Chemistry of the NOx trap technology

8th VERT Forum: Combined particle filter and deNOx-technologies

Dübendorf, March 17, 2017

Blue Technology: Not green enough yet

Blue Technology: Not green enough yet

GDCh/DECHEMA-Sonderkolloquium, Frankfurt, 14. Januar 2016

"Stickoxide: Ist der Diesel noch zu retten?"

7th VERT-Forum, Dübendorf, March 18, 2016

"Can diesel solve its NO and NO_2 problem in time?"

6th Freiburger workshop, Freiburg i.B., 6. Juni 2016

"Europe's NOx problem, a consequence of inefficient diesel-converters and bad exhaust legislation"

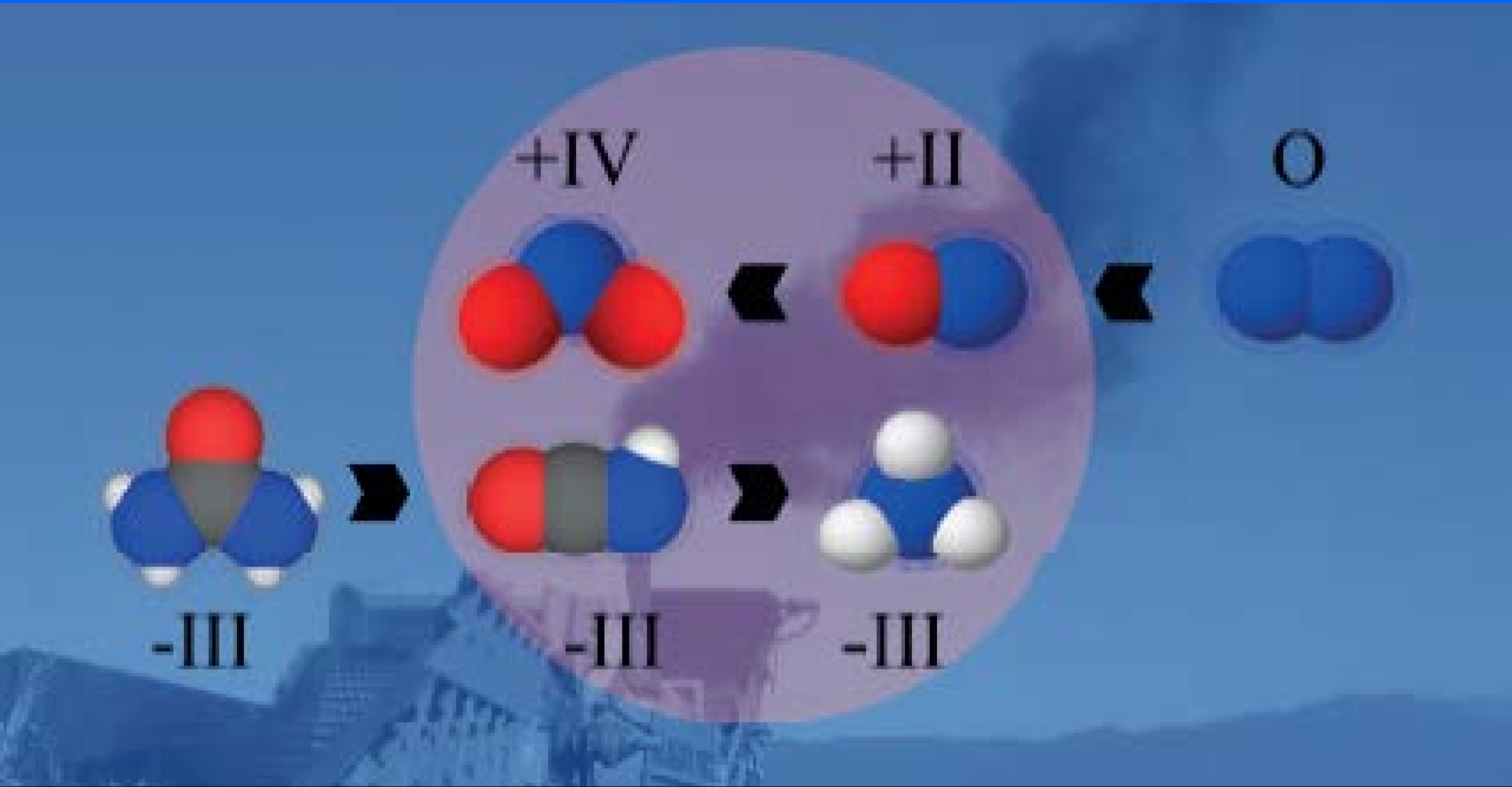
20th ETH conference on CGN, Zürich, June 13-16, 2016

"The particle-NOx trade-off: Two decades of diesel converter technologies have not settled both issues?"

GDCh/DECHEMA/VDI-Expert Forum Frankfurt, 5-6. December 2016

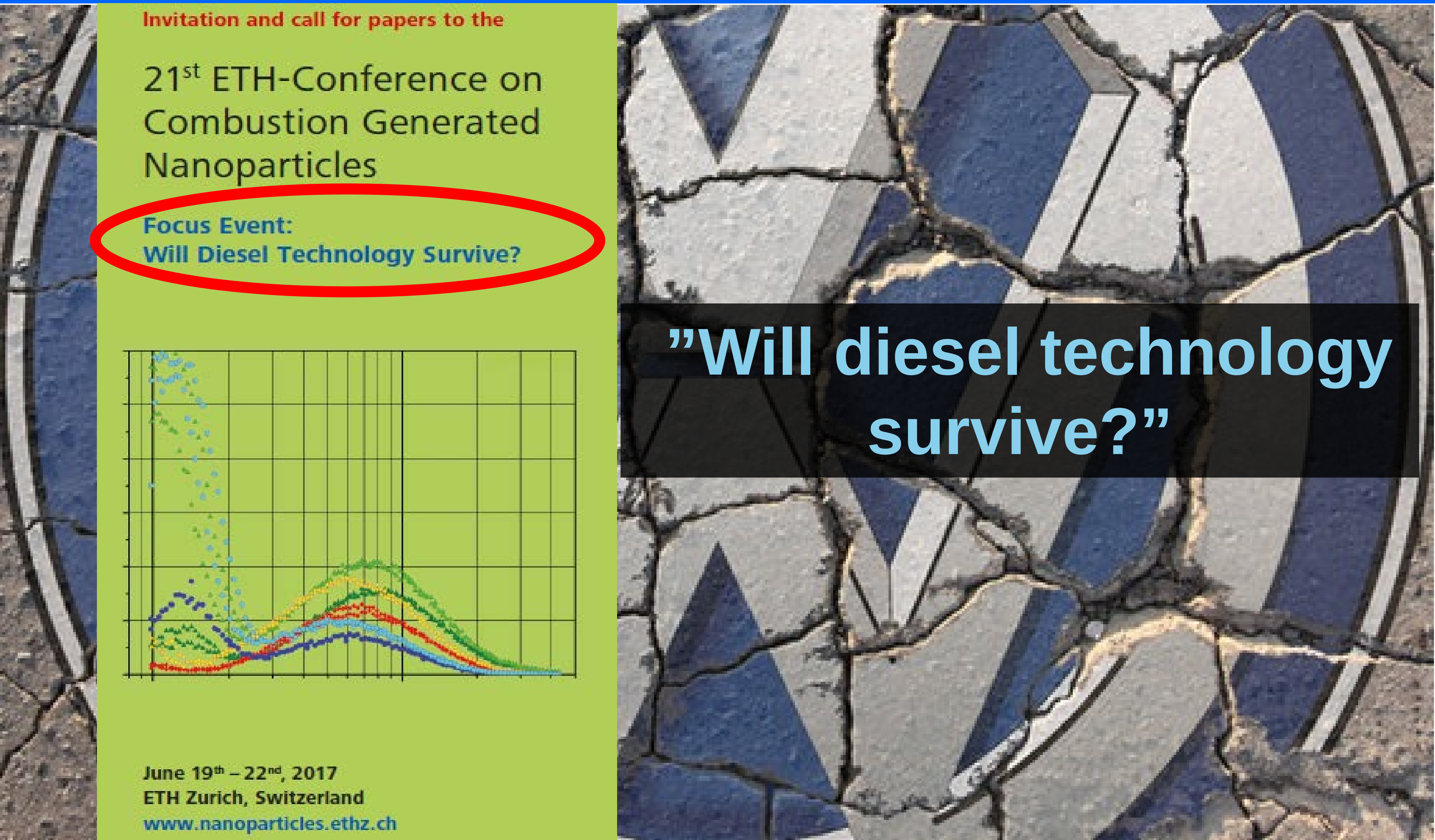
"Efficient filter & deNOx for diesel and GDI vehicles?"

Blue Technology: Not green enough yet

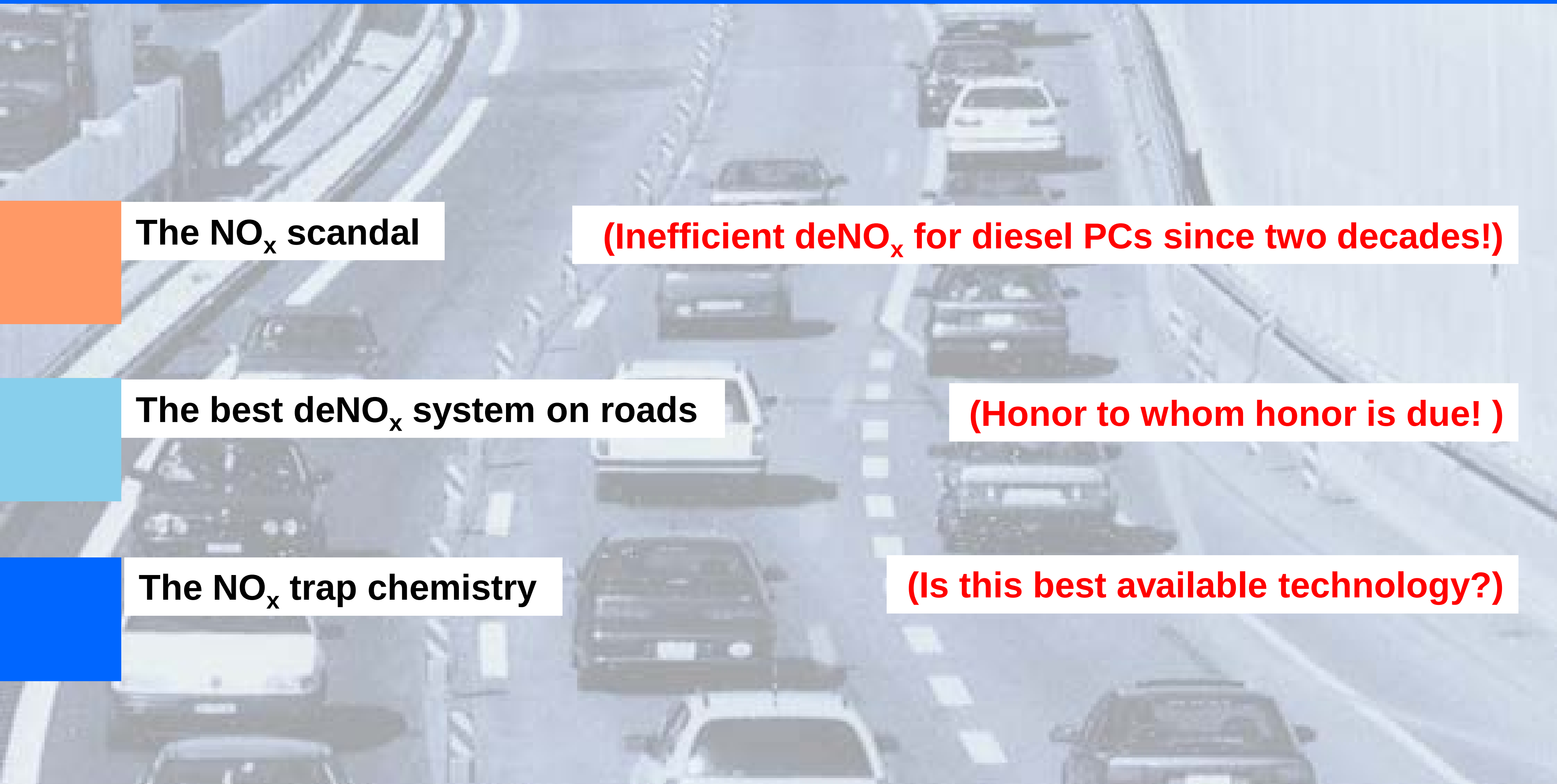


“Will blue technology be green enough in the future?”

Blue Technology: Not green enough yet



Chemistry of the NOx trap technology



The NO_x scandal — **(Inefficient $deNO_x$ for diesel PCs since two decades!)**

The best $deNO_x$ system on roads — **(Honor to whom honor is due!)**

The NO_x trap chemistry — **(Is this best available technology?)**

8th VERT Forum: Combined particle filter and deNOx-technologies

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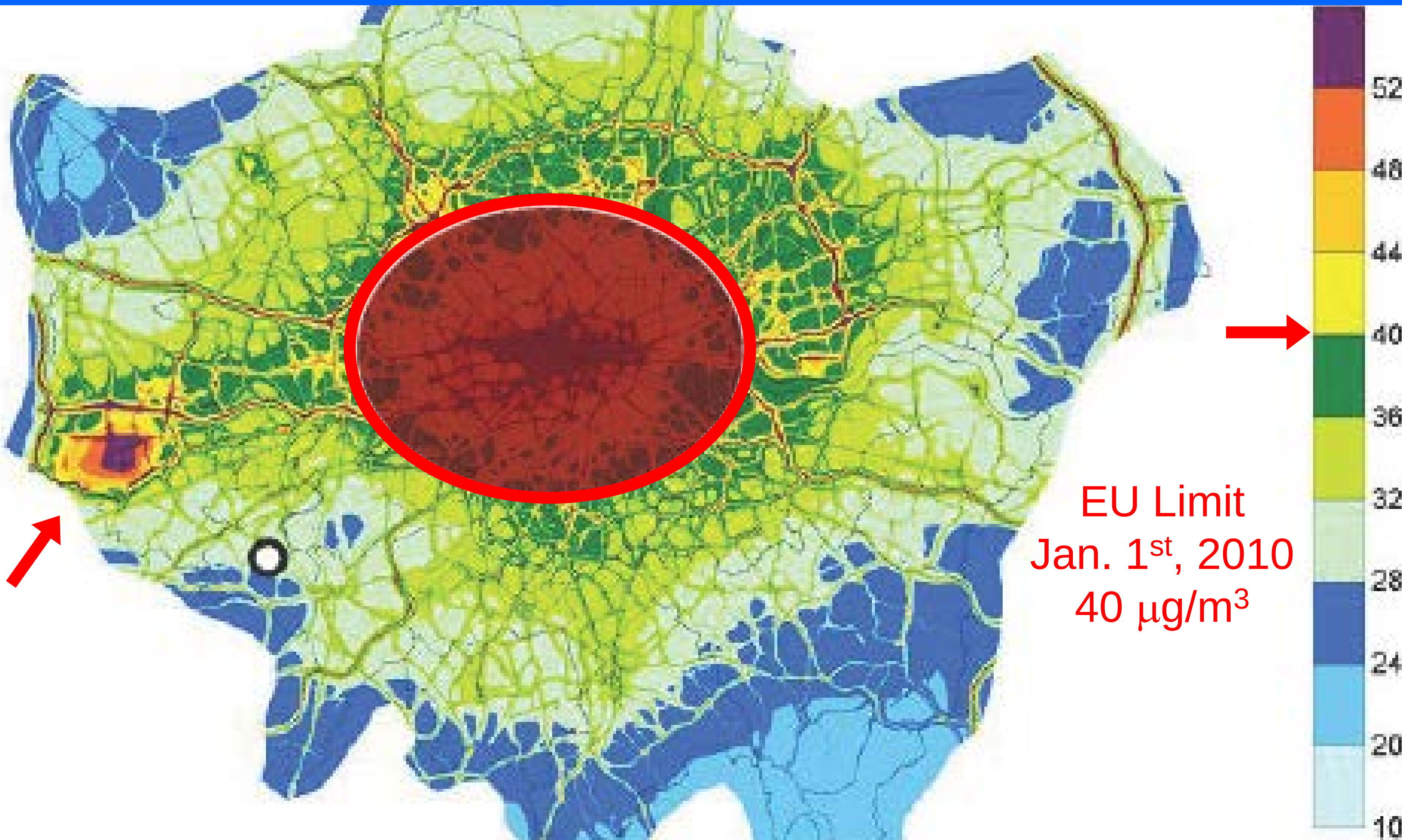
Mean annual NO_2 levels: City of London

