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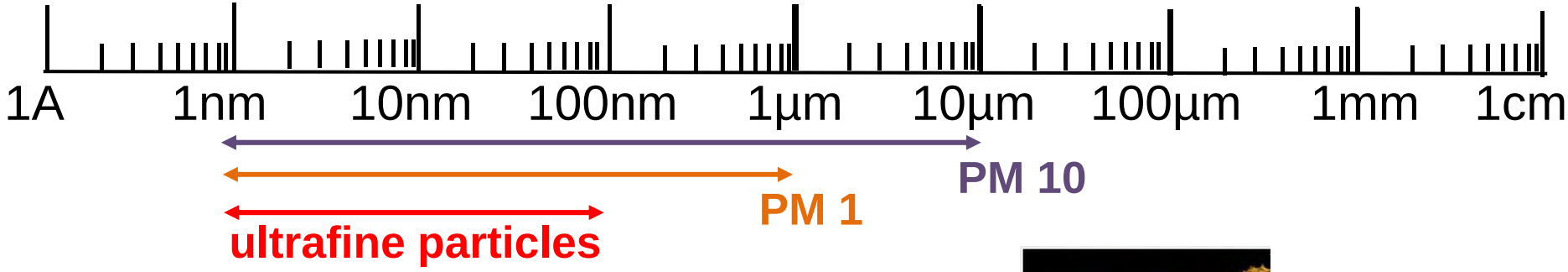
Changes of chemical composition of PM10

and the assessment of long-term trends

A. Ulrich, M.F.D. Gianini, A. Wichser, A. Fischer,
N. Heeb, R. Gehrig, C. Hueglin

Empa, Swiss Federal Laboratories for Materials Science and Technology,, Switzerland
andrea.ulrich@empa.ch

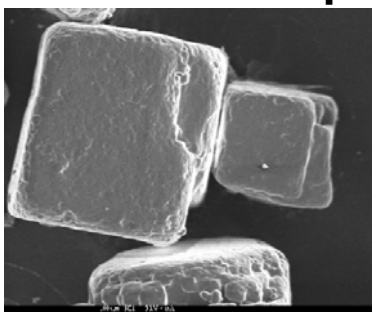
Dimensions of particulate matter in ambient air

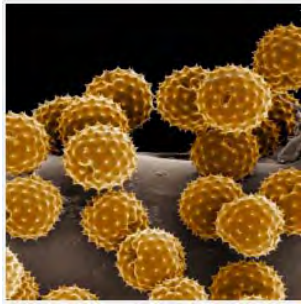


Ammonium sulfate ca. 100 nm

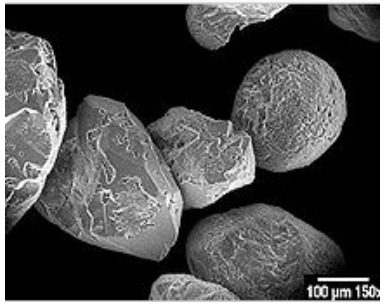
diesel soot ca. 100 nm
combustion generated soot

sea salt 0.2 -10 µm





pollen 10 -100 µm



mineral dust 0.2 -10 µm

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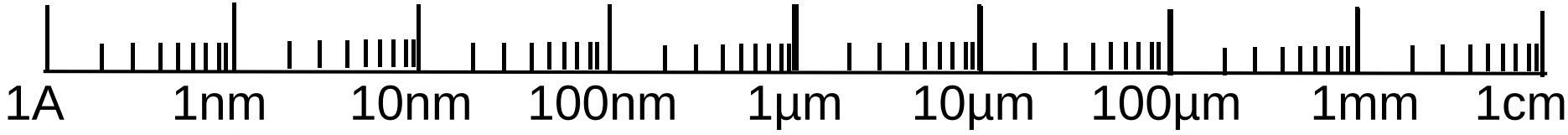
Particle deposition in human lungs



PM 10

PM 1

ultrafine particles

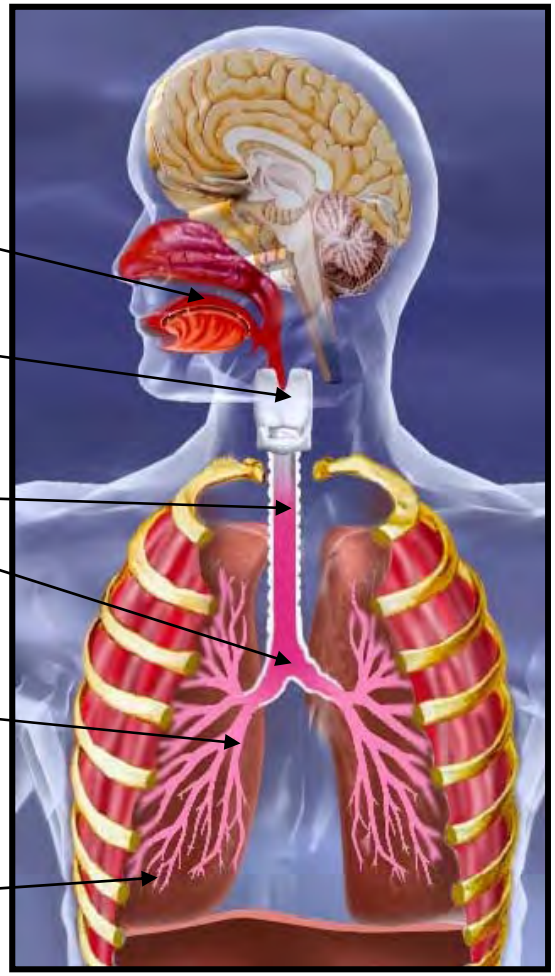
Pharyngeal / mucosa
> 10 µm

Larynx 5 – 6 µm

Trachea /
main bronchia
3 – 5 µm

Terminal bronchia
1 - 4 µm

Alveole < 1 µm



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National Air Pollution Monitoring Network (NABEL)

Basel: suburban

Bern: urban, kerbside

Chaumont: rural, above 1000m asl.

Davos: forest, above 1000m asl.

Dübendorf: suburban

Härkingen: rural, motorway

Jungfraujoch: high-alpine

Lägeren: forest

Lausanne: urban, kerbside

Lugano: urban, background

Magadino: rural

Payerne: rural

Rigi: rural, above 1000m asl.

