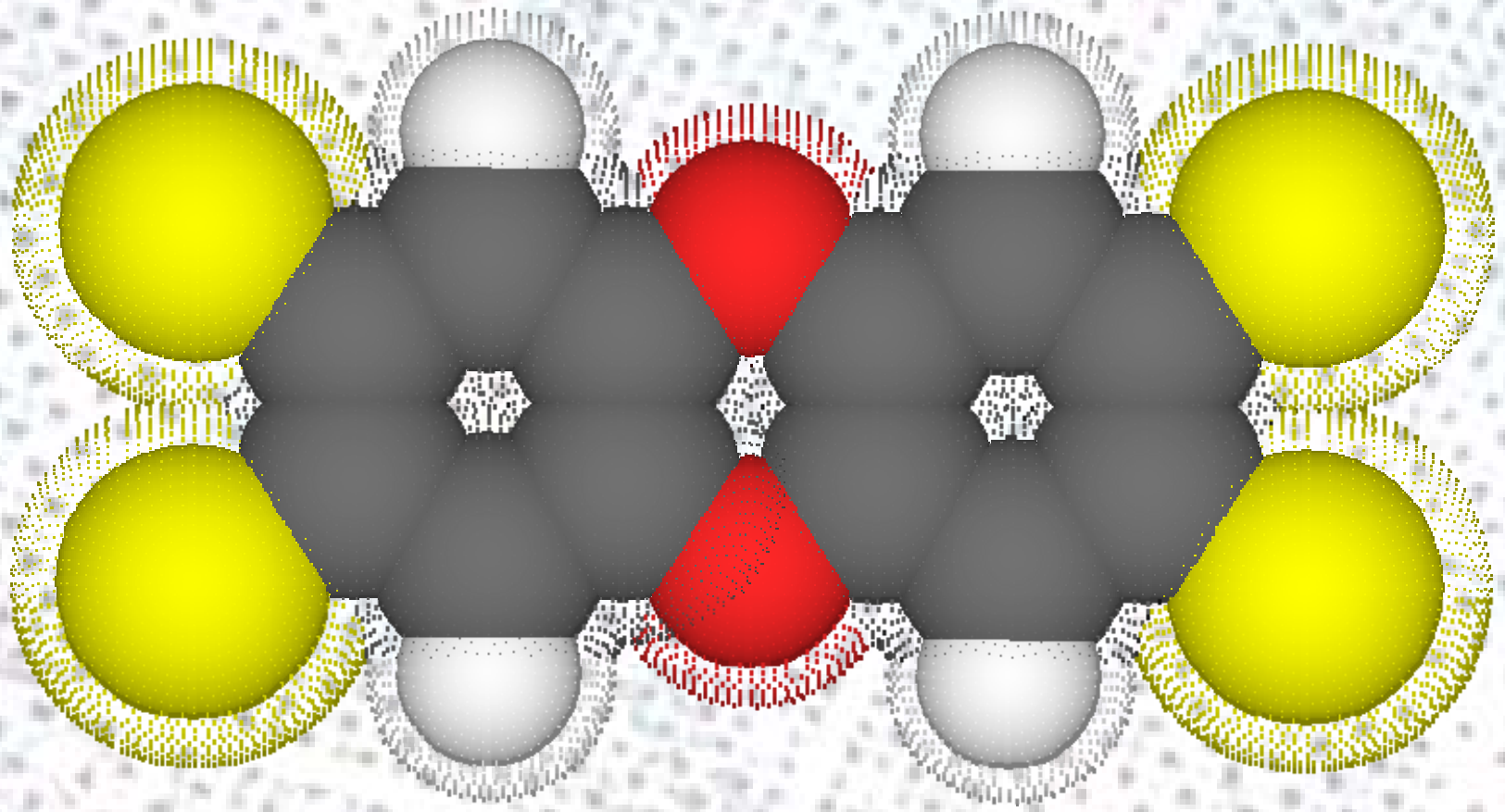
- Thermally stable up to 440°C
- Solid, non-volatile, bound to particles
- Should be removed in DPFs like PAHs unless they are formed *de novo*



PCDD/Fs: toxic at pg-quantities

What are PCDD/Fs?

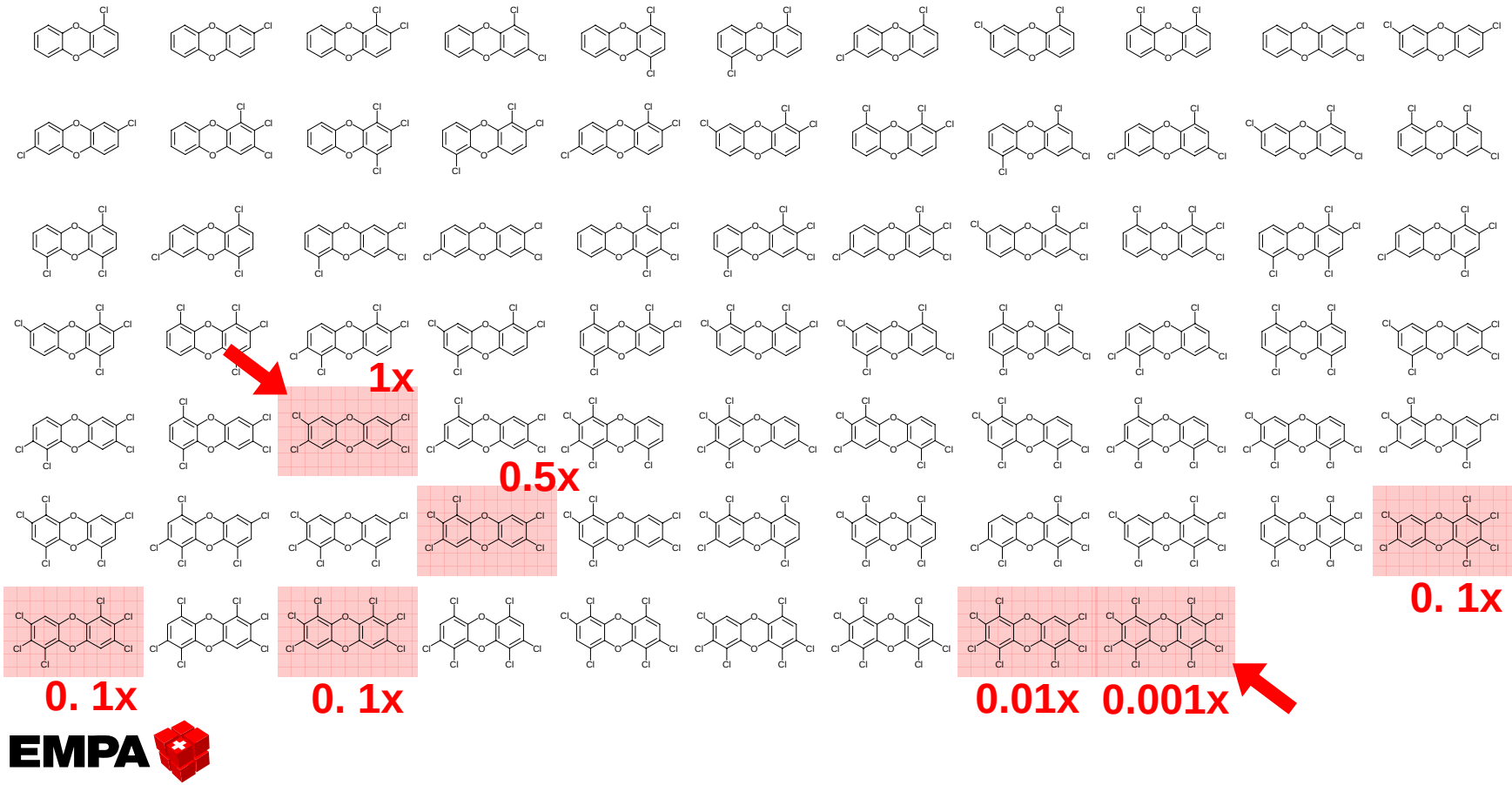
2,3,7,8-Tetrachlorodibenzodioxin - the so-called Seveso-dioxin



Analysis of dibenzodioxins at ultratrace level

Which are the 7 toxic PCDDs?

Chemical structures of polychlorinated dibenzodioxins



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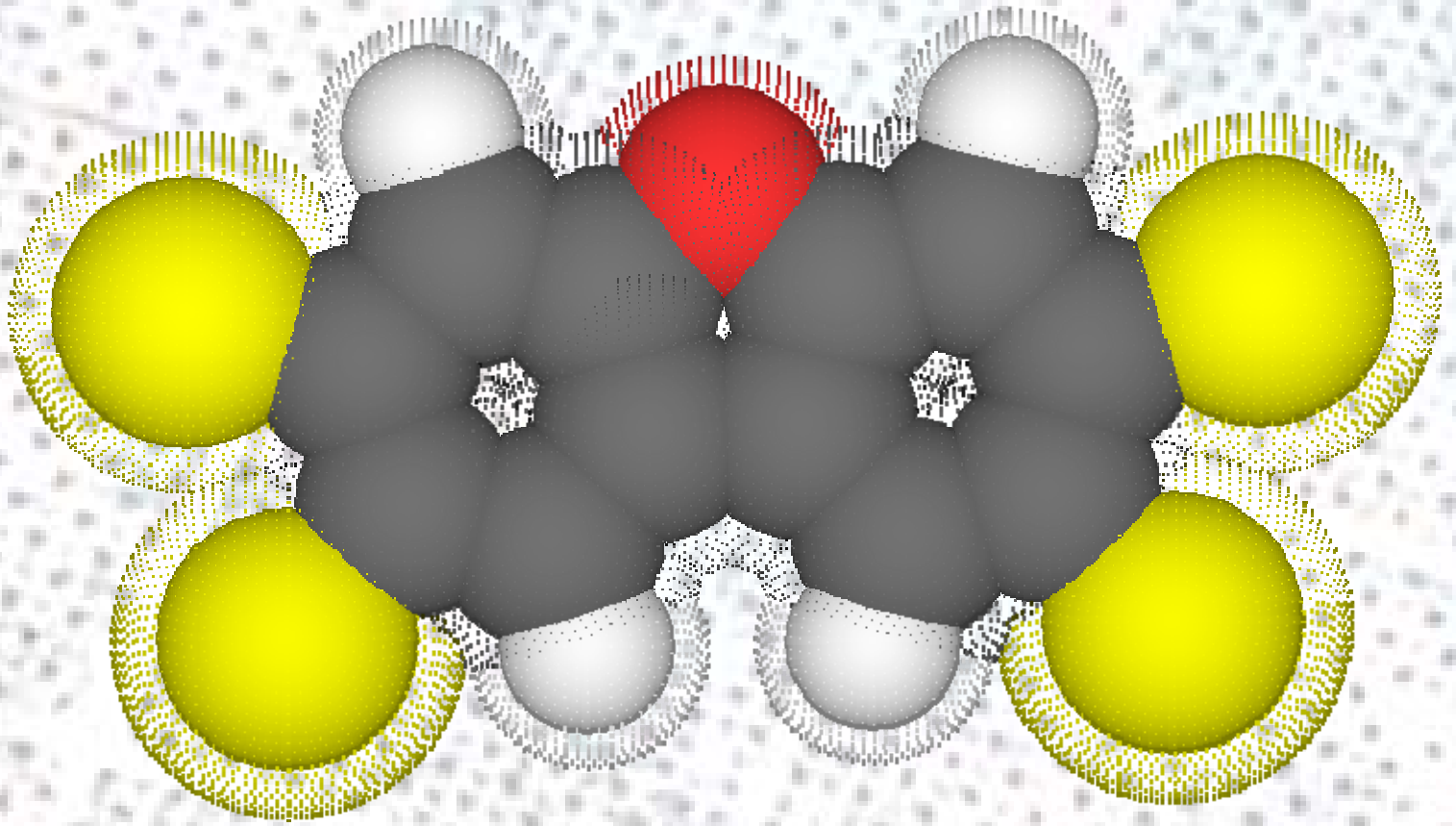
PCDD/Fs: toxic at pg-quantities

What are PCDFs?

