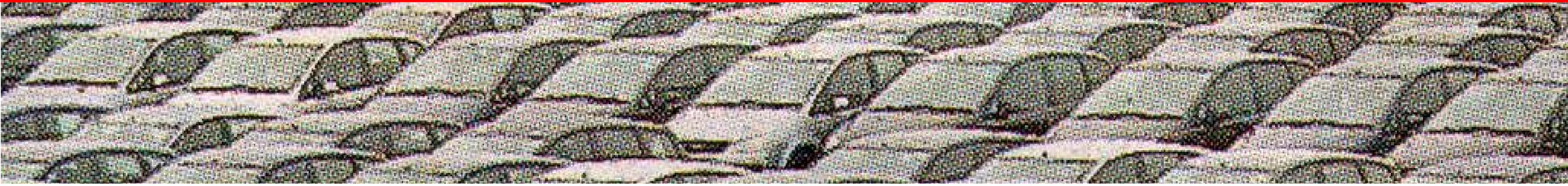
Chemistry-based assessment of combustion exhausts



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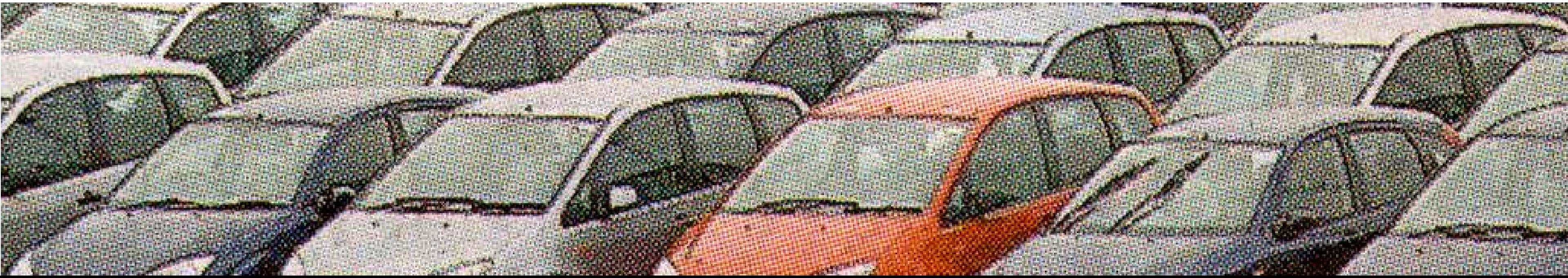


Focus Event: Effect- and toxicity-based assessment of exhausts

Empa, March 16, 2018

Road vehicles on earth

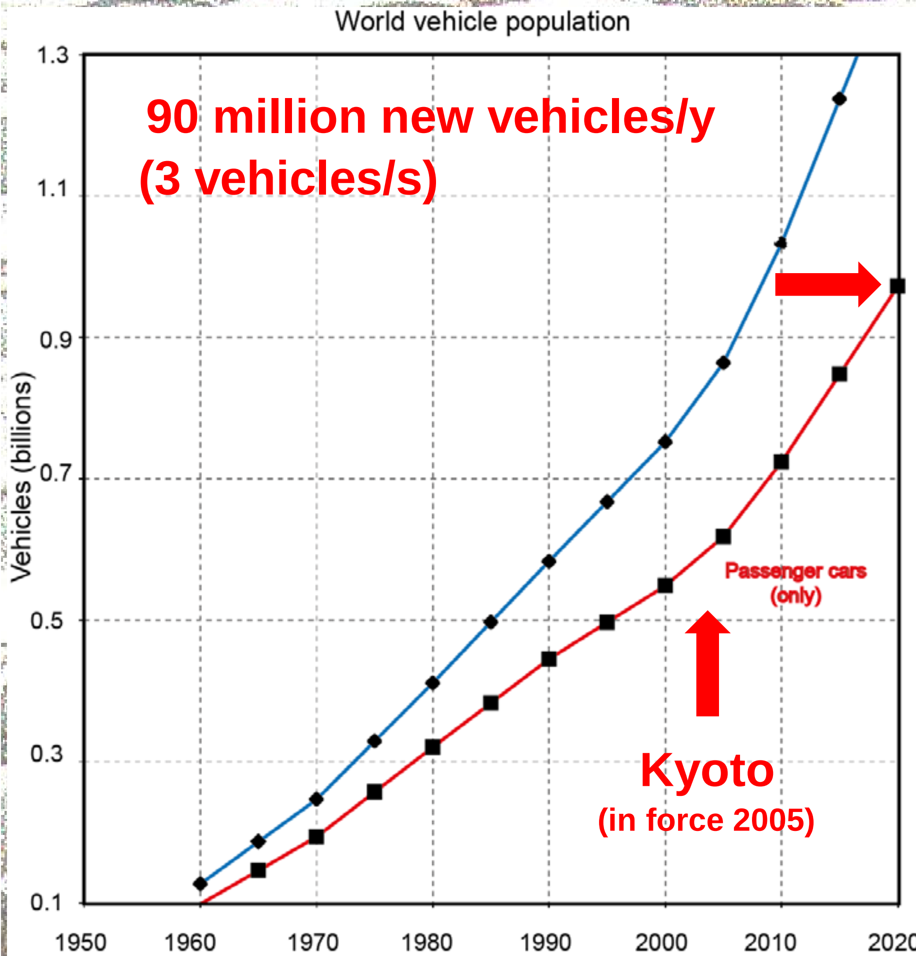
From 0.1 to 1 billion in 60 years

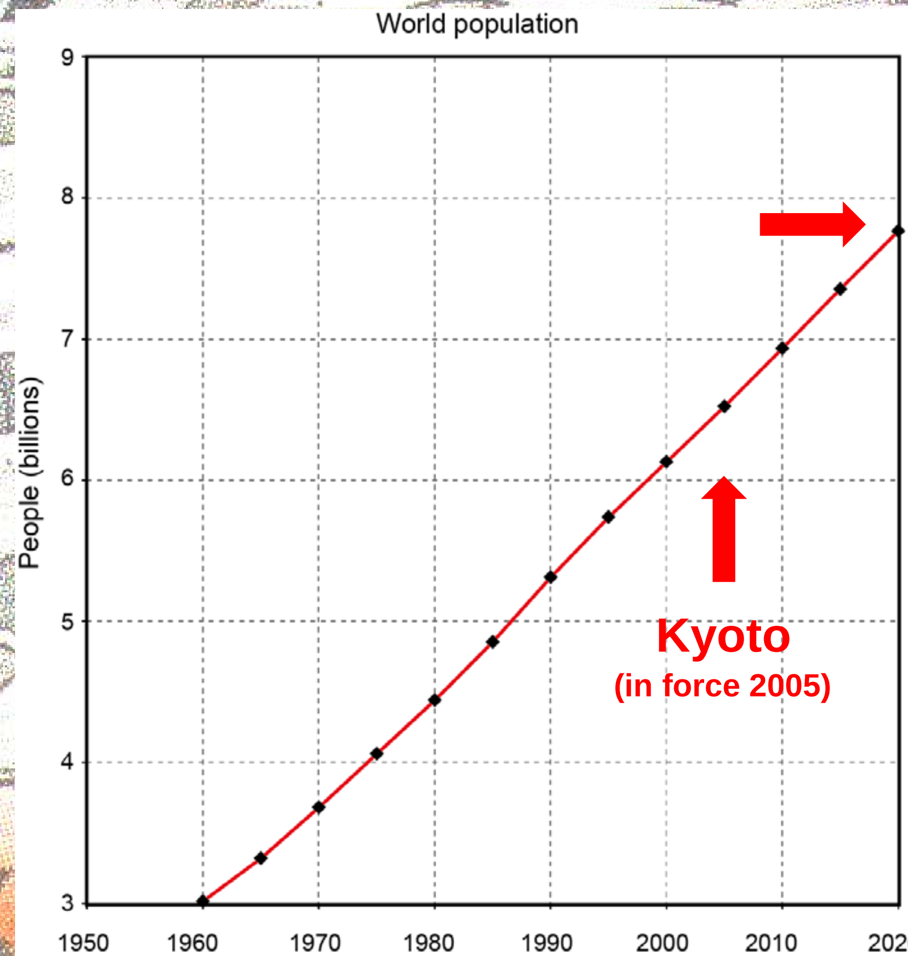
(3800 as I spoke, 86'000 today)

(10 x)

From 3 to 8 billion in 60 years

(3 x)





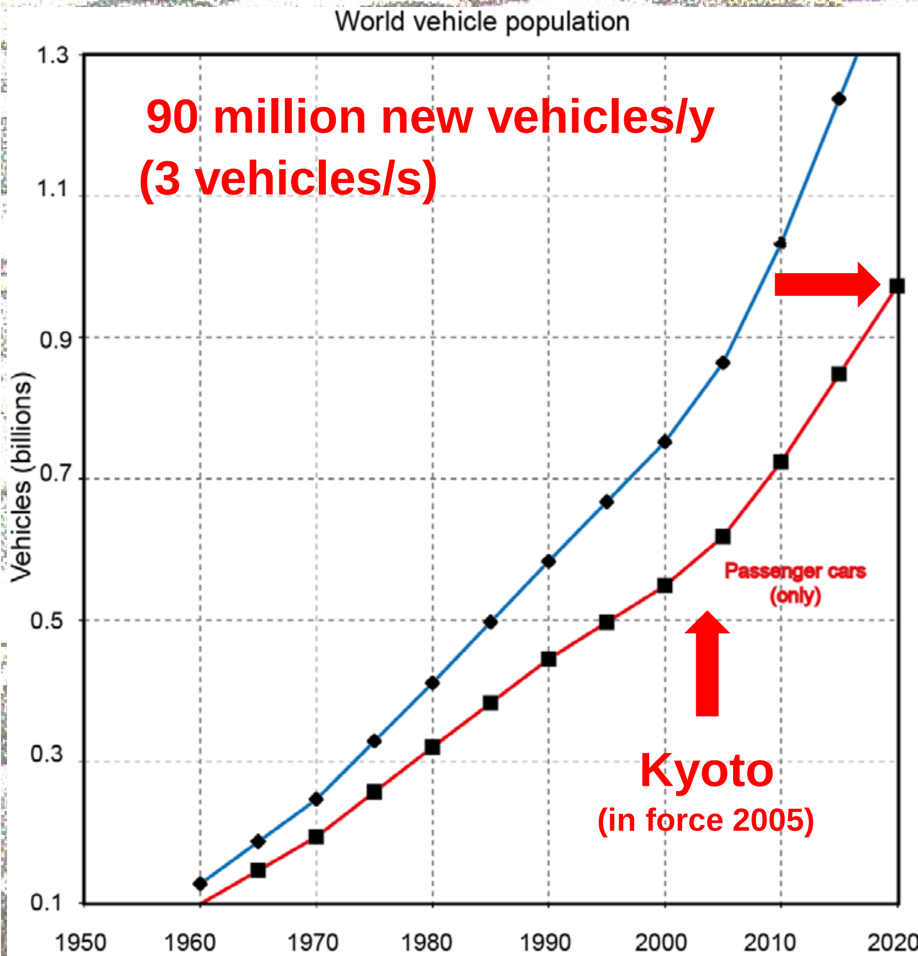
Road vehicles on earth

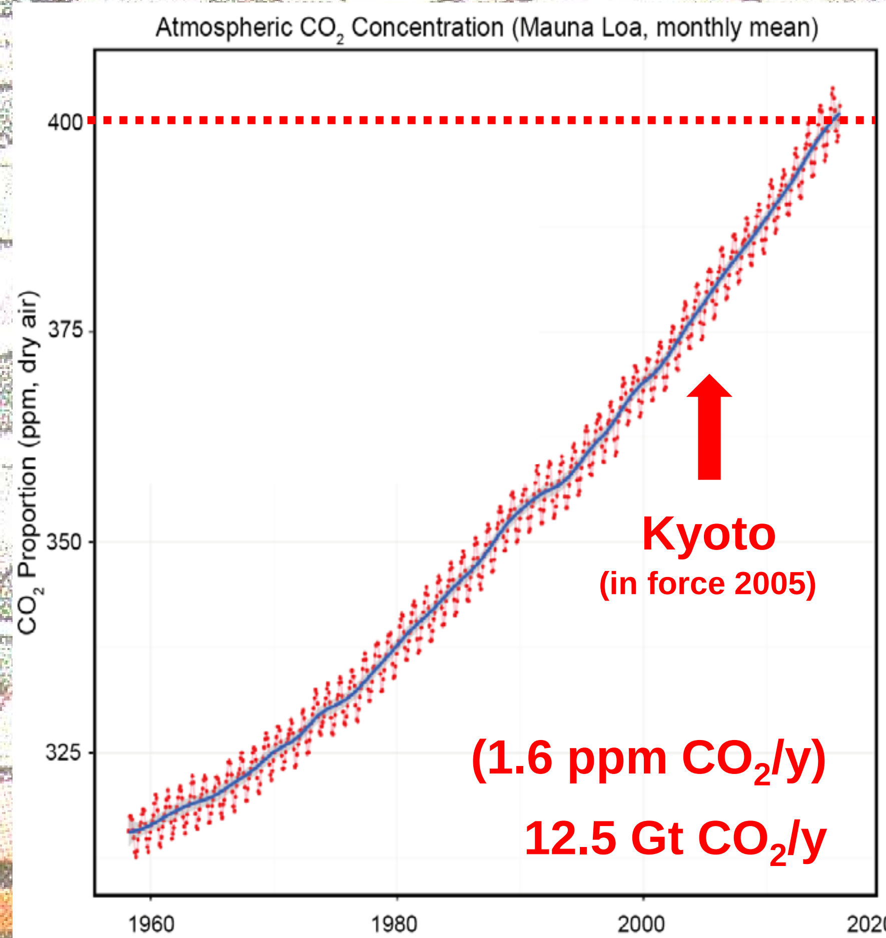
From 0.1 to 1 billion in 60 years

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

(10 x)

From 300 to 400 ppm in 60 years





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

Chemistry-based assessment of combustion exhausts

Combustion of fossil fuels is pure chemistry

The chemistry of fuels — **(What you feed is what you get!)**

The sooting problem — **(Soot is bad news at the nanometer scale)**

Combustion exhaust, ia a toxic cocktail — **(Many ways for intoxication)**

Mass spectrometry is the tool for HAP identification and quantification

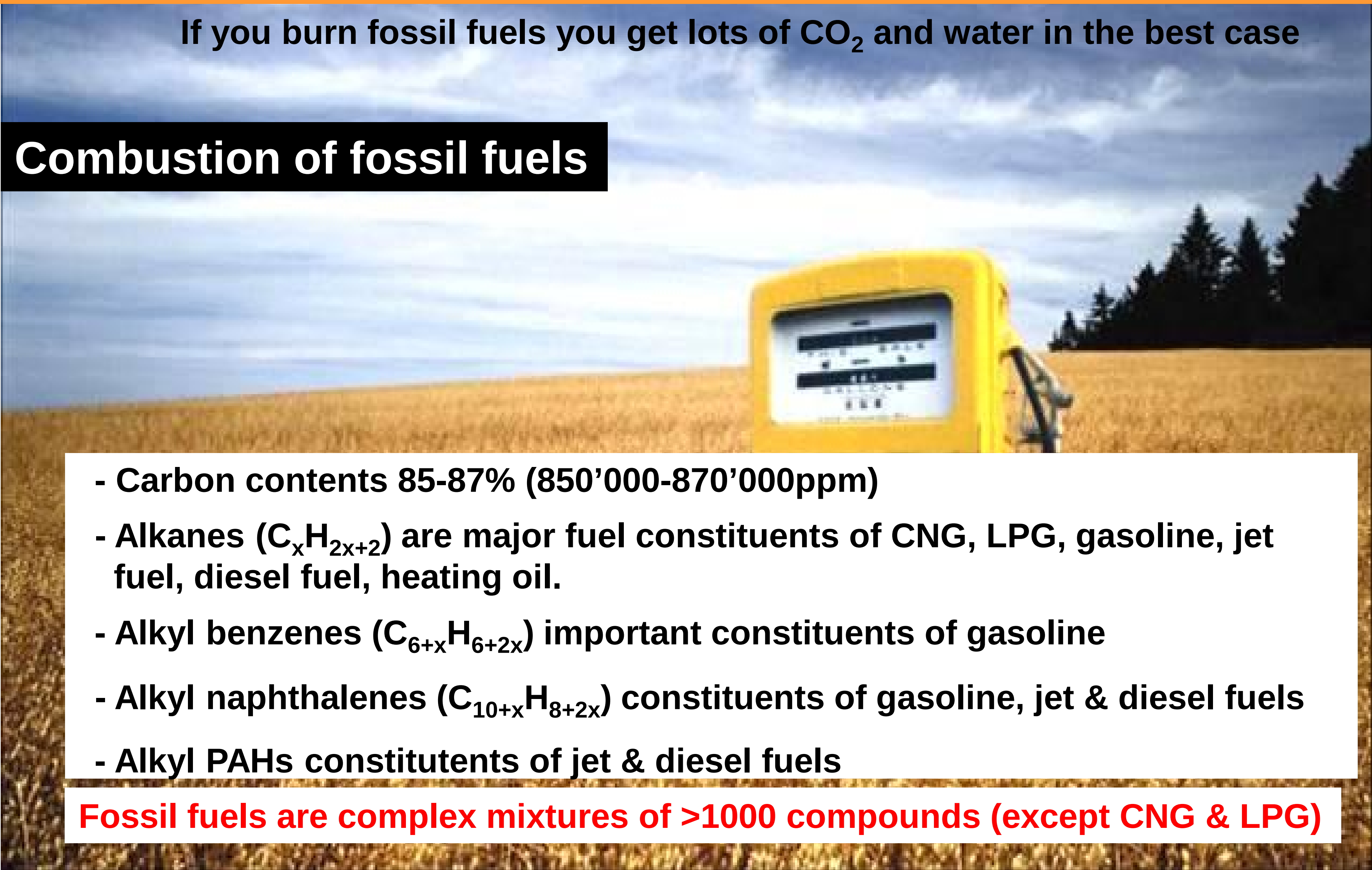
The chemistry of fuels

What you feed is what you get, not one atom is lost!