Sion: rural, motorway

Tänikon: rural

Zürich: urban, background

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Federal Office for the Environment (FOEN)

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Sampling sites

5 different sampling site types

Basel

Suburban

Zurich

Urban background

Bern

Urban kerbside

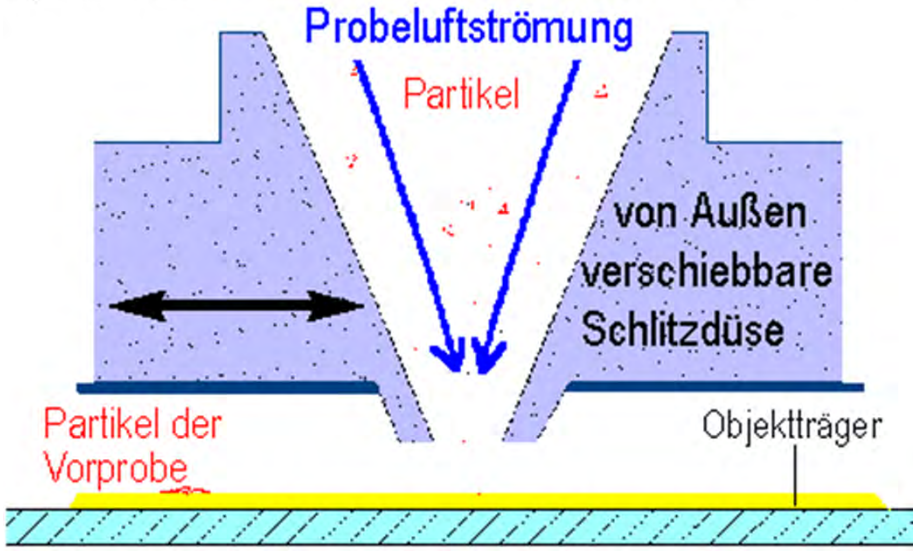
Payerne

Rural – North of the Alps

Magadino

Rural –
South of the Alps

Sampling of PM 10



- Daily PM10 filters:

Site	Sampling period
Basel	04.1998 - 03.1999 08.2008 - 07.2009
Bern	04.1998 - 03.1999 08.2008 - 07.2009
Zürich	04.1998 - 03.1999 08.2008 - 07.2009
Magadino	08.2008 - 07.2009
Payerne	08.2008 - 07.2009

C. Hueglin et al, Atm Environ 2005, 39(4), 637-651
M. Gianini et. al., Atm Environ 2011, submitted

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Analysis of PM 10

- **EC/OC Thermal-optical analysis**
  - EC = elemental carbon (soot)
  - OC = organic carbon
- **Plasma Mass Spectrometry ICPMS**
  - 35 Elements (e.g. Al, V, Fe, Ni, Cu, Se, Rb, Mo,……)
- **Ionic Chromatography IC**
  - 8 Ions (Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-})

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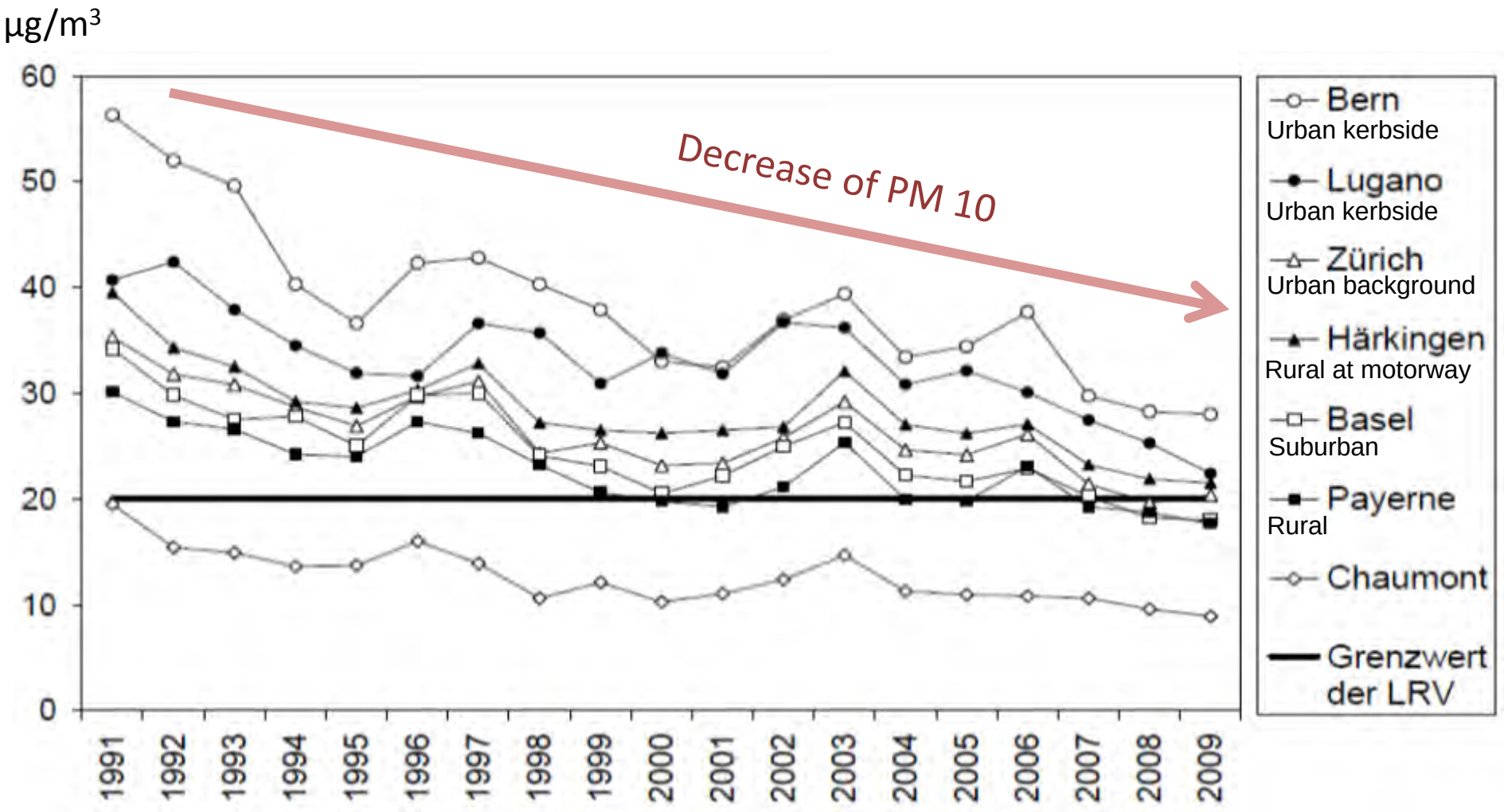
Trend of PM10 (annual mean) from 1991 - 2009



