# Effects of a combined diesel particle filter-deNOx system on reactive nitrogen compounds emissions

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Catalytic diesel particle filters (DPFs) have evolved to a mature environmental technology over the last two decades. Two important filter families can be distinguished. They differ with respect to their oxidation potential and related to this their nitric oxide (NO) and nitrogen dioxide ($NO_2$) emission characteristics. DPFs with high oxidation potential (hox-DPFs) convert NO to $NO_2$, whereas low-oxidation potential DPFs (lox-DPFs) reduce $NO_2$ (Fig. 1, R1). Hox-DPFs typically rely on noble metal catalysts, lox-DPFs on transition metal- or rare earth metal-catalysts.

$$2\,\overset{+\mathrm{II}}{N}O + O_2 \rightleftharpoons 2\,\overset{+\mathrm{IV}}{N}O_2 \qquad (\mathbf{R1})$$

$$2\,\overset{-\mathrm{III}}{N}H_3 + \overset{+\mathrm{II}}{N}O + \overset{+\mathrm{IV}}{N}O_2 \longrightarrow 2\,\overset{\mathrm{O}}{N_2} + 3\,H_2O \qquad (\mathbf{R2})$$

$$4\,\overset{-\mathrm{III}}{N}H_3 + 4\,\overset{+\mathrm{II}}{N}O + O_2 \longrightarrow 4\,\overset{\mathrm{O}}{N_2} + 6\,H_2O \qquad (\mathbf{R3})$$

$$8\,\overset{-\mathrm{III}}{N}H_3 + 6\,\overset{+\mathrm{IV}}{N}O_2 \longrightarrow 7\,\overset{\mathrm{O}}{N_2} + 12\,H_2O \qquad (\mathbf{R4})$$

$$CO(\overset{-\mathrm{III}}{N}H_2)_2 \longrightarrow \overset{-\mathrm{III}}{N}H_3 + H\overset{-\mathrm{III}}{N}CO \qquad (\mathbf{R5})$$

$$H\overset{-\mathrm{III}}{N}CO + H_2O \longrightarrow \overset{-\mathrm{III}}{N}H_3 + CO_2 \qquad (\mathbf{R6})$$

$$H_2O + 2\,\overset{+\mathrm{IV}}{N}O_2 \longrightarrow H\overset{+\mathrm{III}}{N}O_2 + H\overset{+\mathrm{V}}{N}O_3 \qquad (\mathbf{R7})$$

**Fig. 1.** Reactive nitrogen compounds (RNCs) chemistry in combined DPF-deNOx systems

Diesel engines have improved considerably over the years, but their NO and $NO_2$ emissions still affect air quality. In several European cities, ambient air $NO_2$ levels frequently exceed the 40 μg/m$^3$ threshold set by the EU parliament in 2010. $NO_2$ is a strong oxidizing agent involved in the photochemical formation of ozone. At higher concentrations, $NO_2$ induces skin and eye irritations and lung oedema. Long-term effects like asthma and chronic obstruction pulmonary disease are induced by lower $NO_2$ doses.

The implementation of diesel oxidation catalysts (DOCs) and hox-DPFs, which support a substantial $NO_2$ formation, additionally contribute to the persistently high

$NO_2$ levels in many urban environments and along roads. Recent developments of different $deNO_x$ technologies for diesel engines may help to improve the situation.

In this contribution, we will discuss the impact of a combined diesel particle filter-$deNO_x$ system (DPN) on the emissions of reactive nitrogen compounds (RNCs). The DPN consisted of a platinum-coated cordierite filter and a vanadia-based $deNO_x$ catalyst. The latter supported ammonia-based selective catalytic reduction (SCR) chemistry. Figure 1 displays some of the involved SCR chemistry. Both, NO and $NO_2$ are reduced with ammonia ($NH_3$) to dinitrogen ($N_2$) at different stoichiometries (Fig. 1, R2, R3 and R4). Ammonia is produced in situ, either from thermolysis of urea or from hydrolysis of isocyanic acid (HNCO) as shown in Fig. 1 (R5, R6). HNCO and $NH_3$ are both toxic and highly reactive intermediates and, if released, have to be considered as unwanted secondary emissions of the $deNO_x$ system.

We studied emissions of these RNCs and effects of changing urea feed factors ($\alpha$), exhaust temperatures, and residence times. The $deNO_x$ system was only part-time active and urea injection was stopped and restarted twice in the test cycle (Fig. 2, stages 4 and 8).

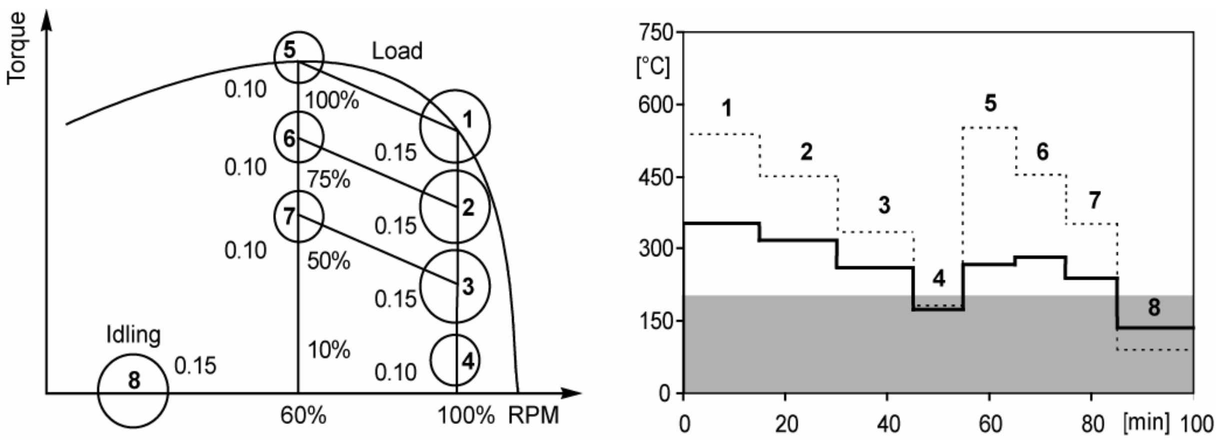


**Fig. 2.** Test cycle and exhaust temperatures before (dashed) and after (solid) a combined DPF-deNOx system

Nevertheless, high mean NO conversion efficiencies of 80%, 95% and 97% were achieved at $\alpha$=0.8, 1.0, and 1.2, respectively, those for $NO_2$ were 43%, 87%, and 99%. HNCO emissions increased from 28 mg/h engine-out to 183, 245, and 258 mg/h at $\alpha$=0.8, 1.0 and 1.2. $NH_3$ emissions increased from <45 to 124, 1820, and 12700 mg/h, respectively, with maxima at highest temperatures and shortest residence times (<0.3 s). Most HNCO is released at intermediate residence times and intermediate temperatures of 300-400 °C.

The investigated DPN represents the most advanced converter system tested so far under the VERT protocol with high conversion efficiencies for particles, NO, $NO_2$, CO, and hydrocarbons. But the release of $NH_3$ and HNCO should be further minimized. Clearly there is a trade-off between deNOx efficiency and secondary emissions. Thus optimized conditions have to be established for different diesel engine applications. The DPN has the potential to lower $NO_x$- and particle-pollution, but risks of increased $NH_3$ and HNCO emissions have to be assessed as well.


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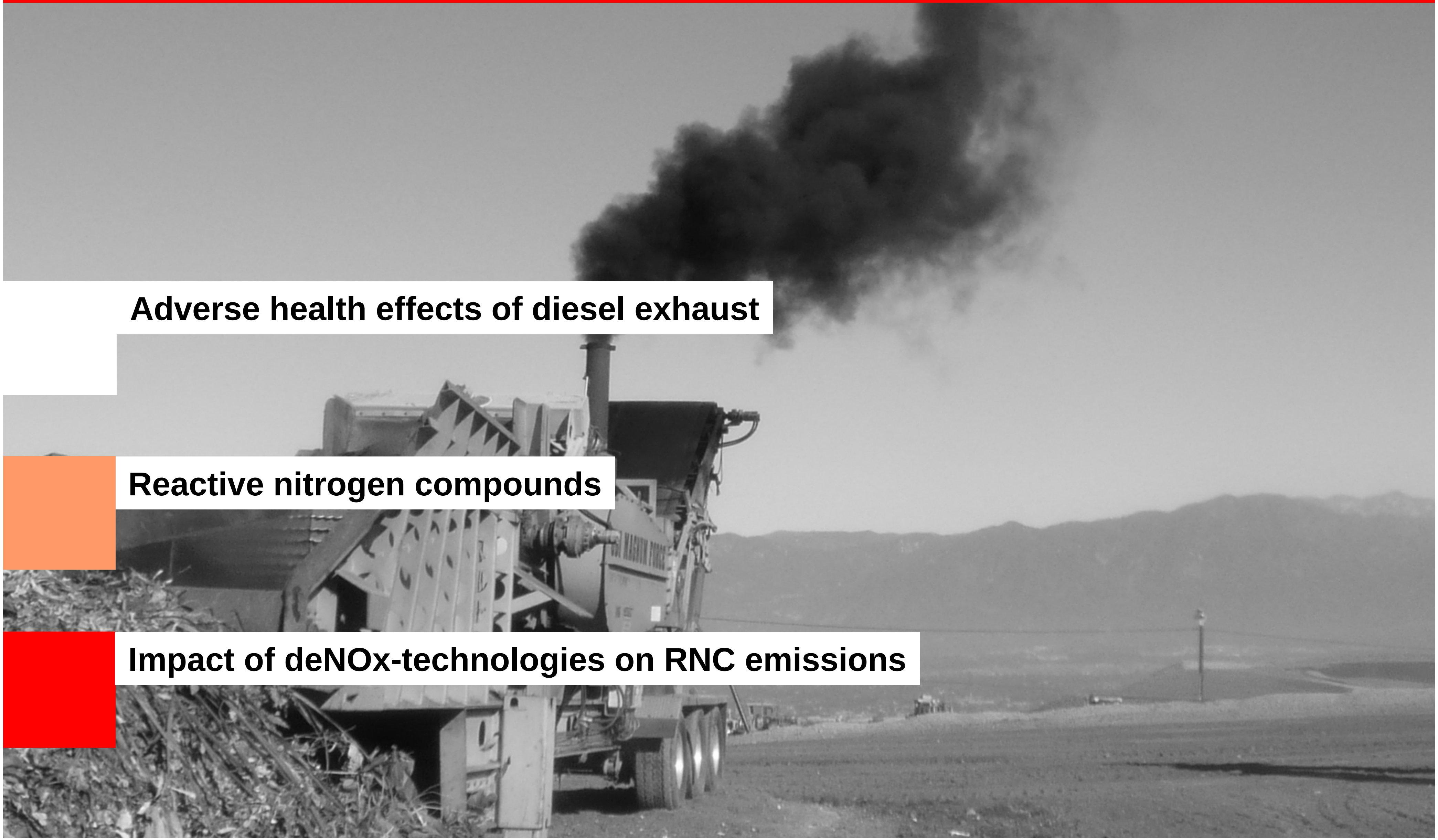
# Effects of a combined DPF-deNO$_x$ system on RNC emissions