The chemistry of fuels

If you burn fossil fuels you get lots of CO_2 and water in the best case

Combustion of fossil fuels



- Carbon contents 85-87% (850’000-870’000ppm)
- Alkanes (C_xH_{2x+2}) are major fuel constituents of CNG, LPG, gasoline, jet fuel, diesel fuel, heating oil.
- Alkyl benzenes ($C_{6+x}H_{6+2x}$) important constituents of gasoline
- Alkyl naphthalenes ($C_{10+x}H_{8+2x}$) constituents of gasoline, jet & diesel fuels
- Alkyl PAHs constitutents of jet & diesel fuels

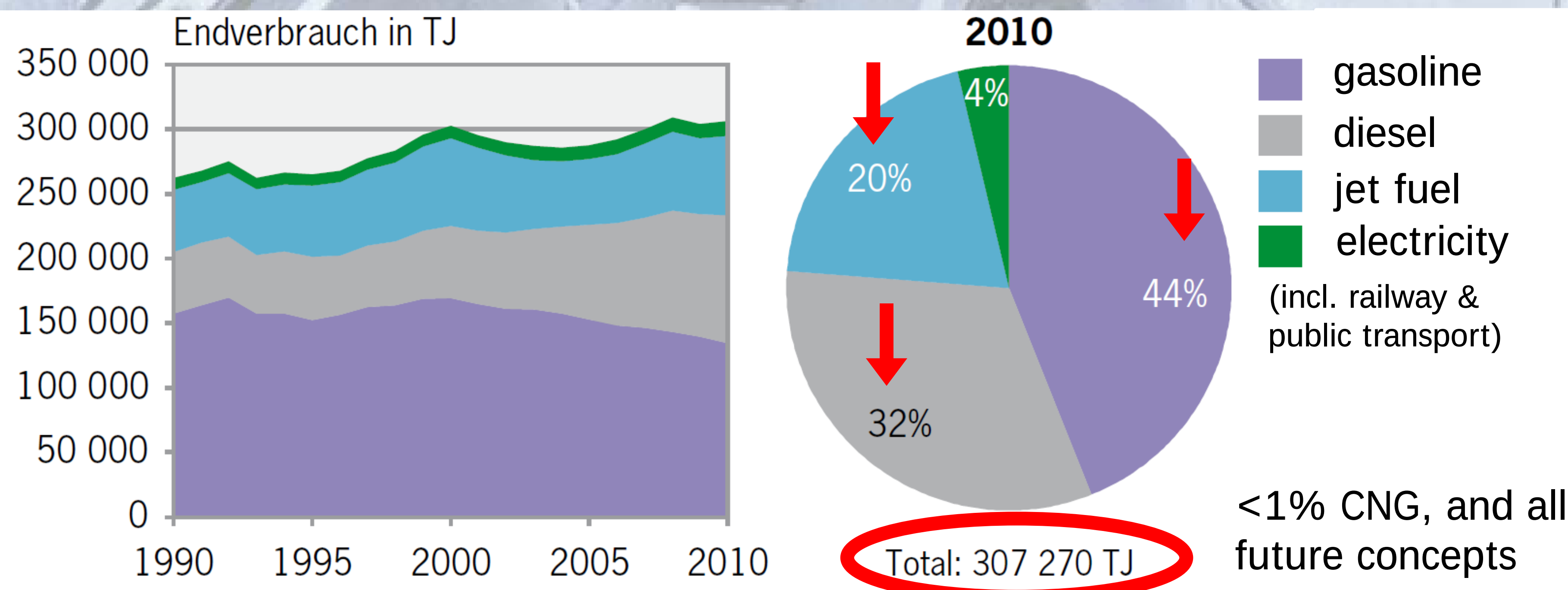
Fossil fuels are complex mixtures of >1000 compounds (except CNG & LPG)

Energy consumption of Swiss traffic

Consumption of gasoline, diesel and jetfuel?

Energy consumption traffic (TJ)

96 % based on fossil fuel!



Traffic accounts for 34% of total Swiss energy consumption(2010)

The chemistry of fuels

If you burn fossil fuels you get lots of CO_2 and water, but stoichiometry matters

Stoichiometric combustion of alkanes:

CH_4	+	2.0	O_2	$\longrightarrow$	1	CO_2	+	2	H_2O
C_2H_6	+	3.5	O_2	$\longrightarrow$	2	CO_2	+	3	H_2O
C_3H_8	+	5.0	O_2	$\longrightarrow$	3	CO_2	+	4	H_2O
C_4H_{10}	+	6.5	O_2	$\longrightarrow$	4	CO_2	+	5	H_2O
C_5H_{12}	+	8.0	O_2	$\longrightarrow$	5	CO_2	+	6	H_2O
C_6H_{14}	+	9.5	O_2	$\longrightarrow$	6	CO_2	+	7	H_2O

$$C_xH_{2x+2} + 1.5x+0.5\ O_2 \longrightarrow x\ CO_2 + x+1\ H_2O$$

The chemistry of fuels

If you burn fossil fuels you get lots of CO_2 and water, but stoichiometry matters

Stoichiometric combustion of alkyl benzenes:

$$C_6H_6 + 7.5\ O_2 \longrightarrow 6\ CO_2 + 3\ H_2O$$

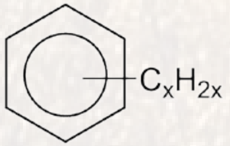
$$C_7H_8 + 9.0\ O_2 \longrightarrow 7\ CO_2 + 4\ H_2O$$

$$C_8H_{10} + 10.5\ O_2 \longrightarrow 8\ CO_2 + 5\ H_2O$$

$$C_9H_{12} + 12.0\ O_2 \longrightarrow 9\ CO_2 + 6\ H_2O$$

$$C_{10}H_{14} + 13.5\ O_2 \longrightarrow 10\ CO_2 + 7\ H_2O$$

$$C_{11}H_{16} + 15.0\ O_2 \longrightarrow 11\ CO_2 + 8\ H_2O$$



$$C_{6+x}H_{6+2x} + 1.5x+7.5\ O_2 \longrightarrow 6+x\ CO_2 + 3+x\ H_2O$$

The chemistry of fuels

If you burn fossil fuels you get lots of CO_2 and water, but stoichiometry matters

Stoichiometric combustion of alkyl naphthalenes:

$$C_{10}H_8 + 12.0\ O_2 \longrightarrow 10\ CO_2 + 4\ H_2O$$

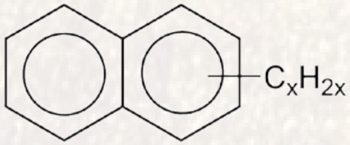
$$C_{11}H_{10} + 13.5\ O_2 \longrightarrow 11\ CO_2 + 5\ H_2O$$

$$C_{12}H_{12} + 15\ O_2 \longrightarrow 12\ CO_2 + 6\ H_2O$$

$$C_{13}H_{14} + 16.5\ O_2 \longrightarrow 13\ CO_2 + 7\ H_2O$$

$$C_{14}H_{16} + 18.0\ O_2 \longrightarrow 14\ CO_2 + 8\ H_2O$$

$$C_{15}H_{18} + 19.5\ O_2 \longrightarrow 15\ CO_2 + 9\ H_2O$$

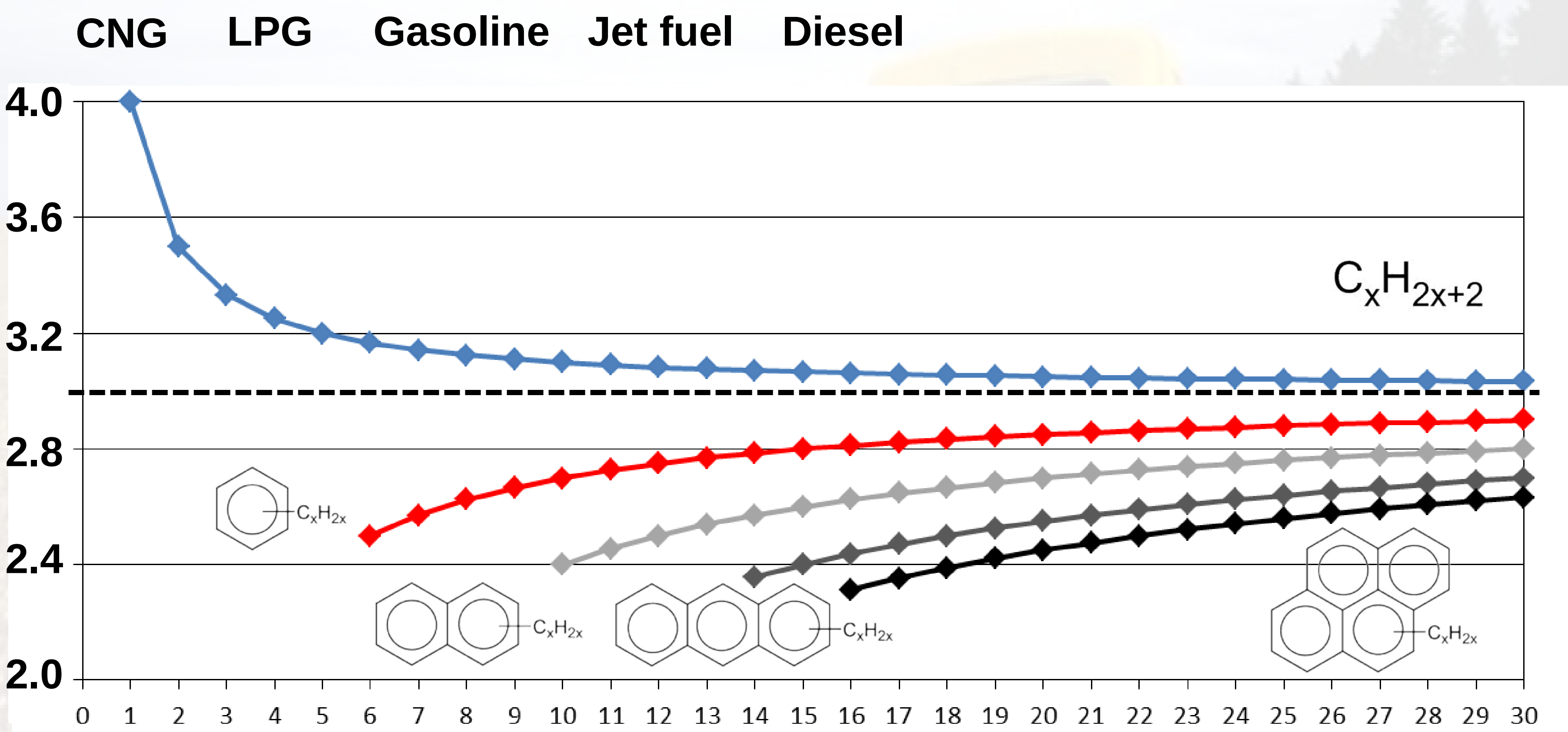


$$C_{10+x}H_{8+2x} + 1.5x+12\ O_2 \longrightarrow 10+x\ CO_2 + 4+x\ H_2O$$

The chemistry of fuels

If you burn mixtures, stoichiometric combustion is difficult to maintain!

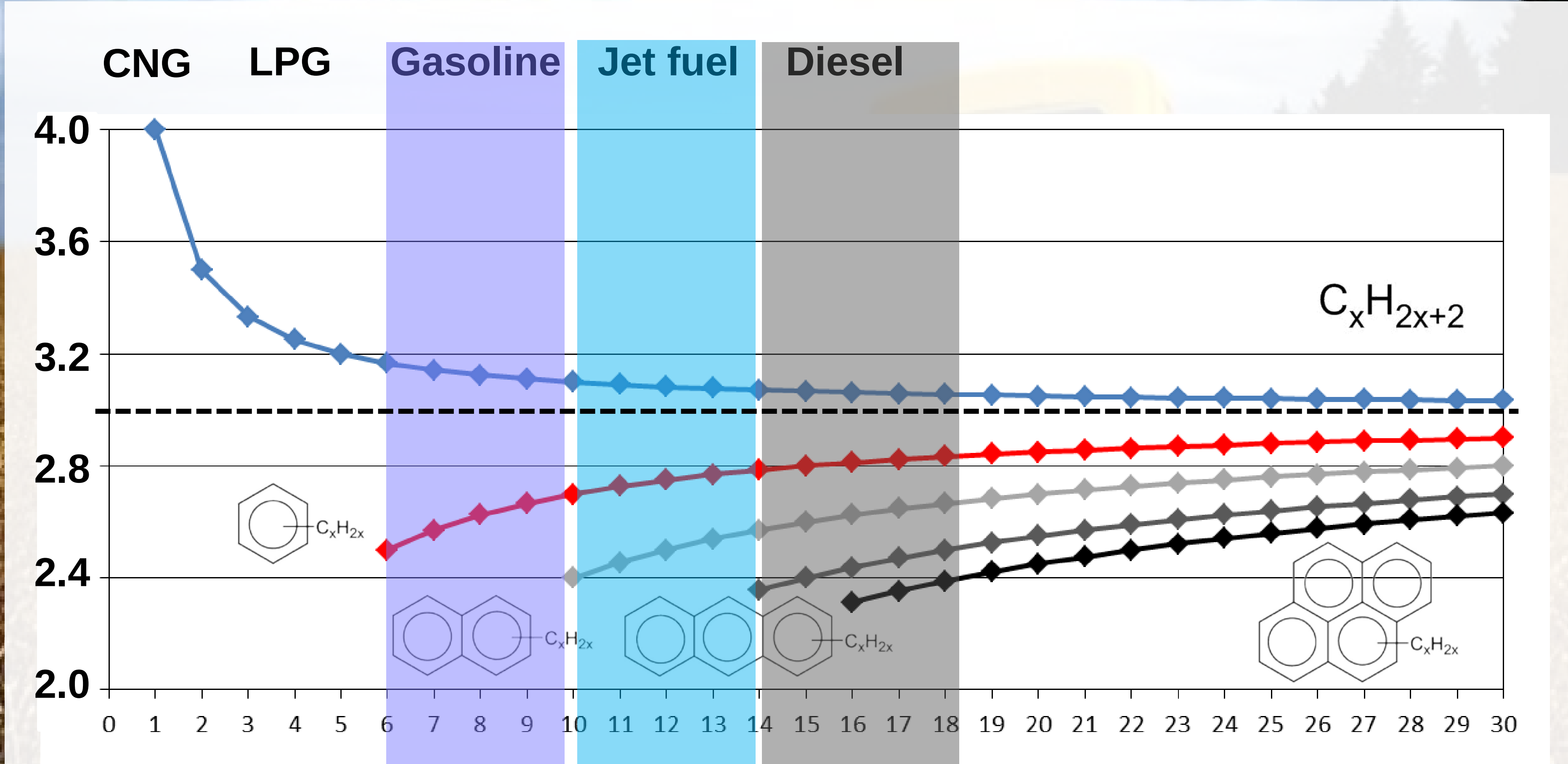
Oxygen to carbon ratio (O/C):



The chemistry of fuels

Sub-stoichiometric combustion results in sooting!

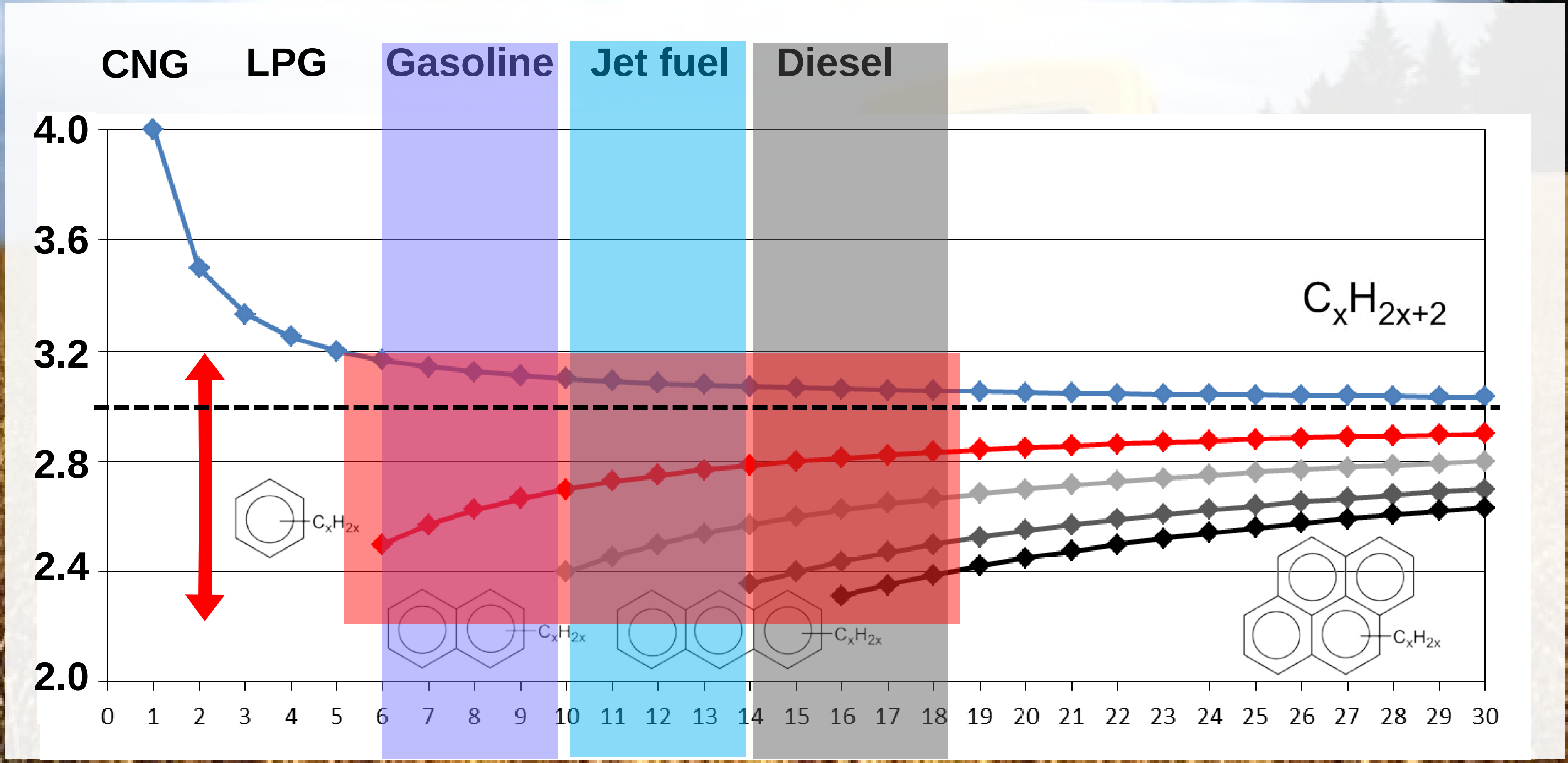
Oxygen to carbon ratio (O/C):