Source: BAFU, Luftbelastung 2009

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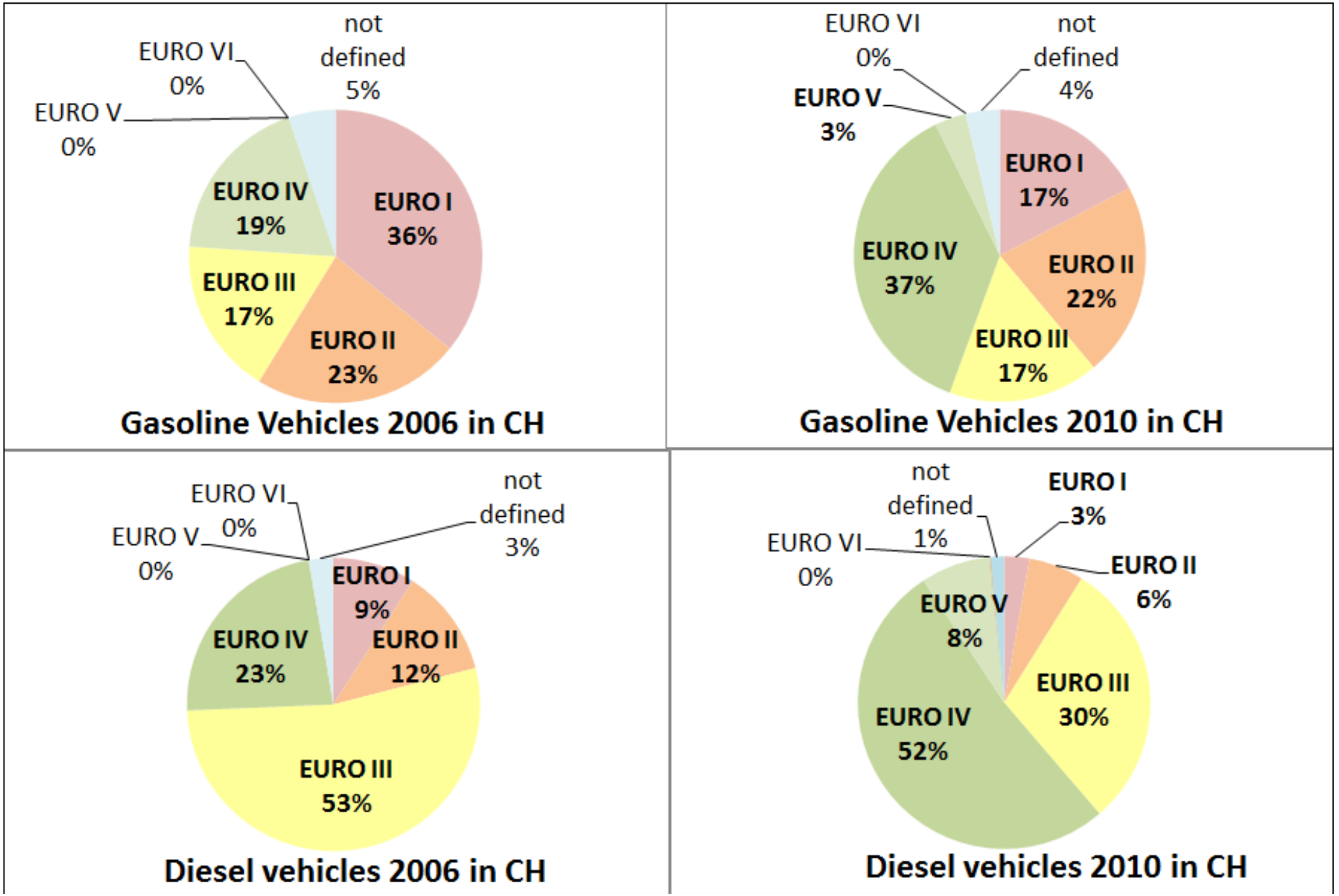
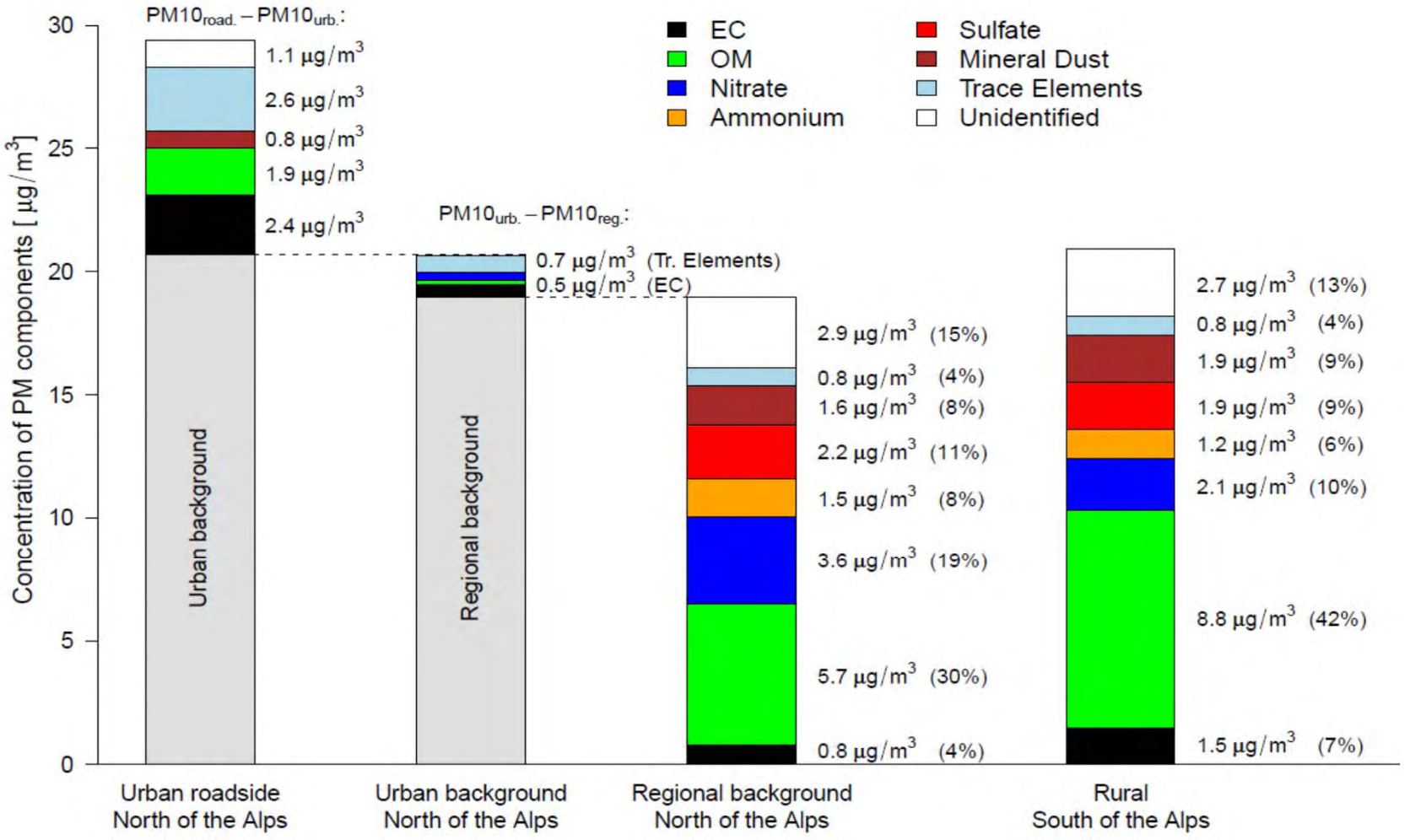
Change of Fleet in CH from 2006 to 2010



Chemical composition of PM10 (Aug. 2008 – Jul. 2009)



Bern – Urban roadside	Zurich – Urban background	Basel - suburban Payerne - rural	Magadino - rural
29.4 µg/m³	20.7 µg/m³	19.0 µg/m³	20.9 µg/m³
		North of the Alps	South of the Alps