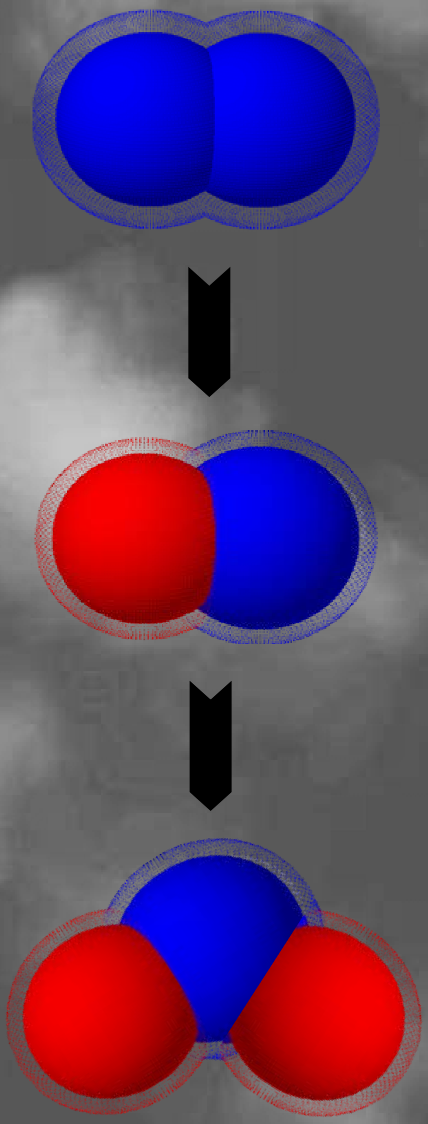


DOCs and hox-DPFs substantially contribute to the NO_2 problem

Adverse health effects of diesel exhaust

Reactive nitrogen compounds

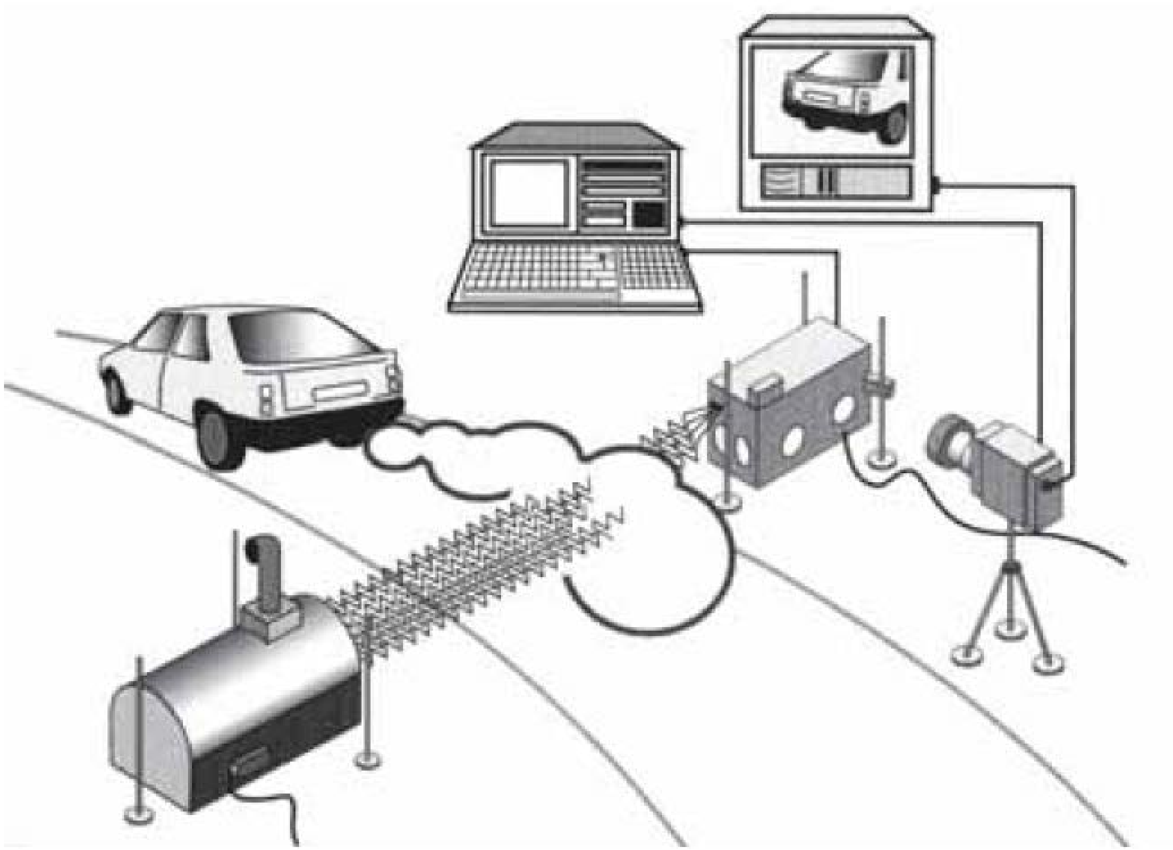
- NO_2 is highly toxic (acute and chronic) (induces oxidative stress, inflammation chronic obstructive pulmonary disease)
- Diesel vehicles with DOCs and hox-DPFs are high NO_2 emitters!



One reason for better deNO_x systems is the increase of NO_2 emissions due to secondary formation in DPFs

From chassis dynamometers to on-road measurements

For example with an FT-IR at the curbside



- **Remote Sensing**
- **Emissions of individual vehicles**
- **NO, CO, HC, CO_2**
- **15 years, 500'000 vehicles**
- **Licence plate recognition**
- **Technology assignment**
- **Detection of high emitters**
- **Field inspection and control**

Gian-Marco Alt, Michael Götsch, Valentin Delb, AWEL, Zürich

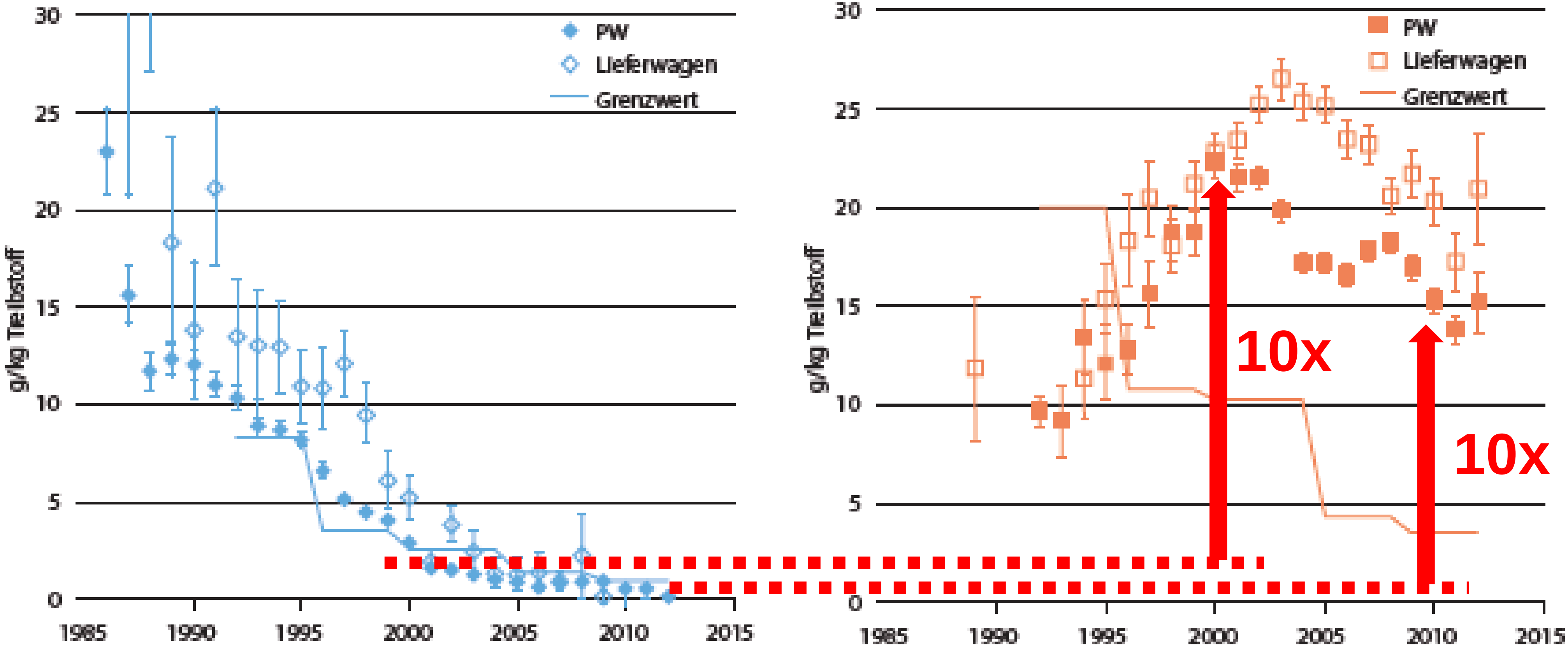
Chen & Borken-Kleefeld Atm. Env. **2014**, 88, 157-164

From chassis dynamometers to on-road measurements

Appearance and reality are far apart! Diesel NO_x 10x higher than gasoline vehicles

NO_x emissions of gasoline & diesel vehicles

The NO_x problem of diesel PCs & LDVs is 20 years old – that's the scandal



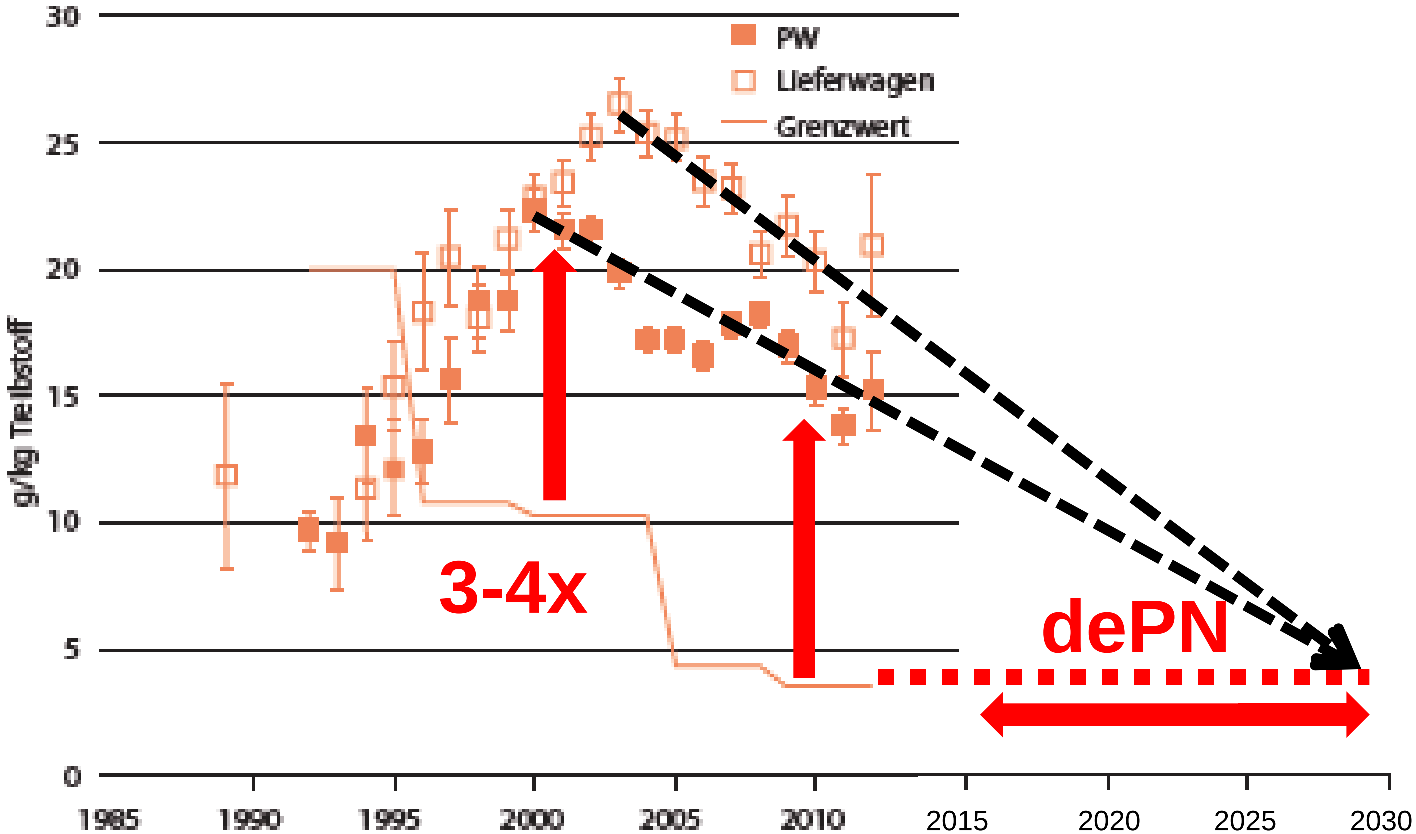
Chen & Borken-Kleefeld Atm. Env. **2014**, 88, 157-164

Can diesel solve its NO and NO2 emission problem in time?

Appearance and reality are far apart! Another 15 years to wait?

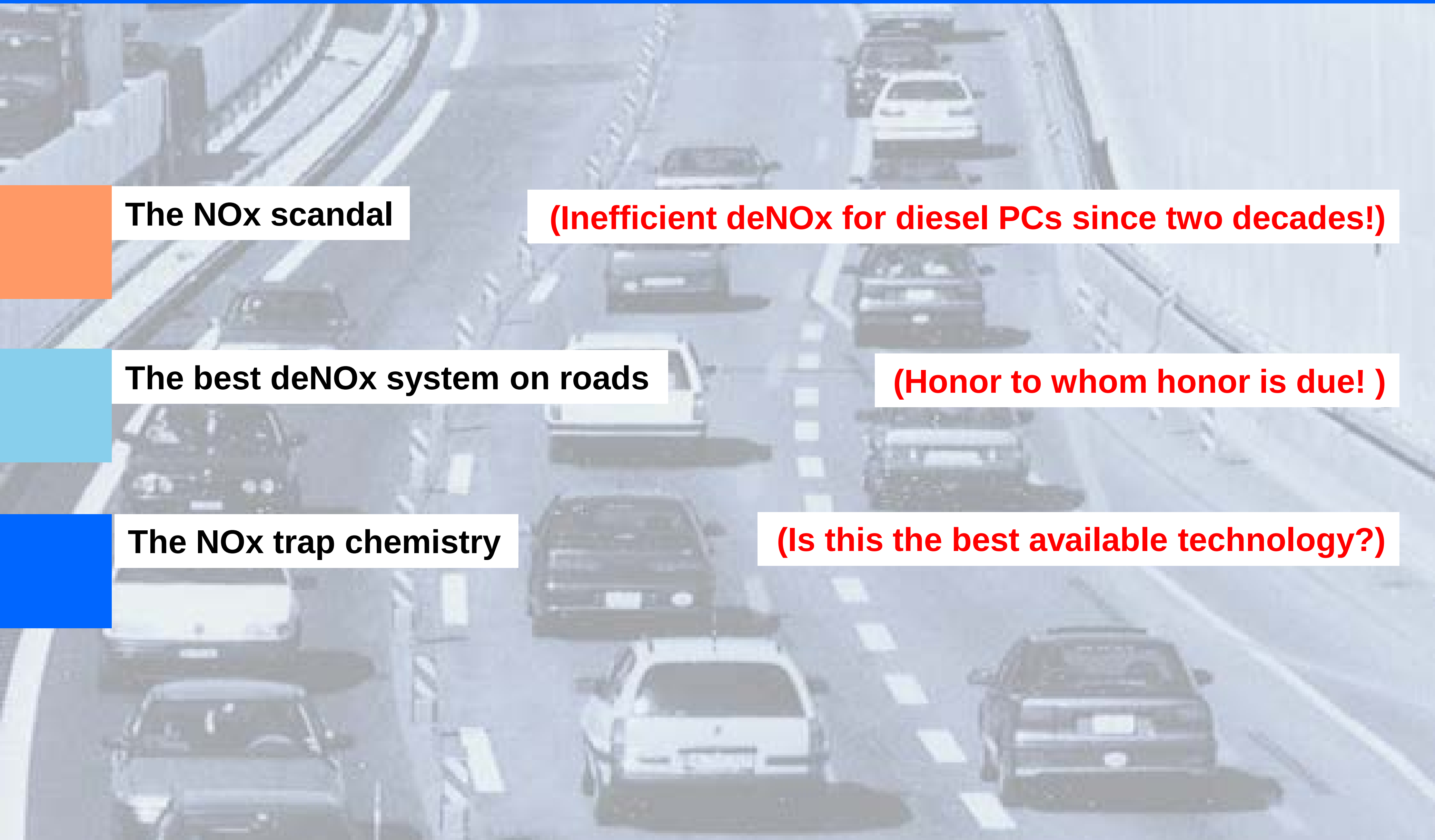
NO_x emissions of diesel vehicles

The NO_x problem of diesel PCs & LDVs is 20 years old – that's the scandal



Is it really 2030 when diesel PC and LDV reach the Euro-6 level introduced in 2009?