The chemistry of fuels

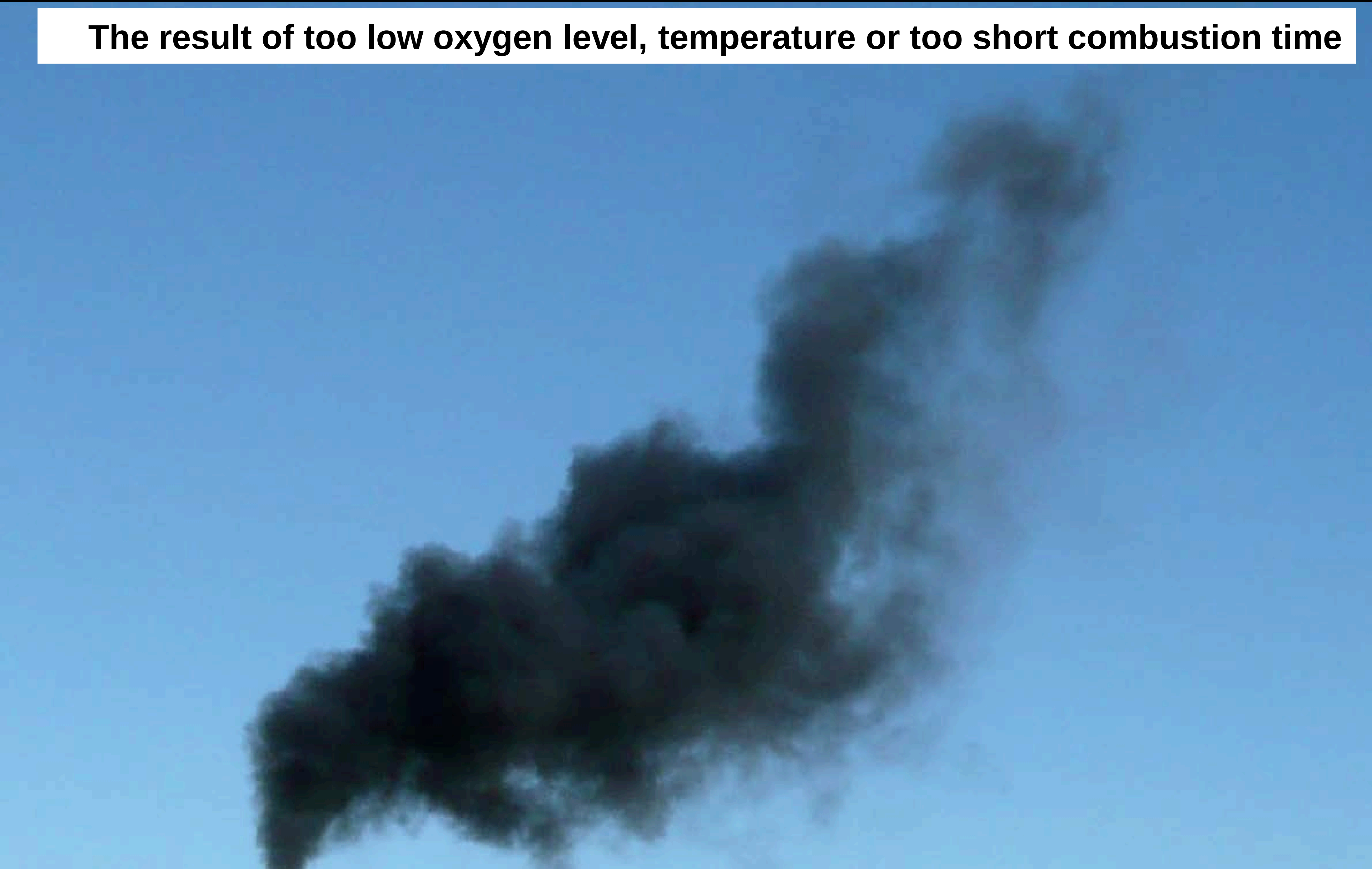
If you burn mixtures, stoichiometric combustion is difficult to maintain!

Oxygen to carbon ratio (O/C):



The sooting problem

The result of too low oxygen level, temperature or too short combustion time



The sooting problem of diesel engines

The result of too low oxygen level, temperature or too short combustion time

The sooting problem of GDI vehicles

GDI fleet properties: Mean GDI fleet (n=7)

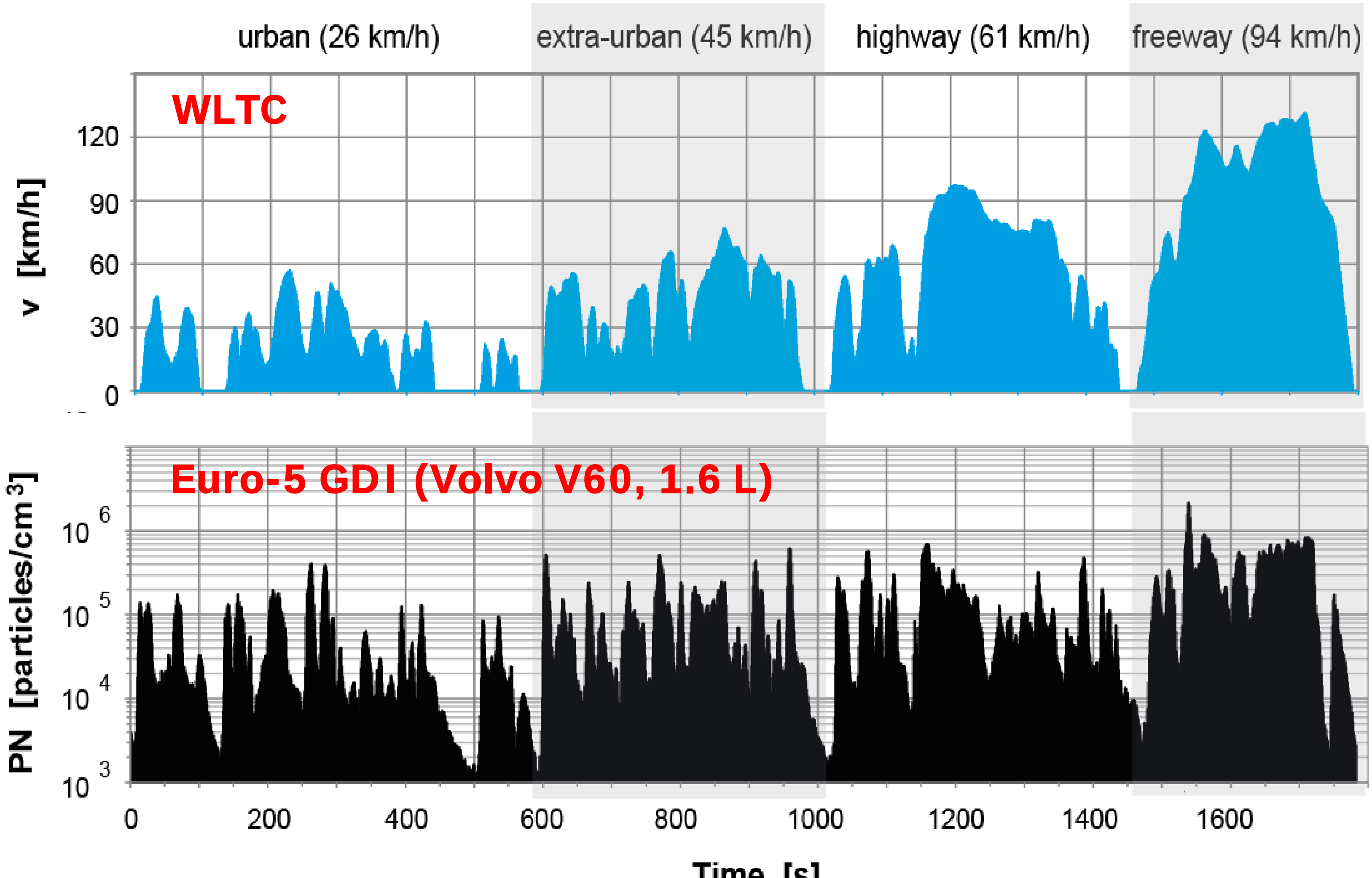
GDI-1:	**Mitsubishi Carisma (1.8 L)**	**Euro-3**
GDI-2:	**VW Golf (1.4 L)**	**Euro-4**
GDI-3:	**Opel Insignia (1.6)**	**Euro-5**
GDI-4:	**Volvo V60 T4F (1.6 L)**	**Euro-5**
GDI-5:	**Opel Zafira (1.6 L)**	**Euro-5**
GDI-6:	**Citroën C4 Cactus (1.2 L)**	**Euro-6**
GDI-7:	**VW Golf VII (1.4 L)**	**Euro-6**

Diesel benchmark (with DOC+DPF, EGR)

DI:	**Peugeot 4008 (1.6 L)**	**Euro-5**

The sooting problem of GDI vehicles

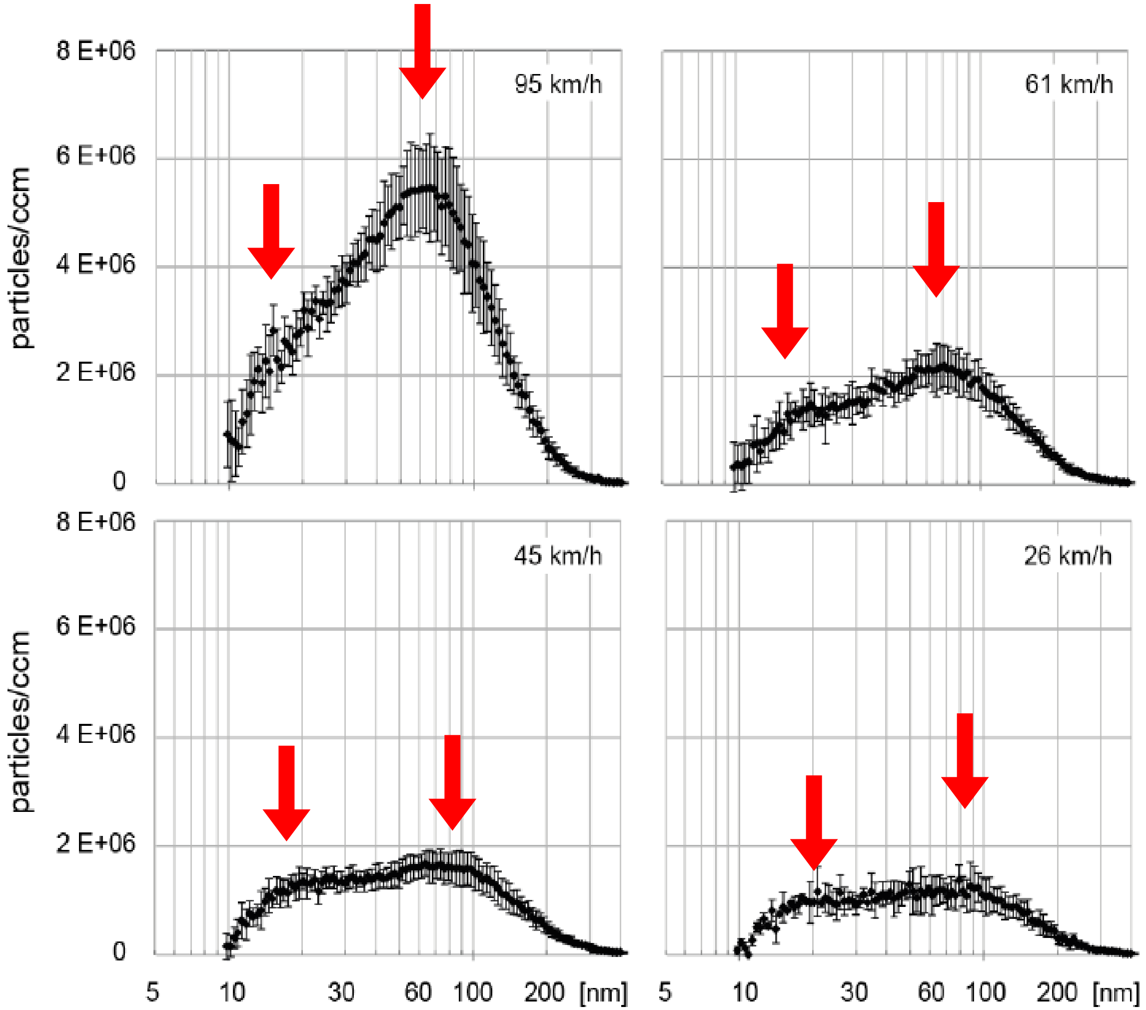
Each transient induces the release of nanoparticles



Nanoparticle emissions of GDI vehicles

GDI particles indeed are nanoparticles of 10-200 nm

- **GDI particles are nano!**
- **Bimodal distribution**
- **Maxima at 20 & 80nm**



Millions of new «sooting stars» are born every year now!

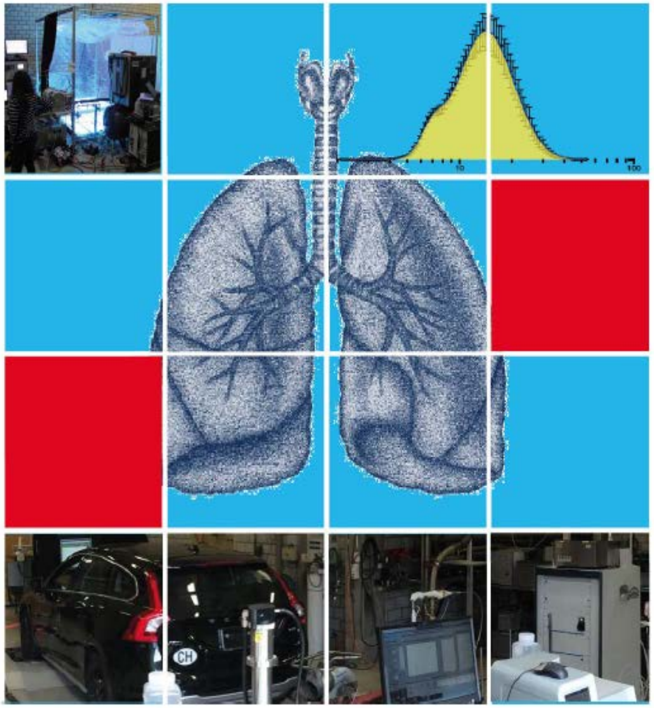
Nanoparticle emissions of GDI vehicles

Europe is flooded with soot nanoparticles of GDI vehicles

GDI vehicles on the rise

- 53 mio GDI vehicles in Europe (2010-2020)
- 30% of the EU fleet will be GDI in 2020

GDI vehicles, on average, release:
700 x more nanoparticles
and 17 x more genotoxic PAHs
than a Euro-5 diesel vehicle with DPF!


GASOMEP: Current Status and New Concepts of **Gas**oline Vehicle Emission Control for **O**rganic, **Me**tallic and **P**articulate Non-Legislative Pollutants

Authors: P. Comte, J. Czerwinski, A. Keller, N. Kumar, M. Muñoz, S. Pieber, A. Prévôt, A. Wichser, N. Heeb

Before you buy a GDI vehicle, please read the GASOMEP report (https://www.empa.ch/web/s604/soot-particles-from-gdi)

Combustion exhausts are toxic cocktails

Many ways to get intoxicated, mostly chronic diseases, only CO kills quickly

Acute toxicity: - CO, reactive nitrogen compounds (RNCs)

Chronic toxicity: - oxidative stress
- inflammation
- chronic obstructive pulmonary disease

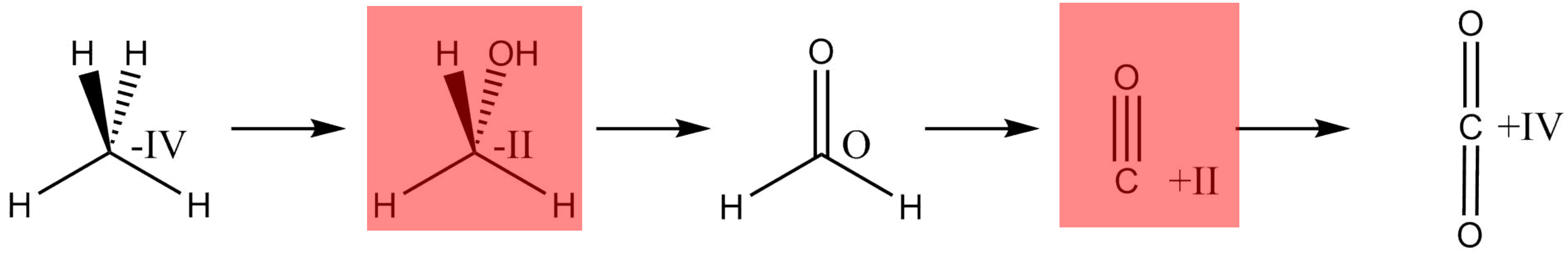
Genotoxicity: - mutations
- cancer

How toxic are combustion exhausts, what can chemical analysis tell us?