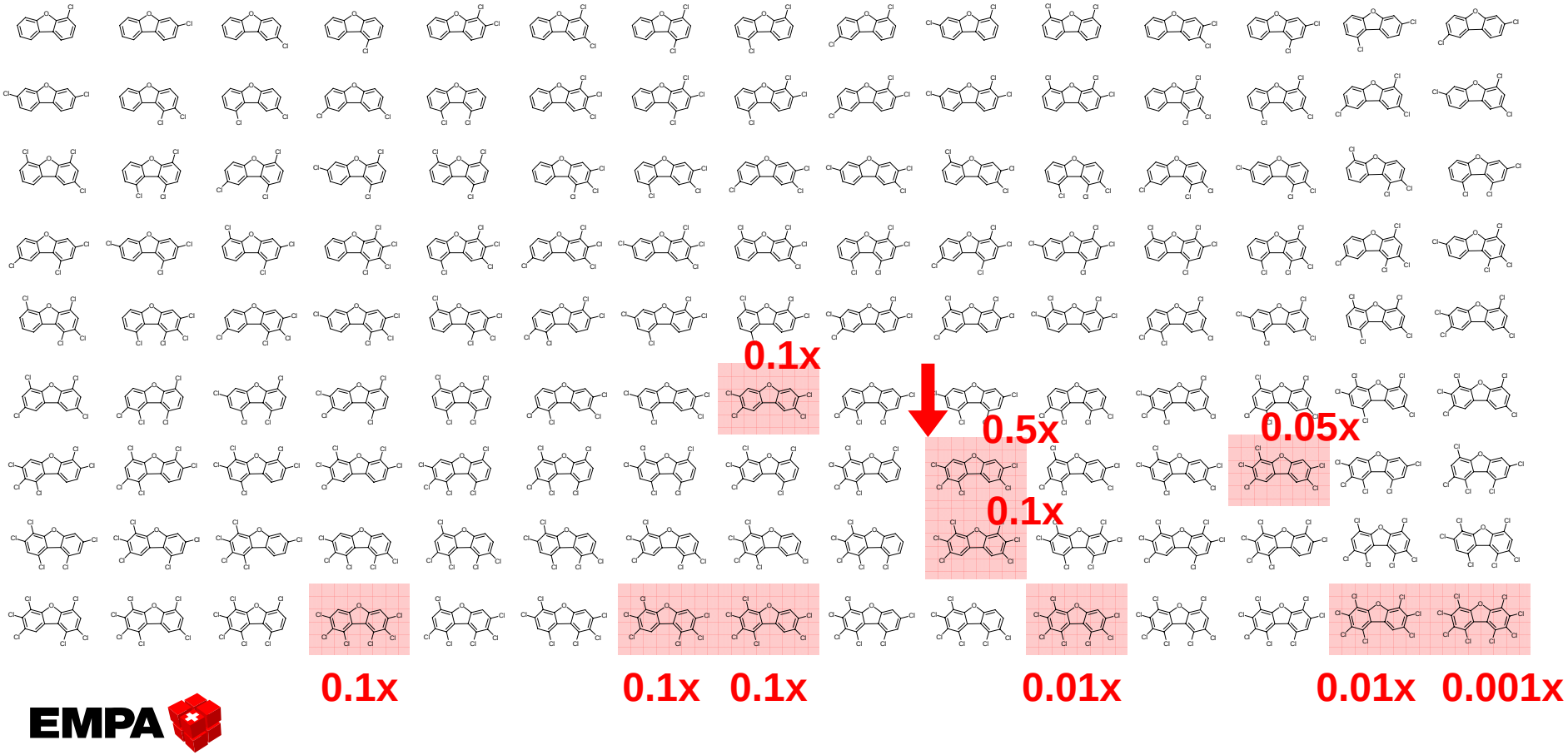
2,3,7,8-Tetrachlorodibenzofuran



Analysis of dibenzofurans at ultratrace level

Which are the 10 toxic PCDFs?

Chemical structures of polychlorinated dibenzofurans



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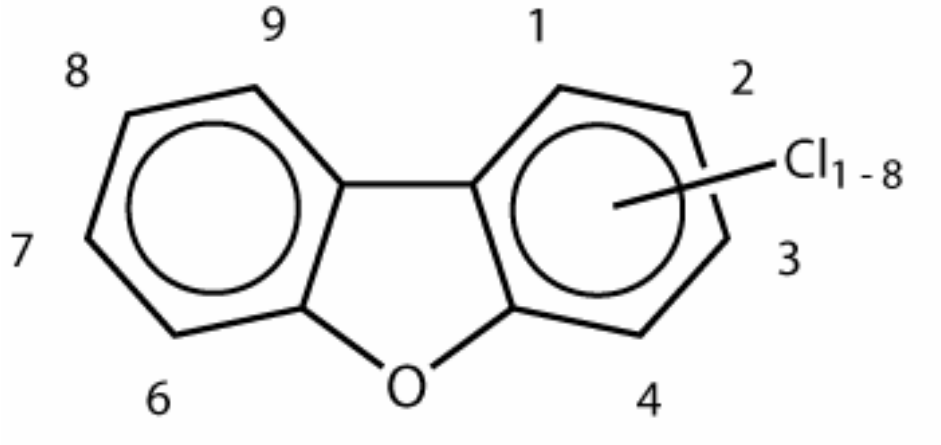
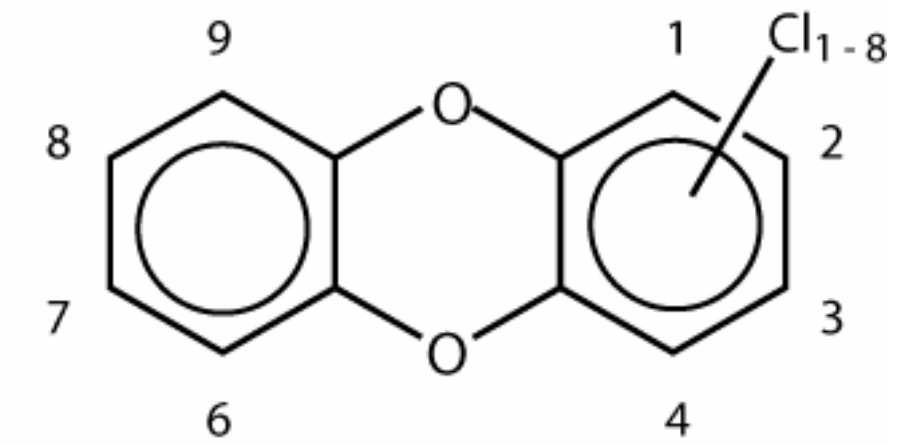
PCDD/Fs: Two classes of compounds

PCDD/Fs are aromatic 3-ring systems related to PAHs?

PCDD/Fs: Two classes of polychlorinated compounds



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



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

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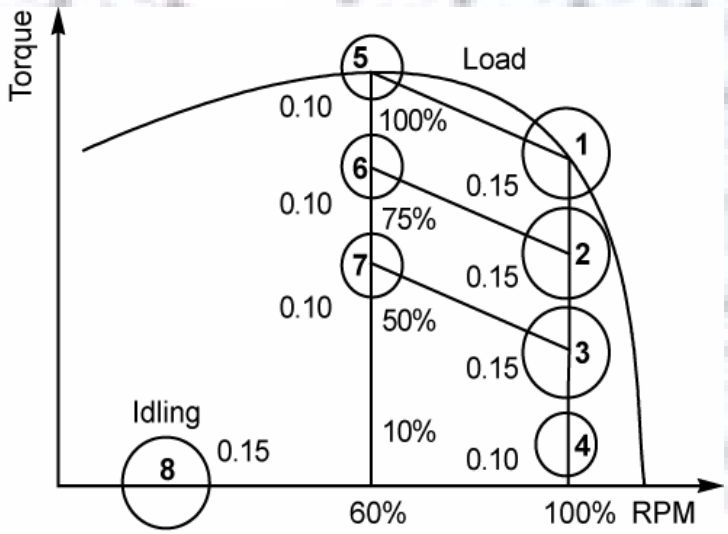
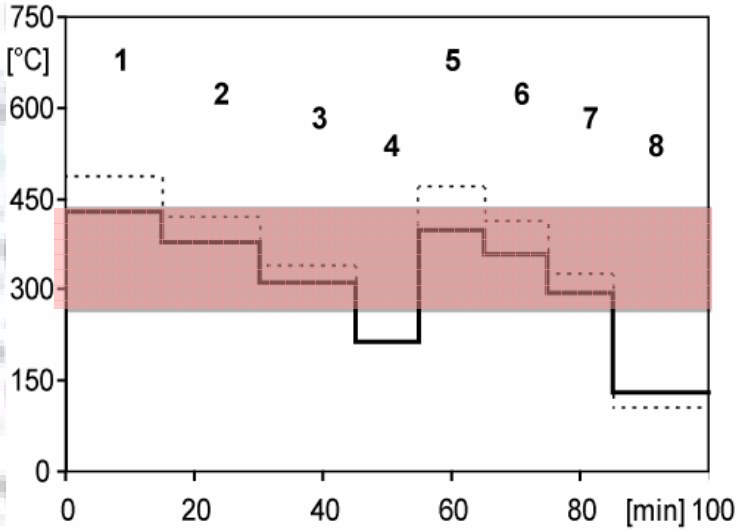
Secondary PCDD/F Formation in DPFs?

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

DPFs: perfect chemical reactors

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





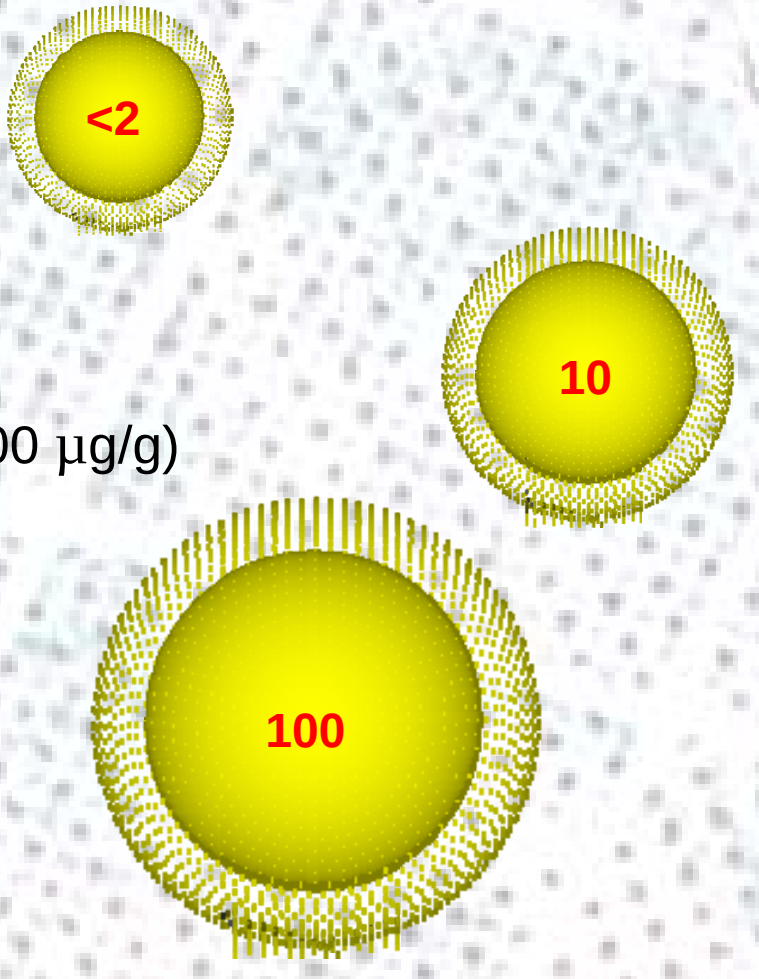
***De novo* formation is possible during 75-80% of operation time in the ISO8178/4 cycle**

Secondary PCDD/F Formation in DPFs?