Chemistry of the NOx trap technology



The NOx scandal (Inefficient deNOx for diesel PCs since two decades!)

The best deNOx system on roads (Honor to whom honor is due!)

The NOx trap chemistry (Is this the best available technology?)

The best deNO$_x$ system on European roads

Honor to whom honor is due

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

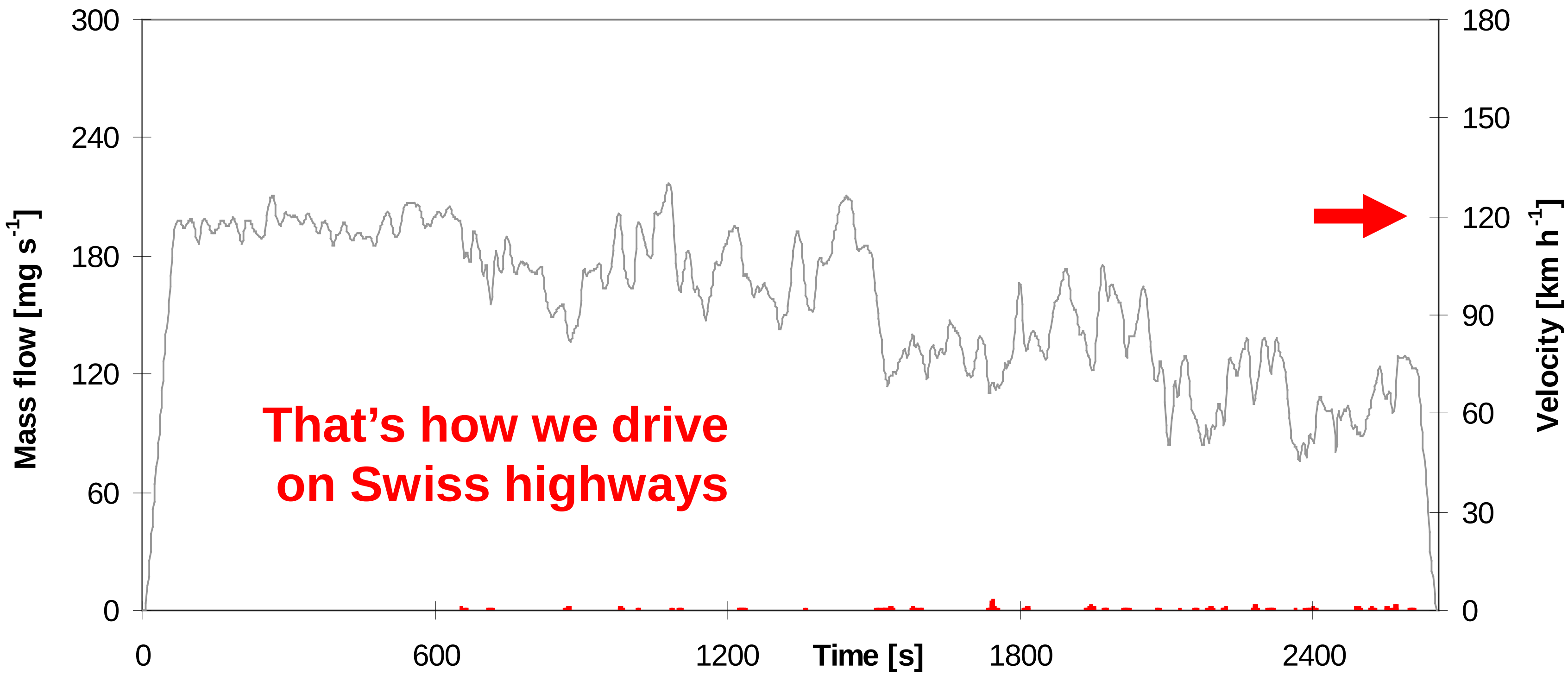
Fuel:
- 95 RON gasoline (specification CEF RF-08-A-85)

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

DeNO$_X$ am Pd/Rh-TWC

Speed limit 120 km h^{-1}

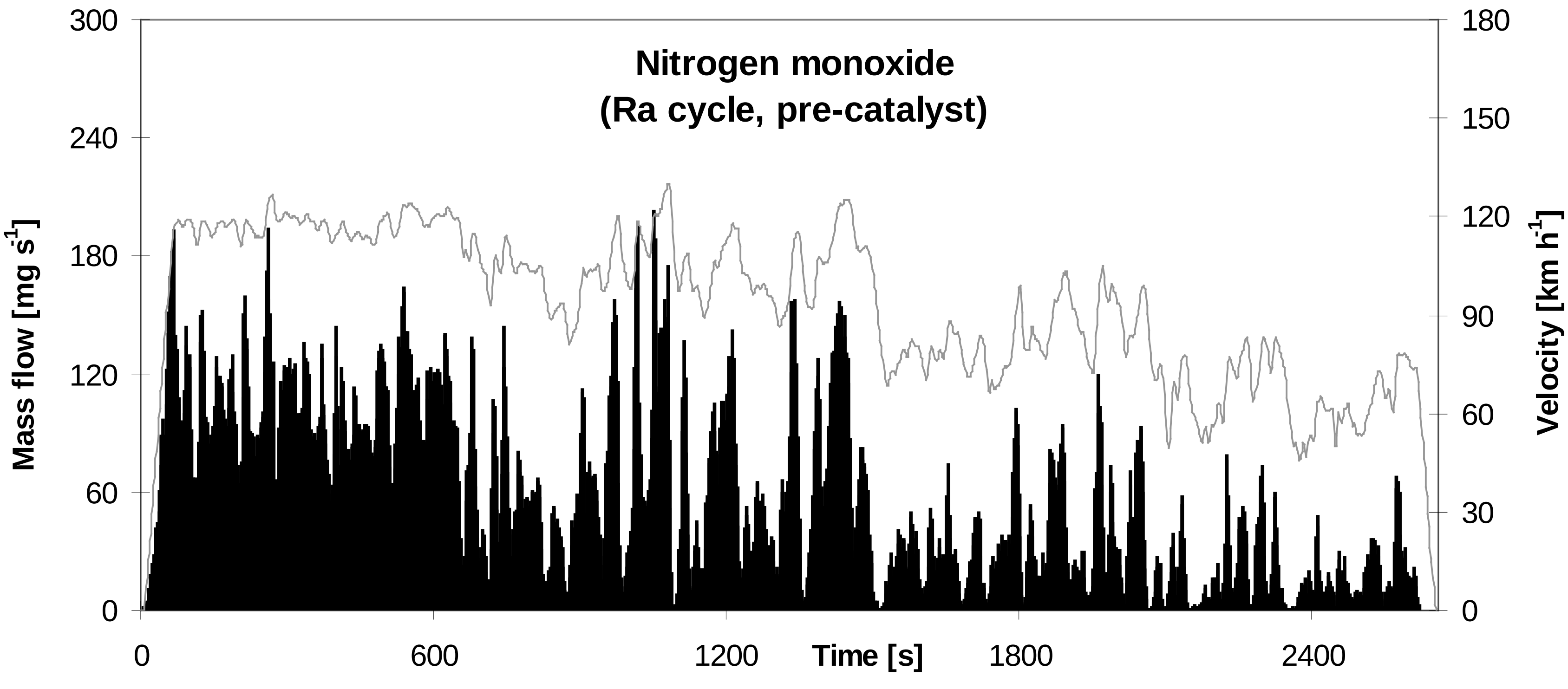
NO emission (BMW, 1.8 l, 1995, EURO-1)



DeNO$_x$ in 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)



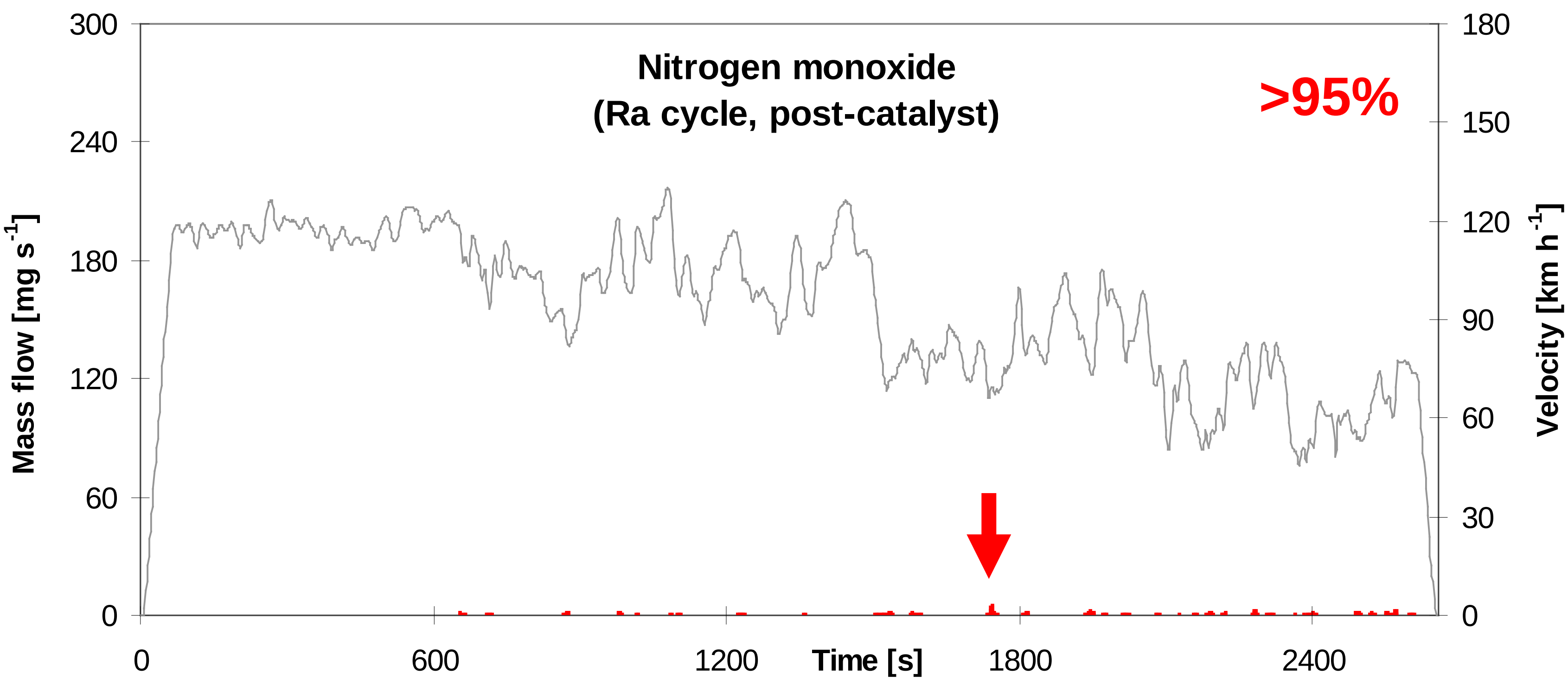
Heeb et al. Atm. Env. 40 (2006) 5986-5997

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

$DeNO_X$ am Pd/Rh-TWC

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

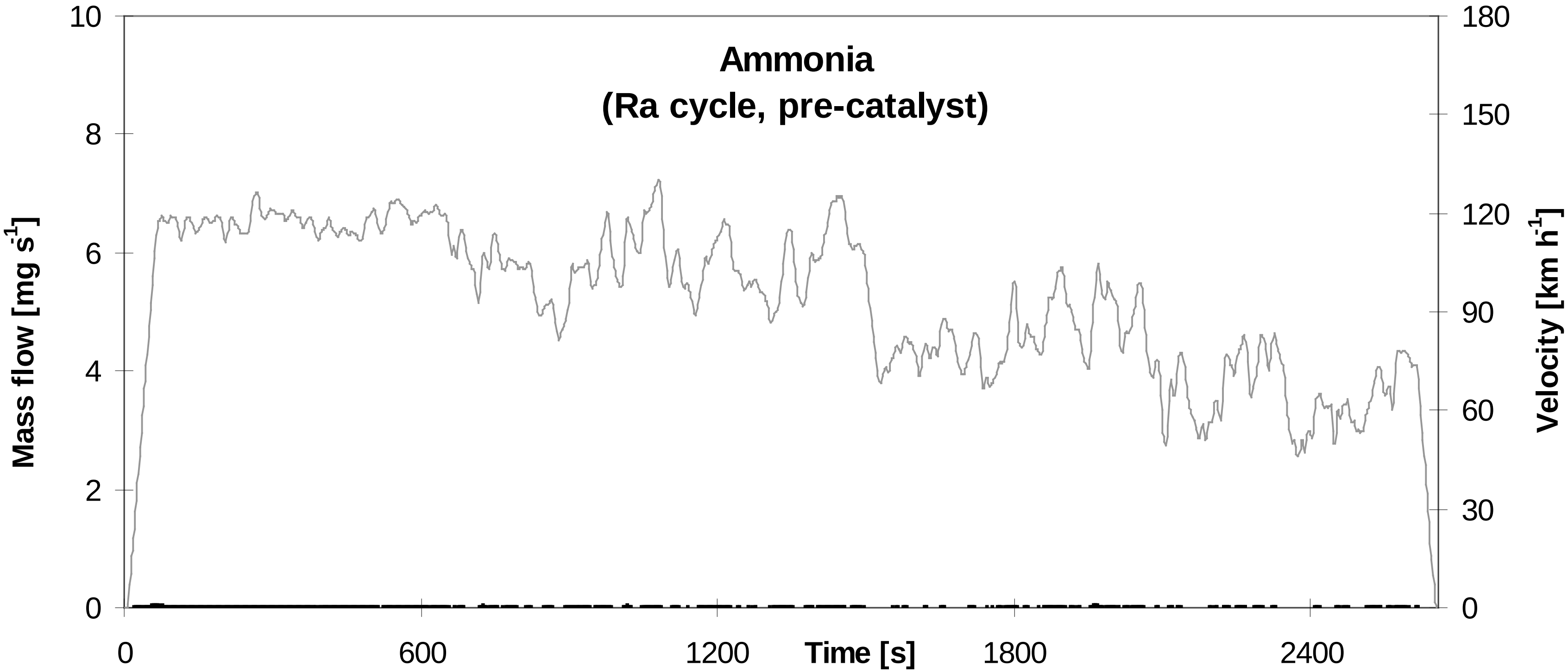
NO emission (BMW, 1.8 l, 1995, EURO-1)



