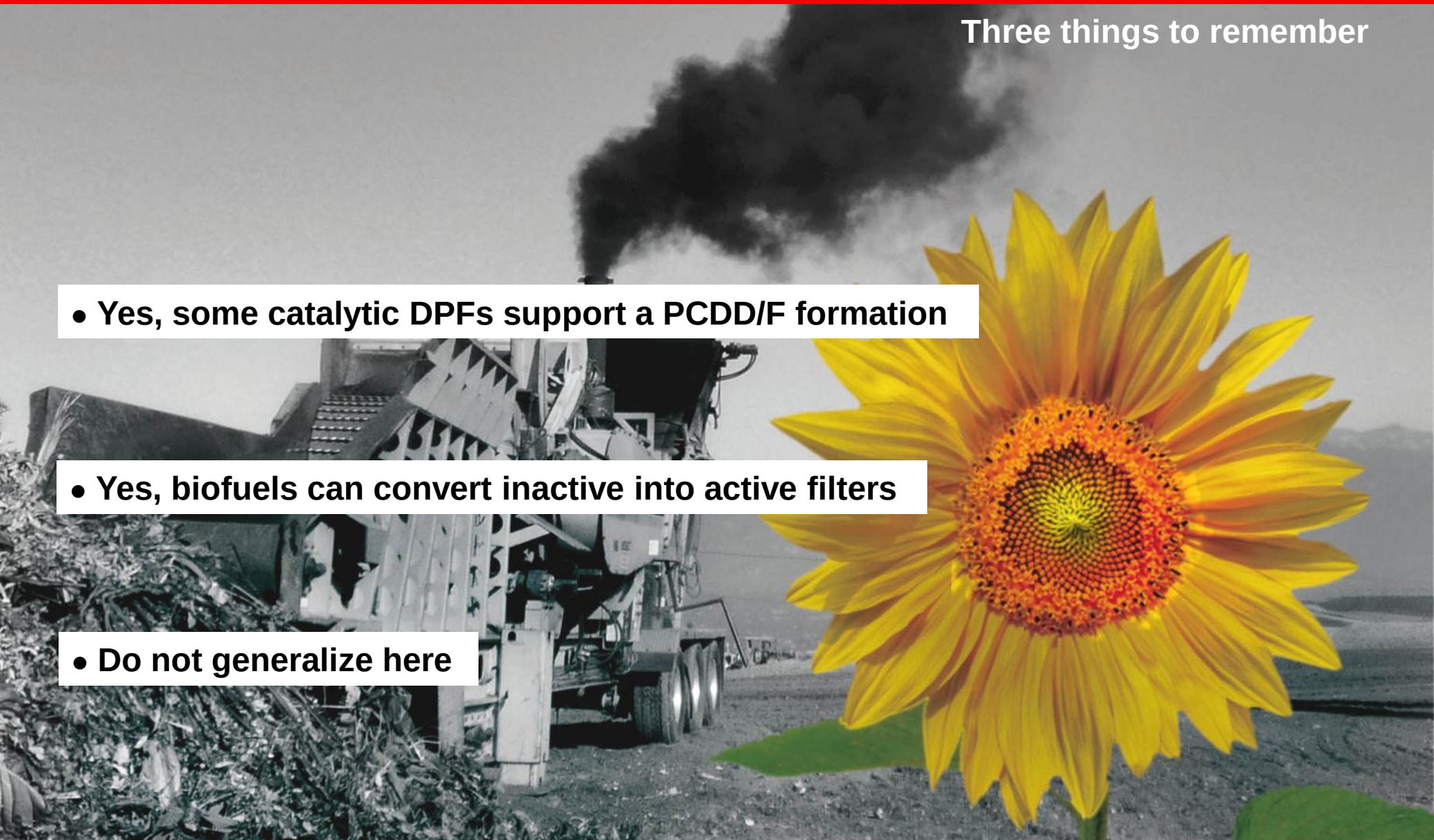
PCDD/Fs are not only generated by copper catalysis: the inconvenient truth about biofuels

6th VERT Forum: Particle Filter Technologies, both for diesel and GDI vehicles

Dübendorf, March 20, 2015

PCDD/Fs are not only generated by copper catalysis: the inconvenient truth about biofuels



Three things to remember

- Yes, some catalytic DPFs support a PCDD/F formation
- Yes, biofuels can convert inactive into active filters
- Do not generalize here

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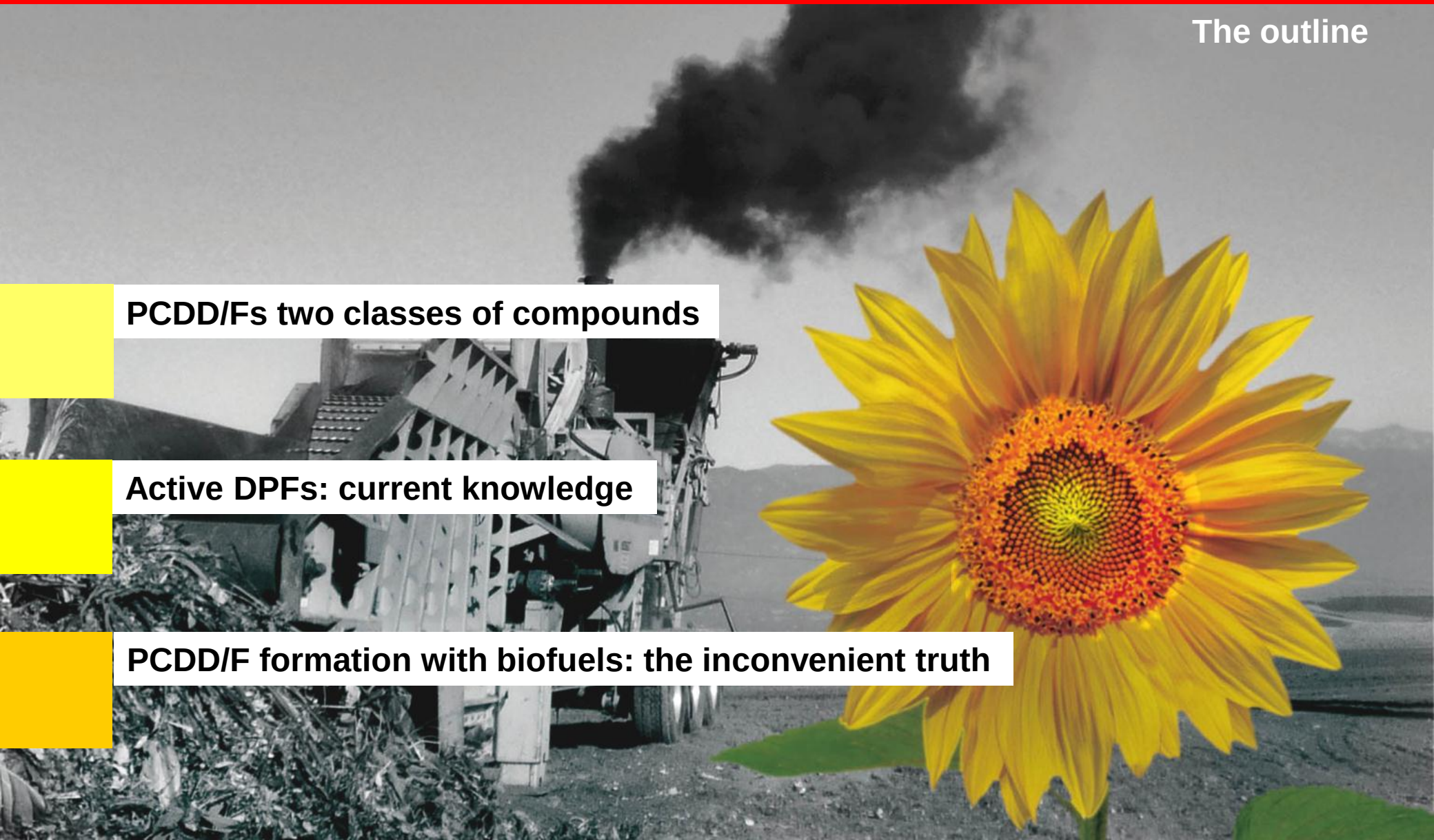


The outline

PCDD/Fs two classes of compounds

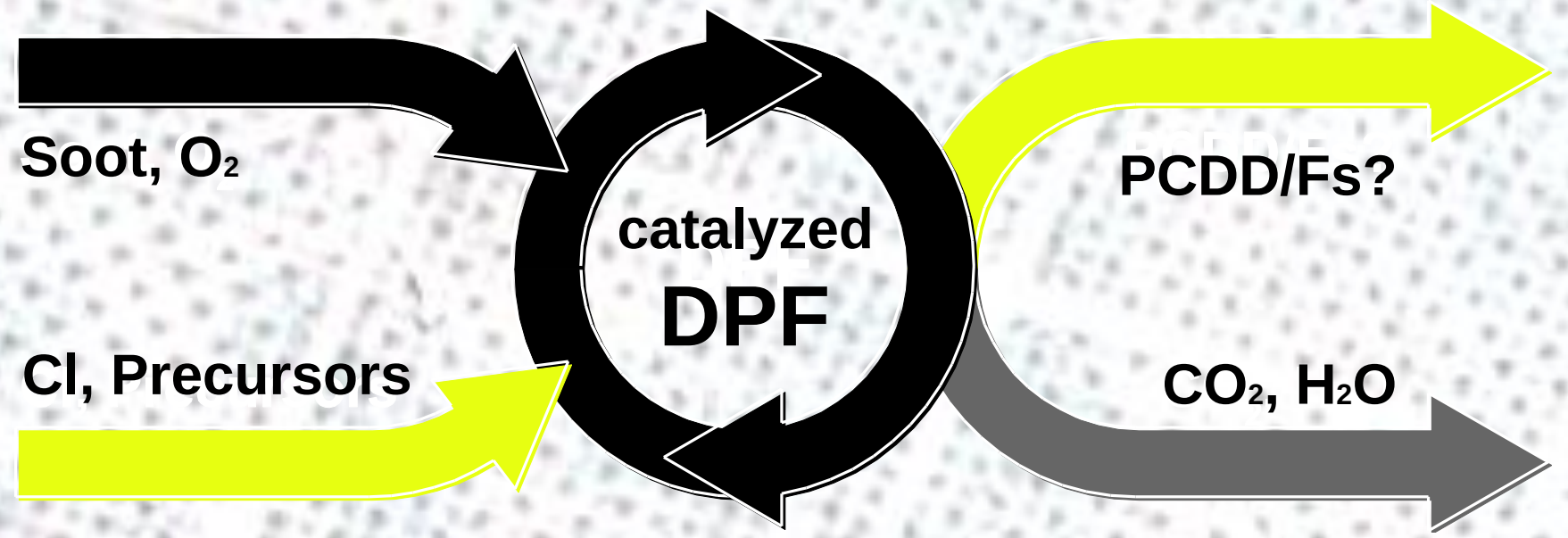
Active DPFs: current knowledge

PCDD/F formation with biofuels: the inconvenient truth

VERT Secondary emissions test

Yes, there are risks for a PCDD/F formation in DPFs - they should be assessed!