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

Potential chlorine sources

- Commercial diesel (<2 µg/g)
- Intake air contains µg quantities of chlorinated hydrocarbons (several µg/m³ 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

Assessment of the PCDD/F-formation potential

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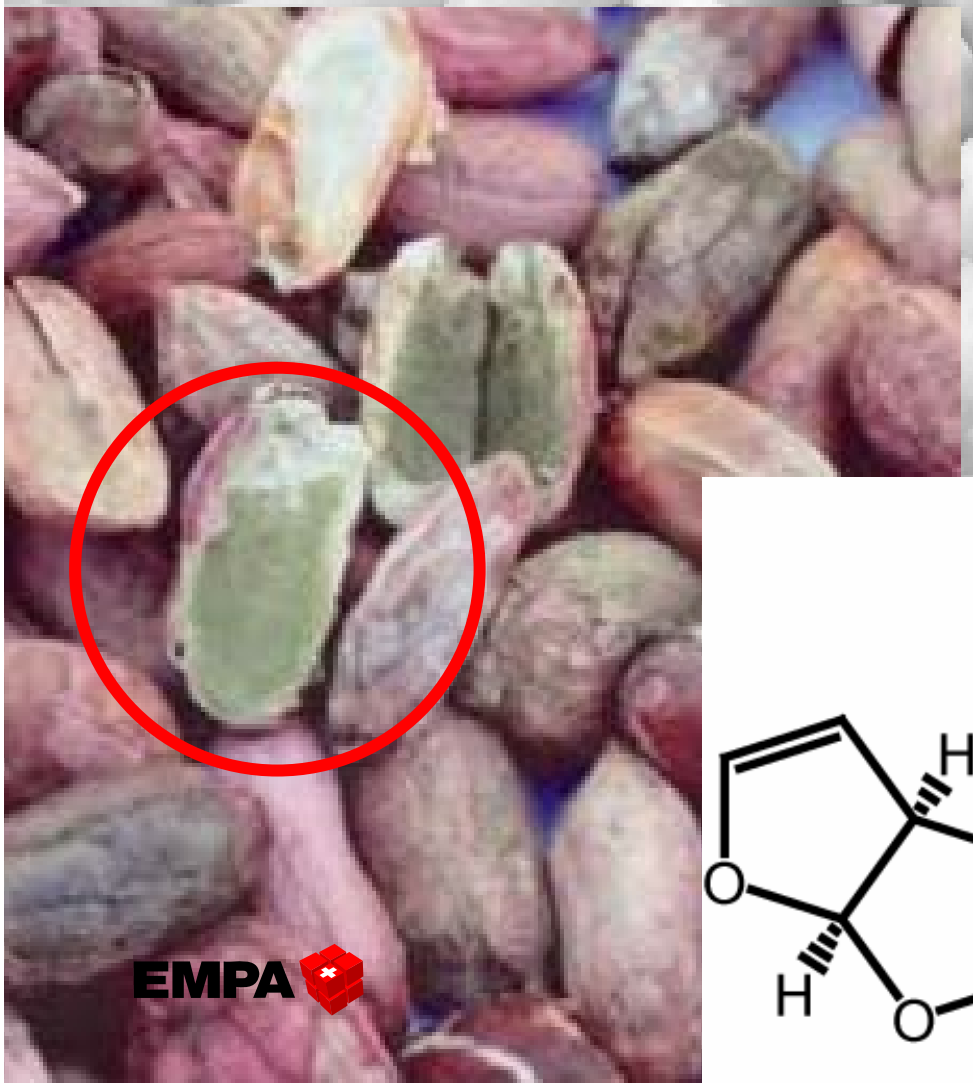
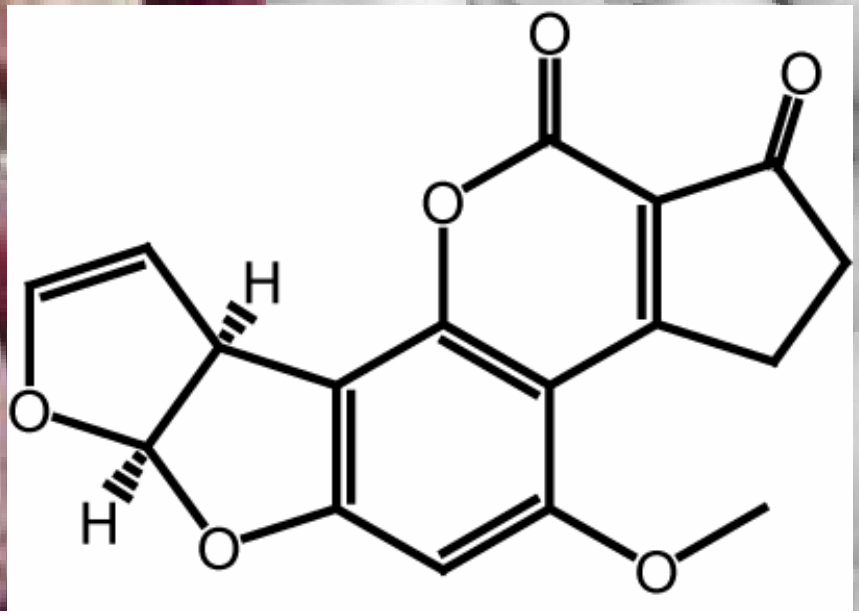
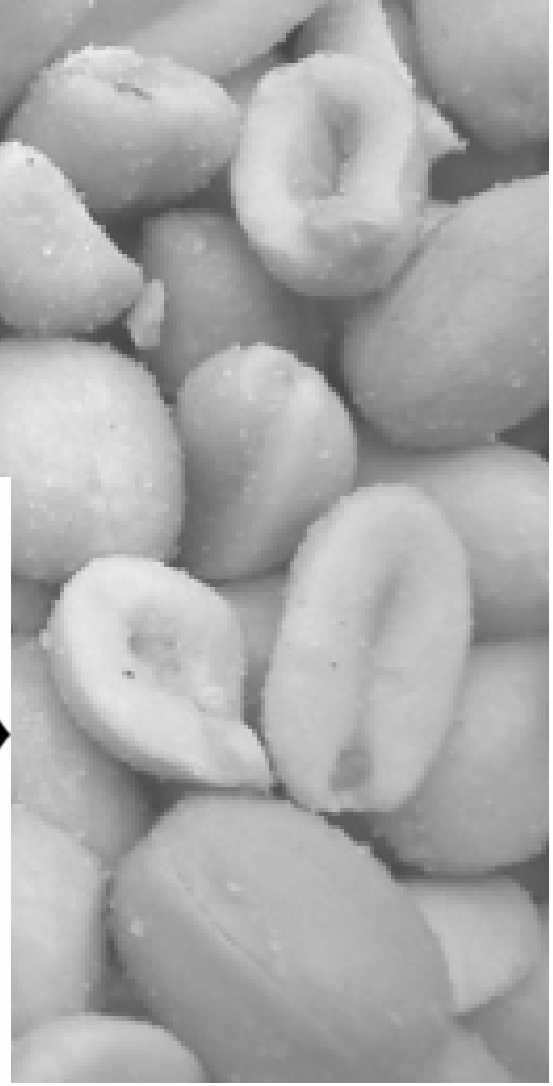
Assessment of the PCDD/F-formation potential

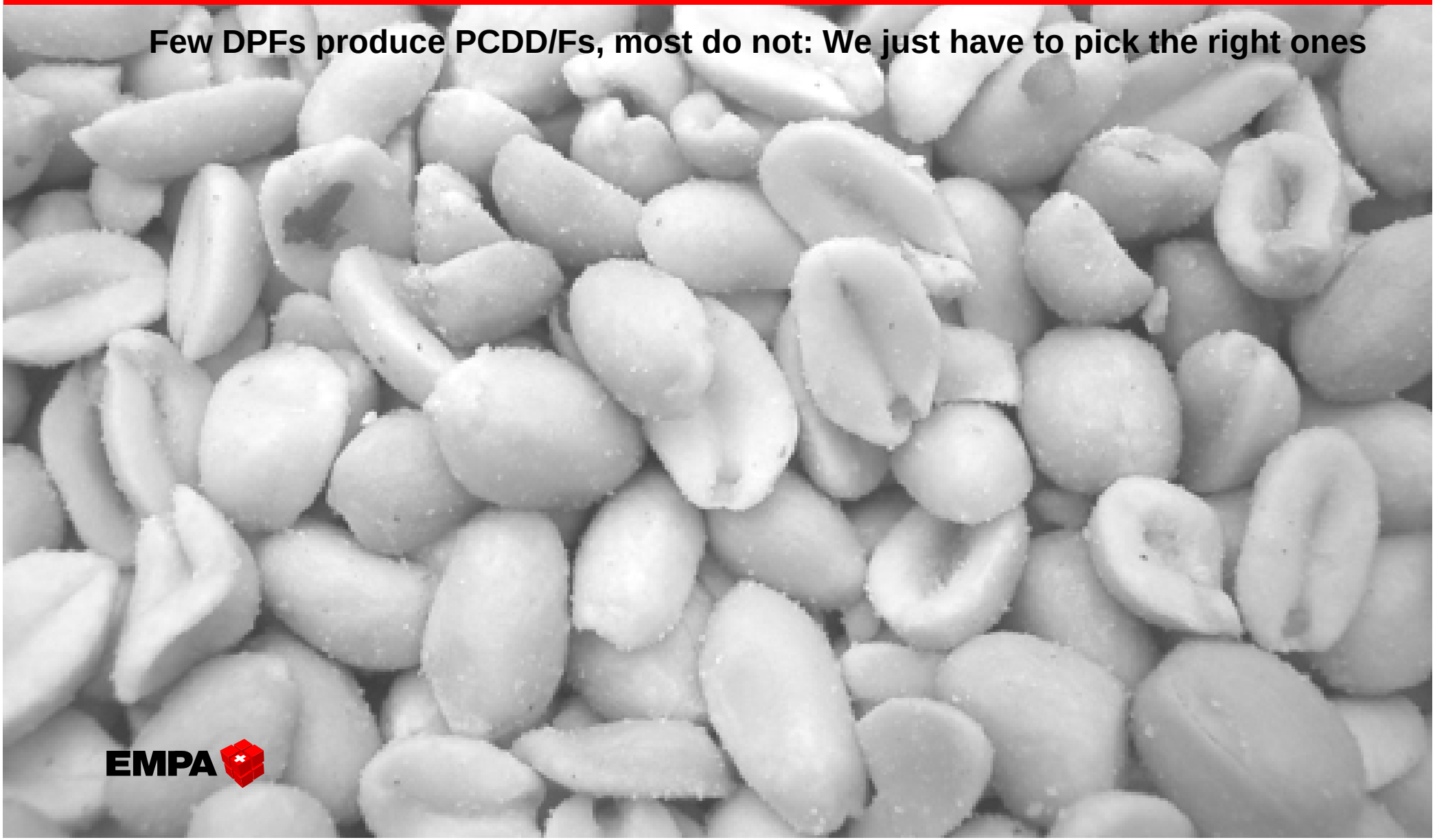
It is like eating peanuts, some peanuts contain aflatoxins, some do not





