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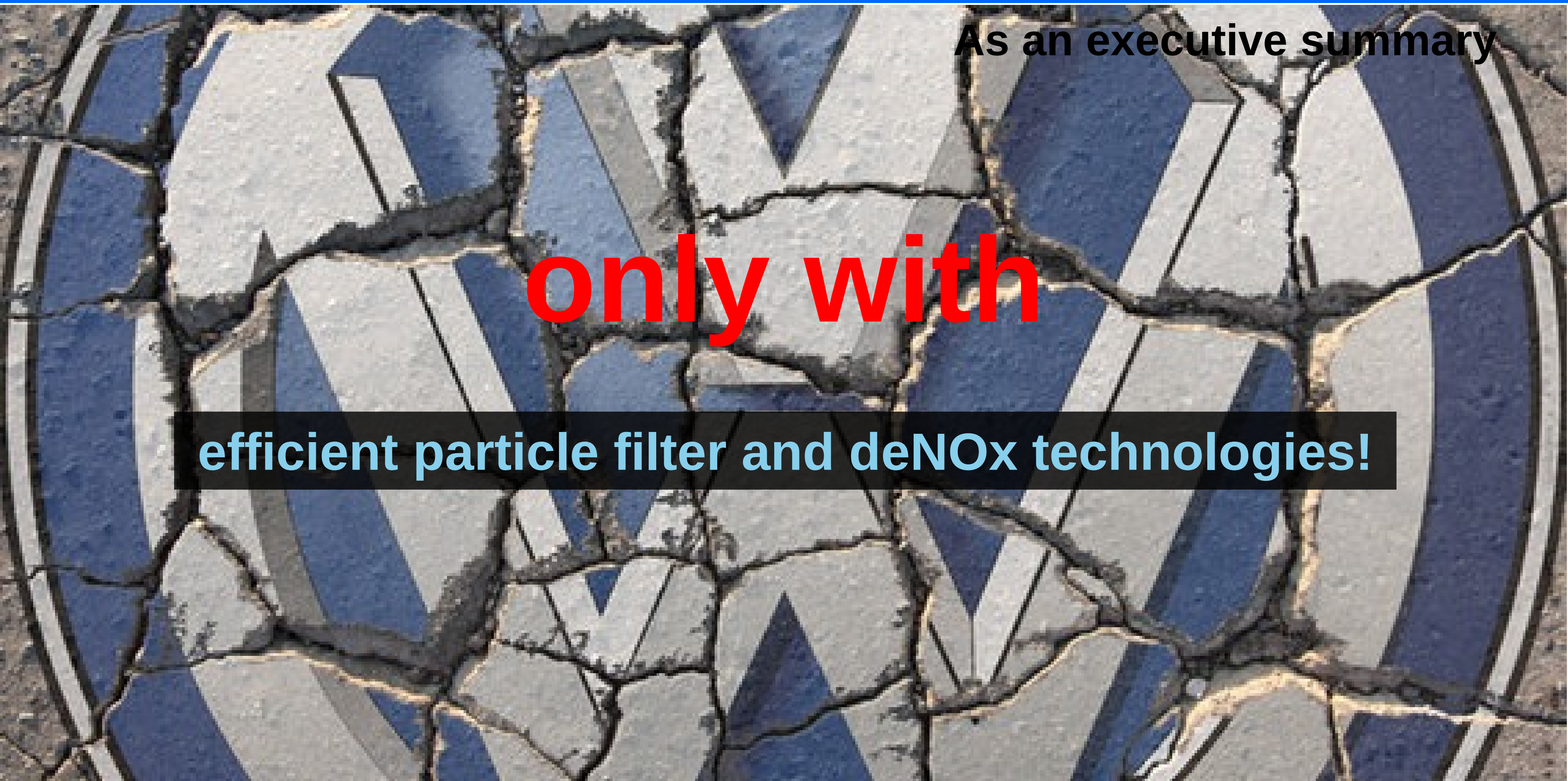
Empa
Materials Science and Technology

Will diesel technology survive?

21st ETH Conference on Combustion Generated Nanoparticles

Zürich, June 19-22, 2017

Will diesel technology survive?



As an executive summary

only with

efficient particle filter and deNOx technologies!

21st ETH Conference on Combustion Generated Nanoparticles

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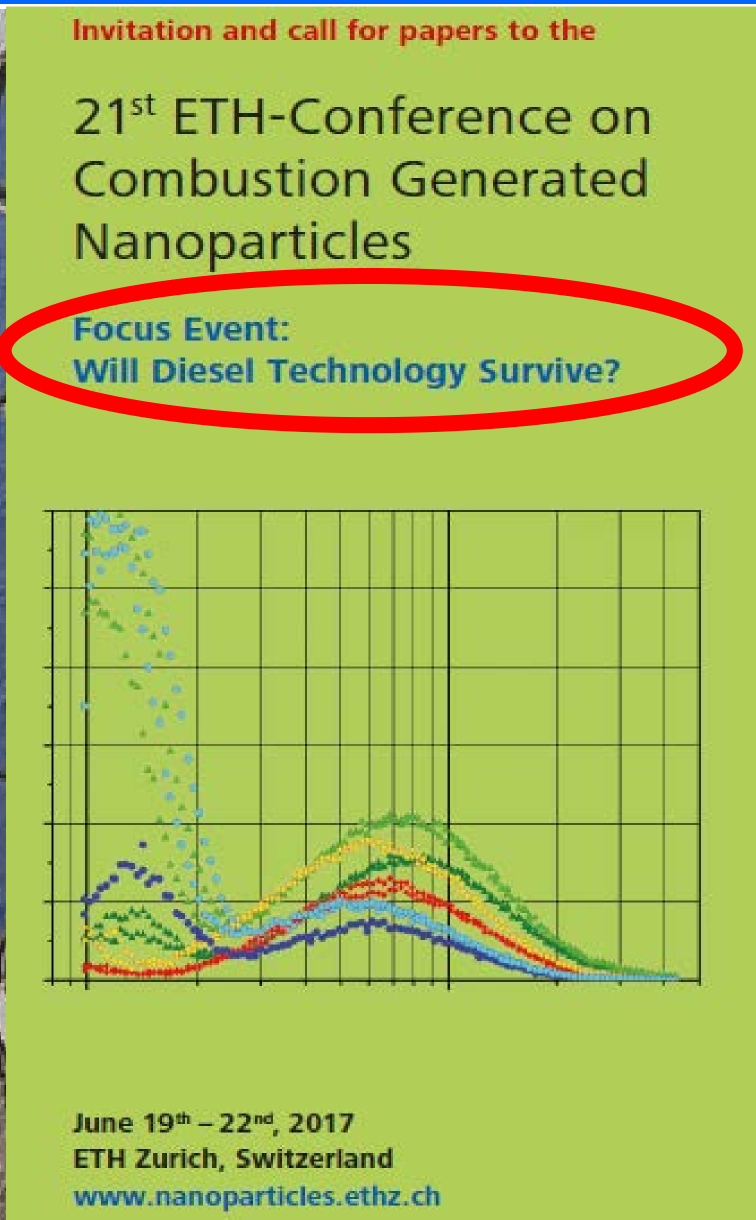
Will diesel technology survive?



1st part: 13:50-15:10

Impact of current diesel technologies

Coffee break 15:10-15:40

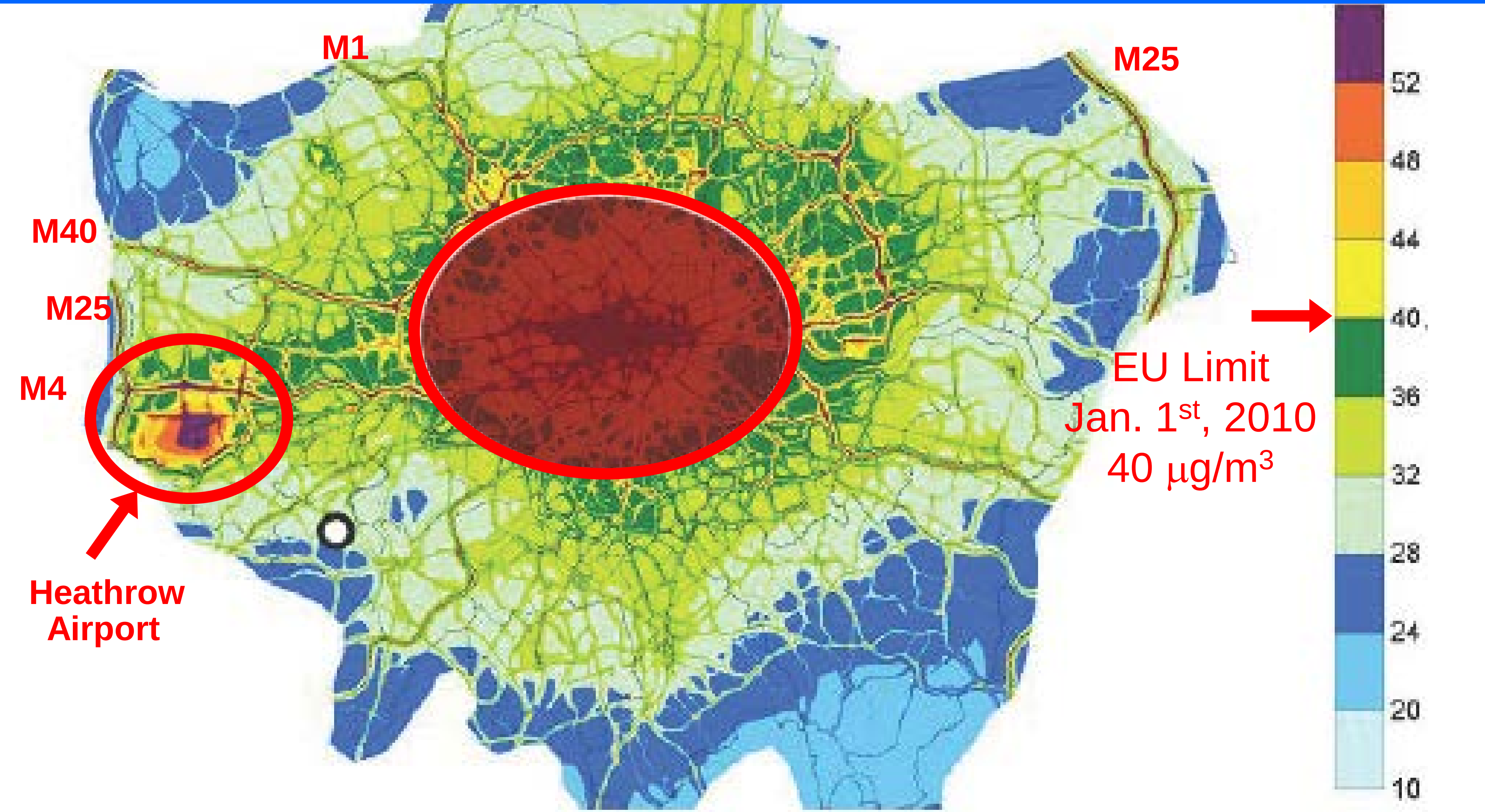
2nd part: 15:40-16:40

The future of diesel technologies

Goodbye: 16:50

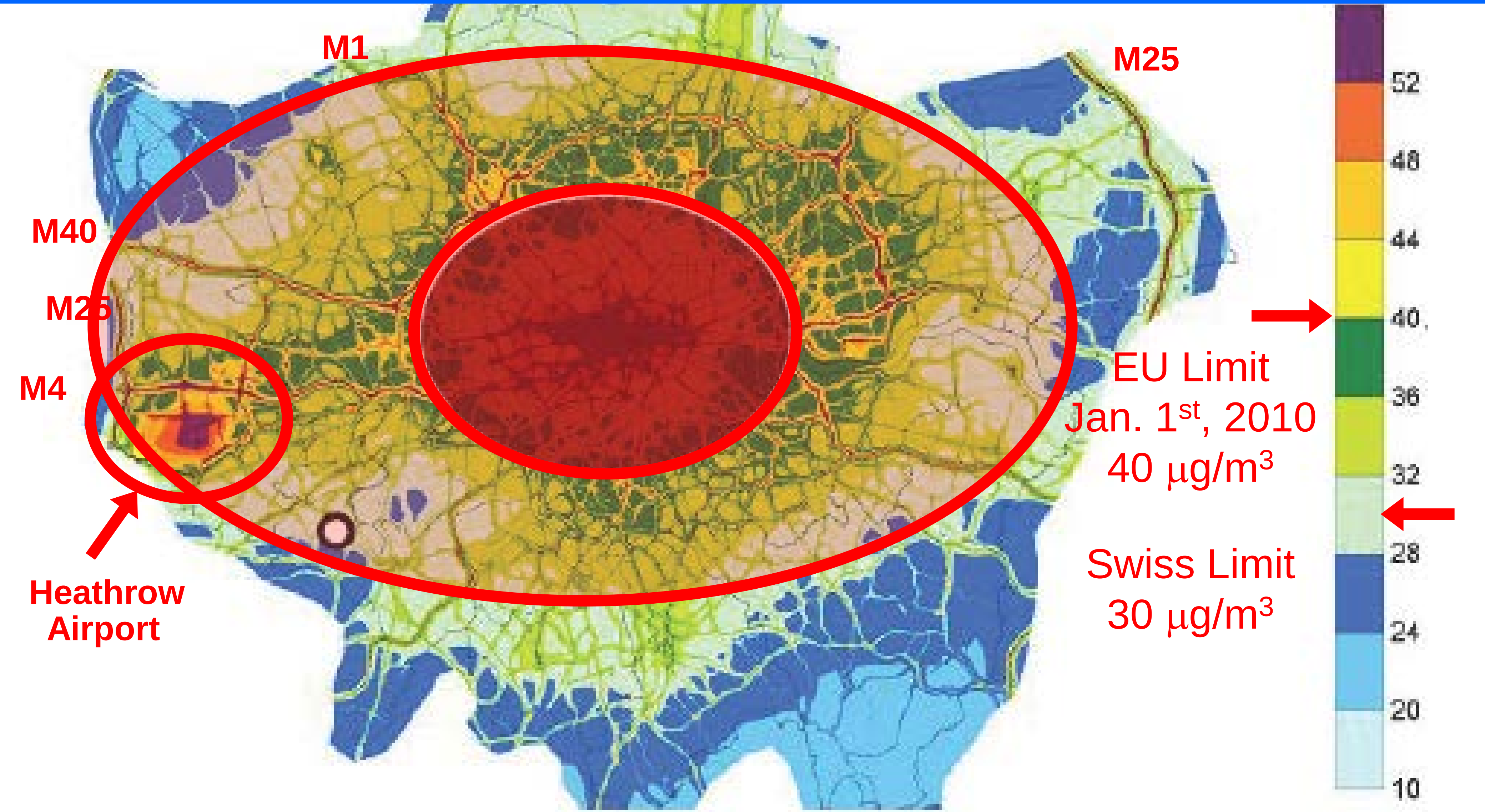
Blue Technology: Not green enough yet

Mean annual NO_2 levels: City of London



The NO_2 problem in central London is severe as in many European cities!

Mean annual NO_2 levels: City of London



From a Swiss perspective, the Brexit will not solve the NO_2 problem!

Blue Technology: Not green enough yet

Nitrogen chemistry of current on-road deNOx technologies

Best deNOx system on European roads — **(Honor to whom honor is due!)**

NOx-trap technology — **(Not very efficient yet)**

Urea-based SCR technology — **(Substantial cold start problems)**

Who knows John J. Mooney?

Who knows John J. Mooney?

- **How to meet the president?**
  2002 National Medal of Technology Award from National Science & Technology Foundation.

  Co-inventor of TWC (1 of the 10 most important inventions in car industry).

  In 1976-2001 TWC avoided 3, 3 & 30 billion tons of HC, NOx and CO emissions.