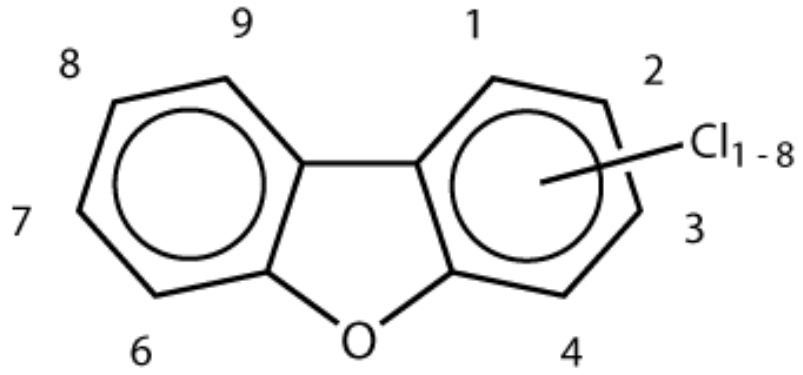
PCDD/F Formation Potential

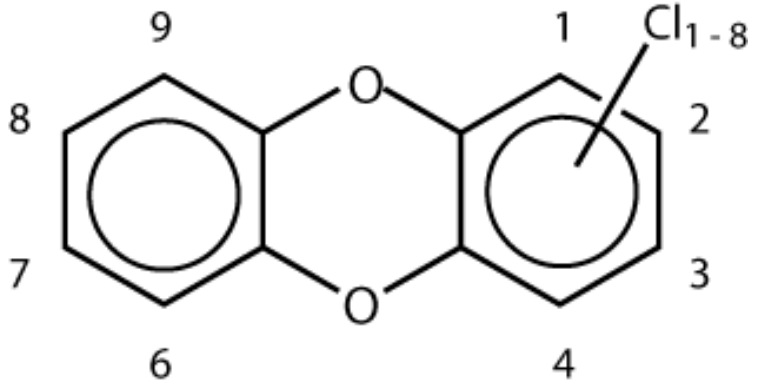


PCDD/Fs: Two classes of compounds

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

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

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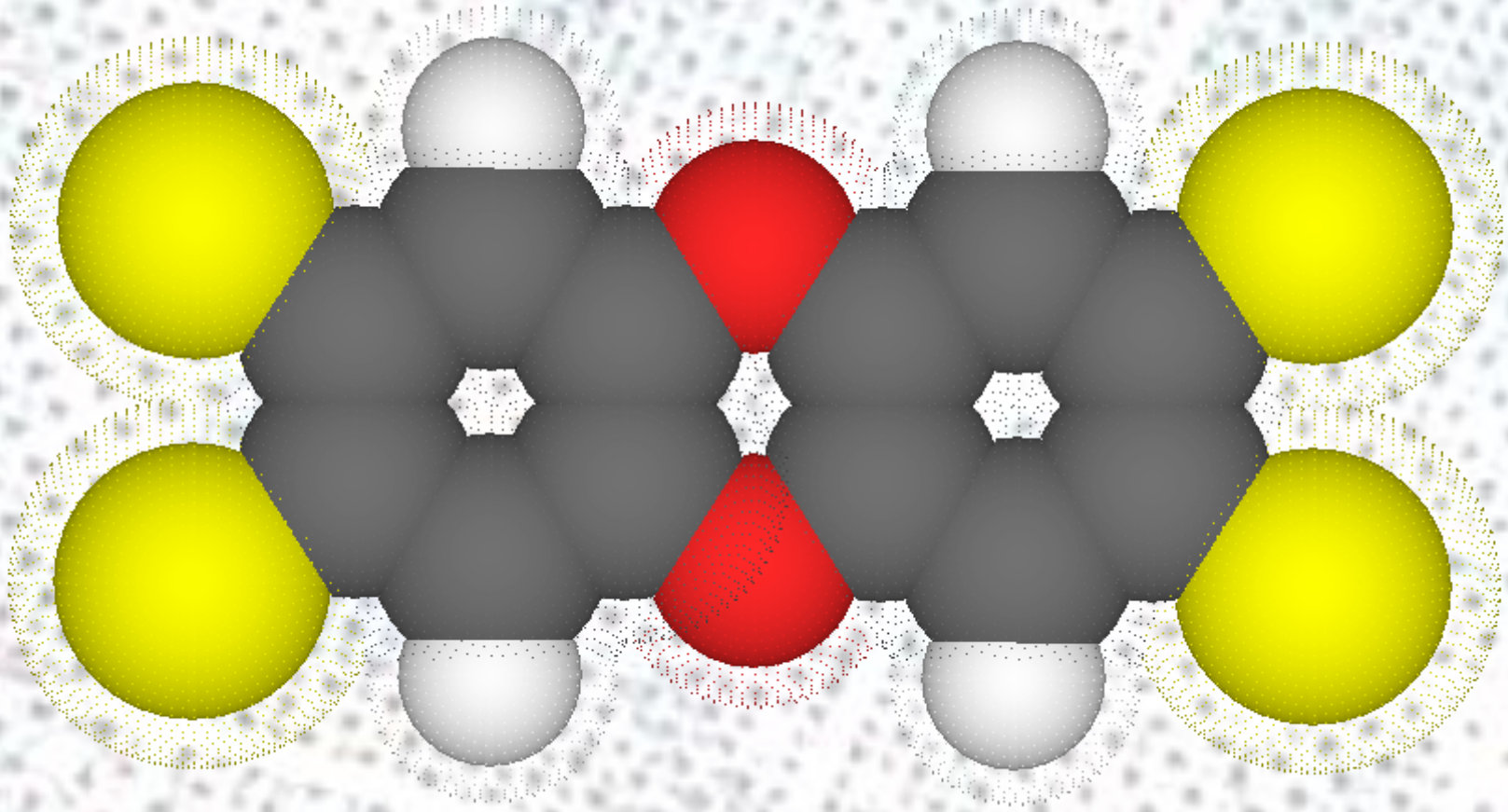
PCDD/Fs: toxic at pg-quantities

2,3,7,8-TCDD – the most toxic congener!

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



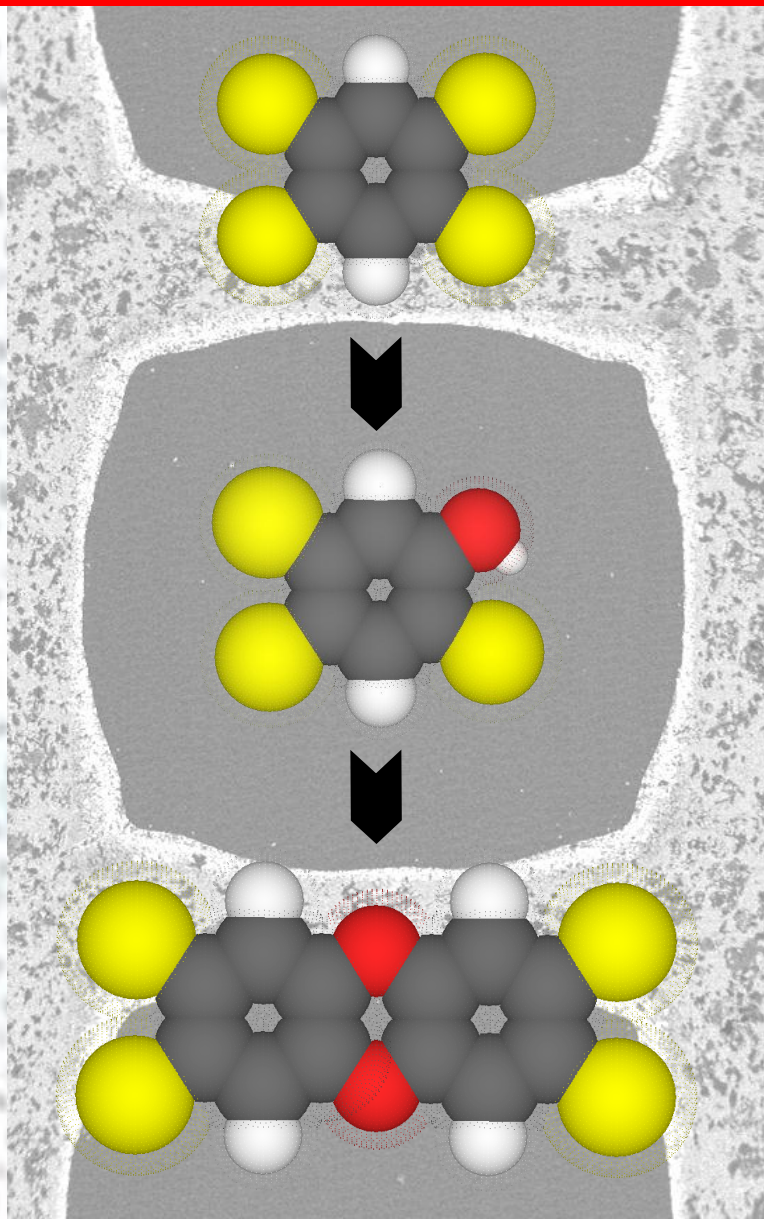
Dioxin formation in Seveso (1976)

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, non-volatile, particle-bound
- Should be trapped in DPFs 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

Attempted assassination of Viktor Yushchenko, former President of the Ukraine

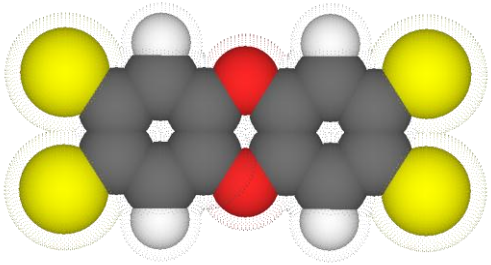
What happened during the 2004 presidential election campain in the Ukraine?

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

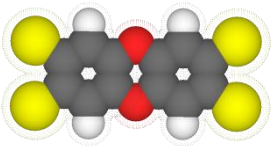
Fat : $TCDD\ (t) = 107'000\ (pg/g\ lw)\ e^{-0.04429\ t}$

$t_{1/2} = 15.7$ months

Attempted assassination of Viktor Yushchenko, former President of the Ukraine

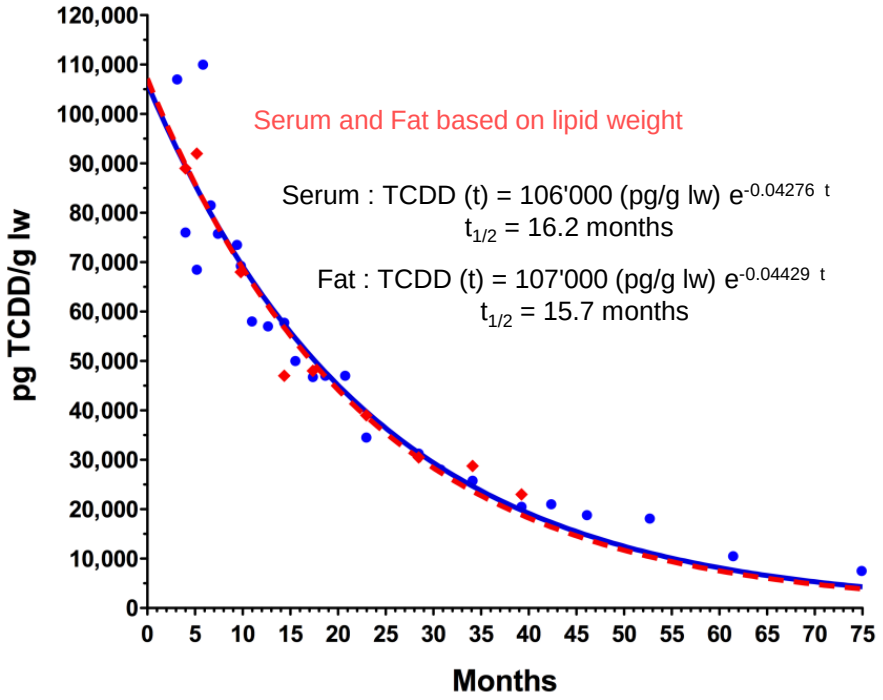
What happened during the 2004 presidential election campain in the Ukraine?

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



- Poisoned Sunday, Sept 5, 2004 Dinner with SBU (Ukrainian National Security)
- Uptake of approximately 1-2 mg 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 quite different pattern!