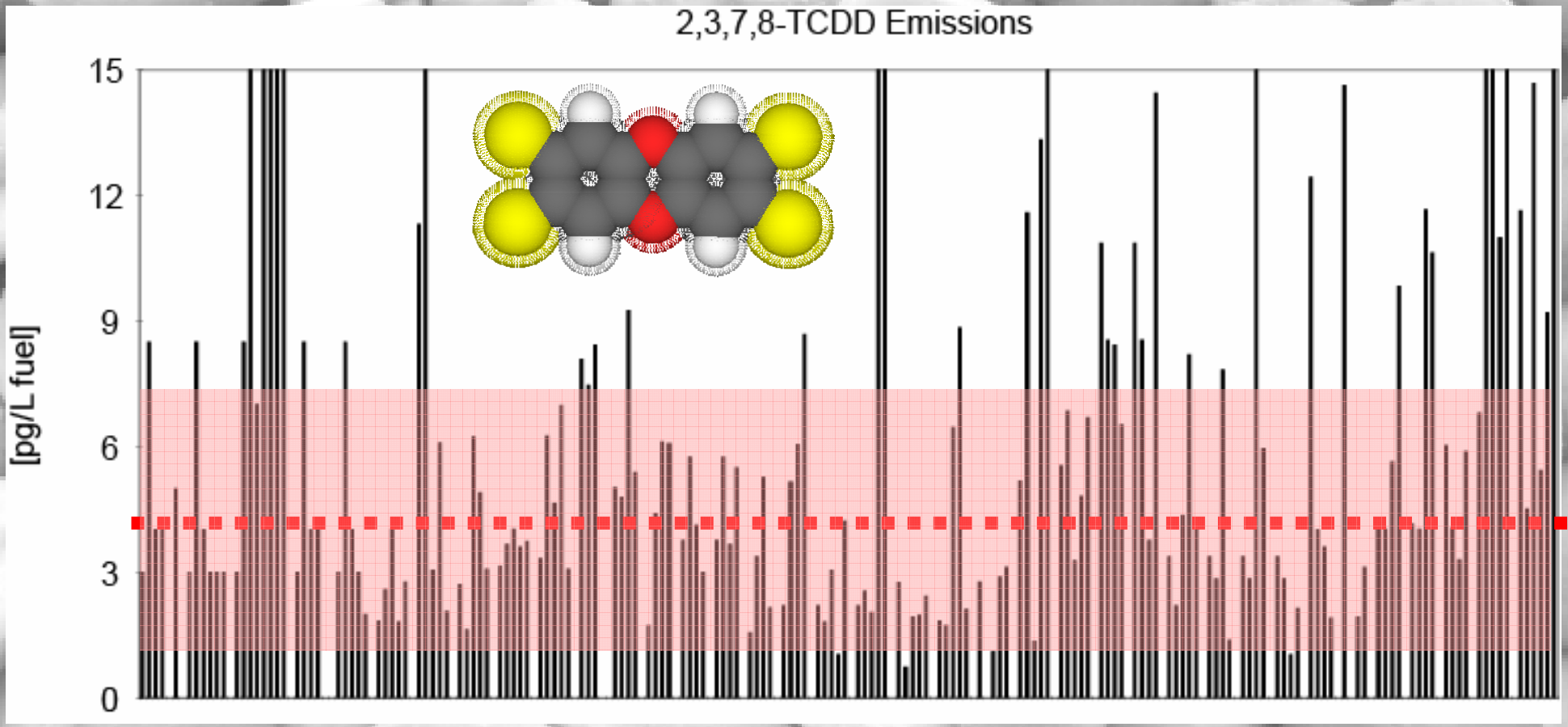


Assessment of the PCDD/F-formation potential



Assessment of the PCDD/F-formation potential

The dioxin formation potential of DPFs has to be investigated experimentally!



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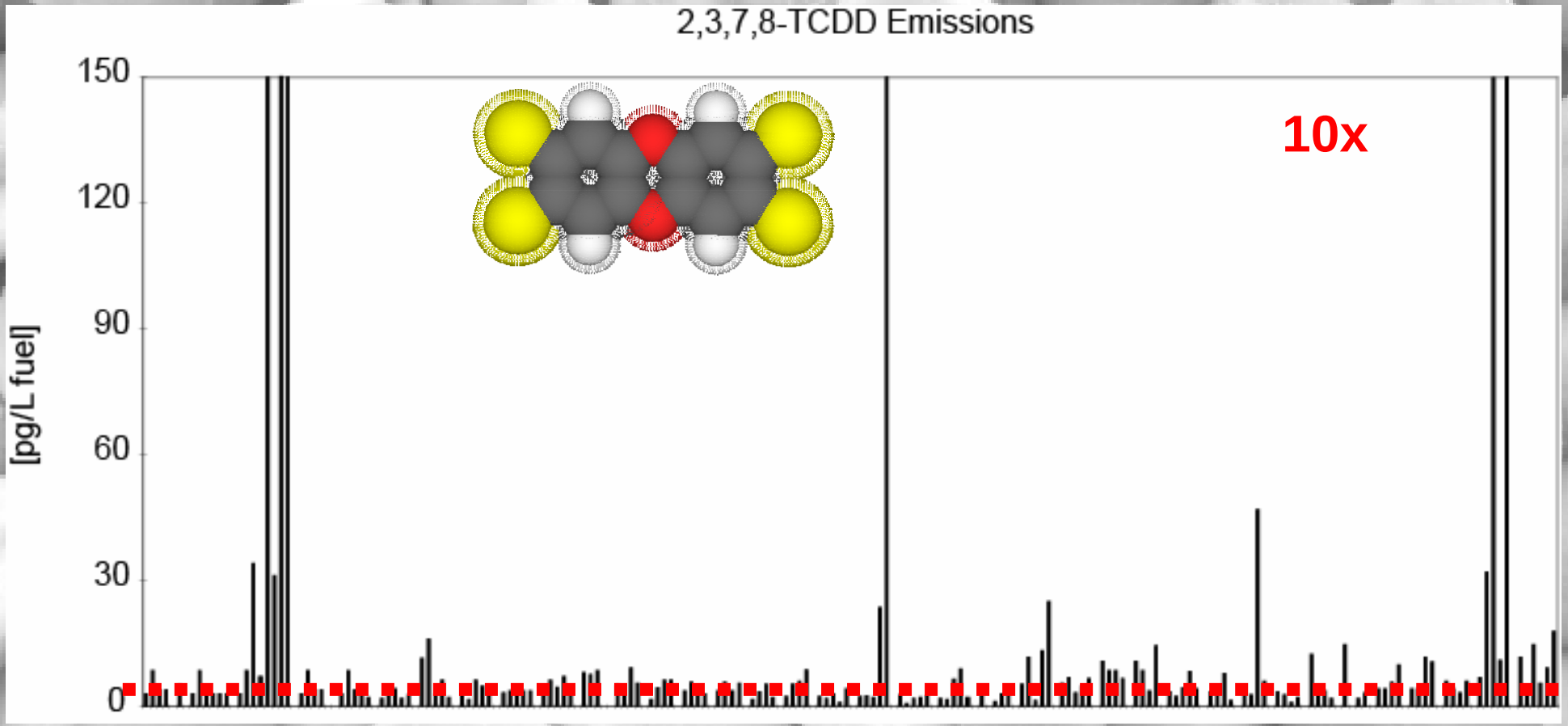
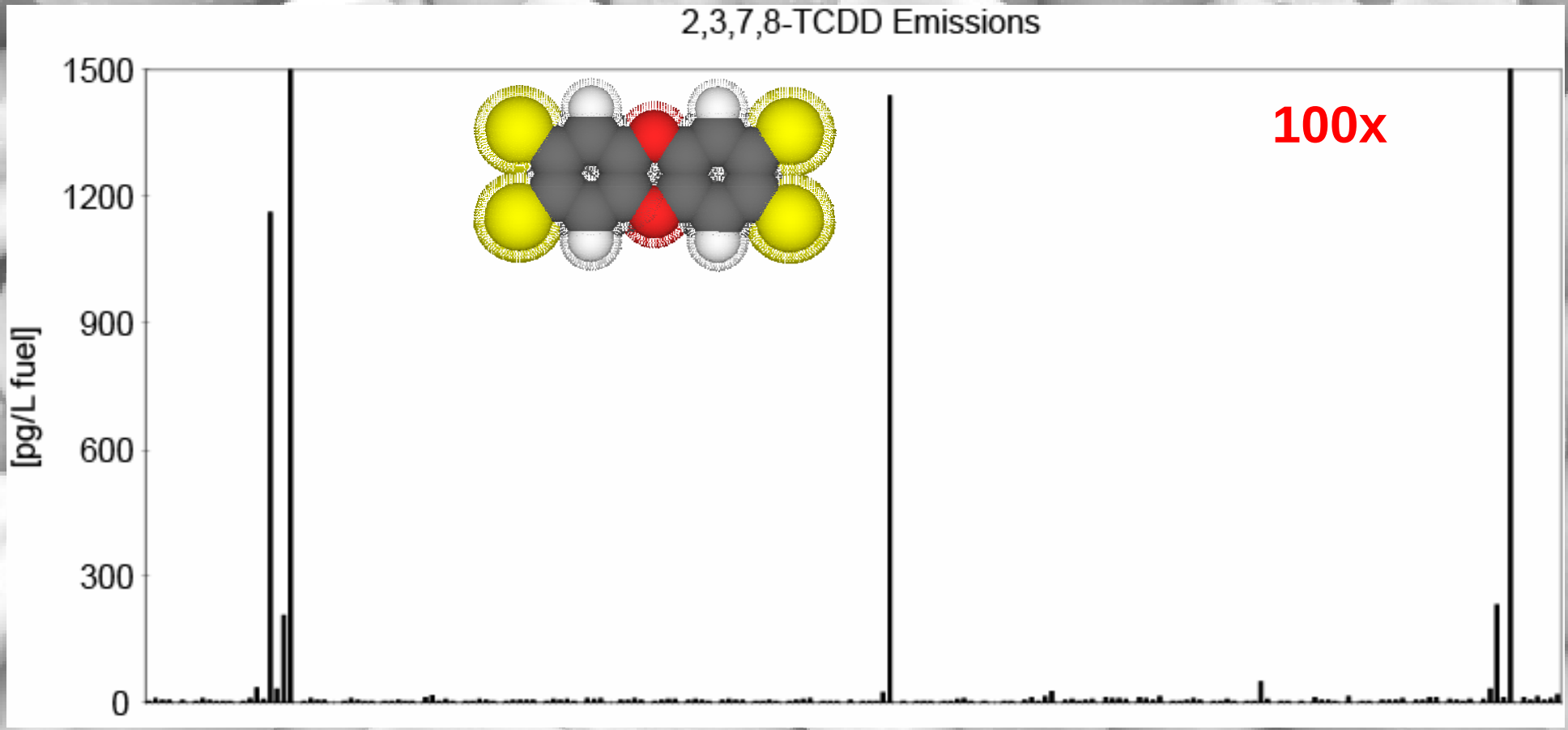


Assessment of the PCDD/F-formation potential

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



Heeb et al. Env. Sci. & Tech. 41 (2007) 5789-5794

Heeb et al. Env. Sci. & Tech. in press (2013)