TWC-induced formation of ammonia

No ammonia before catalyst

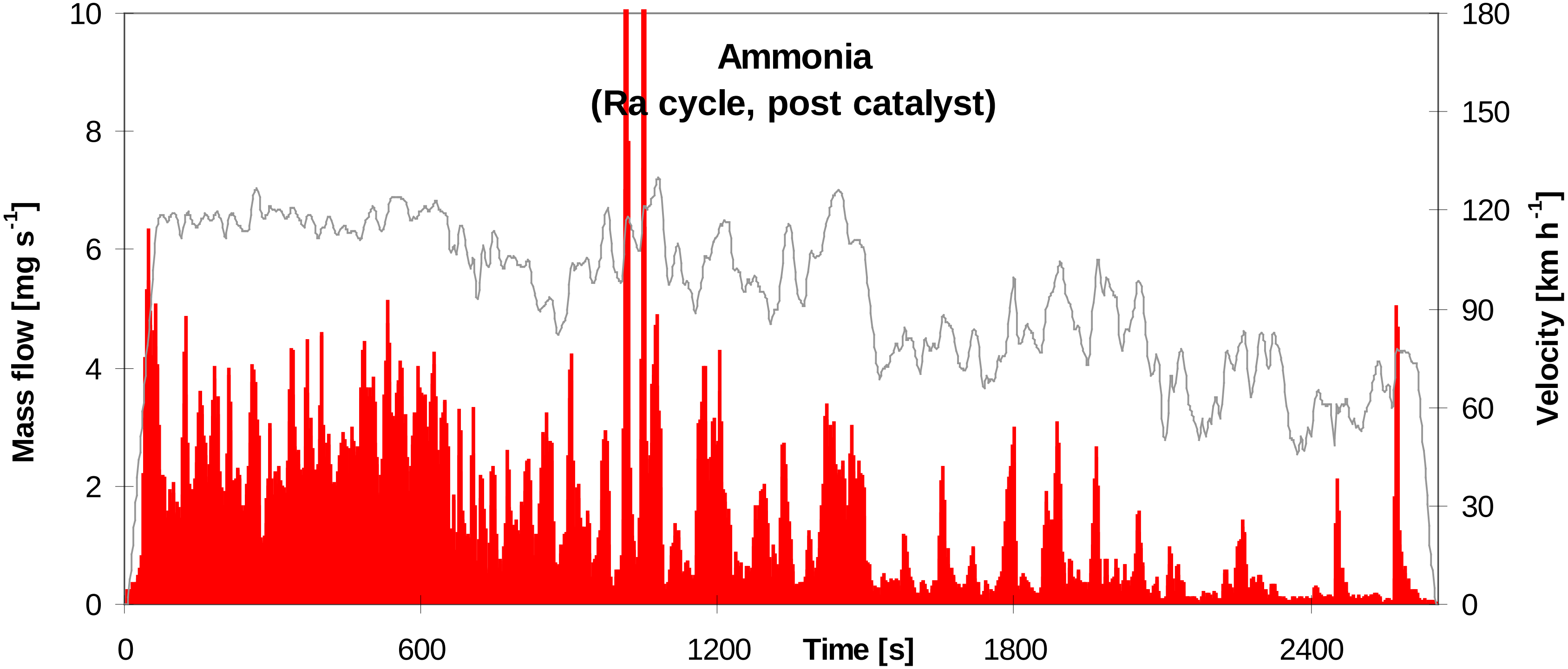
Ammonia emissions (BMW, 1.8 l, 1995, EURO-1)



TWC-induced formation of ammonia

Relevant ammonia emissions post catalyst

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



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TWC in real world application

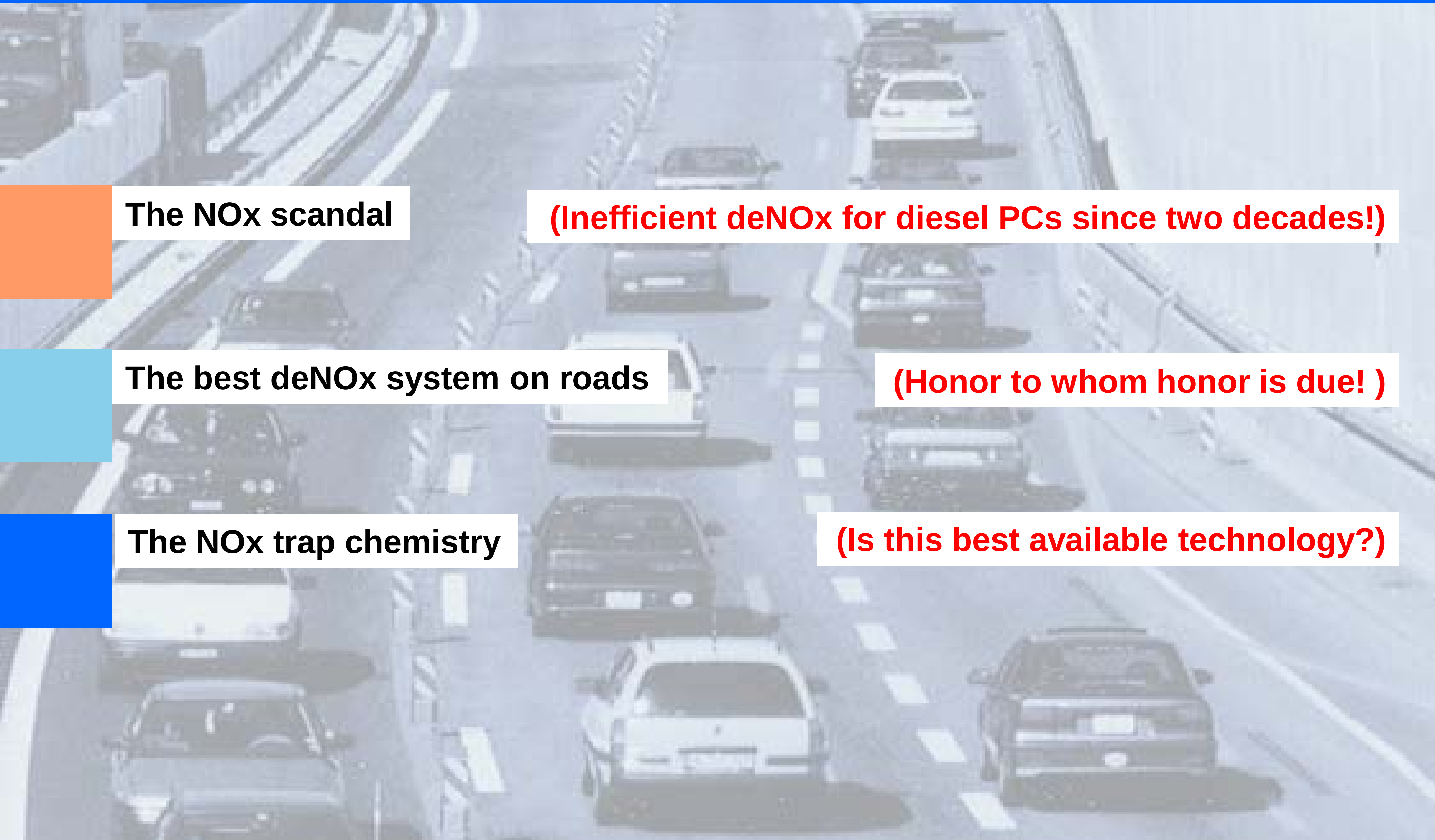
- **Why NH_3 and N_2O?**
  - Which three ways to go?
  - A new try incl. H_2, water gas-shift-reactions and steam reforming
  - Another try with H_2, N_2O and NH_3

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

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

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

Chemistry of the NOx trap technology



The NOx scandal — (Inefficient deNOx for diesel PCs since two decades!)

The best deNOx system on roads — (Honor to whom honor is due!)

The NOx trap chemistry — (Is this best available technology?)

NOx-trap technology

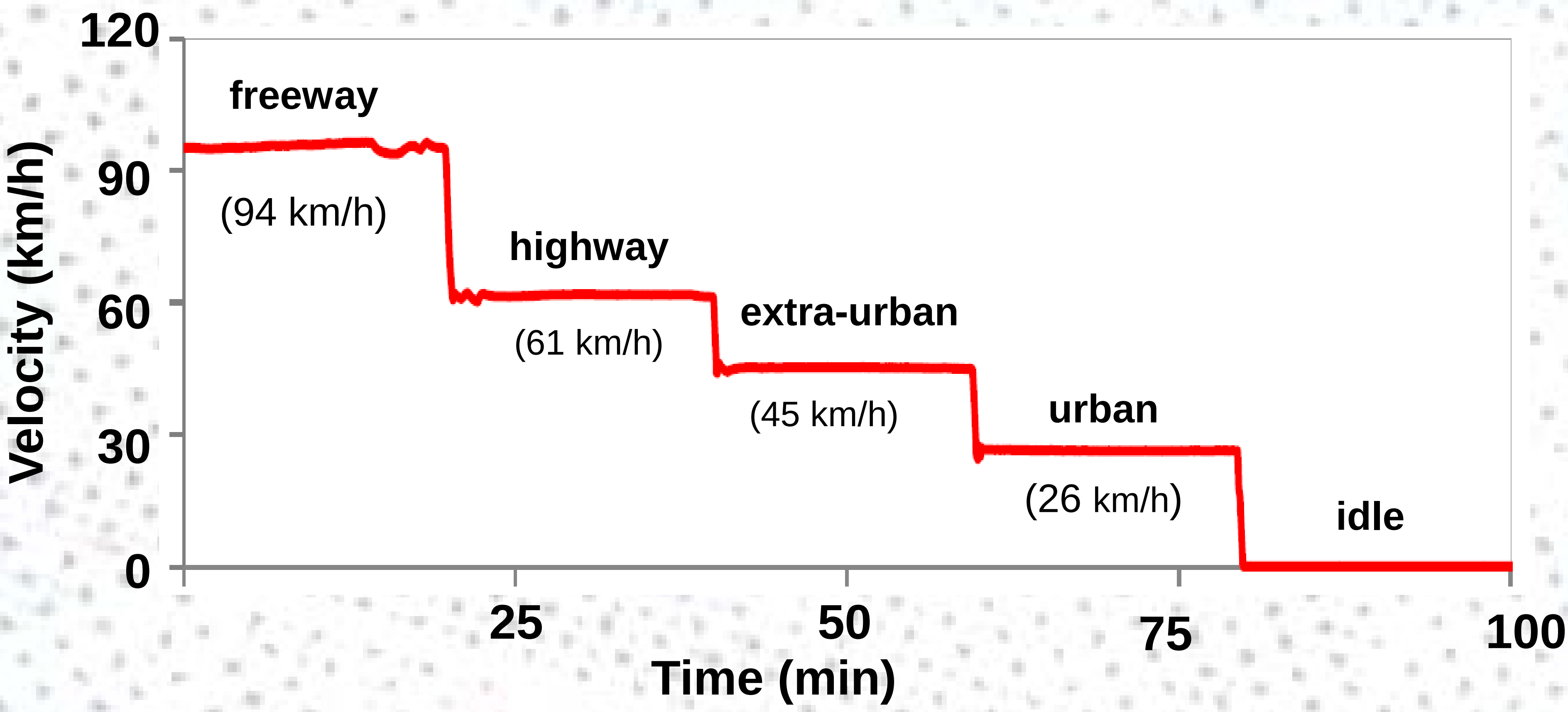
The first in-series GDI vehicle (Mitsubishi Carisma, 1.8 l, Euro-3) with NOx trap technology

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 technology

An ideal cycle to study converter chemistry at its best

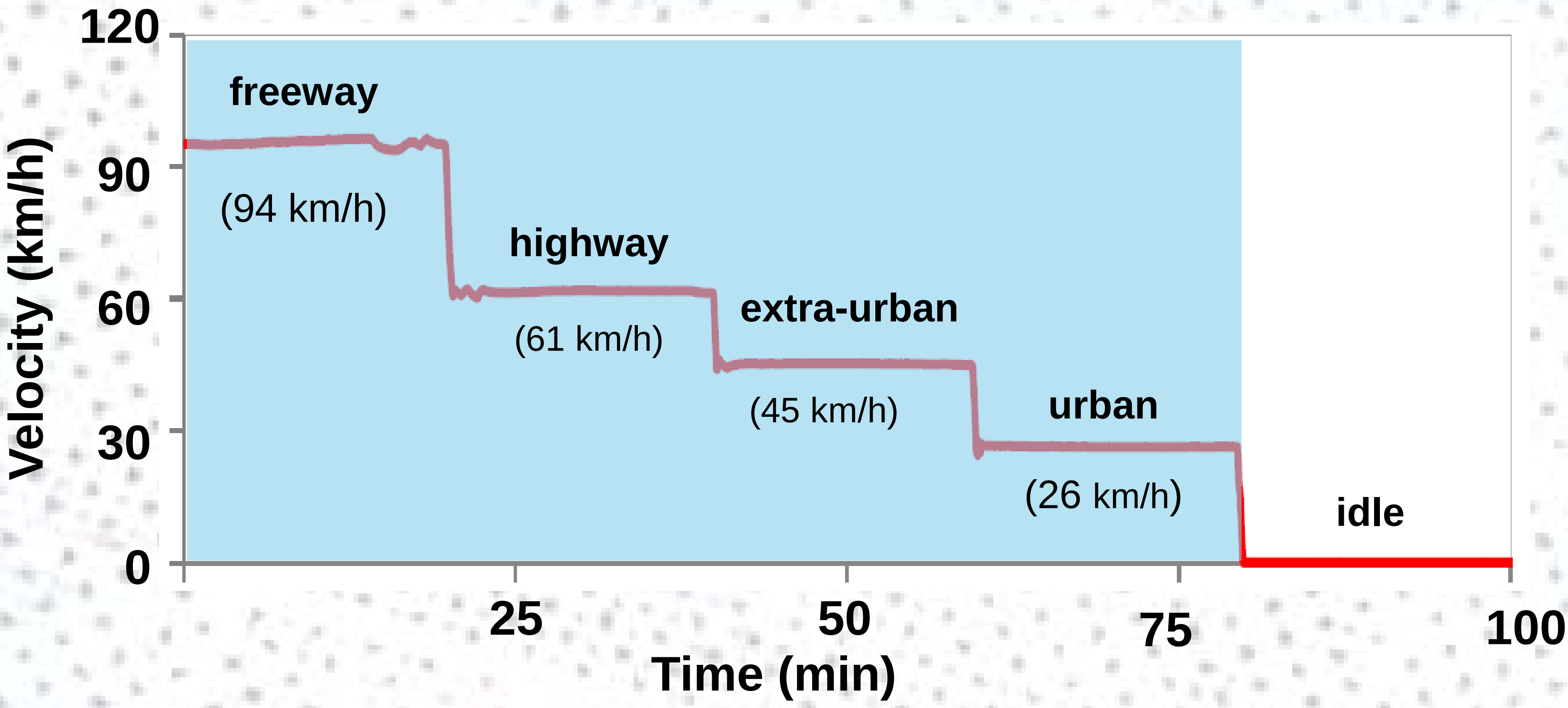
NOx-trap activity in a SSC



NOx-trap technology

An ideal cycle to study converter chemistry at its best

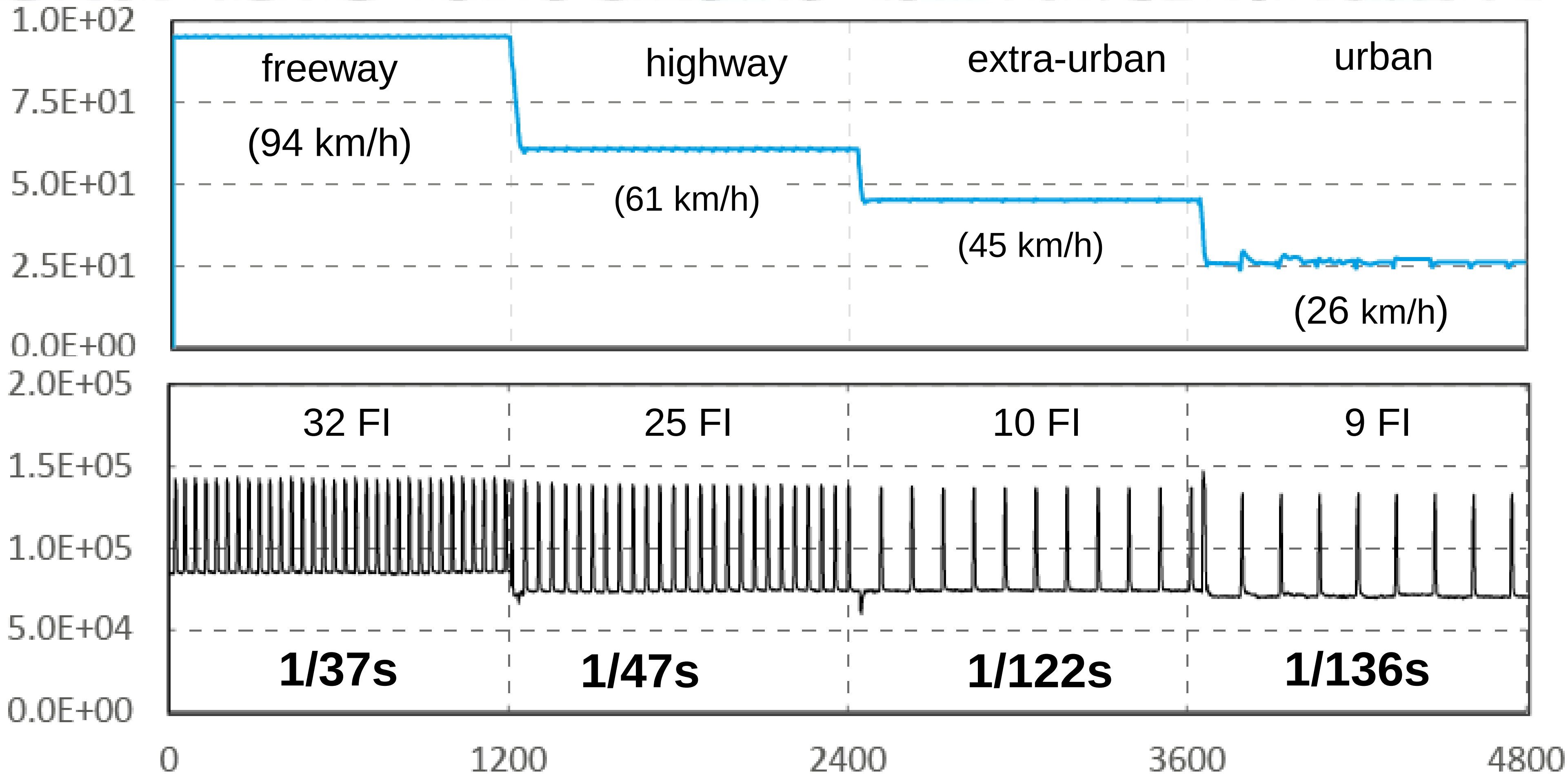
NOx-trap activity in a SSC



NOx-trap chemistry

Extra fuel injections (FI) about every minute!