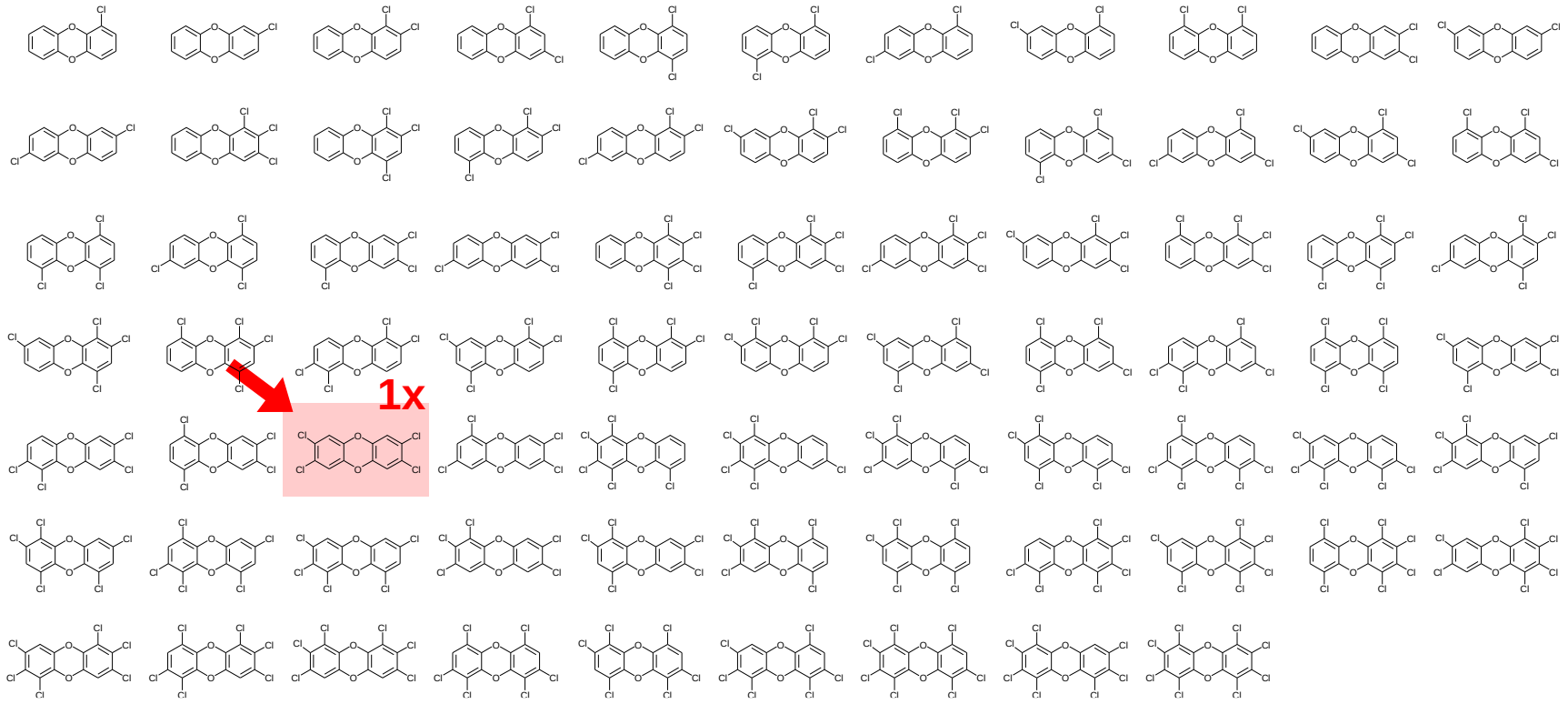


Sorg, O., Zennegg, M. Schmid, P. et al. The Lancet, **2009**, 9696, 1179-85

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



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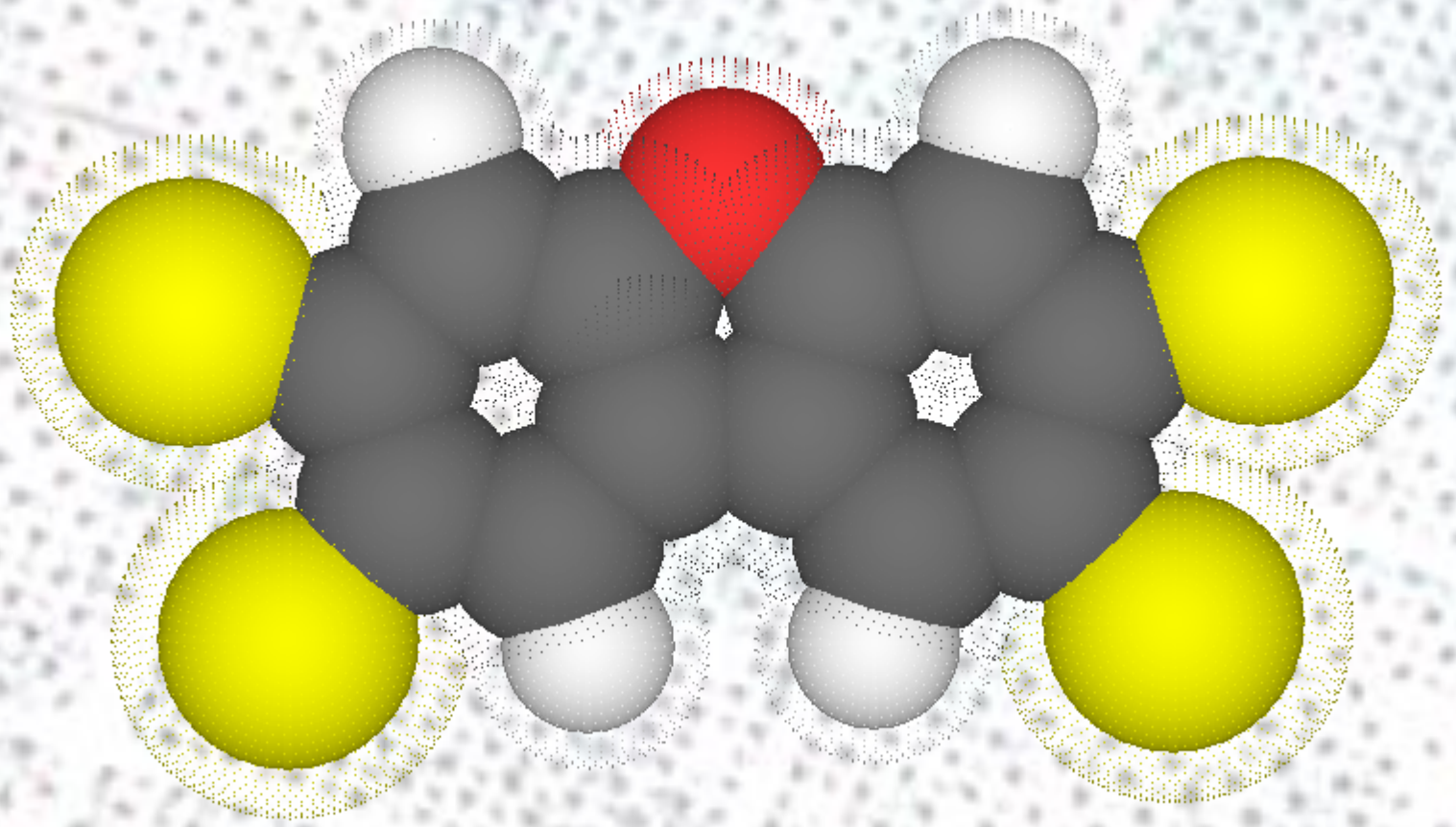
The dibenzofuran class of compounds (PCDFs)

What abuot 2,3,7,8-TCDF?

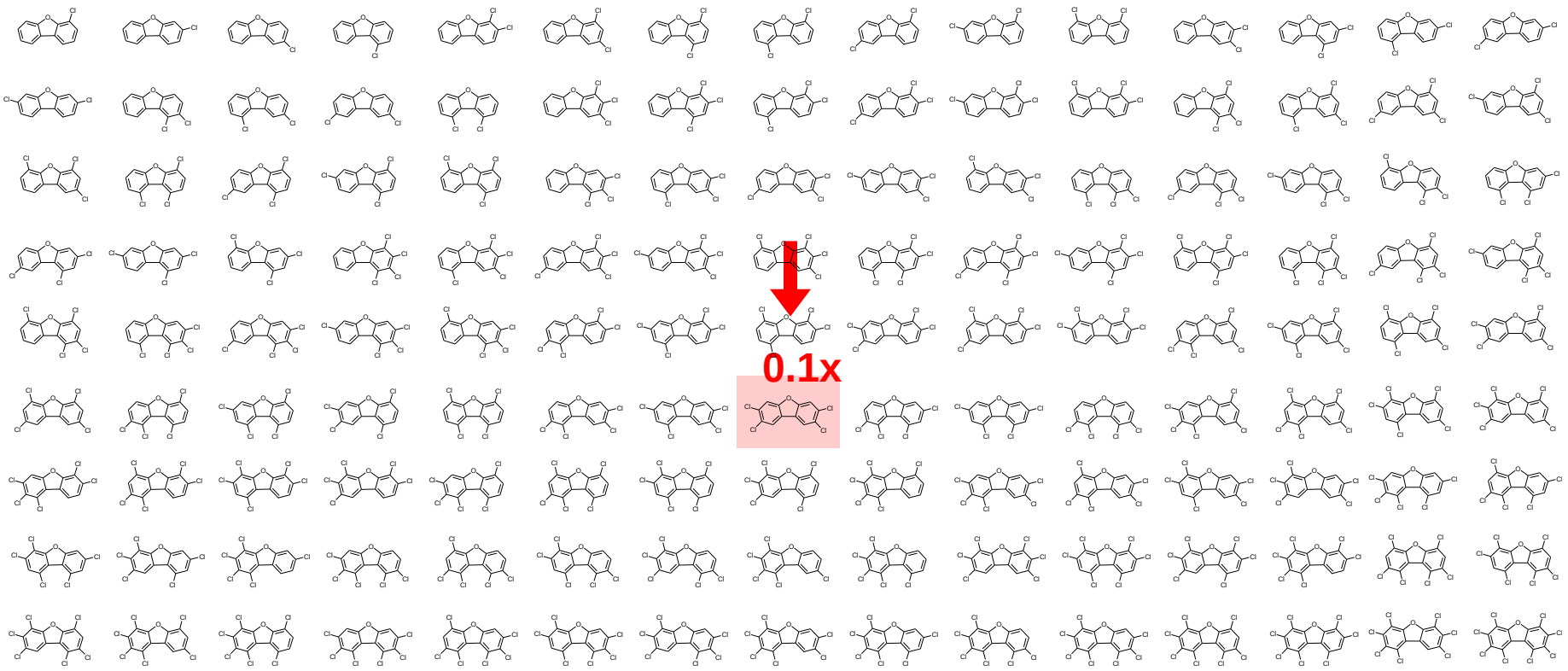
2,3,7,8-Tetrachlorodibenzofuran



The dibenzofuran class of compounds (PCDFs)

Why not 2,3,7,8-TCDF or others of the 135 congeners?

Chemical structures of polychlorinated dibenzofurans



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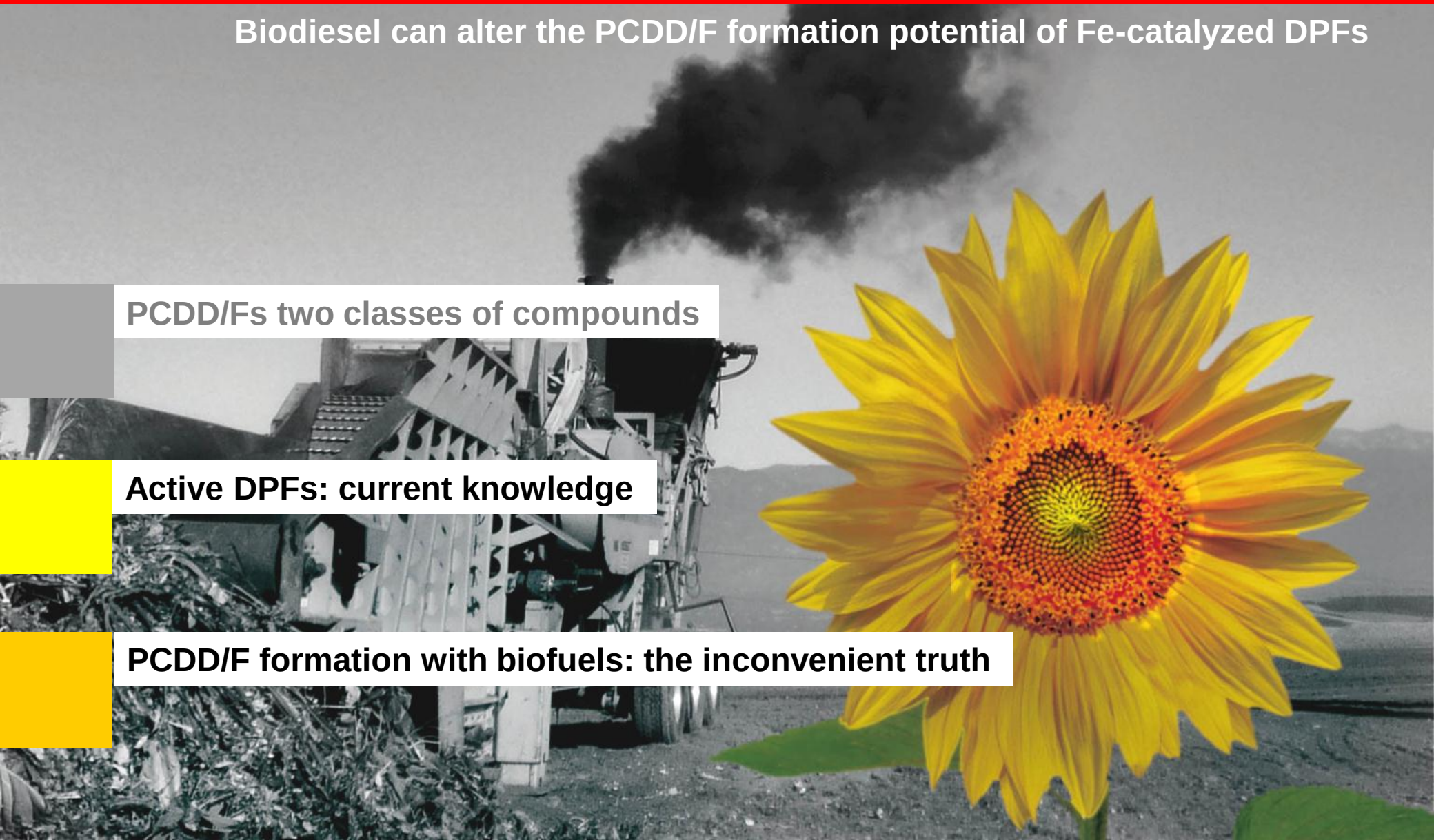
PCDD/Fs are not only generated by copper catalysis: the inconvenient truth about biofuels