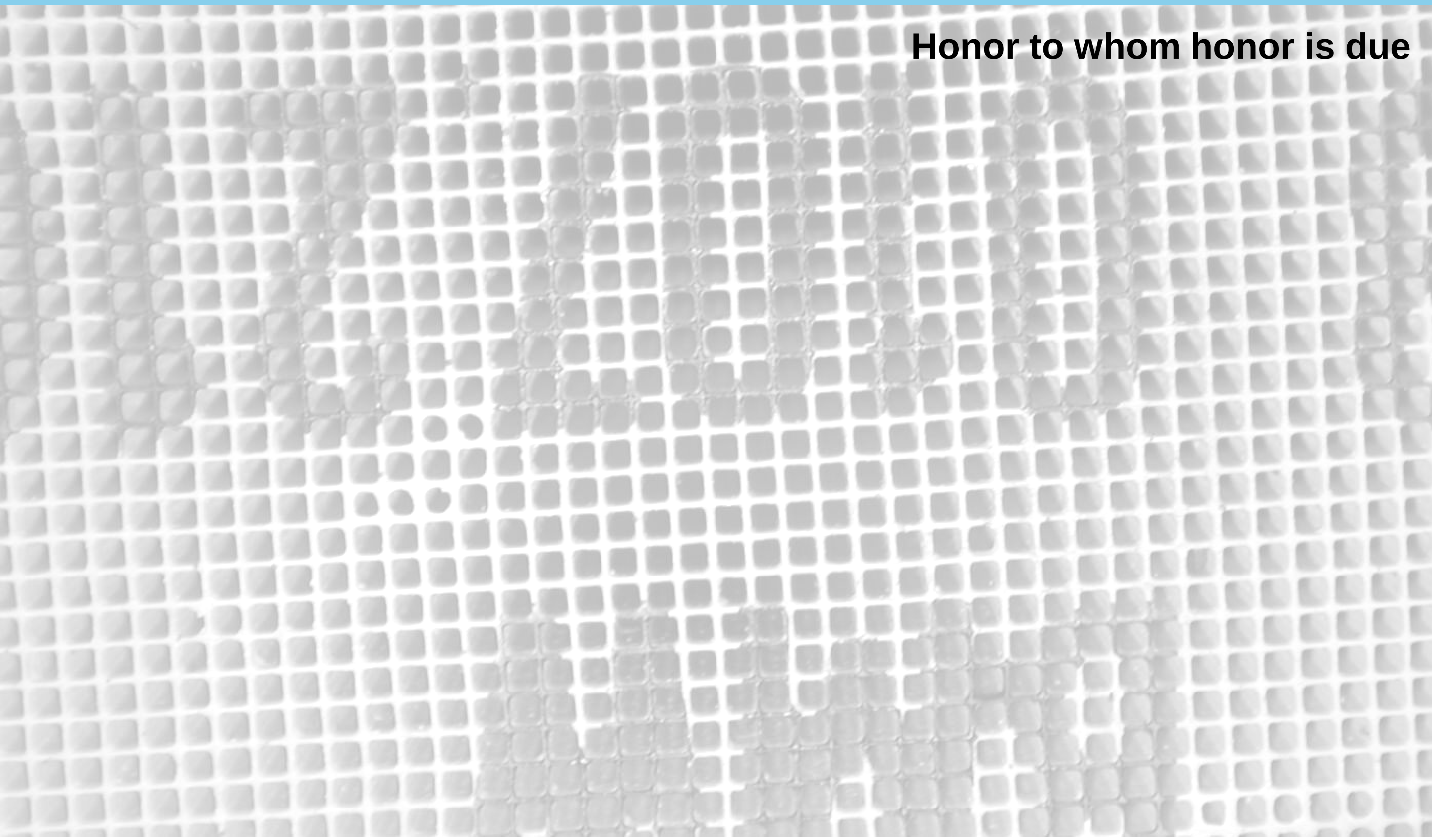
- **Good catalyst design:**
  results in money, honor & fame

Fig. 1: John J. Mooney & Carl D. Keith, Engelhard

Fig. 2: Haren S. Gahndi, Ford Motor Company

The best $deNO_x$-system on European roads

Honor to whom honor is due



DeNO$_X$ on a Pd/Rh-TWC

Dynamometer set-up for time-resolved NO and NH_3 measurements

Vehicle:

- BMW 318 (1.8 l, 1995, Euro-1, mileage 70'000 km)

Fuel:

- 95 RON gasoline (specification CEF RF-08-A-85)

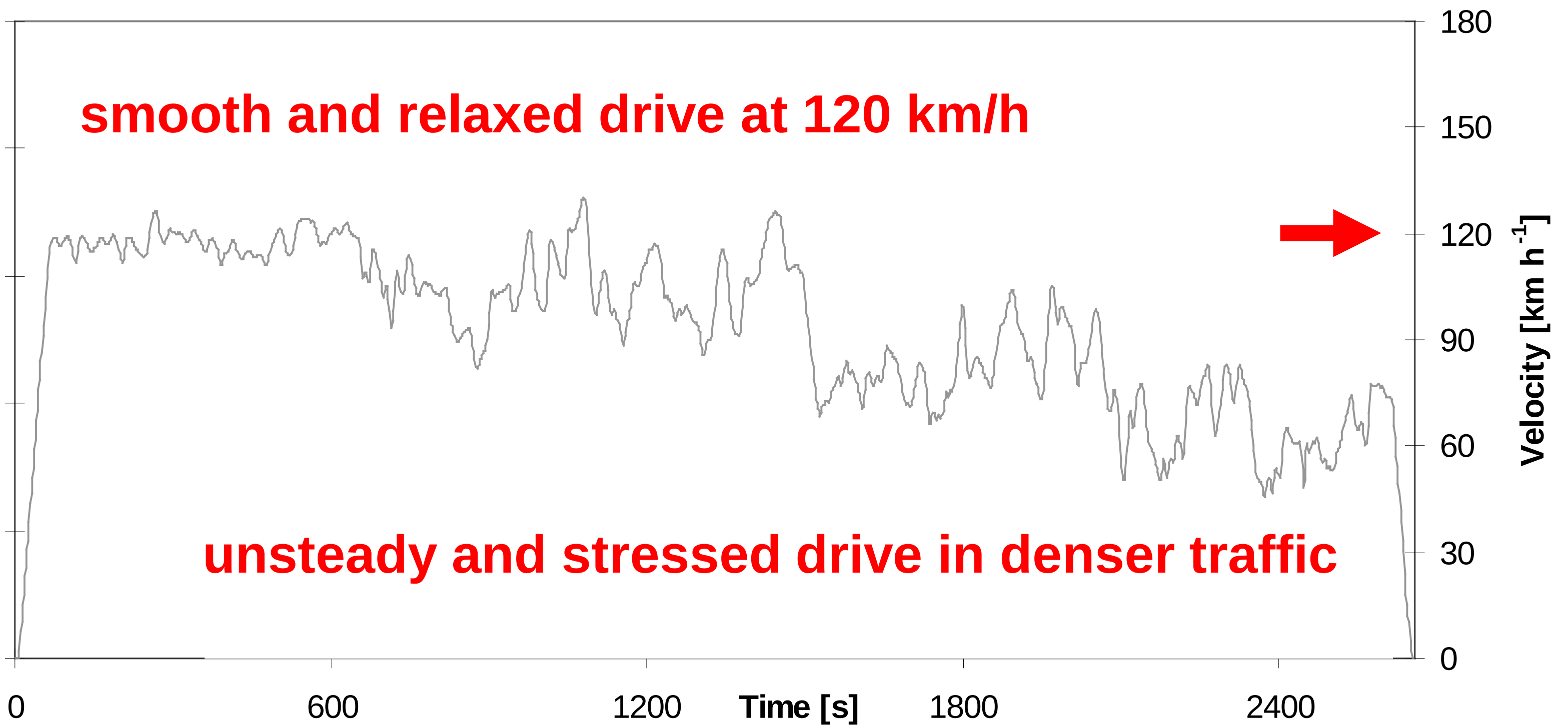
Catalyst:

- New, original spare part TWC
- Two-layered Pd-CeO_2-Al_2O_3/Rh-ZrO_2-Al_2O_3 structure

DeNO$_x$ on a Pd/Rh-TWC

Swiss made driving cycle to mimic highway driving

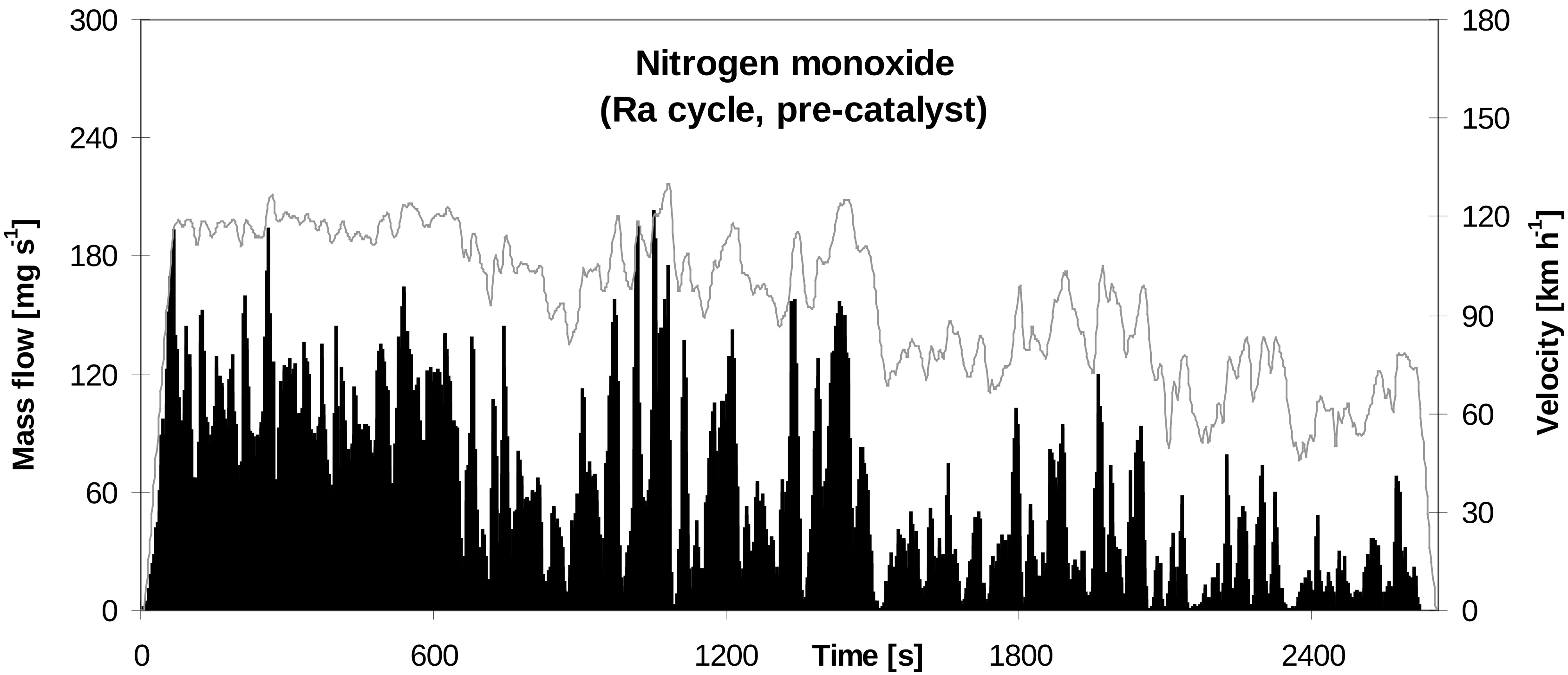
The Swiss highway cycle



DeNO$_X$ on Pd/Rh-TWC

Pre-catalyst NO up to 200 mg s^{-1} at transient highway driving

NO emission (BMW, 1.8 l, 1995, EURO-1)



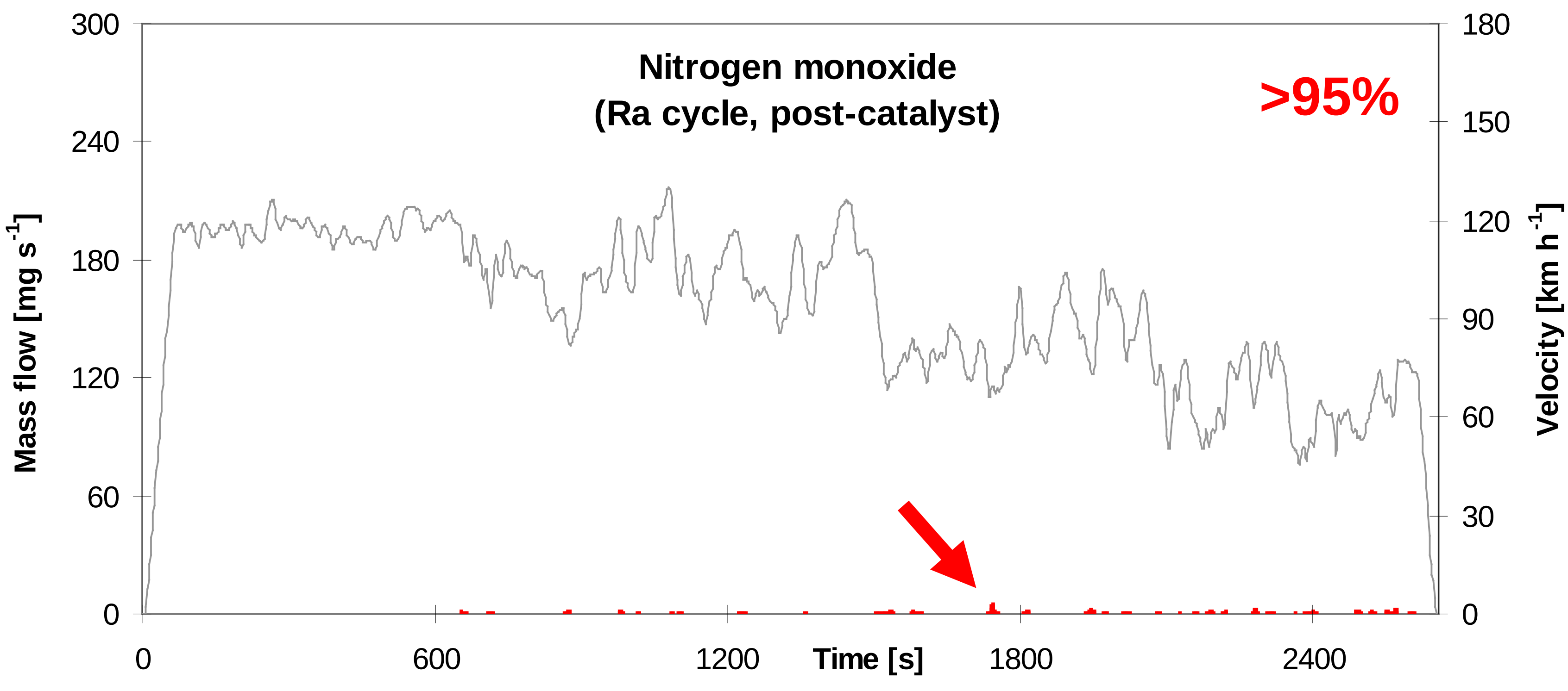
Heeb et al. Atm. Env. 40 (2006) 5986-5997

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

DeNO$_X$ on a Pd/Rh-TWC

Post catalyst less than 6 mg s^{-1}

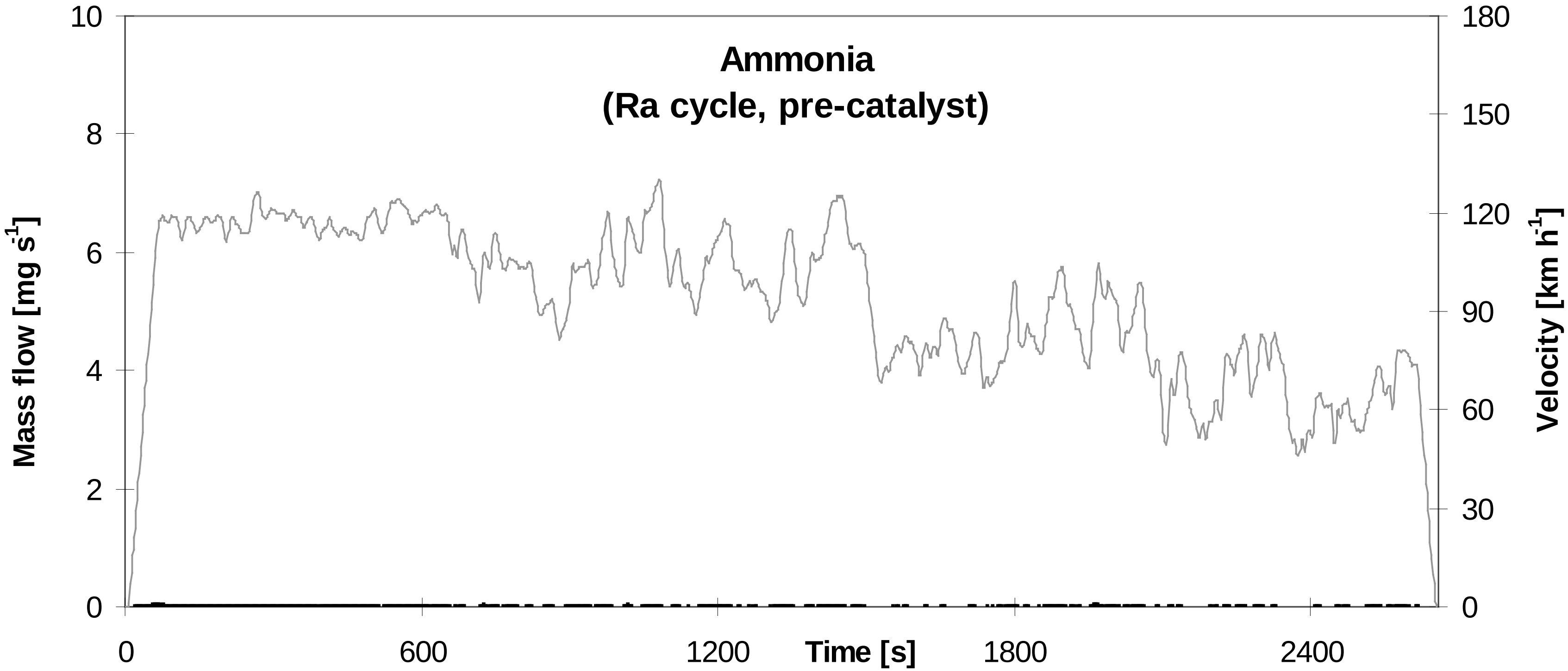
NO emission (BMW, 1.8 l, 1995, EURO-1)