Adverse health effects of combustion exhausts

The simple oxidation of methane can lead several toxic intermediates

Problem: Acute toxicity



non-reactive (persistent)
green house gas
($56 \times CO_2$ in 20 years)

acute toxic
blindness, death
future syn-fuel?

acute toxic
irritant, neurotoxic
genotoxic
class B1 carcinogen

acute toxic
12800 ppm deathly

non-reactive
green house gas

Adverse health effects of combustion exhausts

CO limit 1000 mg/km for gasoline vehicles results in ~1300 mg/m^3 exhaust

Problem: CO intoxication

ppm (mg/m^3)	
35 (44)	- headache, dizziness in 6-8 h
100 (125)	- headache, dizziness in 2-3 h
200 (250)	- headache, dizziness in 2-3 h, loss of judgment
400 (500)	- frontal headache, in 1-2 h
800 (1000)	- dizziness, nausea, convulsion in 45 min in 6 h
1600 (2000)	- dizziness, nausea in 20 min, death <2h
3200 (4000)	- dizziness, nausea in <10 min, death <30 min
6400 (8000)	- dizziness, convulsion, respiratory arrest, death <20 min
12800 (16000)	- unconsciousness after 3 breath, death <3 min

2x

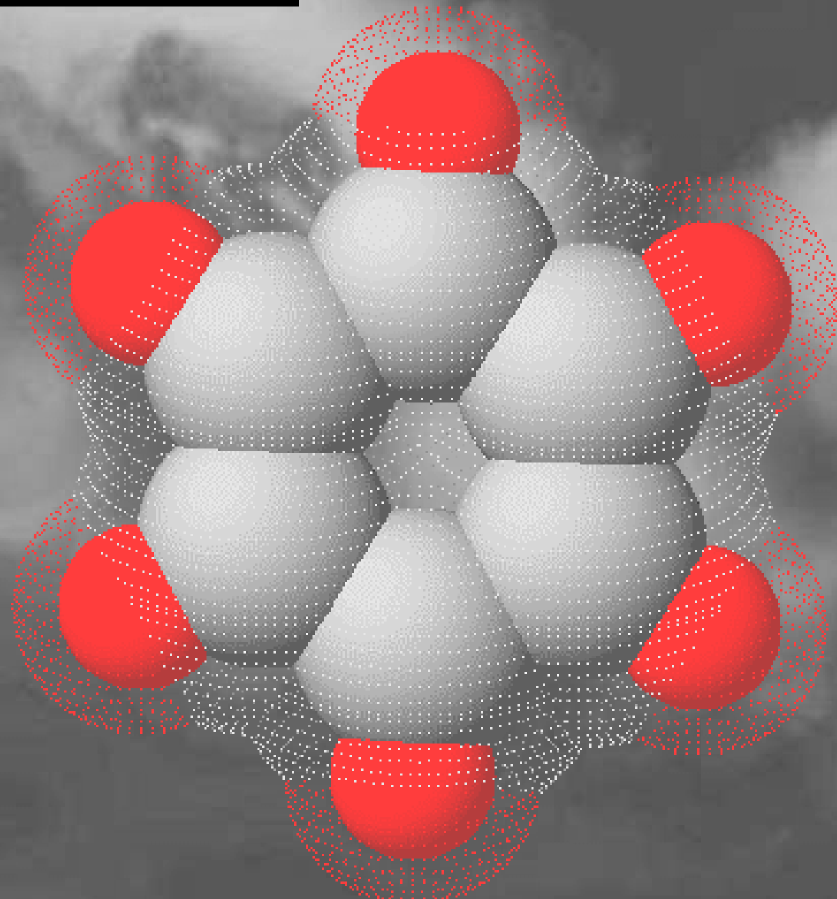
Euro-4,-5,-6 1000 mg/km

Euro-2 2200 mg/km

Adverse health effects of combustion exhausts

Benzene, carcinogenic fuel and exhaust constitutent

Problem: benzene toxicity

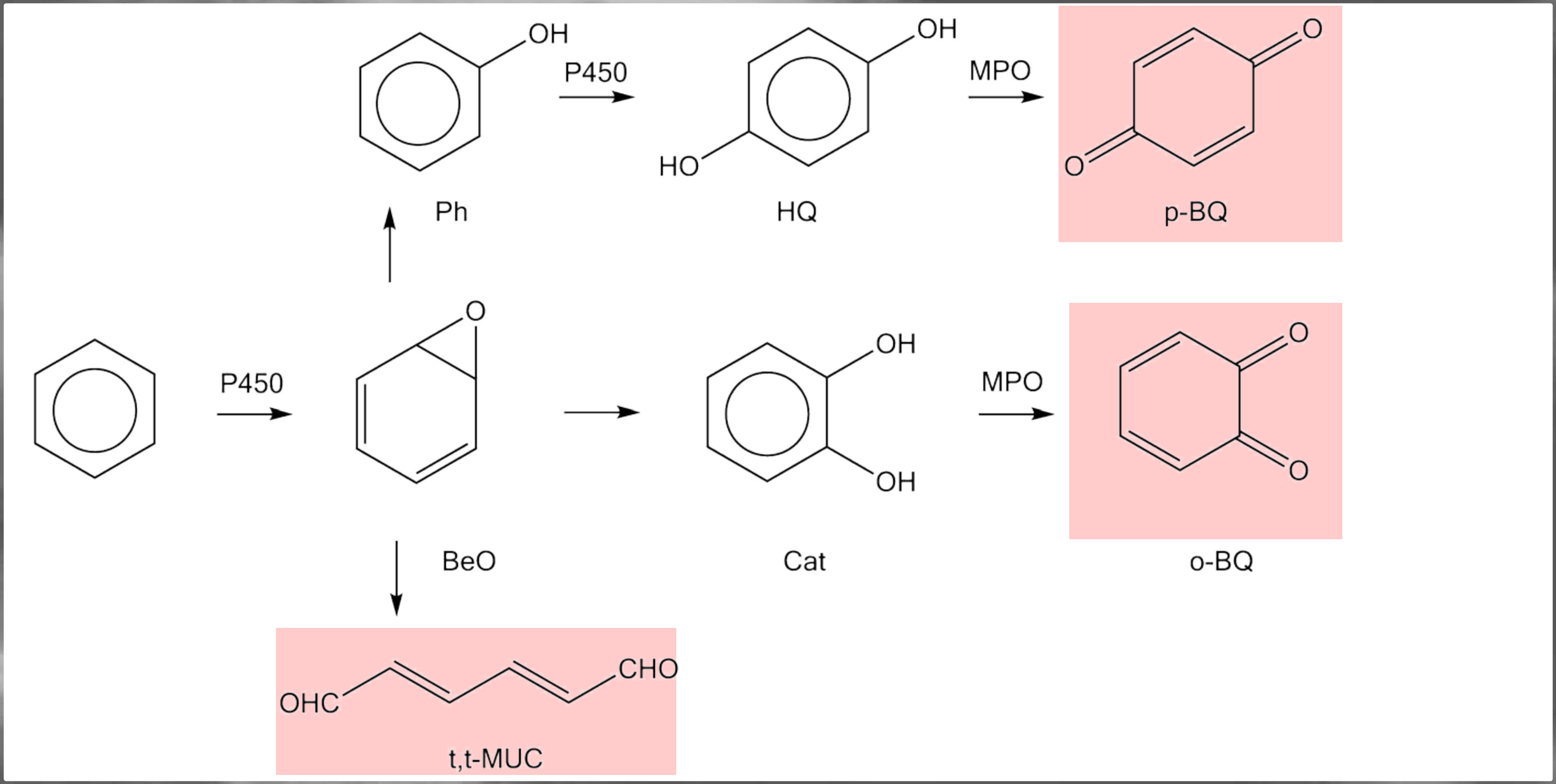


Ambient air EU limit Jan. 1st, 2010, 1 µg benzene/m^3

Adverse health effects of combustion exhausts

Metabolic activation leads to several toxic and reactive intermediates

Benzene activation with human myeloperoxidase (MPO):

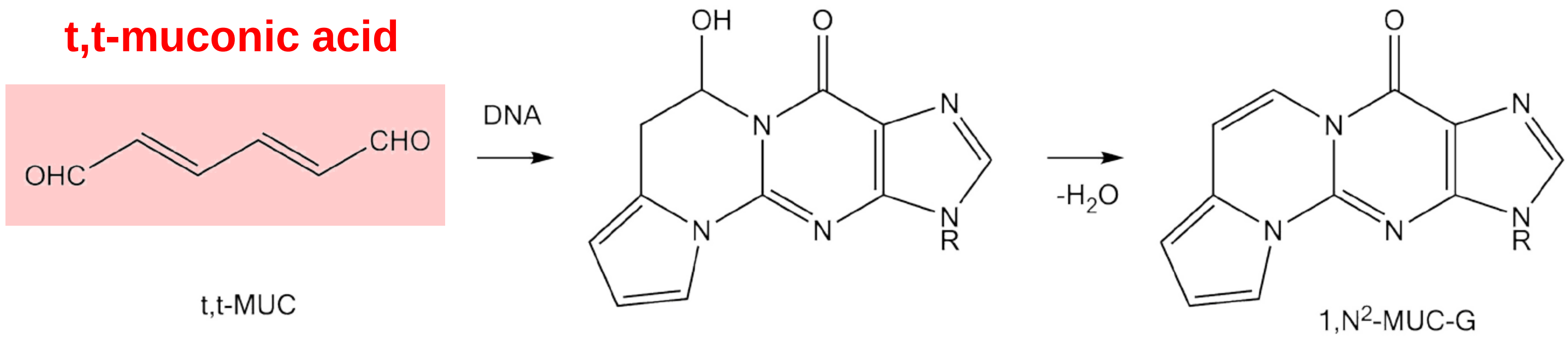


Hang B. J. Nucleic Acids. **2010**, 1-29, doi:10.4061/2010/709521

Adverse health effects of combustion exhausts

Metabolic activation leads to reactive intermediates and DNA adducts

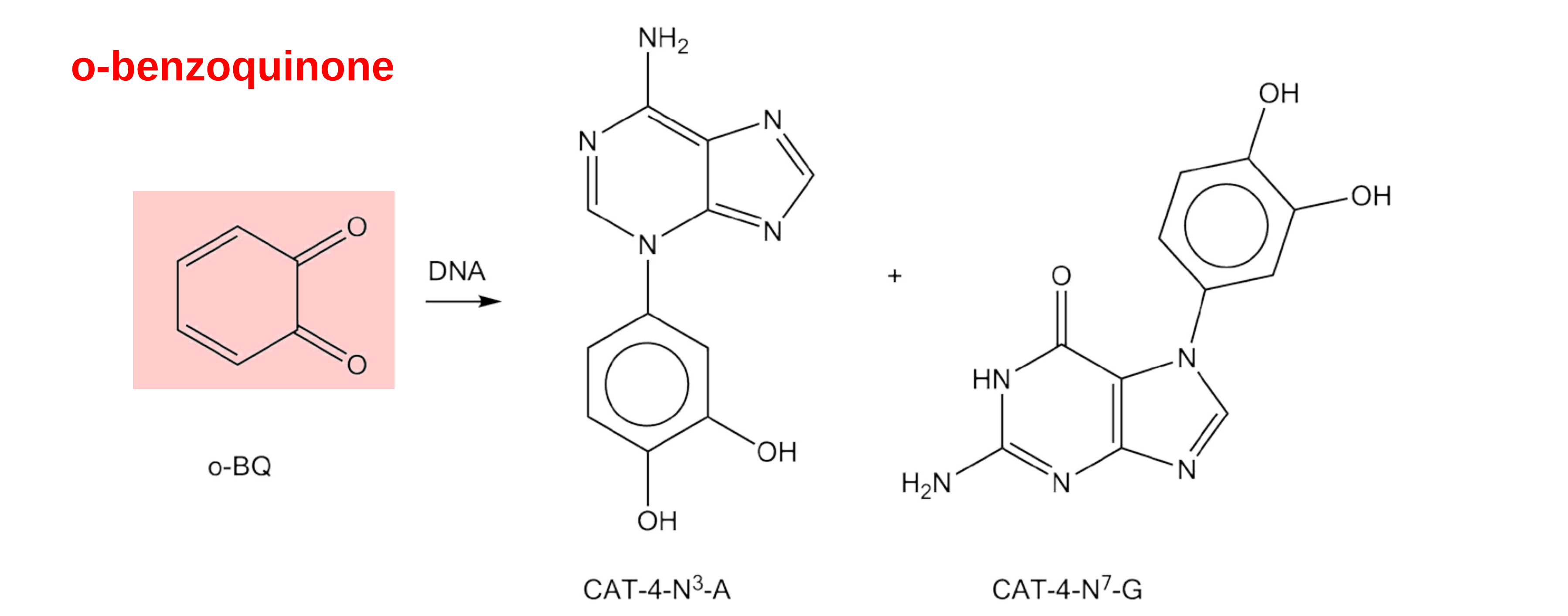
DNA adducts from activated benzene metabolites:



Adverse health effects of combustion exhausts

Metabolic activation leads to reactive intermediates and DNA adducts

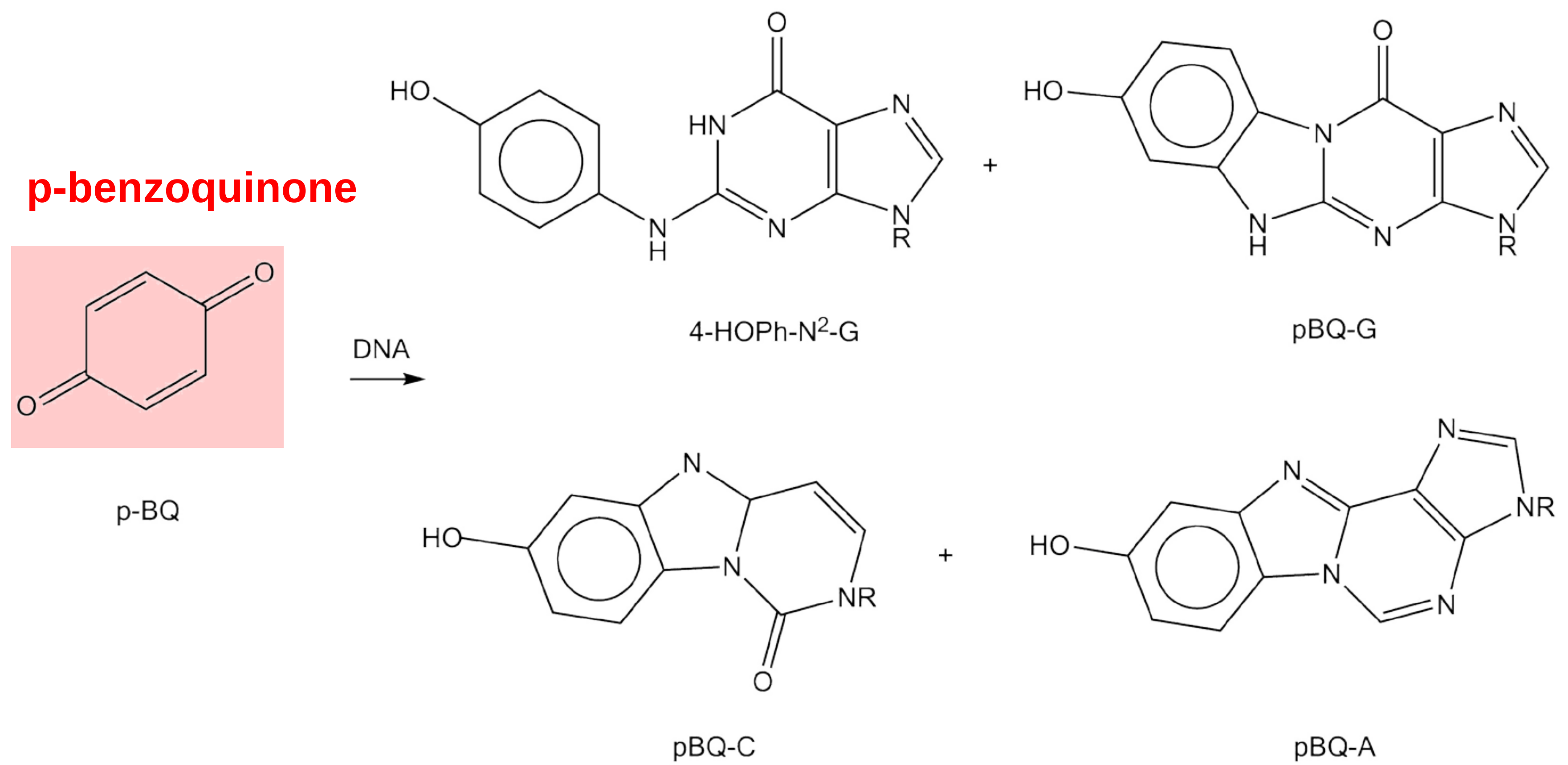
DNA adducts from activated benzene metabolites:



Adverse health effects of combustion exhausts

Metabolic activation leads to reactive intermediates and DNA adducts

DNA adducts from activated benzene metabolites:



Adverse health effects of combustion exhausts

1 precursor, 3 reactive metabolites, 9 DNA adducts

DNA adducts from activated benzene metabolites:

