Materials Science and Technology

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New legislation to guide the world: Where are we now and in which direction should we go?

Mobility is a necessity since *Homo Sapiens Sapiens* left the trees, move in the savanna and lives in cities

New legislation to guide the world: Where are we now and in which direction should we go?

Mobility is a necessity since *Homo Sapiens Sapiens* left the trees, move in the savanna and lives in cities

Agenda

The world motorization degree on the rise

Global trends, the trends in Switzerland

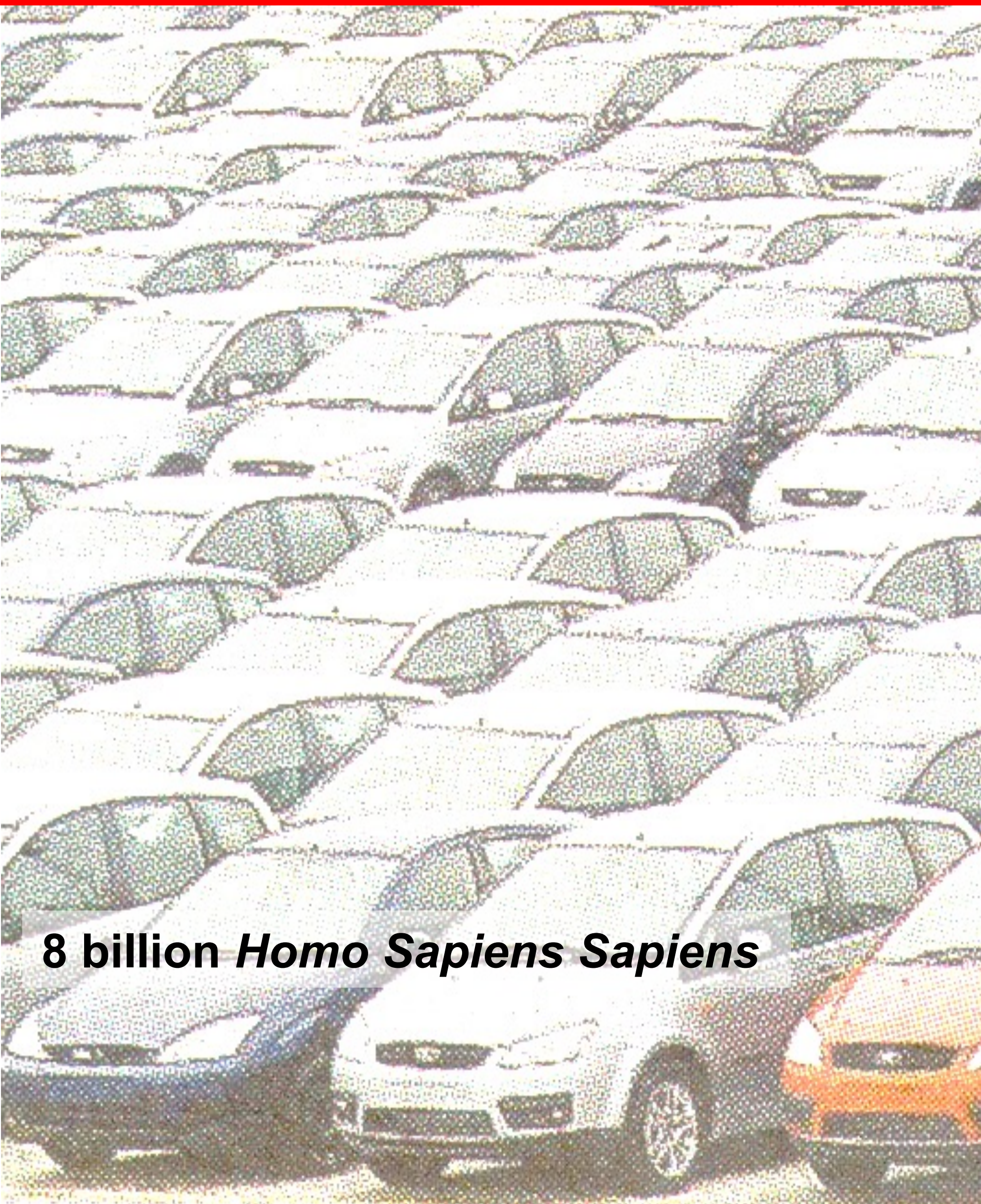
Success and failure of past legislation

Success with TWCs and DPFs, failures with deNOx

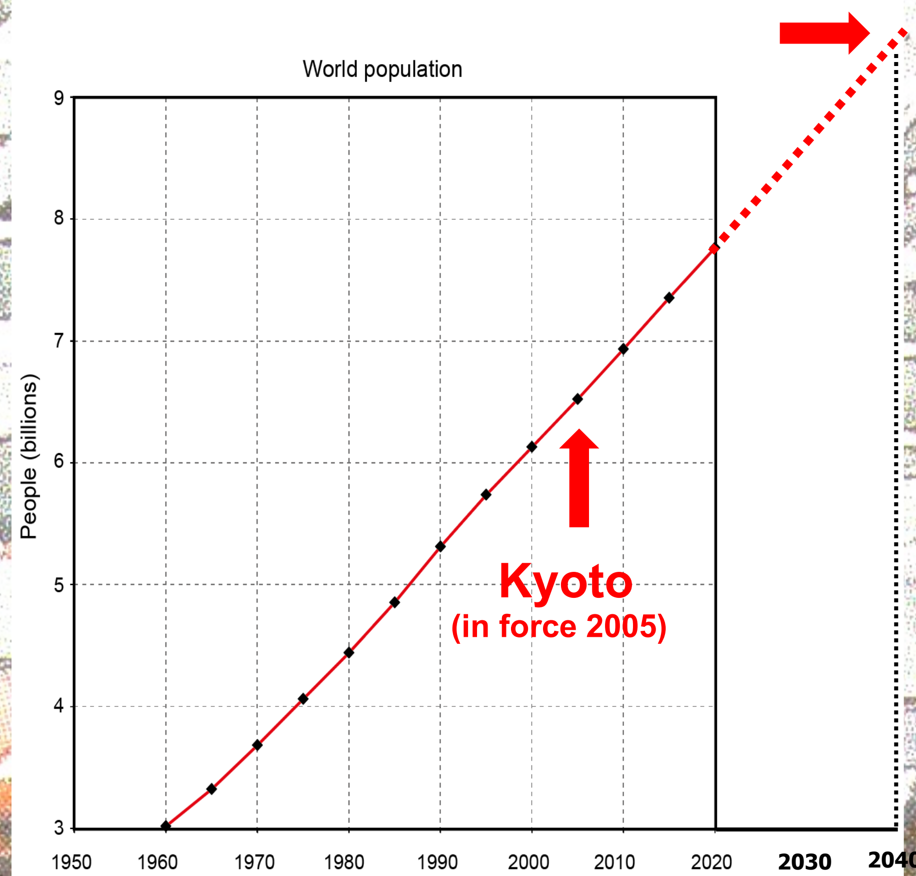
New legislation and new approaches

Toxicity-based, cell-models, multi-media models

Trends on planet earth



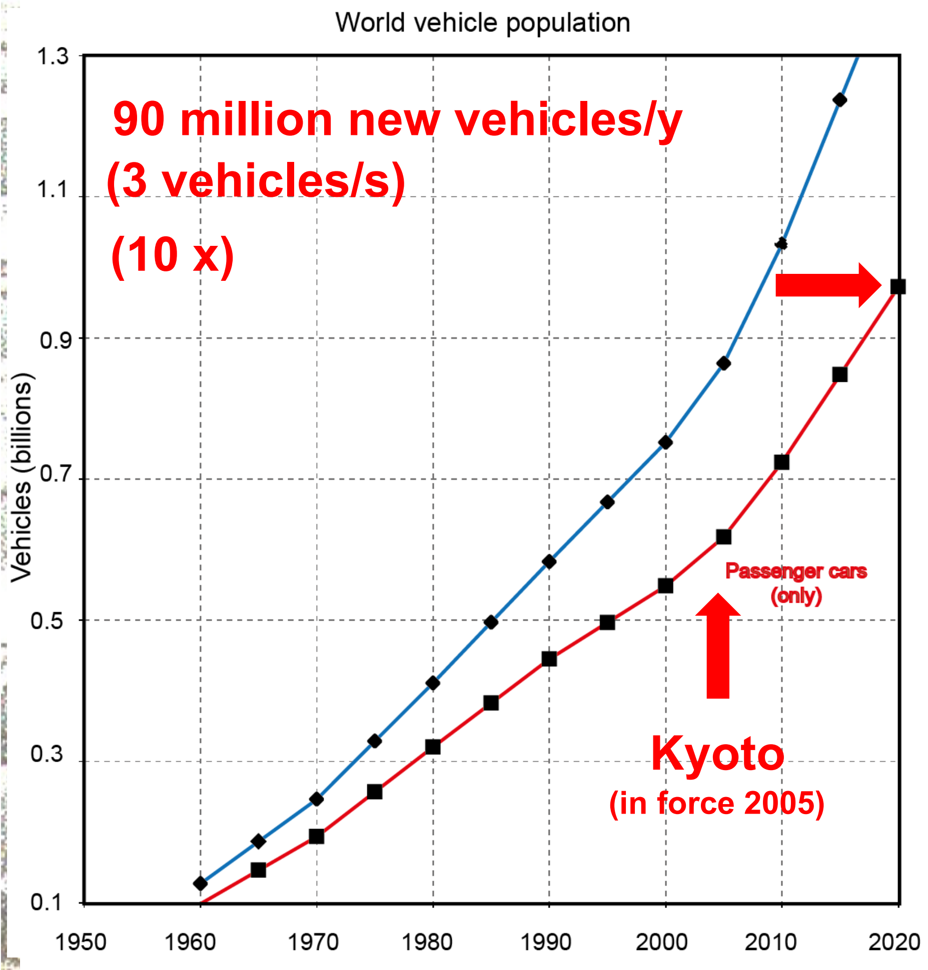
From 3 to 10 billion in 80 years?



Road vehicles on earth

From 0.1 to 1 billion in 60 years

(180 / min, 10'800 / h, 43'200 this afternoon)



Road vehicles on earth

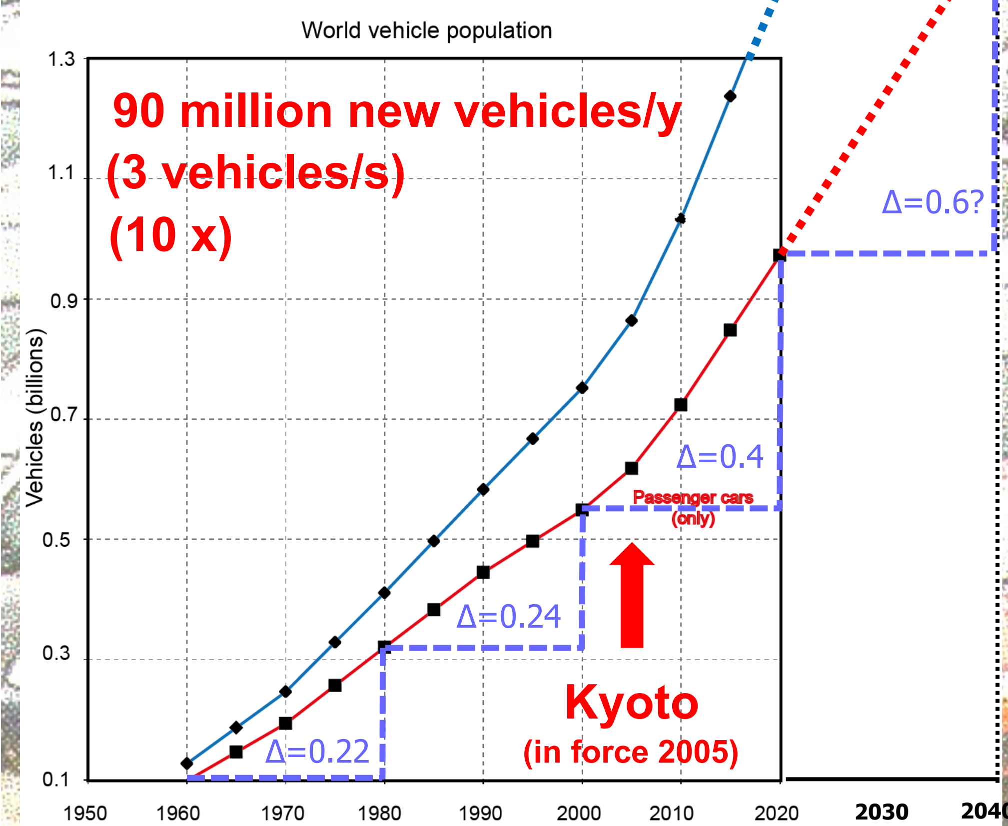
From 0.1 to 2 billion in 80 years?

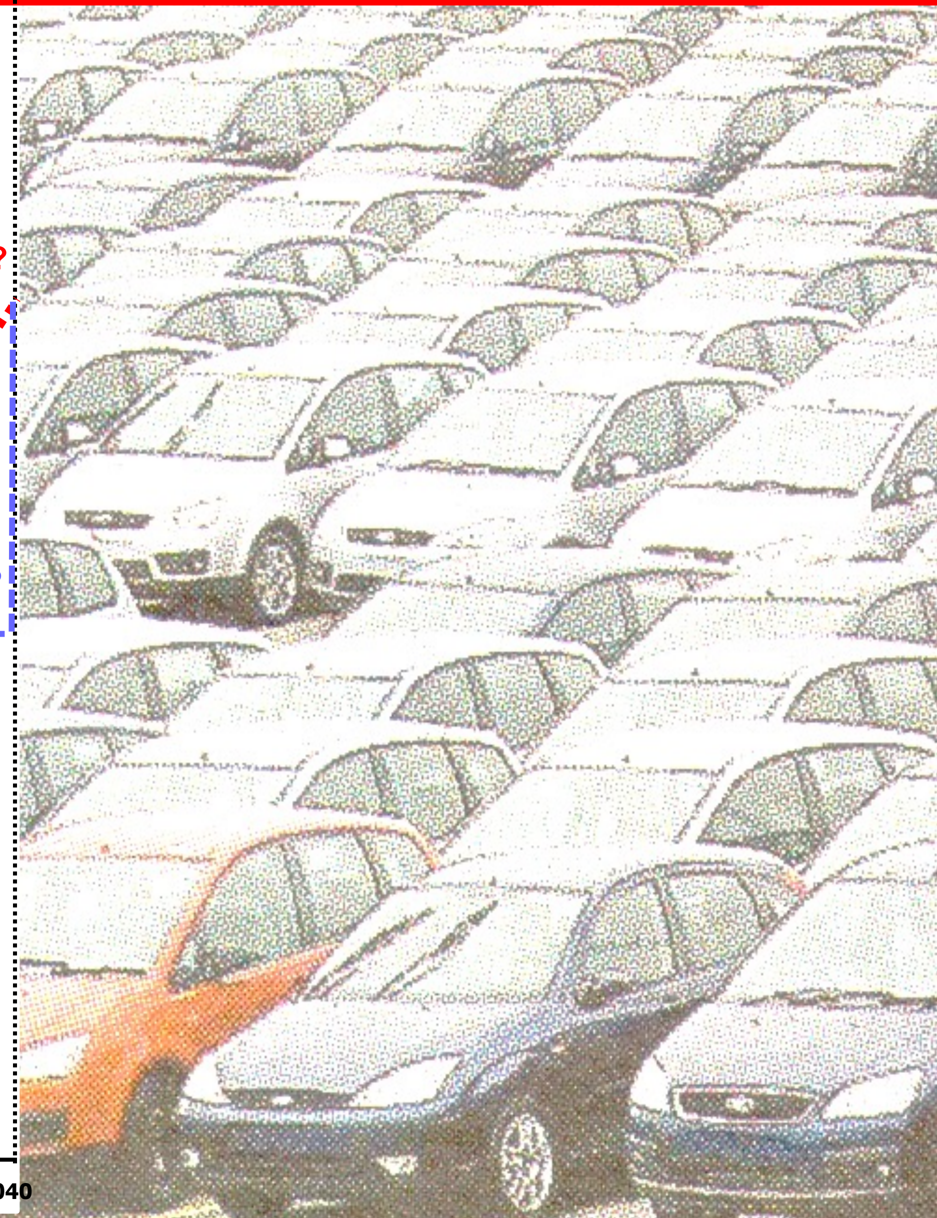
(180 / min, 10’800 / h, 43’200 this afternoon)

2.6 billion vehicles?

1.6 billion PC?

Another 600 millions in the next 20 years?