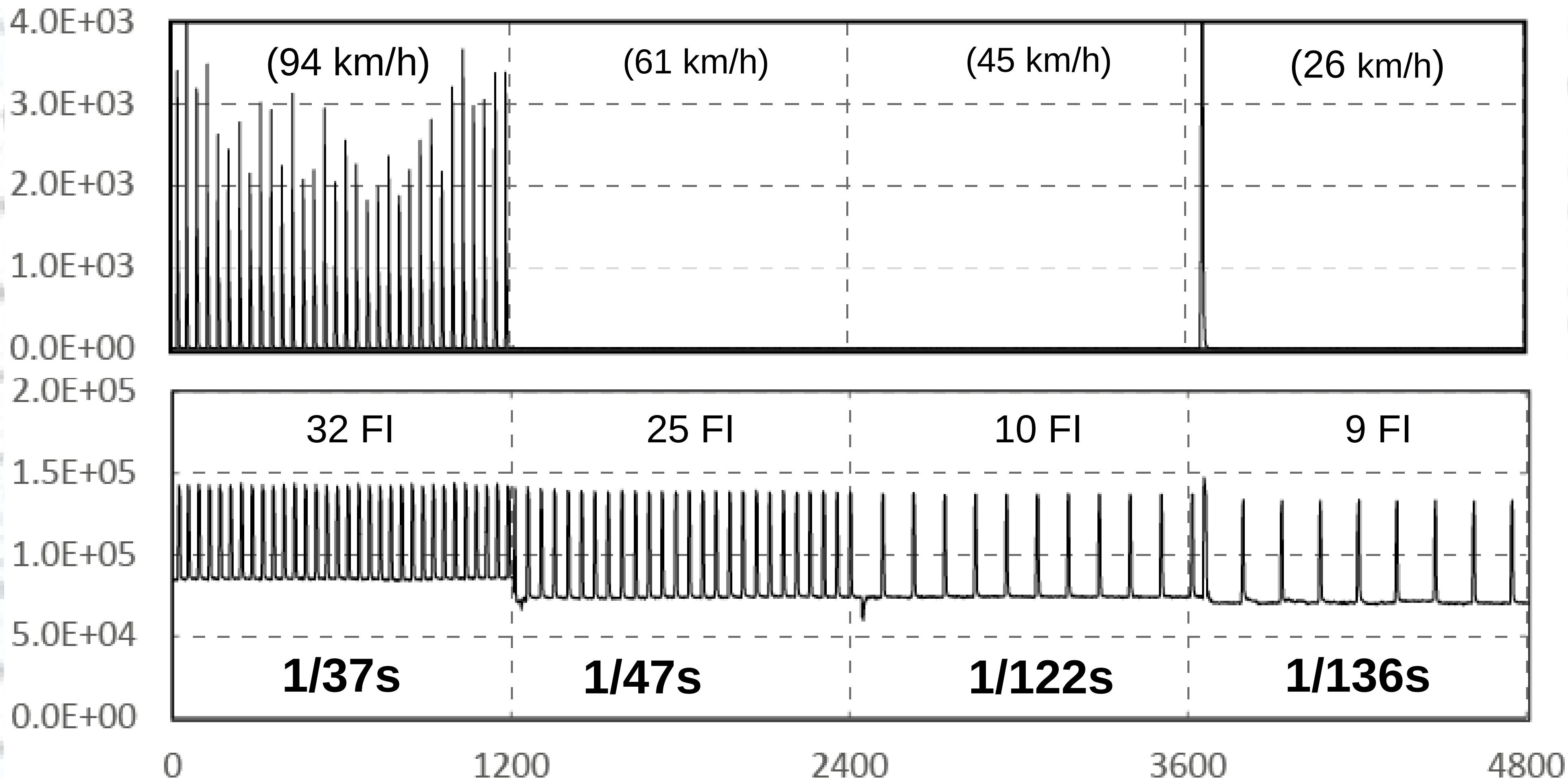
CO_2 emissions in the SSC



NOx-trap chemistry

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

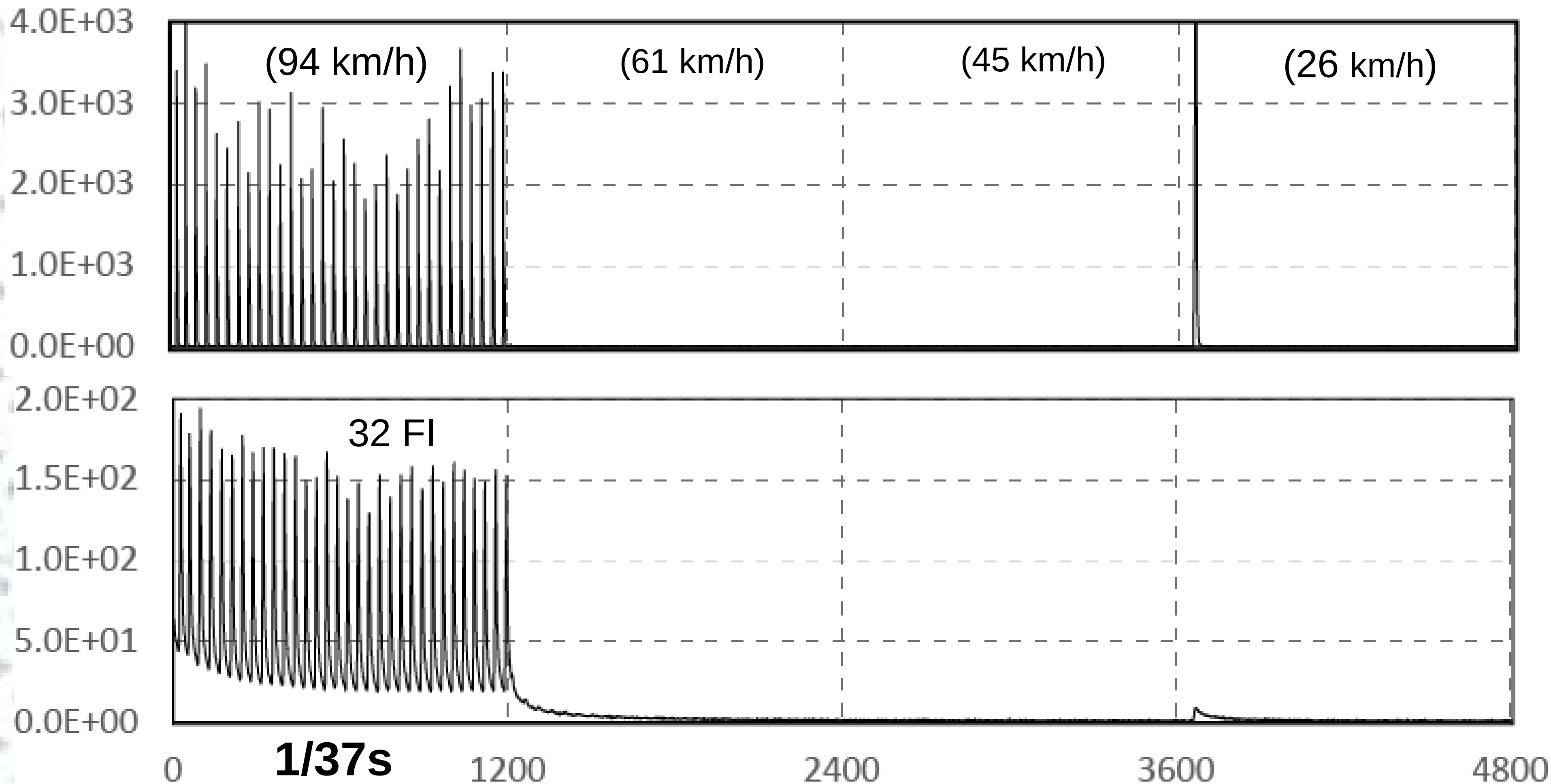
CO and CO_2 emissions



NOx-trap chemistry

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

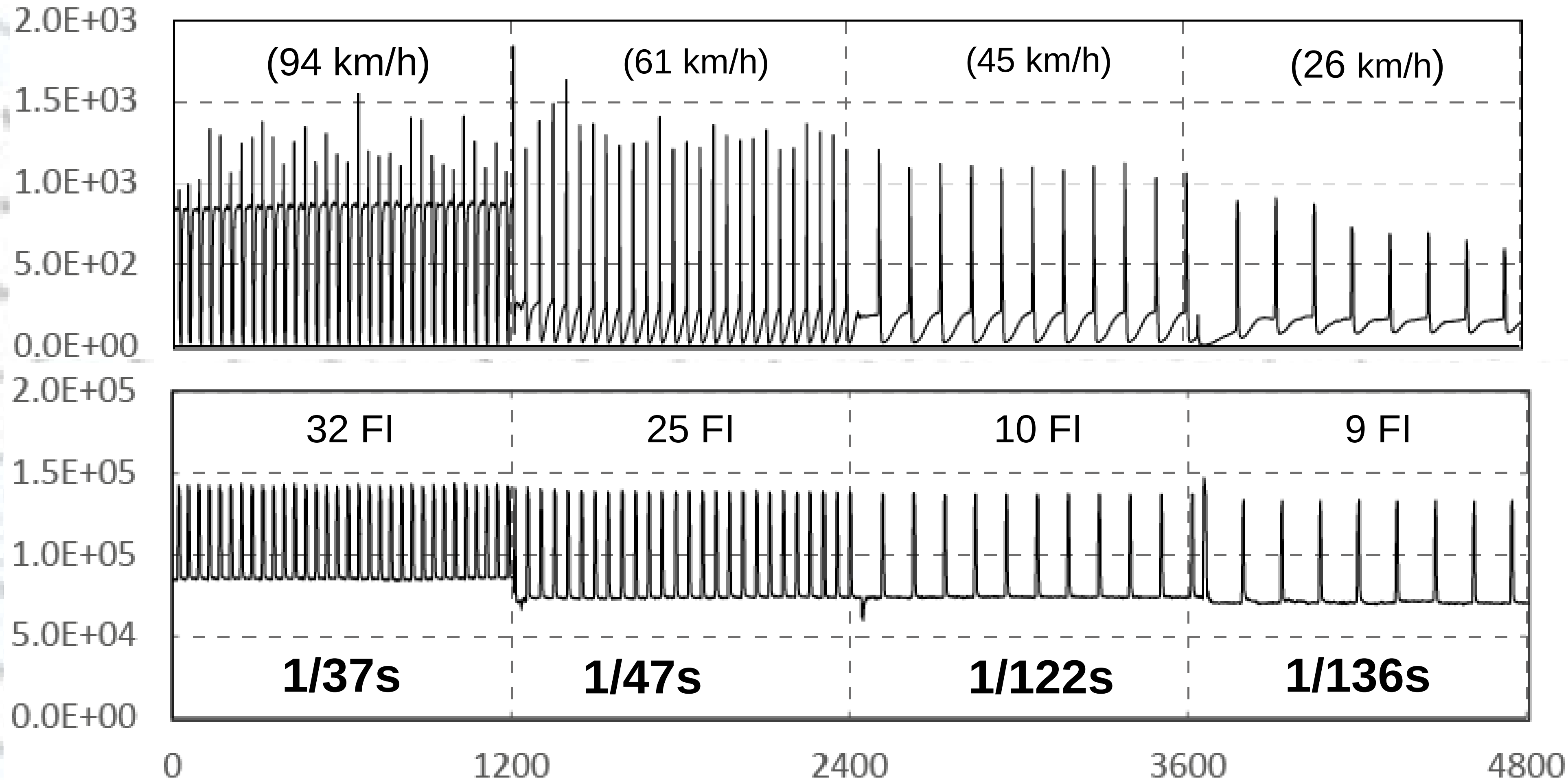
NH_3 and CO emissions



NOx-trap chemistry

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

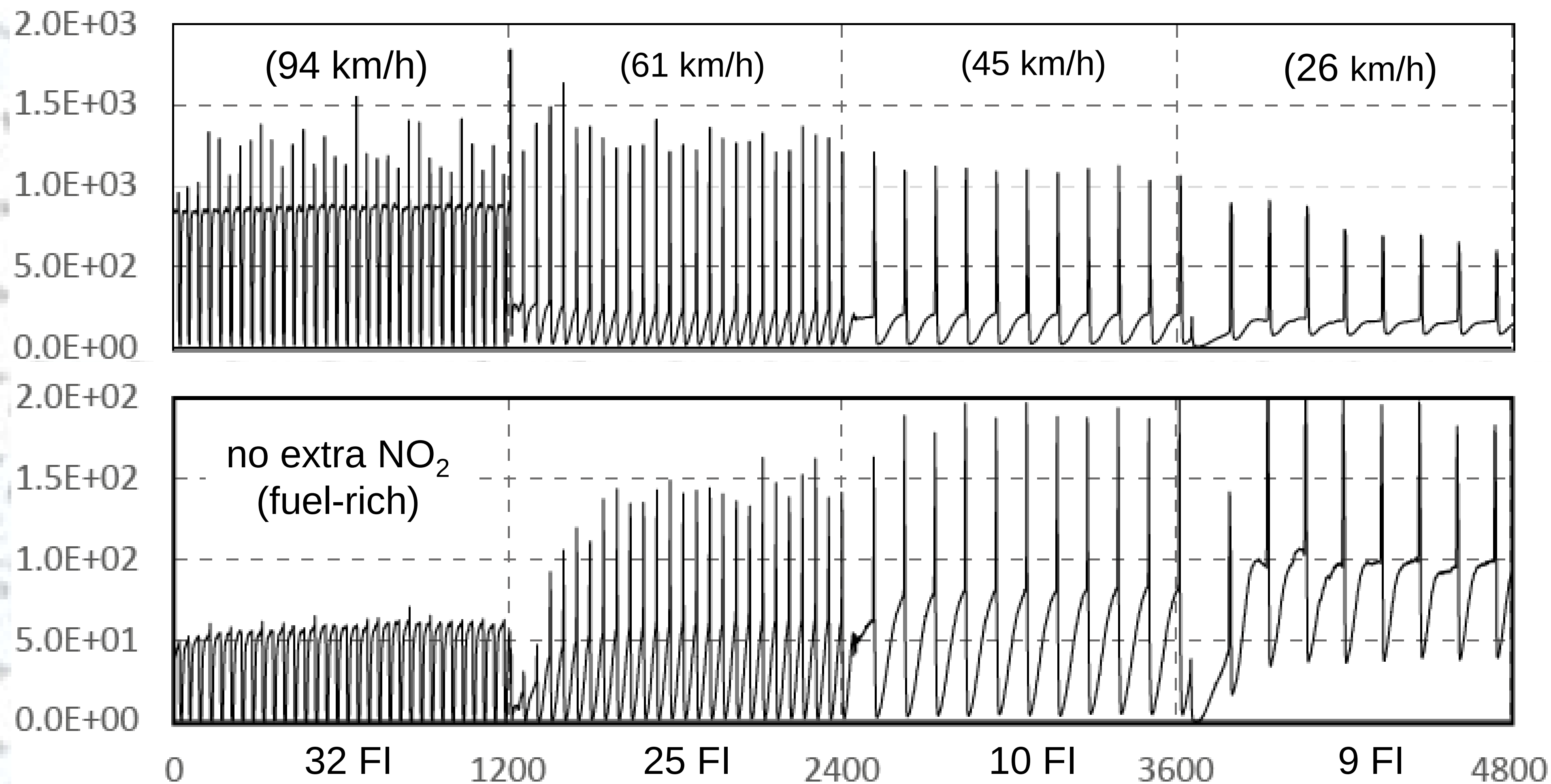
NO and CO_2 emissions



NOx-trap chemistry