1 precursor

↓

3 metabolites

↓

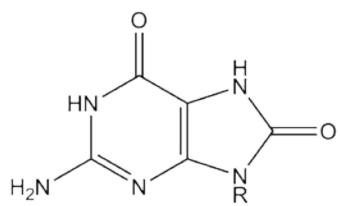
9 DNA adducts to be repaired

↓

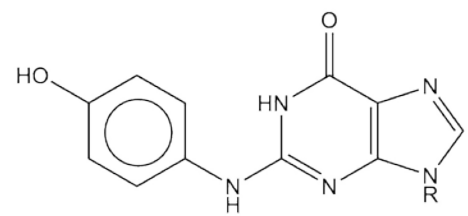
mutagenesis

↓

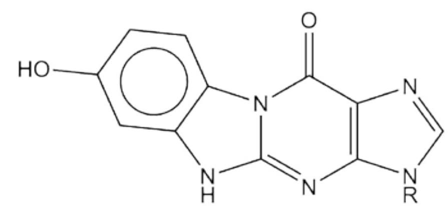
leukemia



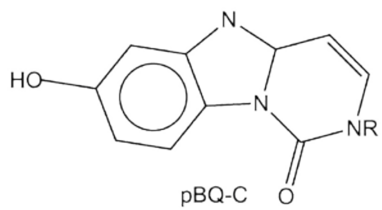
8-Oxo-G



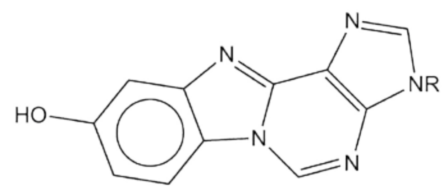
4-HOPh-N^2-G



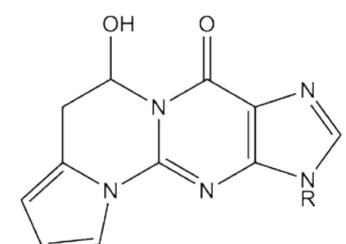
pBQ-G

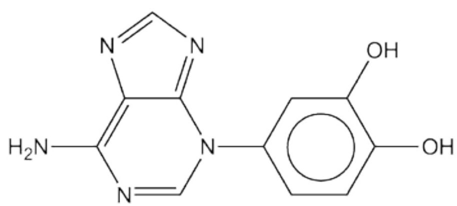


pBQ-C

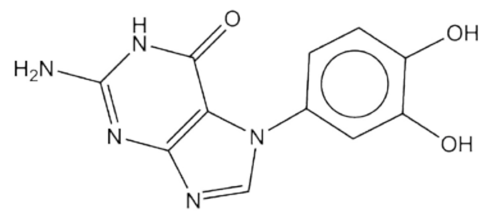


pBQ-A

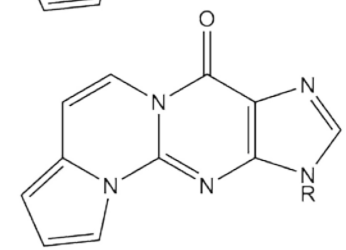




CAT-4-N^3-A



CAT-4-N^7-G

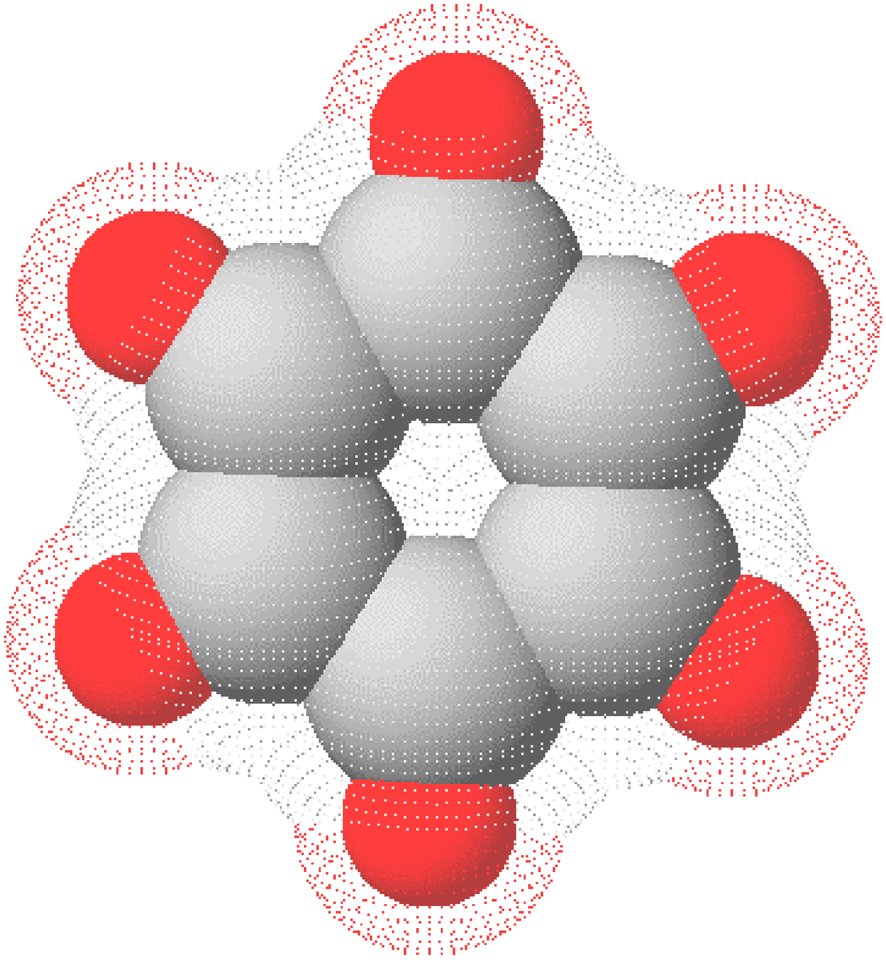


1,N^2-MUC-G

Adverse health effects of combustion exhausts

The good thing about benzene - it is volatile, you might be able to exhale it!

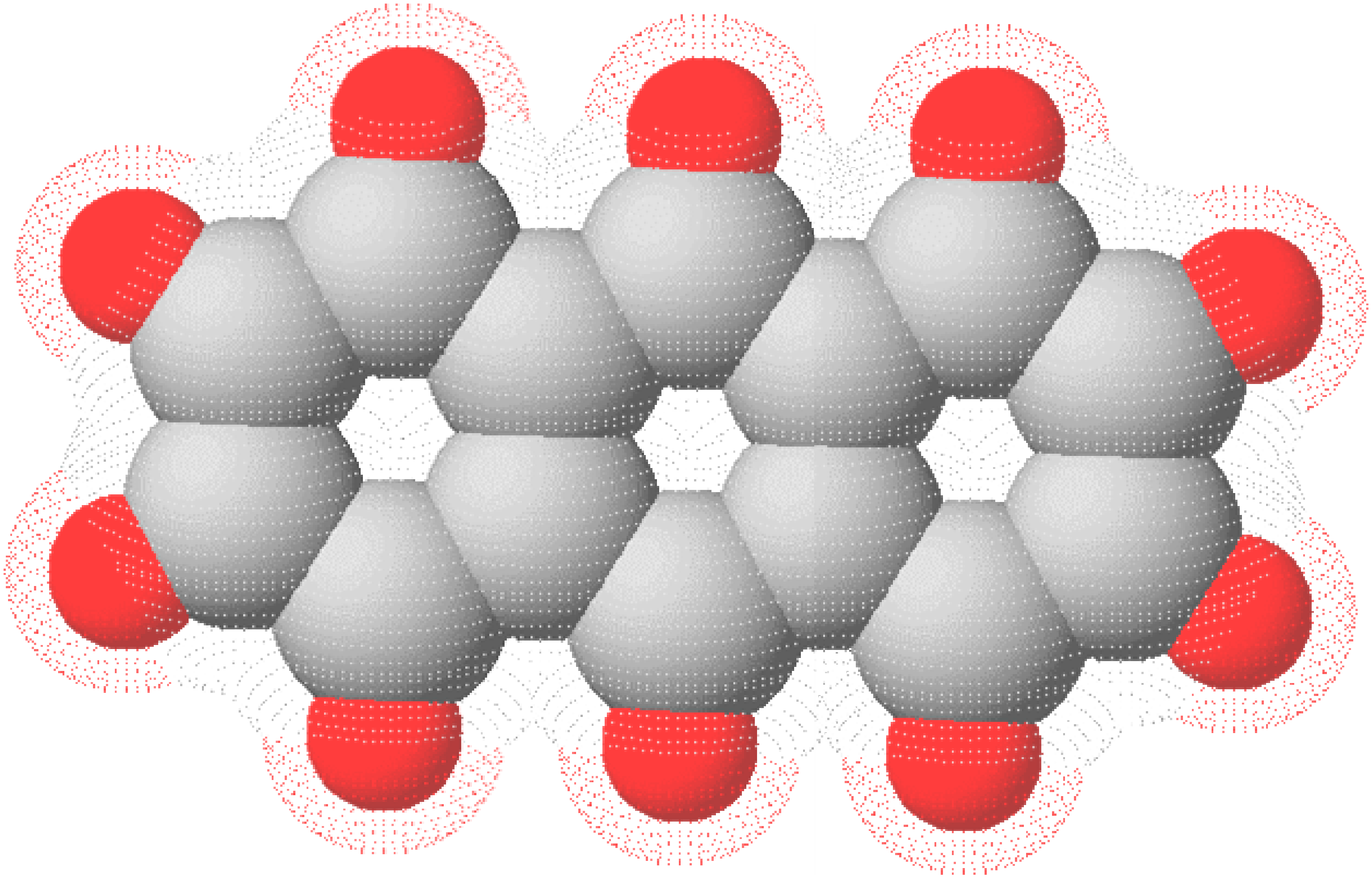
Problem: benzene intoxication



Adverse health effects of combustion exhausts

The bad thing about PAHs - you can't exhale them if they are bound to particles!