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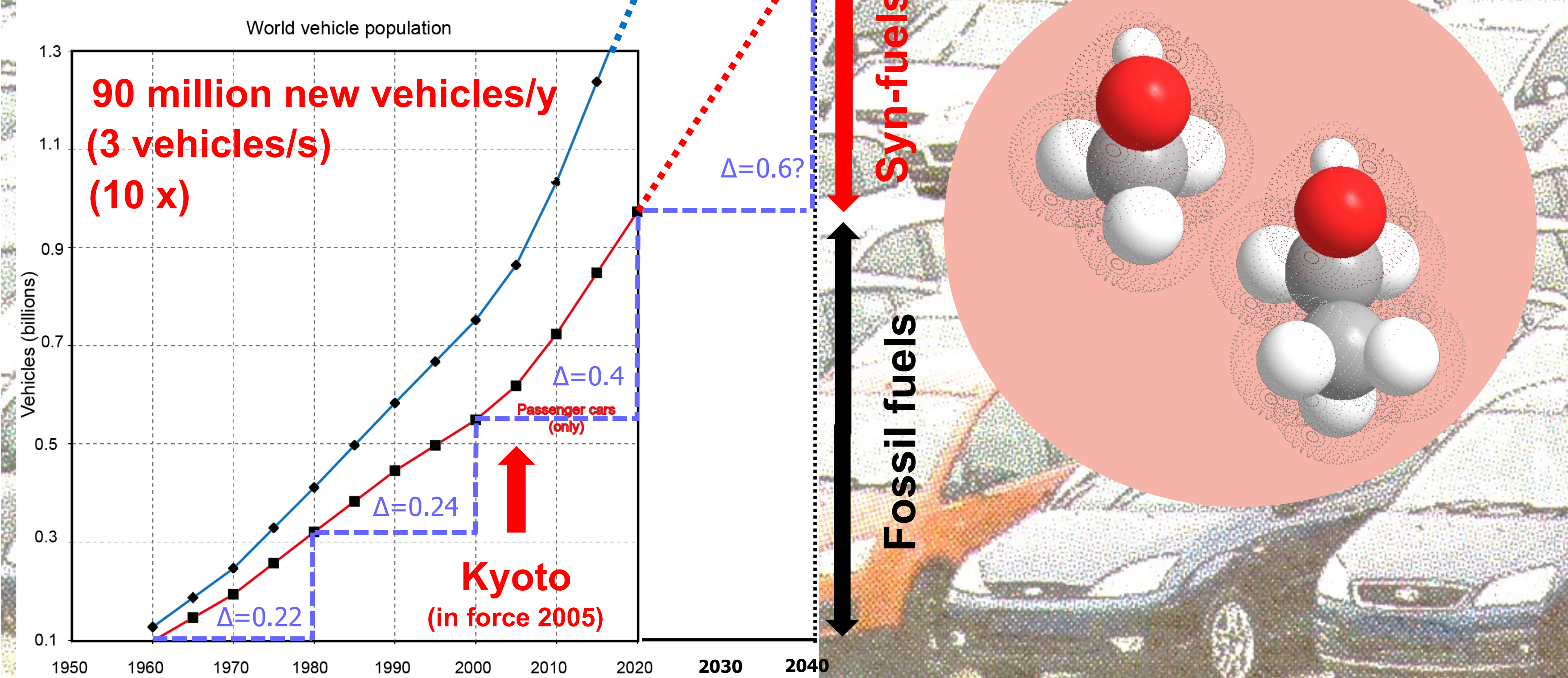

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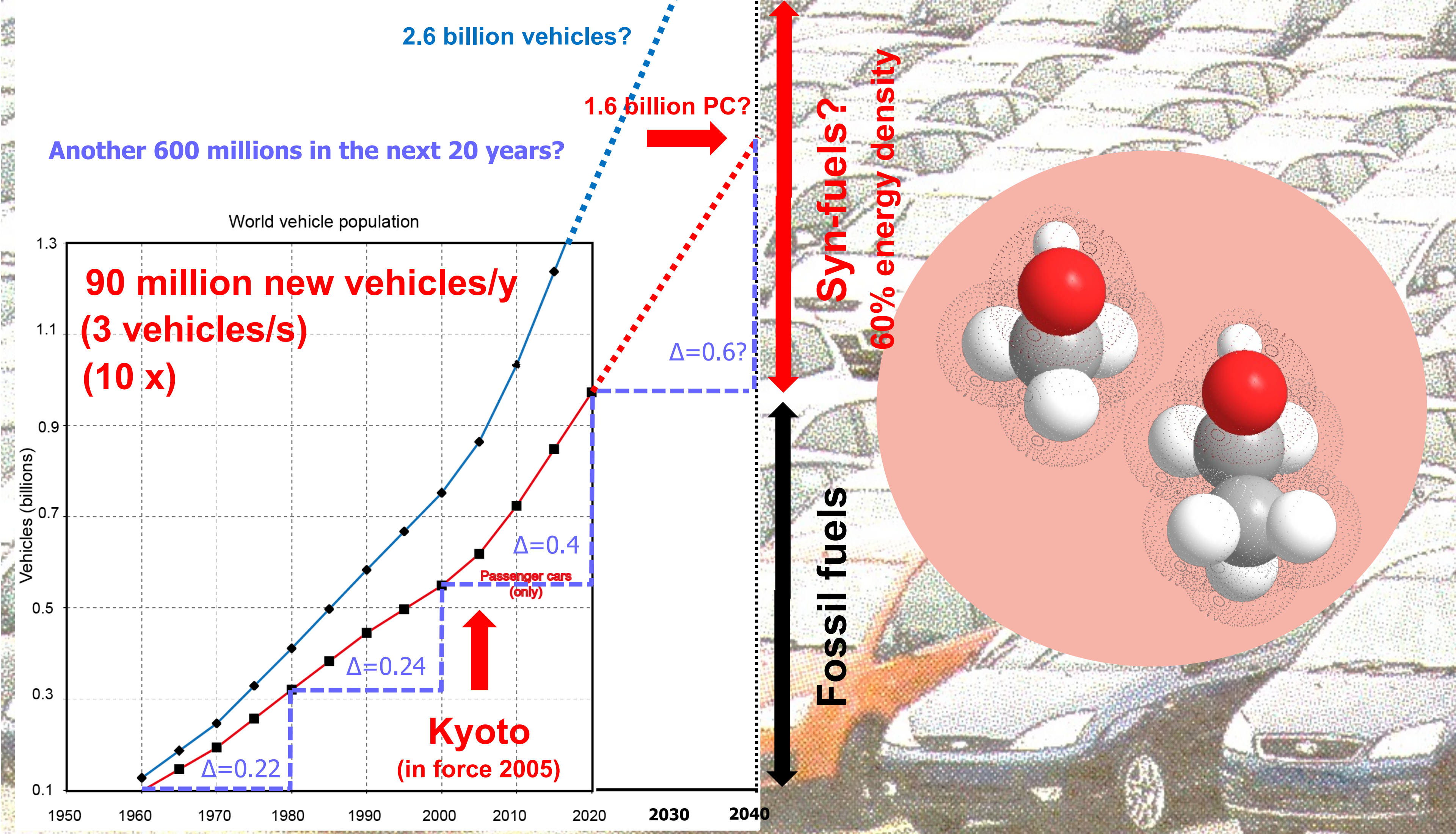

Road vehicles on earth

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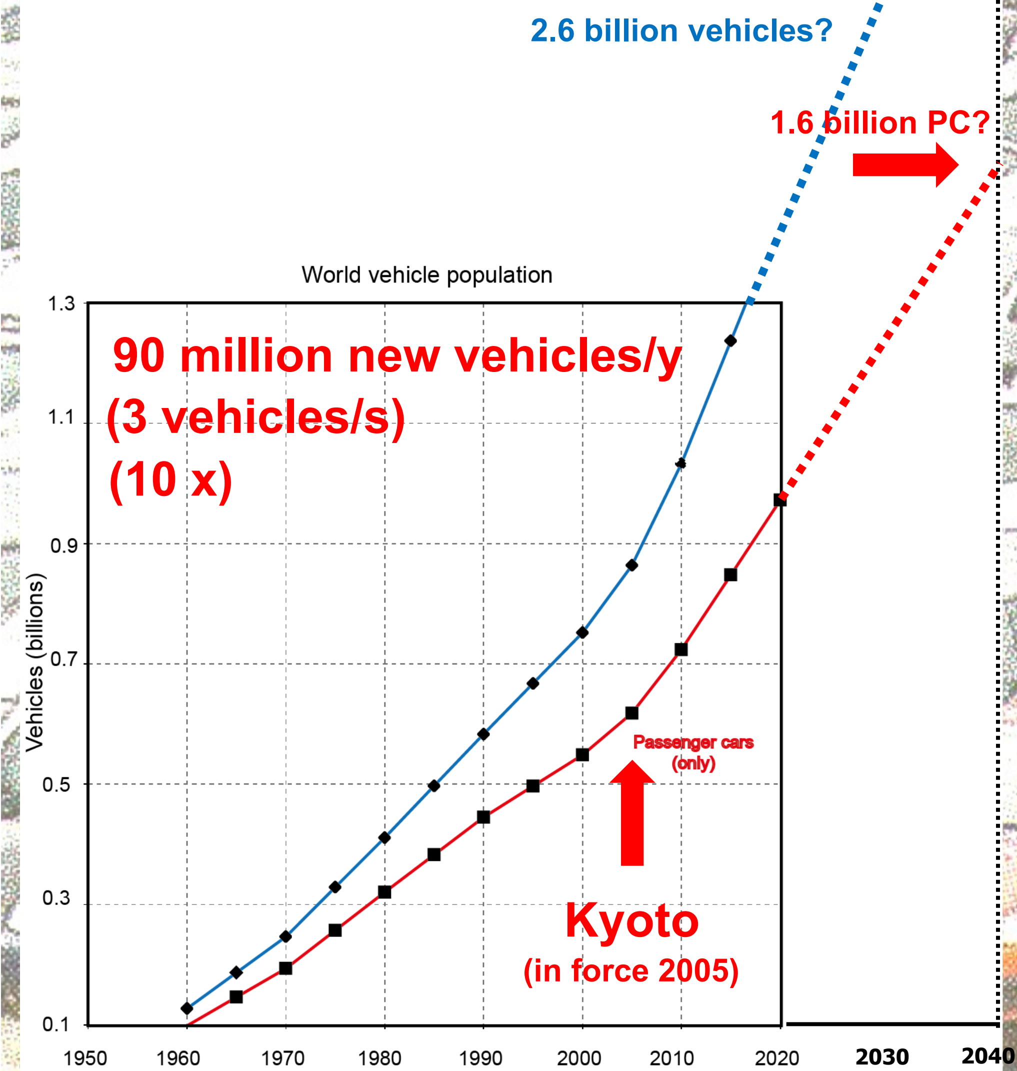
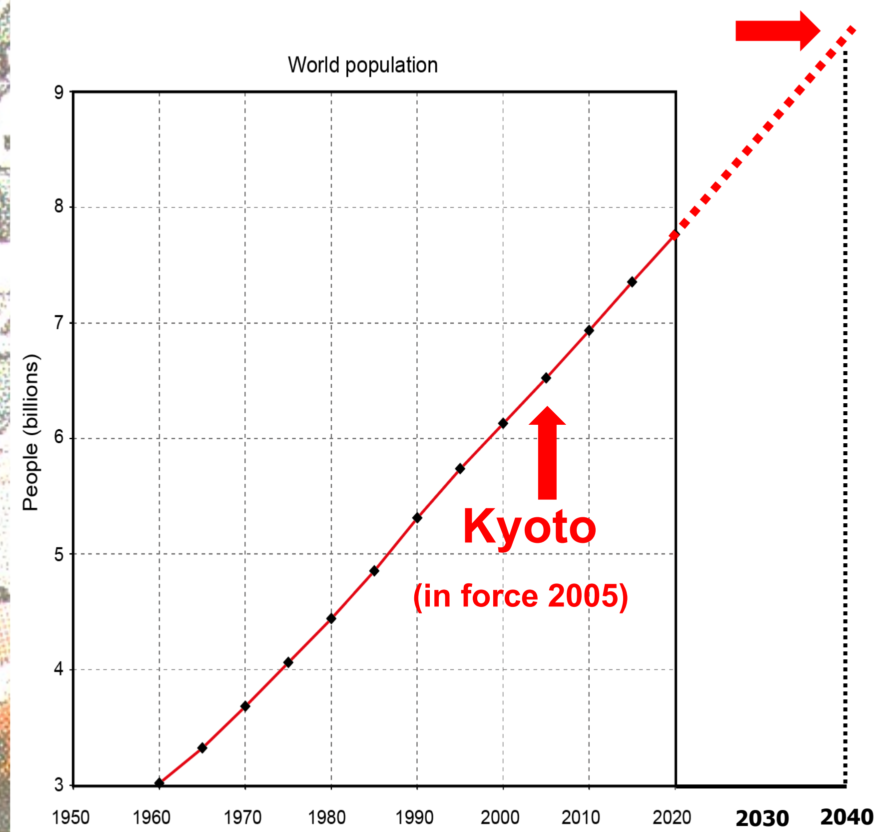


From 3 to 10 billion in 80 years?

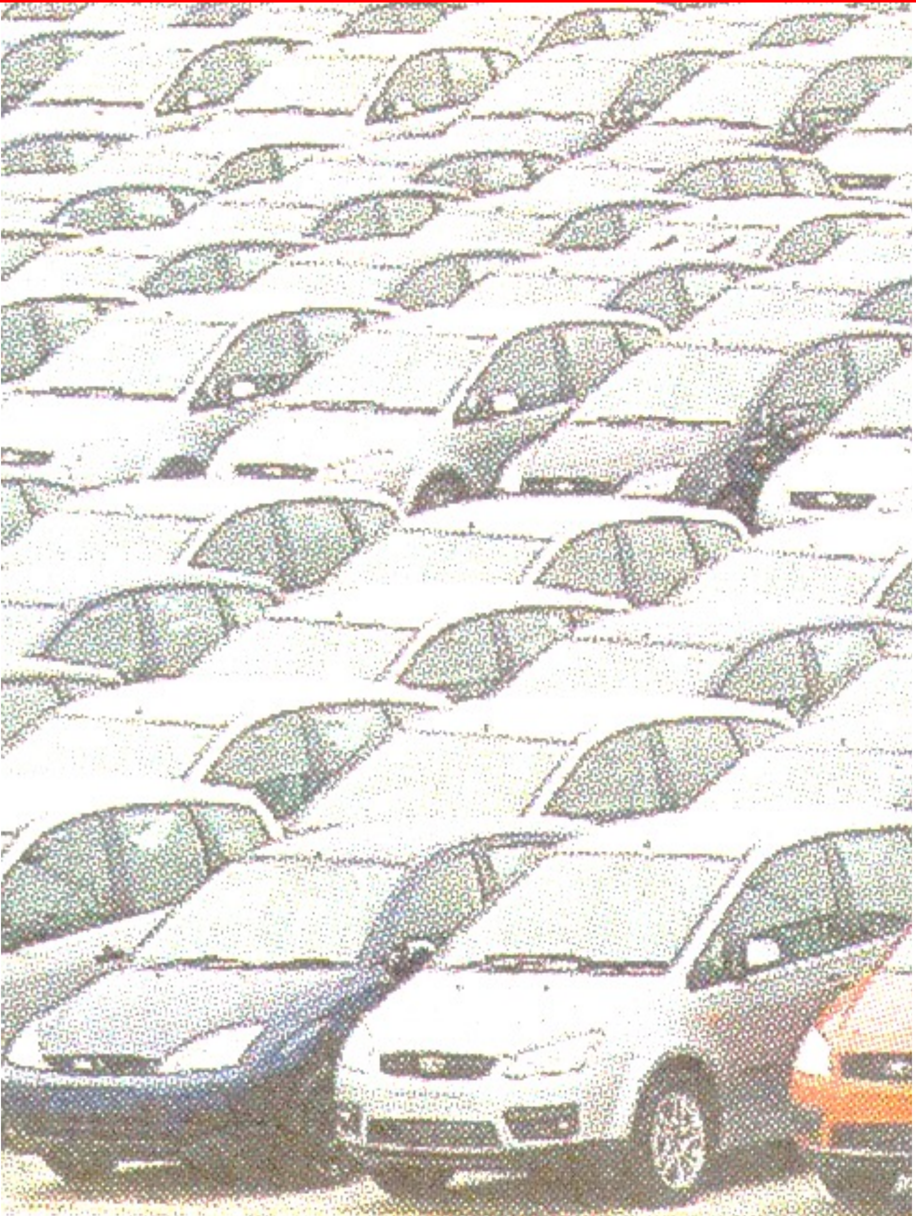
Degree of motorization (PC)