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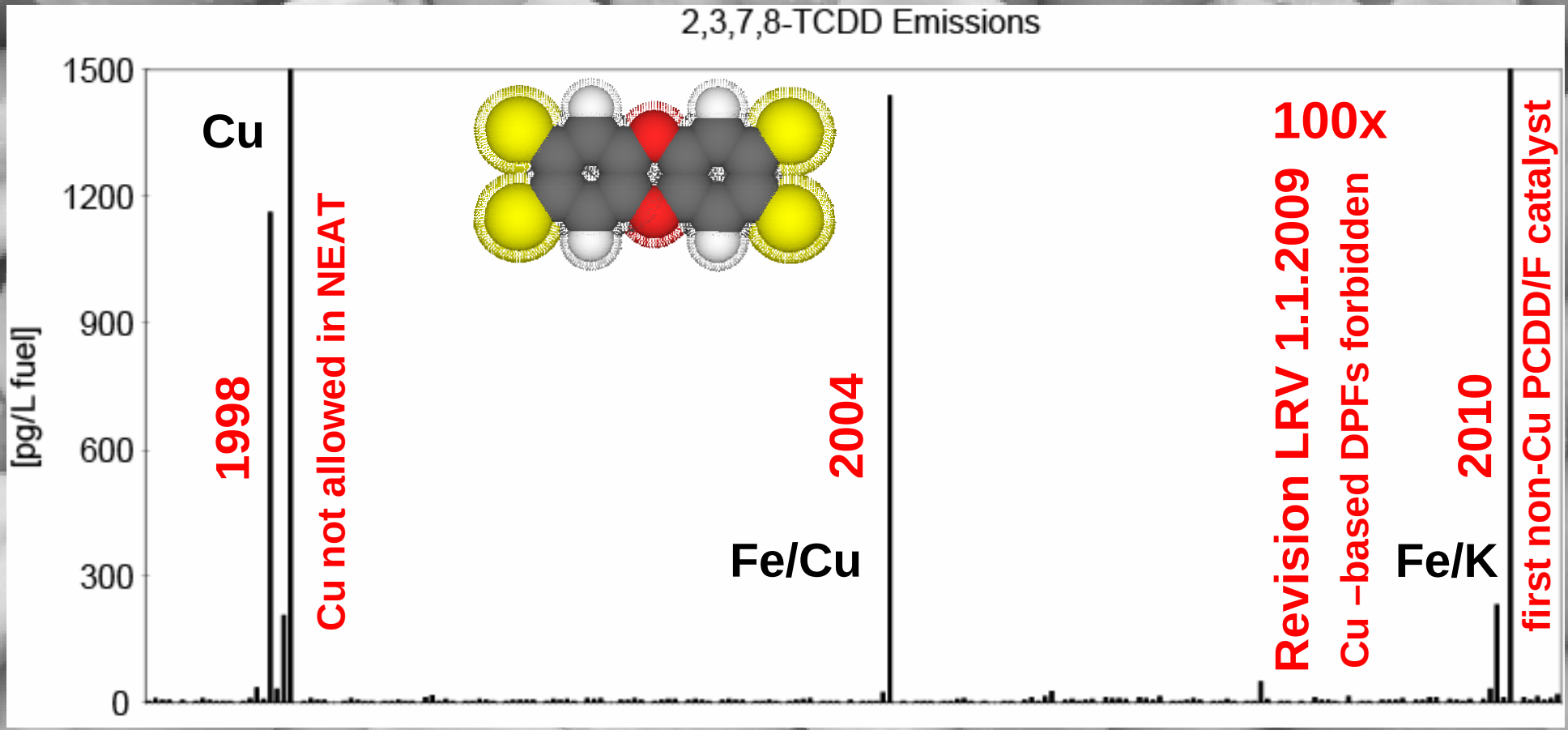
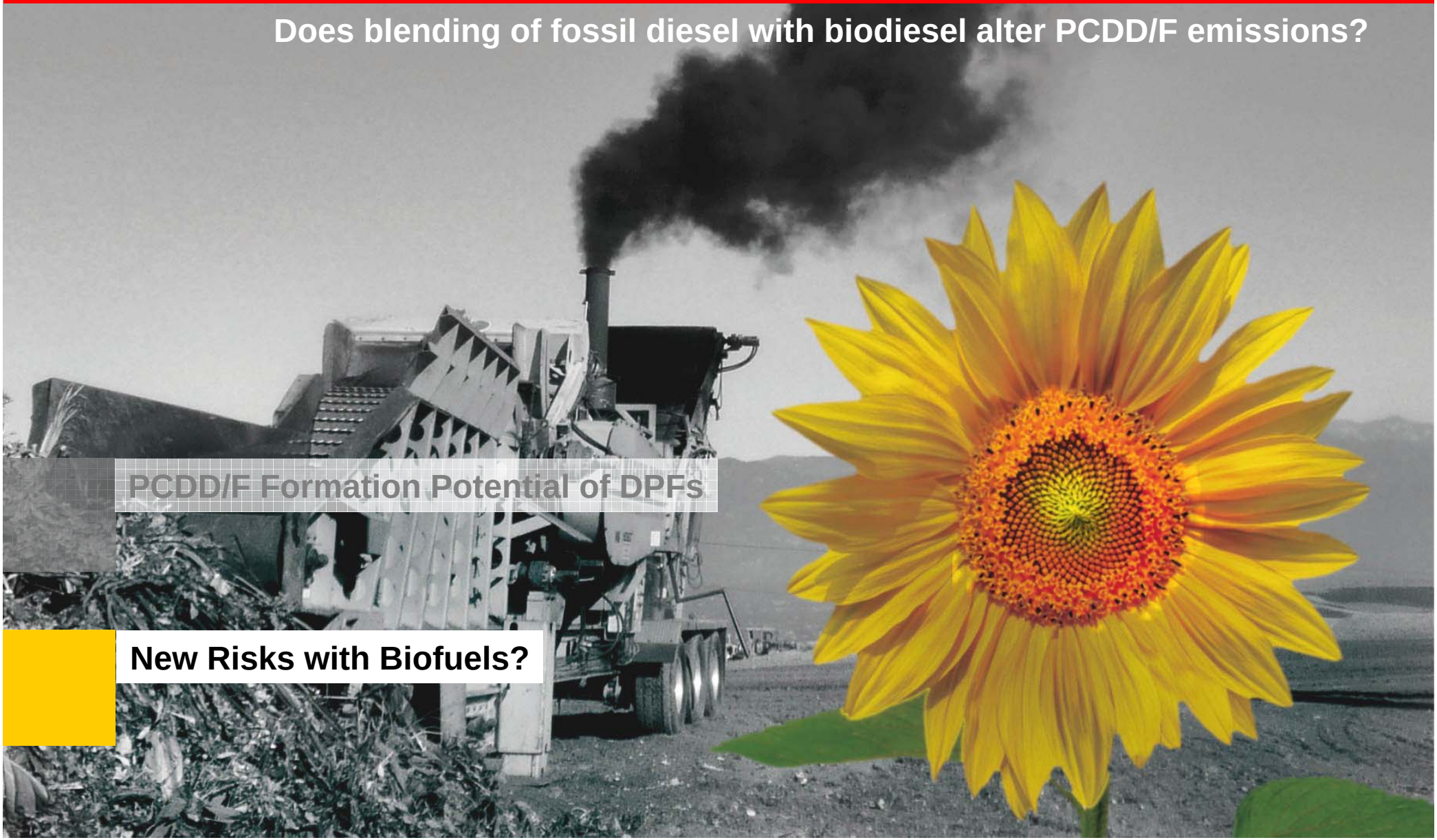


PCDD/F formation in catalytic DPFs: New risks with biofuels?

Does blending of fossil diesel with biodiesel alter PCDD/F emissions?



PCDD/F Formation Potential of DPFs

New Risks with Biofuels?

Benefit / risk assessment of biofuels

Benefit / risk assessment of biofuels

Biofuels are now produced and consumed, weather we like it or not!

Biofuels today:

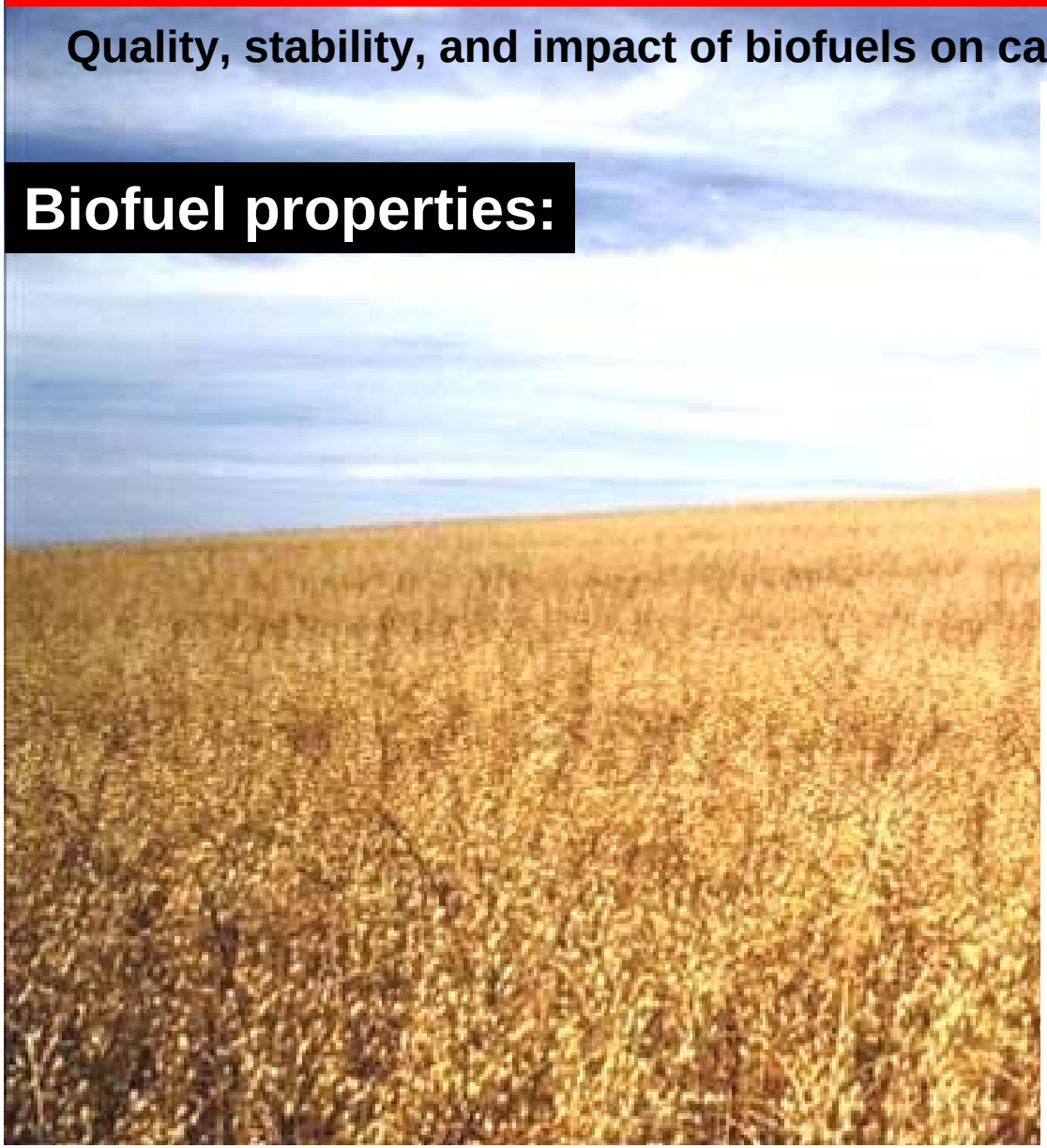
- Several 1st and 2nd generation biofuels are produced today. Bioethanol is a substitute for gasolines and fatty acid methyl esters (FAME) for diesel fuels
- Gasoline and diesel are increasingly blended with biofuels in the EU. Up to 20% in 2020, >2% in 2005, >5% in 2010, (Directive 2003/30 EC, May 8, 2003)
- The global biofuel market is growing, weather we like it or not!

Are biofuels part of a sustainable society?

Benefit / risk assessment of biofuels

Quality, stability, and impact of biofuels on catalytic converter technologies are issues

Biofuel properties:



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Wagistrasse 2 CH-8952 Schlieren Fon:+41-43 433 78 10 Fax:+41-43 433 78 1 www.intertek.ch / schlieren@intertek.com

Test Report No: 110049/02

Client:

Empa
Materials Science & Technology
Abt. 132
Überlandstrasse 129
CH-8600 Dübendorf

Test object: **Fatty acid methyl ester (FAME)**

Date of Receipt: 2010-01-19
Container: 1 can
Designation of sample: Biodiesel 206280
Order from: 2010-01-19
Compiler: Norbert Heeb
Specification: EN 14214

Property	Unit		Result	Limits Low	Limits High	Test Method
Density at 15 °C	kg/m³		884,4	860	900	EN ISO 12185
Viscosity at 40°C	mm²/s		4,759	3,50	5,00	EN ISO 3104
Flash point	°C		174,0	101		EN ISO 3679¹
Oxidation stability, 110°C	h	(!)	1,8	6,0		EN 14112¹ ²
Acid Number	mg KOH/g		<0,01		0,50	EN 14104¹
Phosphorus	mg/kg		0,8		4,0	EN 14107
Carbon residue (10% Dest.)	Mass.%	(!)	0,40		0,30	ISO 10370 mod.¹
Water	mg/kg	(!)	520		500	EN ISO 12937
Particulate matter	mg/kg		2		24	EN 12662
Copper corrosion (50°C)			1a		1	EN ISO 2160
Sulphated ash	g/100g		<0,001		0,02	ISO 3987¹ ²
Sulfur	mg/kg		5,2		10,0	EN ISO 20846
Cetane number			52,3	51,0		ISO 5165
Ester content	Mass.%	(!)	94,4	96,5		EN 14103¹ ²
Iodine Value	g Iod/100g		106,1		120	EN 14111¹
Linolenic Acid methylesters	Mass.%		8,3		12,0	EN 14103¹ ²
Methanol	Mass.%		0,08		0,20	EN 14110¹
Poly unsaturated methylesters (>=4 double bonds)	Mass.%		<1		1	EN 14103¹ ²
Glycerines (GC)						EN 14105¹ ²
Monoglyceride	Mass.%		0,43		0,80	
Diglyceride	Mass.%	(!)	0,74		0,20	
Triglyceride	Mass.%	(!)	2,56		0,20	
Free Glycerol	Mass.%		0,02		0,02	
Total Glycerol	Mass.%	(!)	0,5		0,25	
Group II metals (Ca+Mg)	mg/kg	(!)	5,6		5,0	EN 14538
Calcium	mg/kg		5,2			
Magnesium	mg/kg		0,4			
Group I metals (Na+K)	mg/kg		3,8		5,0	EN 14538²
Sodium	mg/kg		0,4			
Potassium	mg/kg		3,4			

Remark: The test results are only valid for the analysed sample. The utilisation of the report for advertising purposes, or reference to it in publications, requires the permission of Intertek Caleb Brett (Schweiz) AG. Details of the analyses (norms, SOPs), as well as limits of detection and standard deviations can be obtained from Intertek Caleb Brett (Schweiz) AG. Files, including reports, are retained for ten years at Intertek Caleb Brett (Schweiz) AG. The raw data is held at Intertek Caleb Brett (Schweiz) AG for ten years. The sample is held at Intertek Caleb Brett (Schweiz) AG for at least one month after the report has been completed.