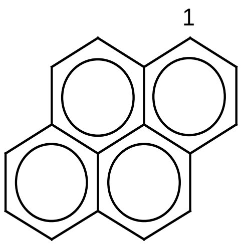
Problem: anthracene toxicity



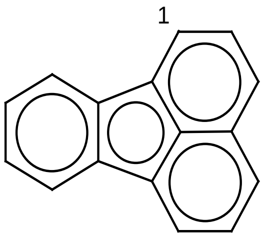
Genotoxic PAHs

Several PAHs are carcinogenic according to the WHO

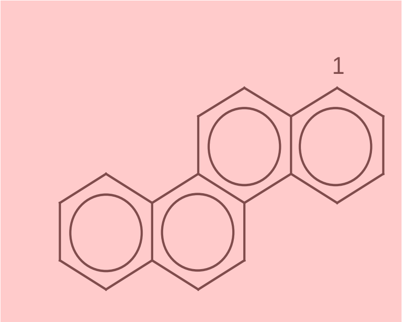
Carcinogenic PAHs



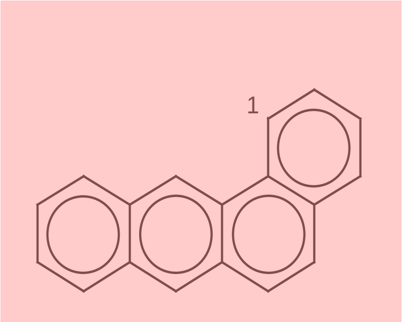
Pyrene



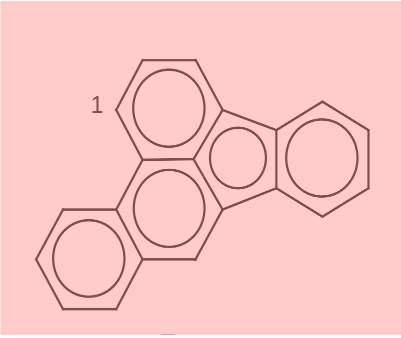
Fluoranthene



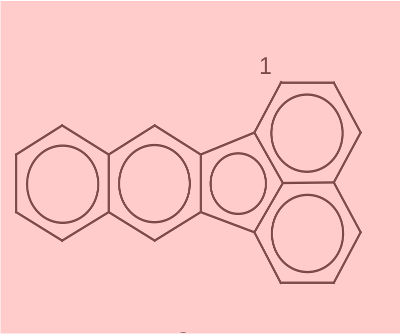
Chrysene



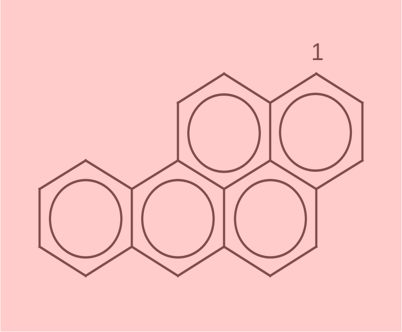
Benz(a)anthracene



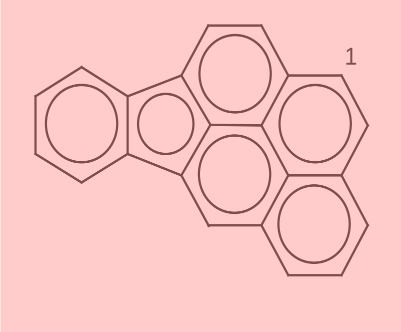
Benzo[b]-
fluoranthene



Benzo[k]-
fluoranthene



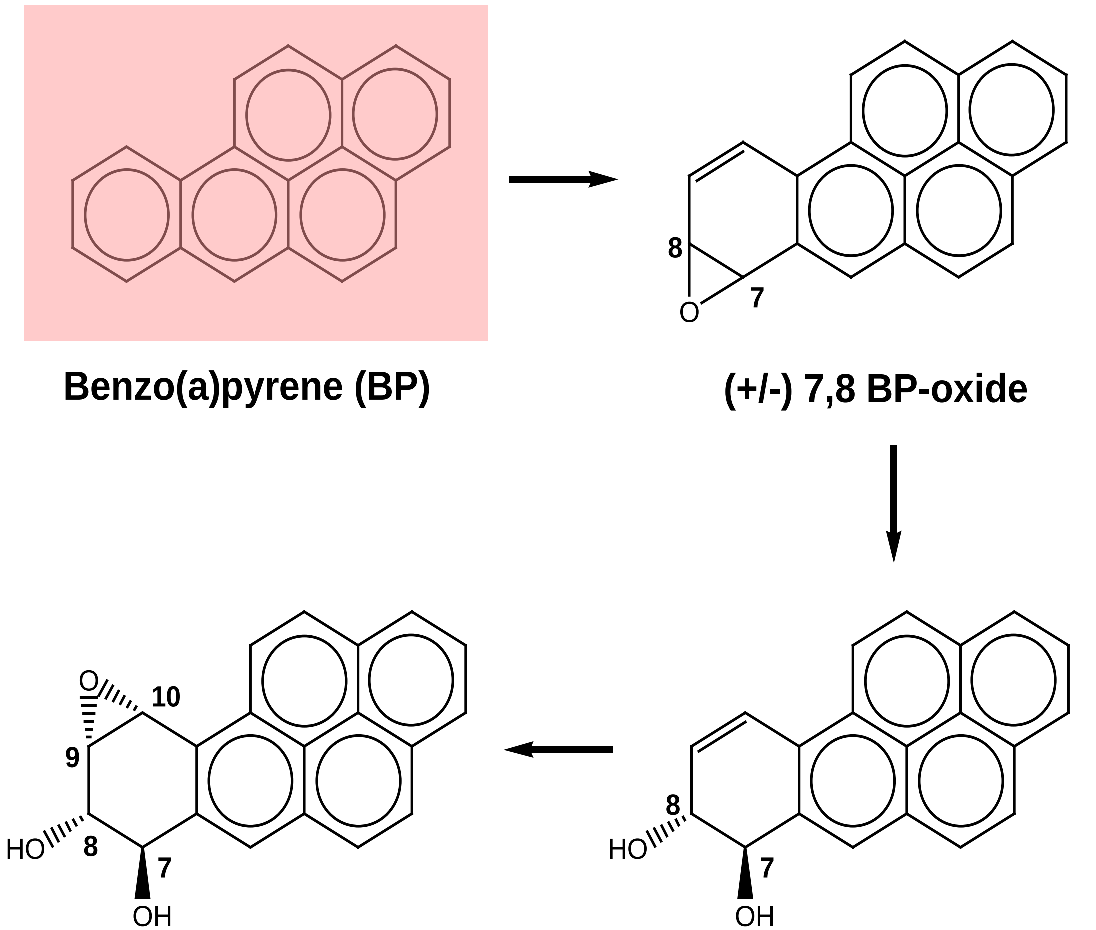
Benzo[a]-
pyrene



Indeno(1,2,3-cd)-
pyrene

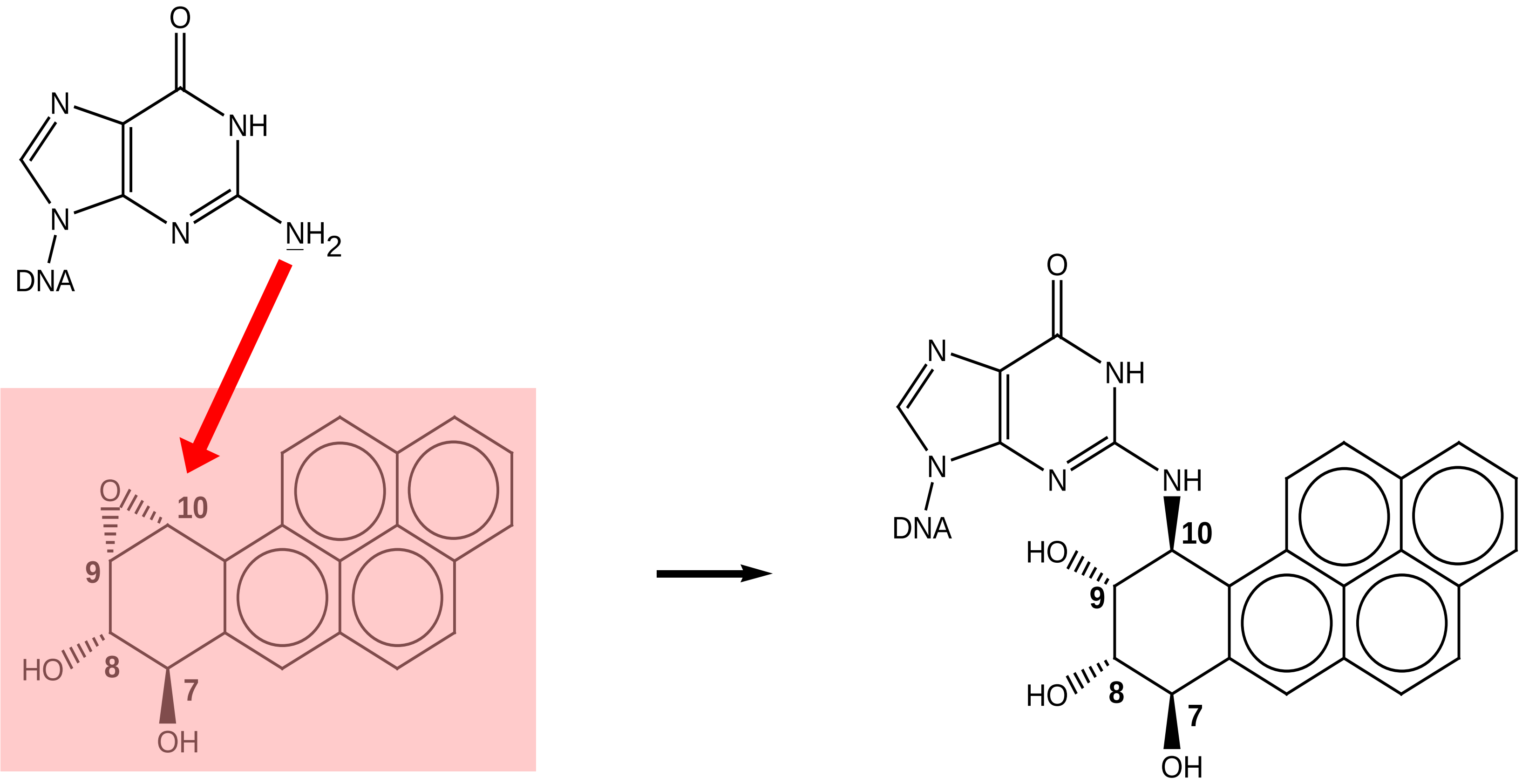
Carcinogenesis from benzo(a)pyrene

Oxidative metabolic activation of benzo(a)pyrene



Carcinogenesis from benzo(a)pyrene

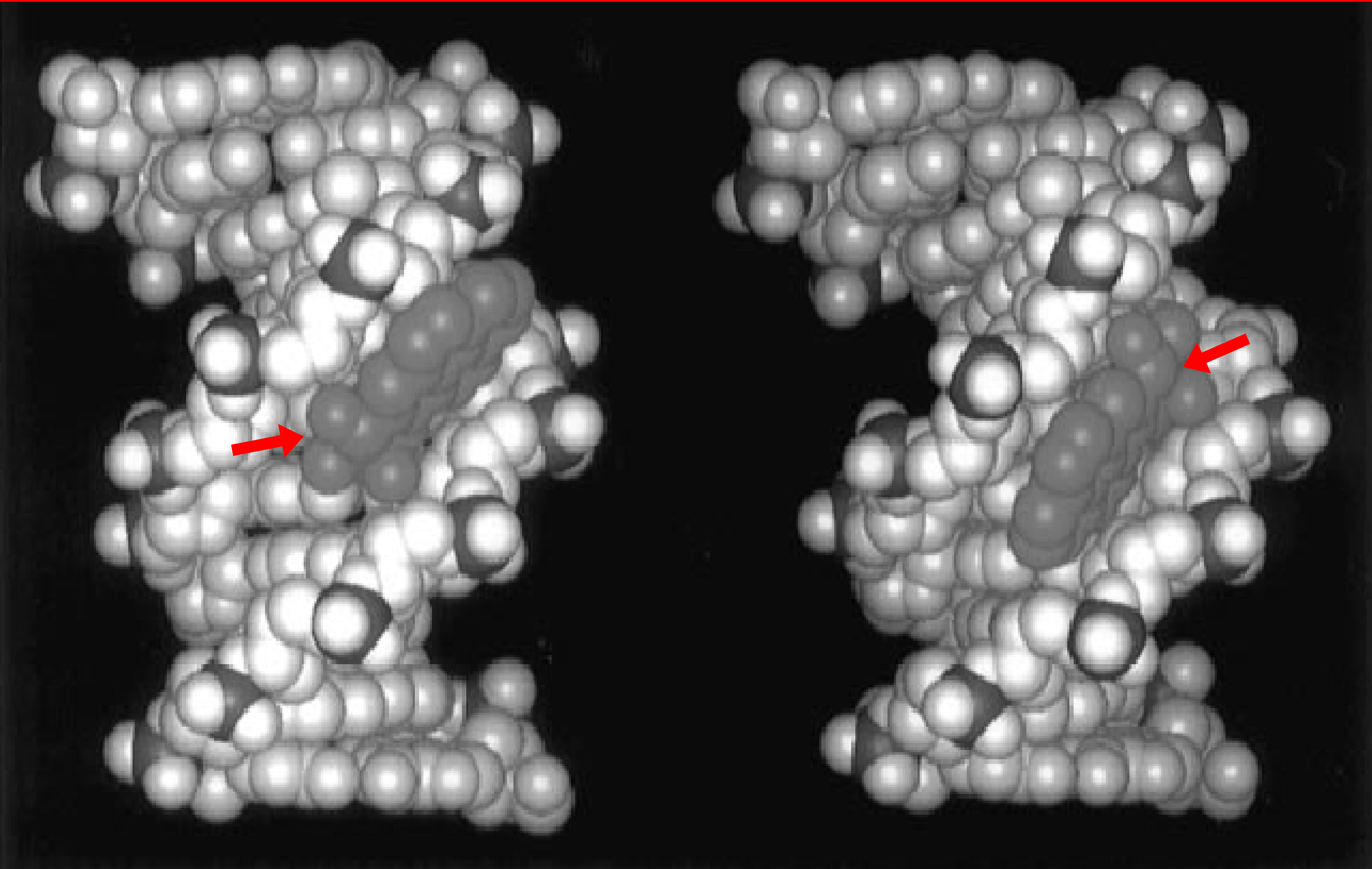
Stereoselective formation of benzo(a)pyrene-DNA-adducts



(+) anti 7R,8S,9S,10R-BP-dihydrodiol-epoxide

(-) 10R trans-anti-[BP]-triol-N2-deoxy-guanosine-adduct

Carcinogenesis from benzo(a)pyrene



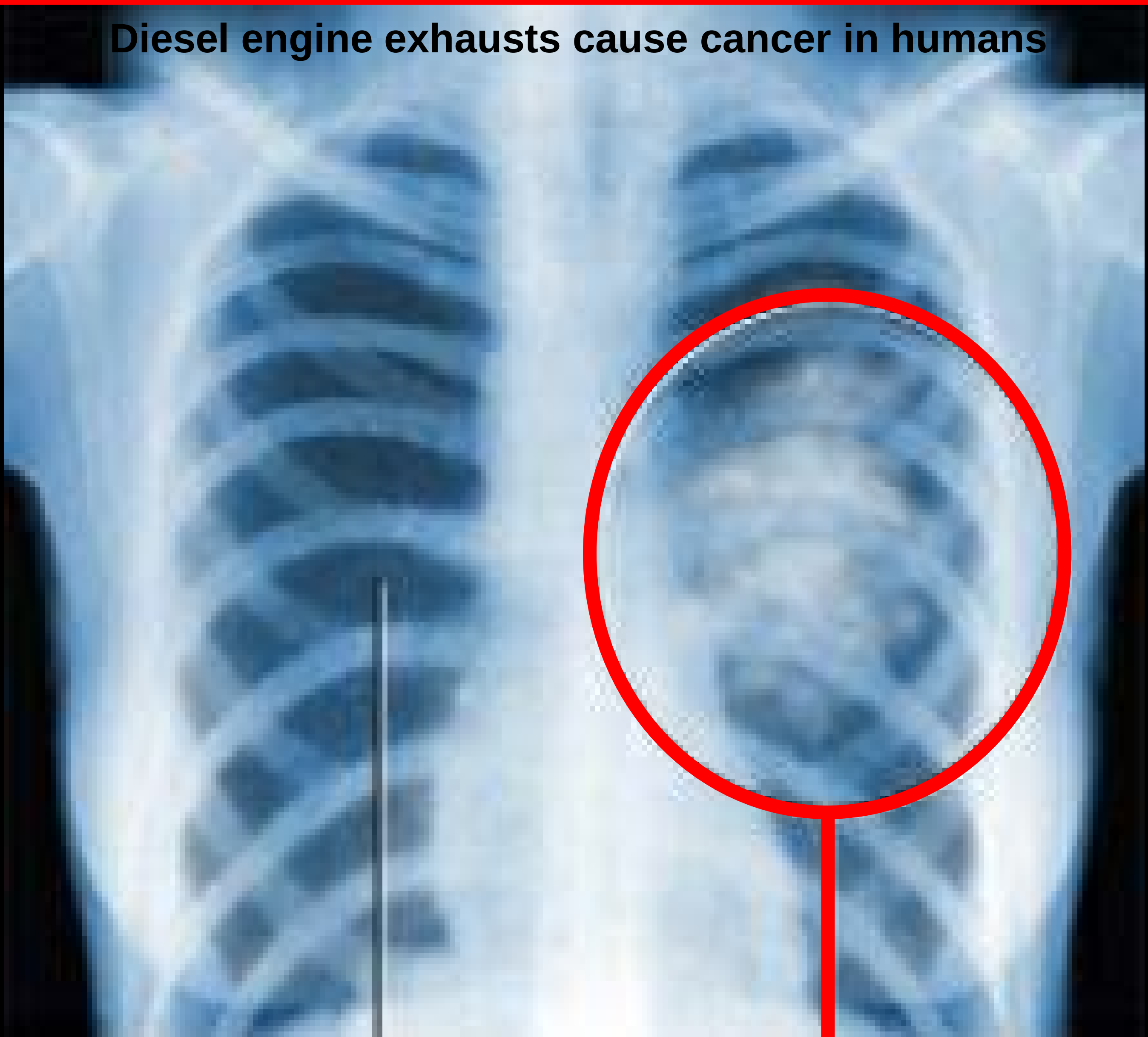
Diesel and GDI nanoparticles act as Trojan horses for genotoxic compounds

Problem: Trojan horse effect

- **Nanoparticles penetrate cell membranes (alveoli, placenta, blood cells) acting like a Trojan horse**

Trojan horse, Harbour of Canakkale, Turkey

World Health Organization, IARC
Diesel engine exhaust: A group 1 carcinogen



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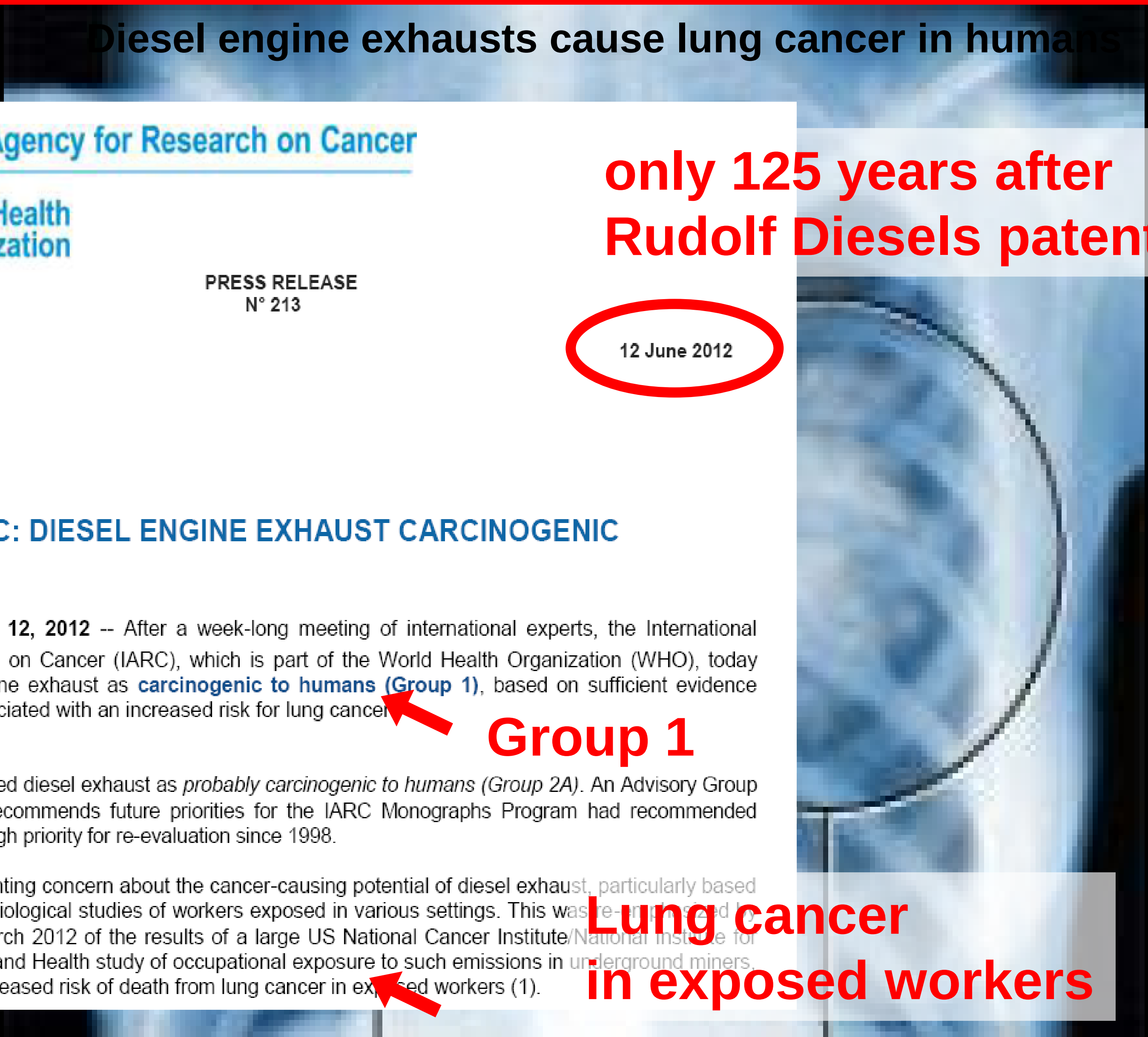

Diesel engine exhausts cause lung cancer in humans

International Agency for Research on Cancer

World Health Organization

PRESS RELEASE
N° 213

12 June 2012

only 125 years after Rudolf Diesels patent!

IARC: DIESEL ENGINE EXHAUST CARCINOGENIC

Lyon, France, June 12, 2012 -- After a week-long meeting of international experts, the International Agency for Research on Cancer (IARC), which is part of the World Health Organization (WHO), today classified diesel engine exhaust as **carcinogenic to humans (Group 1)**, based on sufficient evidence that exposure is associated with an increased risk for lung cancer.

Group 1

Background

In 1988, IARC classified diesel exhaust as *probably carcinogenic to humans (Group 2A)*. An Advisory Group which reviews and recommends future priorities for the IARC Monographs Program had recommended diesel exhaust as a high priority for re-evaluation since 1998.

There has been mounting concern about the cancer-causing potential of diesel exhaust, particularly based on findings in epidemiological studies of workers exposed in various settings. This was re-emphasized by the publication in March 2012 of the results of a large US National Cancer Institute/National Institute for Occupational Safety and Health study of occupational exposure to such emissions in underground miners, which showed an increased risk of death from lung cancer in exposed workers (1).

Lung cancer in exposed workers

World Health Organization, IARC
Diesel engine exhaust: a group 1 carcinogen

Diesel engine exhaust cause cancer in humans

The Diesel Exhaust in Miners Study: A Nested Case–Control Study of Lung Cancer and Diesel Exhaust

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Manuscript received February 16, 2011; revised June 3, 2011; accepted October 21, 2011.

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Background Most studies of the association between diesel exhaust exposure and lung cancer suggest a modest, but consistent, increased risk. However, to our knowledge, no study to date has had quantitative data on historical diesel exposure coupled with adequate sample size to evaluate the exposure–response relationship between diesel exhaust and lung cancer. Our purpose was to evaluate the relationship between quantitative estimates of exposure to diesel exhaust and lung cancer mortality after adjustment for smoking and other potential confounders.

Methods We conducted a nested case–control study in a cohort of 12315 workers in eight nonmetal mining facilities, which included 198 lung cancer deaths and 562 incidence density–sampled control subjects. For each case subject, we selected up to four control subjects, individually matched on mining facility, sex, race/ethnicity, and birth year (within 5 years), from all workers who were alive before the day the case subject died. We estimated diesel exhaust exposure, represented by respirable elemental carbon (REC), by job and year, for each subject, based on an extensive retrospective exposure assessment at each mining facility. We conducted both categorical and continuous regression analyses adjusted for cigarette smoking and other potential confounding variables (eg, history of employment in high-risk occupations for lung cancer and a history of respiratory disease) to estimate odds ratios (ORs) and 95% confidence intervals (CIs). Analyses were both unlagged and lagged to exclude recent exposure such as that occurring in the 15 years directly before the date of death (case subjects)/reference date (control subjects). All statistical tests were two-sided.

Results We observed statistically significant increasing trends in lung cancer risk with increasing cumulative REC and average REC intensity. Cumulative REC, lagged 15 years, yielded a statistically significant positive gradient in lung cancer risk overall (P_{trend} = .001); among heavily exposed workers (ie, above the median of the top quartile [REC ≥ 1005 μg/m³-y]), risk was approximately three times greater (OR = 3.20, 95% CI = 1.33 to 7.69) than that among workers in the lowest quartile of exposure. Among never smokers, odd ratios were 1.0, 1.47 (95% CI = 0.29 to 7.50), and 7.30 (95% CI = 1.46 to 36.57) for workers with 15-year lagged cumulative REC tertiles of less than 8, 8 to less than 304, and 304 μg/m³-y or more, respectively. We also observed an interaction between smoking and 15-year lagged cumulative REC ($P_{interaction}$ = .086) such that the effect of each of these exposures was attenuated in the presence of high levels of the other.

Conclusion Our findings provide further evidence that diesel exhaust exposure may cause lung cancer in humans and may represent a potential public health burden.

J Natl Cancer Inst 2012;104:1–14

12315 workers,
198 lung cancer death
(16 in 1000)

diesel exhaust exposure:
a potential public health burden

Swiss Clean Air Act (LRV): List of carcinogenic compounds

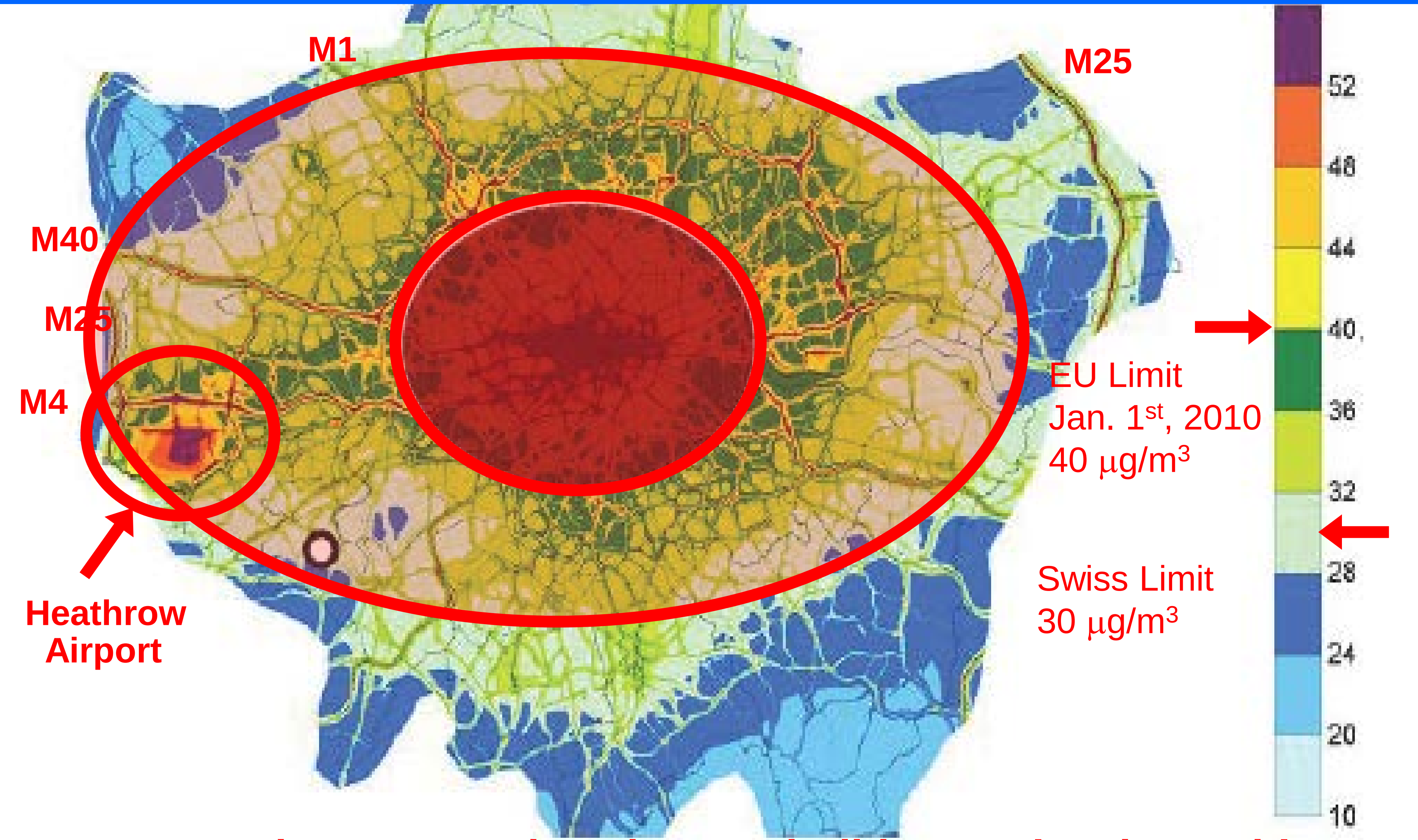
Luftreinhalte-Verordnung (LRV) **814.318.142.1**