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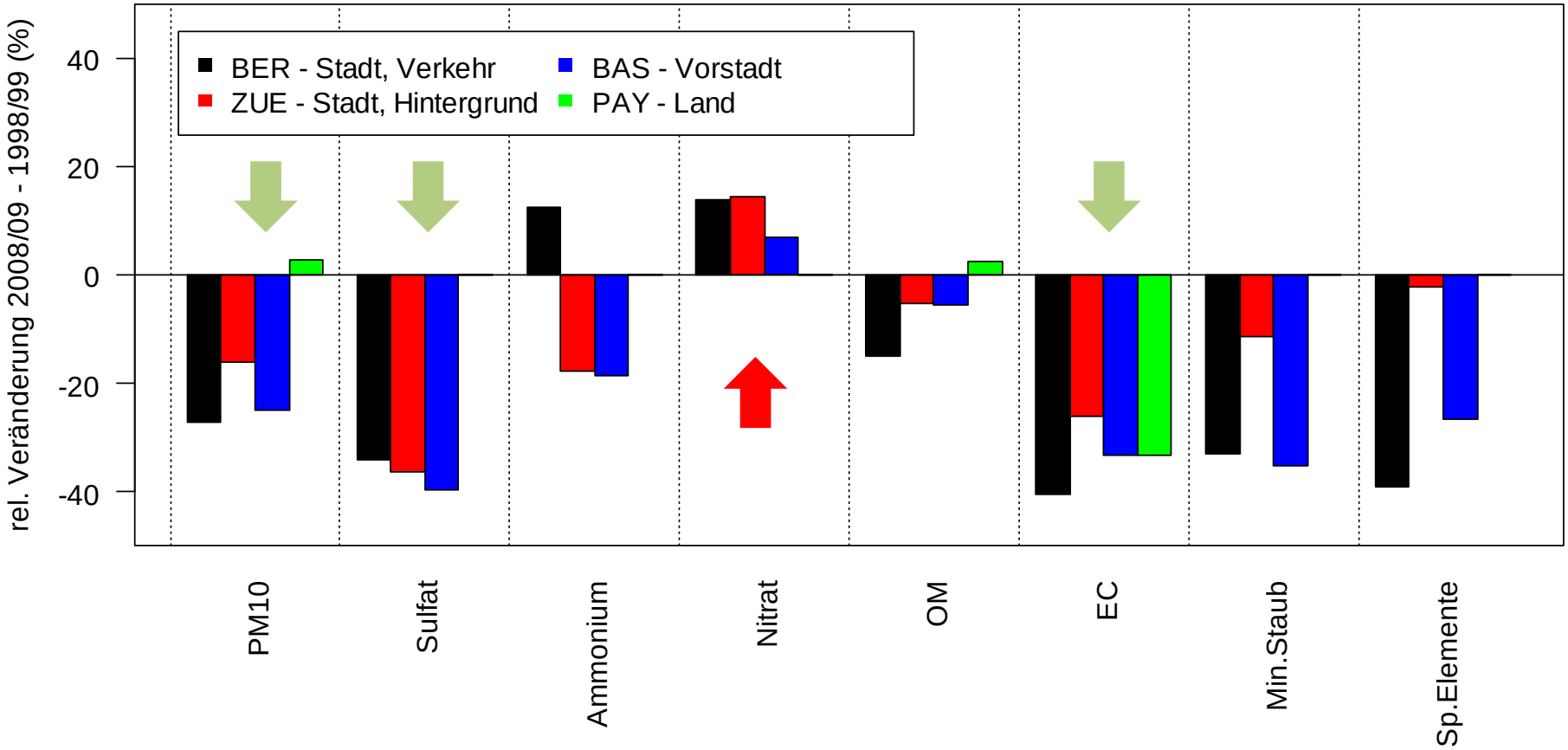
Change in chemical composition of PM10

(1998/1999 – 2008/2009)



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NO_2 air quality standards and guideline values

	Annual mean ($\mu g/m^3$)	*Daily mean ($\mu g/m^3$)*	*Hourly mean ($\mu g/m^3$)*	*½-Hourly mean ($\mu g/m^3$)*
EU	40[a]	---	200[a,b]	---
Switzerland	30	80	---	100[c]
WHO AQG 2005	40[d]	---	200[d]	---