¹ Subconctractor, ² Method not accredited

Benefit / risk assessment of biofuels

Quality, stability, and impact of biofuels on catalytic converter technologies are issues

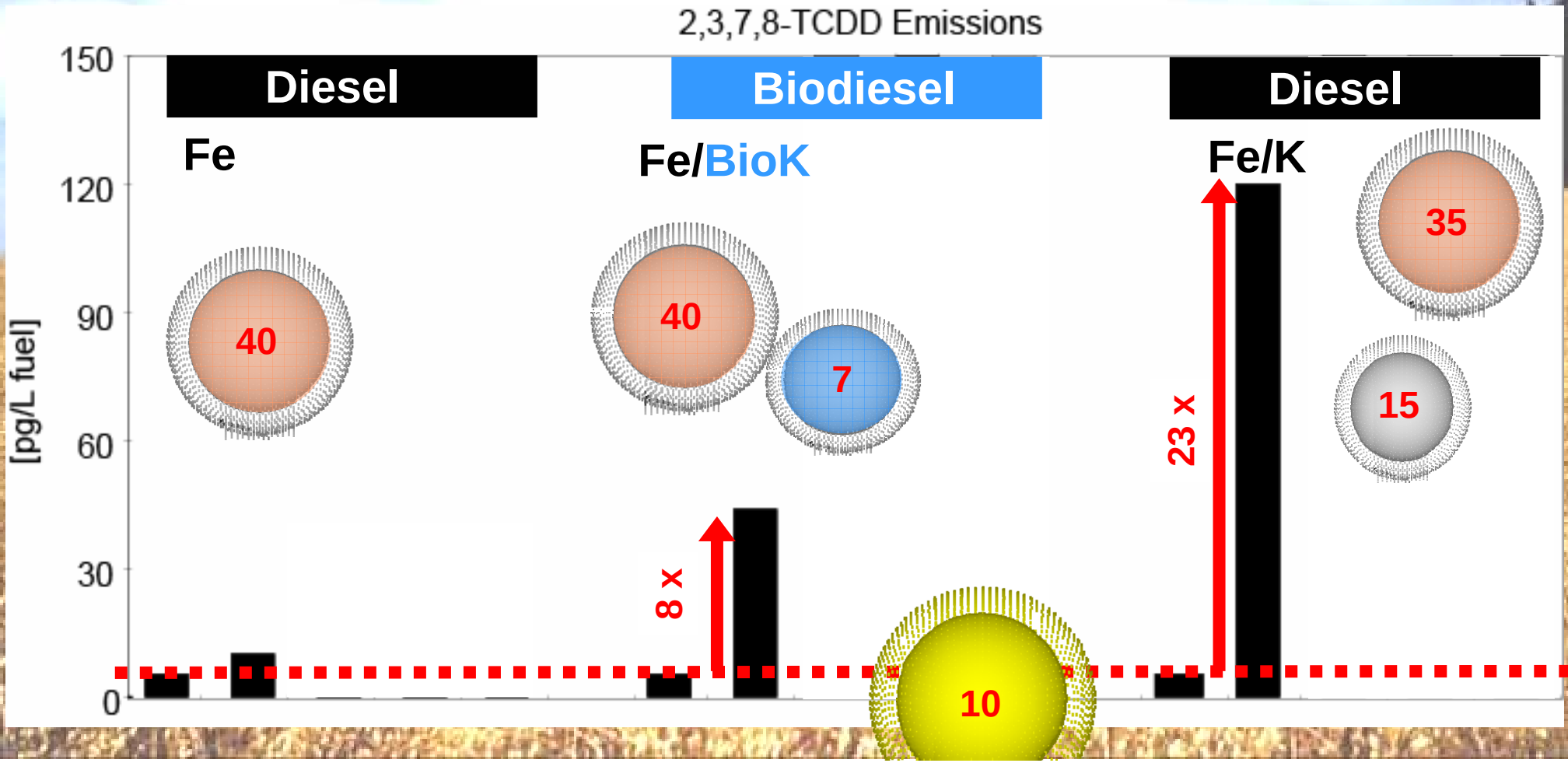
Biofuel compostion:

Property	Unit		Result	Limits Low	Limits High	Test Method
Group II metals (Ca+Mg)	mg/kg	5.2	5,6		5,0	EN 14538
Calcium	mg/kg		5,2			
Magnesium	mg/kg		0,4			
Group I metals (Na+K)	mg/kg		3,8		5,0	EN 14538[2]
Sodium	mg/kg	3.4	0,4			
Potassium	mg/kg		3,4			

New ash components

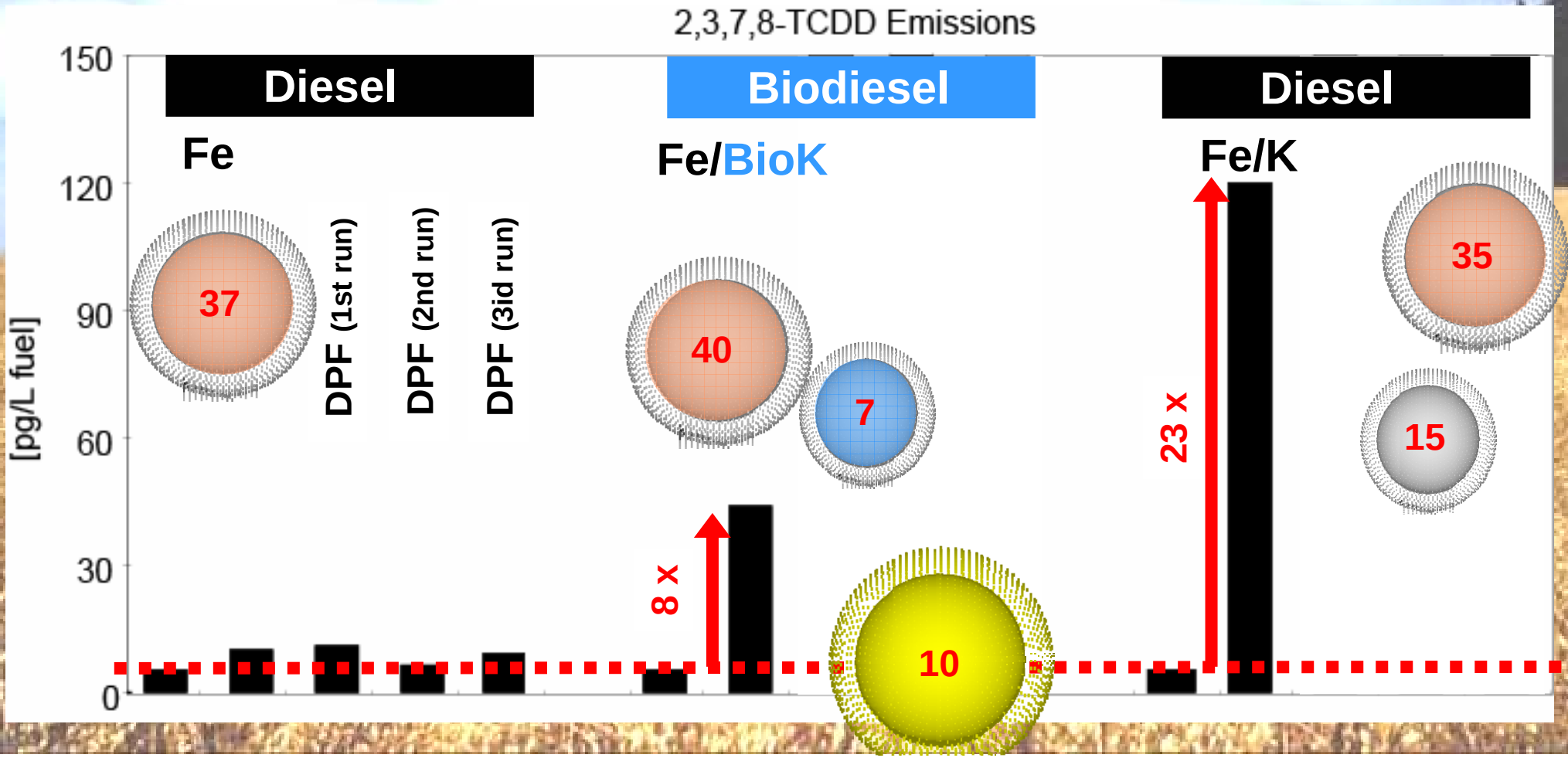
PCDD/F Formation Potential of DPFs: New Risks with Biofuels?

Combustion of diesel with additives without DPF is not allowed. Is 7 ppm K an additive?



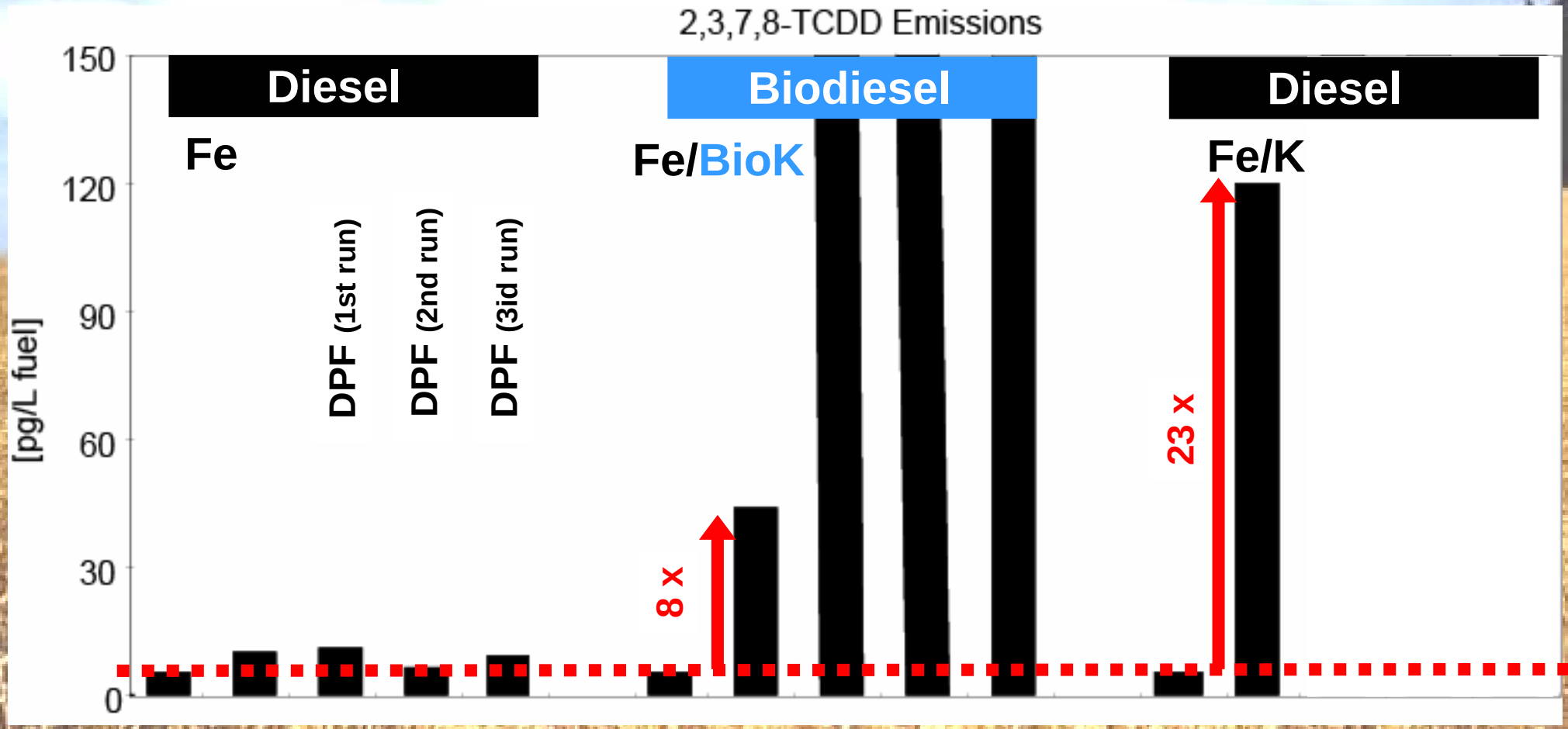
PCDD/F Formation Potential of DPFs: New Risks with Biofuels?