World: 13% in 2020, 16% in 2040

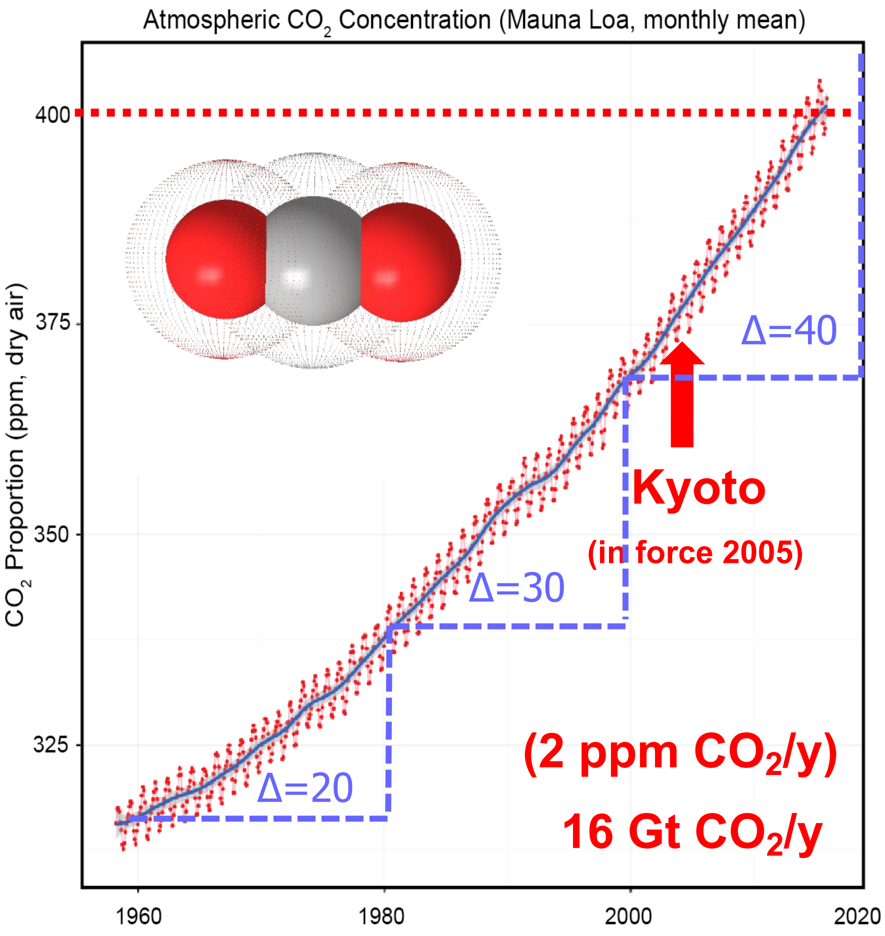
CH: 53% in 2020



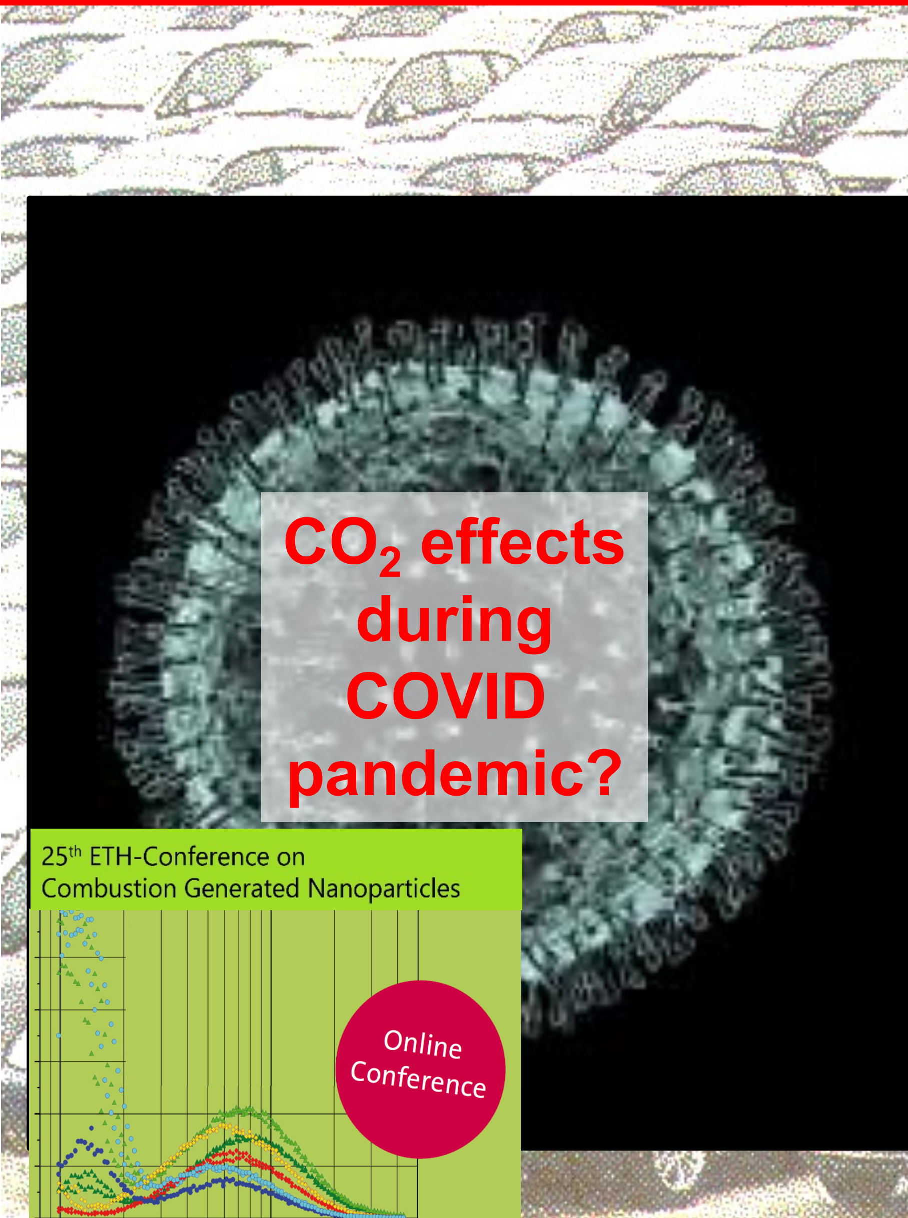
Road vehicles on earth



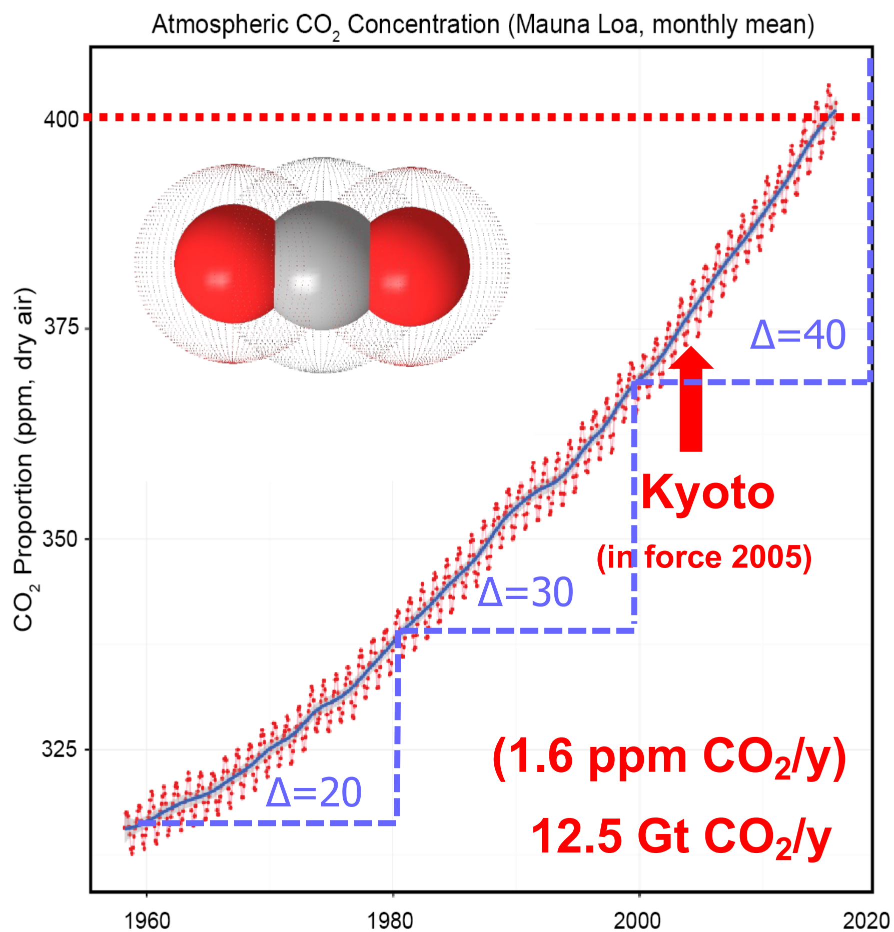
From 310 to 400 ppm in 60 years



Road vehicles on earth

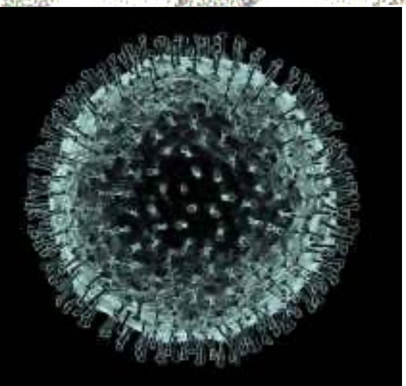


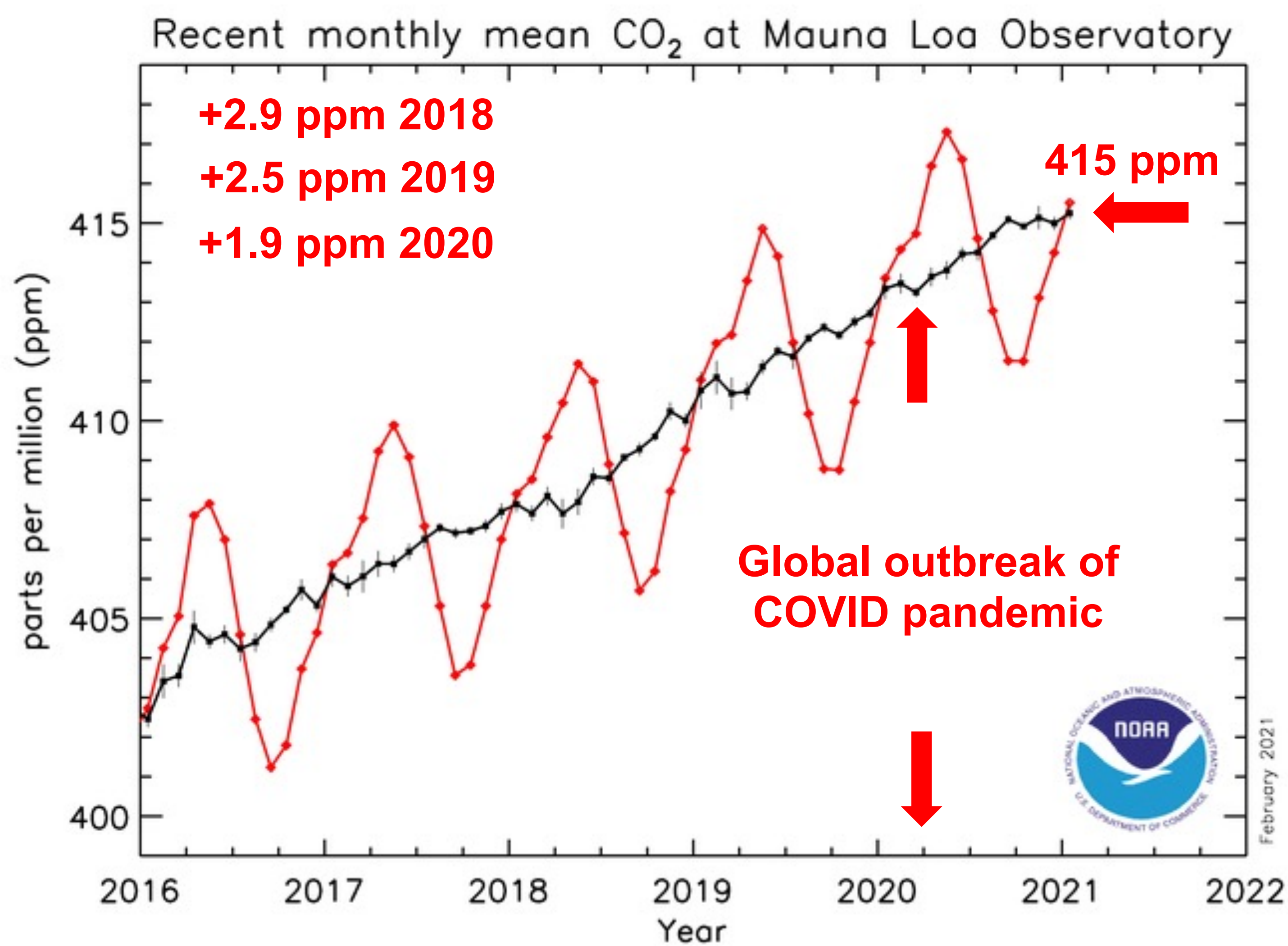
From 310 to 400 ppm in 60 years



Road vehicles on earth

Still an increase of 2 ppm and a new record in 2020!