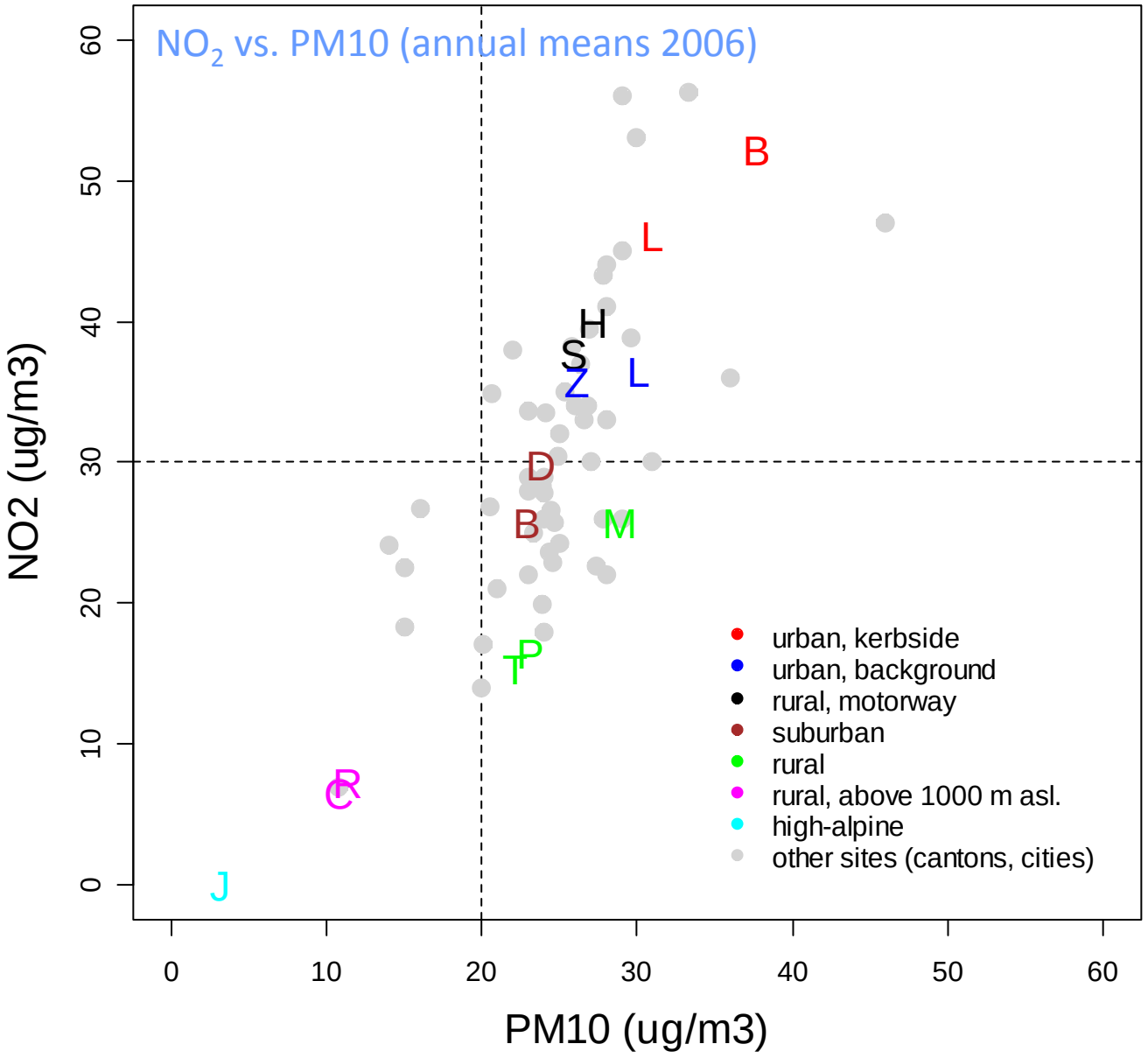
[a] compliance by 1 Jan 2010

[b] not to be exceeded on more than 18 occasions

[c] 95-percentile

[d] Guideline values

NO_2 at Swiss measurement sites



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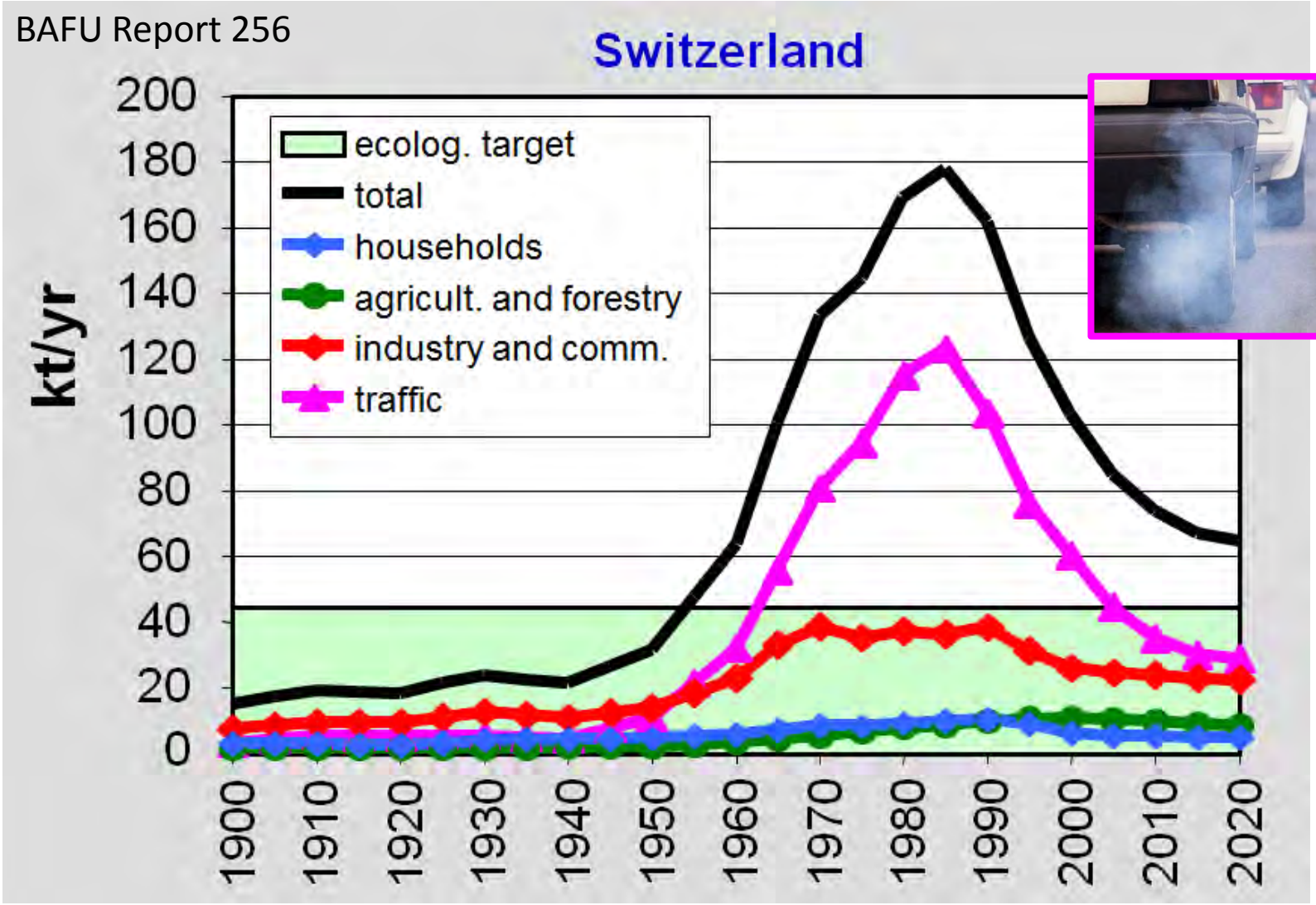
NO_x Sources ($NO_x = NO+NO_2$)

BAFU Report 256



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Trend of annual NO, NO_2, NO_x

at urban roadsite site (Bern)

$$NO + O_3 \xrightarrow{k_1} NO_2 + O_2 \qquad (1)$$

$k_1 = 1.4 \cdot 10^{-12} \cdot \exp(-1310/T) cm^3 s^{-1}$

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad \lambda < 420nm \qquad (2)$$

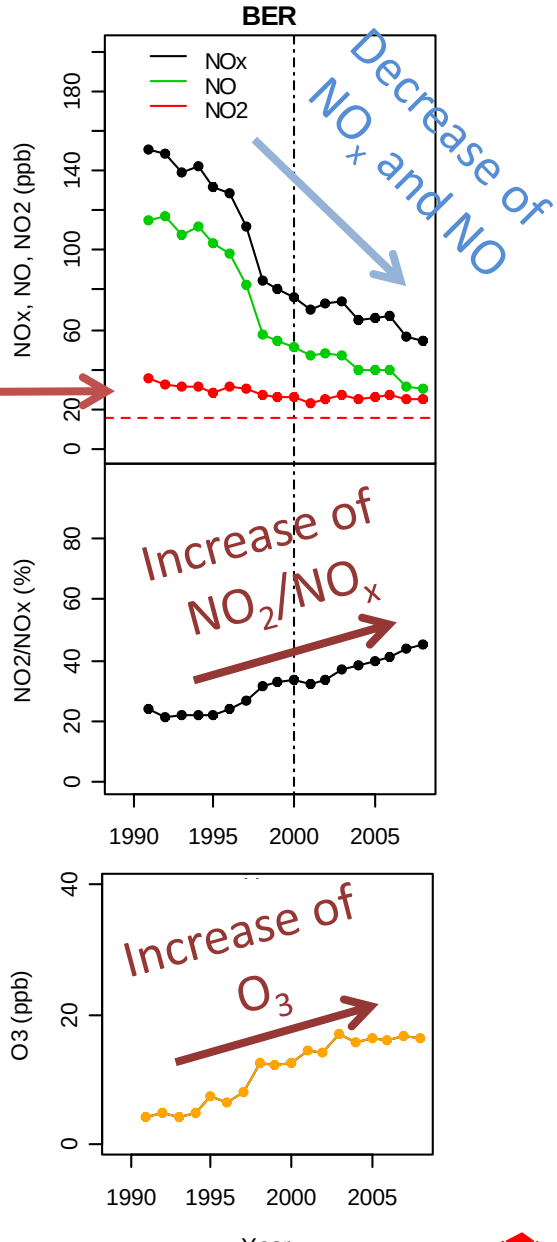
$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (3)$$