Fe-catalyzed DPFs have a low dioxin formation potential, even under worst case



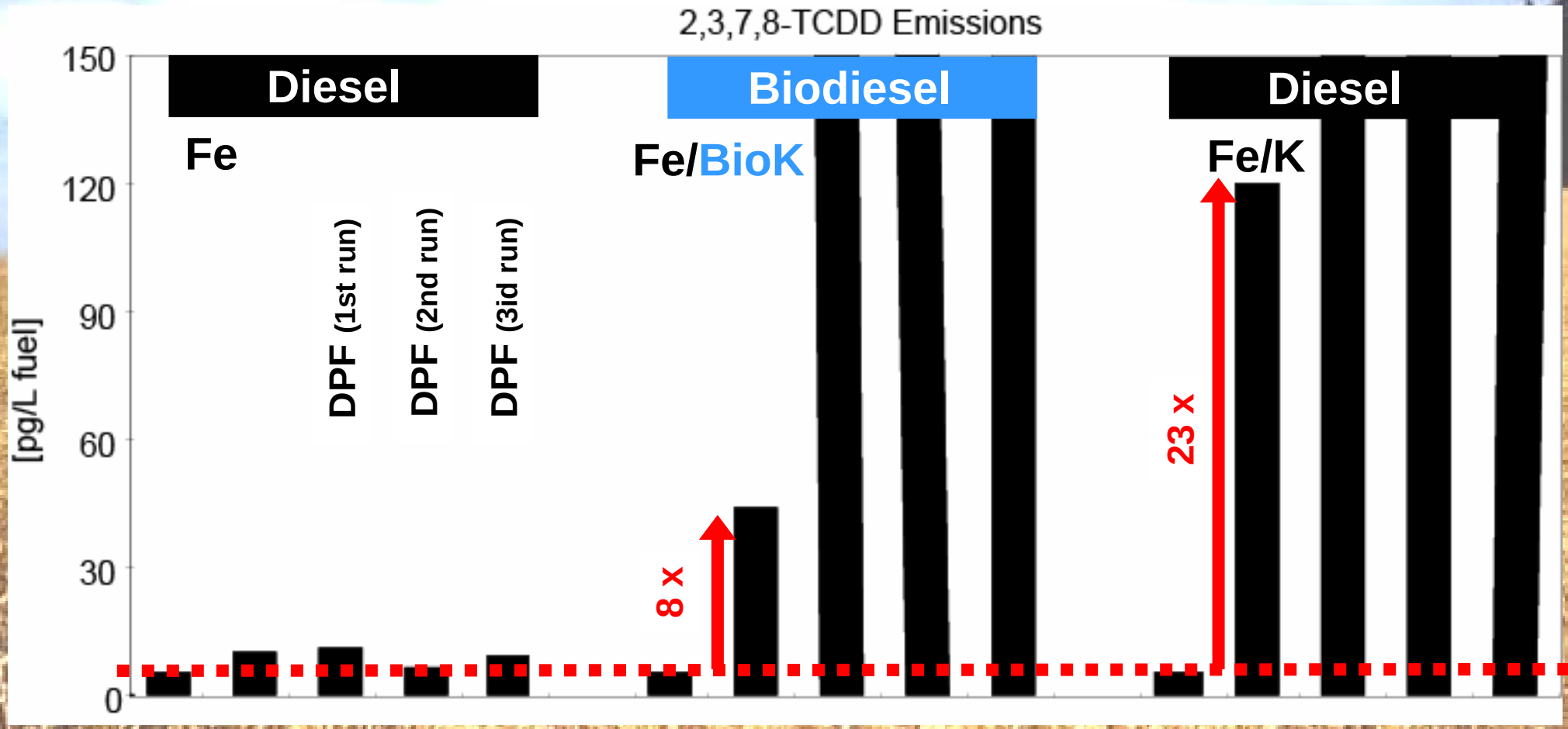
PCDD/F Formation Potential of DPFs: New Risks with Biofuels?

A synergistic effect of the biofuel components and the Fe catalyst.



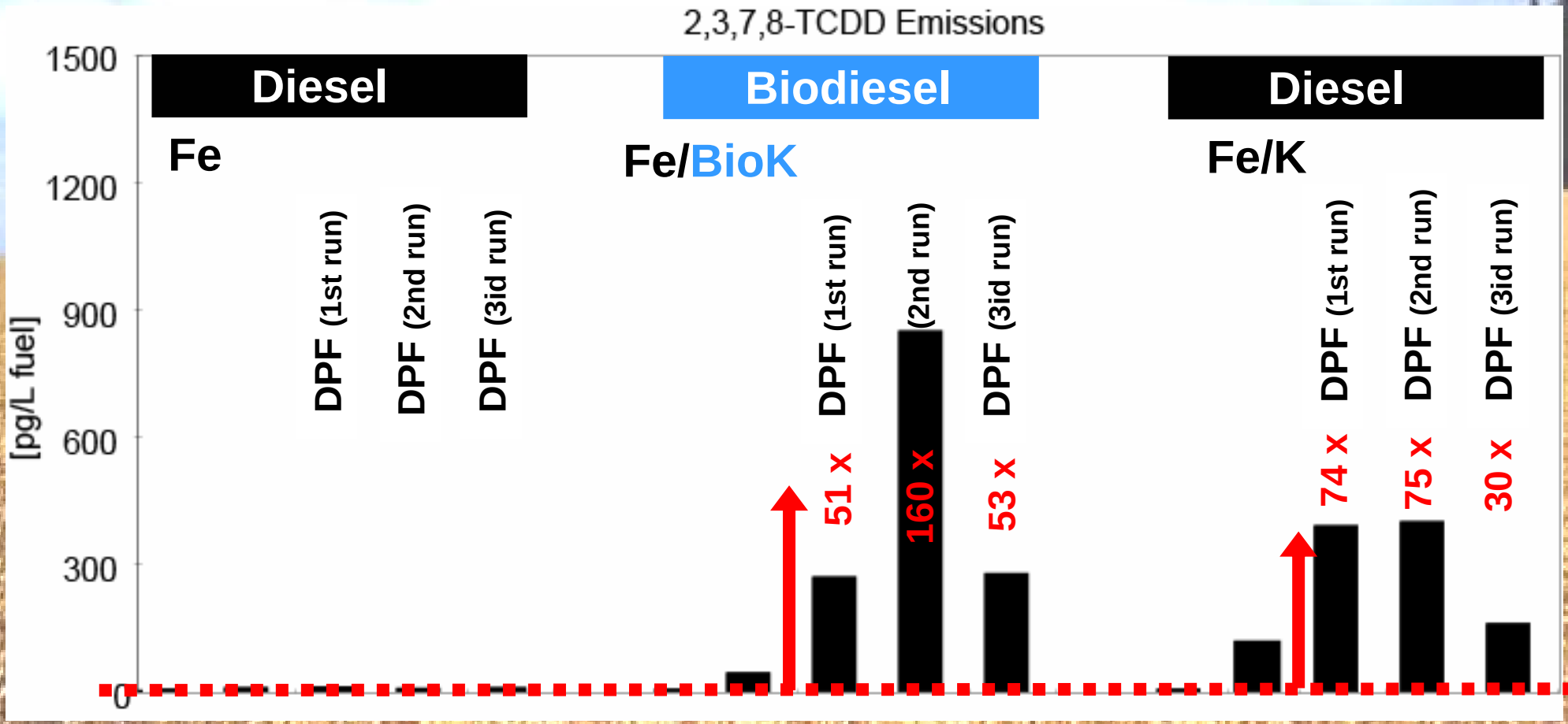
PCDD/F Formation Potential of DPFs: New Risks with Biofuels?

Substantial PCDD/F Formation in both Fe/K-based DPFs



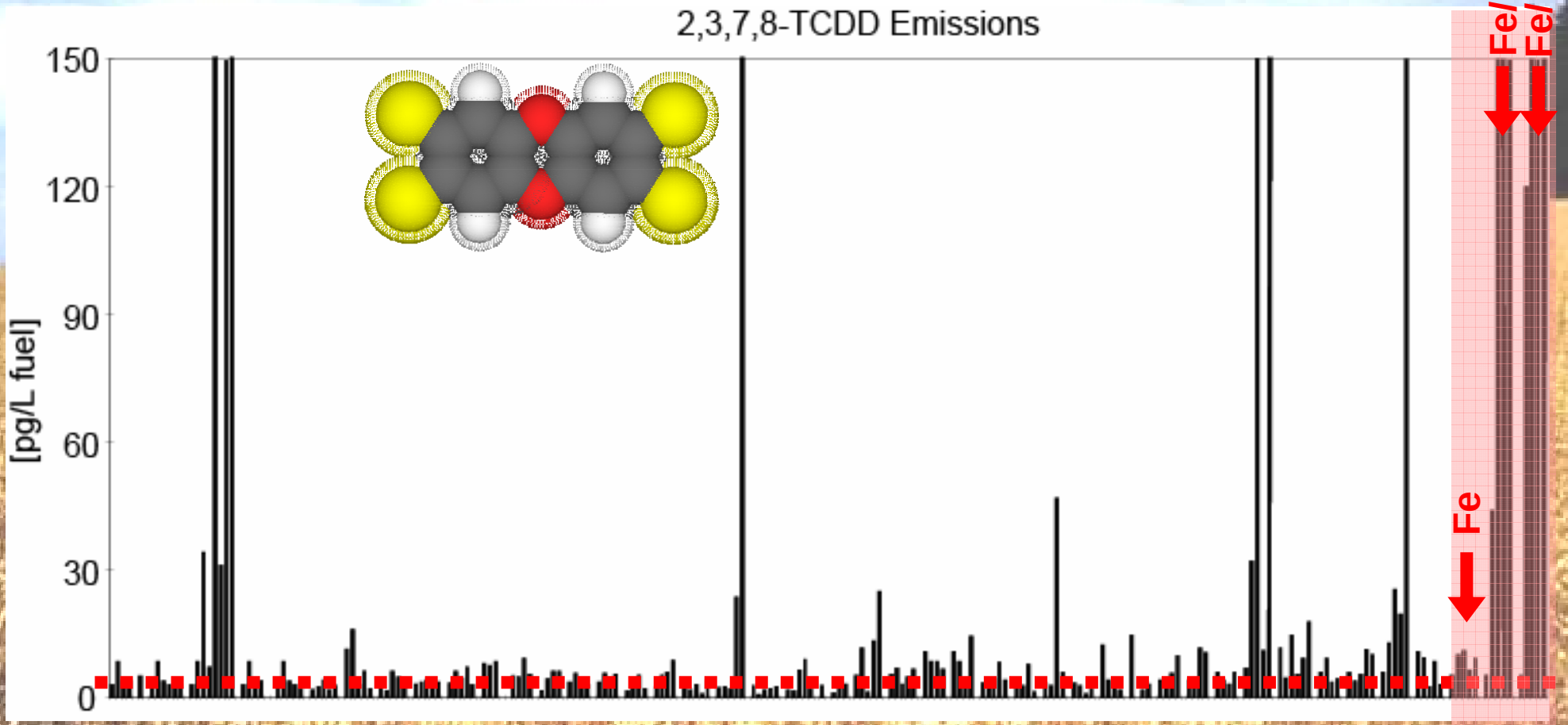
PCDD/F Formation Potential of DPFs: New Risks with Biofuels?