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

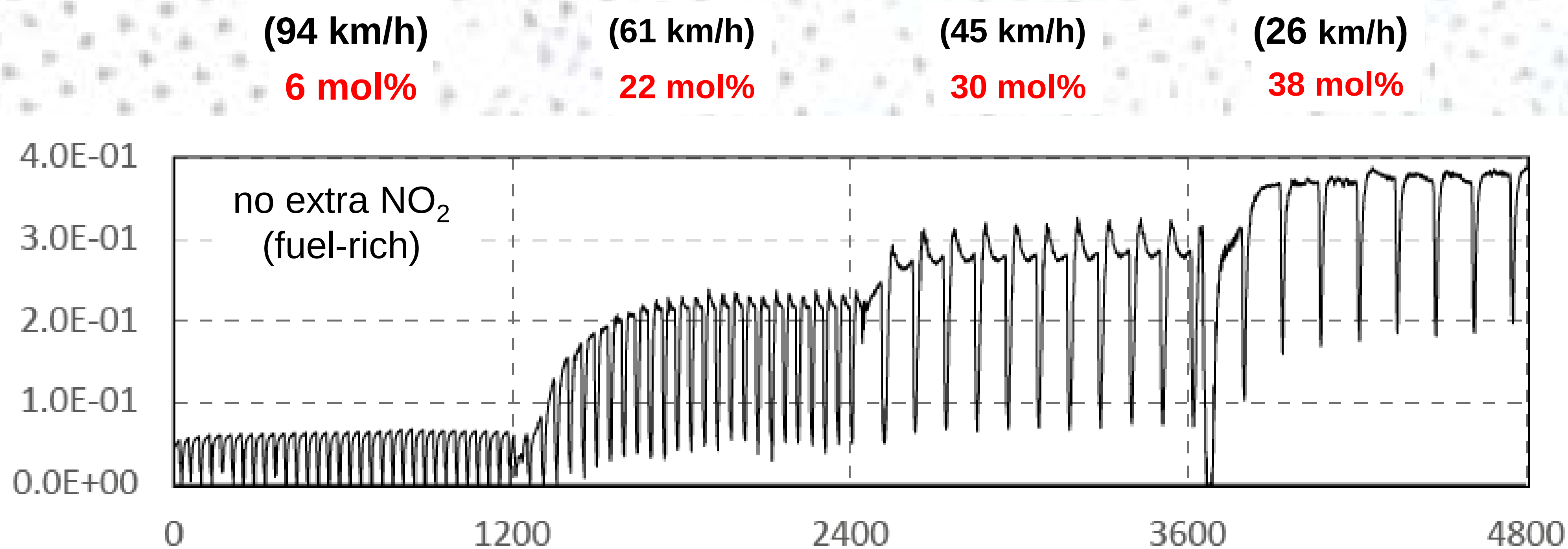
NO and NO_2 emissions



NOx-trap chemistry

NO_2 proportions lowest during extra fuel injections and high temperatures

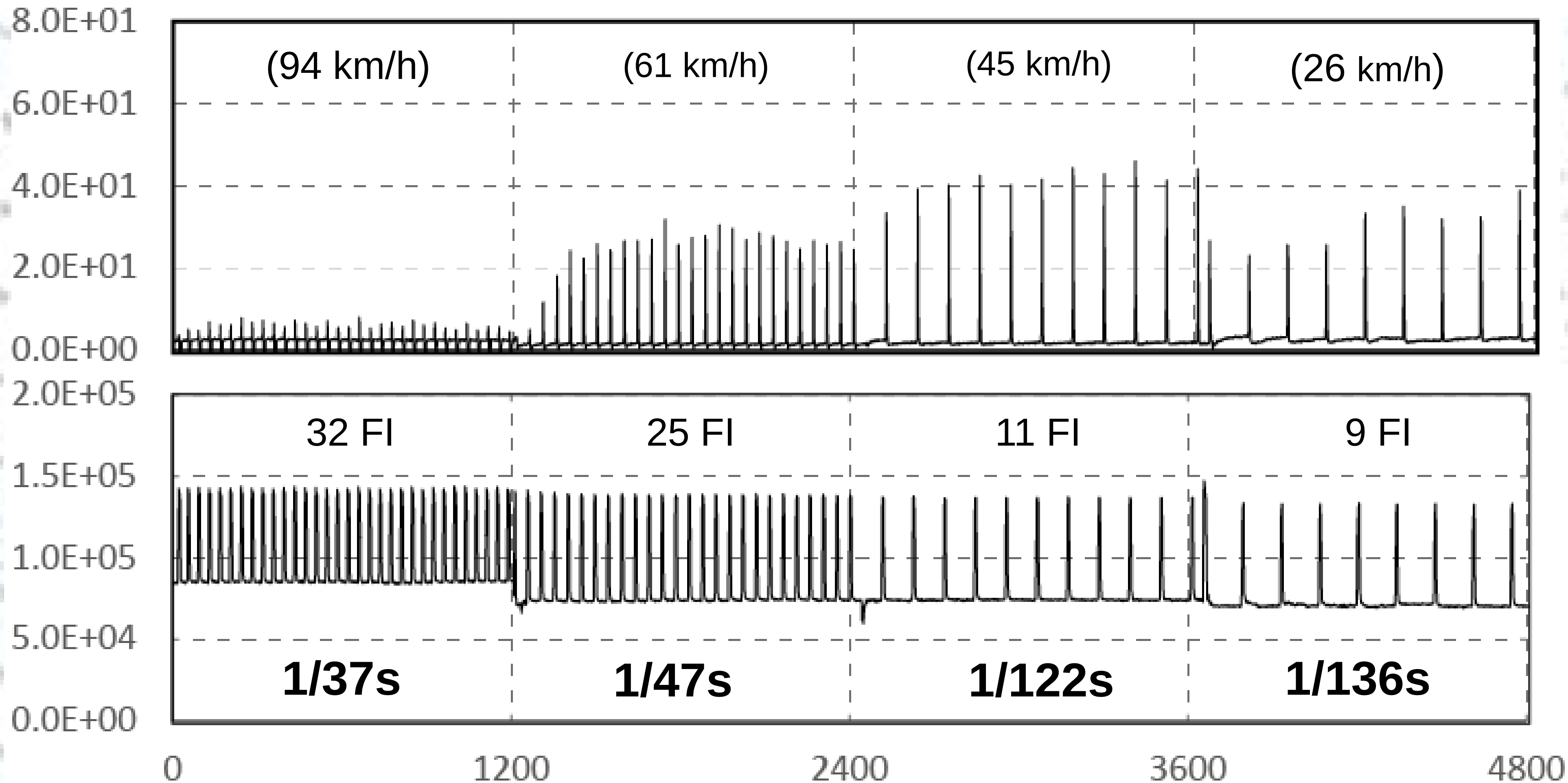
NO_2 proportion



NOx-trap chemistry

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

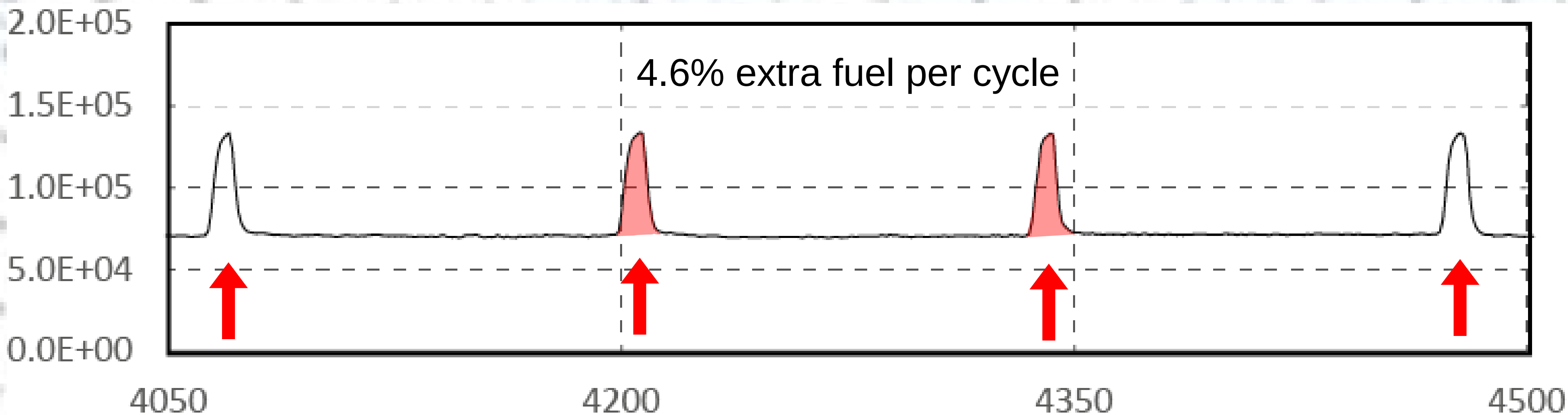
N_2O emissions



NOx-trap chemistry

How much fuel penalty per injection or per store & release cycle?