TWC-induced formation of ammonia

No ammonia before catalyst

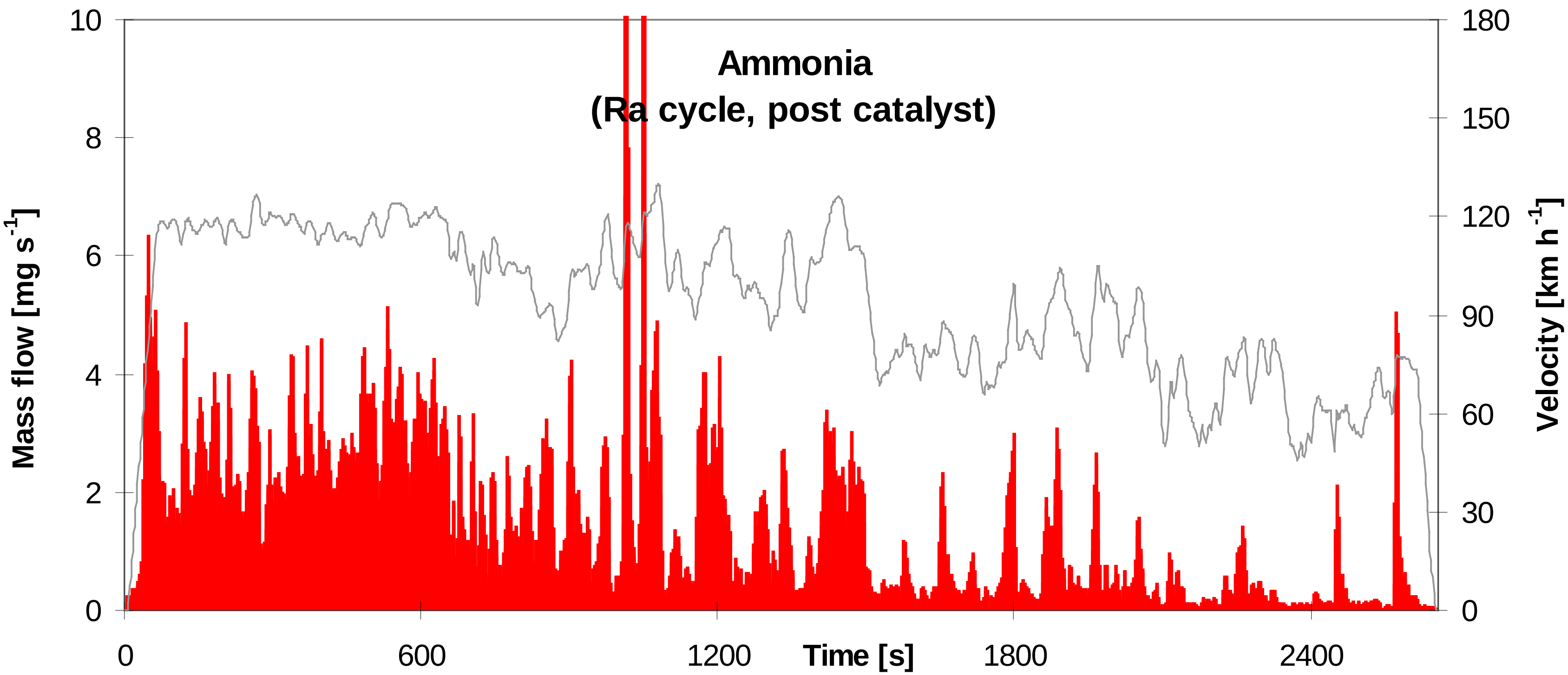
Ammonia emissions (BMW, 1.8 l, 1995, EURO-1)



TWC-induced formation of ammonia

Relevant ammonia emissions post catalyst

Ammonia emissions (BMW, 1.8 l, 1995, EURO-1)



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

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

The best deNO$_x$-system on European roads

What's going on the catalytic surface?

The TWC in theory

- **TWC**
  - Which three ways to go?

$$CO + 1/2\ O_2 \rightleftharpoons CO_2$$

$$HC + O_2 \rightleftharpoons H_2O + CO_2$$

$$NO + CO \rightleftharpoons 1/2\ N_2 + CO_2$$

The TWC in real world application

- **The important role of H_2!**
  - Which three ways to go?
  - A new try with H_2, water gas-shift-reactions and steam reforming

$$CO + 1/2\ O_2 \rightleftharpoons CO_2$$
$$HC + O_2 \rightleftharpoons H_2O + CO_2$$
$$NO + CO \rightleftharpoons 1/2\ N_2 + CO_2$$

$$H_2 + 1/2\ O_2 \rightleftharpoons H_2O$$
$$CO + H_2O \rightleftharpoons H_2 + CO_2$$
$$HC + H_2O \rightleftharpoons H_2 + CO + CO_2$$

The TWC in real world application

- **Why NH_3 and N_2O?**
  - Which three ways to go?
  - A new try incl. H_2, water gas-shift-reactions and steam reforming
  - Another try with H_2, N_2O and NH_3

$$CO + 1/2\,O_2 \rightleftharpoons CO_2$$
$$HC + O_2 \rightleftharpoons H_2O + CO_2$$
$$NO + CO \rightleftharpoons 1/2\,N_2 + CO_2$$

$$H_2 + 1/2\,O_2 \rightleftharpoons H_2O$$
$$CO + H_2O \rightleftharpoons H_2 + CO_2$$
$$HC + H_2O \rightleftharpoons H_2 + CO + CO_2$$

$$NO + H_2 \rightleftharpoons 1/2\,N_2 + H_2O$$
$$NO + HC \rightleftharpoons N_2 + H_2O + CO_2$$
$$NO + 5/2\,H_2 \rightleftharpoons NH_3 + H_2O$$
$$3\,NO + 2\,NH_3 \rightleftharpoons 5/2\,N_2 + 3\,H_2O$$
$$2\,NO + H_2 \rightleftharpoons N_2O + H_2O$$
$$2\,N_2O \rightleftharpoons 2\,N_2 + O_2$$
$$2\,NH_3 \rightleftharpoons N_2 + 3\,H_2$$

NOx-trap technology

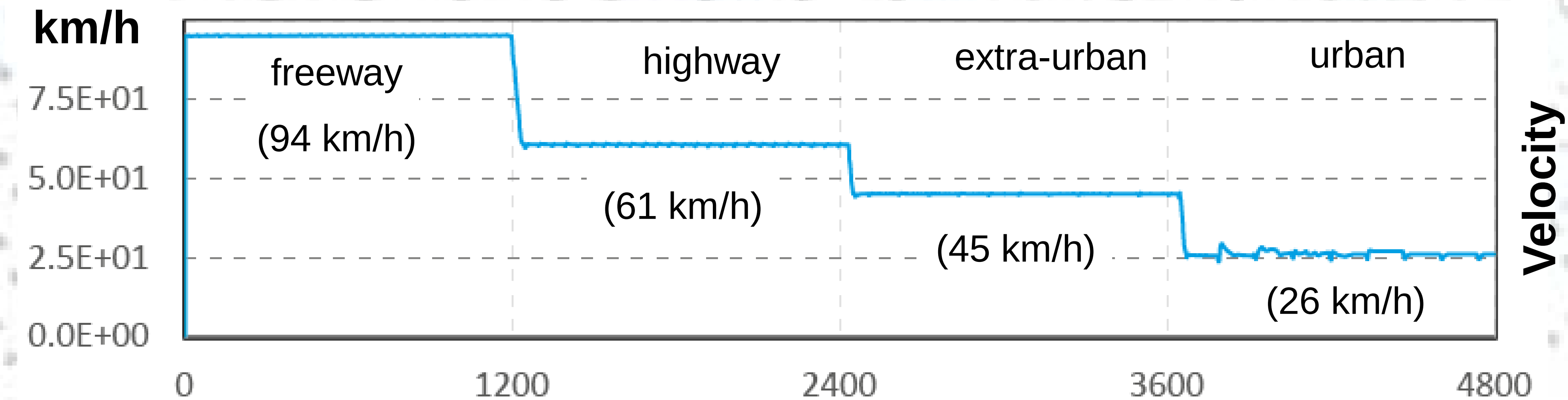
The first GDI vehicle (Mitsubishi Carisma, 1.8L, Euro-3) with NOx trap technology

Vehicle	Mitsubishi Carisma 1.8 GDI
Engine code	4G93
Number and arrangement of cylinder	4 / in line
Displacement cm^3	1834
Power kW	90 @ 5500 rpm
Torque Nm	174 @ 3750 rpm
Injection type	DI
Curb weight kg	1315
Gross vehicle weight kg	1750
Drive wheel	Front-wheel drive
Gearbox	M5
First registration	05.2001
Exhaust	EURO 3

NOx-trap chemistry

An ideal cycle to study converter chemistry at best conditions!

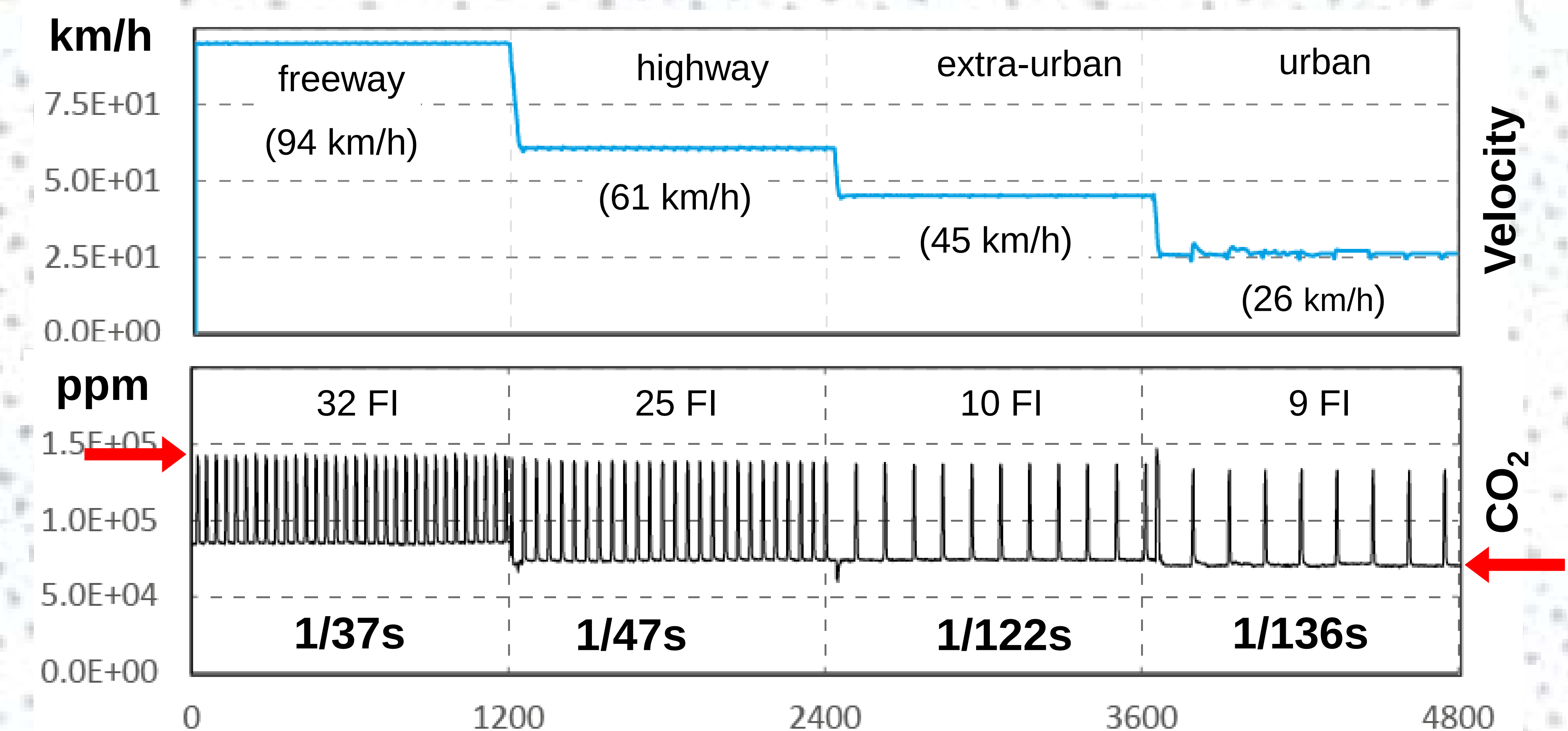
NOx-trap activity at steady driving



NOx-trap chemistry

Extra fuel injections (FI) nearly every minute!

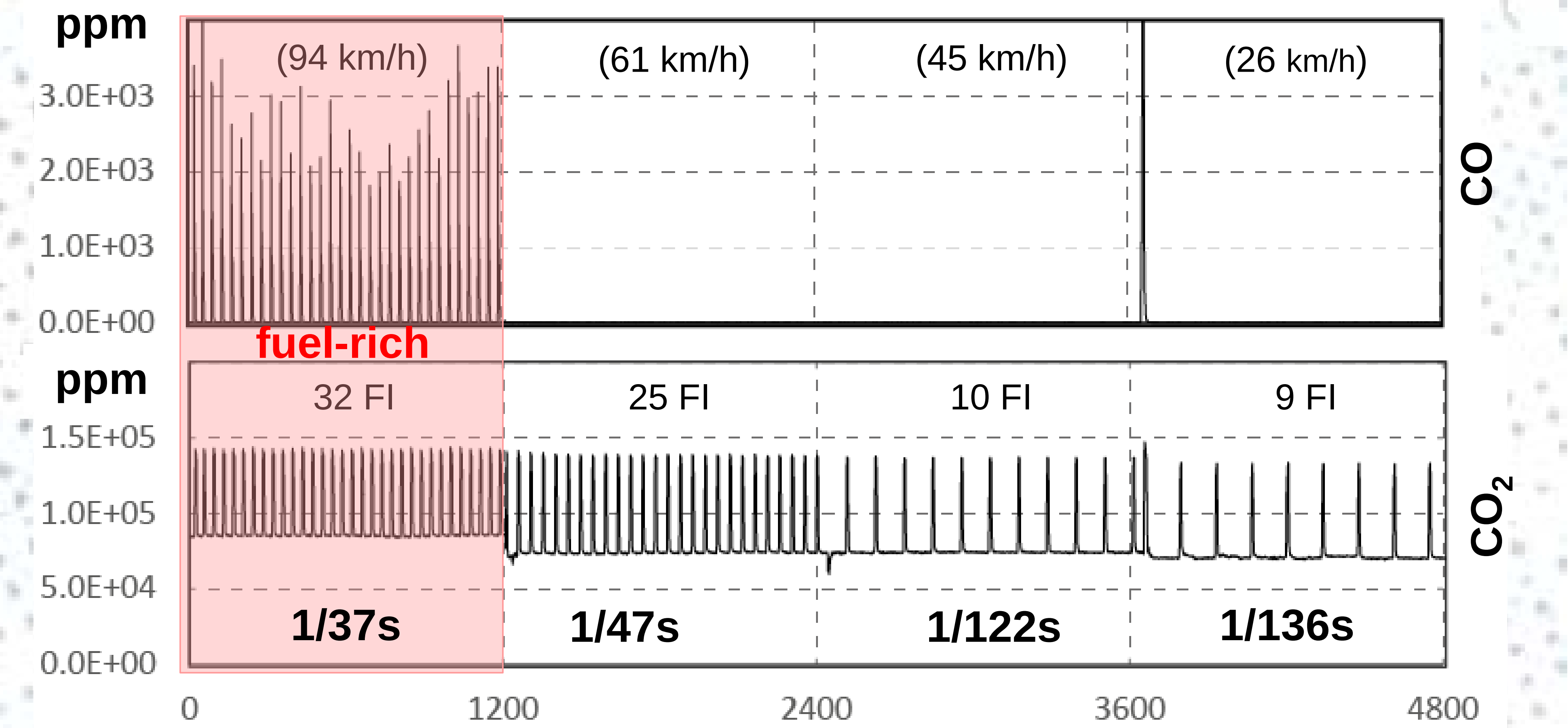
CO_2 emissions at steady driving



NOx-trap chemistry

Extra fuel injections result in extra CO emissions, but only in phase 1!

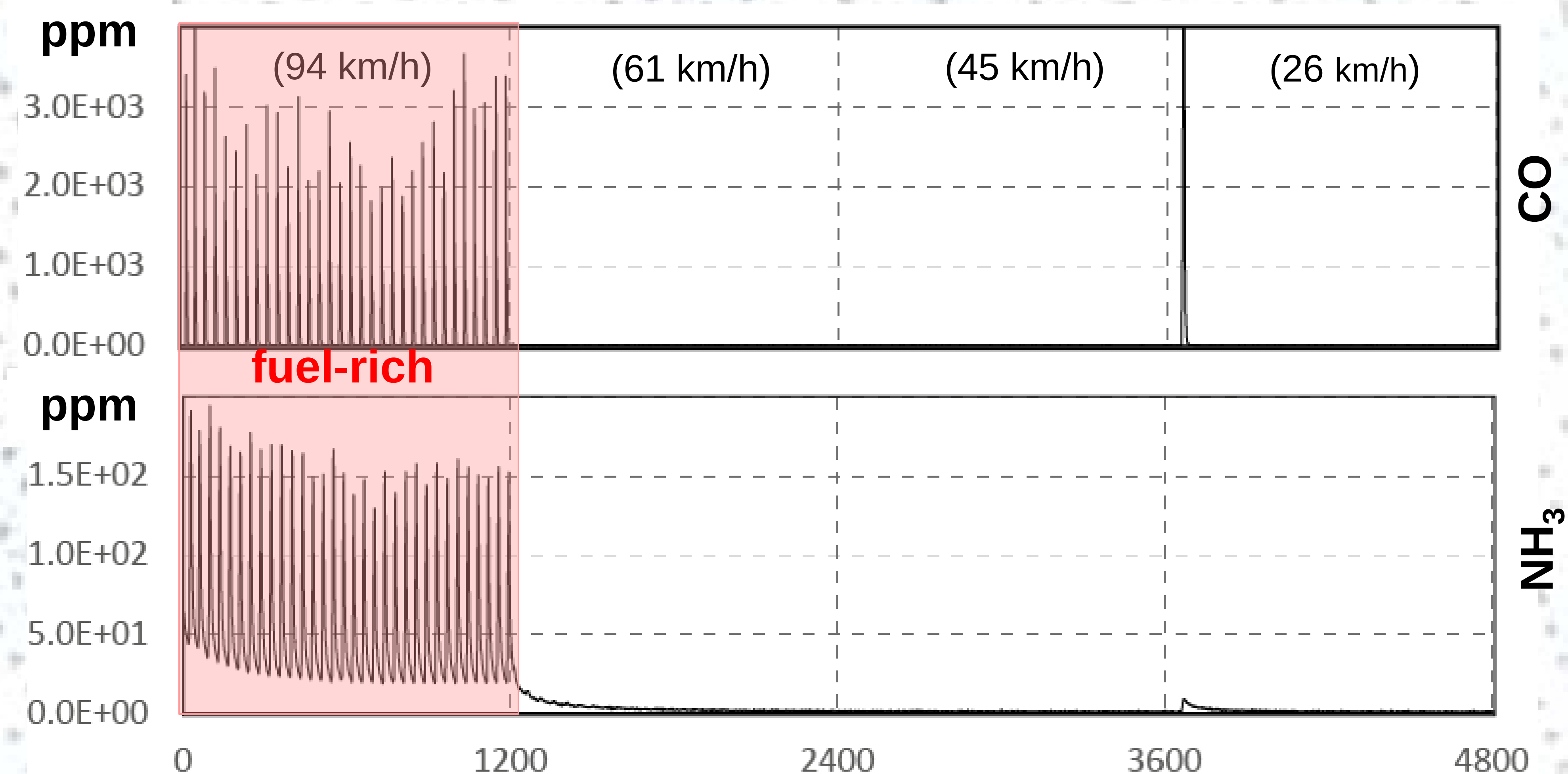
CO and CO_2 emissions



NOx-trap chemistry

Extra fuel injections result in extra CO and NH_3 emissions but only in phase 1!