Nearly two orders of magnitude increase of TCDD emissions in both DPFs



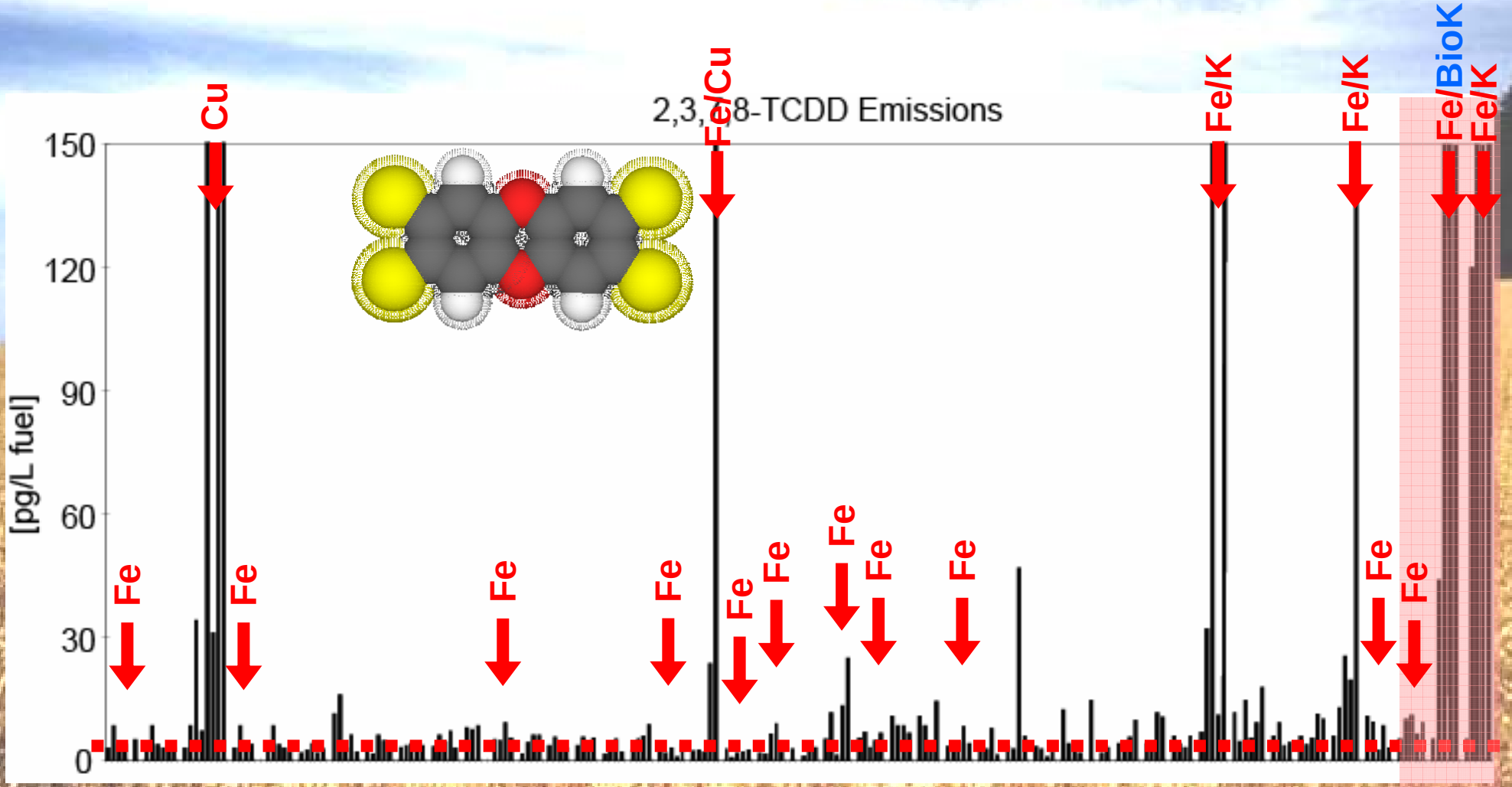
PCDD/F Formation Potential of DPFs: New Risks with Biofuels?

Potassium promotes a PCDD/F formation in Fe-catalyzed DPFs!



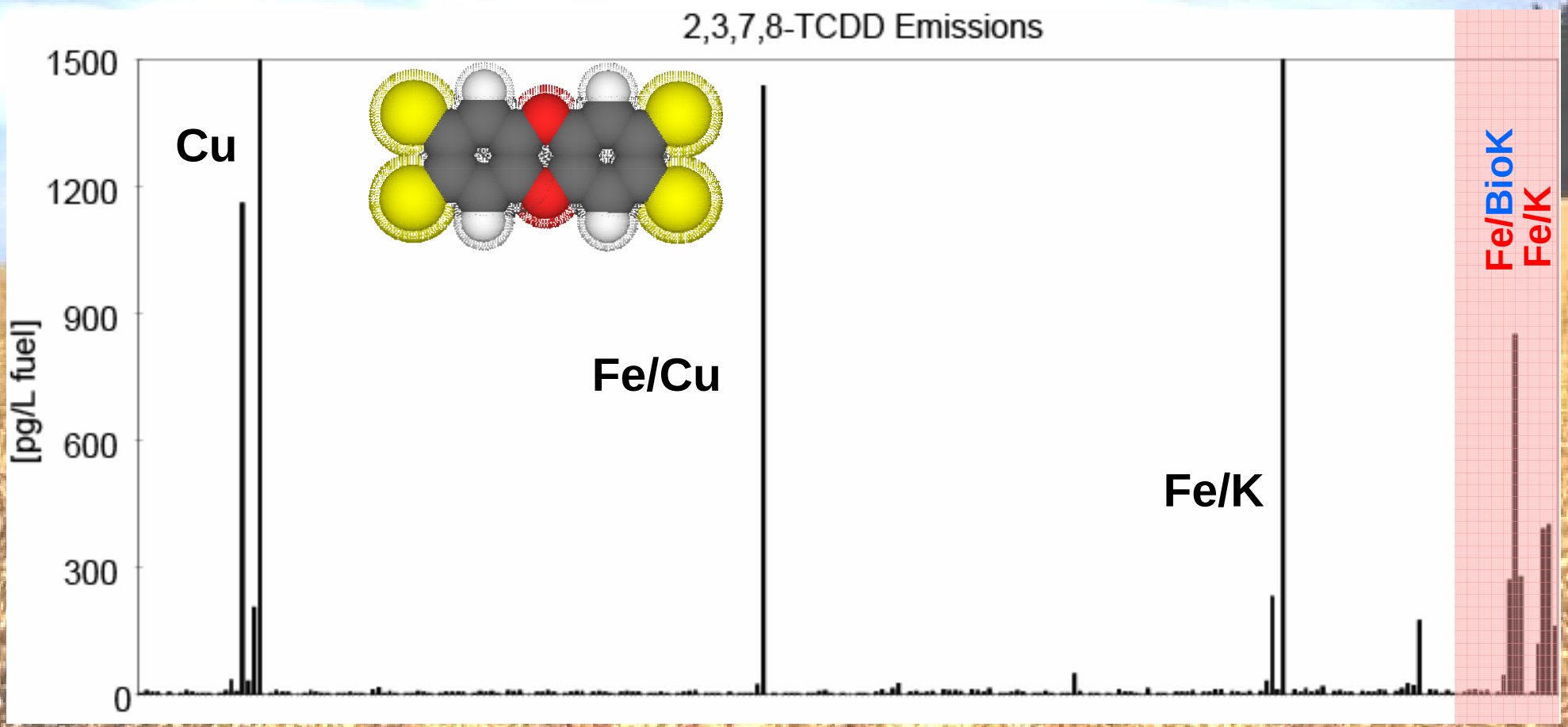
PCDD/F Formation Potential of DPFs: New Risks with Biofuels?

There are more DPFs out with increased PCDD/F risks!



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

Certain DPFs are not compatible with certain biofuels!



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

The PCDD/F formation potential in DPFs is not peanuts!

Conclusions:

- **The chemical nature of the catalyst is most important**
- **Biofuels can alter the dioxin-formation potential of DPFs**
- **There are DPFs out, which may become active over time when used with biofuels**

- **PCDD/F potential of DPFs has to be tested, also with biofuels**

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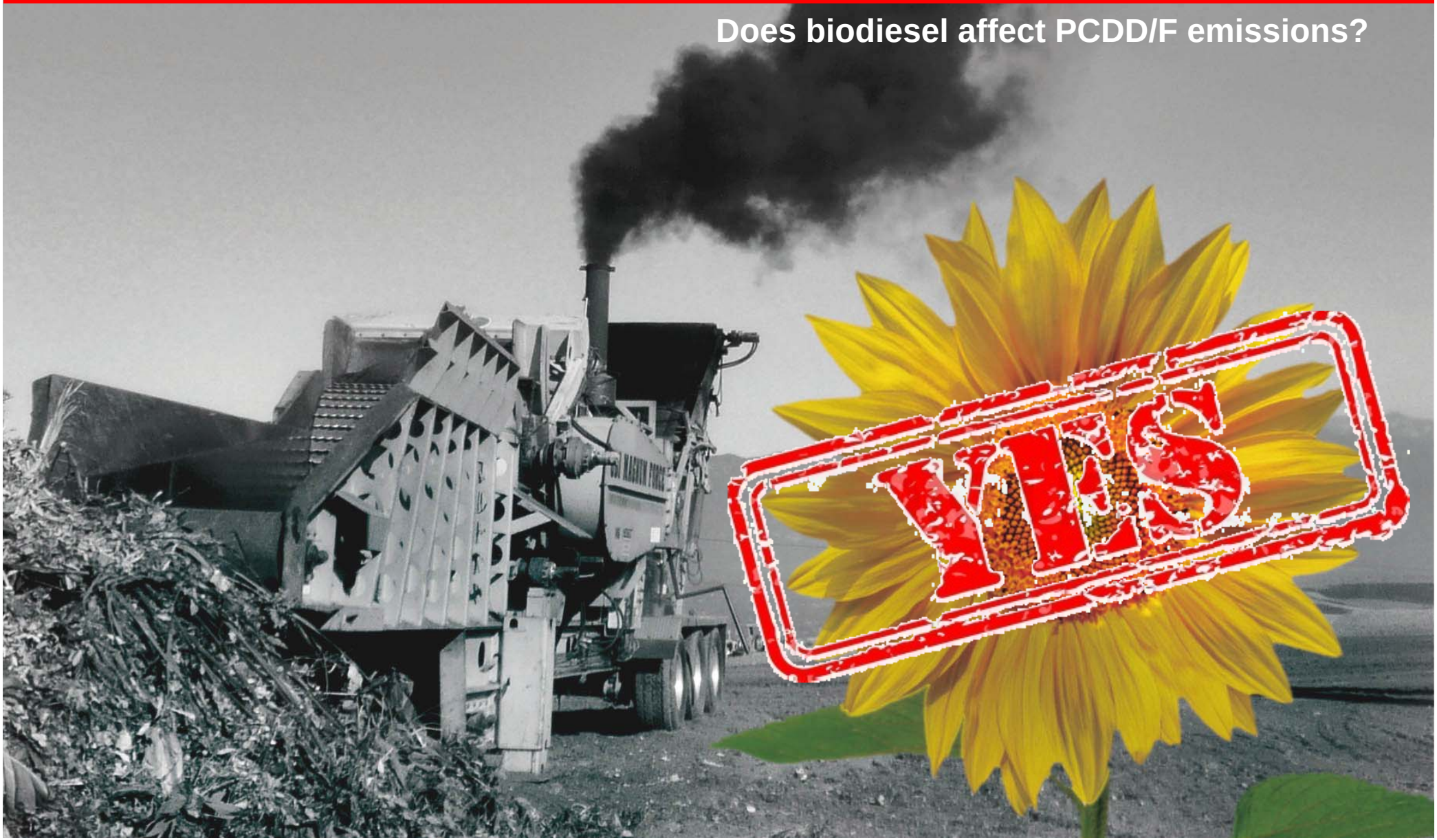
PCDD/F Formation Potential of DPFs: New Risks with Biofuels?



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

A combined effort with many important contributions

Thanks:

- **VERT team:** Andreas Mayer, TTM, Niederrohrdorf

  Jan Czerwinski, Yan Zimmerli, Claudio Chiesura, Sandro Napoli, Tobias Neubert, Thomas Hilfiker, Jean-Luc Petermann, Peter Bonsack, Samuel Bürki, Uni. Appl. Sci., Biel. Markus Kasper, Adrian Hess, Thomas Mosimann, Matter Aerosol, Wohlen Hans Jaeckle, Urs Debrunner, Oliver Schumm, Intertek Caleb Brett, Schlieren.

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