16. ETH-Conference on Combustion Generated Particles

ETH Zurich, June 24-27, 2012

# When DPFs meet deNO$_x$-technologies



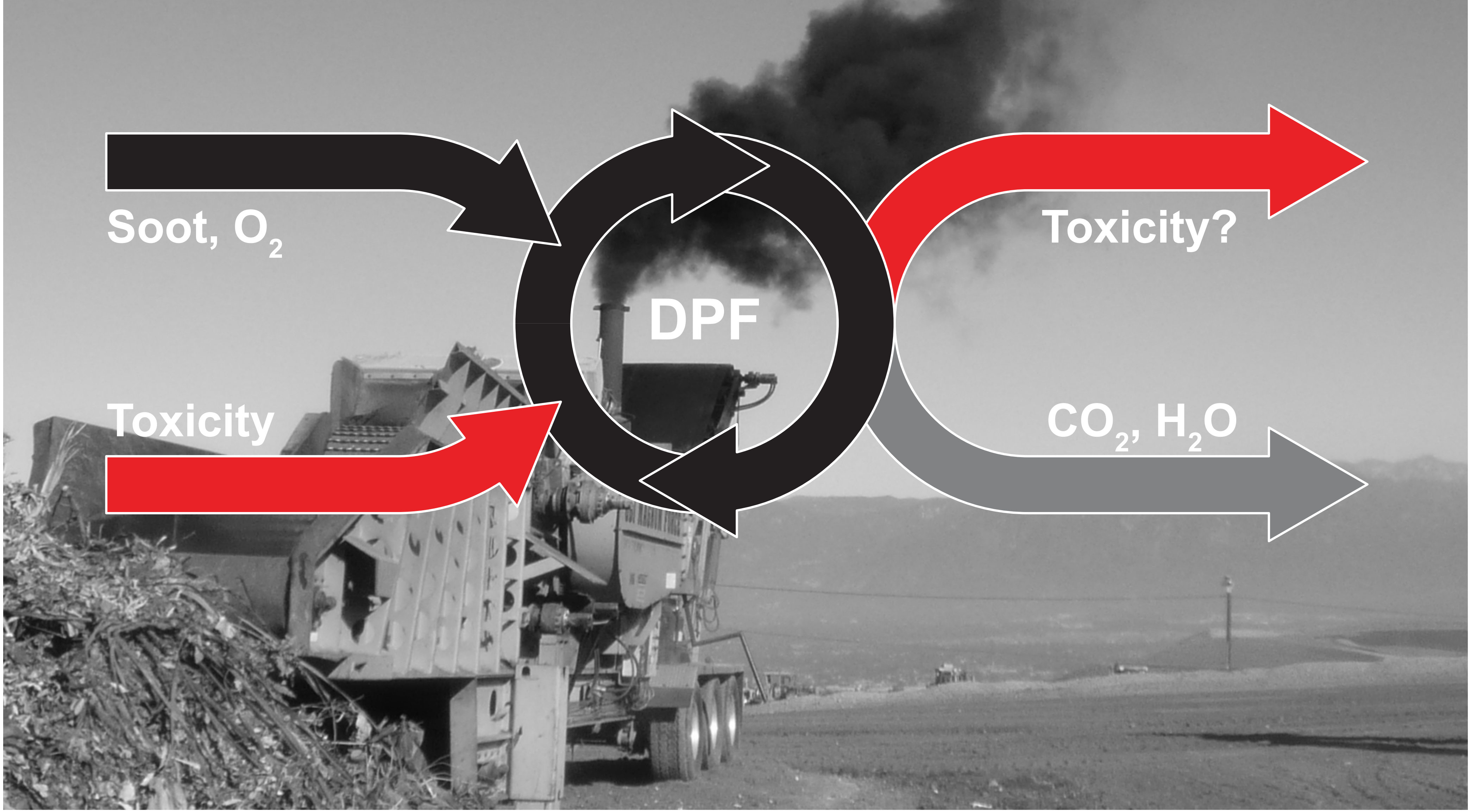
Adverse health effects of diesel exhaust

Reactive nitrogen compounds

Impact of deNOx-technologies on RNC emissions

# Adverse health effects of diesel exhaust

DPFs are very efficient - not only for soot particles!

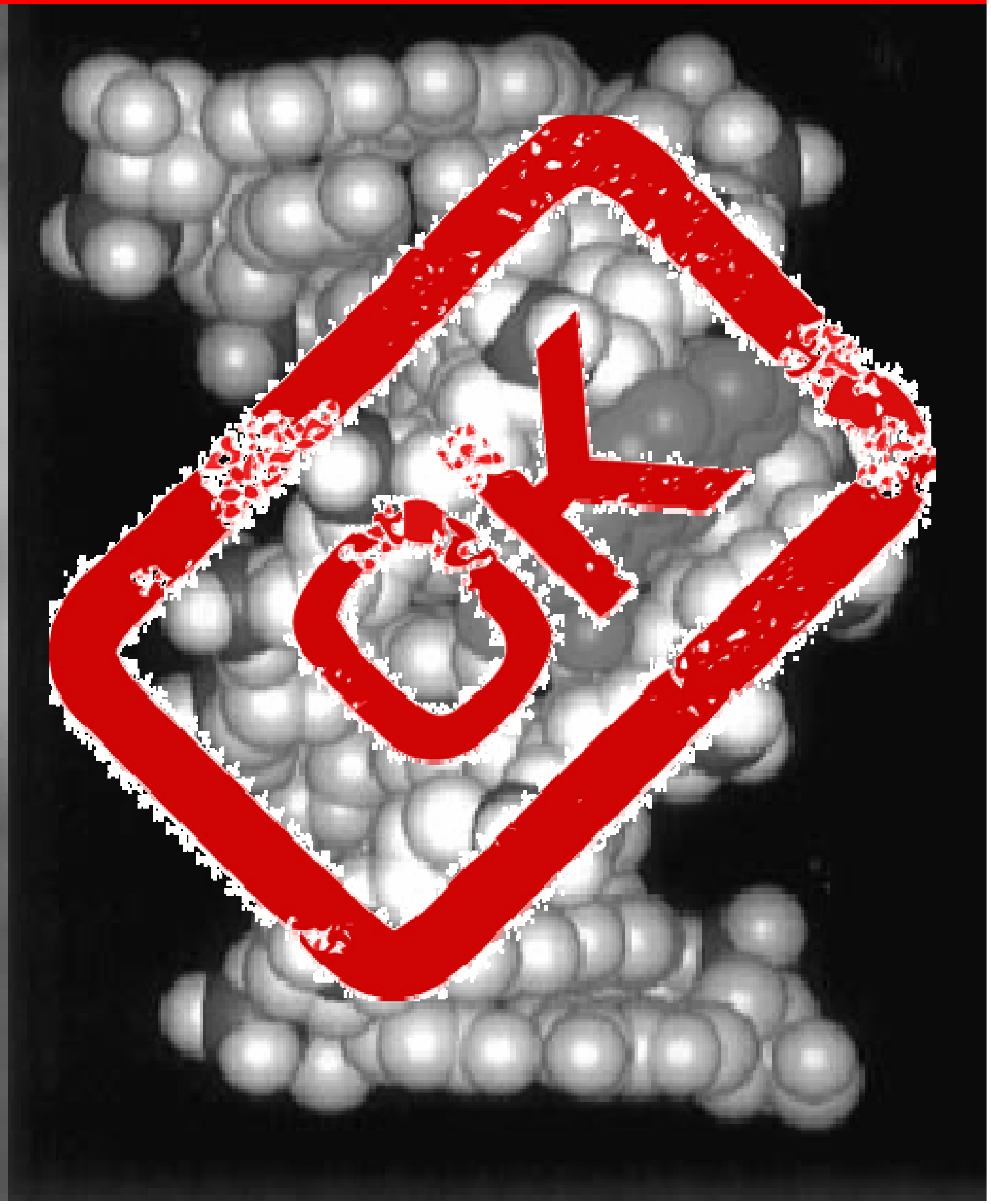


# Adverse health effects of diesel exhaust

## Problem: Genotoxicity

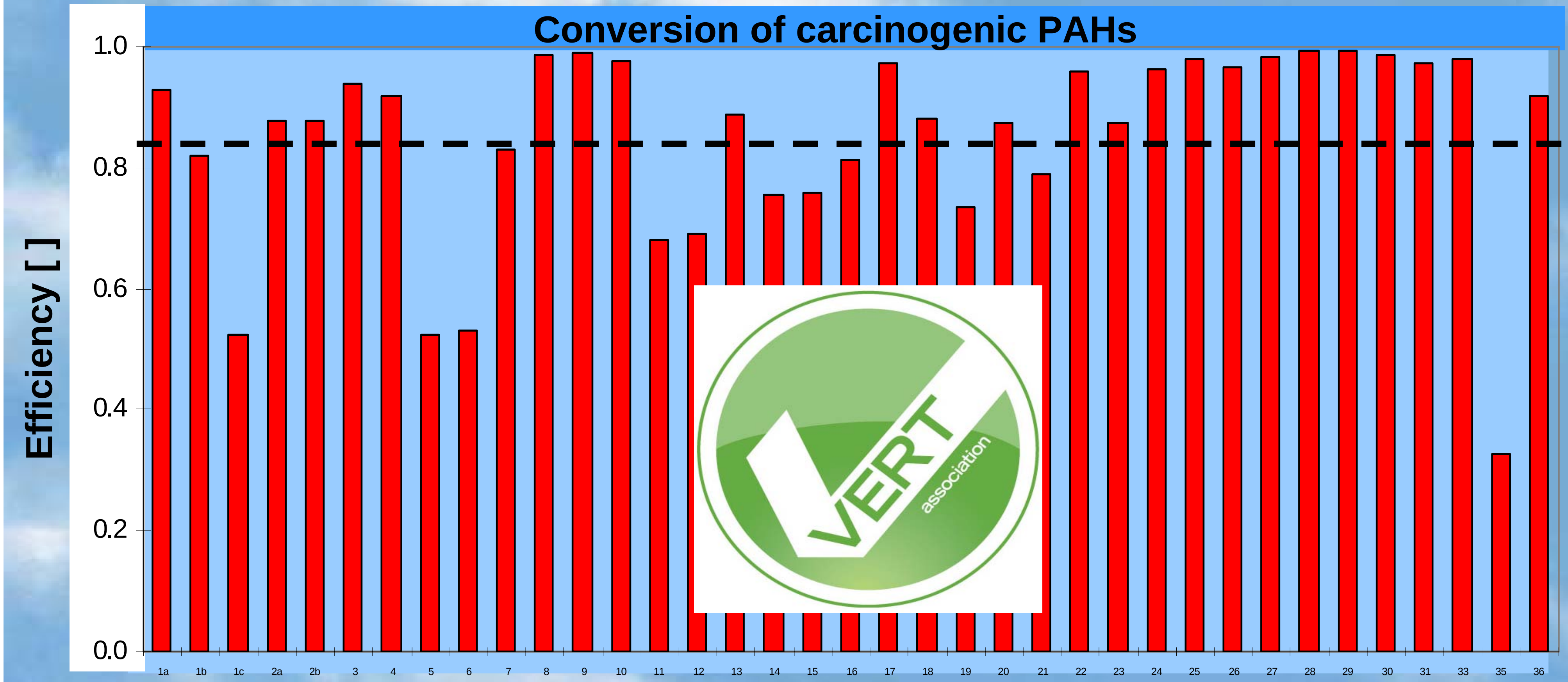
- Diesel exhaust is genotoxic (contains mutagenic and carcinogenic compounds)
- Diesel exhaust classified as group 1 carcinogen inducing lung and bladder cancer in humans (IARC, WHO 2012)
- DPF remove genotoxic compounds up to 98%

Heeb et al. ES&T, **2010**, 42, 3773-3779



# Adverse health effects of diesel exhaust

**All VERT-tested DPFs convert carcinogenic PAHs, most are rather efficient**



# Adverse health effects of diesel exhaust

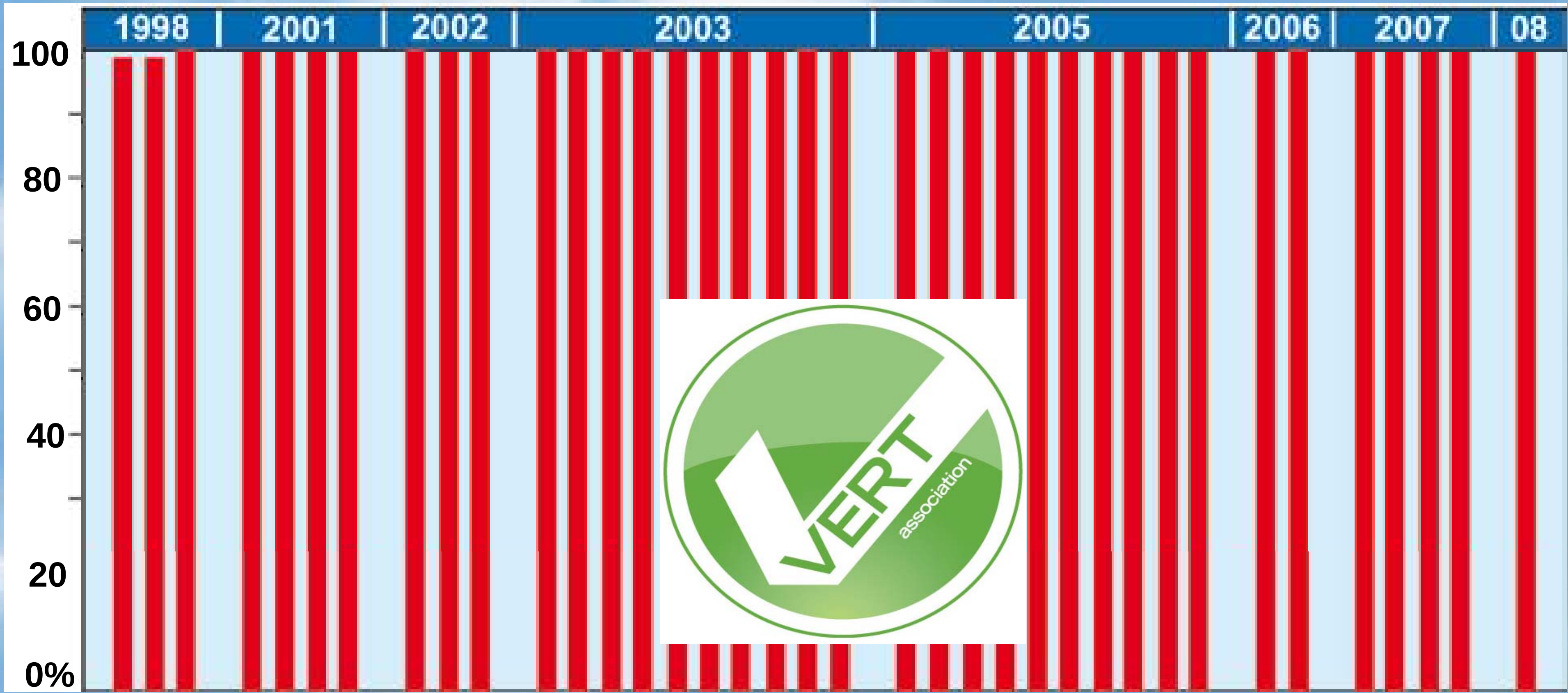
## Problem: Trojan horse effect

- **Nanoparticles penetrate cell membranes (alveoli, placenta, blood cells) acting like a Trojan horse**
- **DPF remove > 98% of nanoparticles**