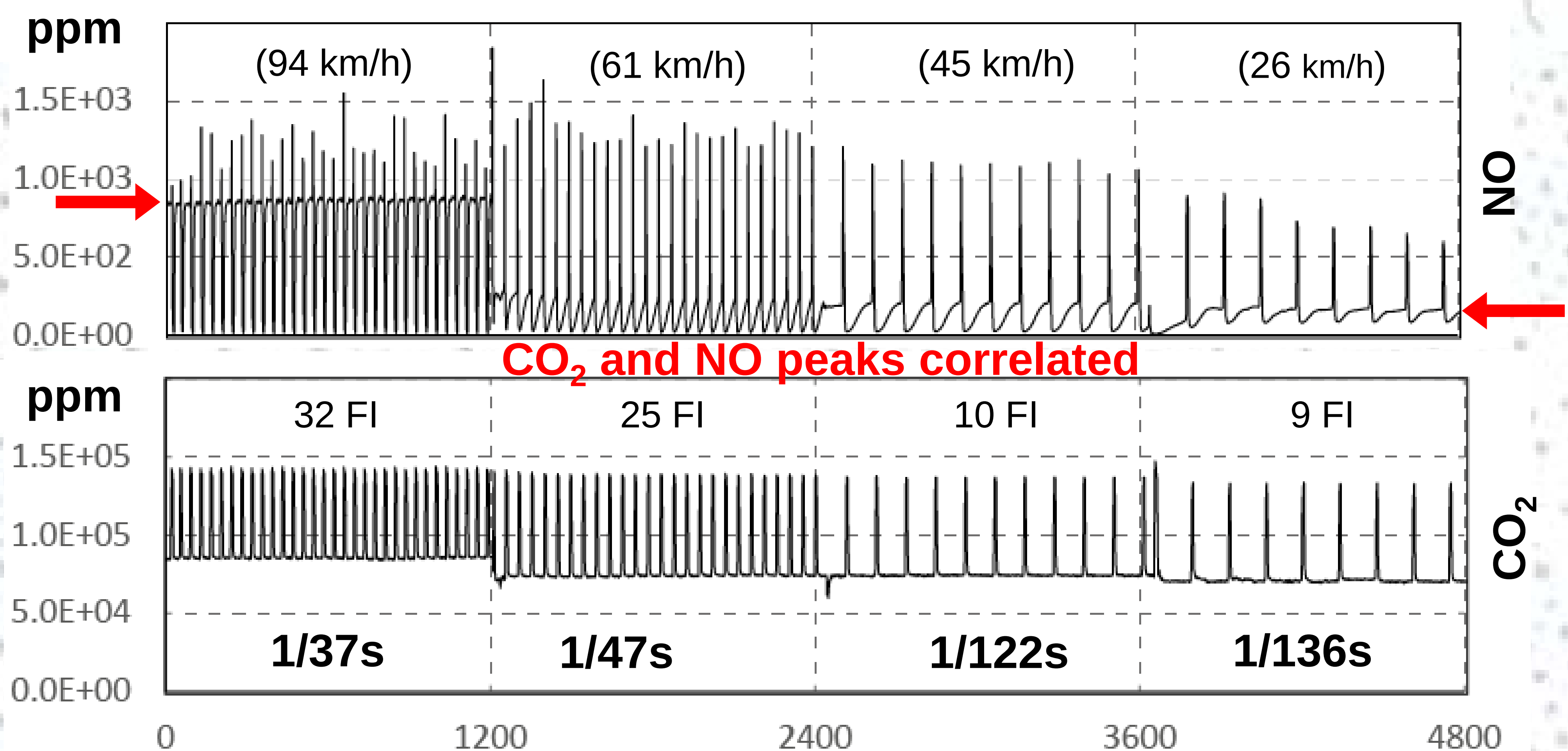
NH_3 & CO emissions



NOx-trap chemistry

NOx trap at work: extra fuel injections result in extra NO emissions

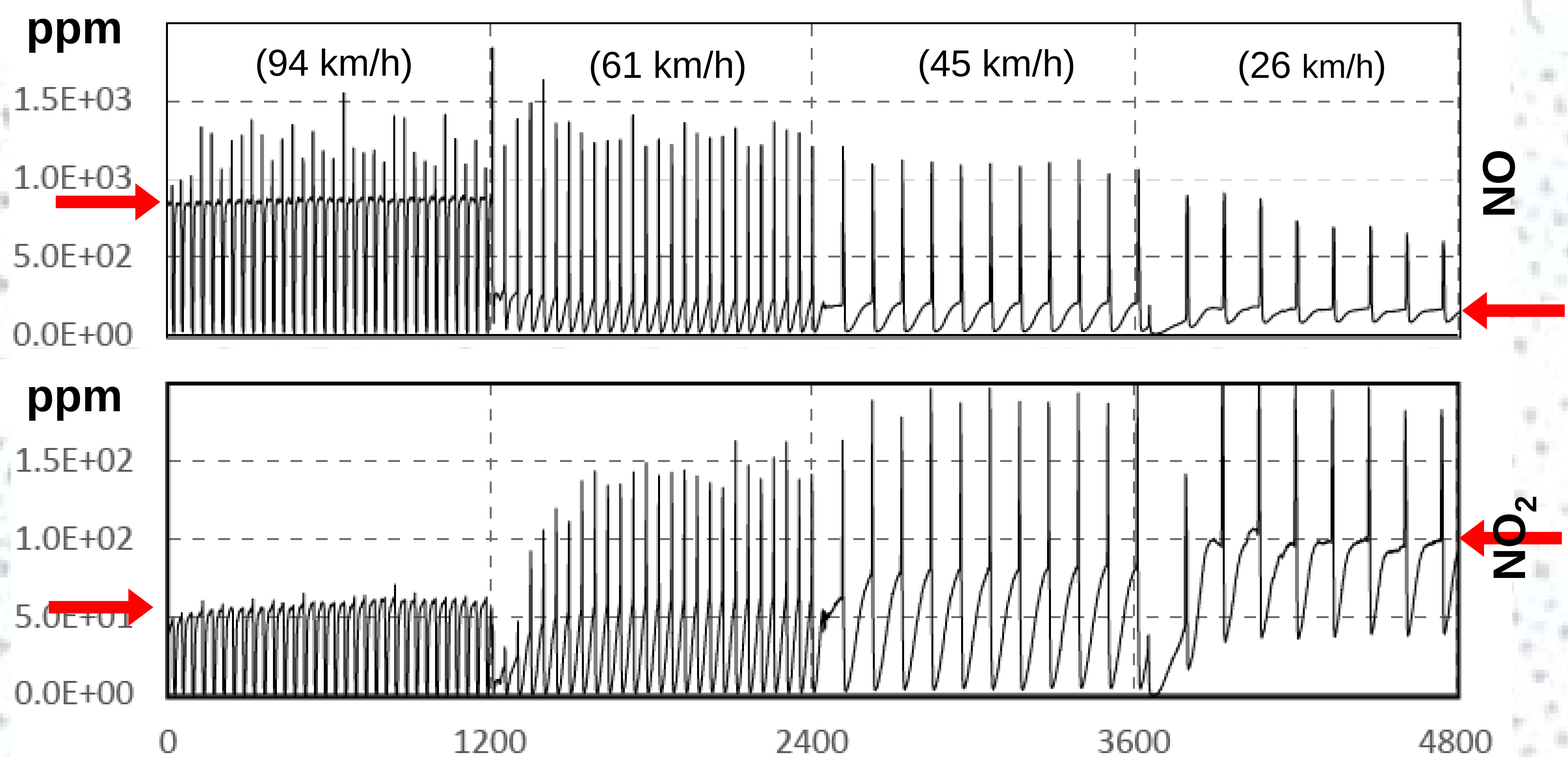
NO and CO_2 emissions



NOx-trap chemistry

NOx trap at work: extra fuel injections result in extra NO and NO_2 emissions

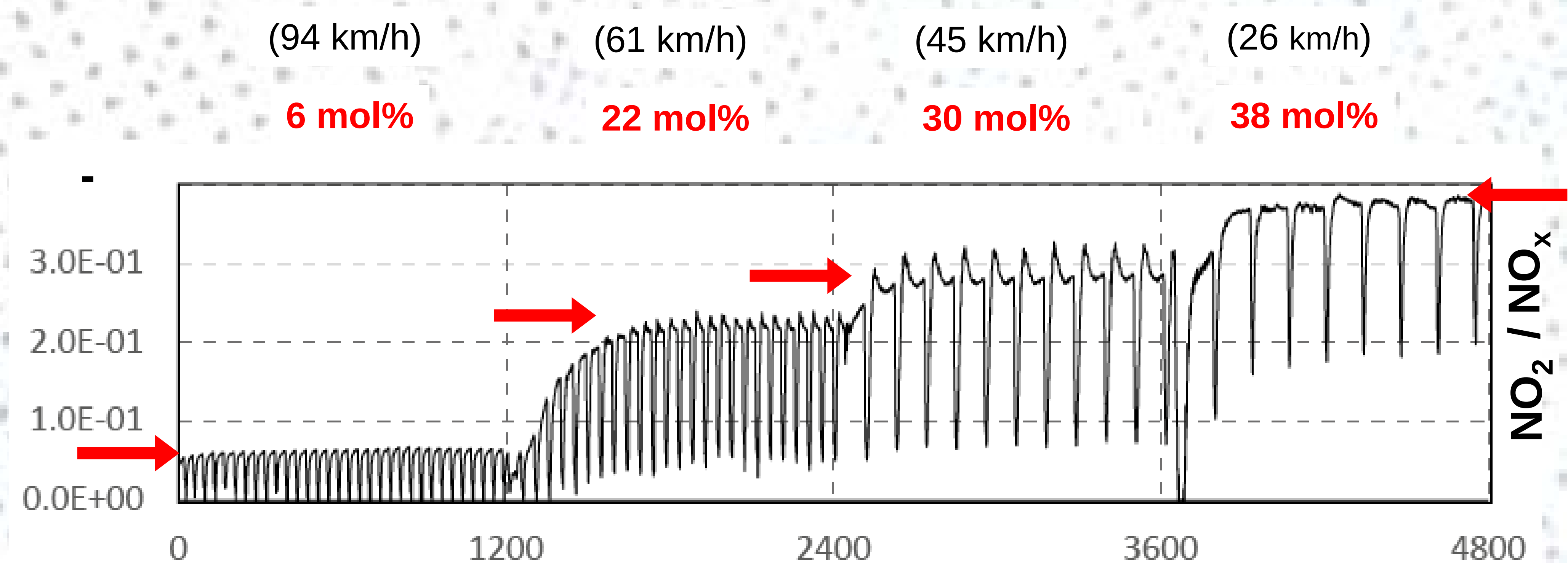
NO and NO_2 emissions



NOx-trap chemistry

NO_2 proportions lowest during extra fuel injections and high temperatures

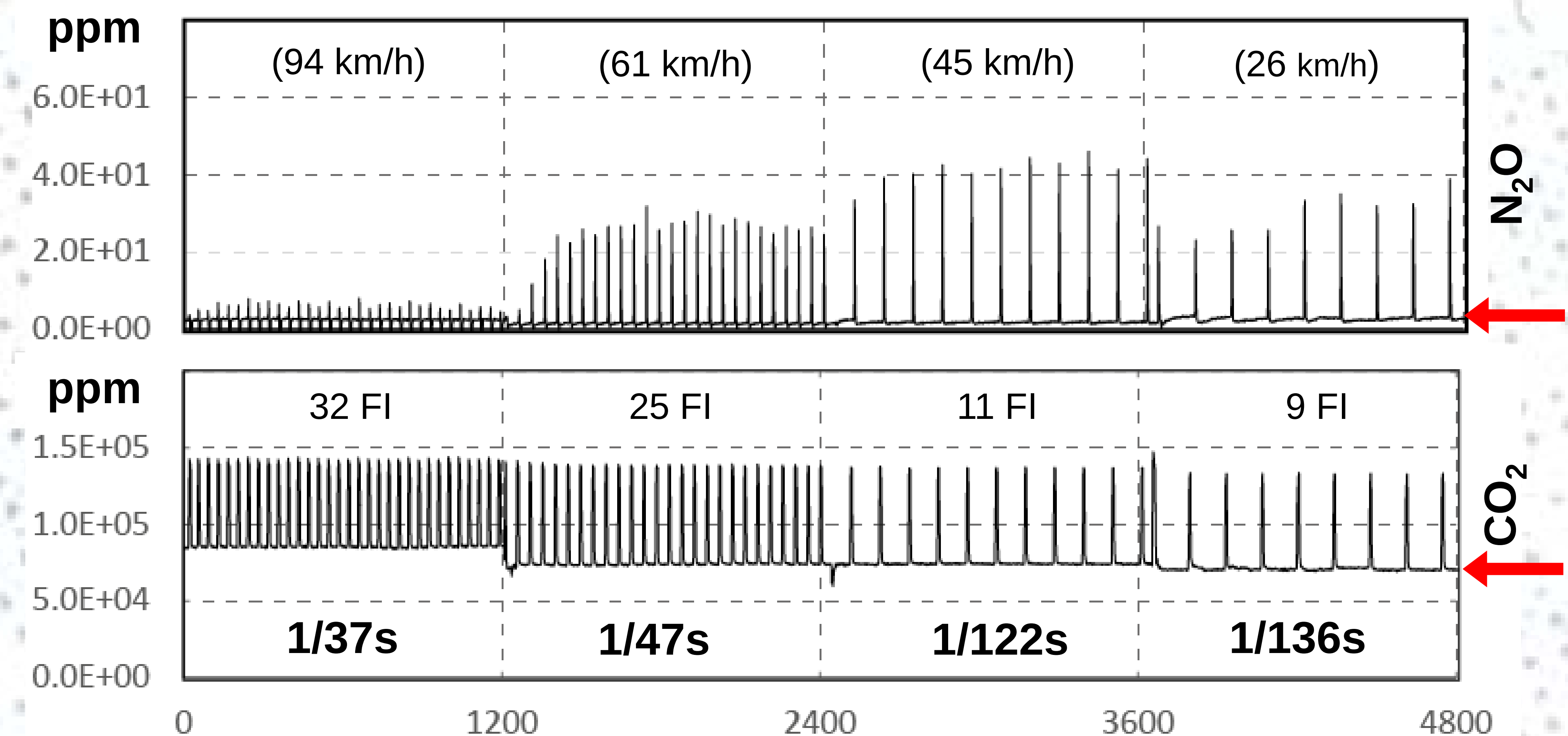
NO_2 proportion in NO_x



NOx-trap chemistry

Not funny, extra fuel injections also result in extra N_2O emissions

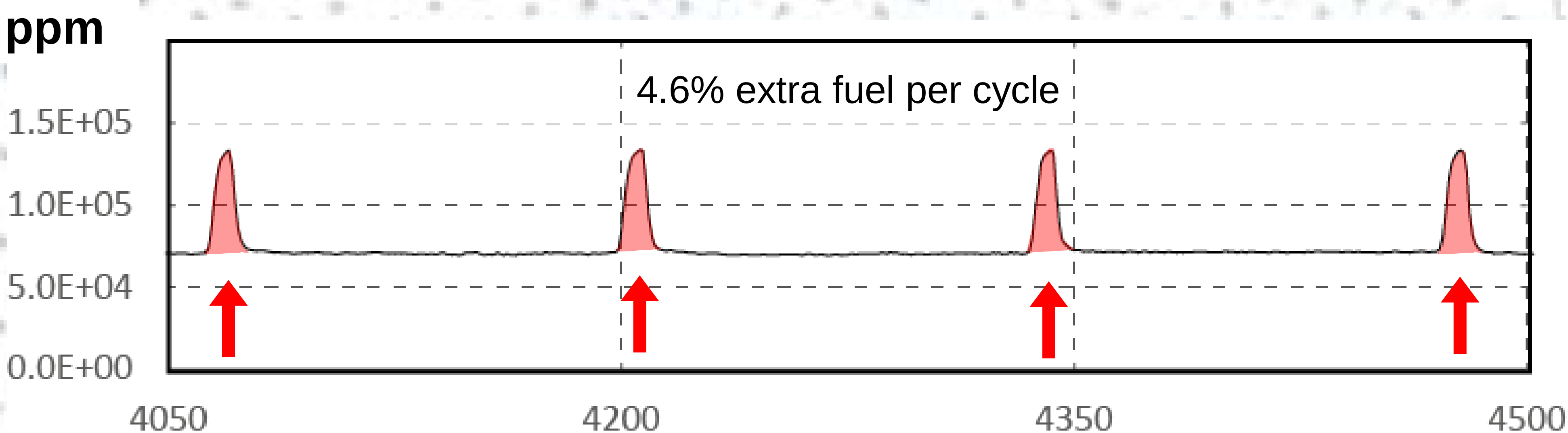
N_2O and CO_2 emissions



NOx-trap chemistry

How much fuel penalty per injection

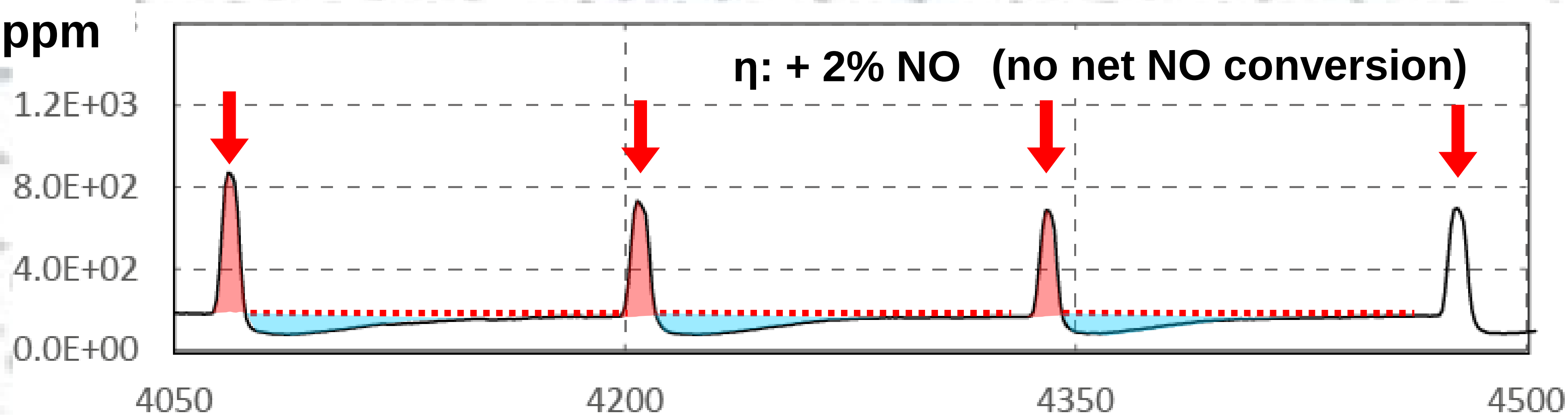
Extra CO_2 at 26 km/h (urban driving)



NOx-trap chemistry

How much deNOx activitiy per injection