Biodiesel can alter the PCDD/F formation potential of Fe-catalyzed DPFs



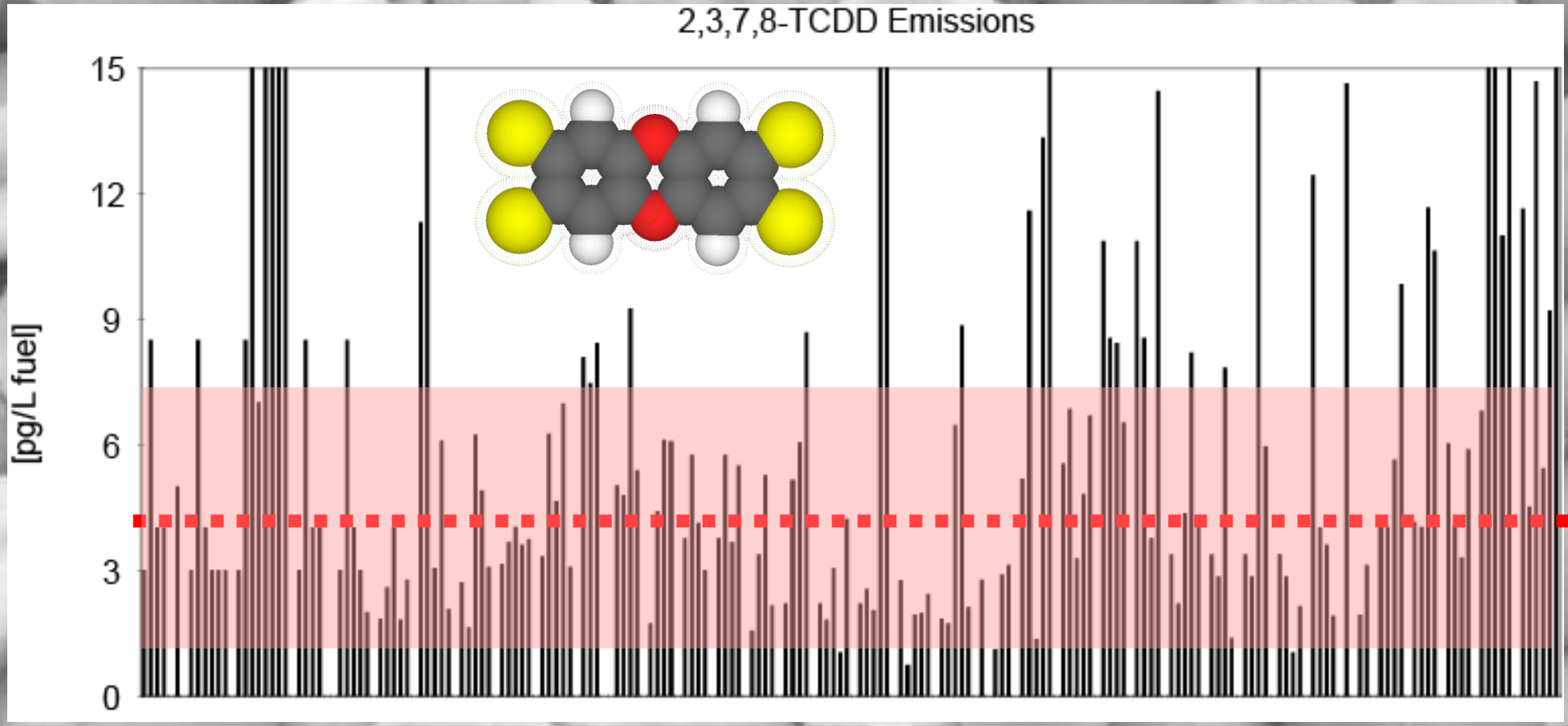
PCDD/Fs two classes of compounds

Active DPFs: current knowledge

PCDD/F formation with biofuels: the inconvenient truth

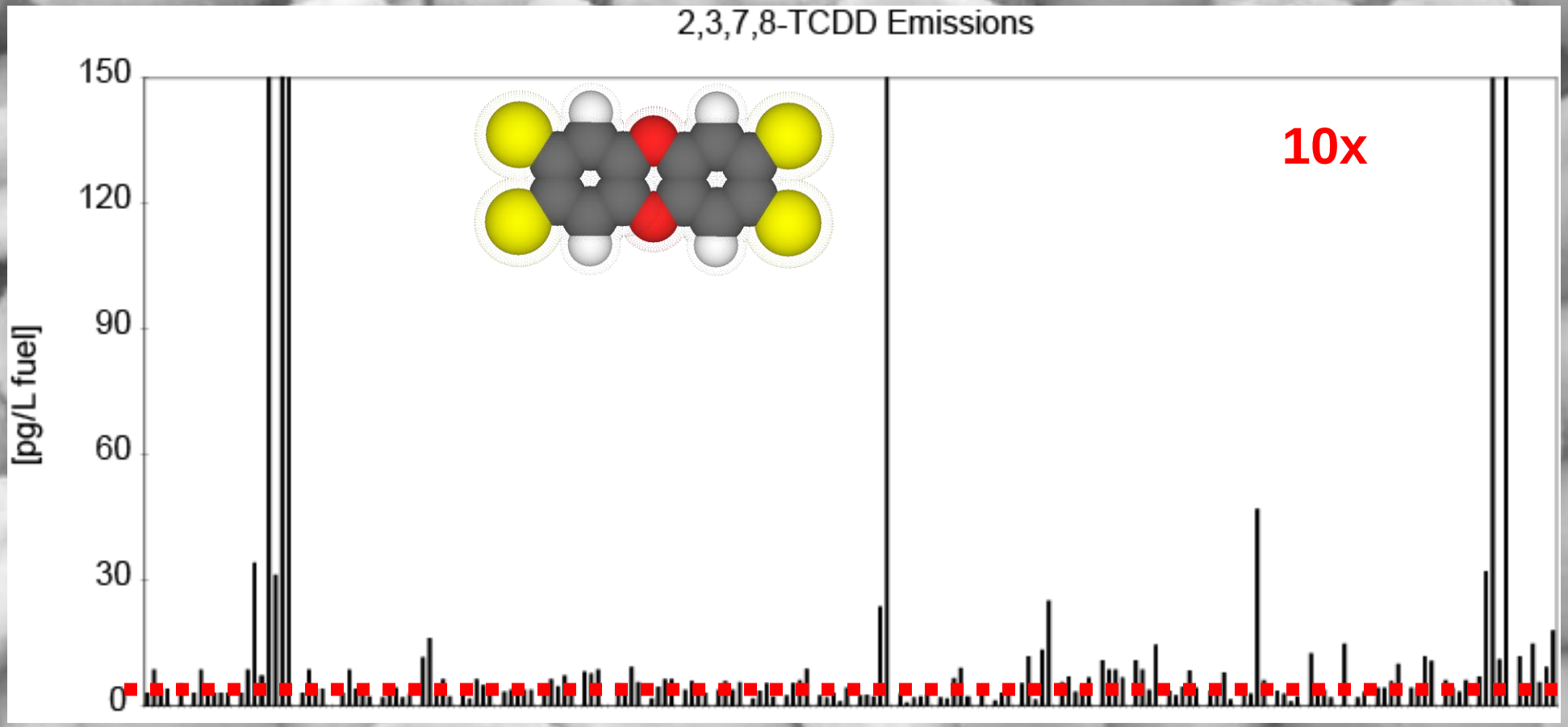
Assessment of the PCDD/F-formation potential

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



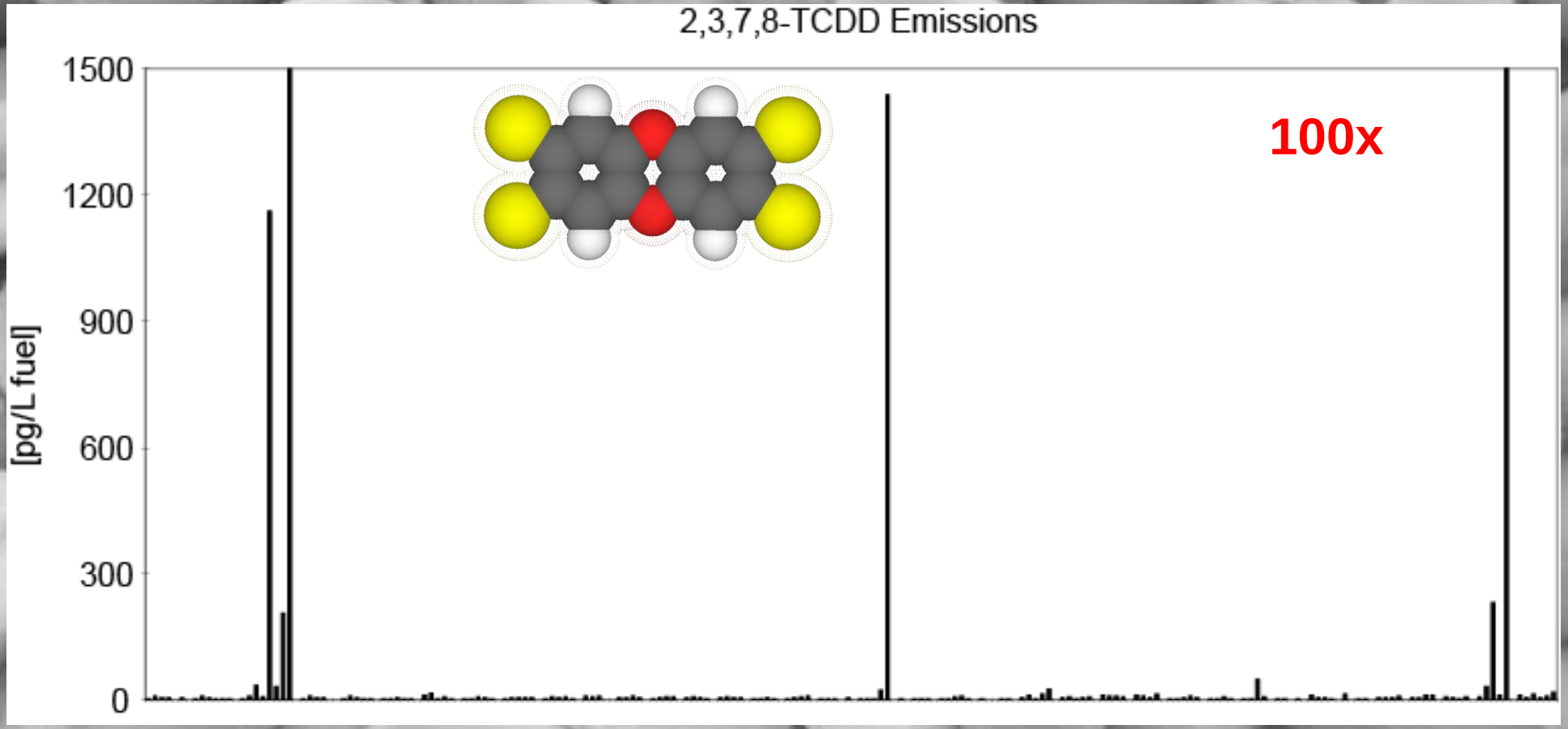
Assessment of the PCDD/F-formation potential

Only few filters exceeded the engine out level?