83 Tabelle von krebserzeugenden Stoffen

Stoff	Summenformel	Klasse
Benzo(a)pyren	$C_{20}H_{12}$	1
Benzol	C_6H_6	3
Dibenz(a, h)anthracen	$C_{22}H_{14}$	1
1,2-Dibromethan	$C_2H_4Br_2$	3
1,4 Dichlorbenzol	$C_6H_4Cl_2$	3
1,2-Dichlorethan	$C_2H_4Cl_2$	3
Dieselruss		3
Diethylsulfat	$C_4H_{10}O_4S$	2

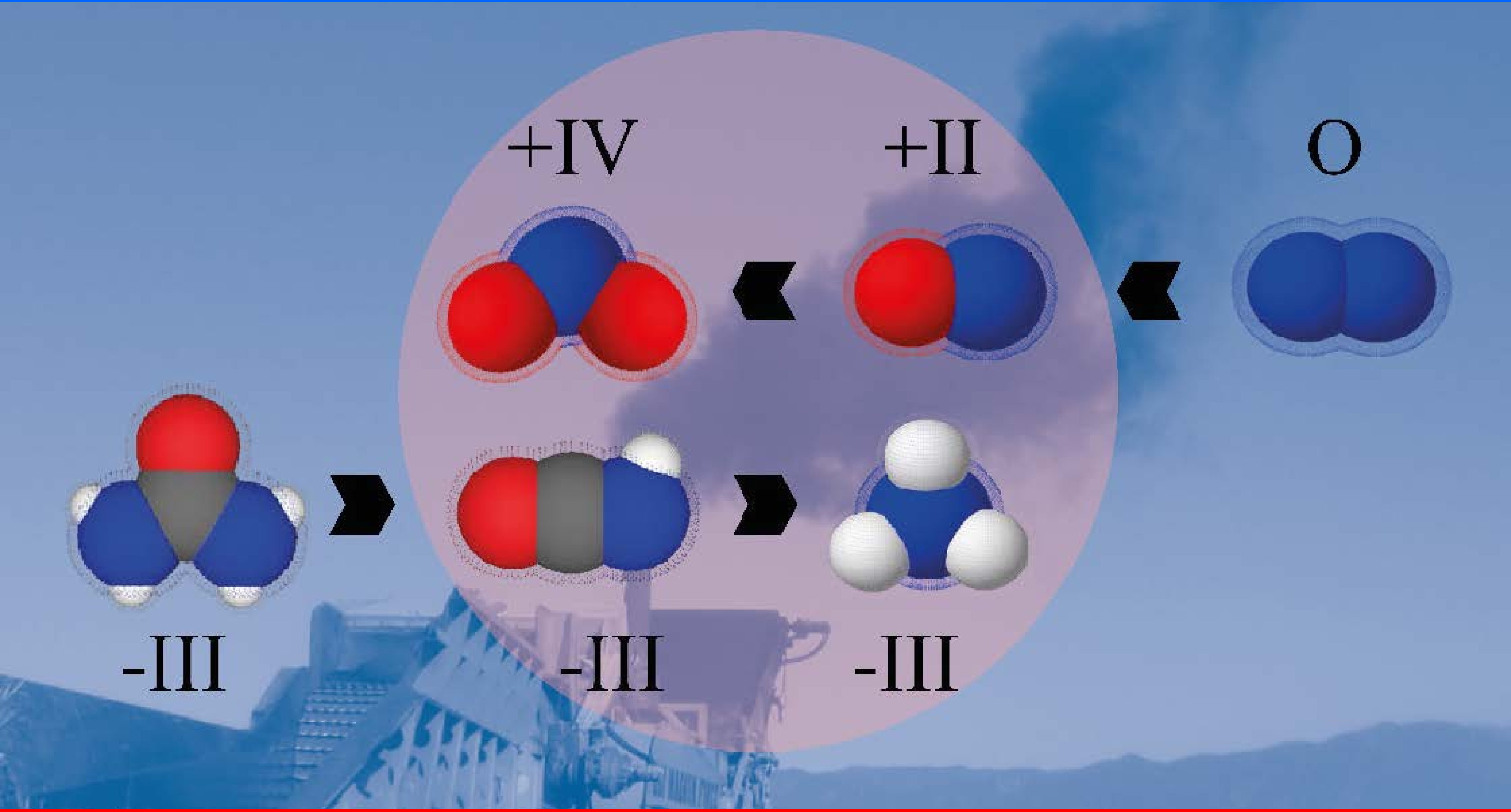
EU ambient air limit Dec. 31st, 2012, 1 ng benzo(a)pyrene/m^3

Mean annual NO_2 levels: City of London



From a Swiss perspective, the Brexit did not solve the problem!

Reactive nitrogen compounds in combustion exhausts

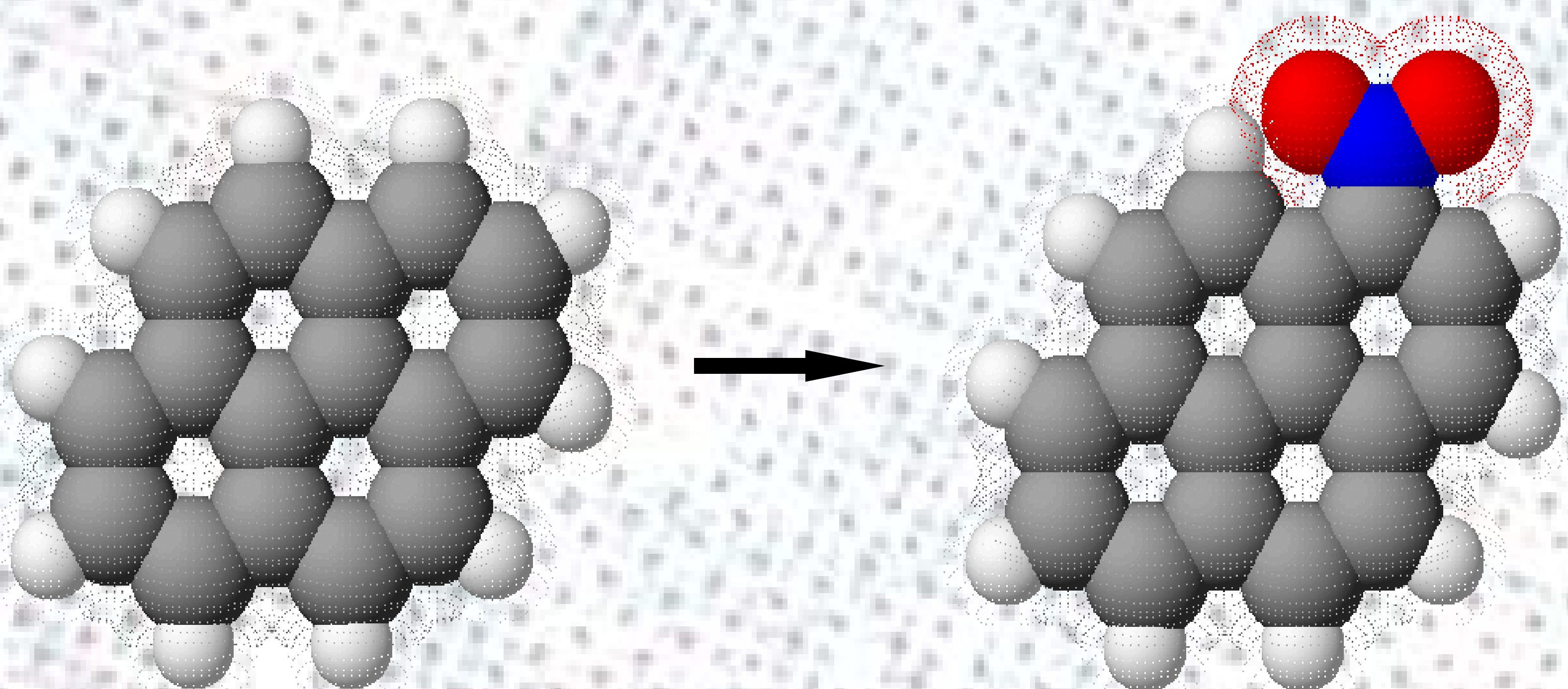


Converter technologies strongly affect RNC levels, but not always to the better

The DPF – a chemical reactor

In one step from a harmless precursor to a mutagen?

Nitration of PAHs



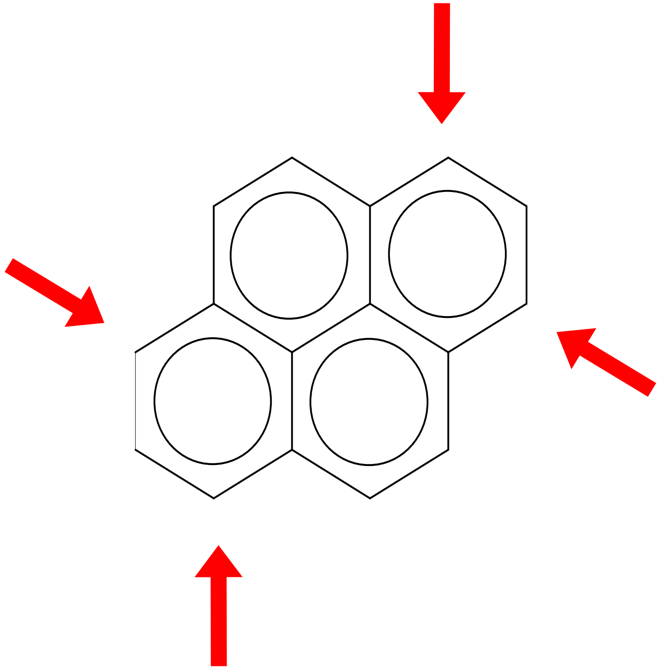
pyrene

1-nitropyrene

The DPF – a chemical reactor

Nitration in alpha-position?

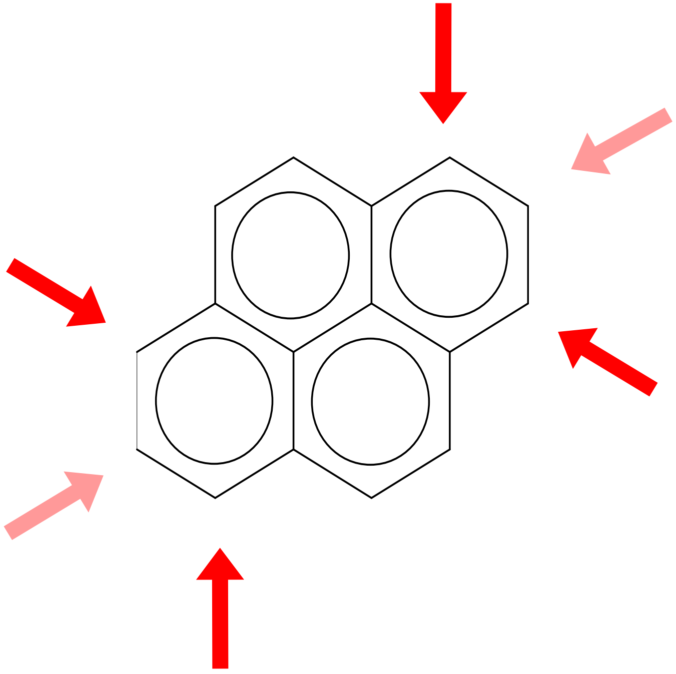
Regioselective nitration of pyrene



The DPF - a chemical reactor

or in beta-position?

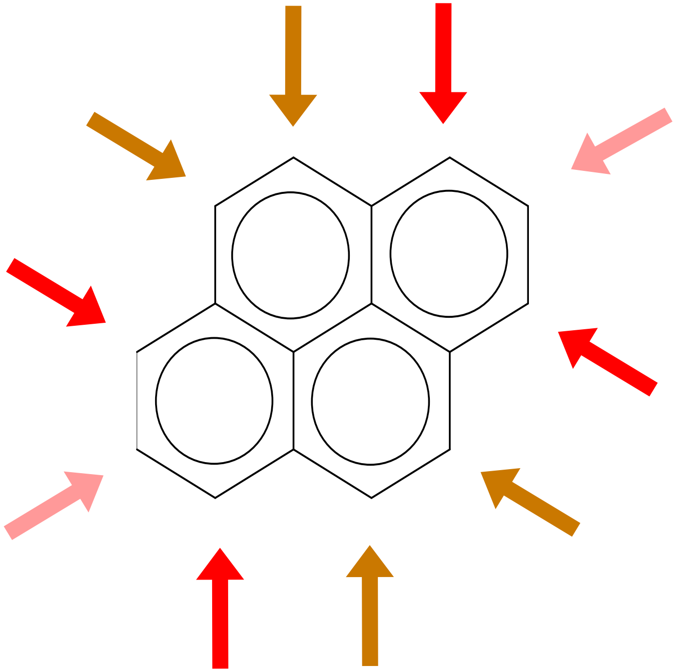
Regioselective nitration of pyrene



The DPF - a chemical reactor

or in gamma-position?

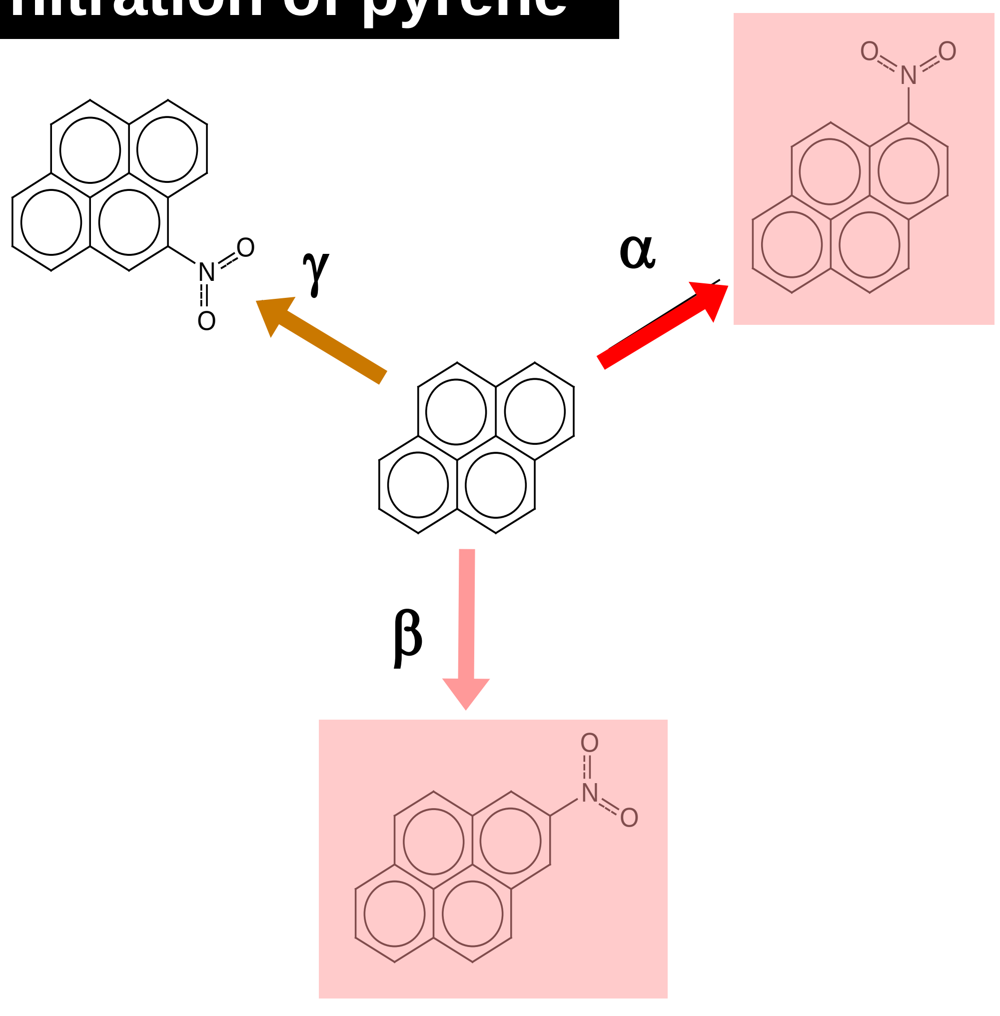
Regioselective nitration of pyrene



The DPF - a chemical reactor

Two of the three isomers are mutagenic.