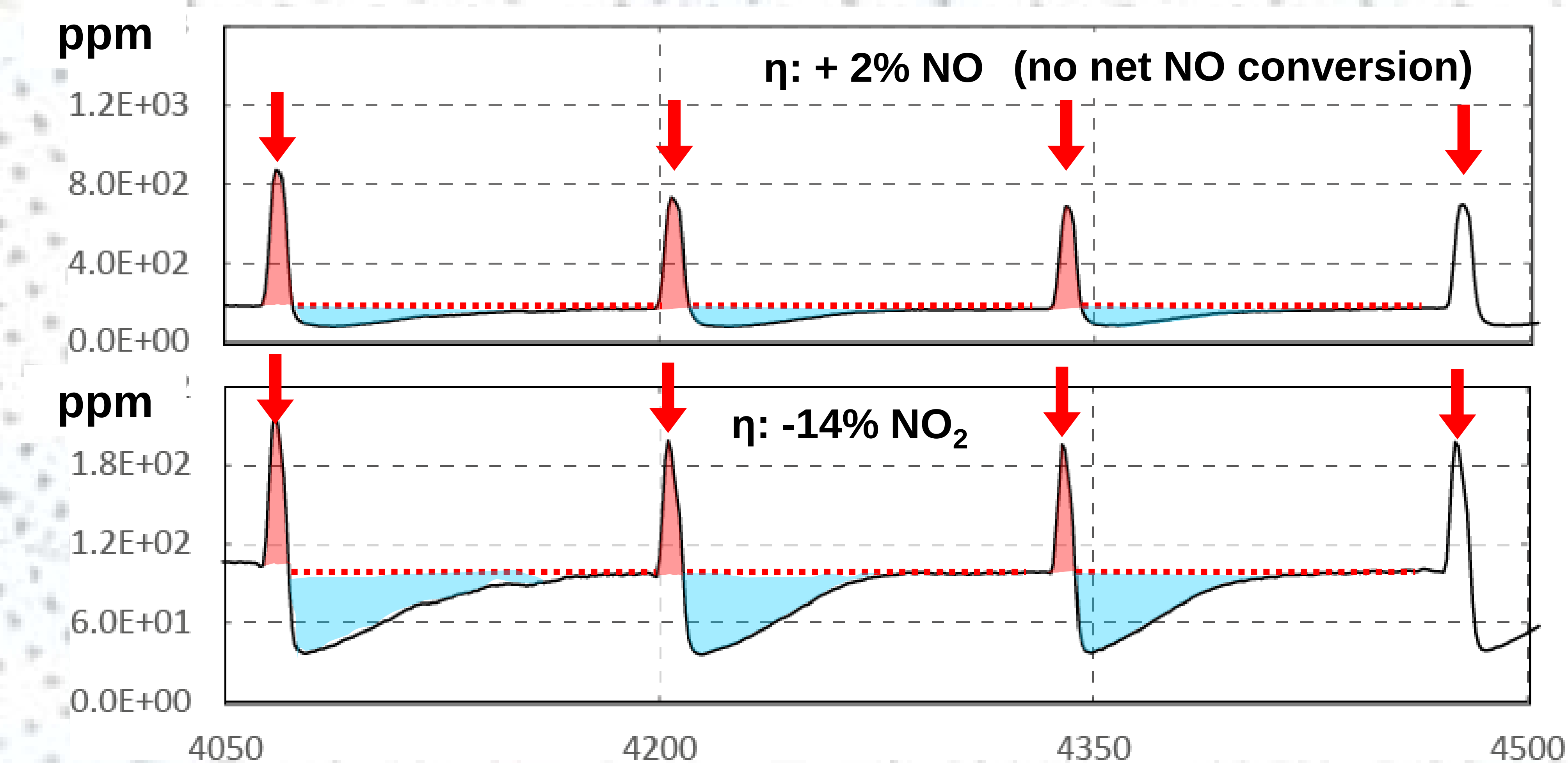
deNO activity at 26 km/h



NOx-trap chemistry

How much deNOx activitiy per injection

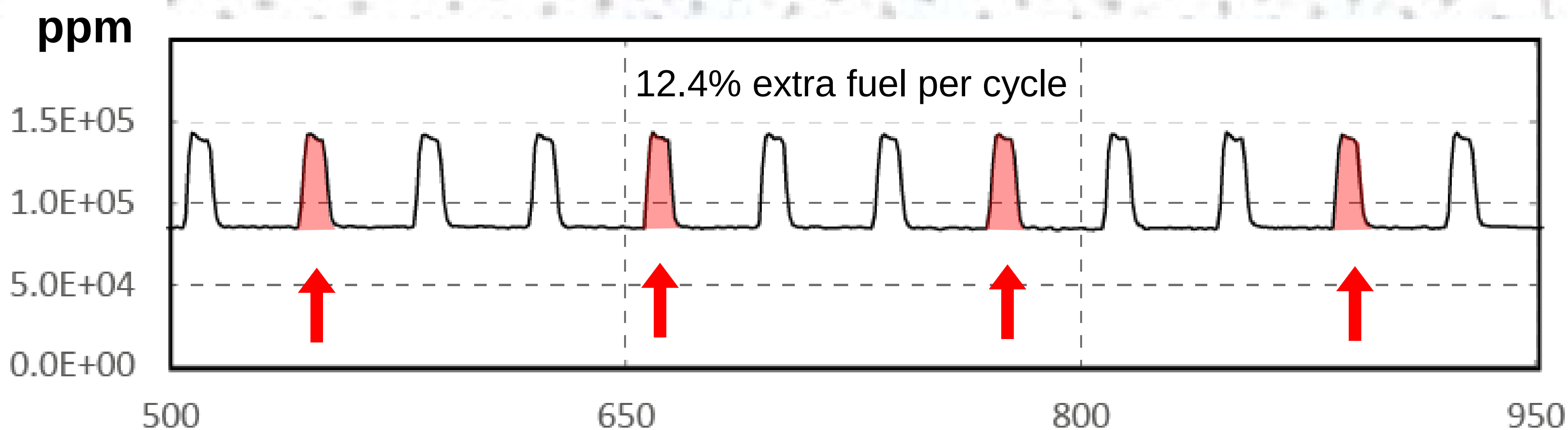
deNO and deNO$_2$ activity at 26 km/h



NOx-trap chemistry

How much fuel penalty per injection

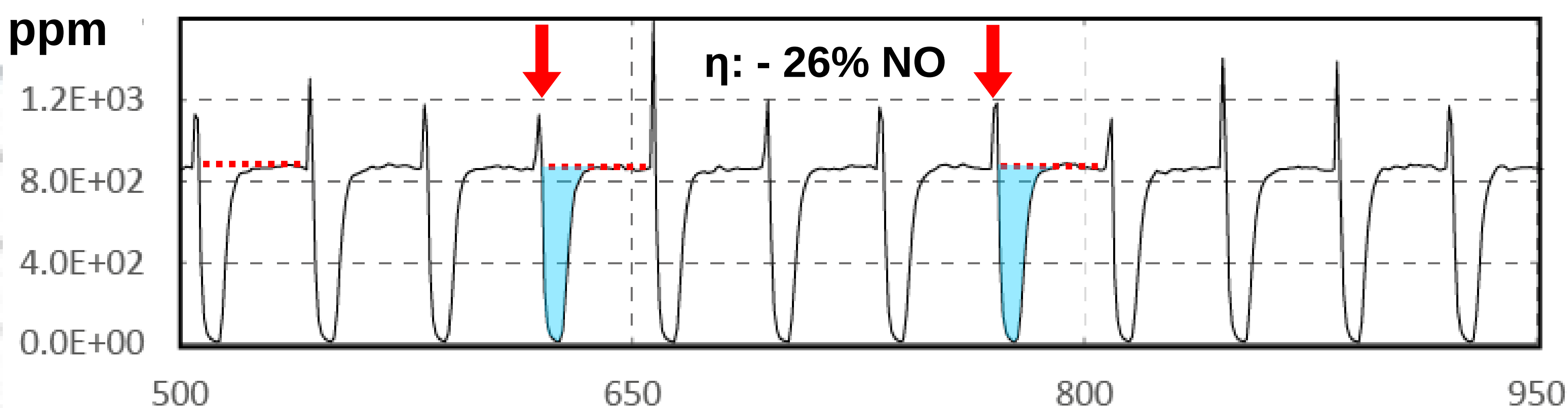
CO_2 at 94 km/h (motorway)



NOx-trap chemistry

How much deNOx activitiy per injection

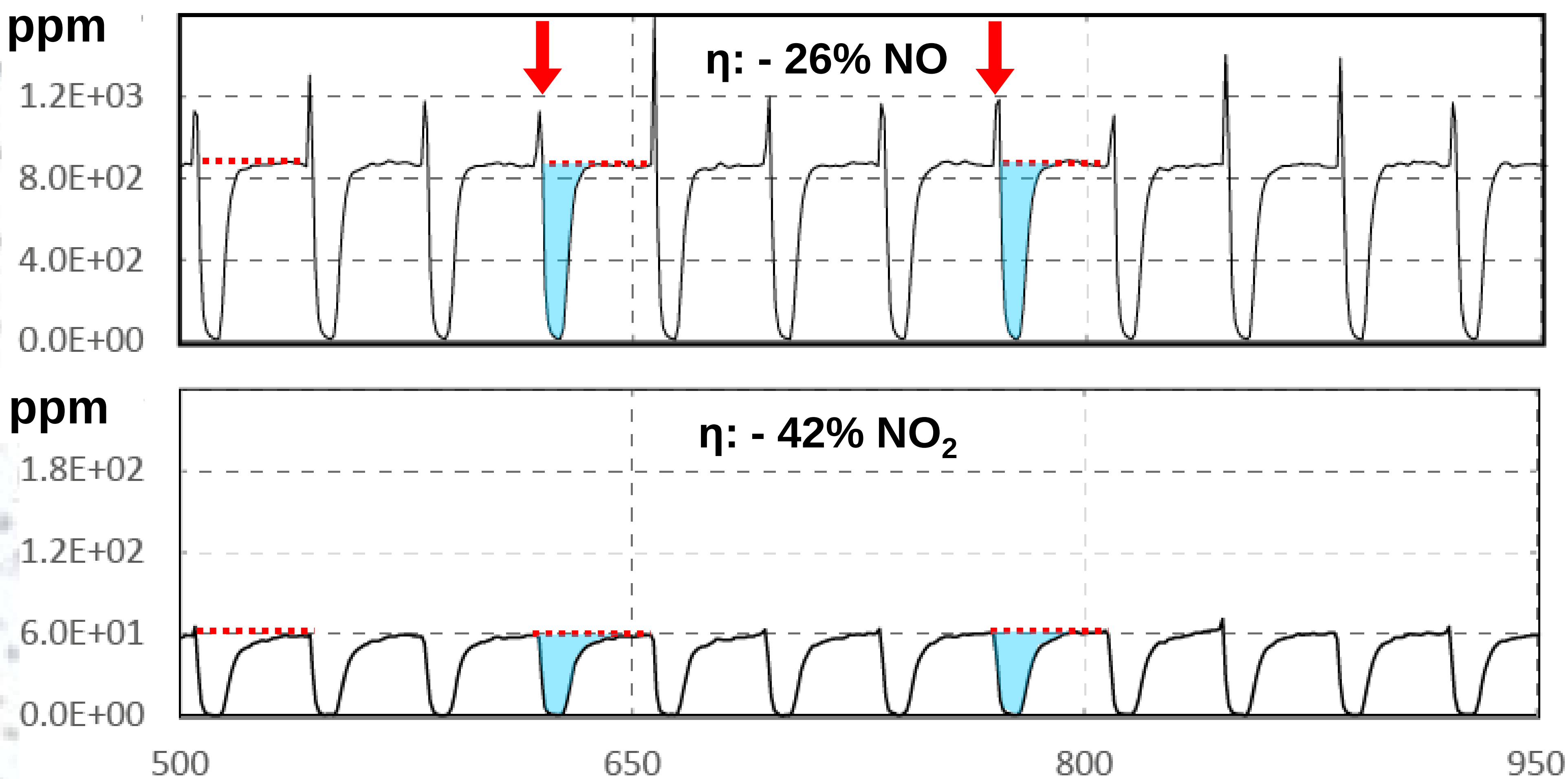
deNO activity at 94 km/h



NOx-trap chemistry

How much deNOx activitiy per injection

deNO and deNO$_2$ activity at 94 km/h



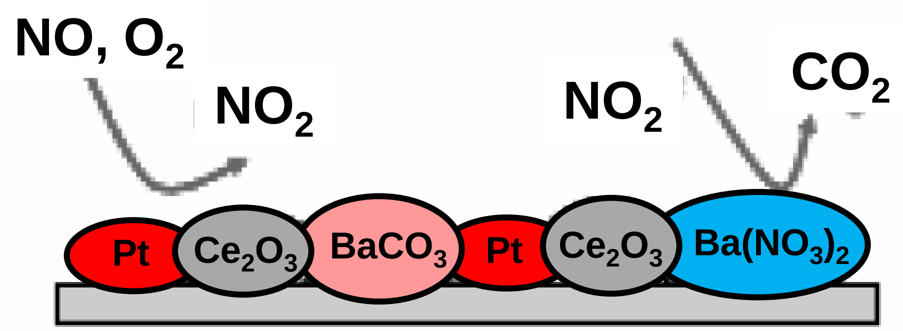
NOx-trap technology

Low NO_x storage capacity, not very sulfur tolerant, its more a SO_x than a NO_x trap

NOx-trap cycle

$\lambda > 1\ (lean)$ T: 150-450 °C

1. NO- & NO_2-oxidation to NO_3^-
2. Store as $Ba(NO_3)_2$



NOx-trap technology

Low NO_x storage capacity, not very sulfur tolerant, its more a SO_x than a NO_x trap