Trojan horse, Harbour of Canakkale, Turkey

# Adverse health effects of diesel exhaust

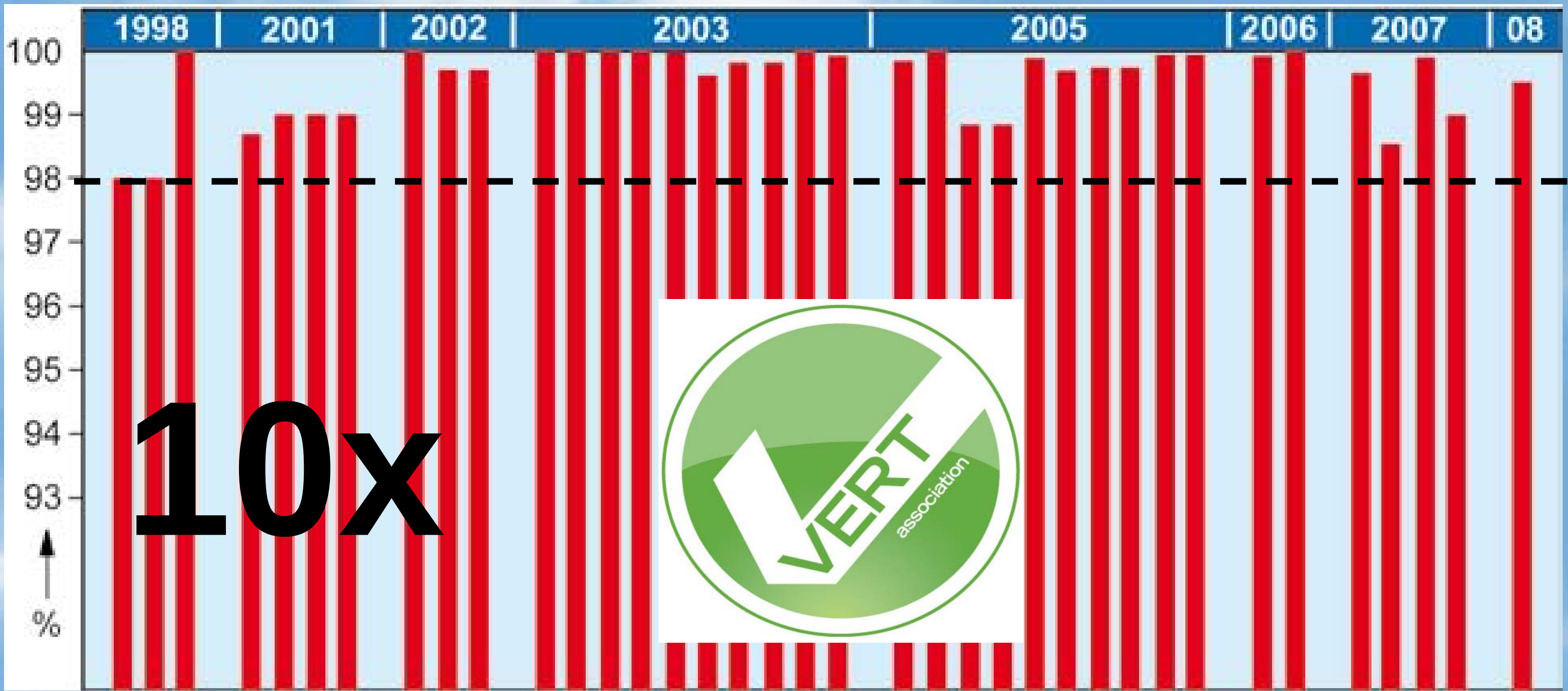
**more than 40 VERT-tested DPFs. All approved systems are excellent particle filters**




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

# Adverse health effects of diesel exhaust

**You have to zoom in to see differences**

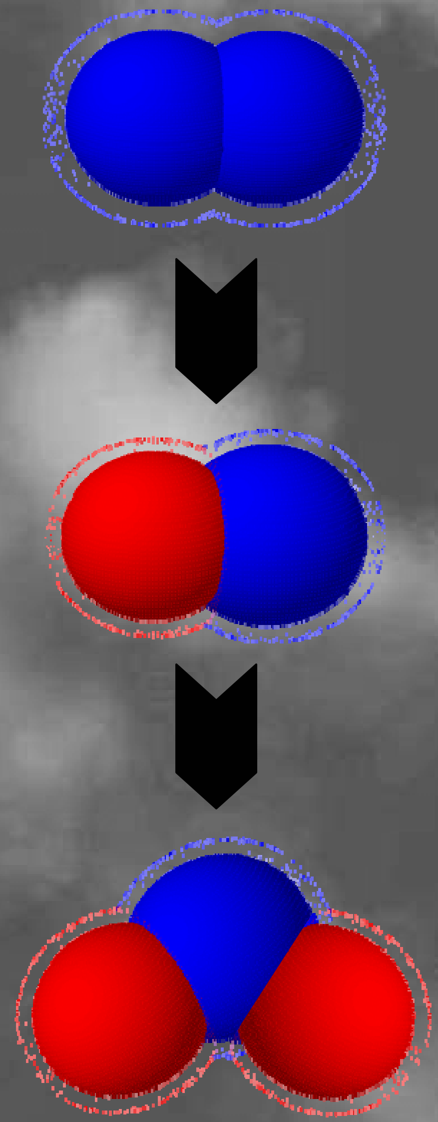



Mayer et al. MTZ, **2009**, 70, 72-79

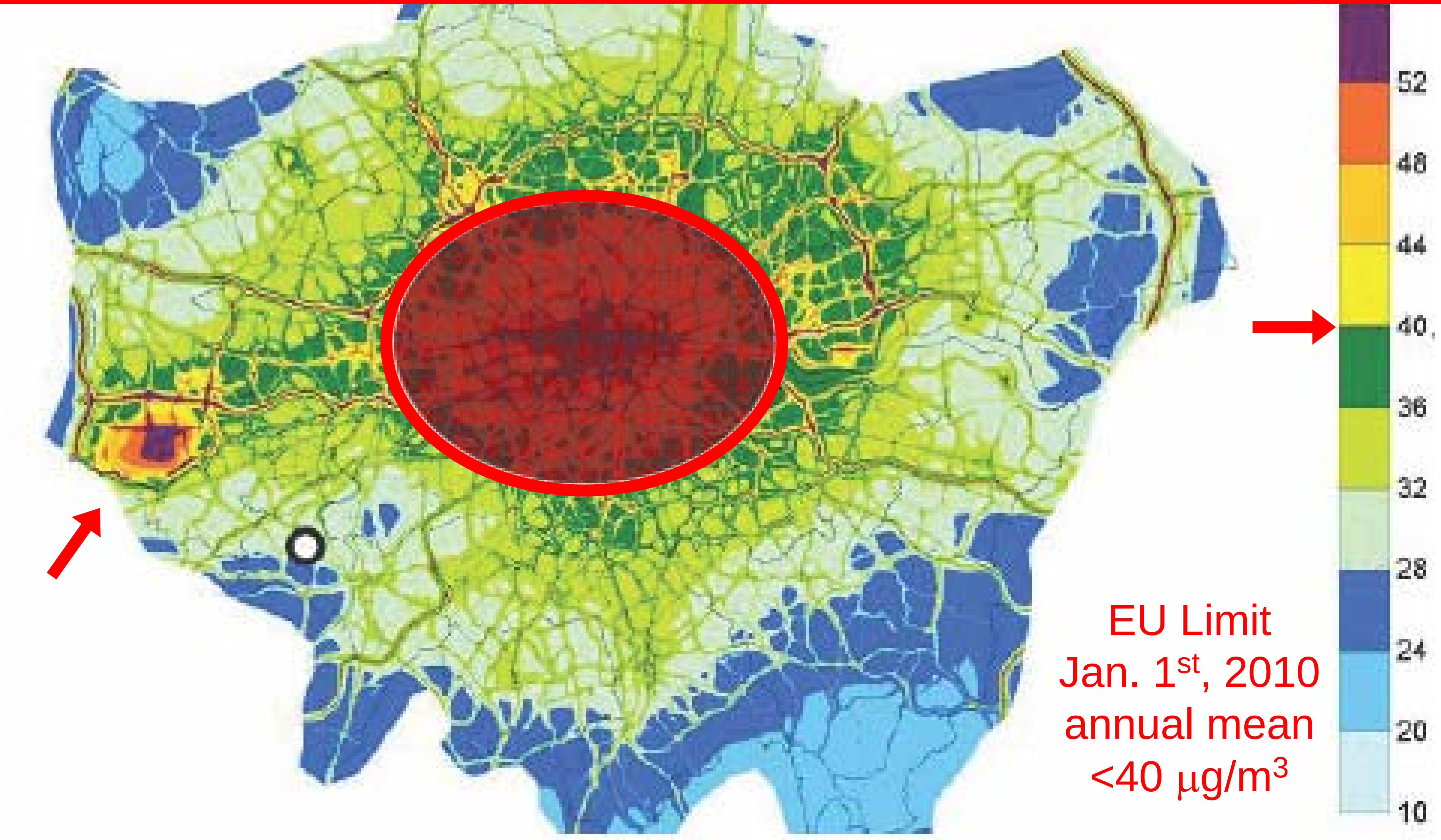
# Adverse health effects of diesel exhaust

## Problem: Reactive nitrogen compounds

- **NO and $NO_2$ induce acute and chronic toxicity (oxidative stress, inflammatory responses, chronic obstructive pulmonary desease, COPD)**
- **hox-DPF increase $NO_2$ emissions**
- **deNOx technologies are needed!**