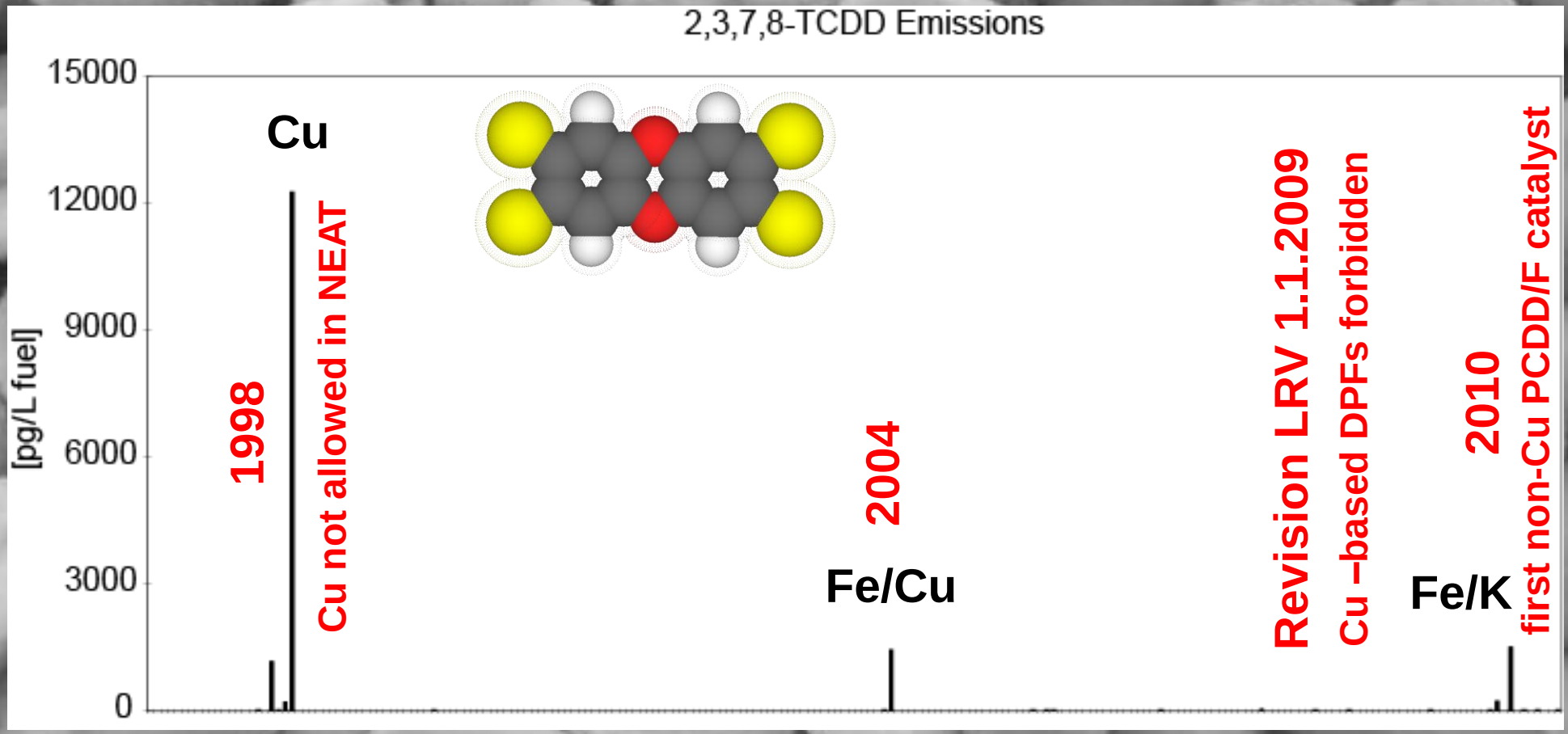
Assessment of the PCDD/F-formation potential

Only 3 of the 37 tested DPFs induced a PCDD/F formation?



Assessment of the PCDD/F-formation potential

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

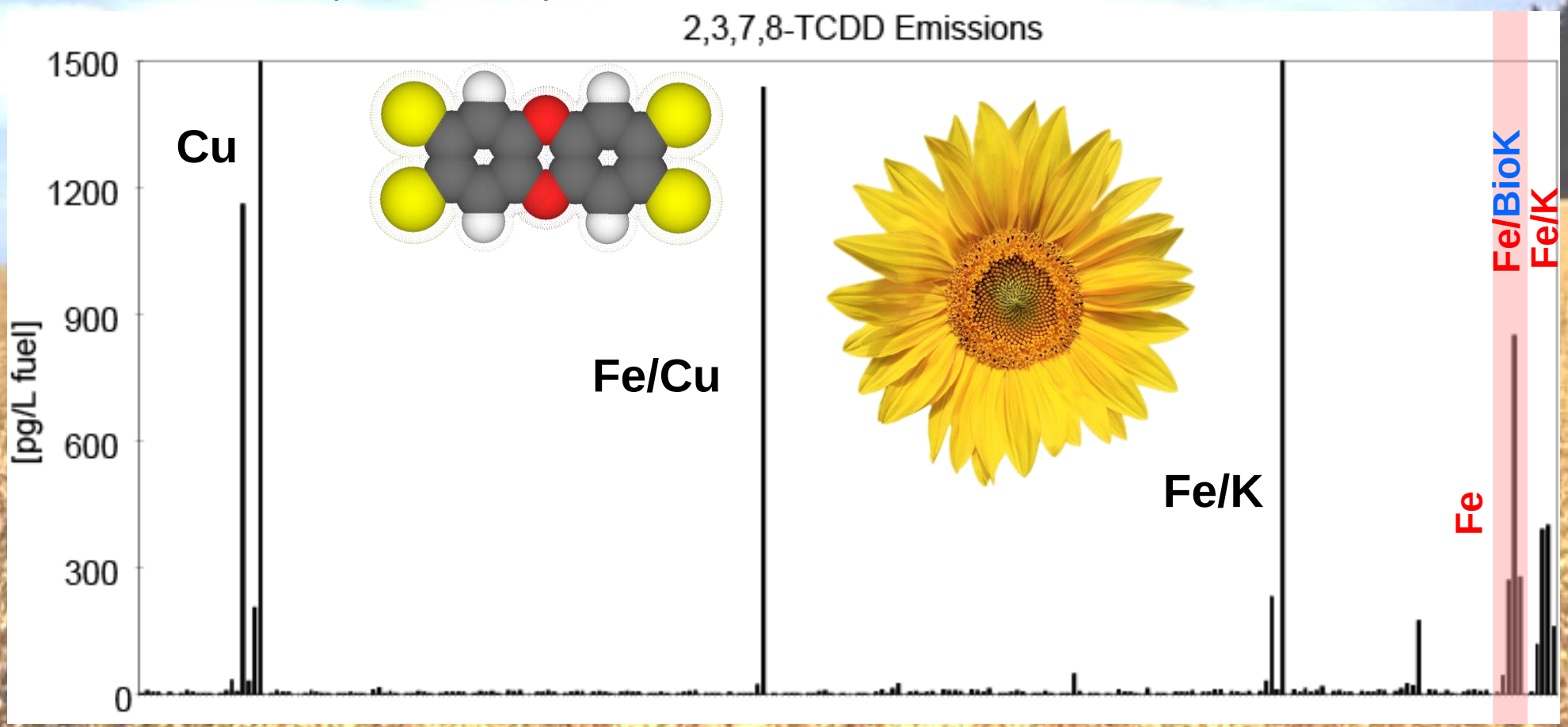


PCDD/F Formation Potential of DPFs: New Risks with Biofuels?

Certain DPFs are not compatible with certain biofuels!

It's fossil fuel! (fossilized biofuel)

It's bio!



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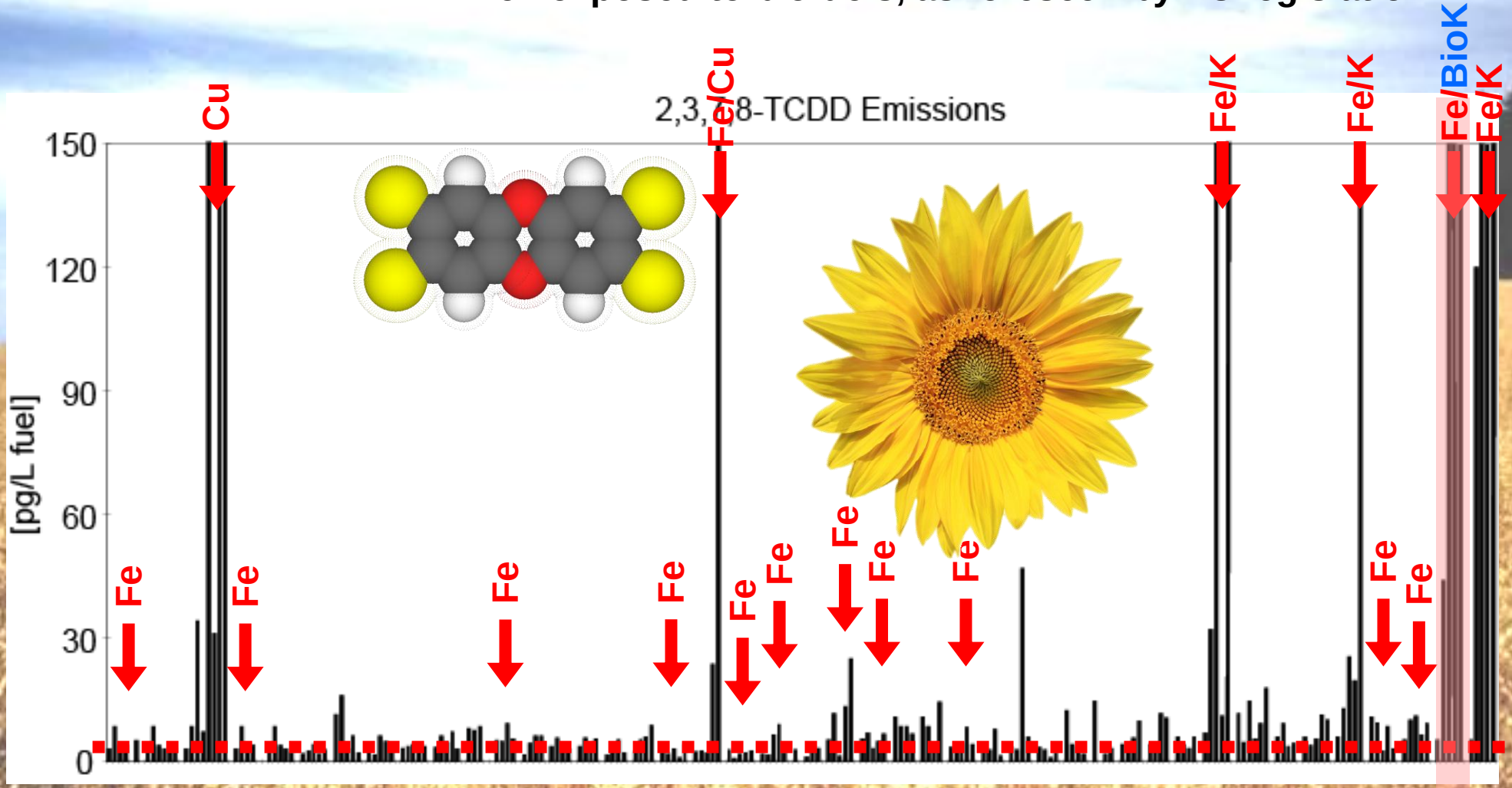
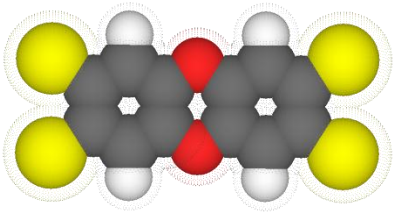
Possibly thousands of vehicles with Fe-catalyzed DPFs might become active, when exposed to biofuels, as foreseen by EU legislation!