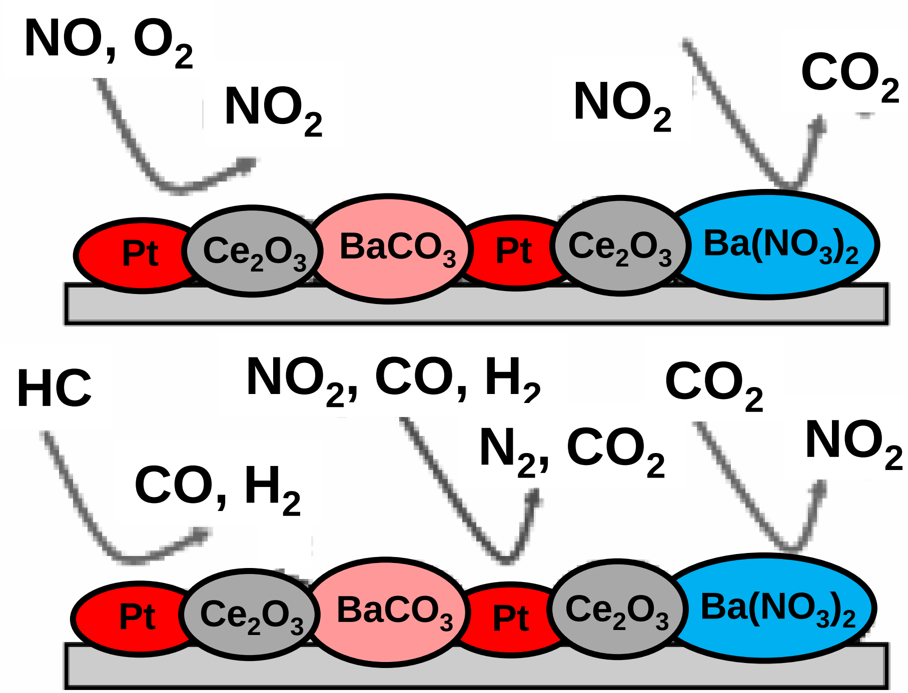
NOx-trap cycle

$\lambda > 1$ (*lean*) **T: 150-450 °C**

1. NO- & NO_2-oxidation to NO_3^-
2. Store as $Ba(NO_3)_2$

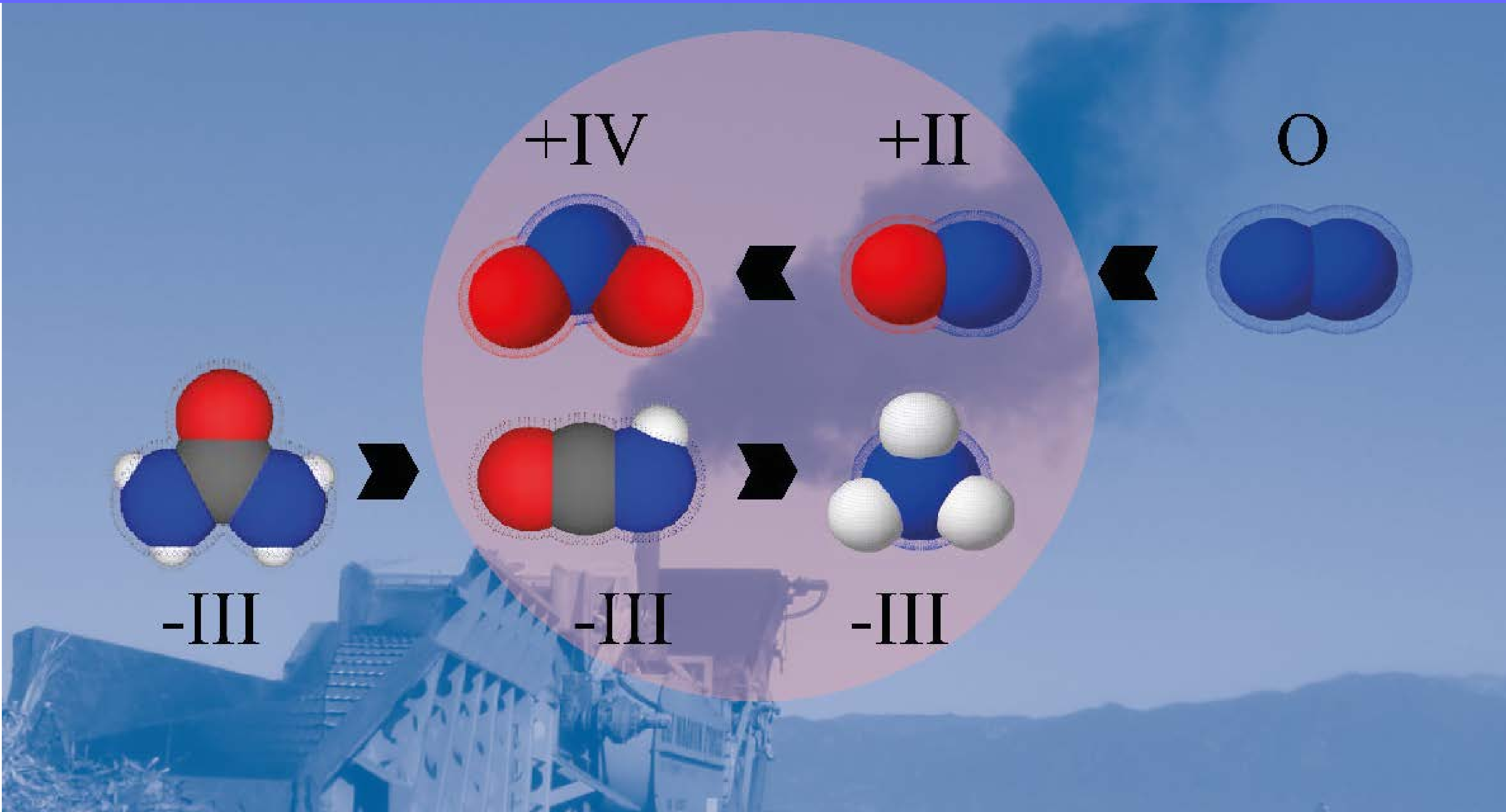
$\lambda < 1$ (*rich*) **T: 200-500 °C**

3. Post injections of fuel
4. NO_3^- reduction with H_2, HC etc.



Similar chemistry in the NO_x trap with secondary formation of N_2O and NH_3

Urea-based SCR



Currently the most efficient deNOx system for diesel engines

Urea-based SCR

At least two steps to decompose and hydrolyze urea

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

$$2\,NH_3 + NO + NO_2 \rightarrow 2\,N_2 + 3\,H_2O \qquad (2)$$

$$4\,NH_3 + 4\,NO + O_2 \rightarrow 4\,N_2 + 6\,H_2O \qquad (3)$$

$$8\,NH_3 + 6\,NO_2 \rightarrow 7\,N_2 + 12\,H_2O \qquad (4)$$

$$CO(NH_2)_2 \rightarrow NH_3 + HNCO \qquad (5)$$

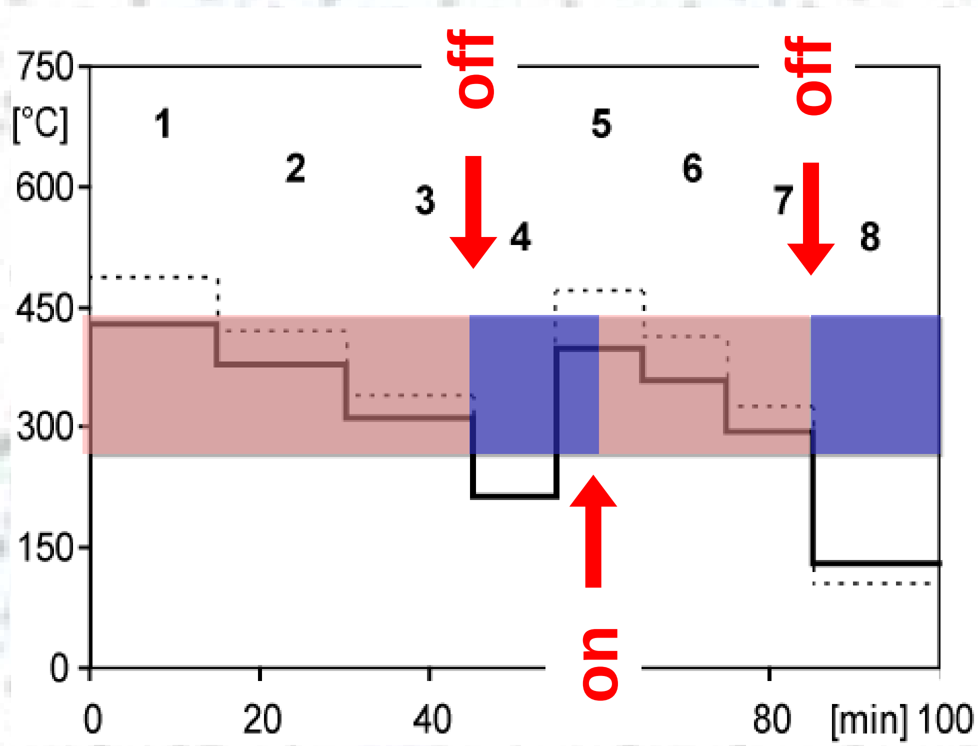
$$HNCO + H_2O \rightarrow NH_3 + CO_2 \qquad (6)$$

Per ton of NO to be reduced, one needs at least 1 ton of urea!

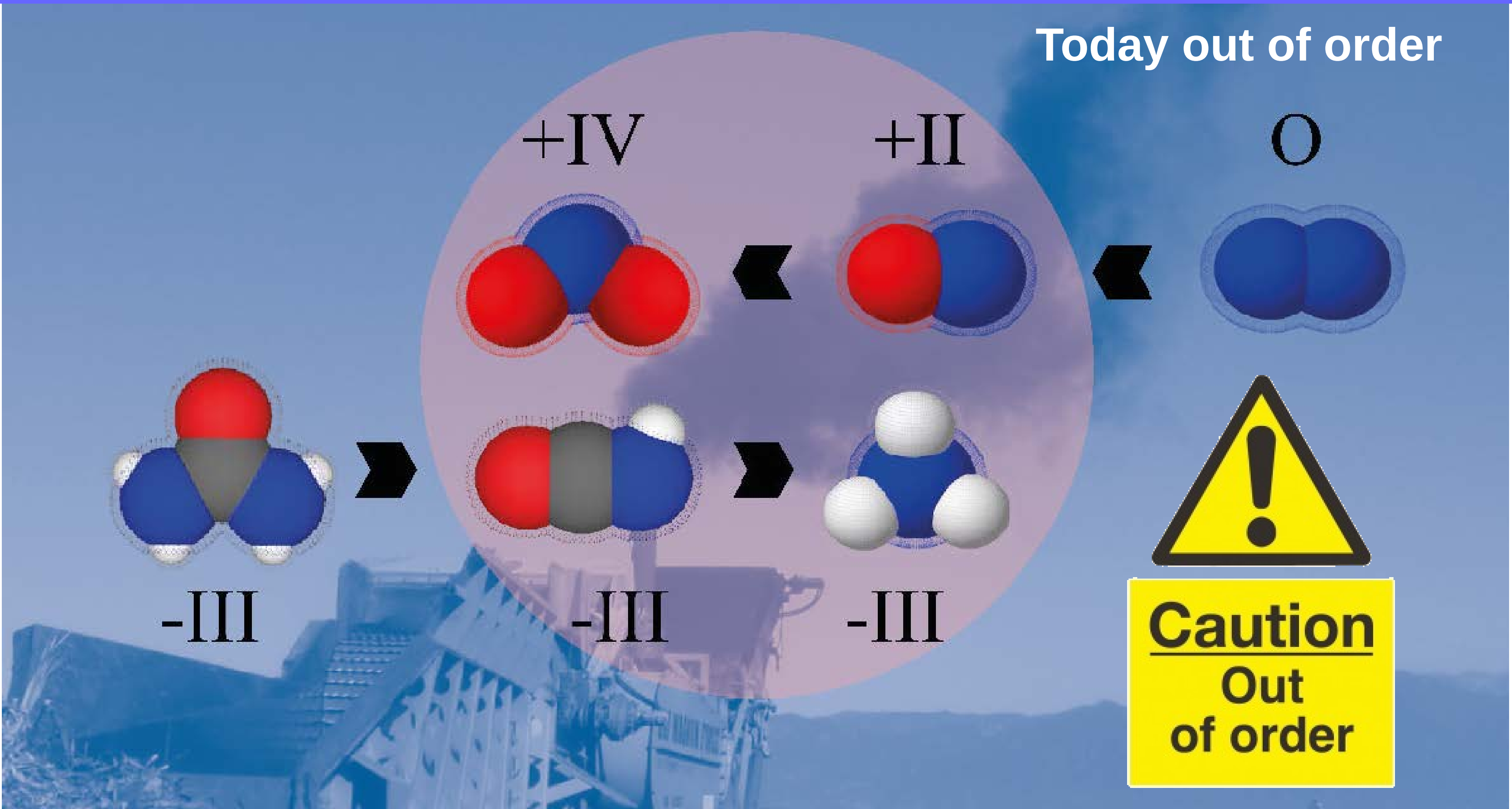
Exhaust temperatures in the ISO 8178/4 C1 cycle

Urea-based $deNO_x$-systems are active only for about 60-80% of the operating time

$DeNO_x$-system active >200°C



Urea-based SCR



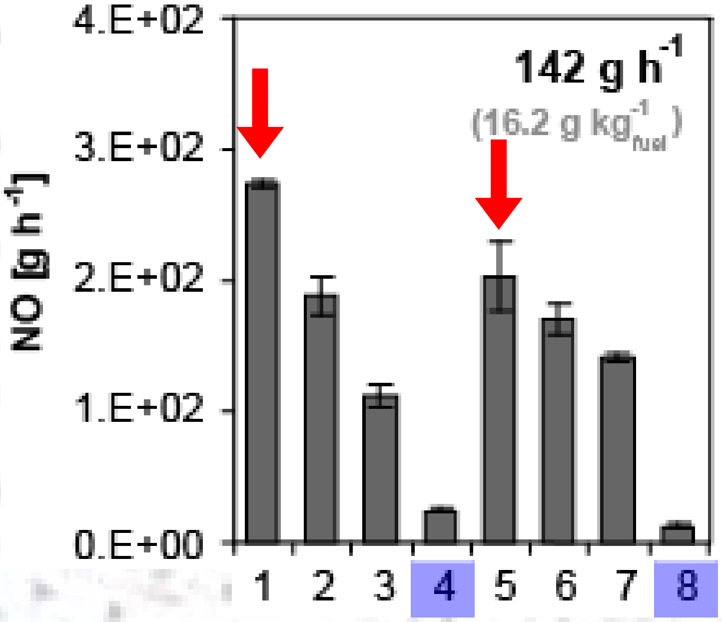
Currently the most efficient deNOx system for diesel engines

DeNO$_x$ Efficiencies: A best case scenario

Highest NO emissions at highest loads and temperatures (IVECO, 3.0 L, 100 kW, V-SCR)

Nitric oxide (NO)

engine-out



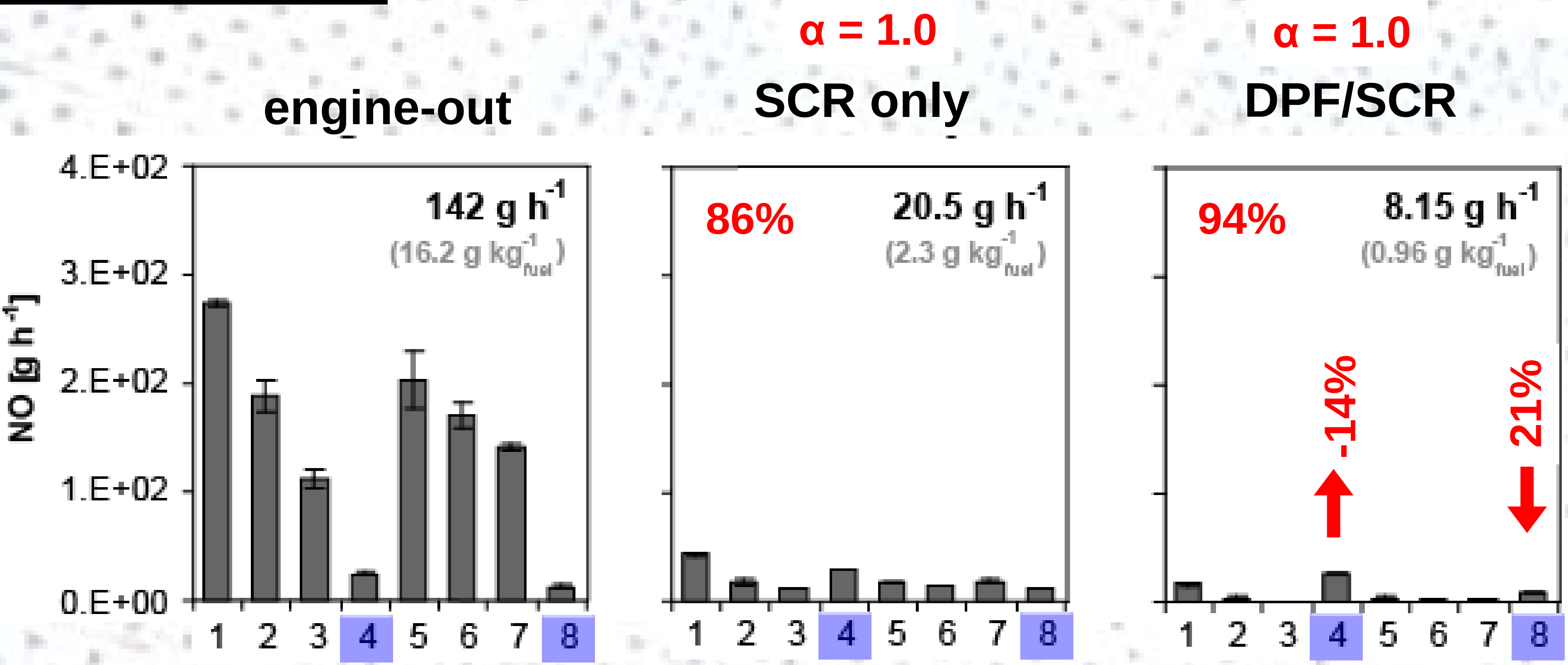
Heeb et al. Atm. Env. 45 (2011) 3203-3209

Heeb et al. Environ. Sci. Techol. 46 (2012) 13317-13325

DeNO$_x$ Efficiencies: A best case scenario

High NO conversion efficiencies can be achieved at alpha = 1.0!