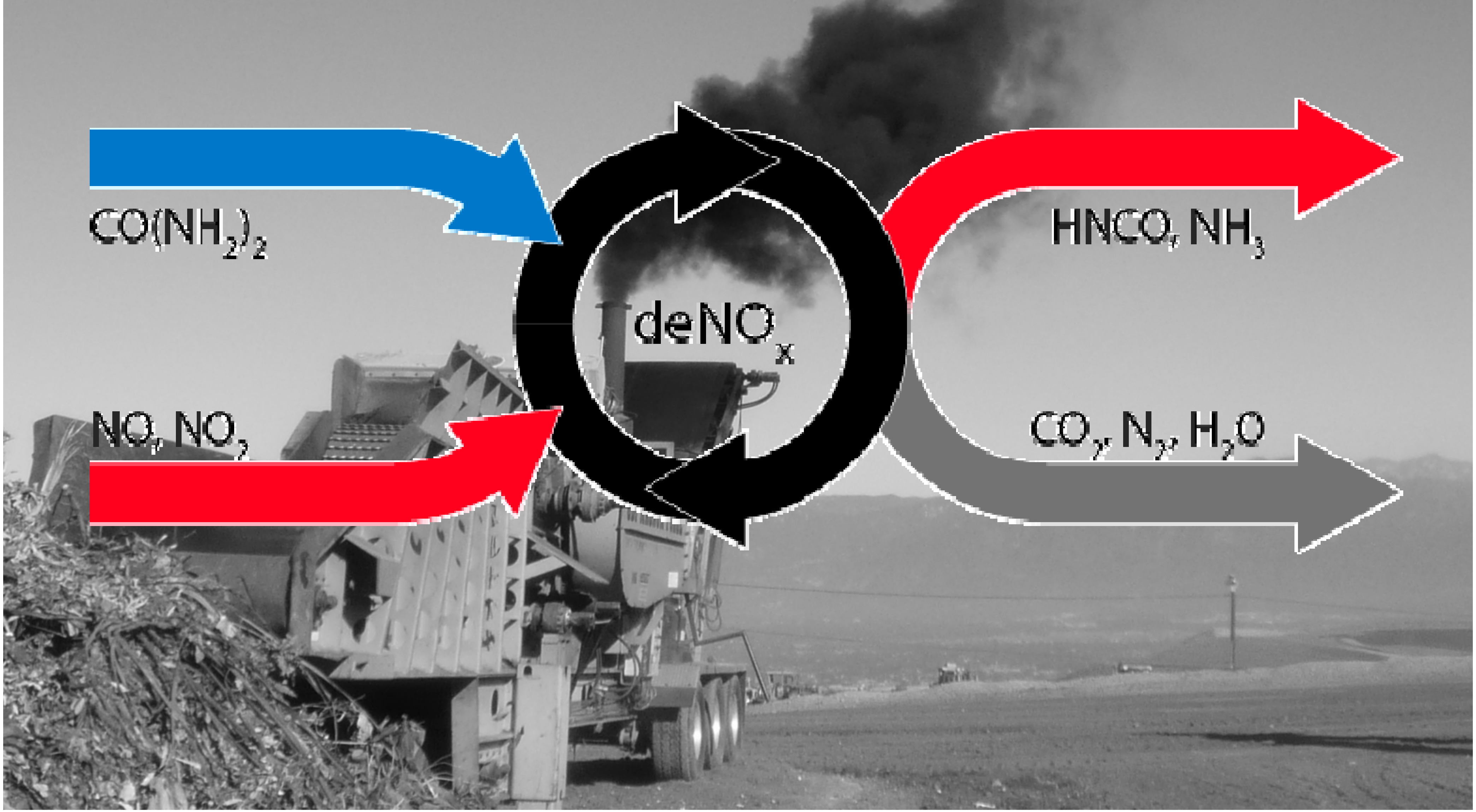
# Mean annual $NO_2$ levels of the City of London




- http://www.dft.gov.uk/pgr/aviation/environmentalissues/heathrowsustain/monitoringandmeasure2911?page=6

# Urea-based SCR

**Impact of deNOx-technologies on RNC emissions?**



# Urea-based SCR

**At least two steps to decompose and hydrolyze urea**

$$2\,NO + O_2 \rightleftharpoons 2\,NO_2 \qquad \textbf{(1)}$$

$$2\,NH_3 + NO + NO_2 \longrightarrow 2\,N_2 + 3\,H_2O \qquad \textbf{(2)}$$

$$4\,NH_3 + 4\,NO + O_2 \longrightarrow 4\,N_2 + 6\,H_2O \qquad \textbf{(3)}$$

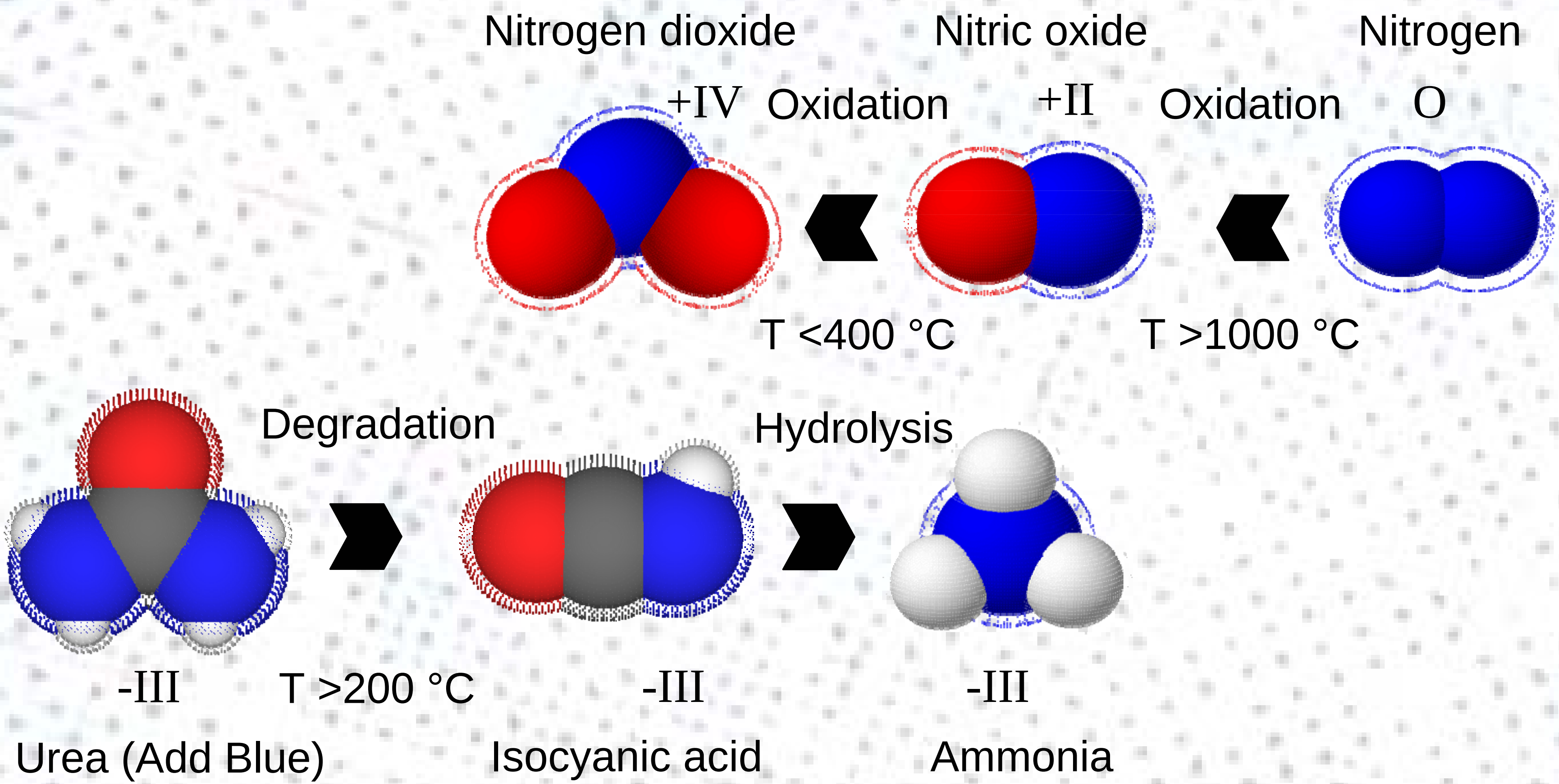
$$8\,NH_3 + 6\,NO_2 \longrightarrow 7\,N_2 + 12\,H_2O \qquad \textbf{(4)}$$

$$CO(NH_2)_2 \longrightarrow NH_3 + HNCO \qquad \textbf{(5)}$$

$$HNCO + H_2O \longrightarrow NH_3 + CO_2 \qquad \textbf{(6)}$$

# Reactive nitrogen compounds (RNCs)

**What are reactive nitrogen compounds?**



# Reactive nitrogen compounds (RNCs)

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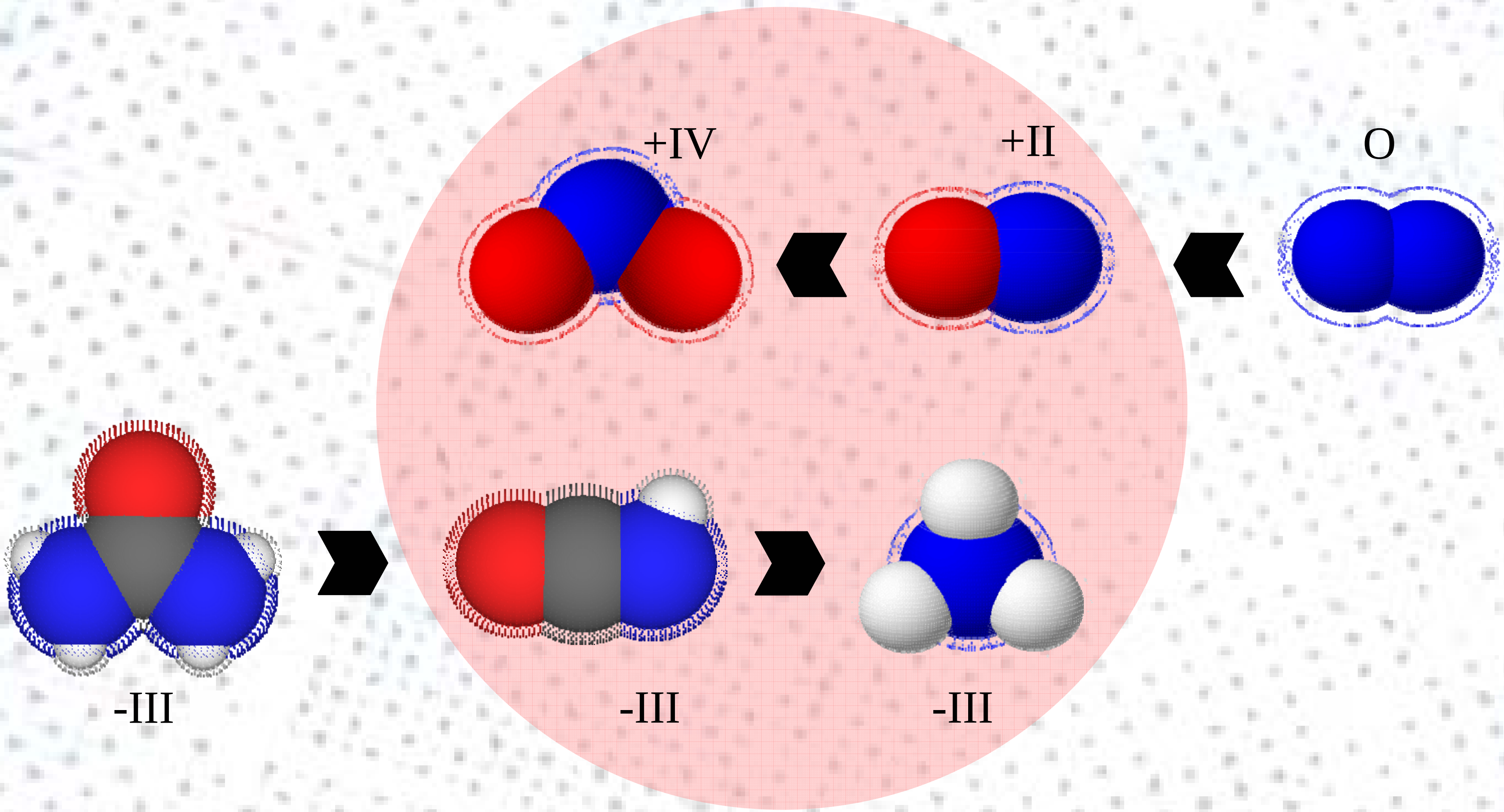
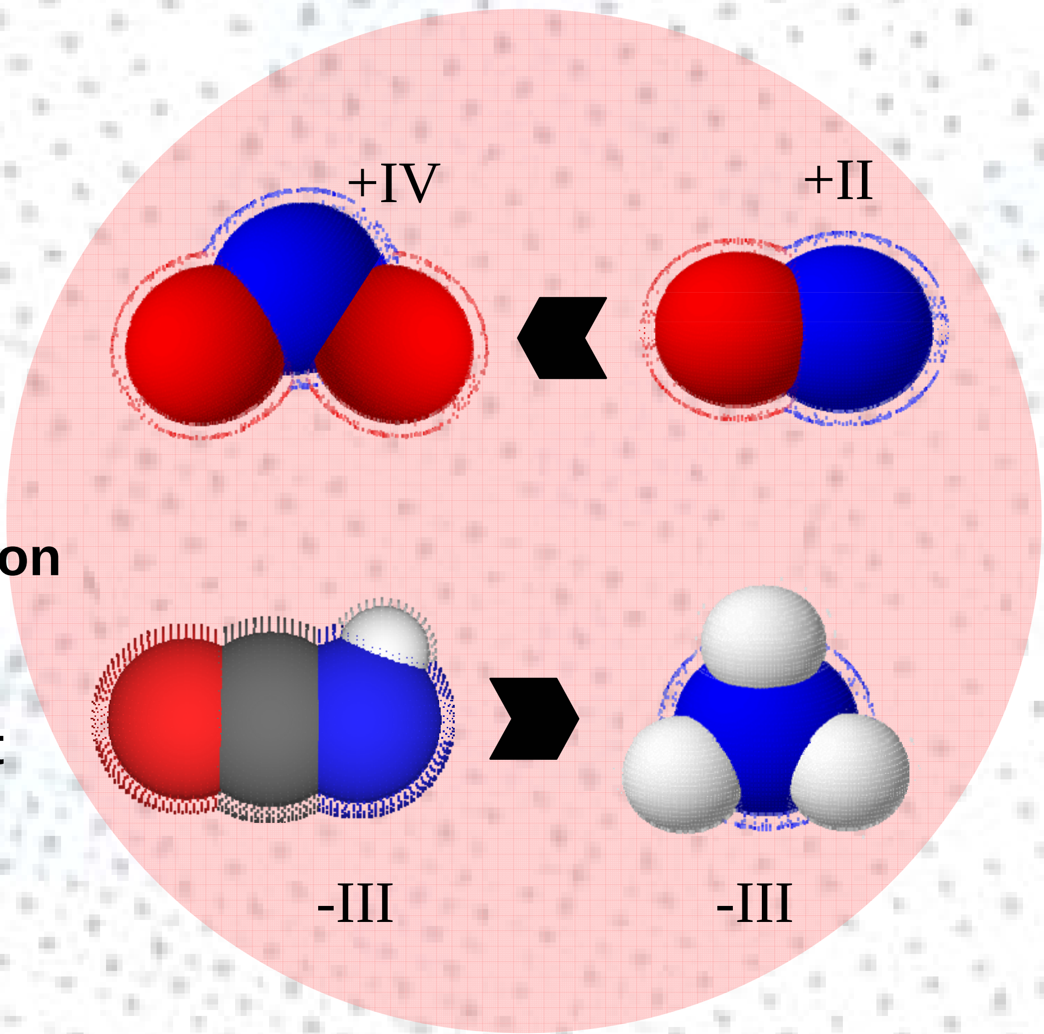