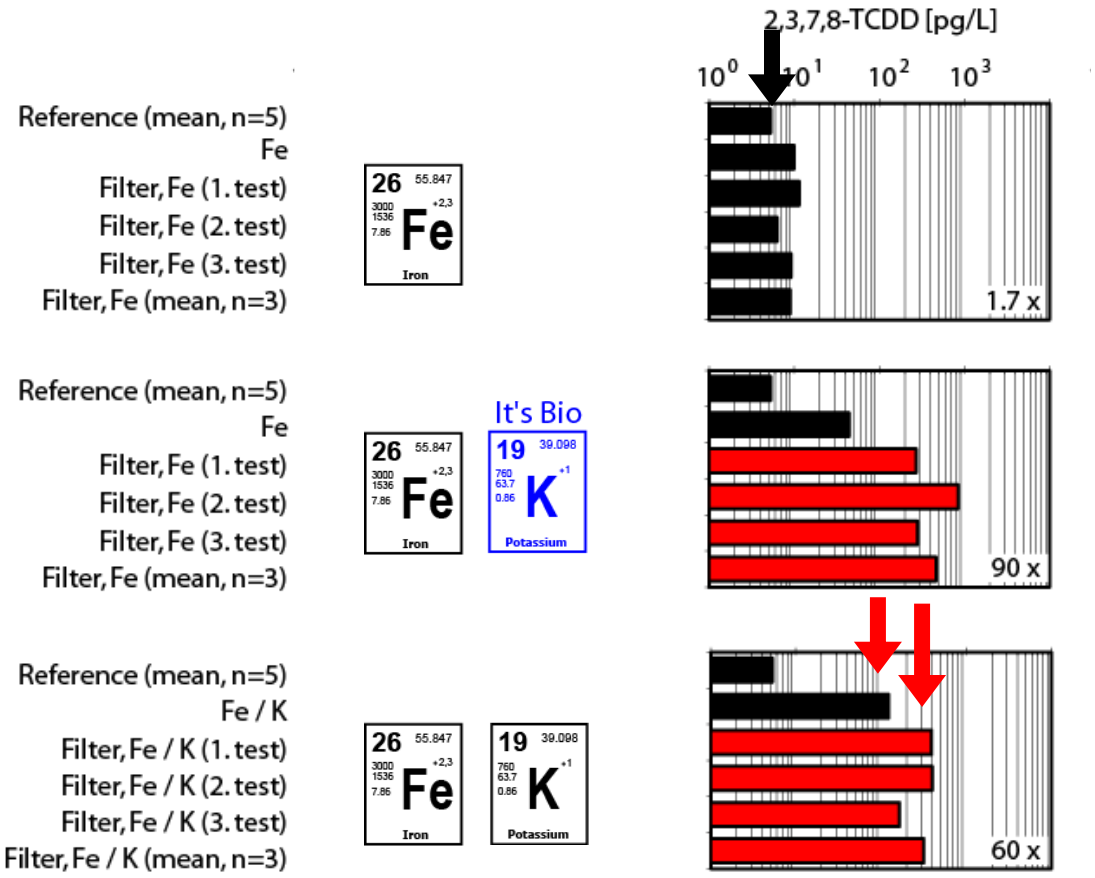


PCDD/F Formation Potential of DPFs: New Risks with Biofuels?

Potassium, independent of its origin, converts an inactive into an active Fe-DPF

Fold increase compared to reference

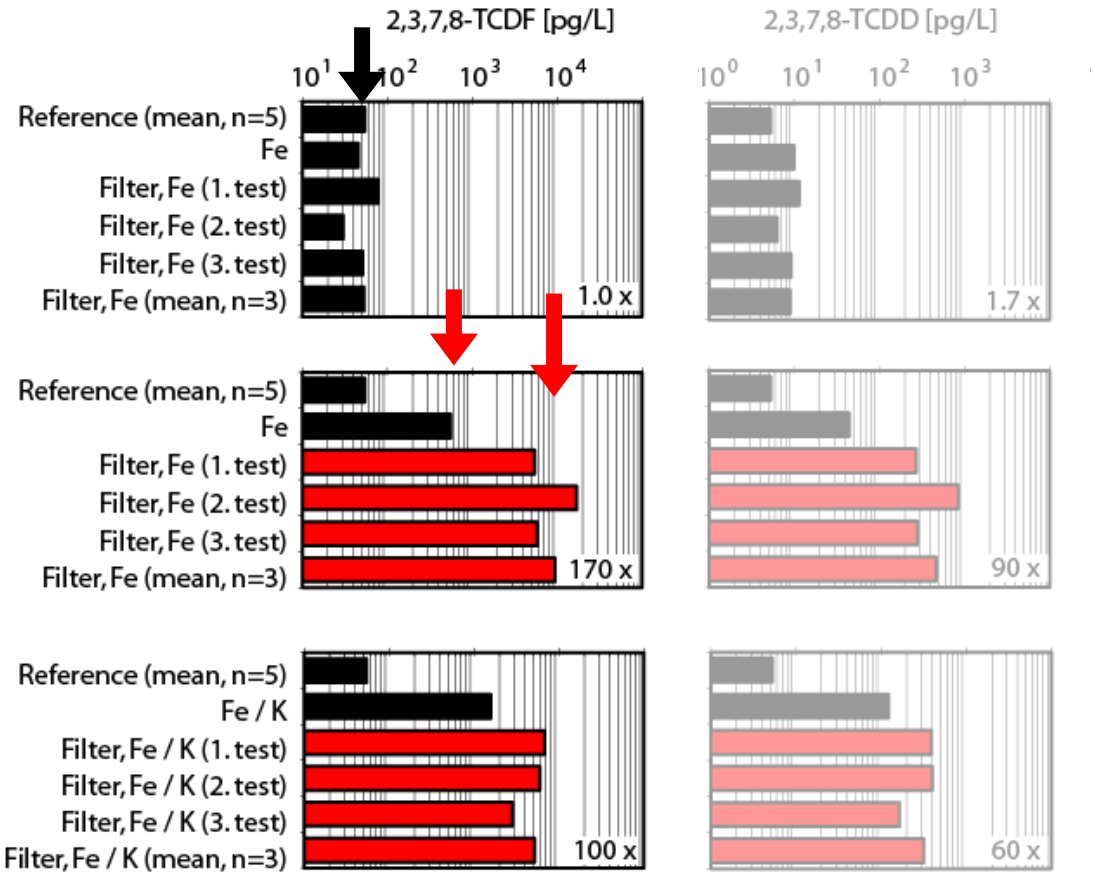


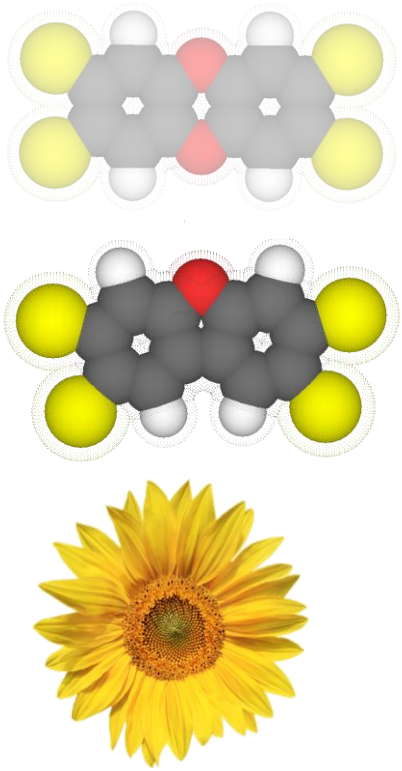


PCDD/F Formation Potential of DPFs: New Risks with Biofuels?

What about 2,3,7,8-TCDF?

Fold increase compared to reference

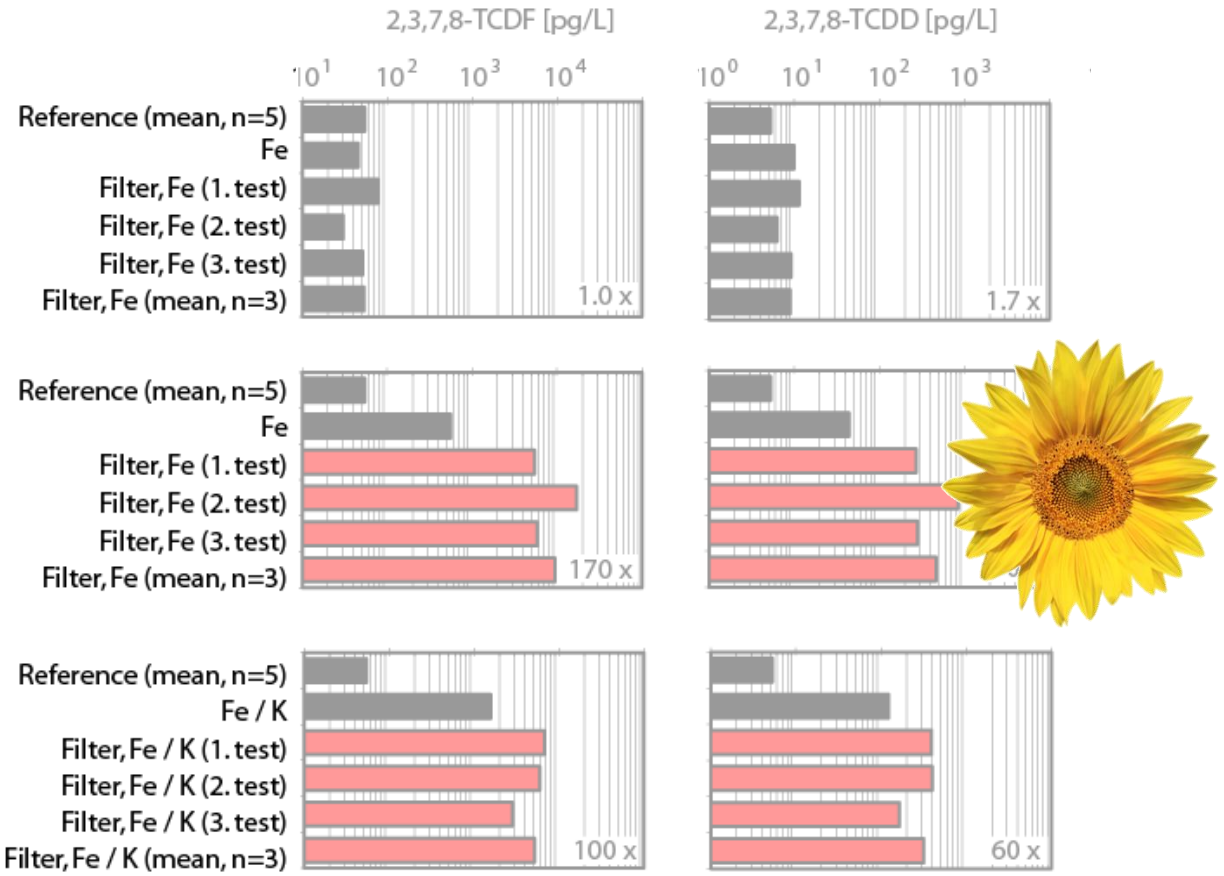


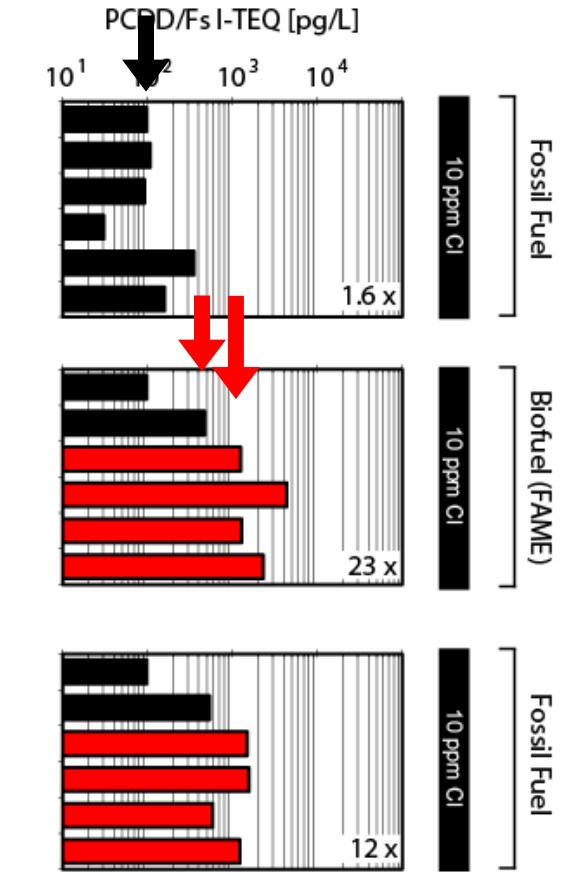


PCDD/F Formation Potential of DPFs: New Risks with Biofuels?