Nitric oxide (NO)



Heeb et al. Atm. Env. 45 (2011) 3203-3209

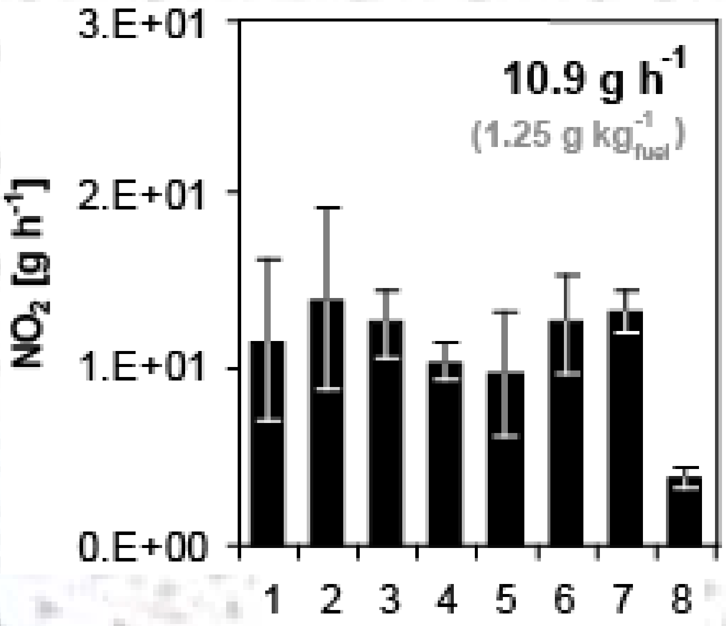
Heeb et al. Environ. Sci. Techol. 46 (2012) 13317-13325

DeNO$_x$ Efficiencies: A best case scenario

Low engine-out NO_2 emissions, only 3% on average

Nitrogen dioxide (NO_2)

engine-out

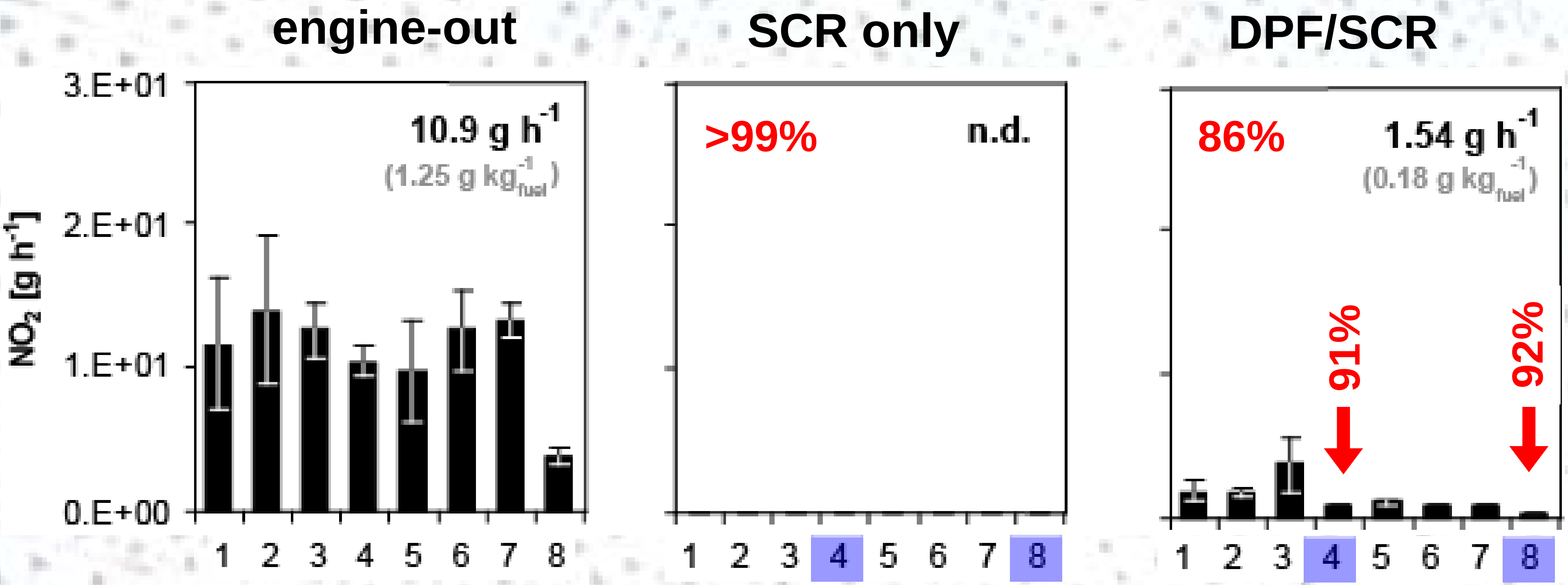


~3% NO2 und 97% NO Anteile

$DeNO_x$ Efficiencies: A best case scenario

High $deNO_2$ efficiencies can be achieved at alpha = 1.0!

Nitrogen dioxide (NO_2)

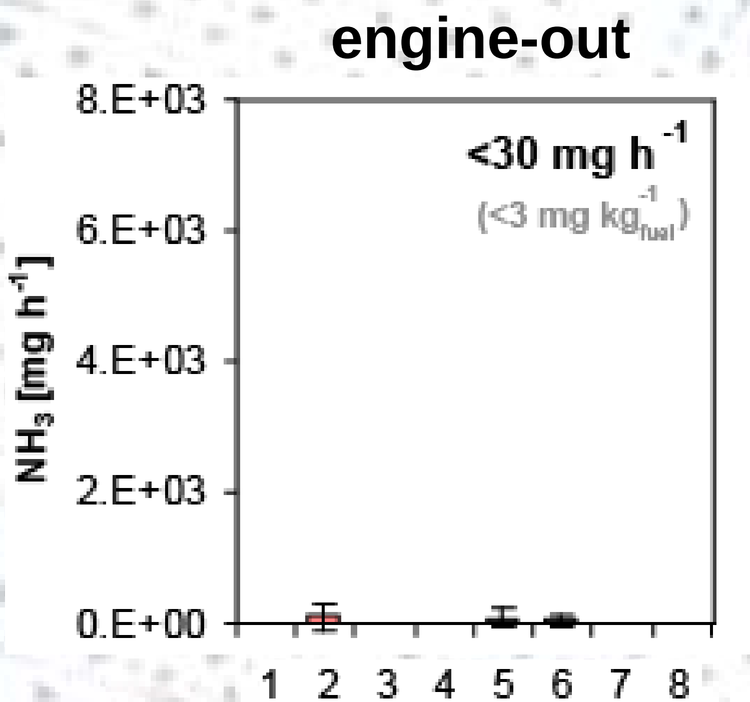


~3% NO_2 und 97% NO Anteile

Secondary pollutants of $DeNO_x$-technologies

Not much engine-out ammonia!

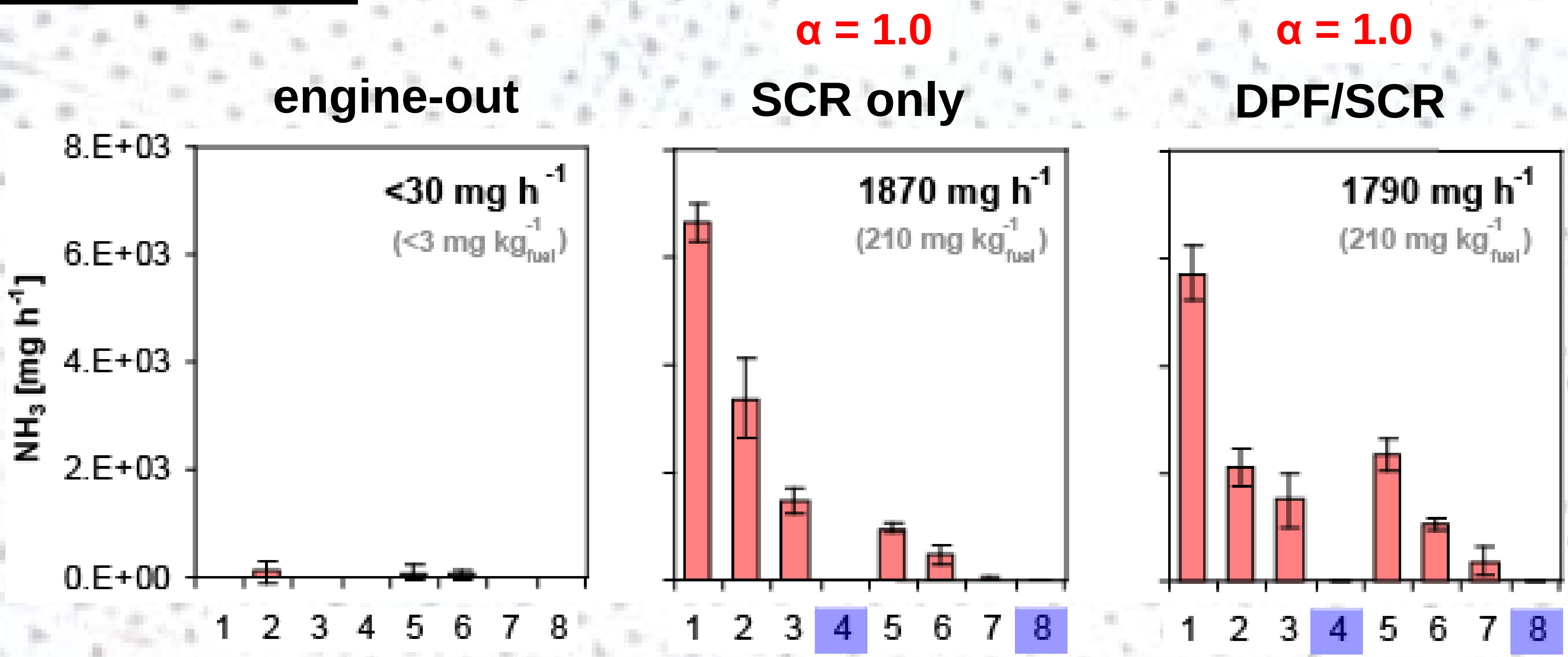
Ammonia (NH_3)



Secondary pollutants of $DeNO_x$-technologies

Substantial ammonia emissions with active SCR at alpha = 1.0!

Ammonia (NH_3)

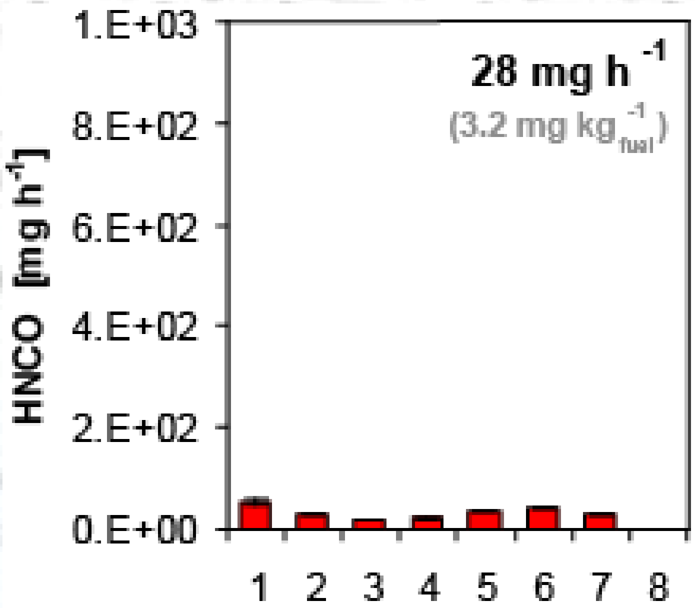


Secondary pollutants of DeNO$_x$-technologies

Some isocyanic acid in engine-out exhaust!

Isocyanic acid (HNCO)

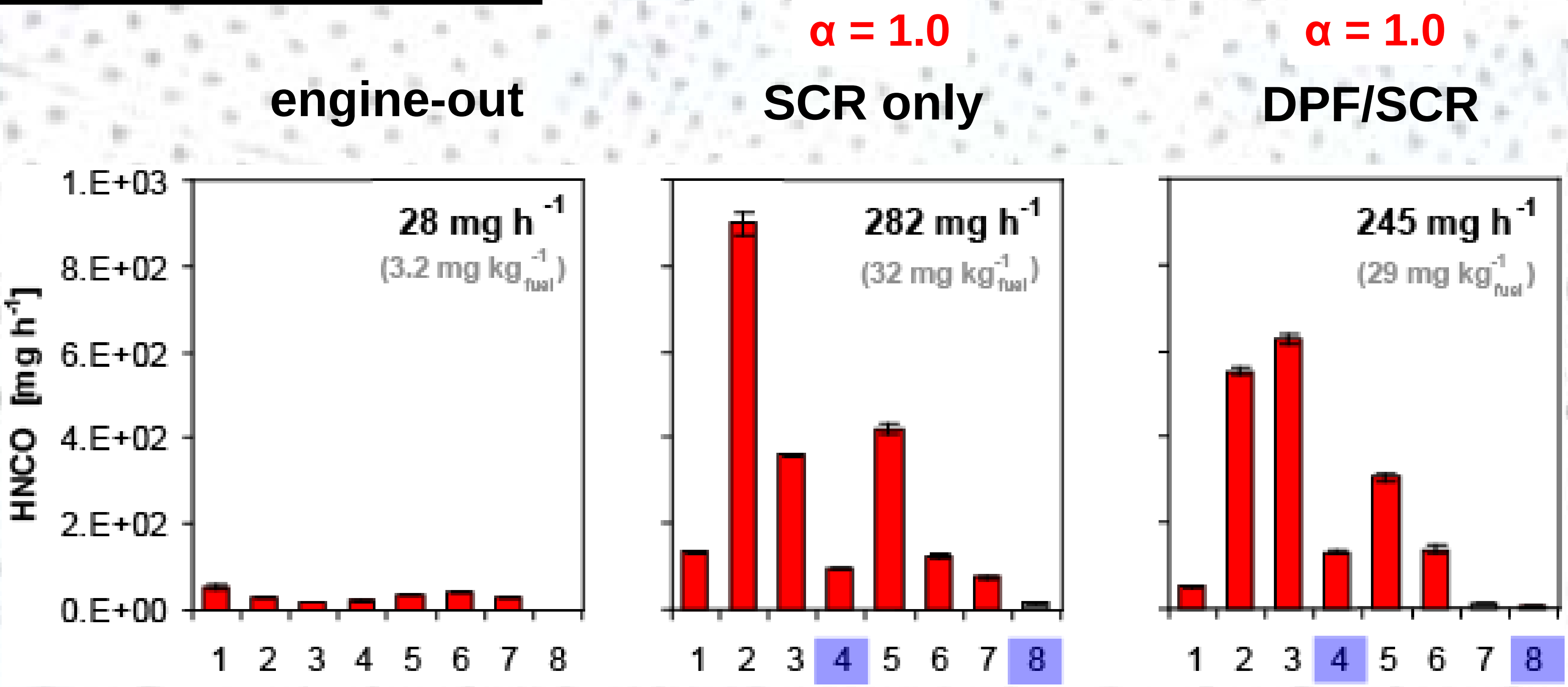
engine-out



Secondary pollutants of $DeNO_x$-technologies

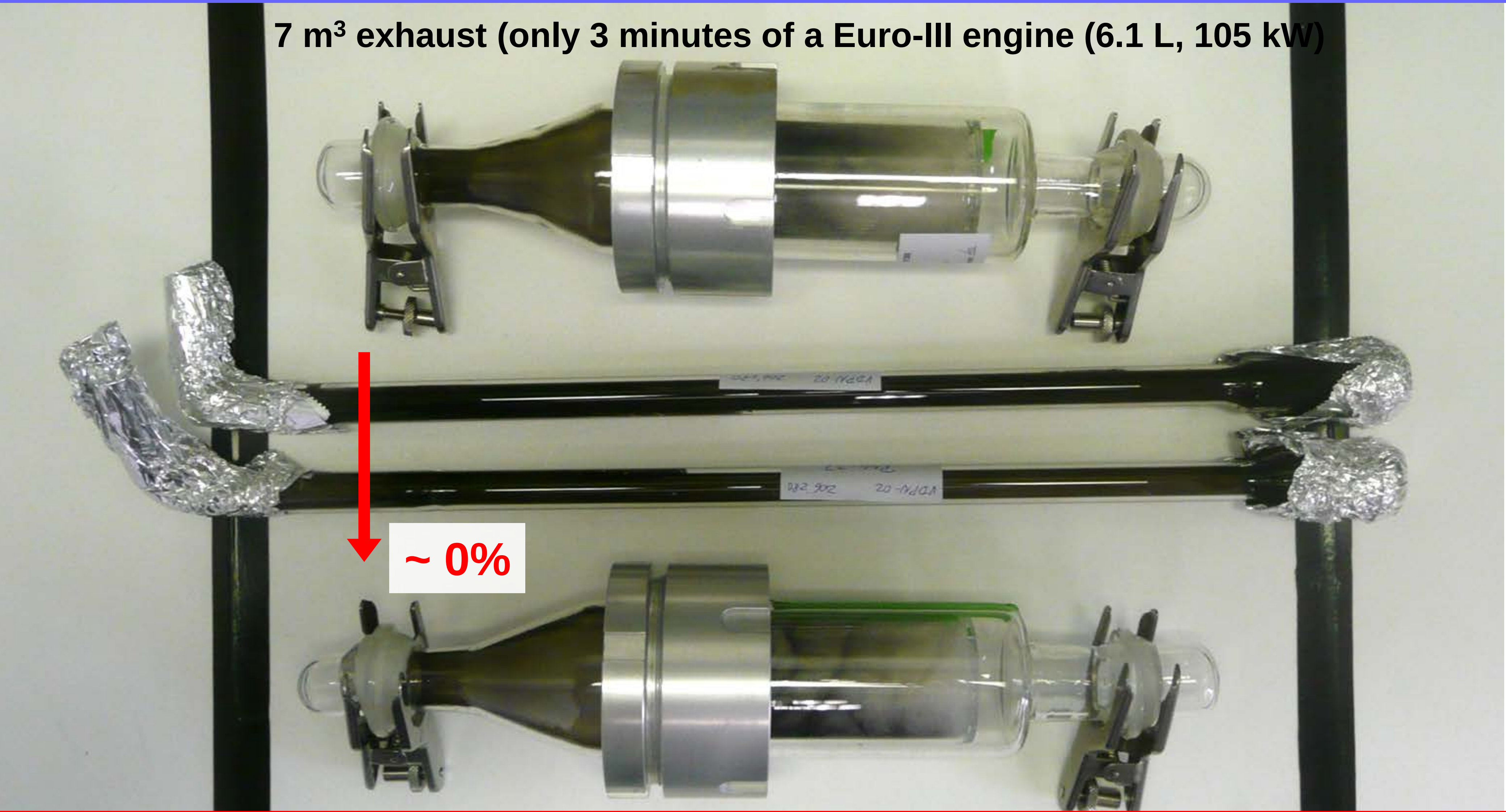
Considerable amounts of isocyanic acid emissions with active SCR!