# Reactive nitrogen compounds (RNCs)

**What are reactive nitrogen compounds?**

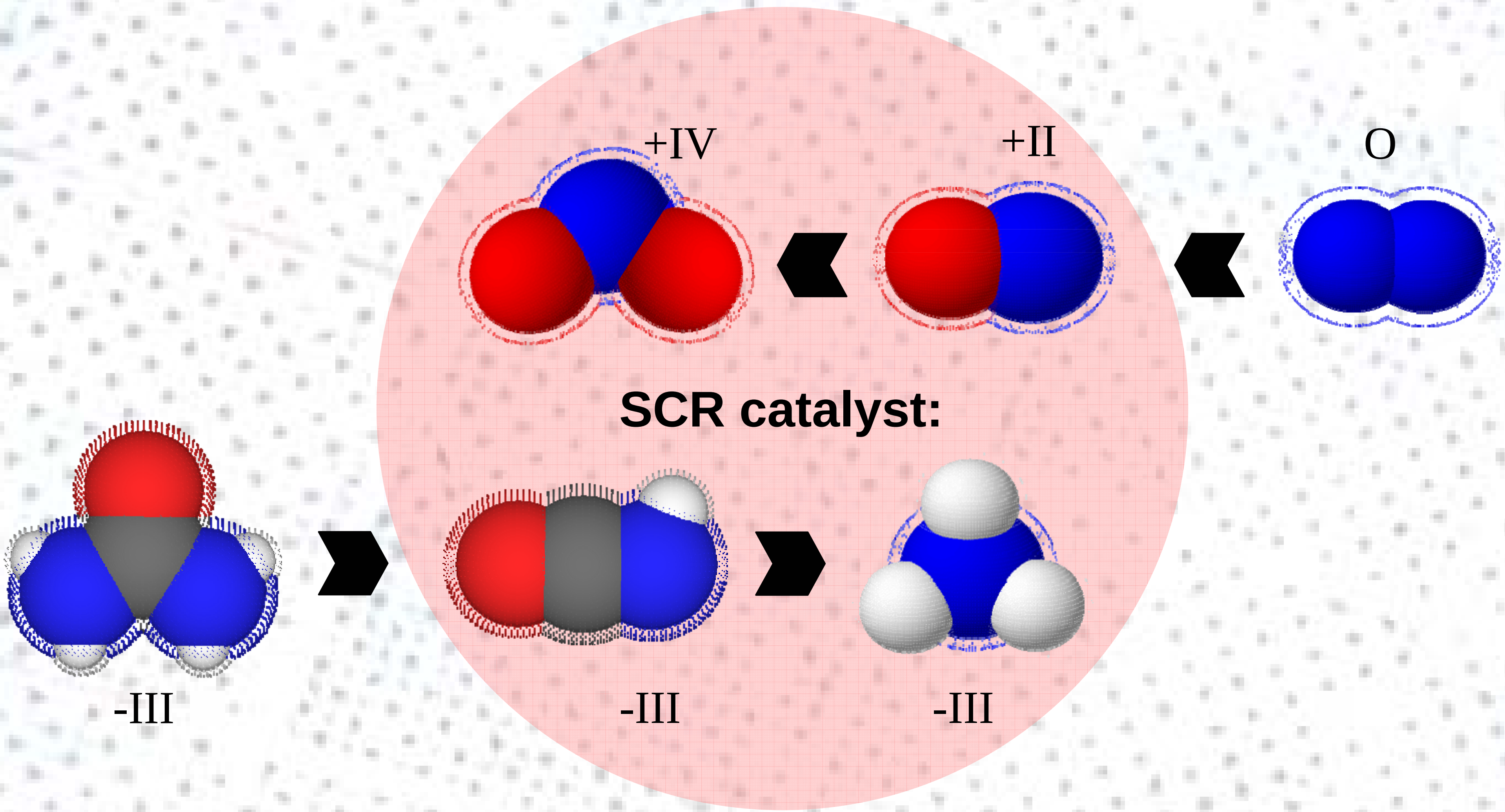
**RNCs are:**

- **highly reactive**
- **short life time**
- **fast transformation**
- **acute toxicity**
- **difficult to detect**



# Urea-based SCR

They are also key molecules of the urea-based SCR chemistry



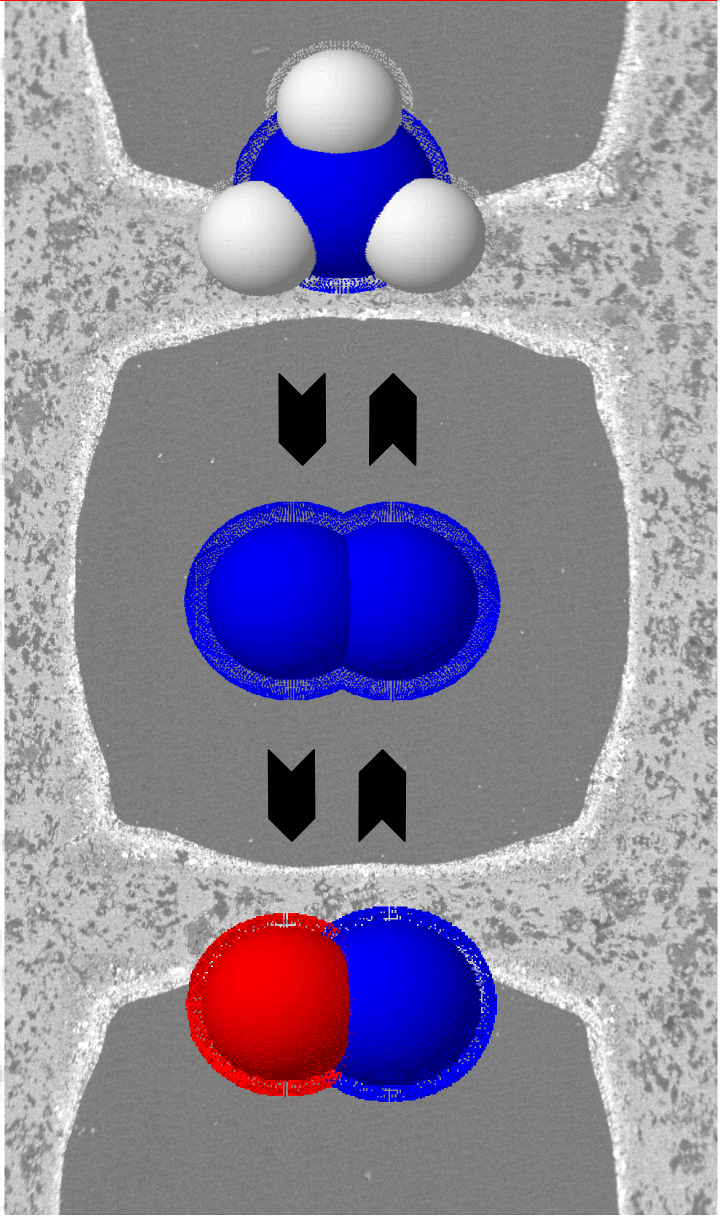
# Secondary pollutants of deNOx-technologies

**The $NH_3$ problem**

- $NH_3$ - a toxic air pollutant
- Eutrophication of soils and surface waters
- Involved in the formation of secondary aerosols

**Risks**

- On-board formation of $NH_3$
- $NH_3$ slip at transient engine operation
- Over dosage of urea



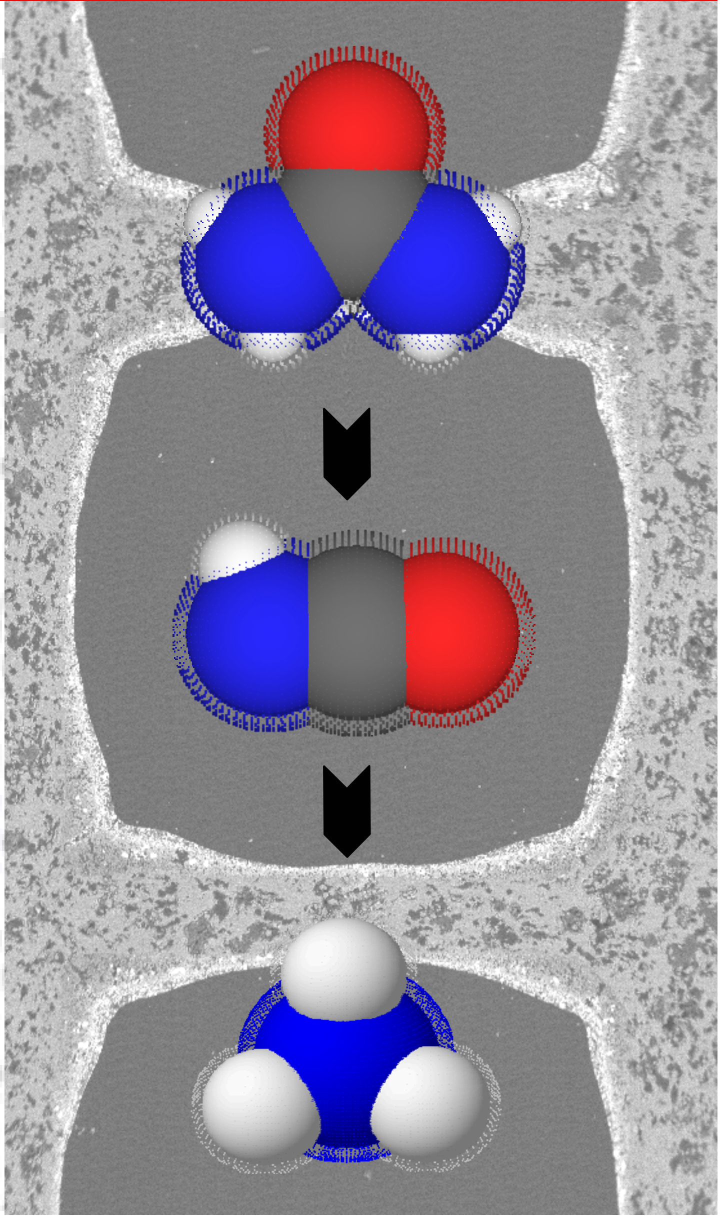
# Secondary pollutants of deNOx-technologies