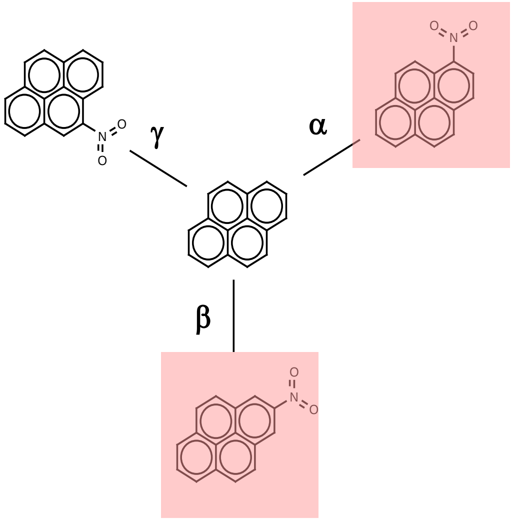
Regioselective nitration of pyrene



The DPF - a chemical reactor

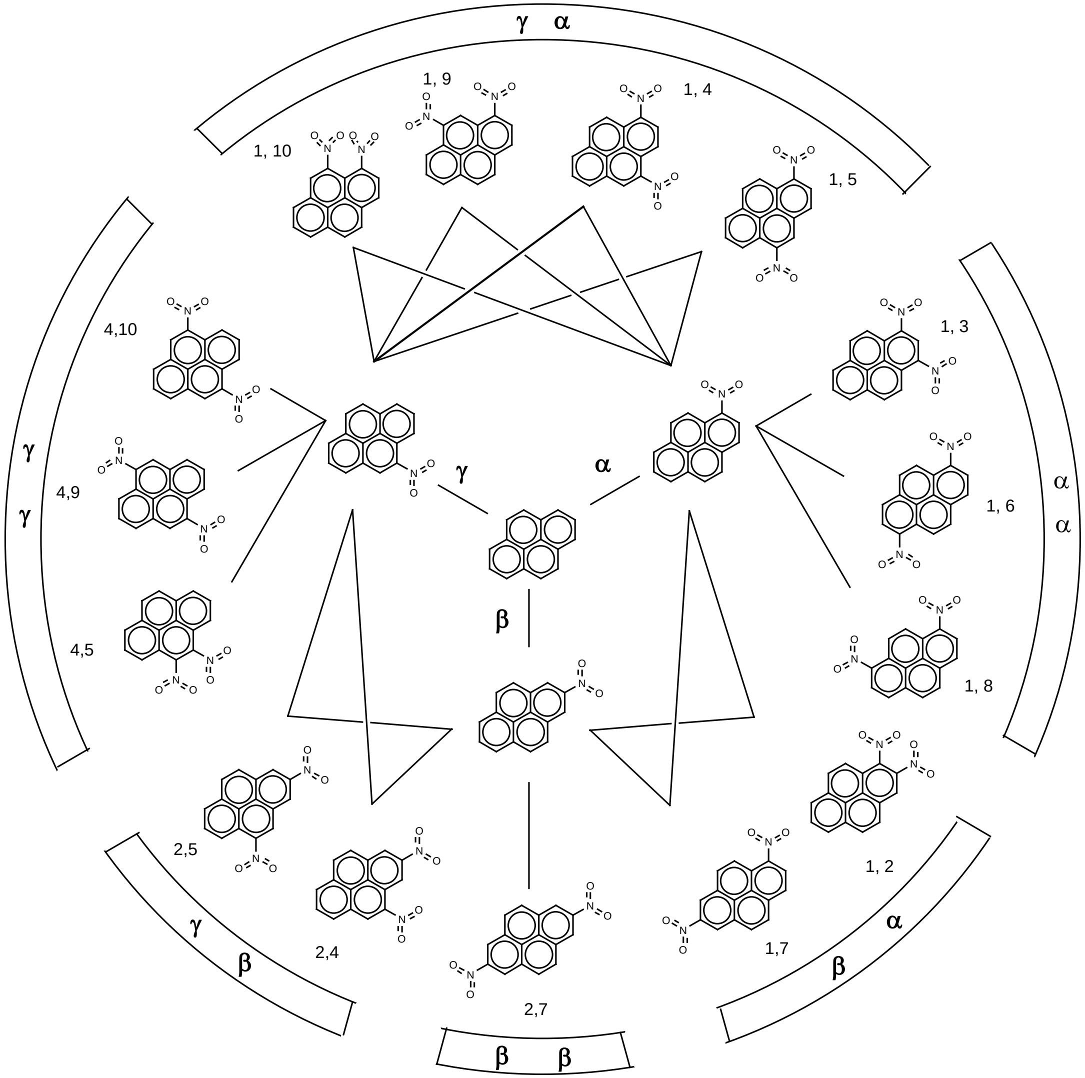
If nitration is possible ones, why not twice?

Nitration of nitropyrenes



The DPF - a chemical reactor

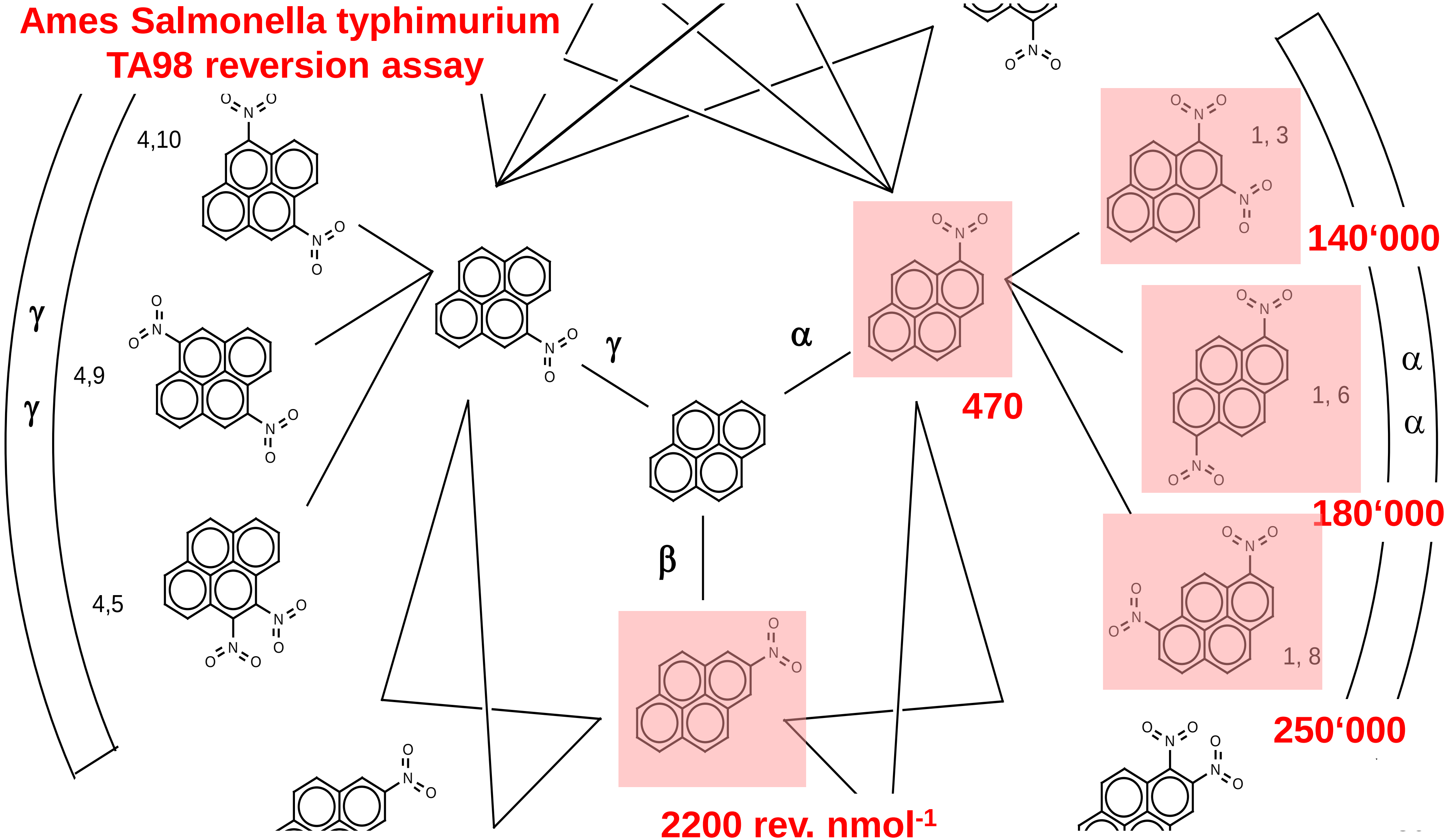
From one precursor to 3 nitropyrenes to 15 dinitropyrenes?



The DPF - a chemical reactor

The most potent direct-acting mutagens known are dinitropyrenes

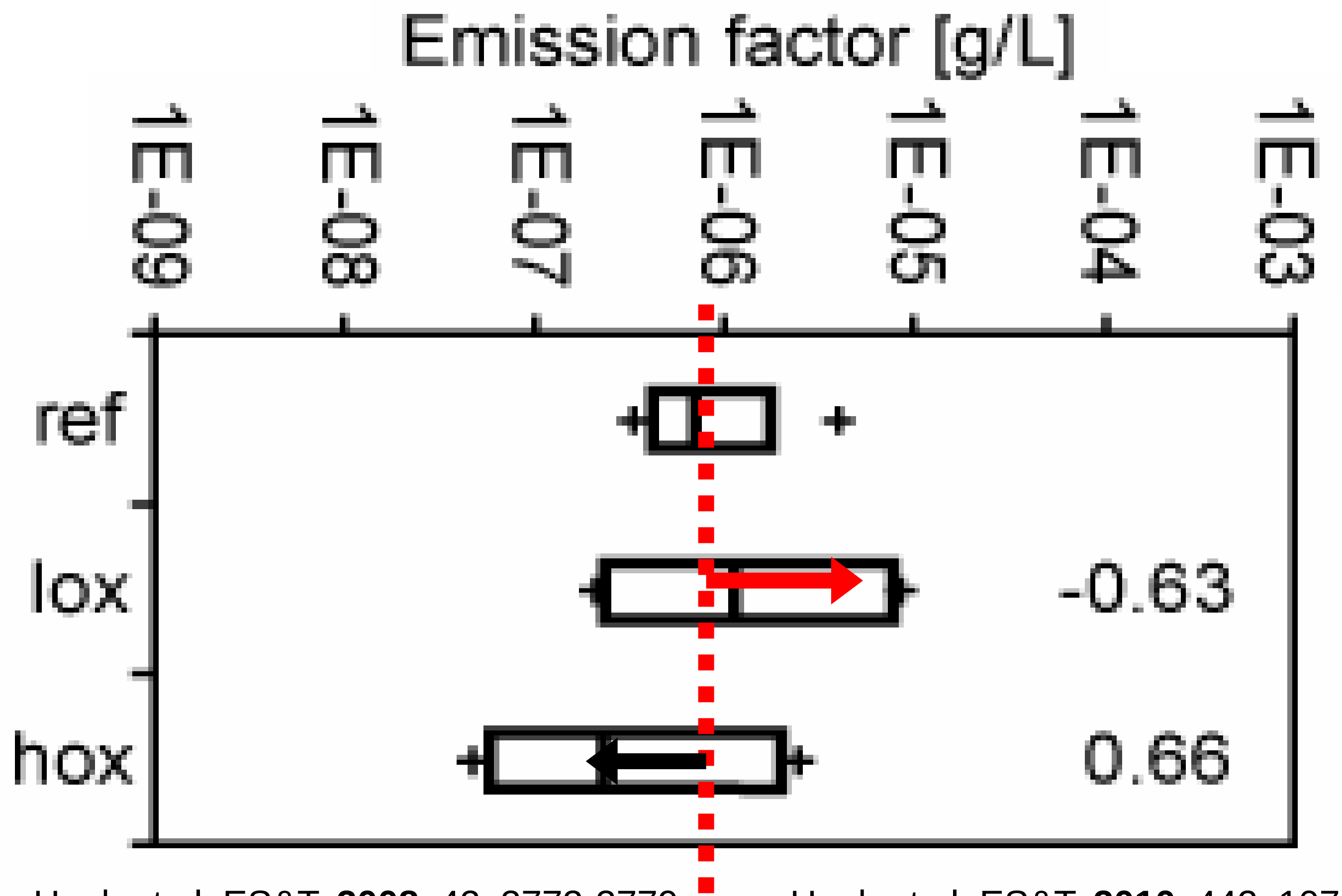
Ames Salmonella typhimurium TA98 reversion assay

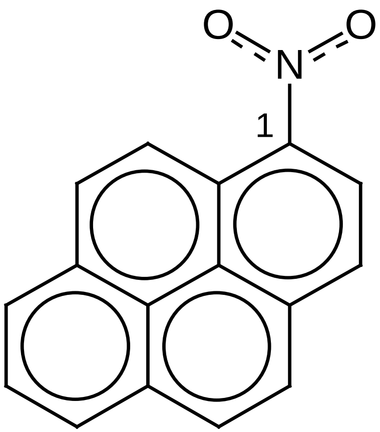


Genotoxic Nitro-PAHs

Low oxidation potential DPF can support 1-nitro-pyrene formation!

DPF-induced nitration of PAHs





Heeb et al. ES&T, **2008**, 42, 3773-3779

Heeb et al. ES&T, **2010**, 442, 1078-1084

Chemistry-based assessment of combustion exhausts

Combustion of fossil fuels is pure chemistry

- **The chemistry of fuels** — (What you feed is what you get!)
- **The sooting problem** — (Soot is bad news at the nanometer scale)
- **Combustion exhaust, ia a toxic cocktail** — (Many ways for intoxication)
- **Mass spectrometry is the tool for HAP identification and quantification**

Chemistry-based assessment of combustion exhausts by HRMS, a powerful tool

HR-MS is all we need for chemical hazard assessment of exhausts

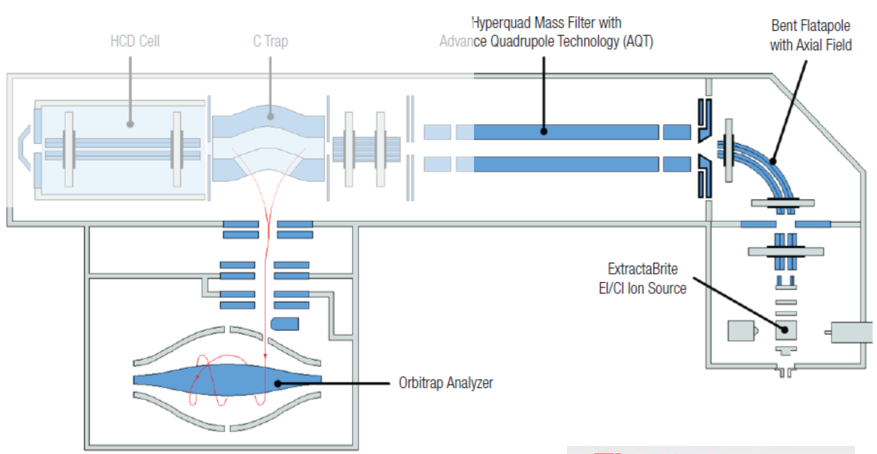
High resolutions mass spectrometry: Is all we need for quantitative analysis at the pg-level

GC-/ LC-HR-MS (Orbitrap)

High sensitivity
(both EI and NCI mode)

Higher selectivity
(chemical noise supression, 120’000 resolution)

Full scan mode – all in one run
(shorter sampling times, less elaborate sample clean-up, better results)



HR-MS is the ideal tool for chemical hazard assessment of exhausts

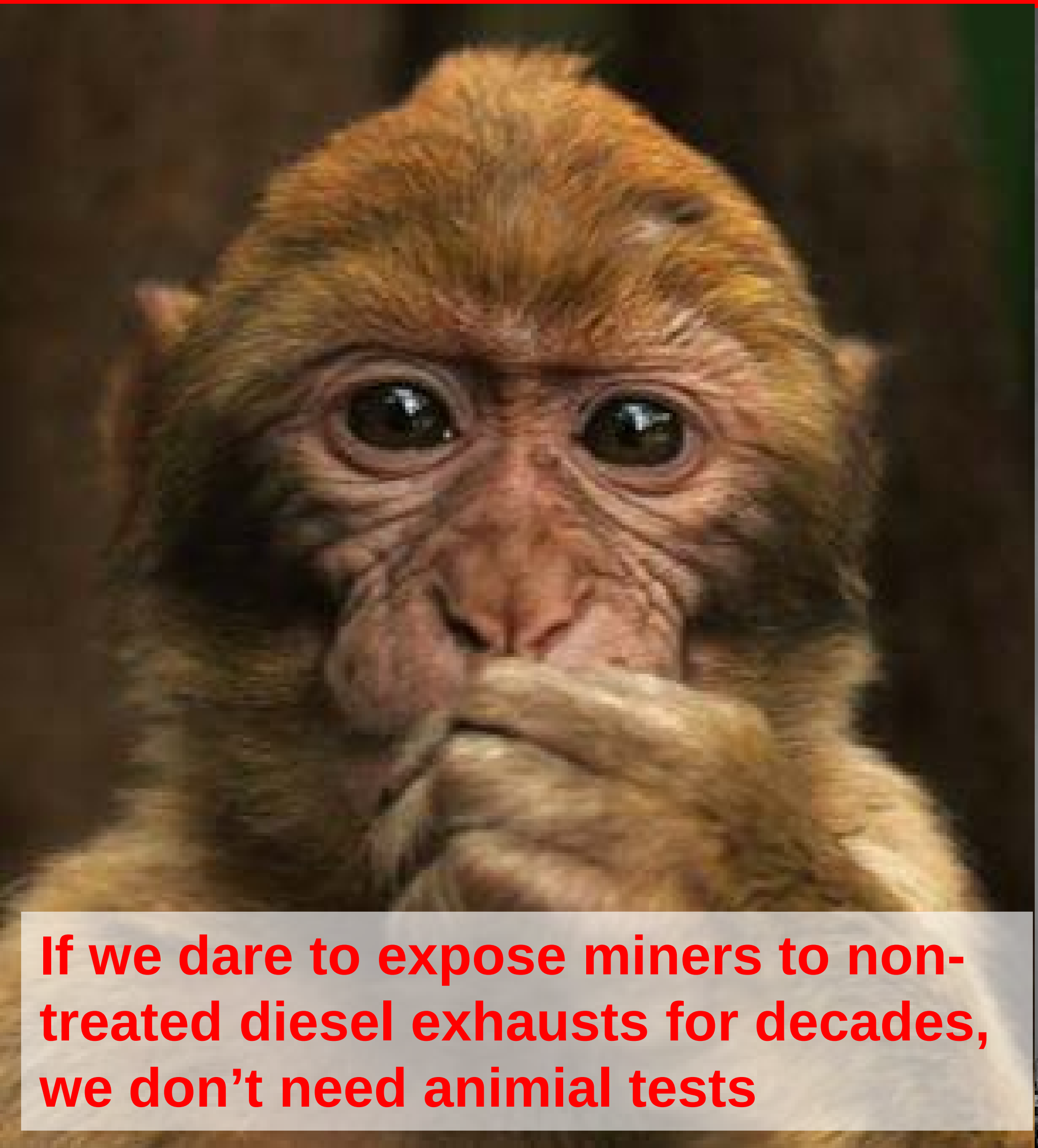
Thermo SCIENTIFIC ORBITRAP

Chemistry-based assessment of combustion exhausts by HRMS, a powerful tool

Hazard assessment of combustion exhausts by chemical analysis

***in vitro* cell culture tests are helpful too**

Chemistry-based assessment of combustion exhausts



If we dare to expose miners to non-treated diesel exhausts for decades, we don’t need animial tests

Chemistry-based assessment of combustion exhausts

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