(1) – (3) tend to establish an equilibrium, the Photostationary State (Leighton, 1961)

$$\frac{[NO_2]}{[NO]} = \frac{k_1[O_3]}{J_{NO_2}}$$

Total oxidant $O_x = NO_2 + O_3$ conserved in eqs. (1) – (3)

NO2 stable



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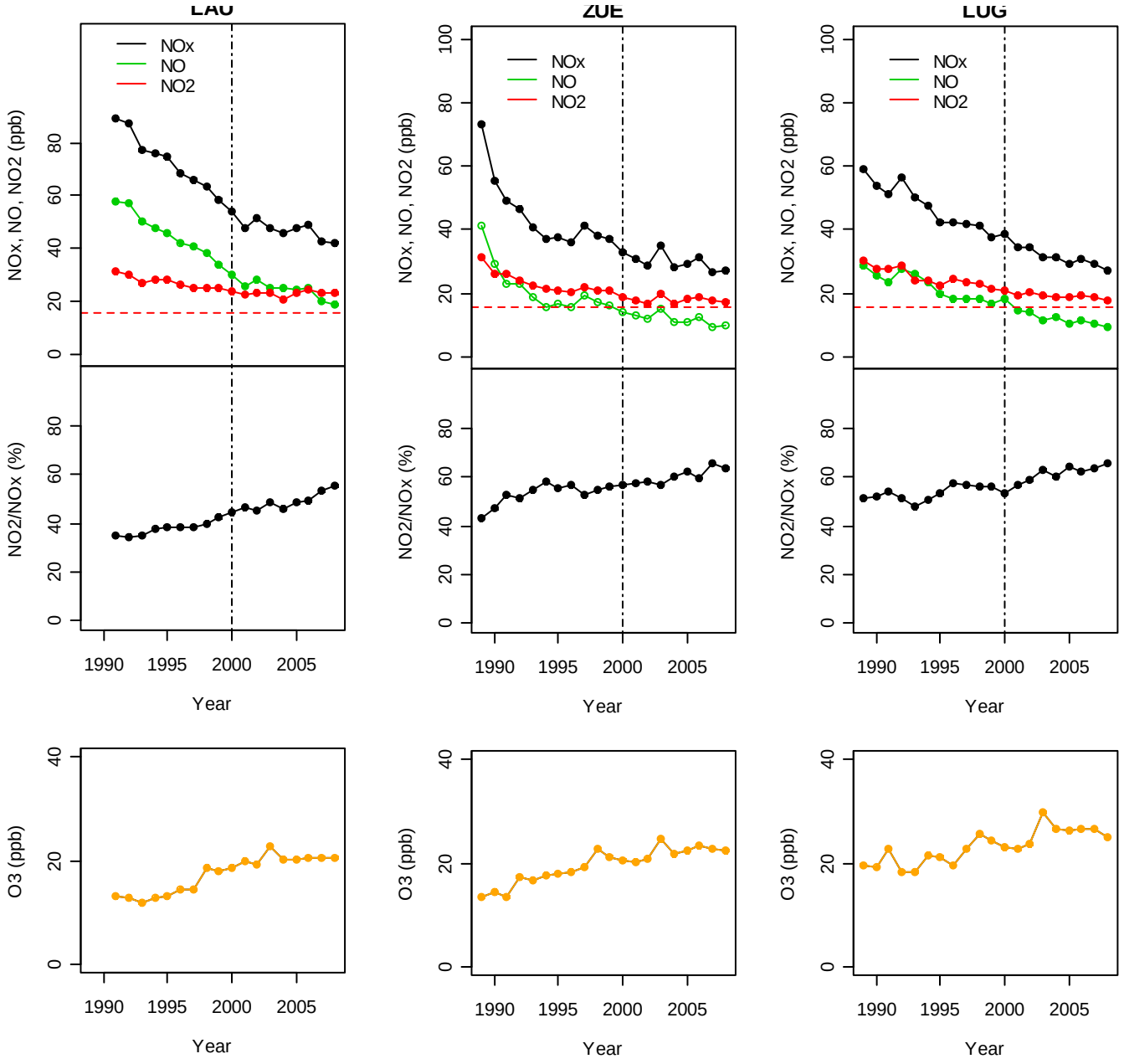
Trend of annual NO, NO_2, NO_x at other urban sites