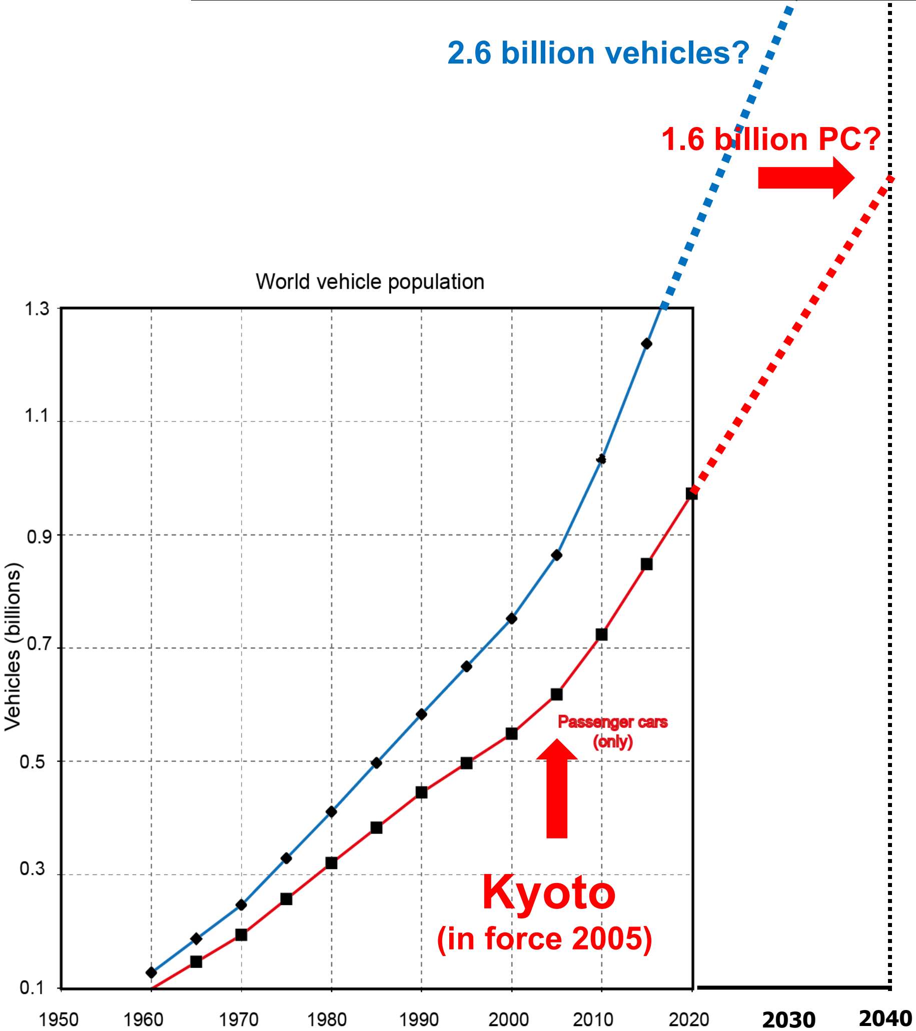


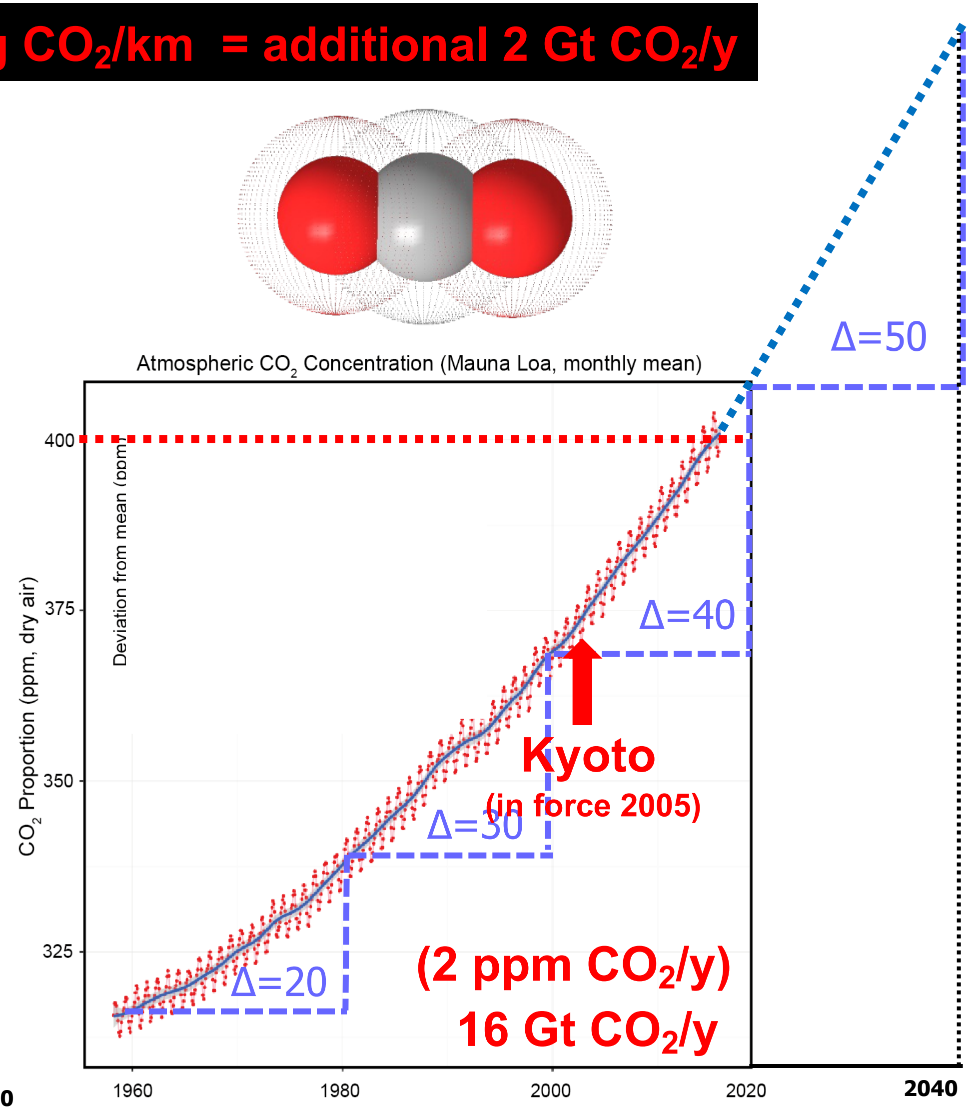


Road vehicles on earth

From 0.1 to 2 billion in 80 years? **From 310 to 460 ppm in 80 years?**

10^9 vehicles x 10^4 km/y x 200 g CO_2/km = additional 2 Gt CO_2/y

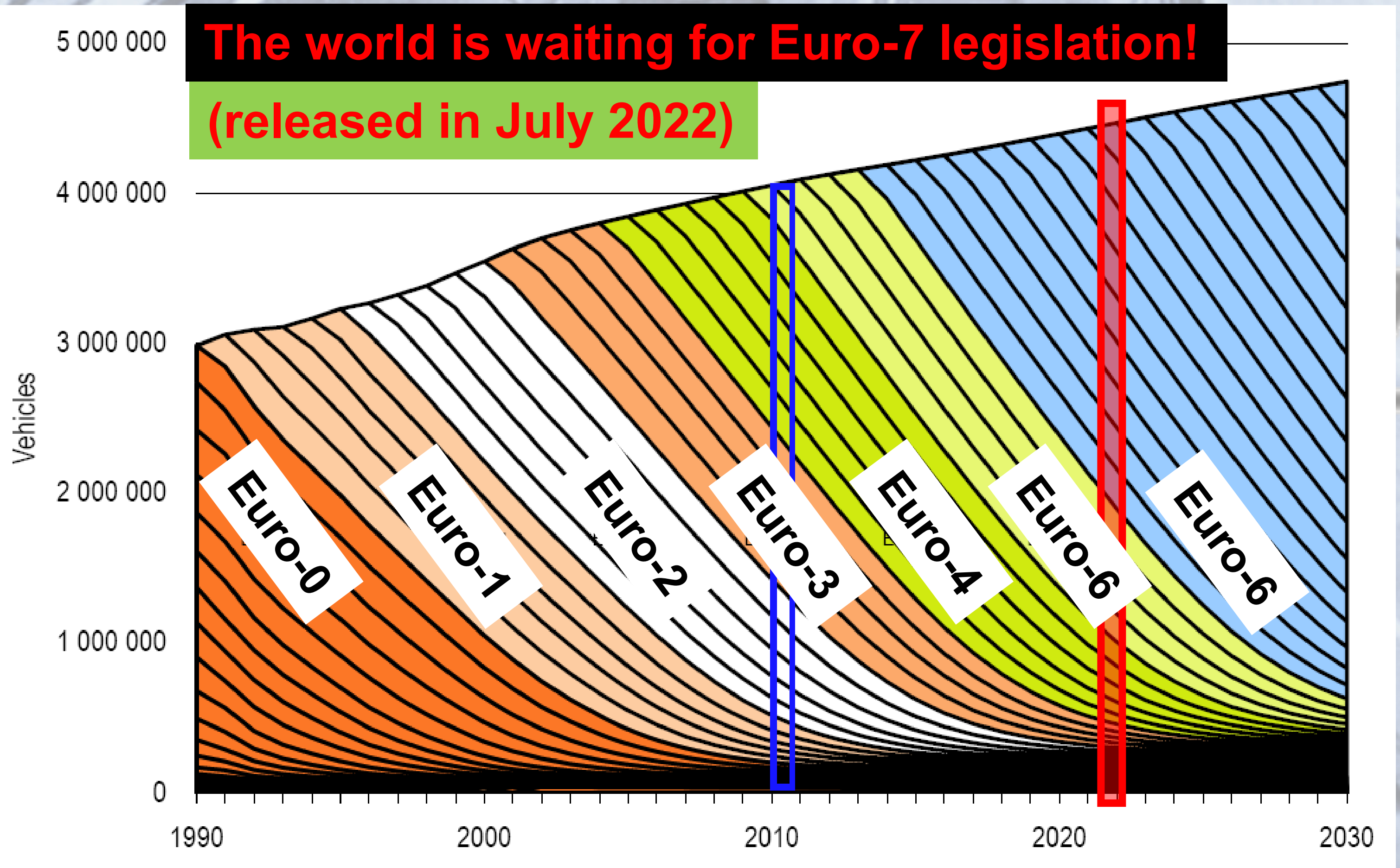




Trends of the Swiss road traffic

In 2022, mainly Euro-4, Euro-5 and Euro-6 vehicles

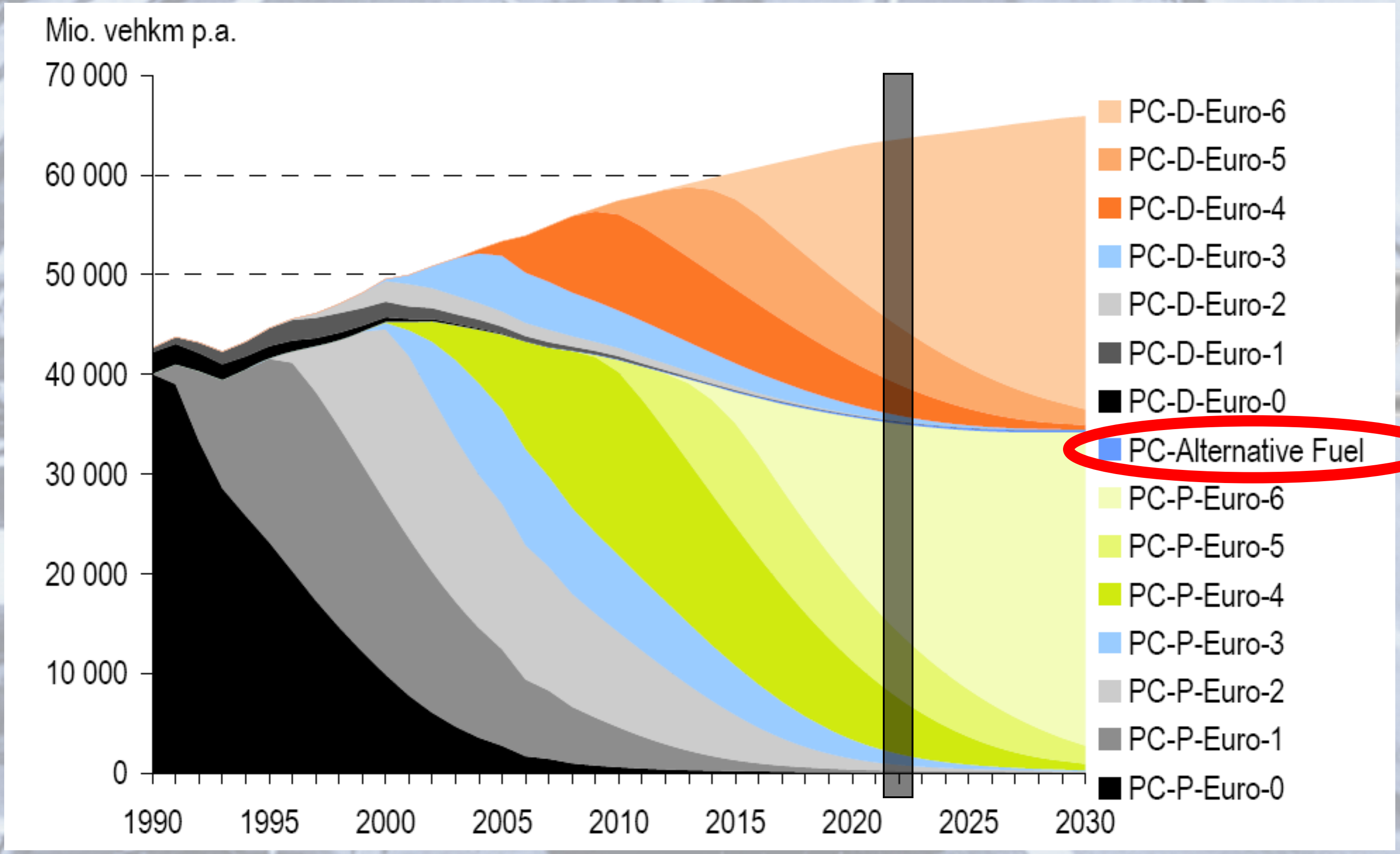
Distribution of technology levels



Trends of the Swiss road traffic

From 3% diesel cars in 1990 to 43% in 2019: <1% alternative fuel vehicles!

Mileage per vehicle class (million vehicle km/y)



Swiss vehicle legislation:
From U.S.- to Euro-based legislation

From 65 down to 1 g CO/km, form 8.2 to 0.1 gTHC/km, from 4.7 to 0.06 gNOx/km

Limits for gasoline vehicles (1974-2019)

Tab. 2 > Emission limit values for petrol-driven passenger cars (induced ignition)

Standard	Stage	Entry into effect[1]	Measurement cycle	Emission limit values						
				CO [g/km]	NMHC [g/km]	THC [g/km]	NO_x [g/km]	$THC+NO_x$ [g/km]	PM [mg/km]	PN [#/km]
ECE 15	ECE 15.00	01.1974	ECE 15	30–65	-	5.1–8.2	-	-	-	-
	ECE 15.01	09.1975	ECE 15	24–52	-	4.3–7.0	-	-	-	-
	ECE 15.02	10.1977	ECE 15	24–52	-	4.3–7.0	3.0–4.7	-	-	-
	ECE 15.03	10.1980	ECE 15	19–42	-	3.8–6.2	2.5–4.0	-	-	-
AGV	AGV 82	10.1982	FTP 72	24.20	-	2.10	1.90	-	-	-
	AGV 86	10.1986	FTP 72	9.30	-	0.90	1.20	-	-	-
FAV 1	FAV 1–1	10.1987	FTP 75	2.10	-	0.25	0.62	-	-	-
TAFV 1	EURO 2	10.1995/96	NEDC	2.20	-	-	-	0.50	-	-
	EURO 3	01.2000/01	NEDCm	2.30	-	0.20	0.15	-	-	-
	EURO 4	01.2005/06	NEDCm	1.00	-	0.10	0.08	-	-	-
	EURO 5	09.2009/10	NEDCm	1.00	0.068	0.10	0.06	-	5.0/4.5[2, 3]	-
	EURO 6	09.2014/15	NEDCm	1.00	0.068	0.10	0.06	-	5.0/4.5[2, 3]	[4]

[1] First date: valid for the homologation of new vehicle types. Second date: valid for initial entry into circulation of new vehicles.
[2] Limits for particle mass for induced ignition engines only apply to vehicles with direct injection.
[3] Revised measurement procedure to be introduced before the limit of 4.5 mg/km is implemented.
[4] New measurement procedure to be introduced before the limit is implemented.
[5] For vehicles with induced ignition engines with direct injection, a limit value for particle number is to be specified before 1 September 2014.

Only GDI with PN limit!

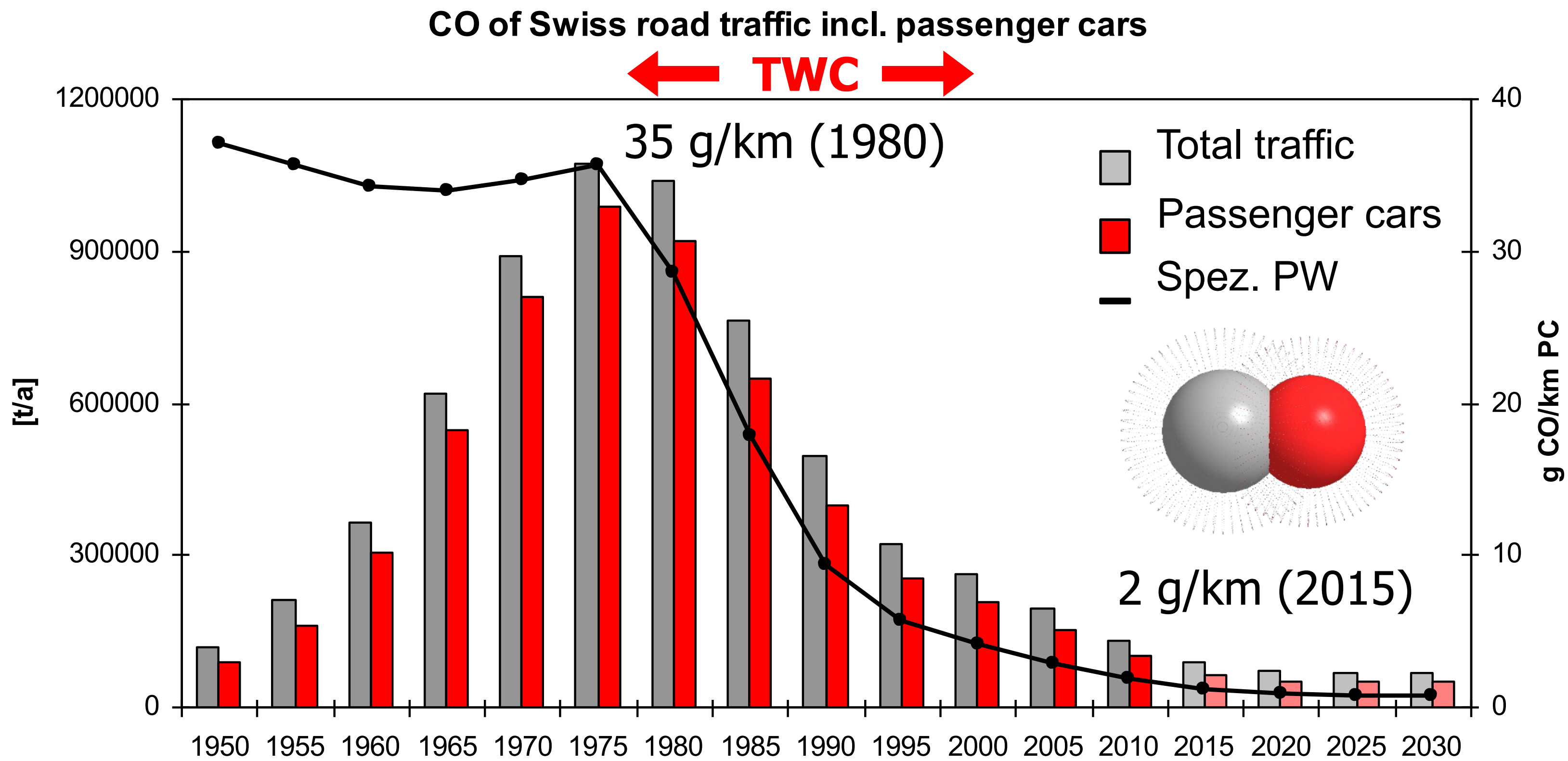
10x!

2014-2017 6x10e12 #/km
>2017 6x10e11 #/km

Emissions of Swiss road traffic

CO, a problem of passenger cars! What happened in the 80ies?

CO emissions (MAC: 35 mg/m³, 15 min)

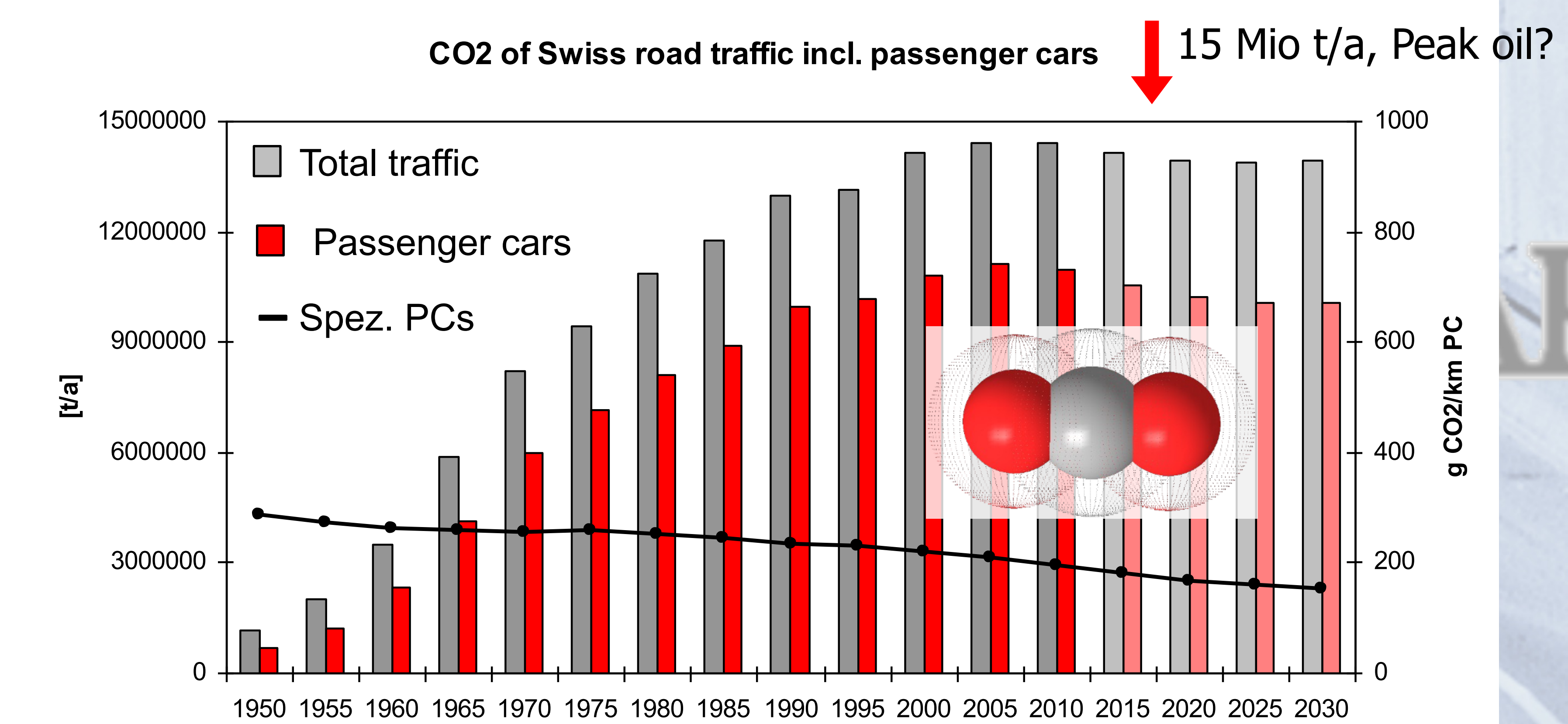


In 40 years from 35 down to 2 g/km

Emissions of the Swiss road traffic

No fuel consumption legislation, no reduction of CO_2 emissions

CO_2 emissions of the road traffic



Not much improvements!

In 80 years from 300 down to 170 g/km

Trends on planet earth

“You’ll never drive alone”

Global trends

The majority of the world population:

- lives in urbanized areas
- is exposed to combustion-engine exhausts
- suffers from heat waves due to rising temperatures especially in cities

Decarbonization of the mobility sector is needed to break these trends

New legislation to guide the world: Where are we now and in which direction should we go?