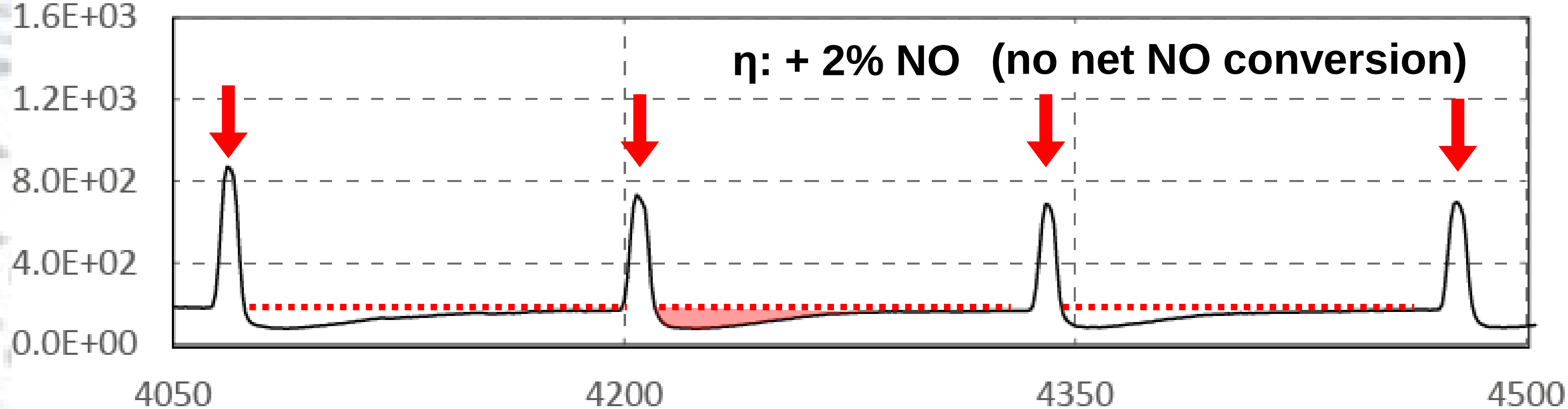
CO_2 at 26 km/h



NOx-trap chemistry

How much deNO activitiy per injection

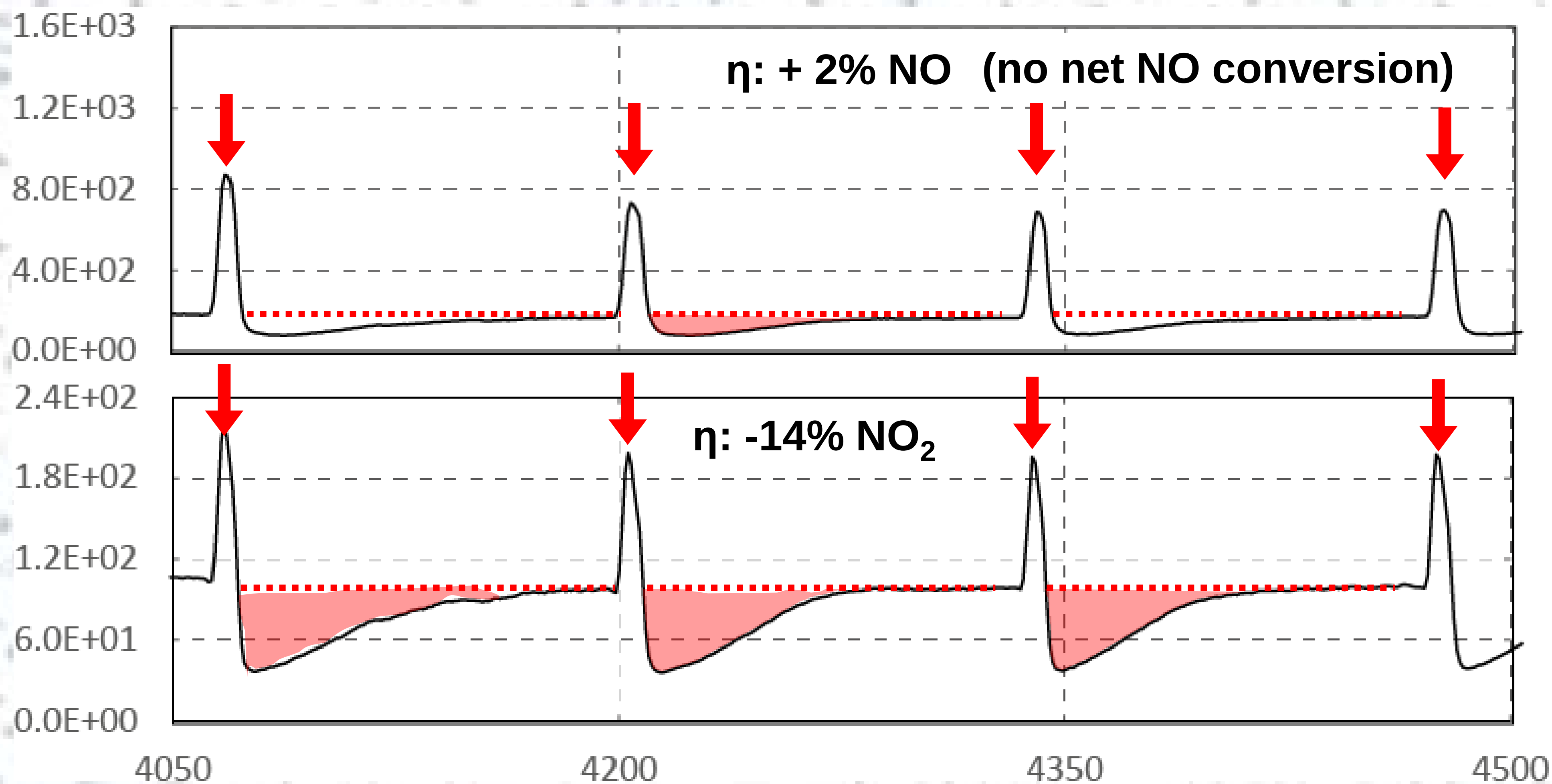
deNO activity at 26 km/h



NOx-trap chemistry

How much deNO activitiy per injection

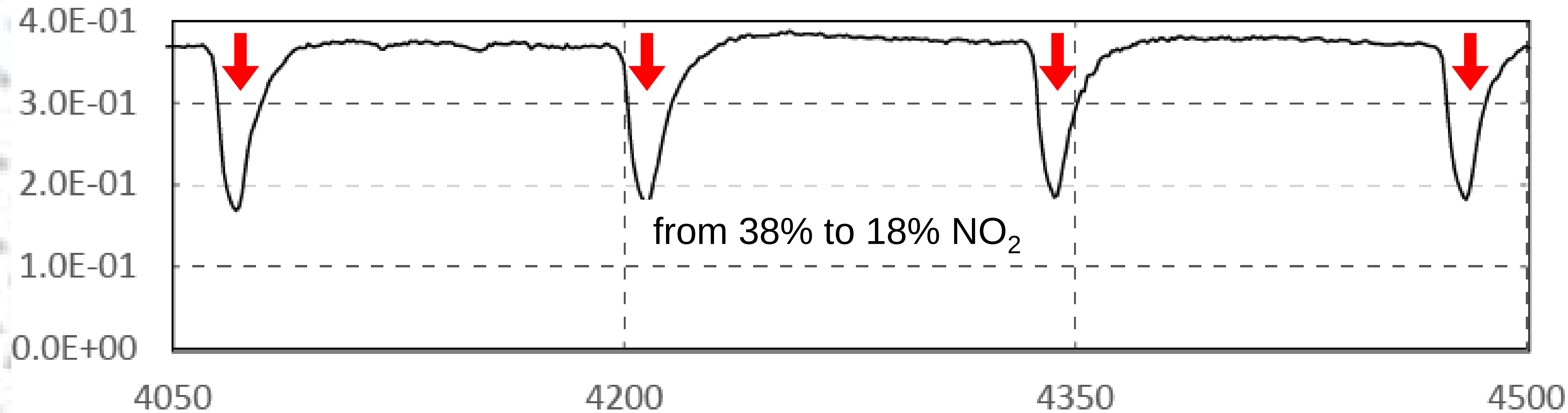
deNO and deNO$_2$ activity at 26 km/h



NOx-trap chemistry

NO_2 proportion drops during fuel injection

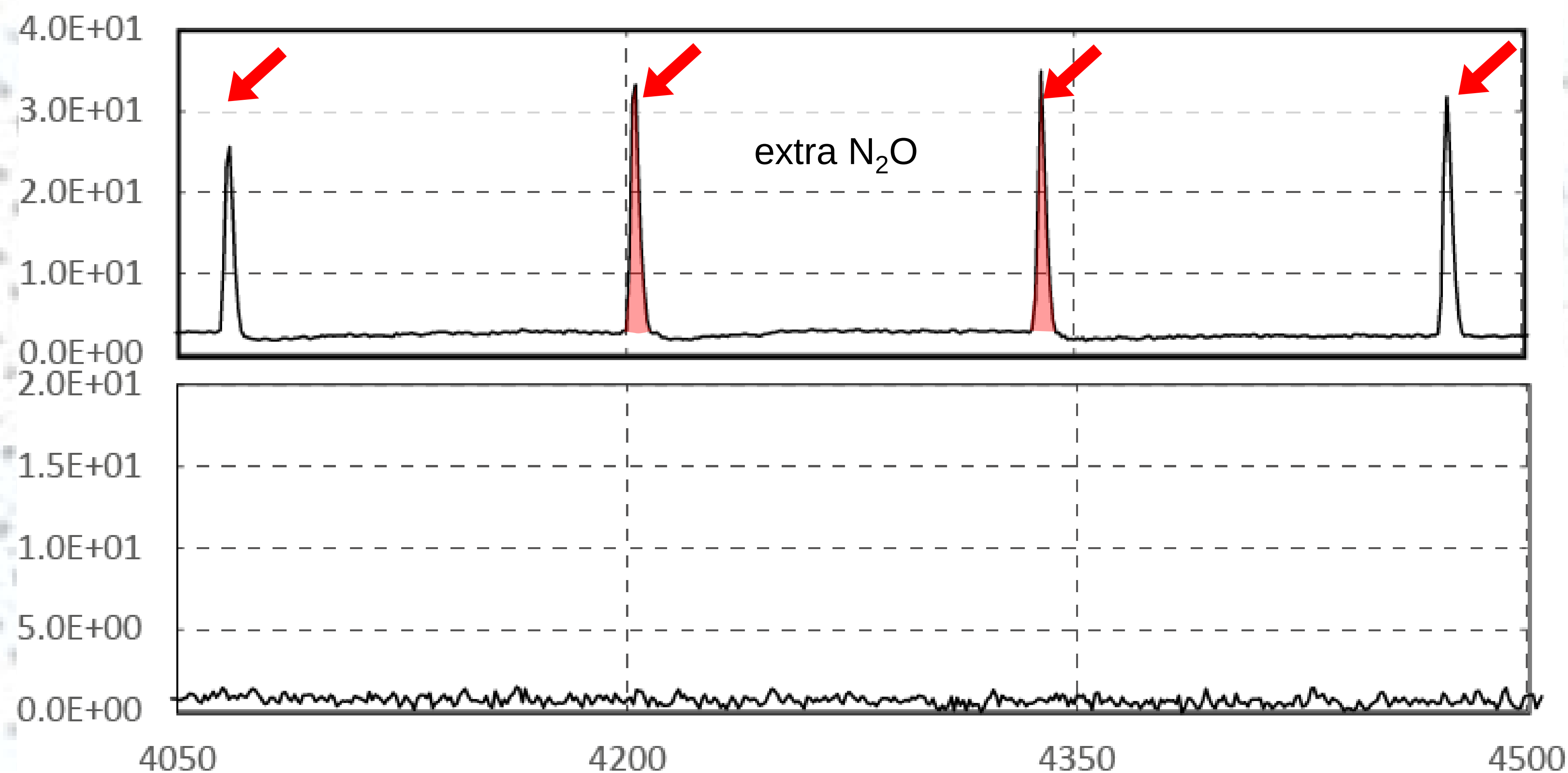
NO_2 proportion at 26 km/h



NOx-trap chemistry

No NH_3 formation, but secondary N_2O formation during fuel injection

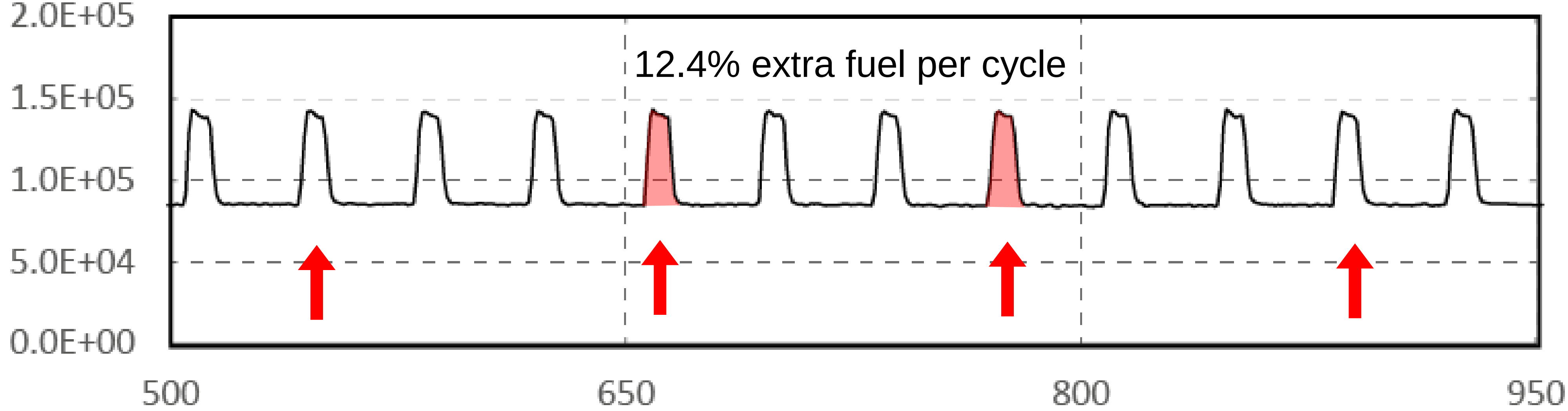
N_2O and NH_3 at 26 km/h



NOx-trap chemistry

How much fuel penalty per injection

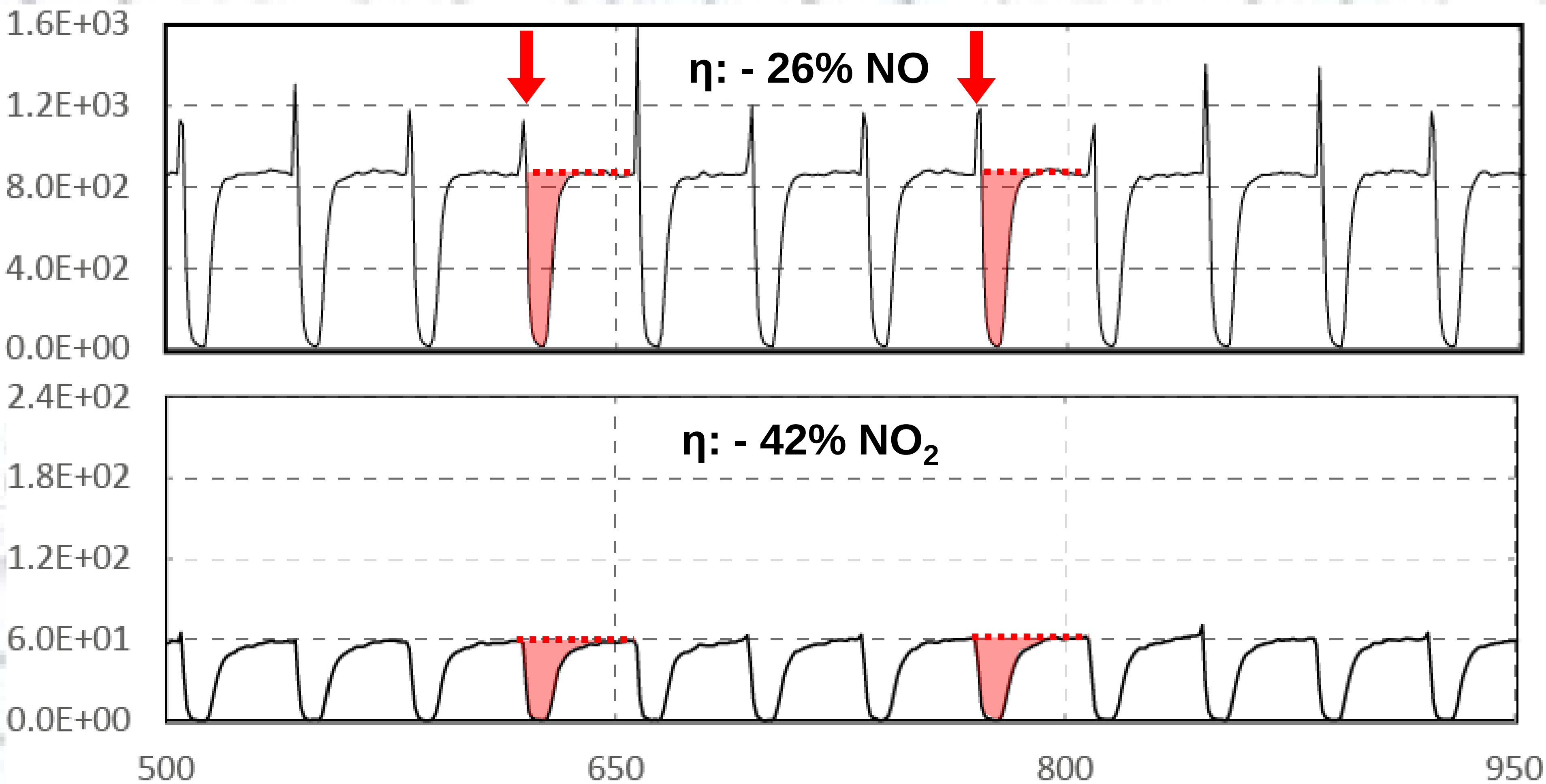
CO_2 at 94 km/h (fuel rich conditions)