## The HNCO problem

- Isocyanates are toxic
- Highly reactive, react with -OH, $-NH_2$, and -SH groups (molecules of life)
- Methyl isocyanate accident Bhopal, India (42 t released on 3.12.1984)

## Risks

- On-board HNCO formation
- Over dosage of urea
- Reacts with other exhaust constituents to form secondary pollutants



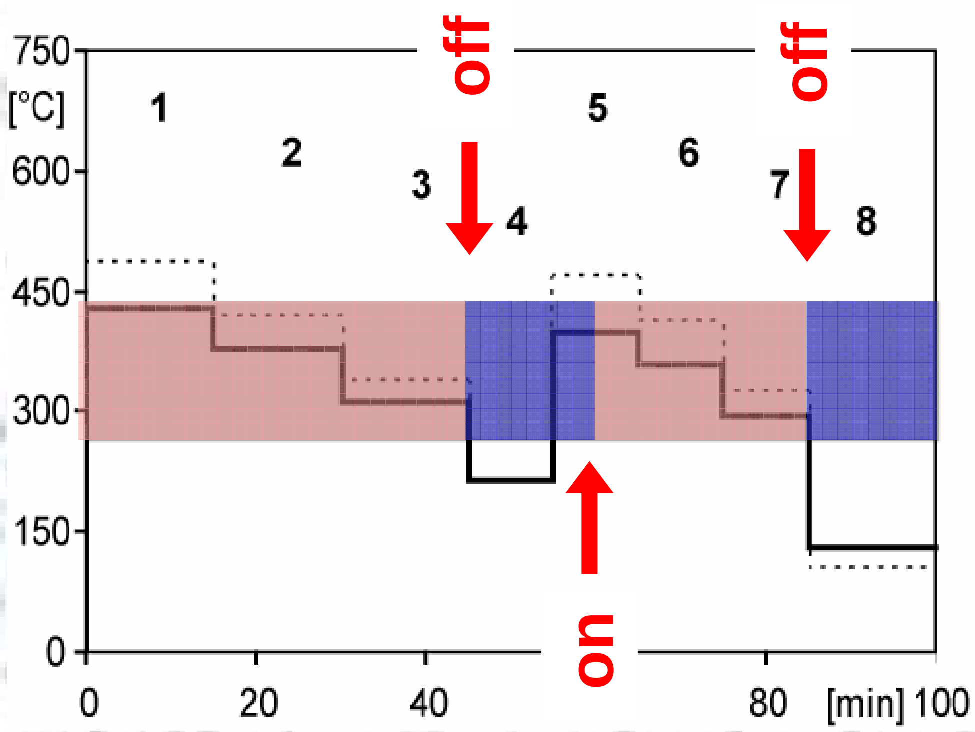
# The combined DPF-deNO$_x$ system – a chemical factory?

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

# Exhaust temperatures in the ISO 8178/4 C1 cycle

**The deNOx-system is only part-time active (60-80%)**

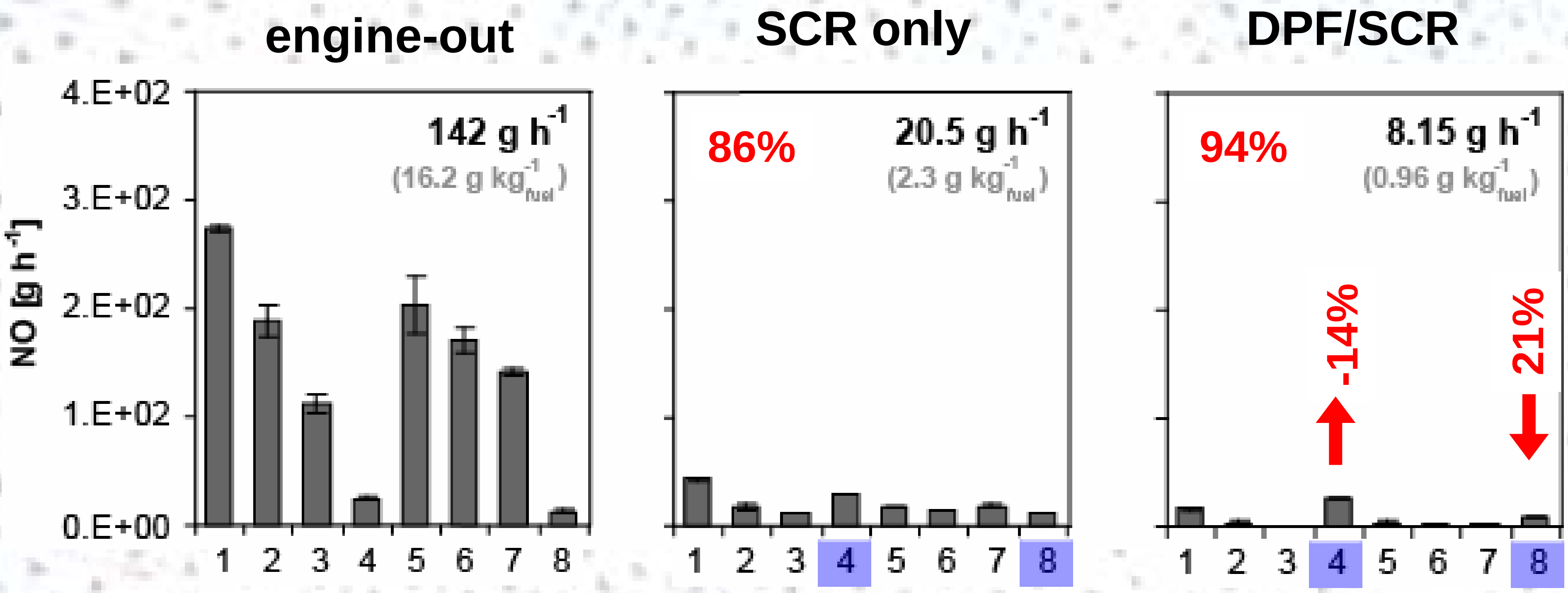
**Urea-based deNOx-system active >200°C**



# DeNO$_x$ Efficiencies

**High NO conversion efficiencies can be achieved!**

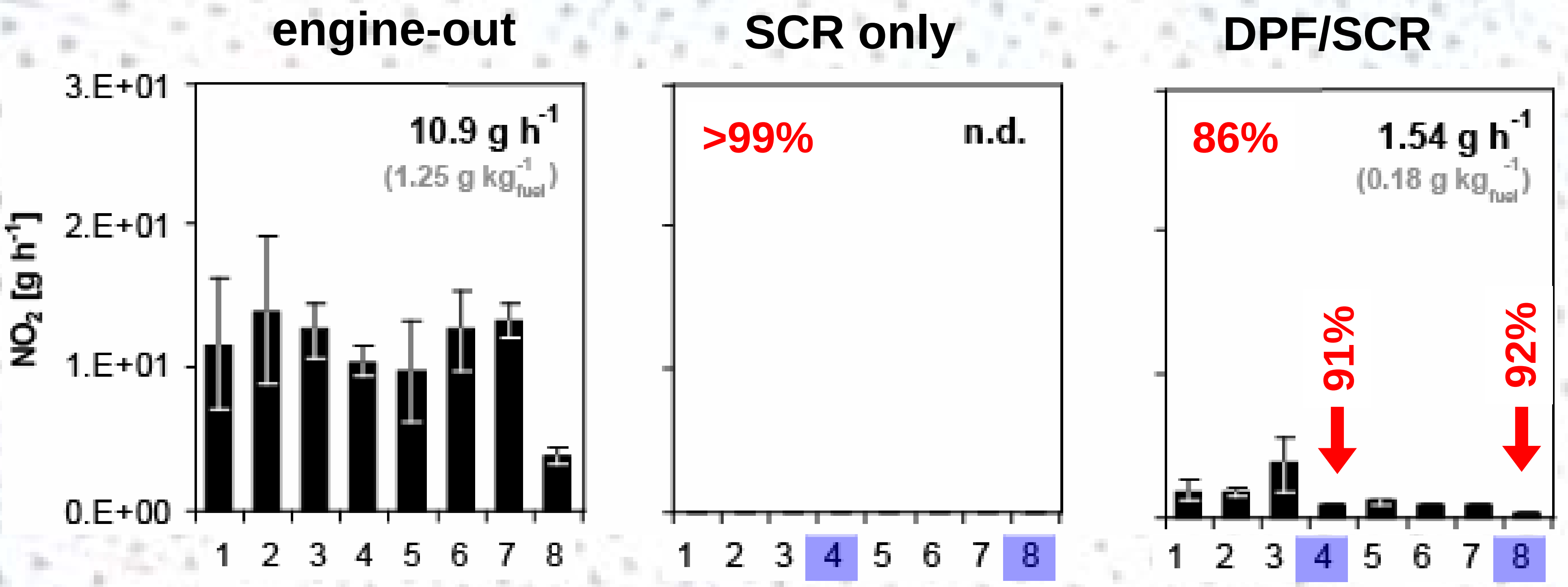
## Nitric oxide (NO)



# $DeNO_x$ Efficiencies

**High efficiencies for $NO_2$ even with intense $NO_2$ formation in the DPF!**

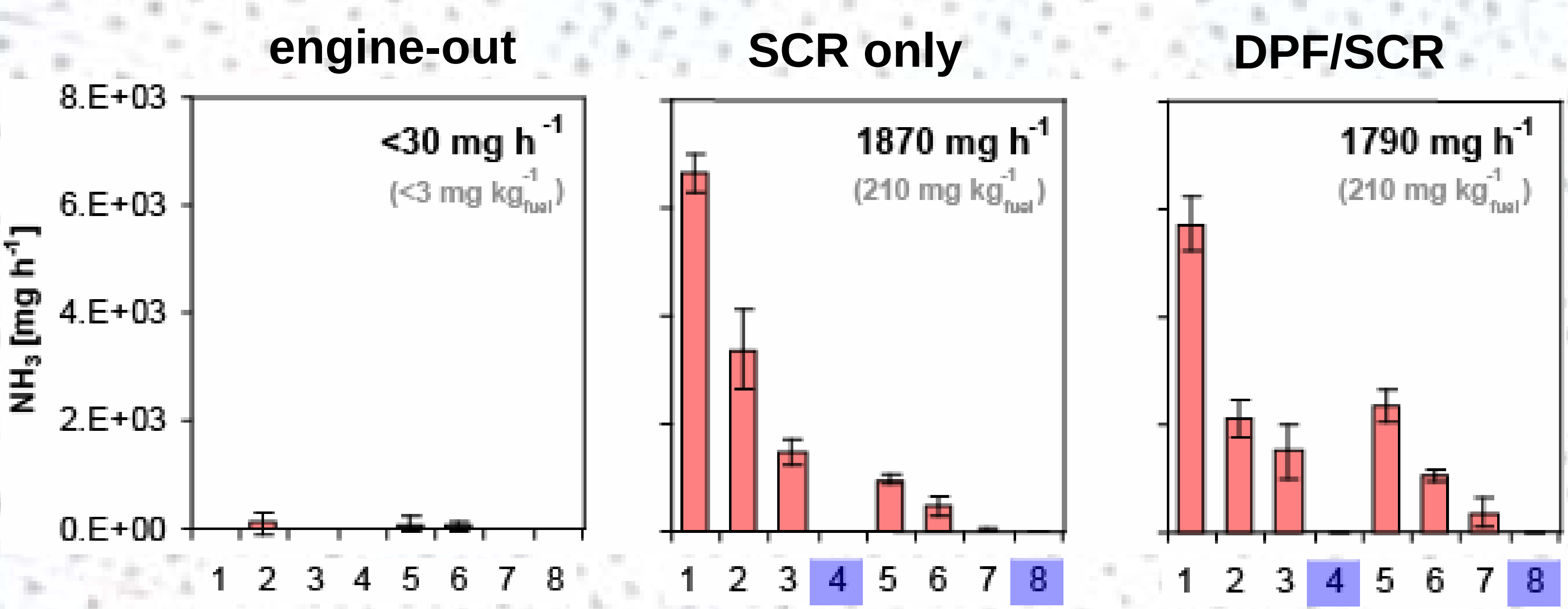
## Nitrogen dioxide ($NO_2$)