Mobility is a necessity since *Homo Sapiens Sapiens* left the trees and have to move in the savanna

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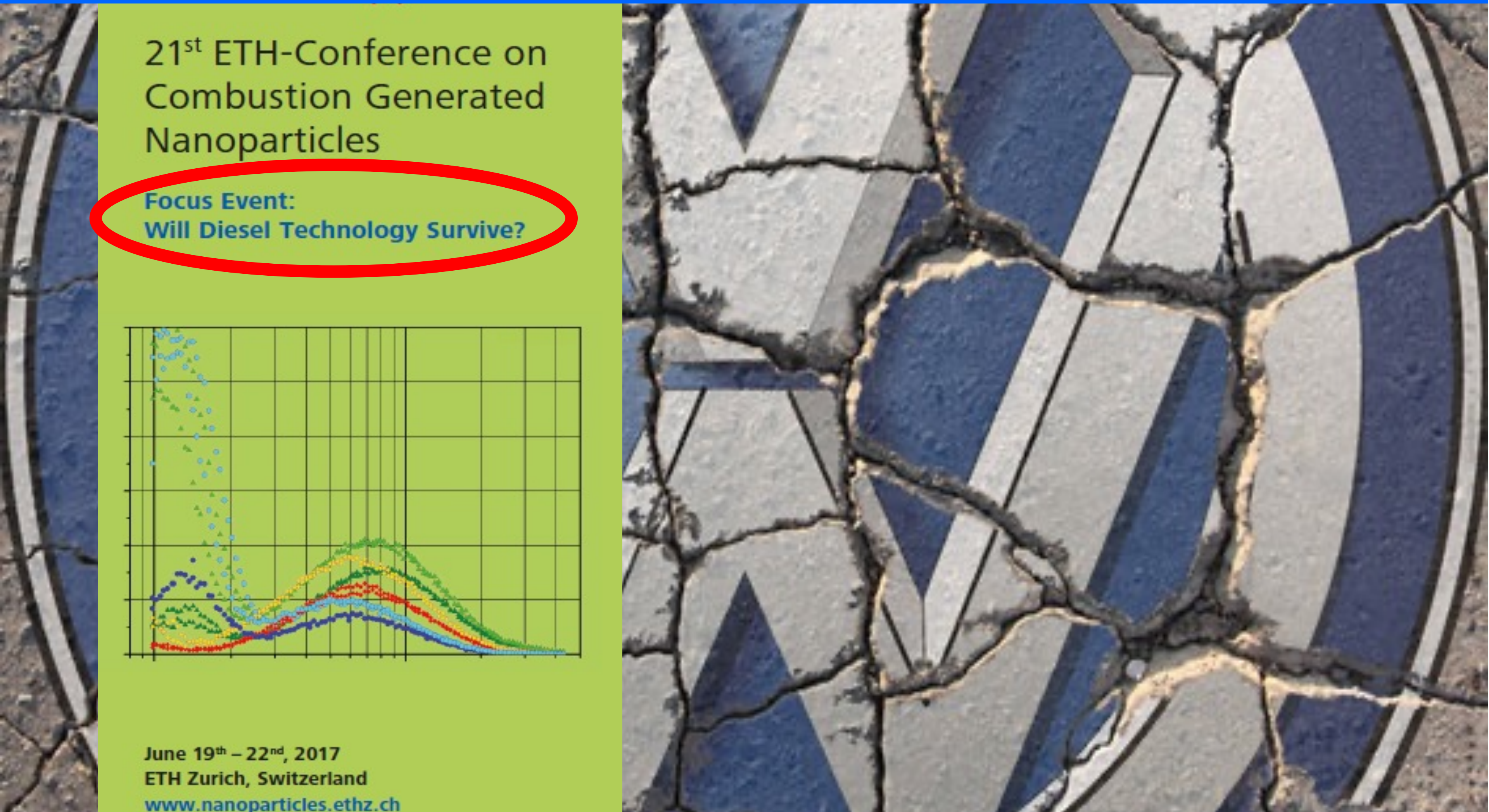
Toxicity-based, cell-models, multi-media models

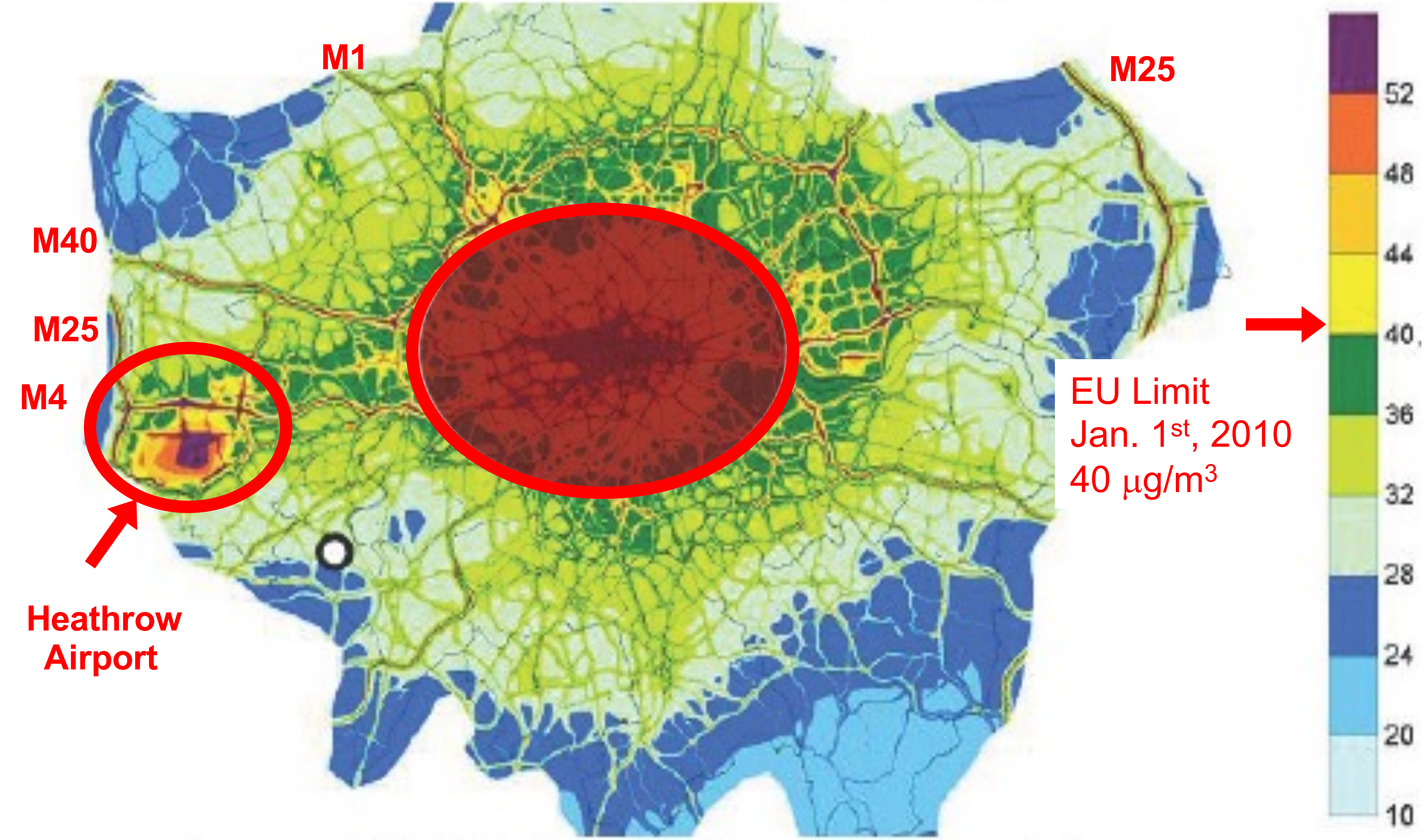
Will diesel technology survive?



21st ETH Conference on Combustion Generated Nanoparticles

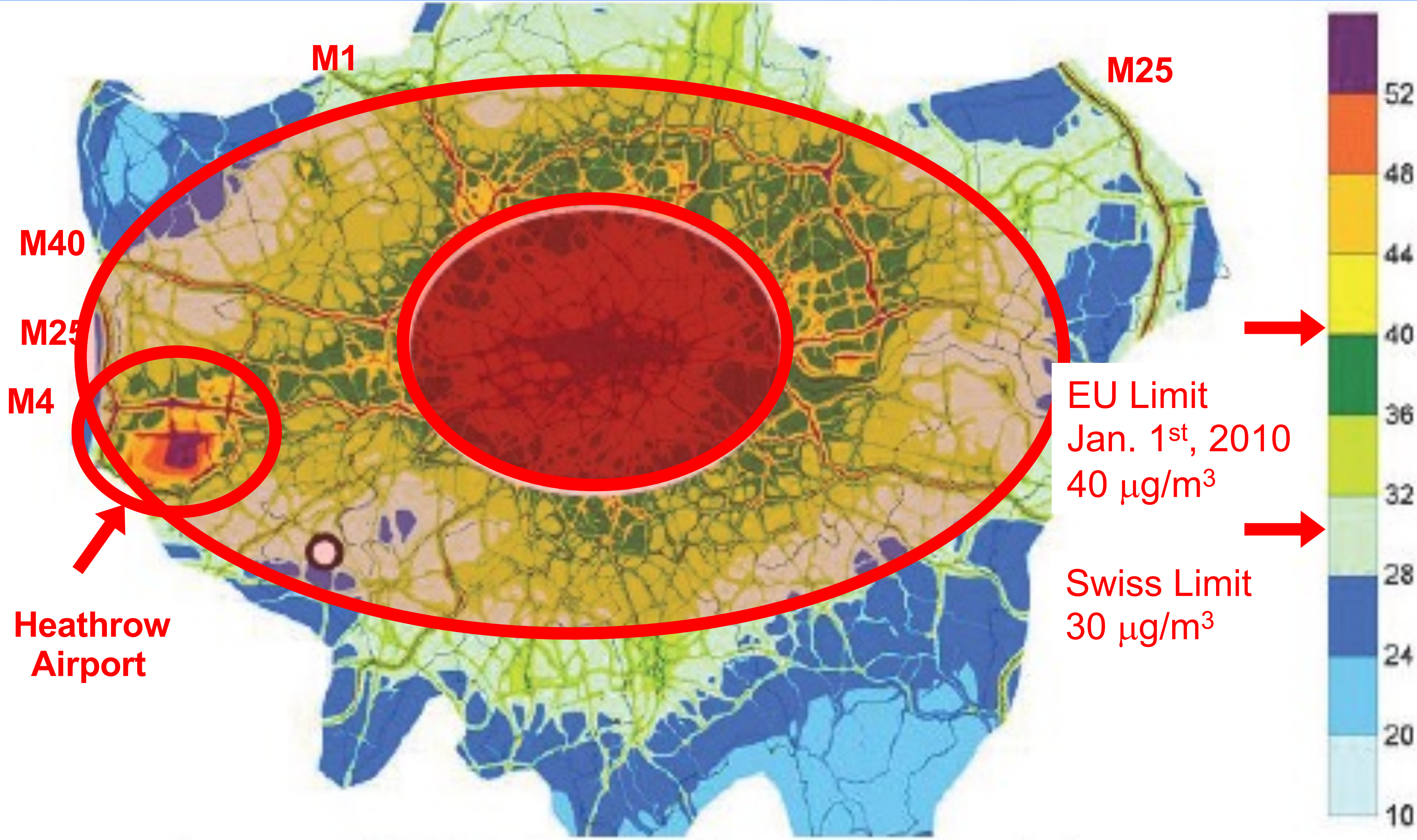
Zürich, June 19-22, 2017

Mean annual NO_2 levels: City of London



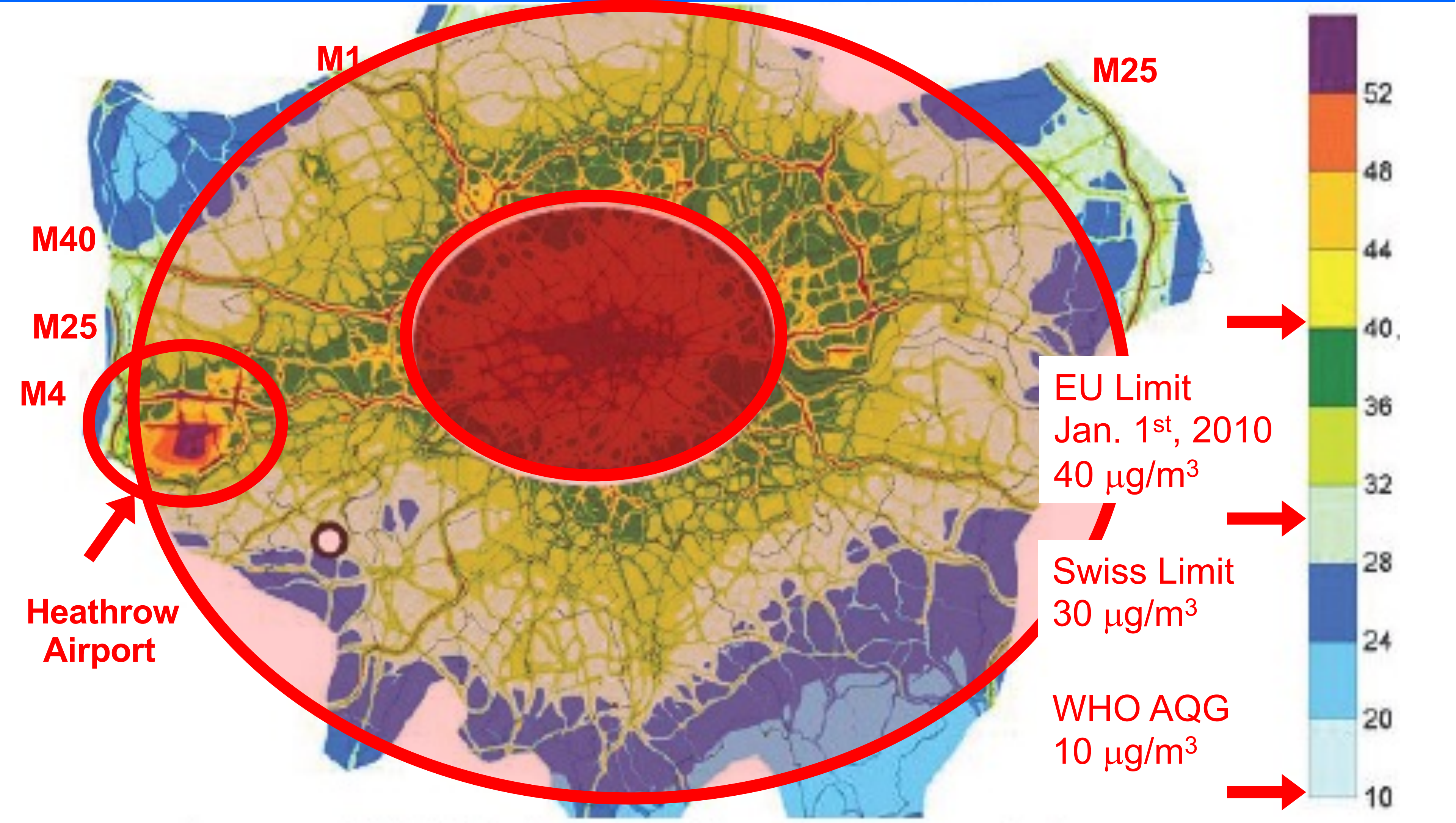
The NO_2 problem in central London is severe, as it is in many European cities!

Mean annual NO_2 levels: City of London



From a Swiss perspective, the NO_2 problem is even more severe!

Mean annual NO_2 levels: City of London



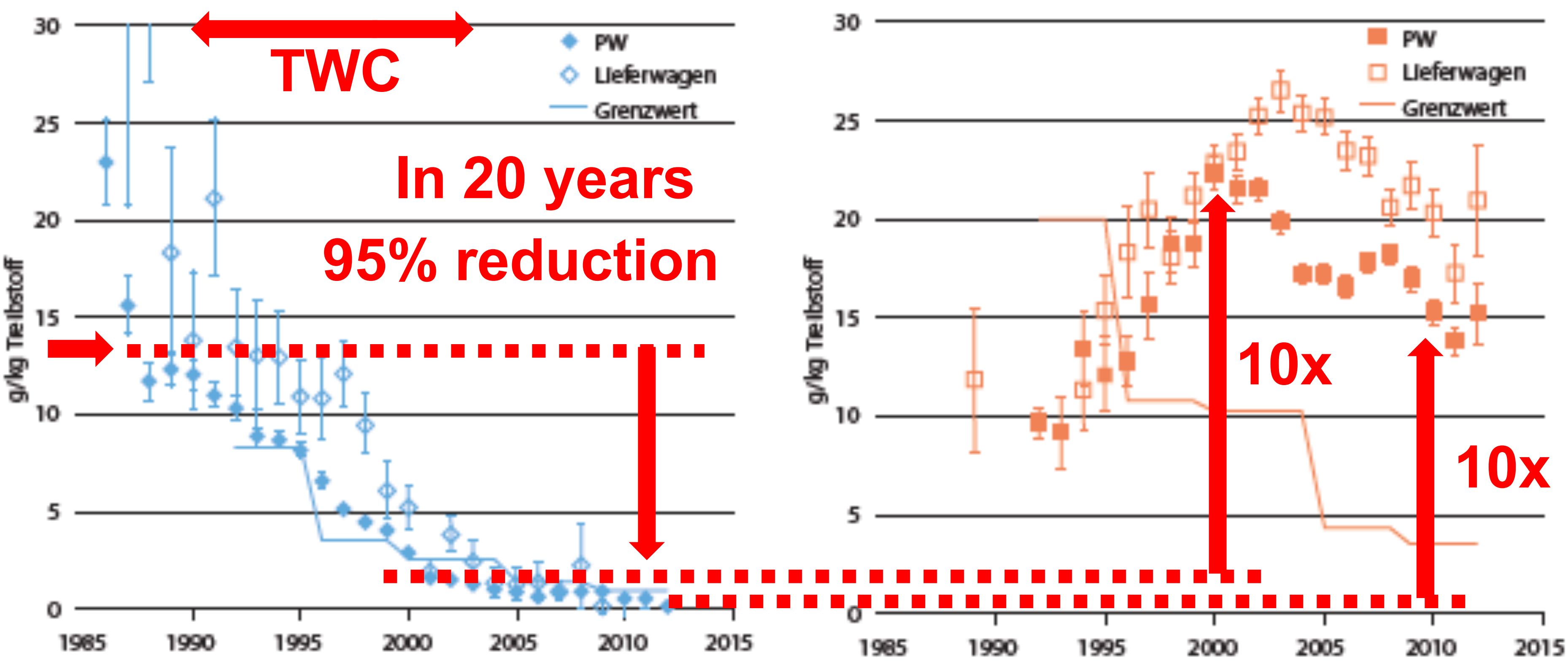
The new WHO air quality guideline will be a major challenge for all cities!