NOx-trap chemistry

How much deNO 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

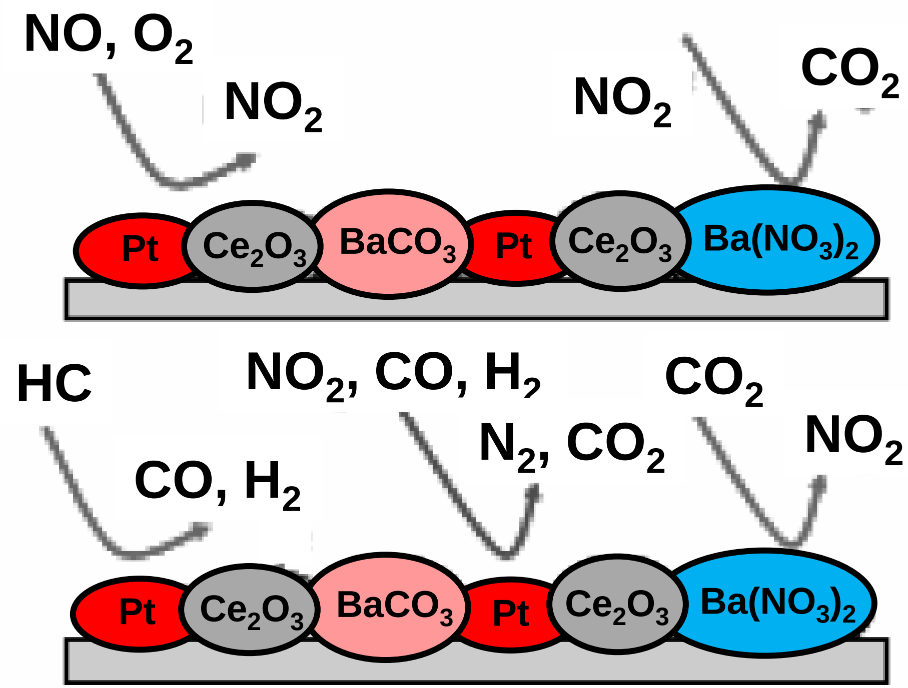
NOx-trap cycle

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

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

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

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

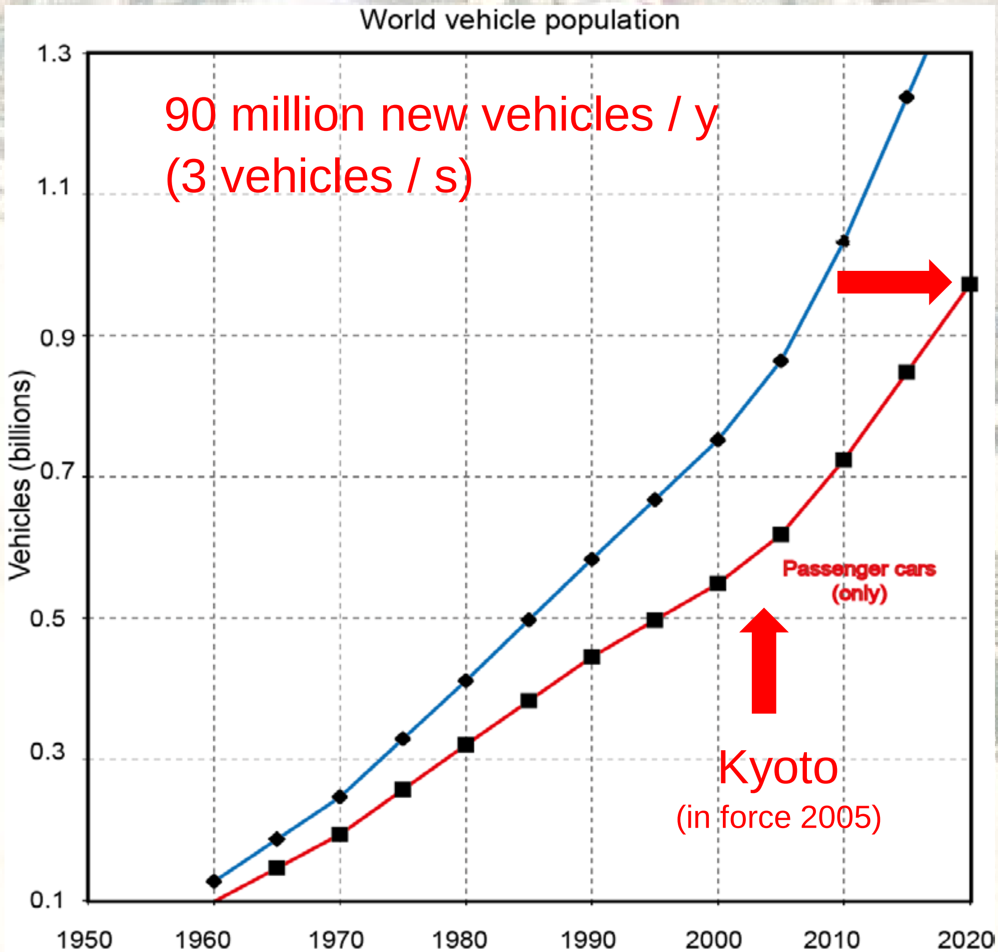


Similar chemistry in the NO_x trap with
Secondary formation of N_2O and NH_3

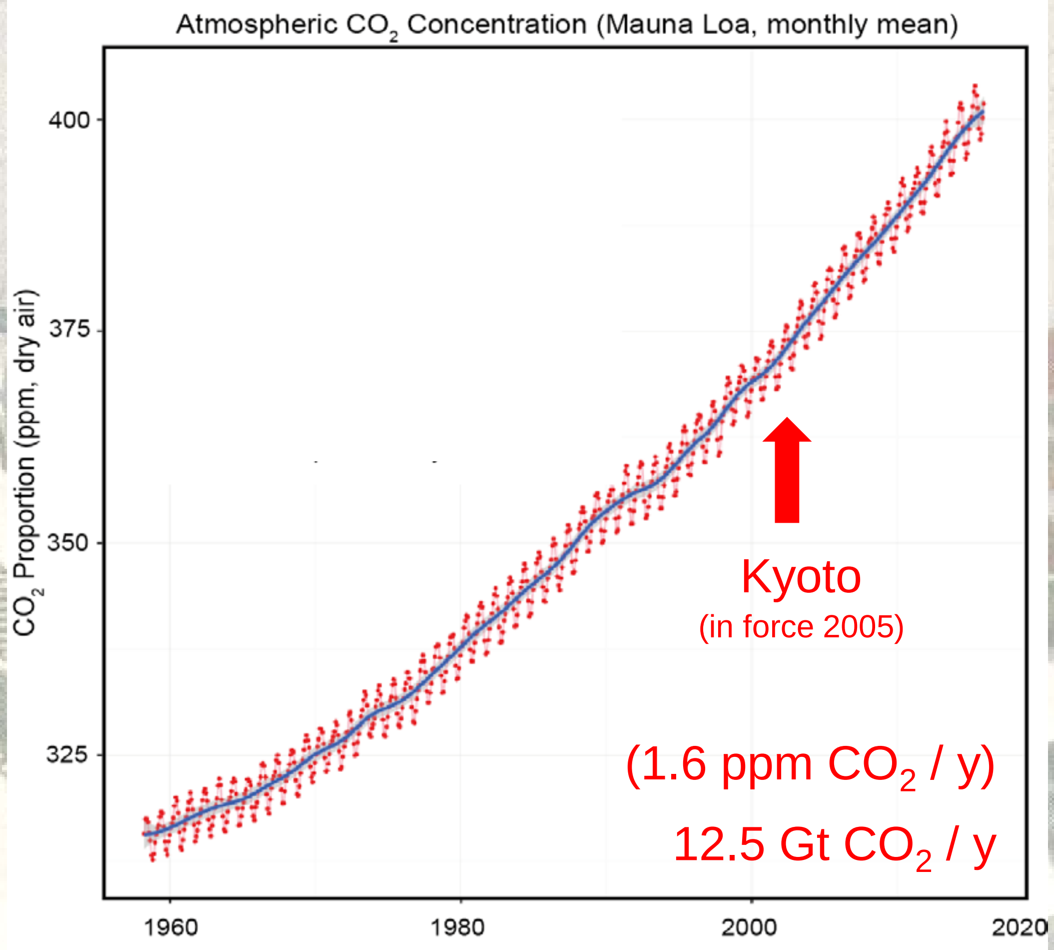
Road vehicles on earth

From 0.1 to 1 billion in 60 years

(3800 as I spoke, 37'000 this morning)

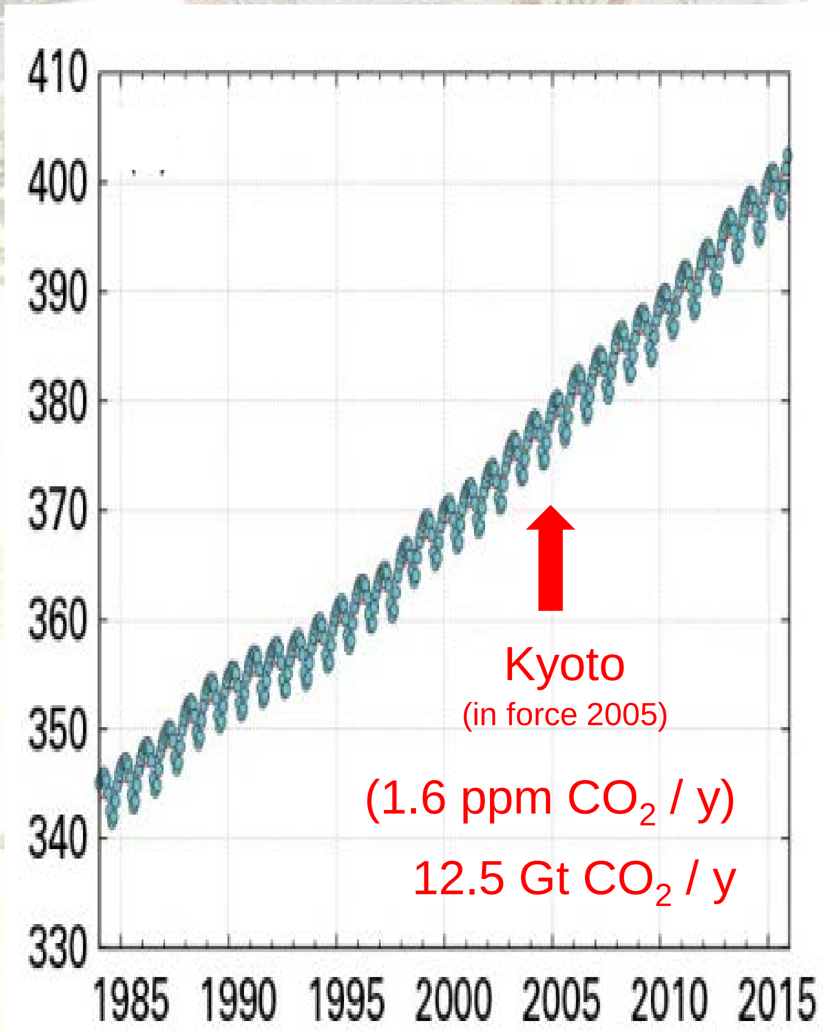


From 310 to 410 ppm in 60 years



CO_2 in earth atmosphere

From 345 to 400 ppm in 30 years



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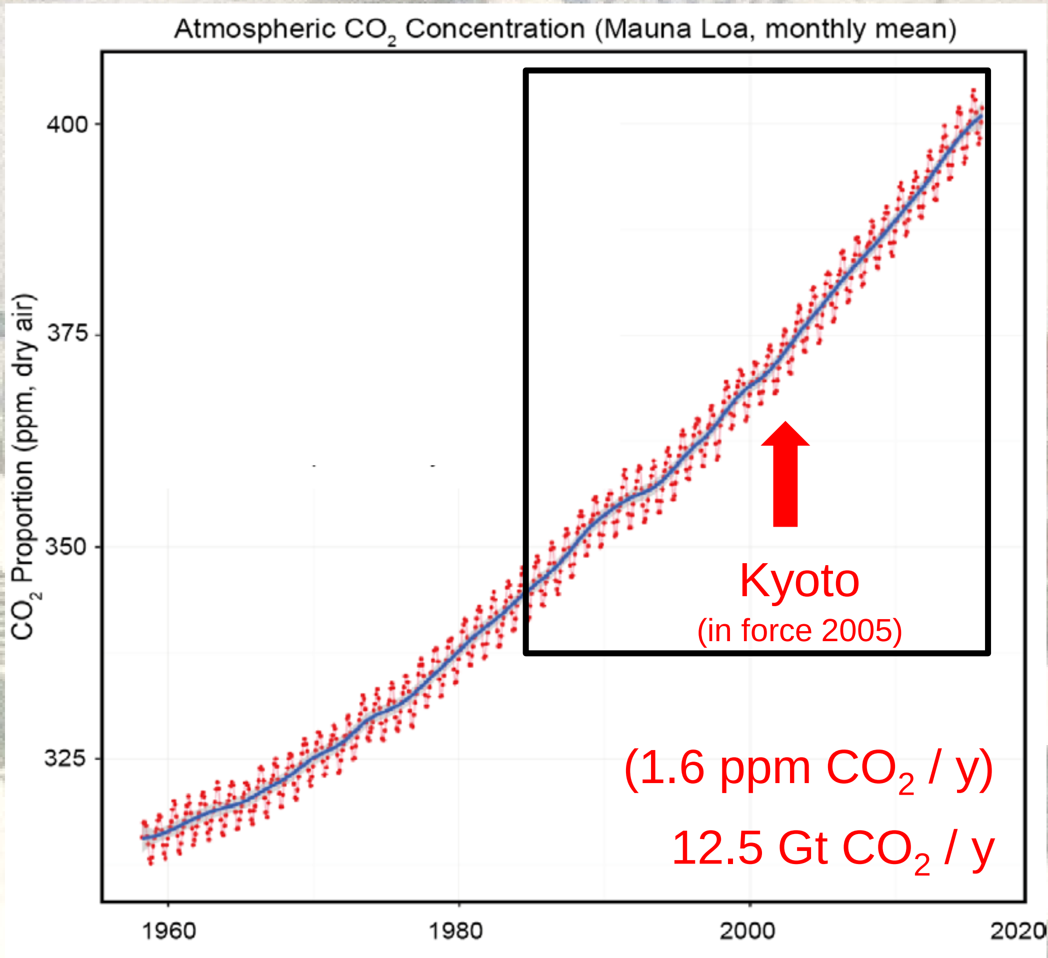
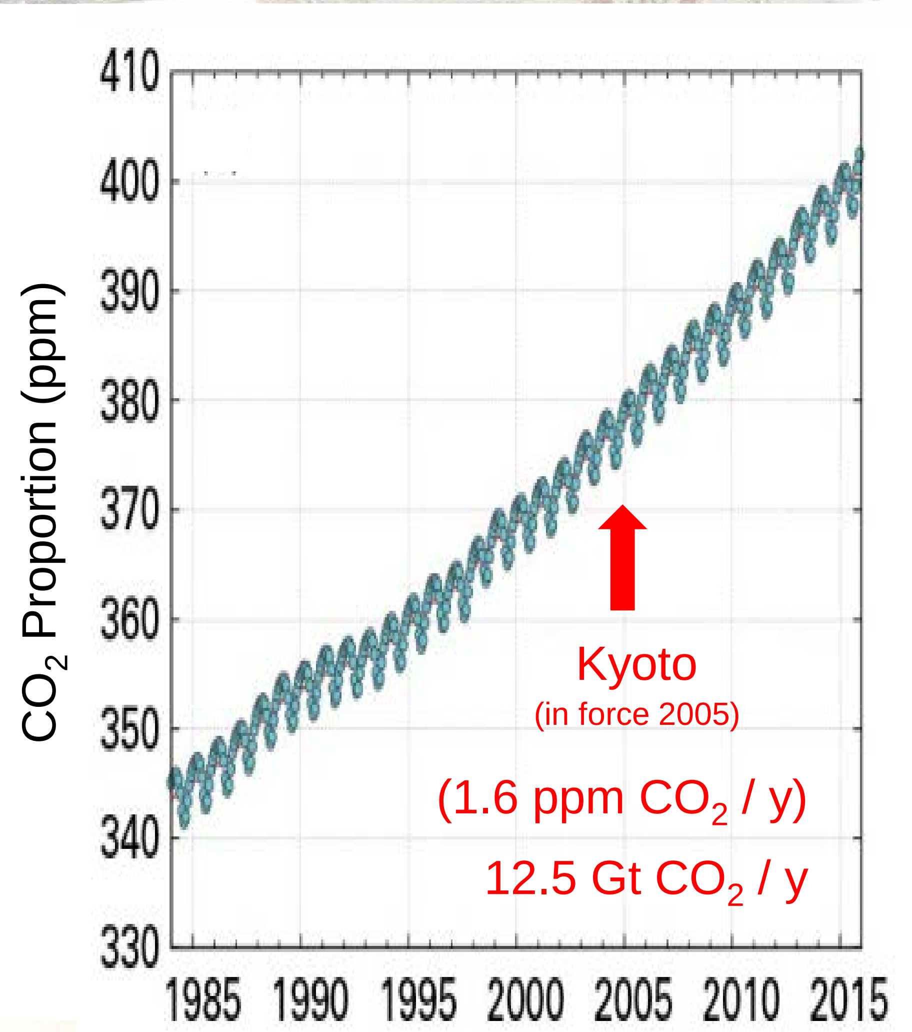
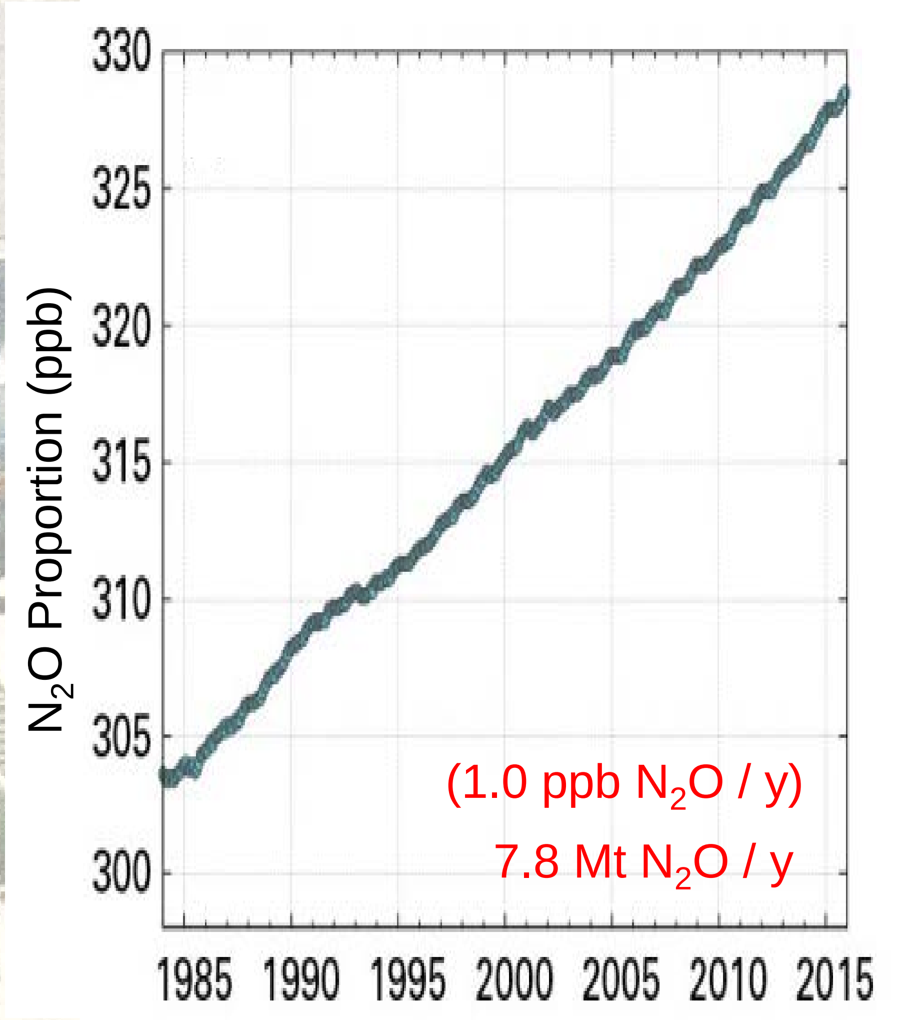


CO_2 and N_2O in earth atmosphere

From 345 to 400 ppm in 30 years



From 303 to 328 ppb in 30 years



Blue Technology: Not green enough yet

GASOMEP: Current status and new concepts of gasoline vehicle emission control

- **Thanks to**
  - **Davide Bleiner, Lukas Emmenegger, Regula Haag, Peter Honegger, Joachim Mohn, Maria Munoz, Juanfernando Angel Ramelli, Cornelia Seiler, Peter Schmid, Heinz Vonmont, Adrian Wichser, Kerstin Zeyer, Empa**
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  - **Andreas Mayer, TTM**

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