# Secondary pollutants of deNOx-technologies

**Substantial ammonia emissions with active SCR!**

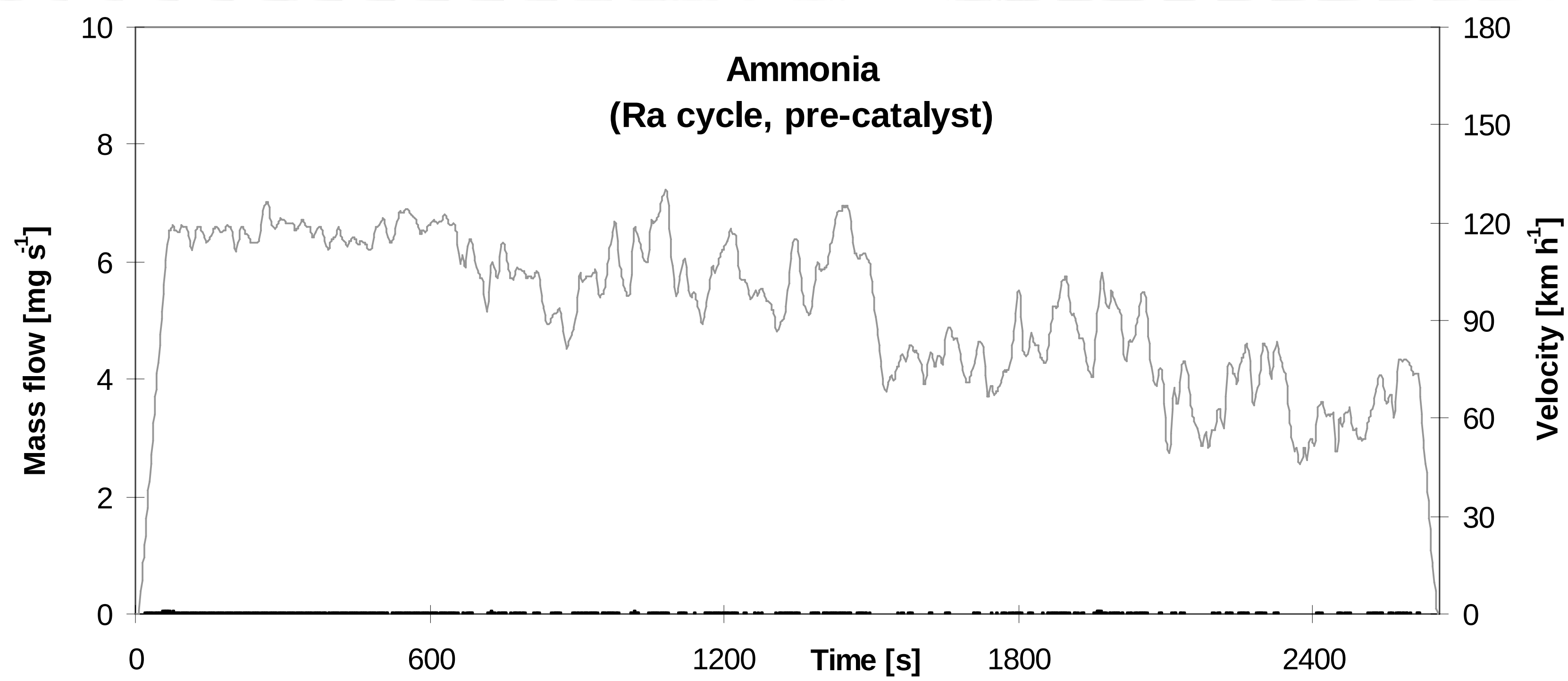
**Ammonia ($NH_3$)**



# Secondary pollutants of deNOx-technologies

**No ammonia before catalyst**

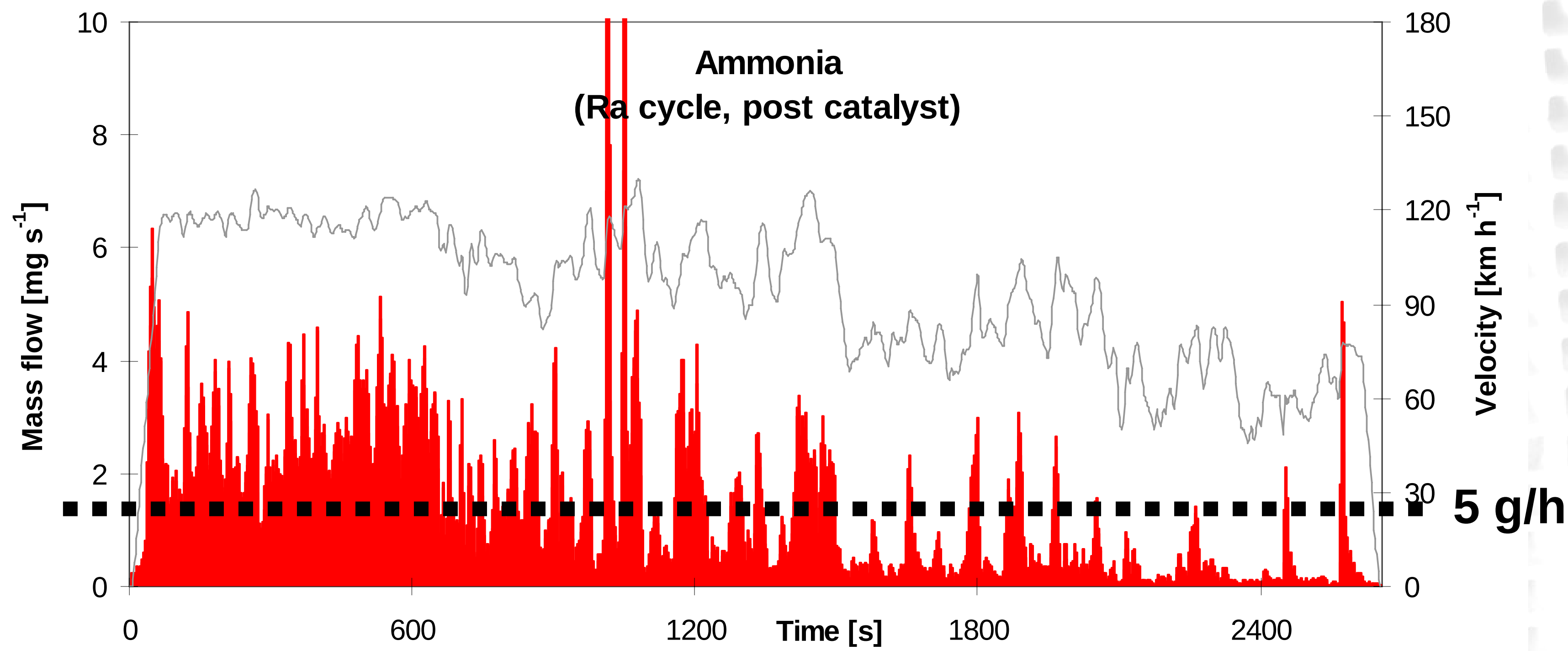
## Ammonia formation in a Pd/Rh-TWC (BMW, 1.8 l, Euro-1)



# Secondary pollutants of deNOx-technologies

**How much $NH_3$ emissions have we already accepted from the TWC technology?**

## Ammonia formation in a Pd/Rh-TWC (BMW, 1.8 l, Euro-1)



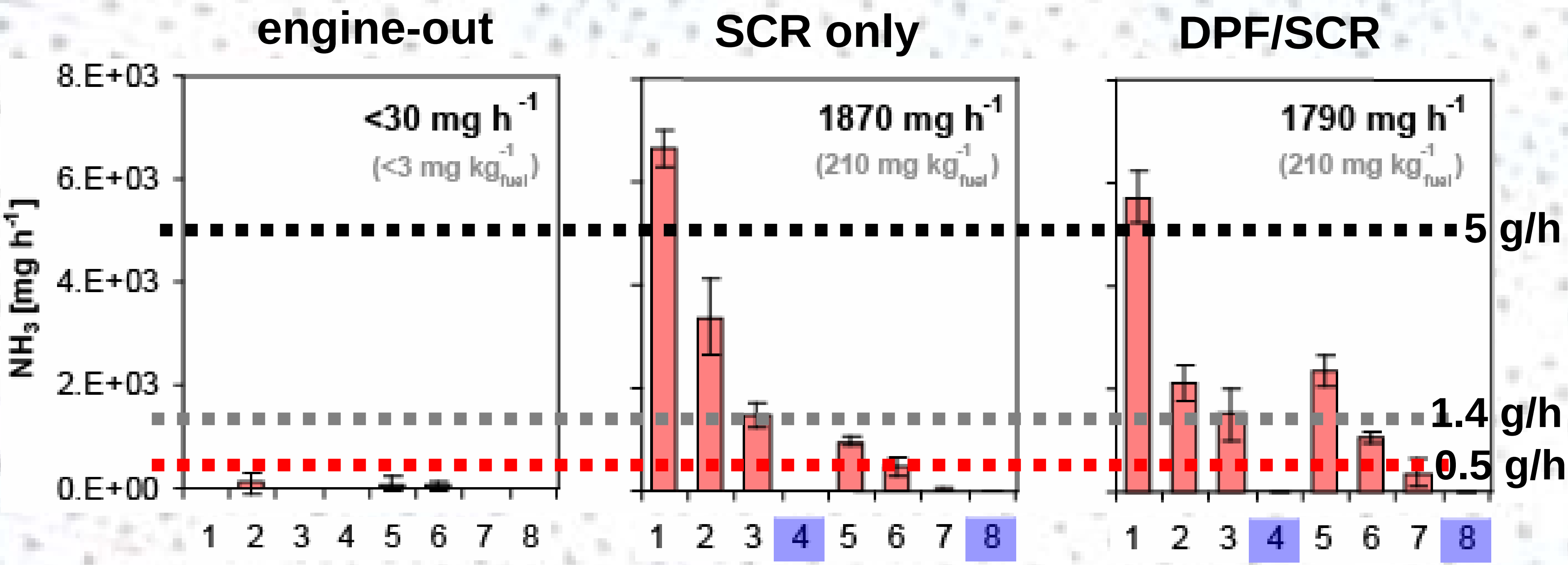

Heeb et al. Atm. Env. 40 (2006) 3750-3763
Heeb et al. Atm. Env. 40 (2006) 5986-5997

Heeb et al. Atm. Env. 42 (2008) 2543-2554

# Secondary pollutants of deNOx-technologies

**Substantial ammonia emissions with active SCR!**

**Ammonia ($NH_3$)**



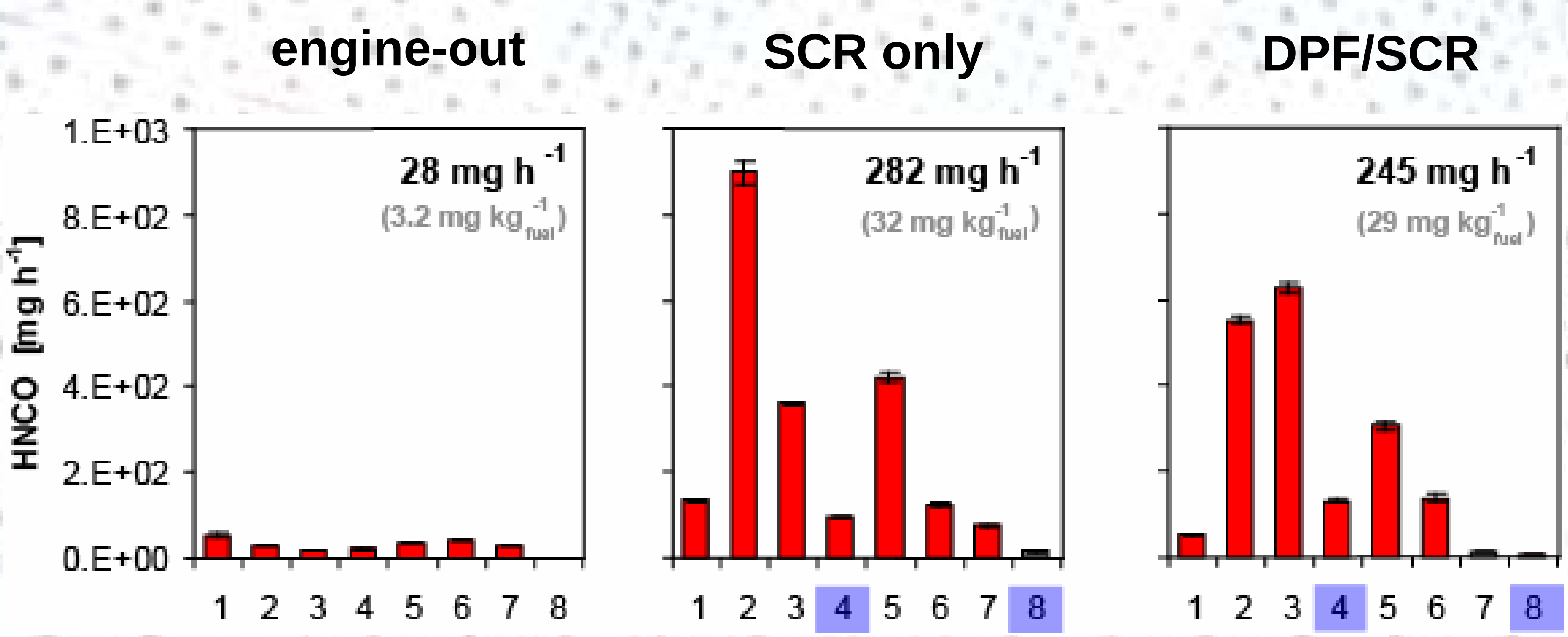

Heeb et al. Atm. Env. 40 (2006) 3750-3763
Heeb et al. Atm. Env. 40 (2006) 5986-5997