Decrease of NO_x and NO

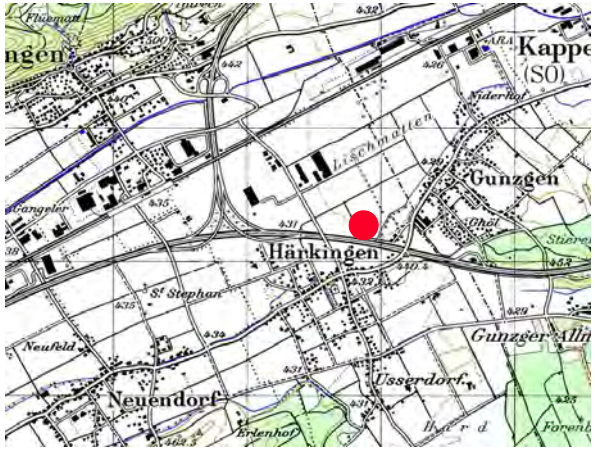
NO2 konstant or less decrease

Increase of NO_2/NO_x

Increase of O_3

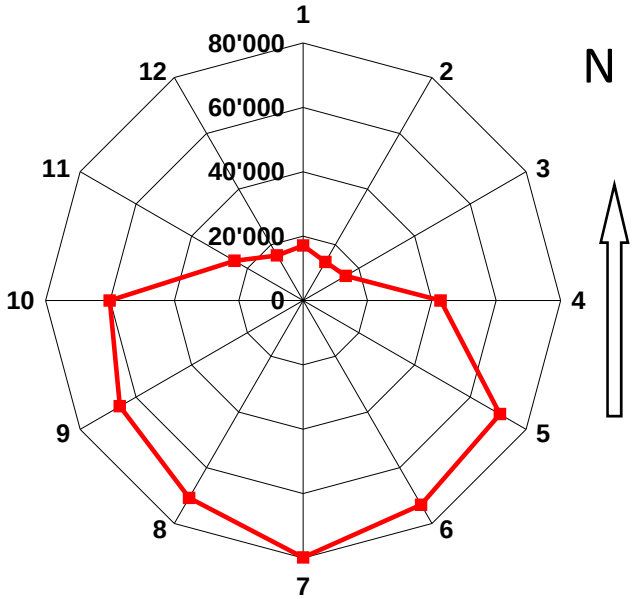


Haerkingen: A rural site 20m from a motorway

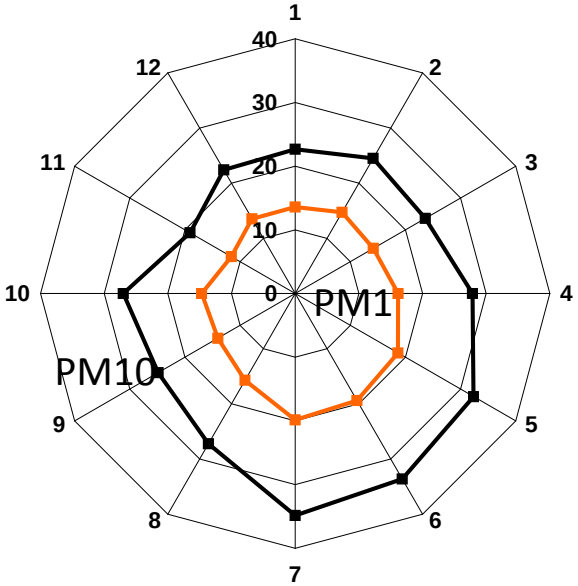


View to eastern direction

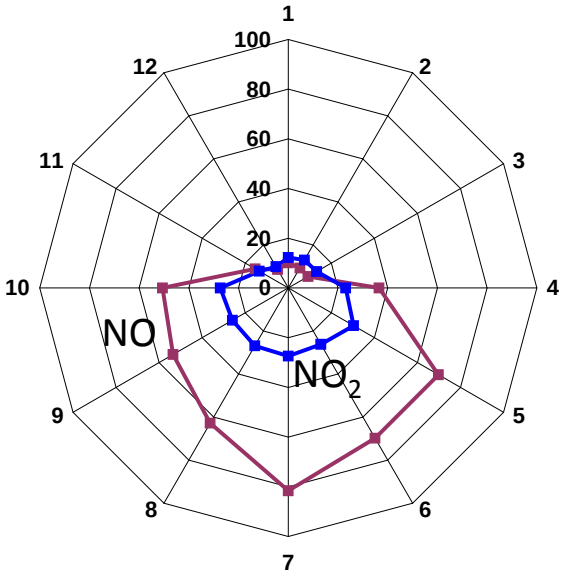
View to north-eastern direction



particle number conc. (#/cm^3)



PM10 and PM1 (µg/m^3)



nitrogen oxides (ppb)

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Possible Reasons

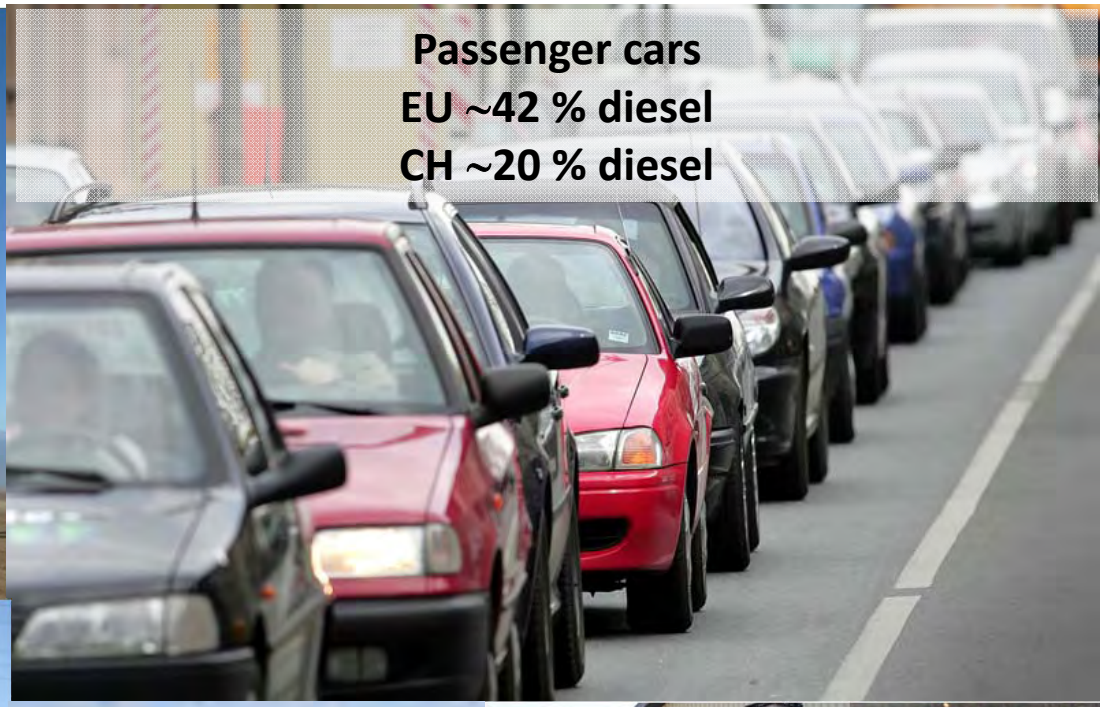
- Reduced S in Fuel from 350 ppm to <10 ppm
  SO_2 replaced by NO_x-species in redox processes

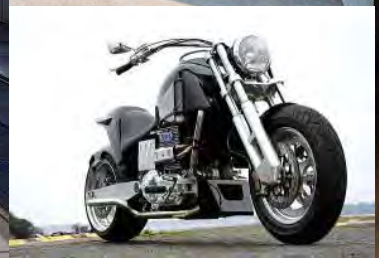
Sulphur Limits in CH			
Fuel	**2001**	**2005**	**since 2004**
Petrol	150 ppm	50 ppm	additonal levy for all fuels with S content >10 ppm
Diesel	350 ppm	50 ppm	additonal levy for all fuels with S content >10 ppm

- Increase of diesel vehicles in Switzerland from 3 to 25 %
  measure in car import to fulfill demands for CO_2 reduction
- Diesel vehicles equipped with oxidation catalysts and diesel particle filter (DPF)