Smaller effects on the 17 toxic PCDD/Fs!

Fold increase compared to reference

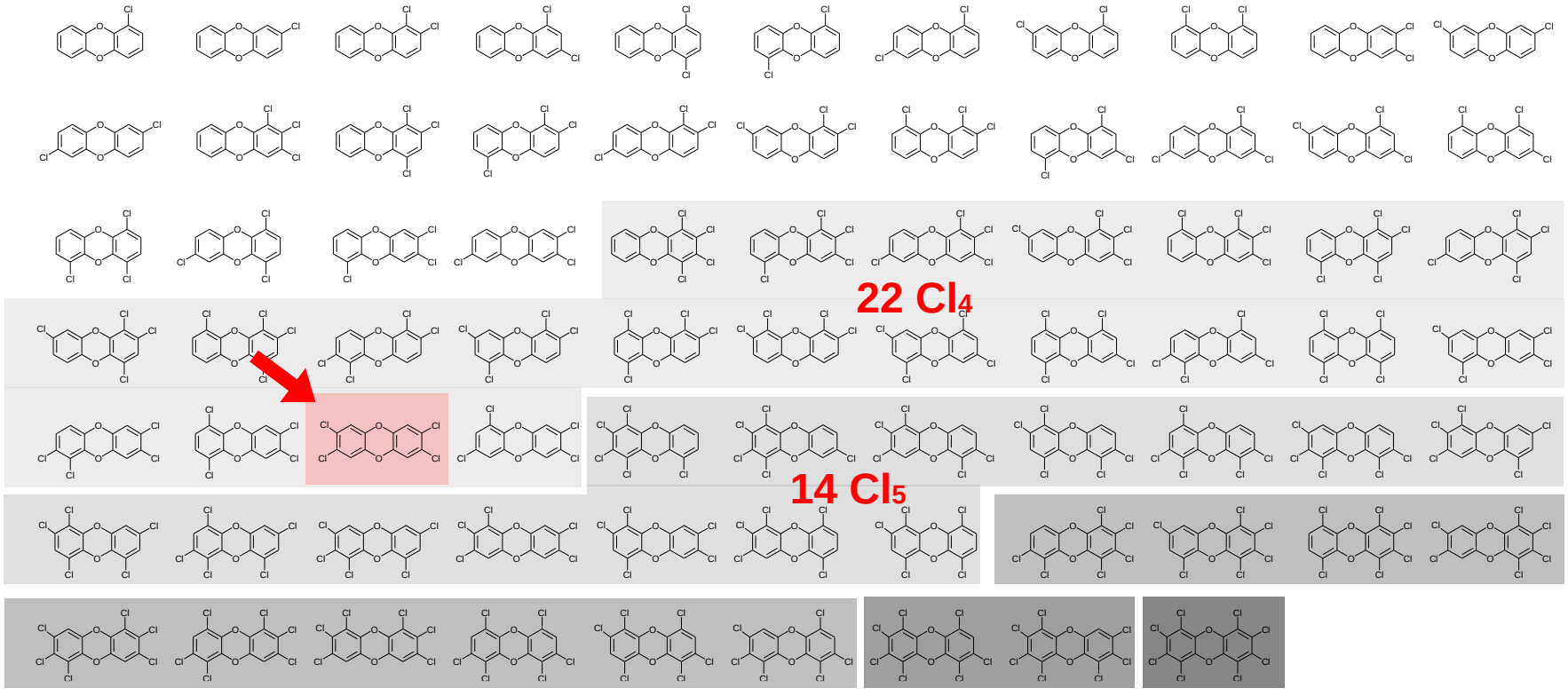




Assessment of the PCDD/F-formation potential

Why not assessing congener classes like Cl_4-, Cl_5-, Cl_6-, Cl_7- & Cl_8DDs?

Chemical structures of polychlorinated dibenzodioxins



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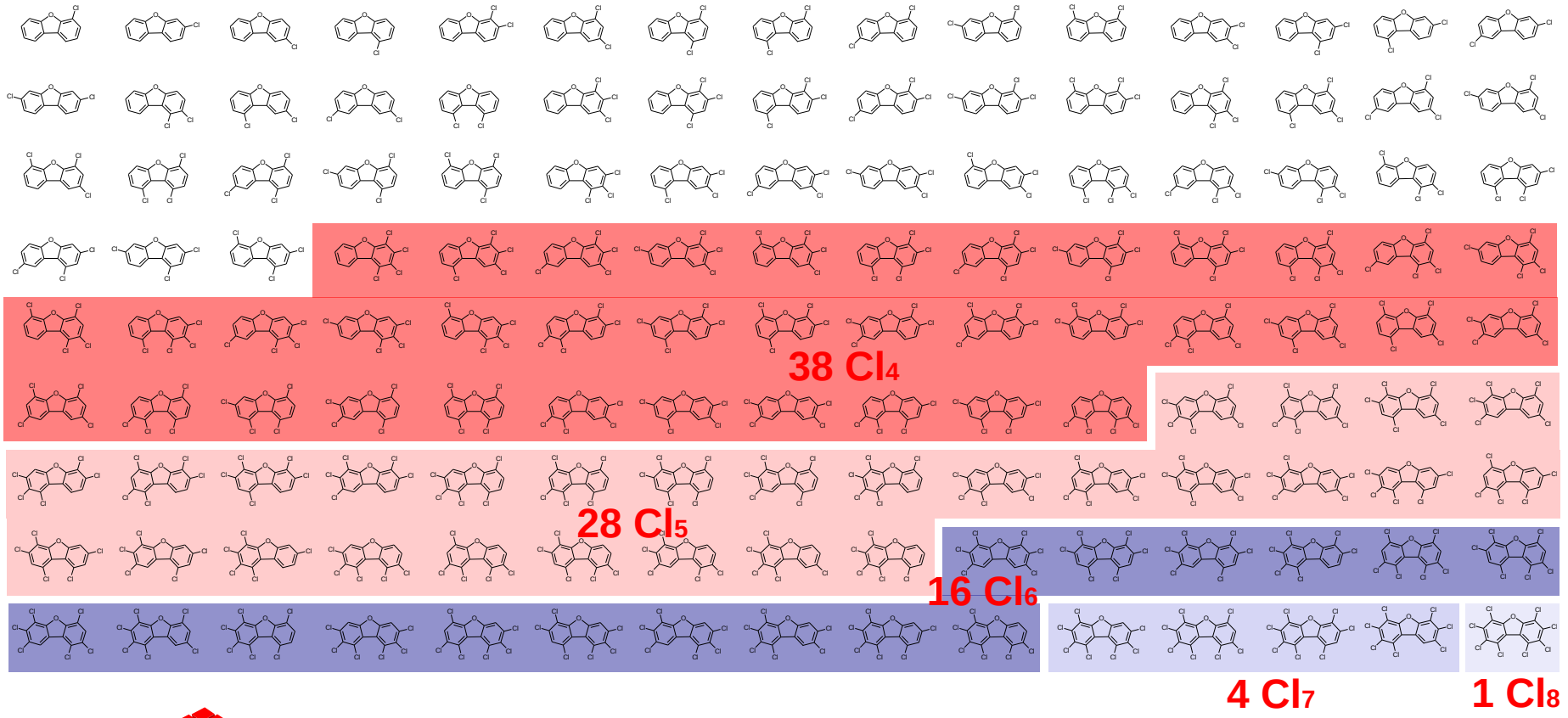

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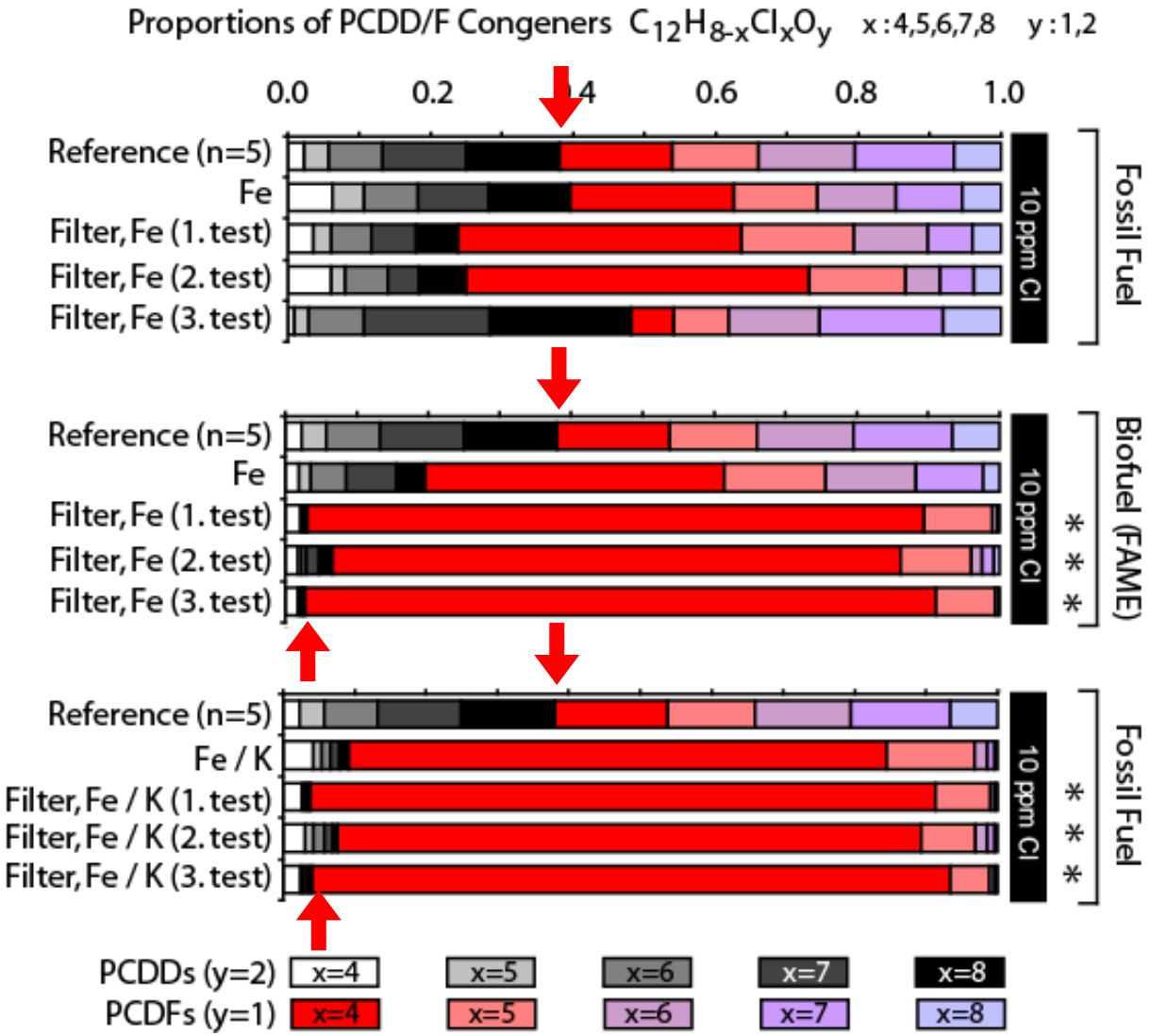
Analysis of congener patterns



Pattern changes?

40% PCDDs / 60% PCDFs

not much change!