Livingston et al. Atm. Env. 43 (2009) 3326-3333
Heeb et al. Atm. Env. 42 (2008) 2543-2554

# Secondary pollutants of deNOx-technologies

**Increased isocyanic acid emissions with active SCR!**

## Isocyanic acid (HNCO)




Heeb et al. Atm. Env. 40 (2011) 3203-3209

# Swiss National Accident Insurance (SUVA): Exposure limits at workplaces

**Maximum tolerable workplace concentration 0.02 mg/m3 not to be exceeded for 15 min**

## MTWC of isocyanates

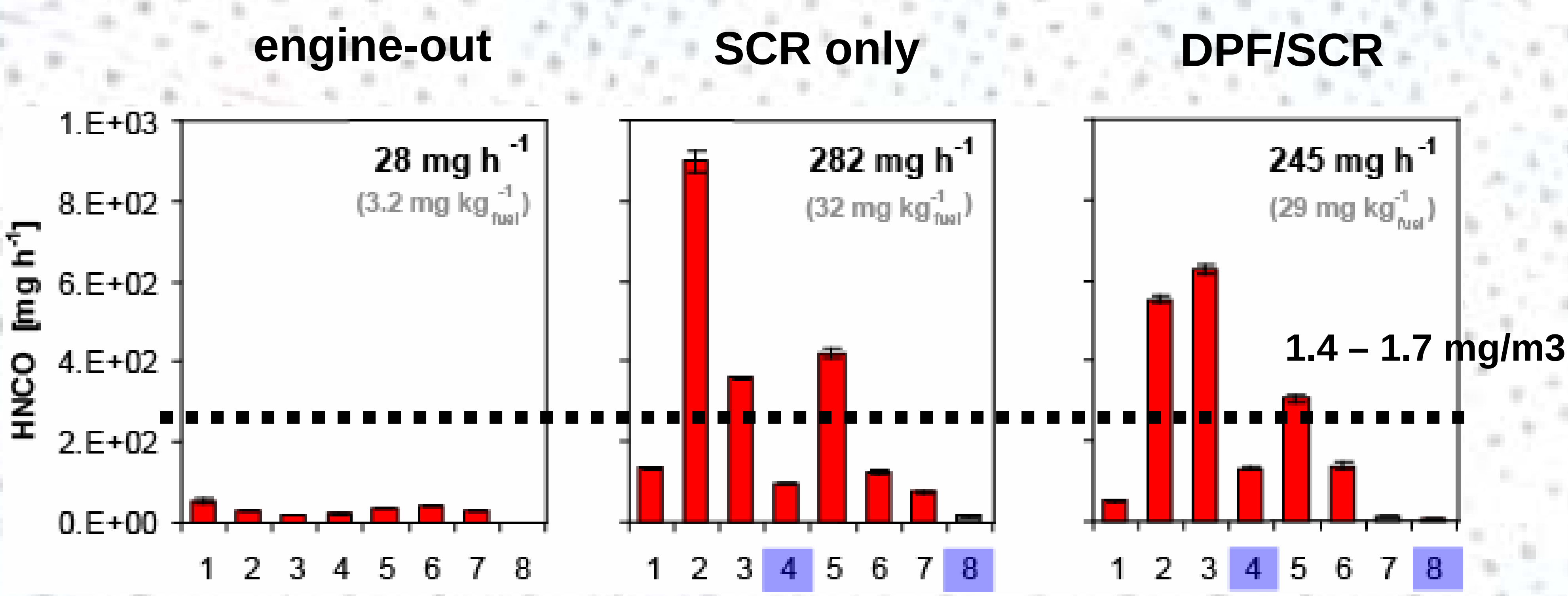
| Stoff [CAS-Nummer] | MAK-Wert | | Kurzzeitgrenzwerte | | |
|---|---|---|---|---|---|
| | ml/m³ (ppm) | mg/m³ | ml/m³ (ppm) | mg/m³ | Zeitl. Begrenzung (Häufigkeit x Dauer in min./Schicht) |
| Isocyanate (Monomere und Präpolymere) (als Gesamt-NCO gemessen) | | 0,02 | | 0,02 | 15 min |

SUVA, Swiss National Accident Insurance Organization, 2011. Grenzwerte am Arbeitsplatz. Available at: http://www.suva.ch.

# Secondary pollutants of deNOx-technologies

**Isocyanic acid emissions 70-85 x above MTWC**

## Isocyanic acid (HNCO)




Heeb et al. Atm. Env. 40 (2011) 3203-3209

# The combined DPF-deNO$_x$ system – a chemical factory?

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

**Are DPN systems the ultimate solution?**

**VERT-goals:**

- Benefit/risk assessment of converter technologies
- Effectiveness on regulated pollutants
- Effects on toxic exhaust gas constituents
- Potential for secondary emissions (poisoning)

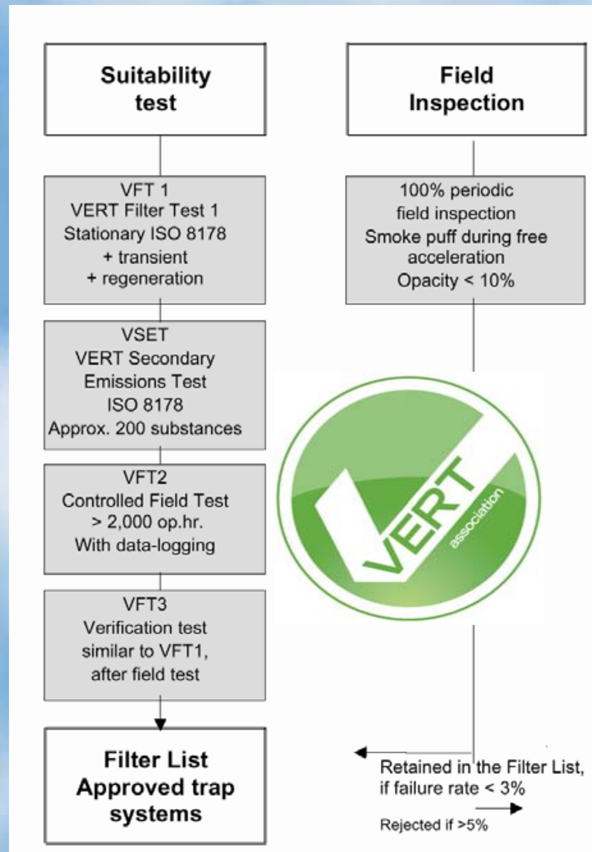
# VERT approval for combined DPF-deNO$_x$ systems

**The VERT approach is also suitable for benefit/risk assessments of DPN systems**

## Requirements for combined systems

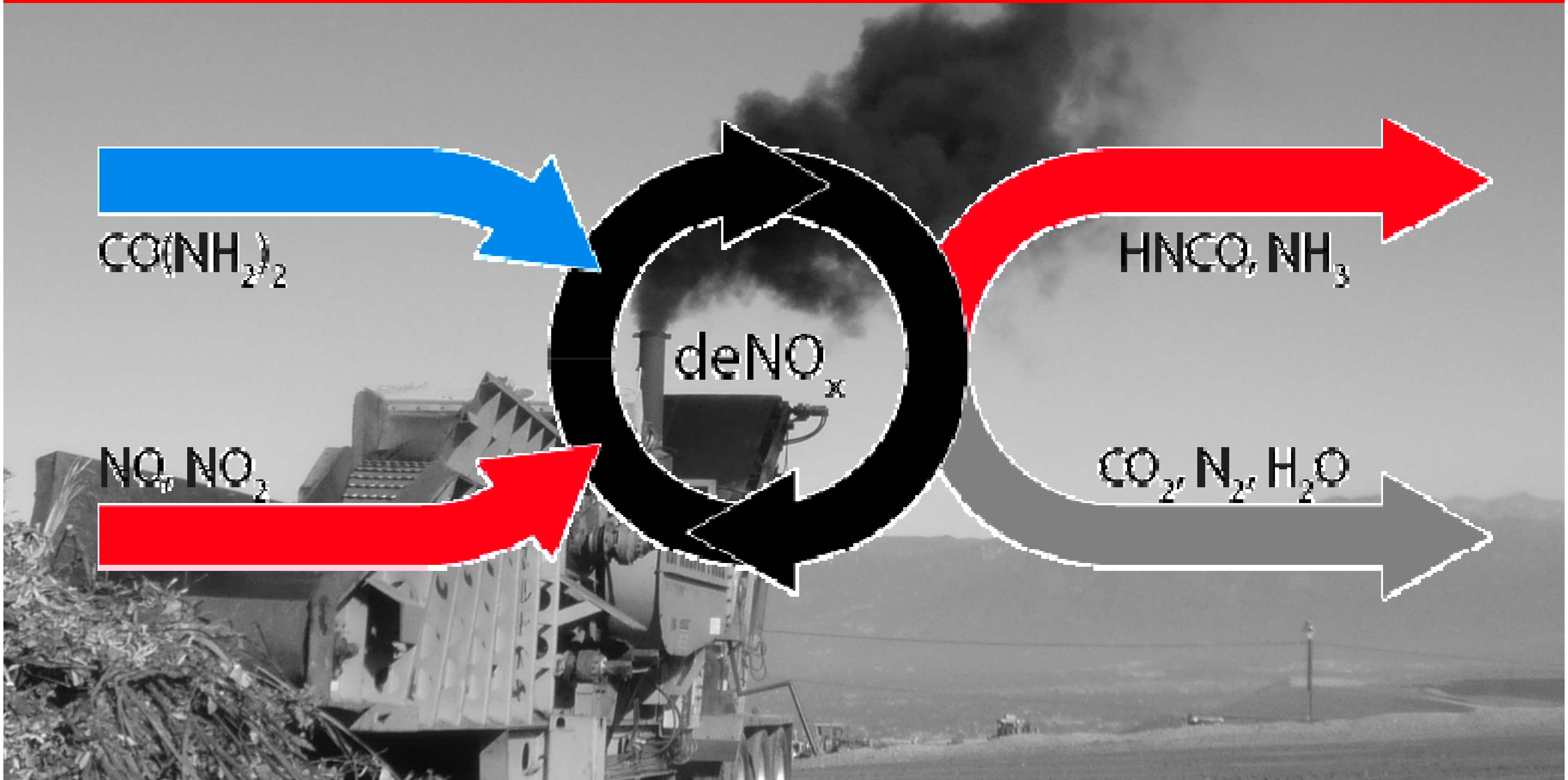
### Approved DPNs should:

- Reduce PM- & PN-emissions (>98%)
- Reduce genotoxic compounds (a.m.a.p.)
- Have low risks of secondary emissions
- Reduce NO and $NO_2$ emissions (>? %)




Combined systems are considered as DPFs with additional features. They have to fulfill the same VERT standards as DPFs.

# When DPFs meet $deNO_x$-technologies




DPFs are now BAT to detoxify diesel exhaust.
Combinations with appropriate $deNO_x$-technologies will be the future!

# Effects of a combined DPF-deNO$_x$ system on RNC emissions

**A combined effort with many important contributions**

## Thanks:

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