From chassis dynamometer to on-road measurements

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

NOx-emissions of gasoline- & diesel-vehicles

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

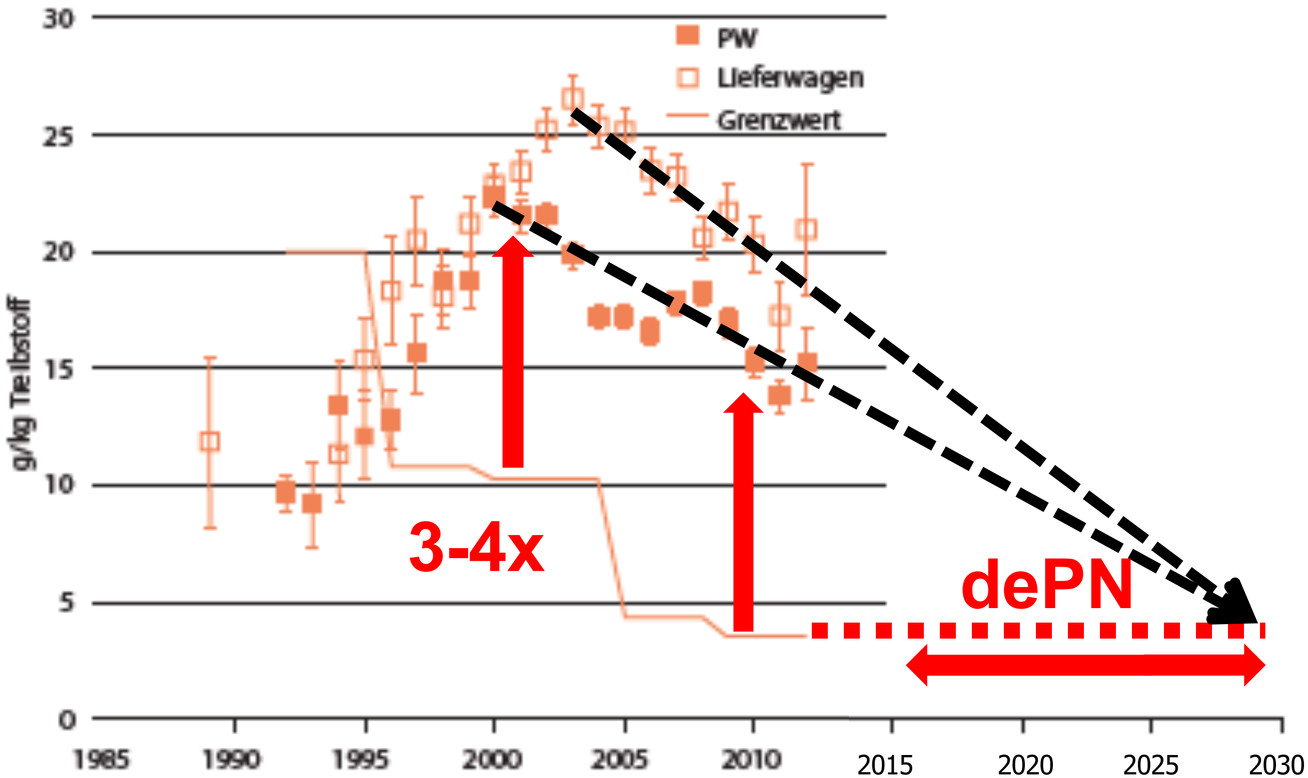


The NOx-problem of diesel vehicles is 20 years old – that's the scandal

Can diesel solve its NO_x problem in time?

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

NO_x-emissions of diesel-vehicles



Is it 2030 when diesel PC and LDV reach Euro-6 level on roads?

The NOx-problem of diesel vehicles is 20 years old – that's the scandal

Diesel deNOx on roads: The blue technology was not green enough

How they did it?

How They Did It: An Analysis of Emission Defeat Devices in Modern Automobiles

Moritz Contag[*], Guo Li[†], Andre Pawlowski[*], Felix Domke[‡], Kirill Levchenko[†], Thorsten Holz[*], and Stefan Savage[†]

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[†] University of California, San Diego, {gul027, klevchen, savage}@cs.ucsd.
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Moritz Contag, Andre Pawlowski, Torsten Holz, Ruhr-Univer

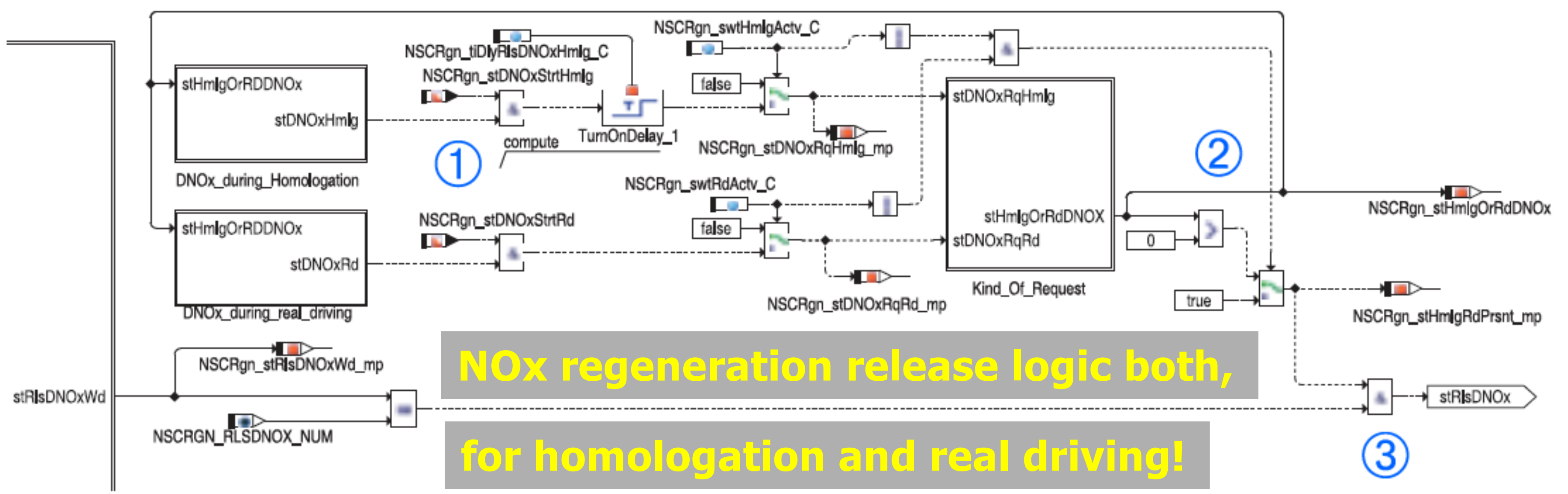
Guo Li, Kirill Levchenko, UC San Diego

Felix Domke, Leibzig

Contag et al. 38th IEEE Symposium (2017) 231-250, How They Did It: Defeat Devices in Modern Automobiles

Diesel deNOx on roads:
The blue technology was not green enough

How they did it? – The Fiat approach, work on NOx regeneration or not



NOx regeneration release logic both,

for homologation and real driving!

Fig. 5: NO_x regeneration release logic combining the start and release signals from the homologation and real driving logic to compute the single regeneration release signal `stRlsDNOx`. Demand and release conditions are computed separately for the homologation and real driving logic ①. The output of the `Kind_of_Request` block is non-zero if either of the homologation or real driving signals is `true` ②. The final release signal `stRlsDNOx` is only asserted ③ if either the homologation or real driving release signals is `true`. Blue numbers ① through ③ added by authors. From function sheet EDC17C69 P 1264 for Fiat 500X. Copyright Robert Bosch GmbH.

Contag et al. 38th IEEE Symposium (2017) 231-250, How They Did It: Defeat Devices in Modern Automobiles

Diesel deNOx on roads:
The blue technology was not green enough

What can we learn from "diesel-gate" with respect to new legislation

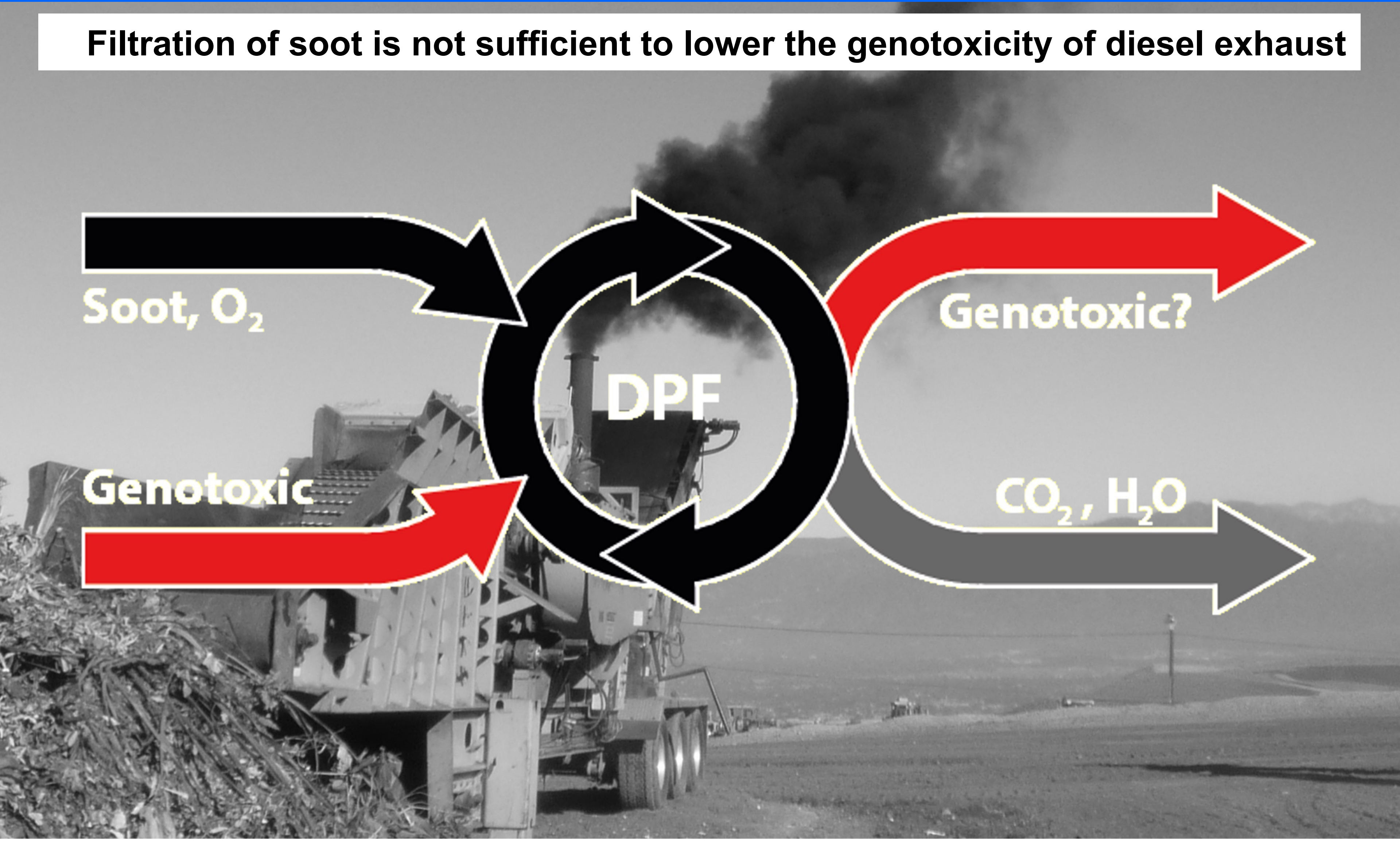
- Chassis dynamometer measurements are not enough
- Cycle beating (optimization) was a problem
- Engine-control units were manipulated to deactivate deNOx-systems (defeat devices)
- On-board diagnostics is not enough

New periodical technical inspection (NPTI) is needed

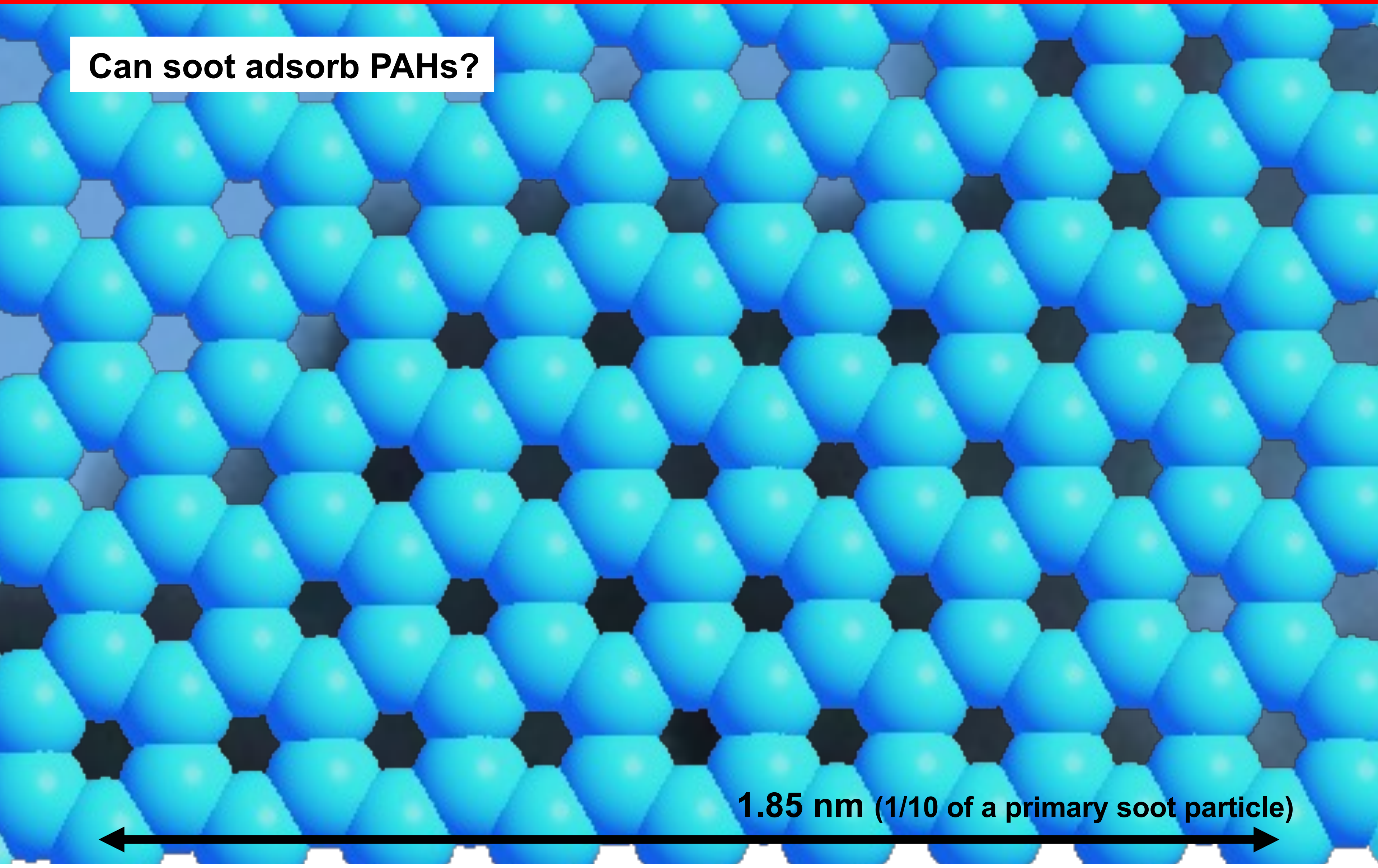
Pascal Buerkenhoudt: Cleaner air due to vehicle approval or vehicle inspection?

New converter technology, new risks for secondary pollutants

Filtration of soot is not sufficient to lower the genotoxicity of diesel exhaust



Soot-catalyzed chemistry



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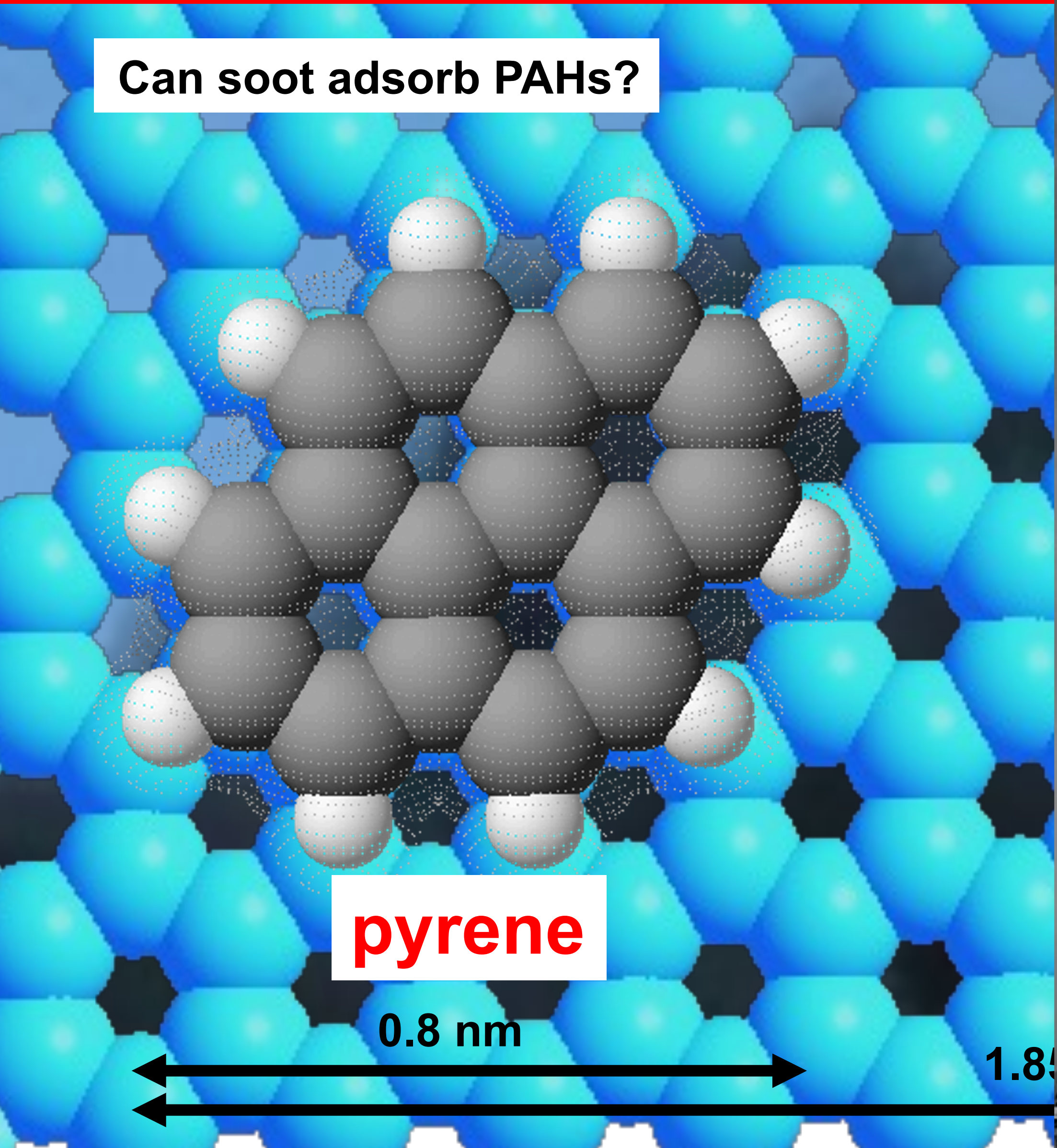
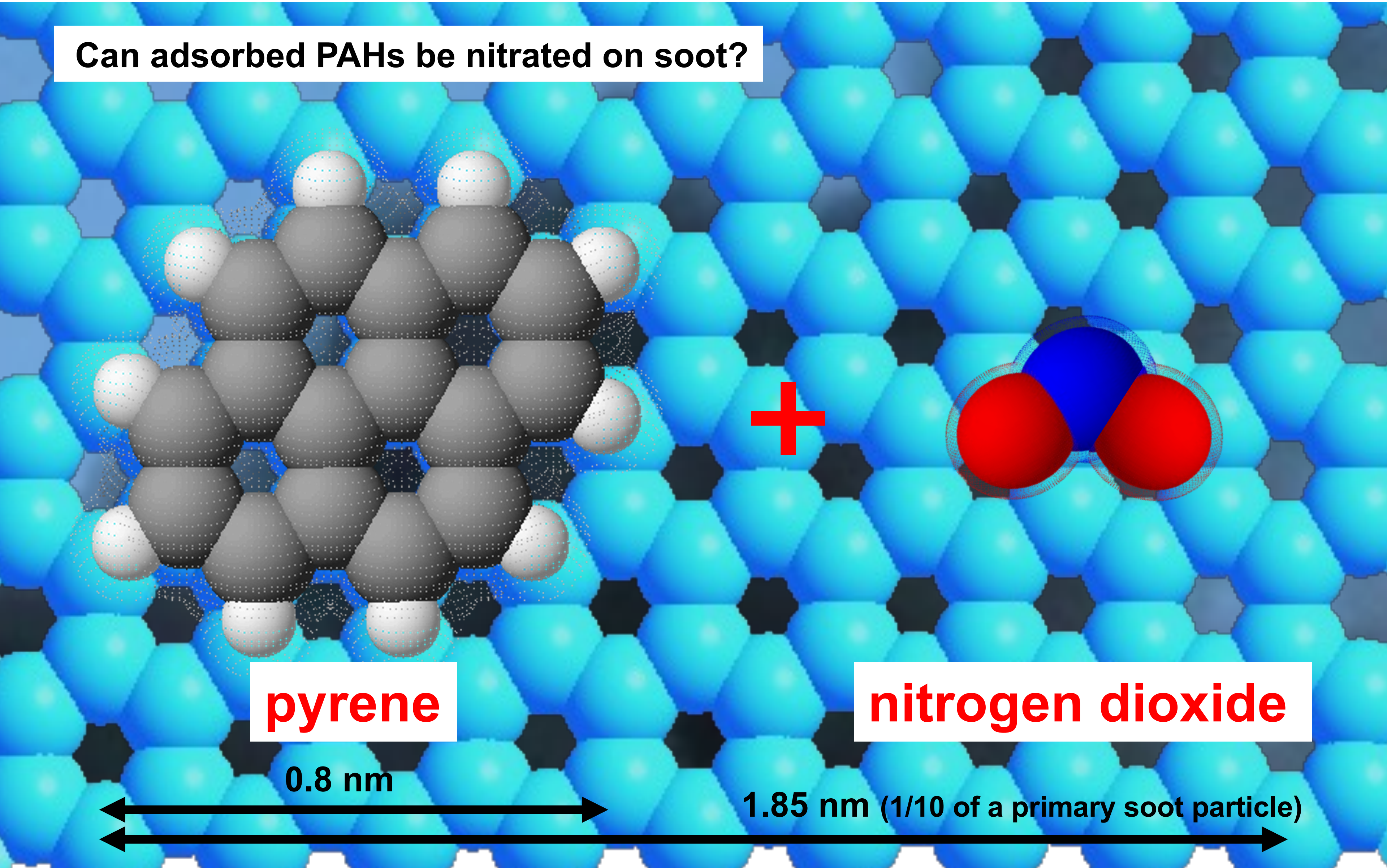