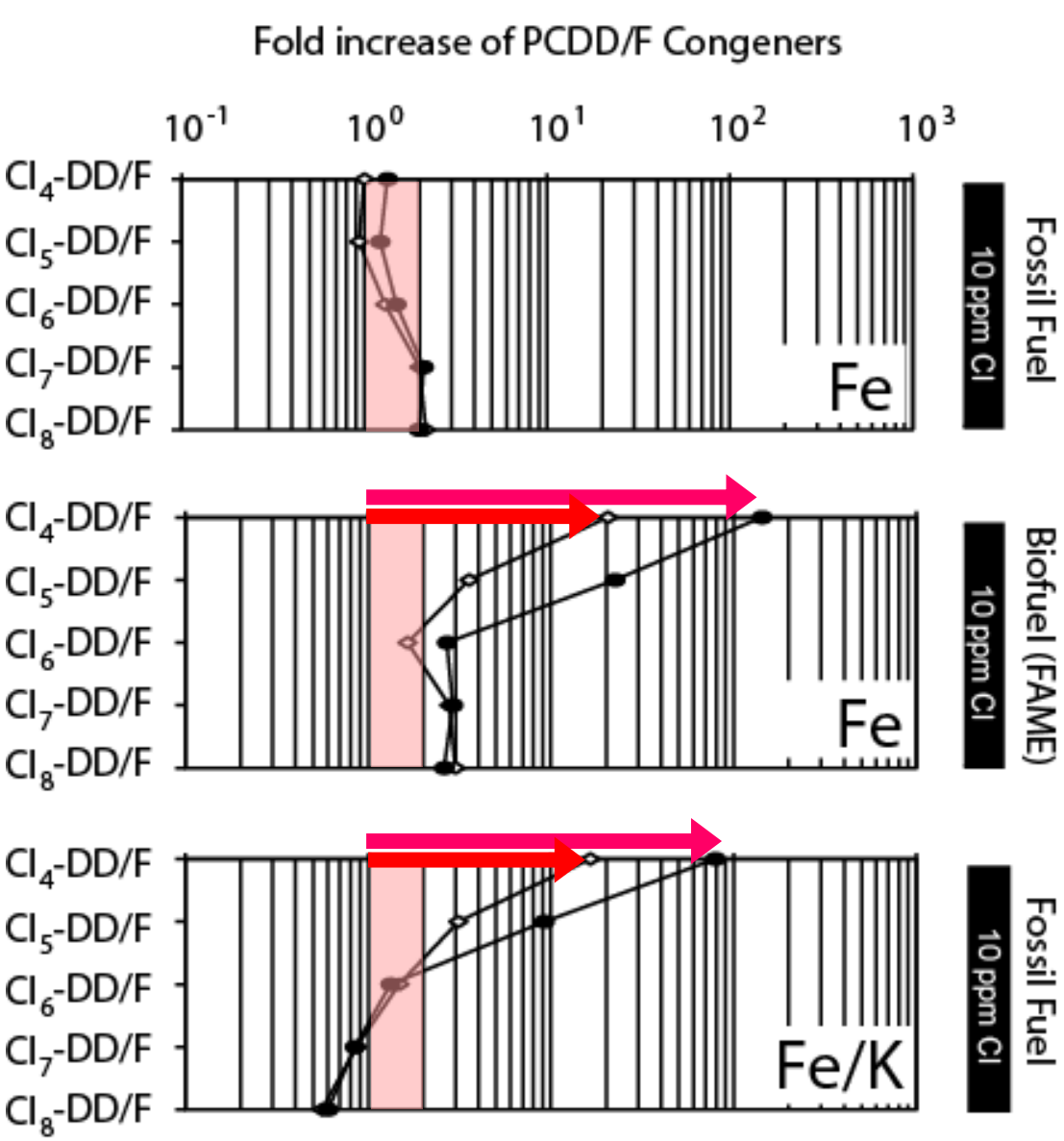
5% PCDDs / 95% PCDFs

things get red with biofuel!

5% PCDDs / 95% PCDFs

Fe/K and Fe/BioK similarl!

Congener-specific effects



Preferential formation of TCDFs!

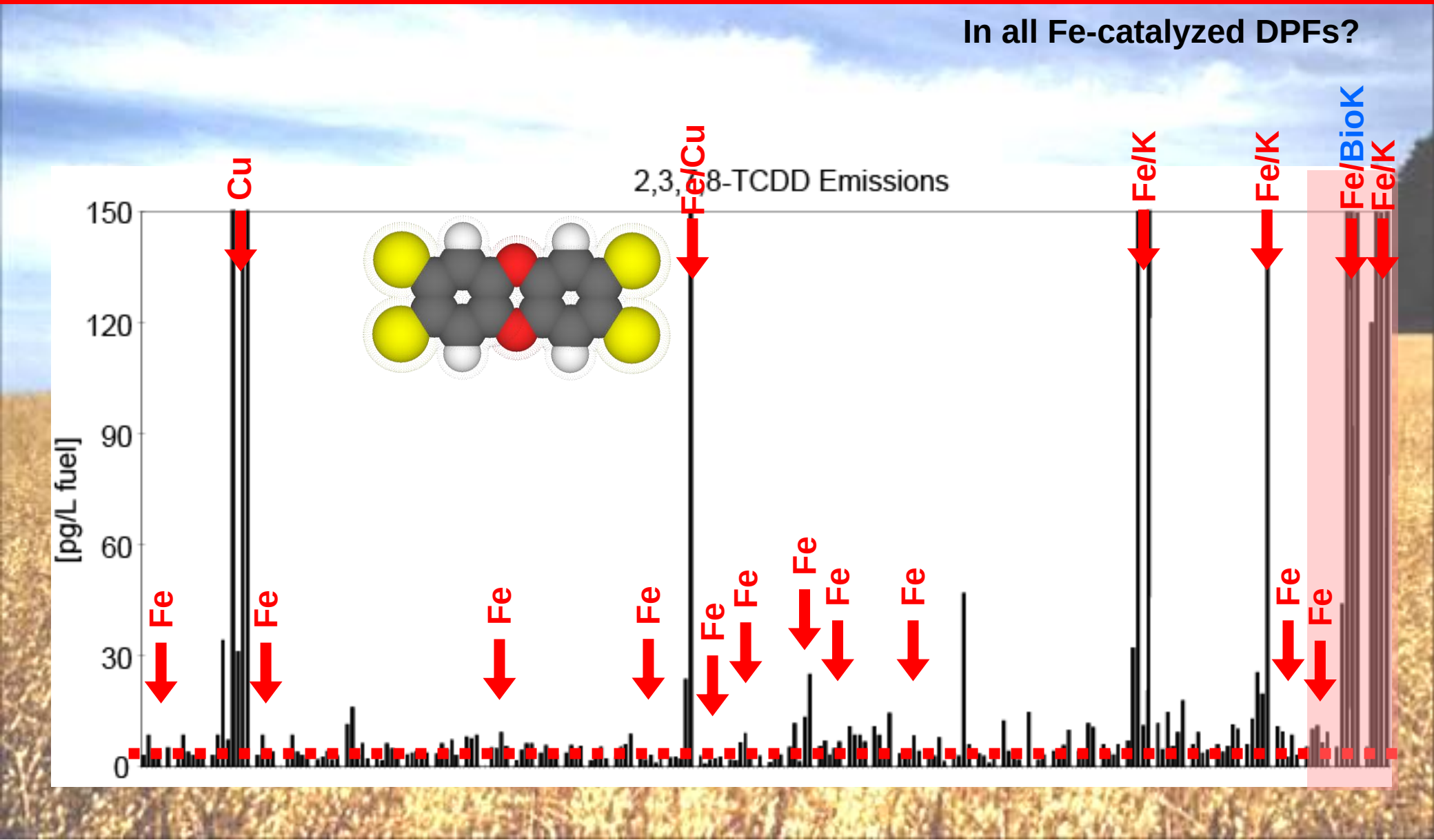
140 x increase of Cl_4-DFs
20 x increase of Cl_4-DDs

80 x increase of Cl_4-DFs
16 x increase of Cl_4-DDs

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?



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Conclusions:

- PCDD/F formation in DPFs is a potential risk
- The chemical nature of the catalyst is important
- Biofuels can alter the PCDD/F potential of DPFs
- There are DPFs out, which may become active over time when exposed to biofuel exhausts

PCDD/F potential of any new type of DPF has to be tested, also with biofuels

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PCDD/Fs are not only generated by copper catalysis: the inconvenient truth about biofuels

A combined effort with many important contributions

Thanks:

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- **Filter-, catalyst-, engine & vehicle manufacturers**:

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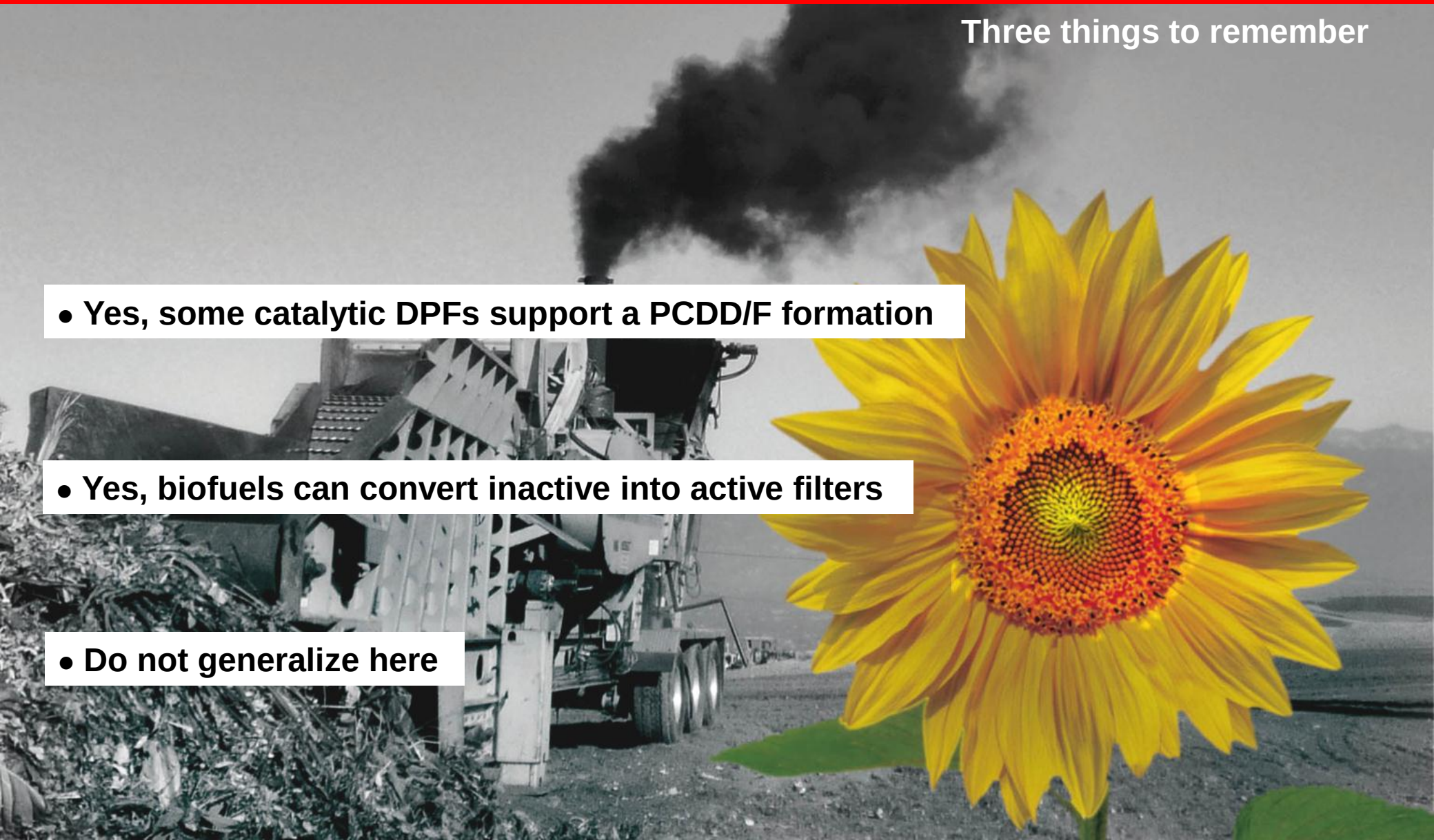

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- Yes, biofuels can convert inactive into active filters
- Do not generalize here