Isocyanic acid (HNCO)



Heeb et al. Atm. Env. 45 (2011) 3203-3209

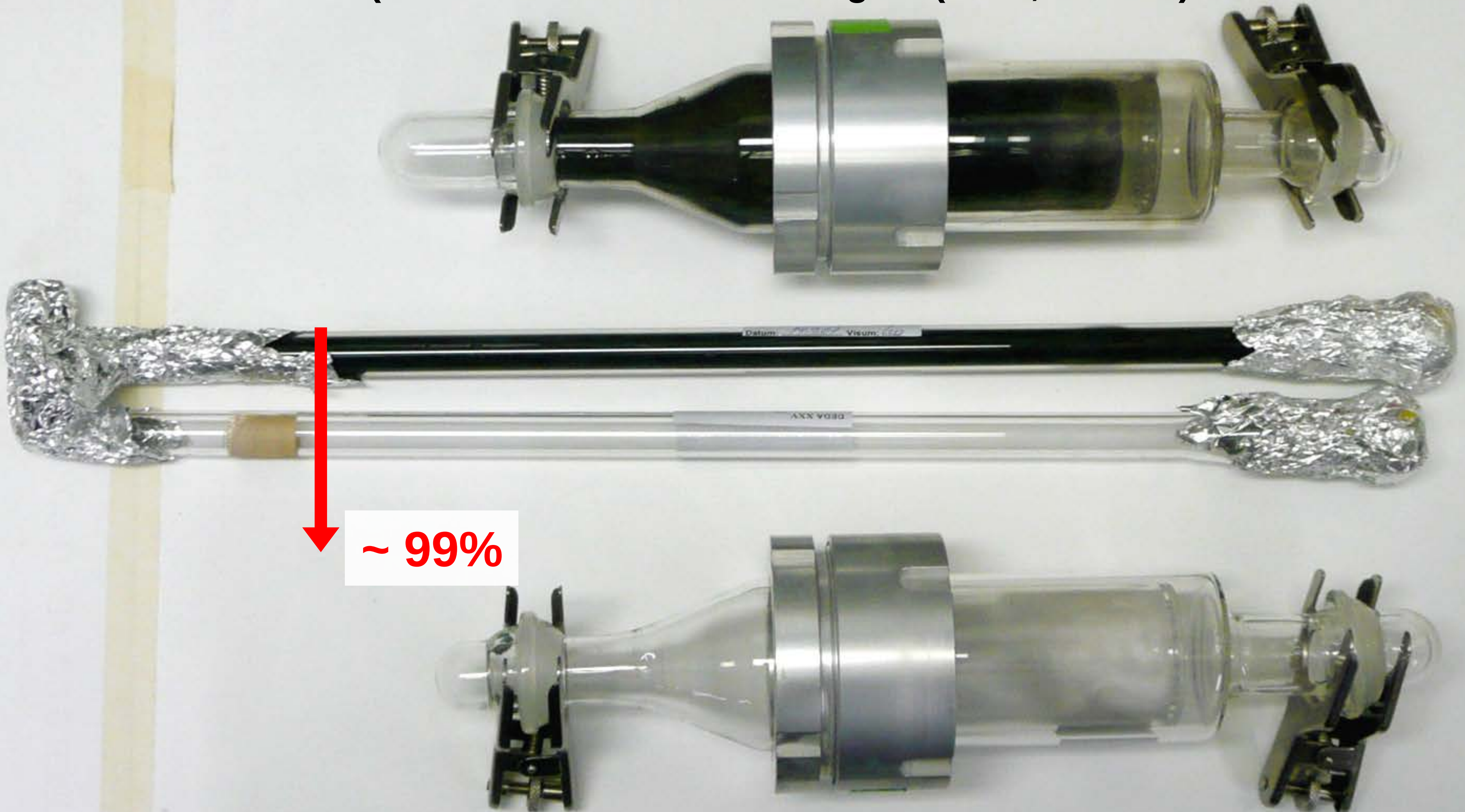
The visible effect of an SCR-system



For years thousands of Euro-III, -IV, -V HDVs without filters!

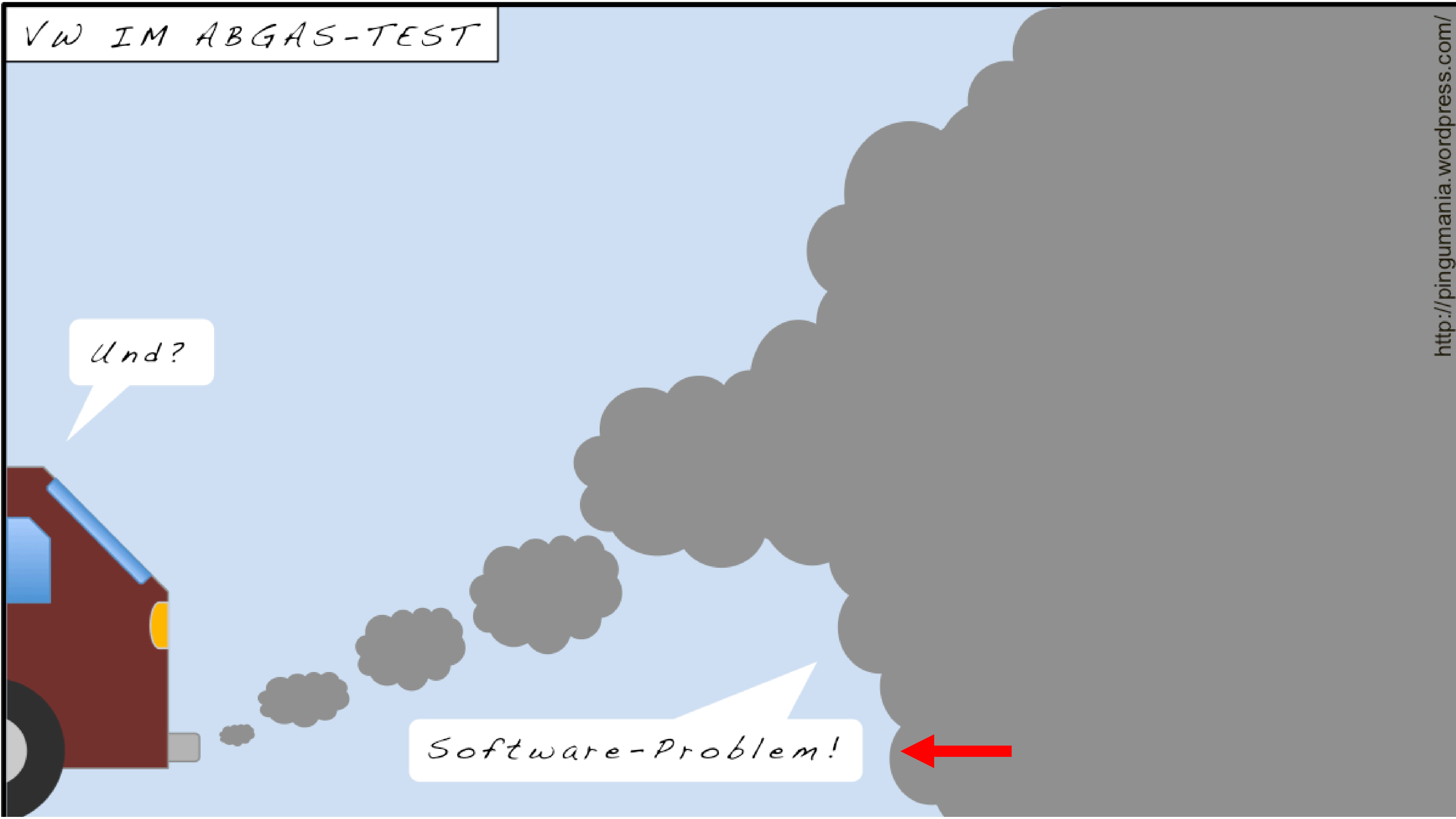
The visible effect of a particle filter

7 m^3 exhaust (3 minutes of an Euro-III engine (6.1 L, 105 kW)

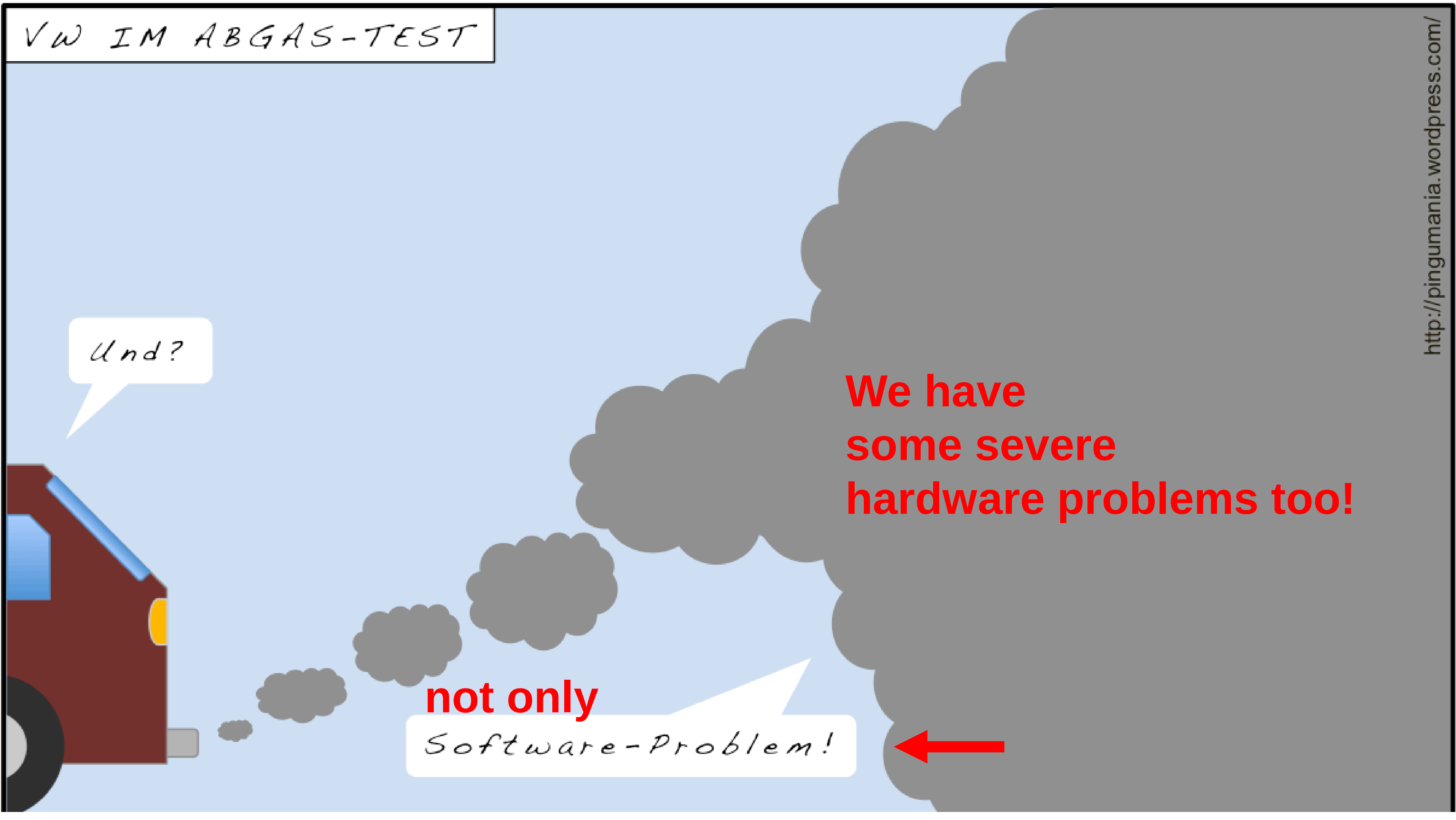


At least Euro-VI HDVs now have both filters and deNOx!

Blue Technology: Not green enough yet



Blue Technology: Not green enough yet



Blue Technology: Not green enough yet

Year two after the VW scandal!

“Will blue technology be green enough in the future?”

There’s quite some work ahead of us, especially at urban driving conditions!

Blue Technology: Not green enough yet

A combined effort with many important contributions

Thanks:

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- **Governement**: Peter Bonsak, Philipp Hallauer, Giovanni D'Urbano, Felix Reutimann, Max Wyser, Gerhard Leutert, Martin Schiess, Swiss Fed. Office for Environment, Bern
  Thomas Gasser, Heinz Berger, Gerhard Stucki, Swiss Federal Road Office
- **Filter- & catalyst manufacturers**: >50 diesel particle filters, 4 deNOx-systems

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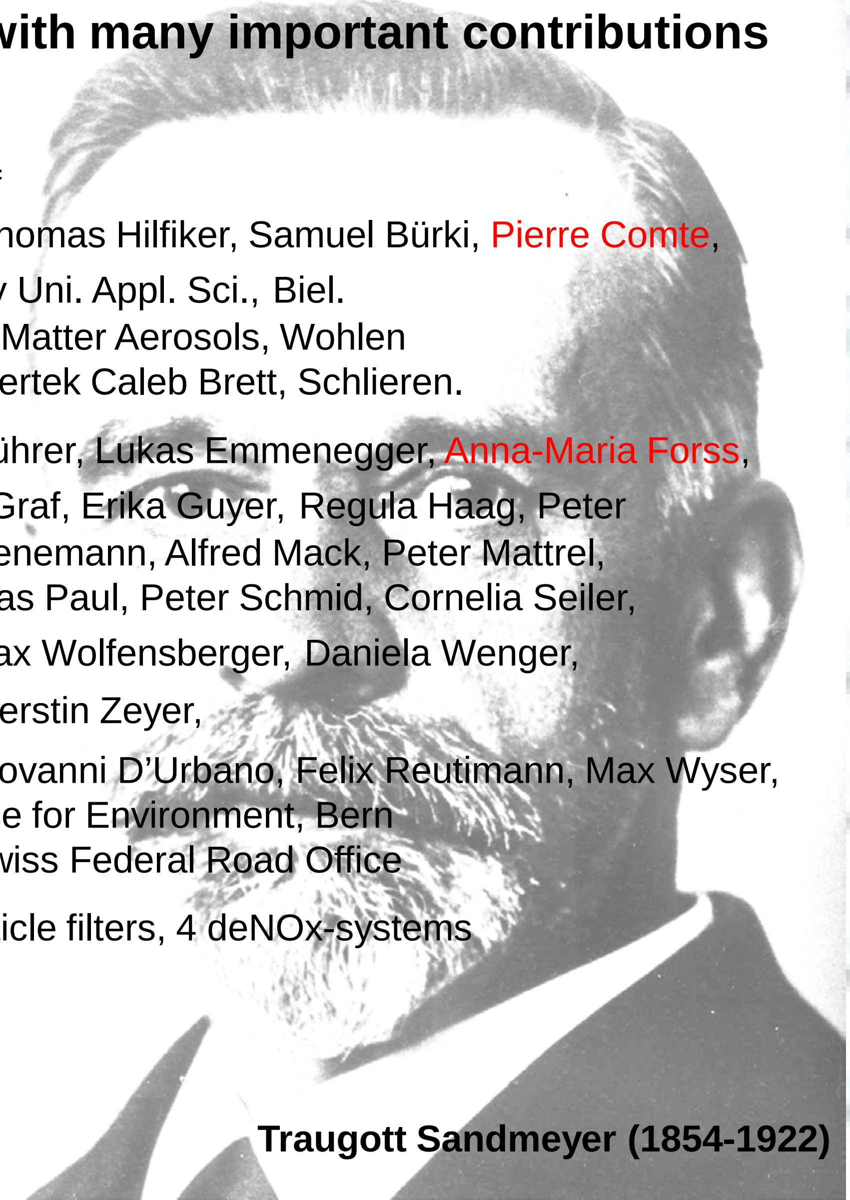

Traugott Sandmeyer (1854-1922)