Soot-catalyzed nitration of PAHs



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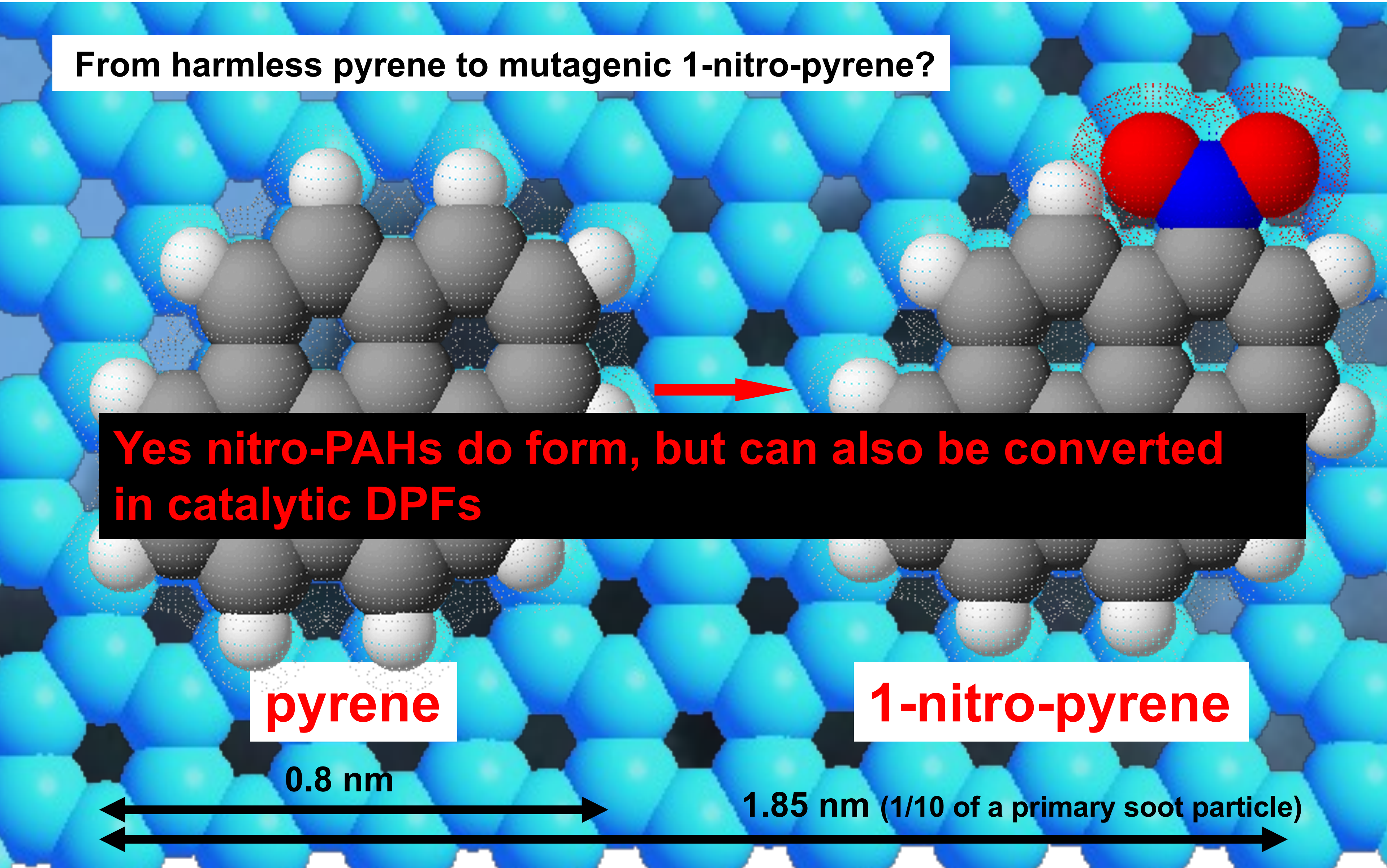
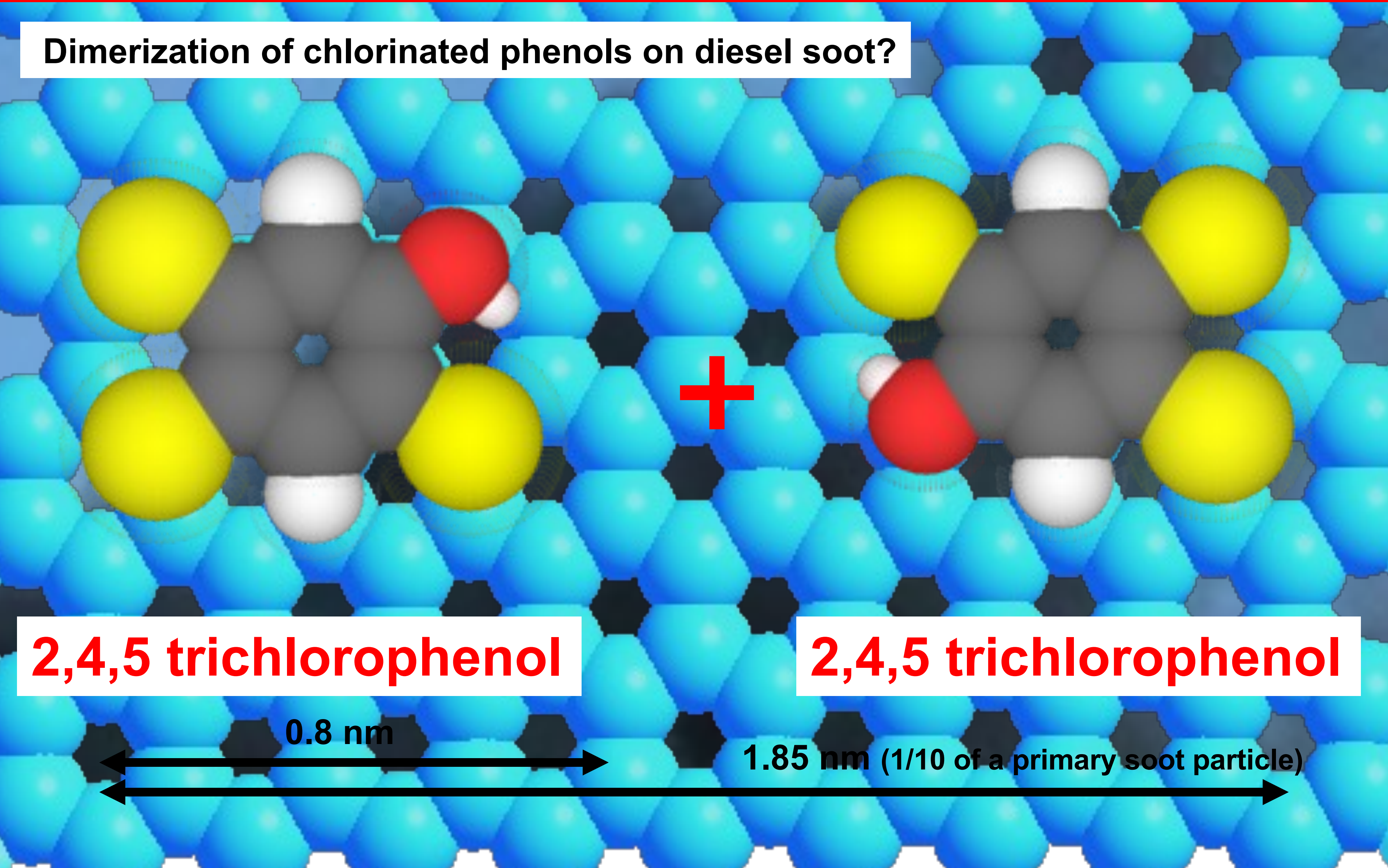
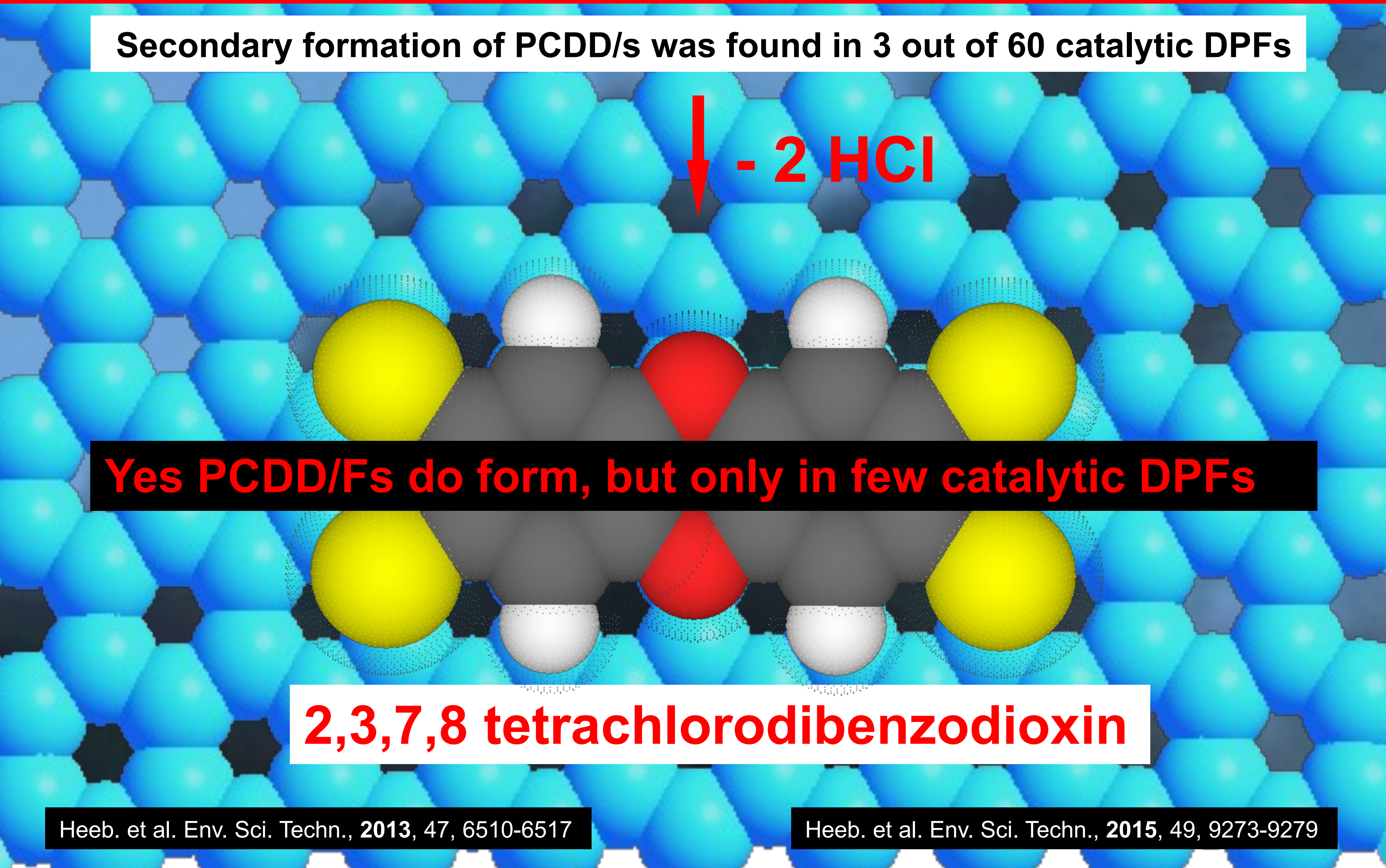


Metal-catalyzed dioxin formation in DPFs



Metal-catalyzed dioxin formation in DPFs

Secondary formation of PCDD/s was found in 3 out of 60 catalytic DPFs



Yes PCDD/Fs do form, but only in few catalytic DPFs

2,3,7,8 tetrachlorodibenzodioxin

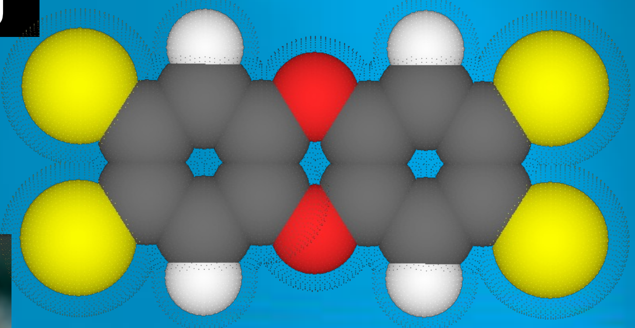
Heeb. et al. Env. Sci. Techn., **2013**, 47, 6510-6517

Heeb. et al. Env. Sci. Techn., **2015**, 49, 9273-9279

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

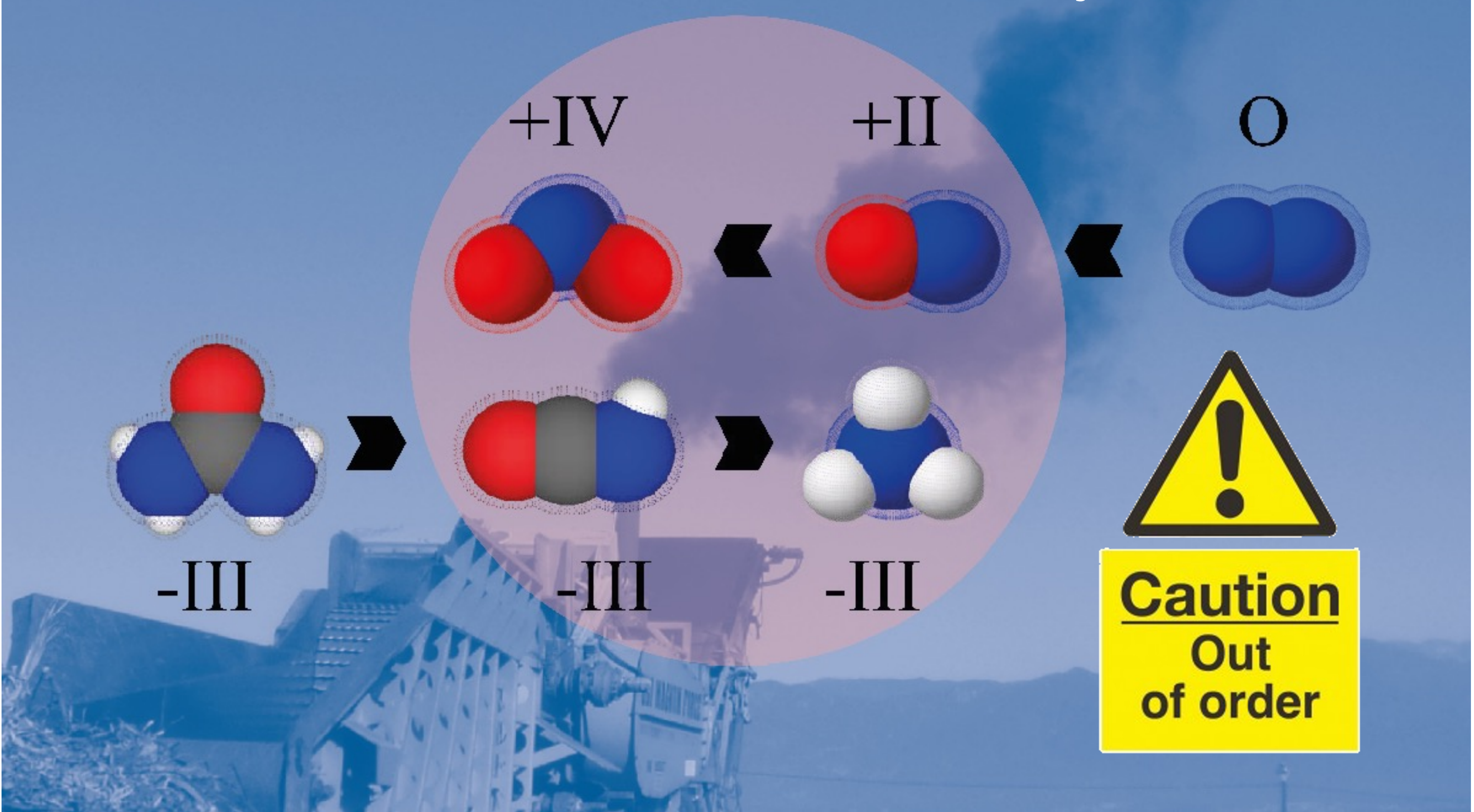


Yes, Victor Yushchenko was poisend with 2,3,7,8-TCDD

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

Urea-based SCR – various reactive nitrogen species (RNCs) on board

But sometimes just out of order



Currently the most efficient deNOx system for diesel engines

Urea-based SCR – various reactive nitrogen species (RNCs) on board

Various steps to decompose and hydrolyze urea and to reduce NO and NO_2!

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

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

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

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

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

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

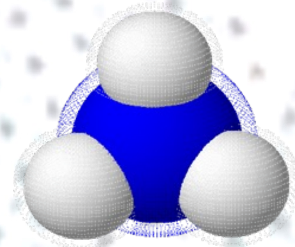
$$HNCO + H_2O \longrightarrow NH_3 + CO_2 \qquad (6)$$

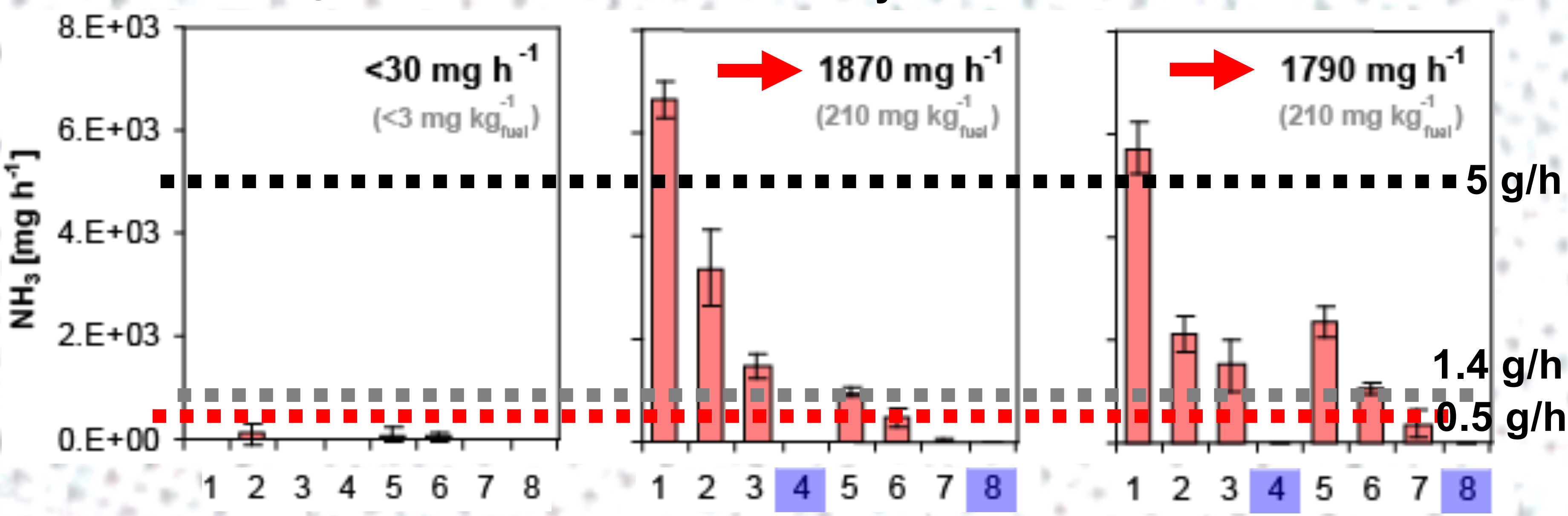
Simplified reaction scheme, quite complex chemistry

Secondary pollutants of DeNO$_x$-technologies

Substantial ammonia emissions with active SCR at α = 1.0!

Ammonia (NH_3)





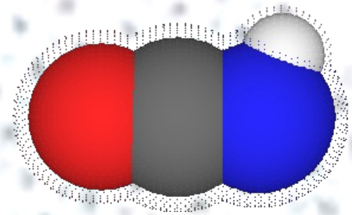
Heeb et al. Atm. Env. 40 (2006) 3750-3763
Heeb et al. Atm. Env. 40 (2006) 5986-5997
Livingston et al. Atm. Env. 43 (2009) 3326-3333
Heeb et al. Atm. Env. 42 (2008) 2543-2554

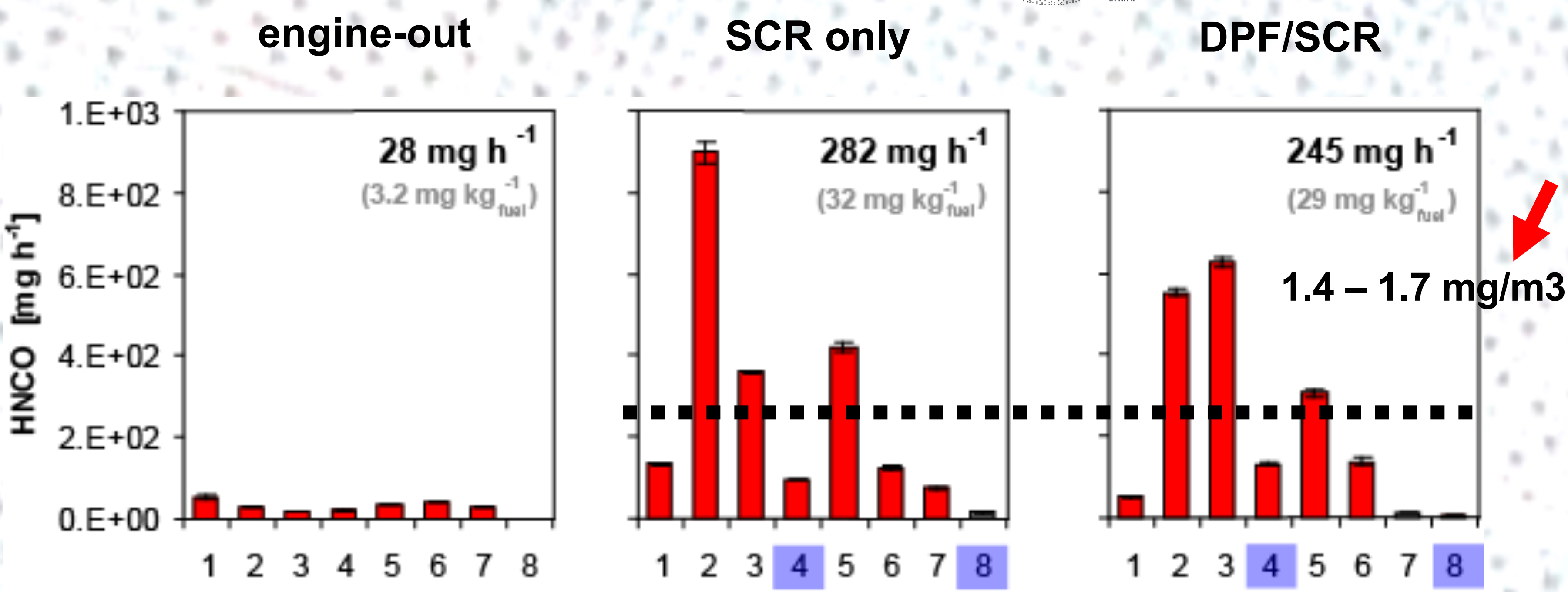
There are no limits for NH_3 despite relevant emissions!

Secondary pollutants of DeNO$_x$-technologies

Isocyanic acid emissions 70-85 x above MAK

Isocyanic acid (HNCO)





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

There are no limits for HNCO despite relevant emissions!

Success and failure of past legislation

Current exhaust legislation is not effect-based!

- Implementation of transient, real-world driving cycles
  - Optimization (cycle-beating), re-programming of ECUs, defeat-devices
- Challenging emission limits favored implementation of catalytic converters
  - Success with TWCs and DPFs, failures with diesel deNOx
- Combination of catalytic converter technologies is complex
  - New risks for secondary pollutants

Good legislation and challenging emission limits are keys to cleaner exhausts and promote the implementation of better technology

New legislation to guide the world: Where are we now and in which direction should we go?

Mobility is a necessity since *Homo Sapiens Sapiens* left the trees and have to move in the savanna

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Toxicity-based, cell-models, multi-media models

New legislation and new approaches

Current exhaust legislation is not effect-based!

- **Specific legislation for toxic compounds**
  - **Toxicology-based legislation, differentiation of harmfuel and harmless**
- **Assess new mass technologies and fuels comprehensively**
  - **Toxicological and environmental risks**

Specific legislation for toxic compounds

What is toxic should be regulated at the emission source, workplace and ambient

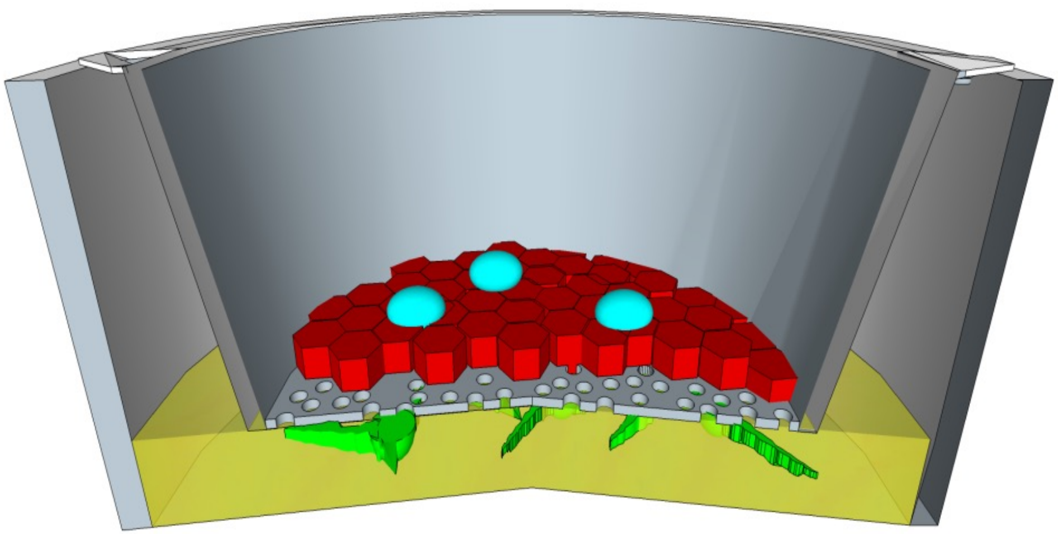
Specific legislation for toxic compounds

Some examples

- Toxicology-based occupational health legislation
- Exposure levels and time, maximum workplace concentrations
- Precautionary principle, also in the Swiss chemicals legislation

In vitro-cell culture models – powerful tools to assess exhaust toxicity

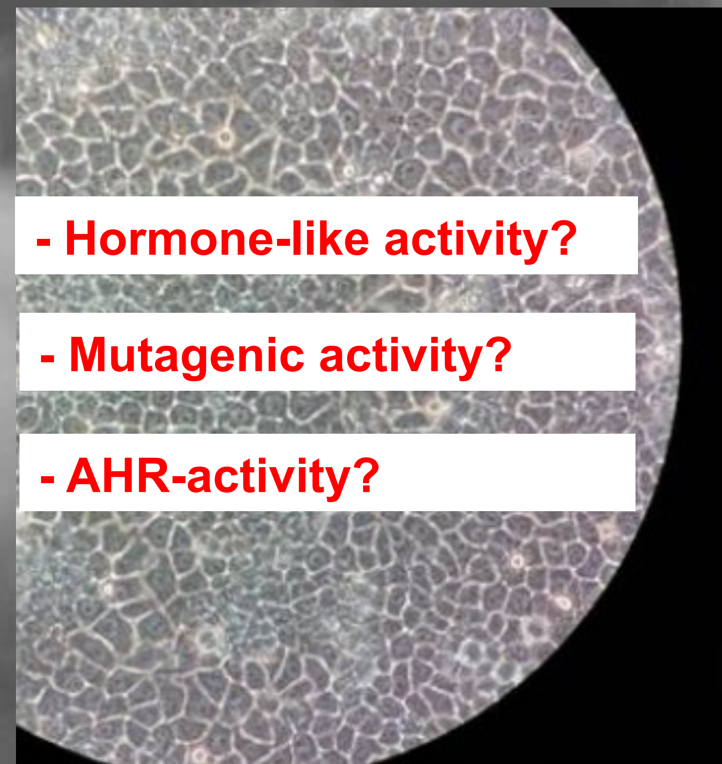
3D-human cell model of the epithelial airway barrier



Macrophages (from human blood)
Bronchial epithelial cells (16HBE14o- cell line)
Dendritic cells (from human blood)

Rothen-Rutishauser et al., 2005. Am. J. Resp. Cell Mol. Biol

Rat hepatoma cell models (ER- & DR-CALUX)



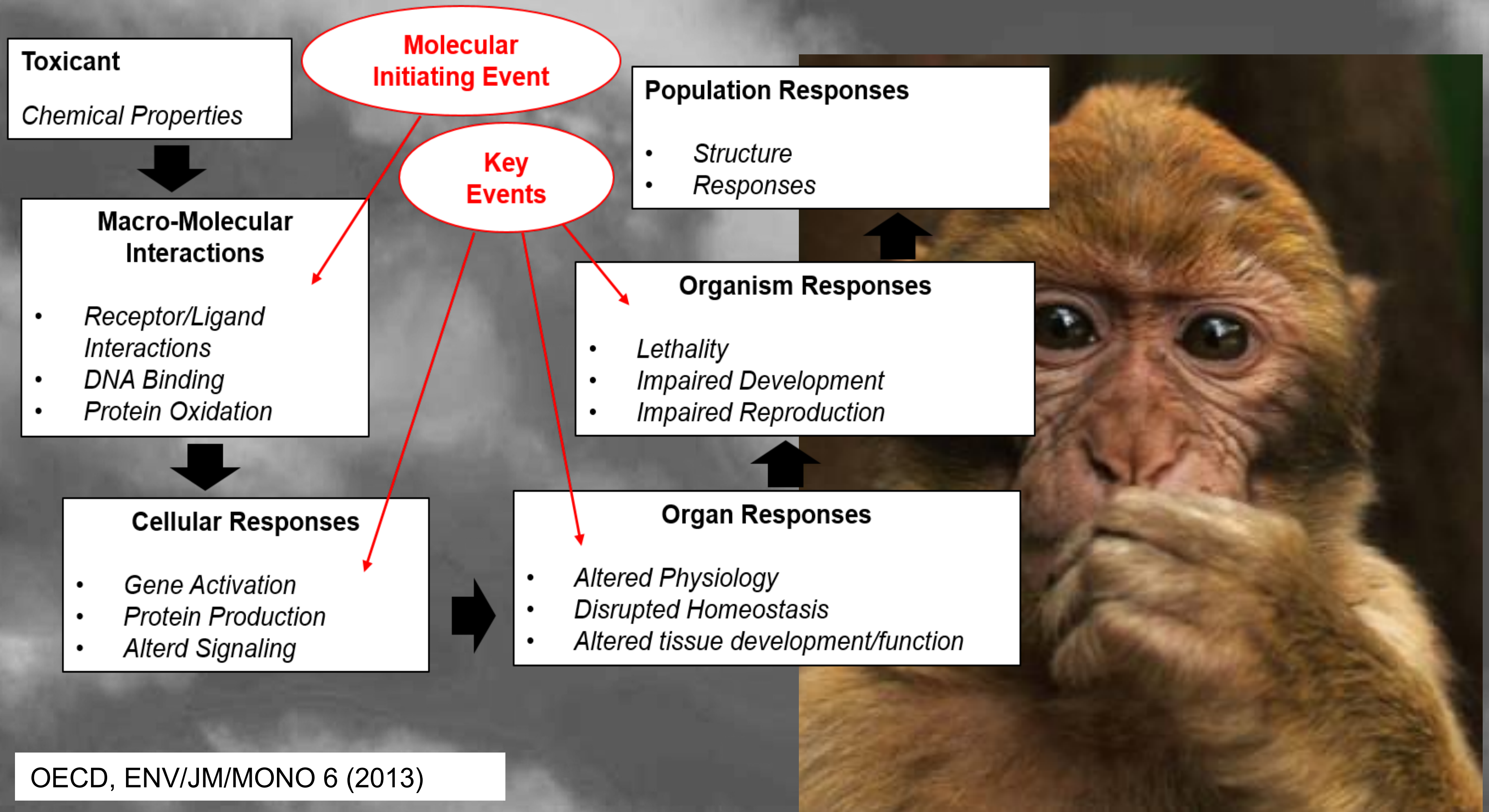
- Hormone-like activity?
- Mutagenic activity?
- AHR-activity?

Wenger et al. ES&T 42 (2008) 2992-2998

Wenger et al. ABC 42 (2008) 2021-2029

Adverse effects on humans - From cells to organs, organism and populations

Adverse effects on animals and humans



OECD, ENV/JM/MONO 6 (2013)

New legislation to guide the world: Where are we now and in which direction should we go?

Mobility is a necessity since *Homo Sapiens Sapiens* left the trees and have to move in the savanna

Agenda

The world motorization degree on the rise

Global trends, the trends in Switzerland

Success and failure of past legislation

Success with TWCs and DPFs, failures with deNOx

New legislation and new approaches

Toxicity-based, cell-models, multi-media models