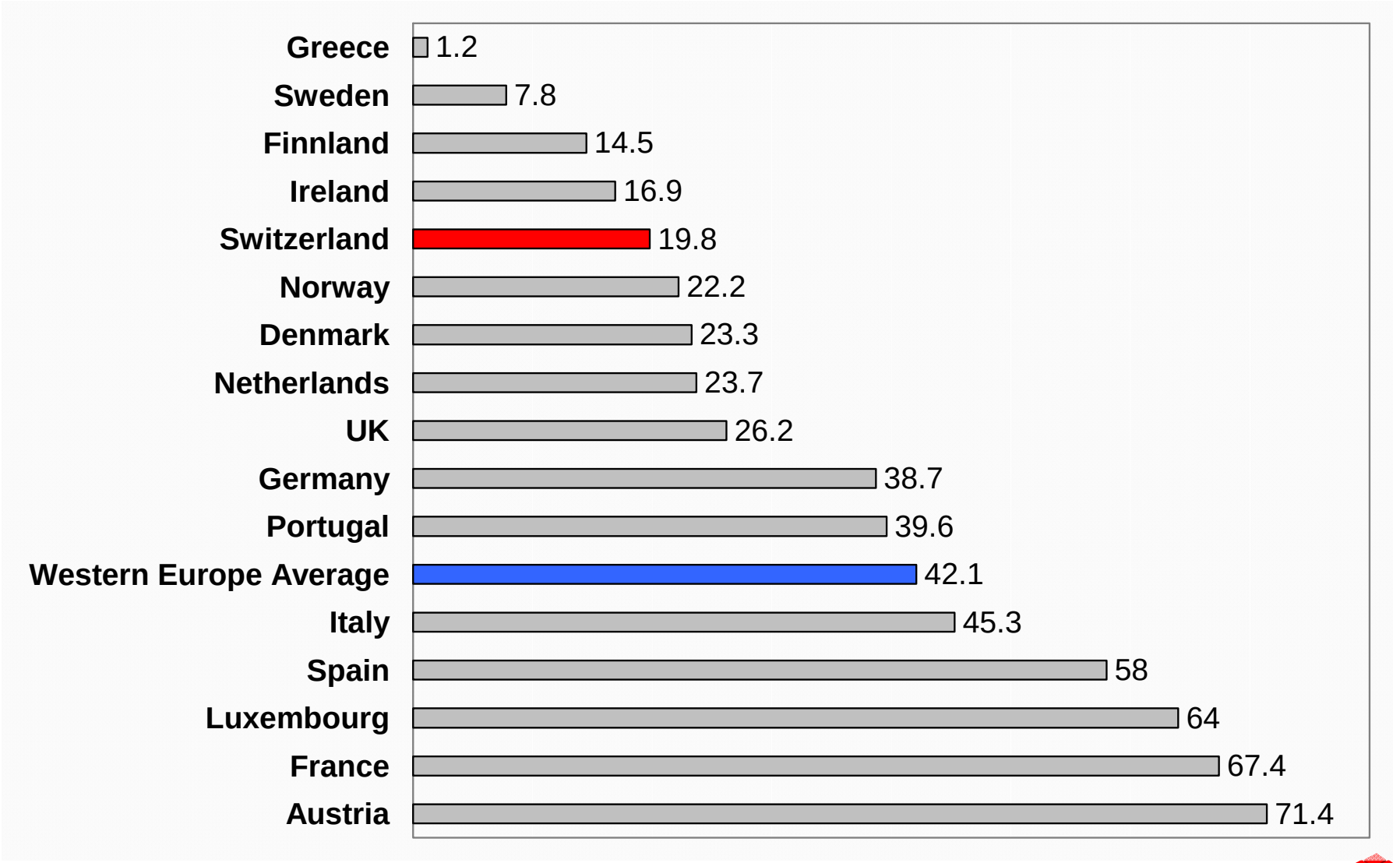
Denovo formation of NO_2 in some types of DPFs?
NO oxidation from reduction to oxidation argent

Diesel vehicle types (2008)

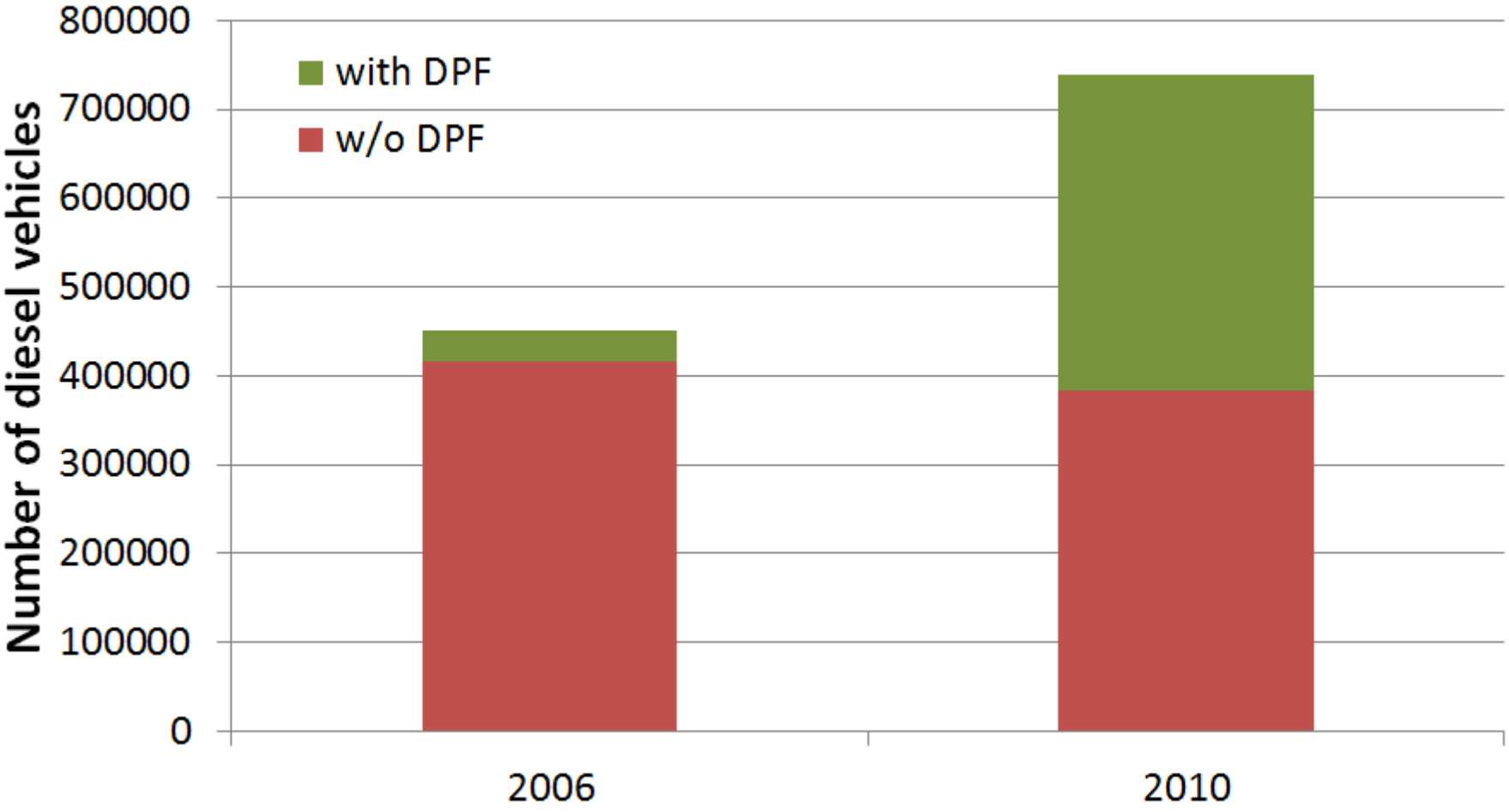




Percentage of diesel personal cars in Europe (2008)



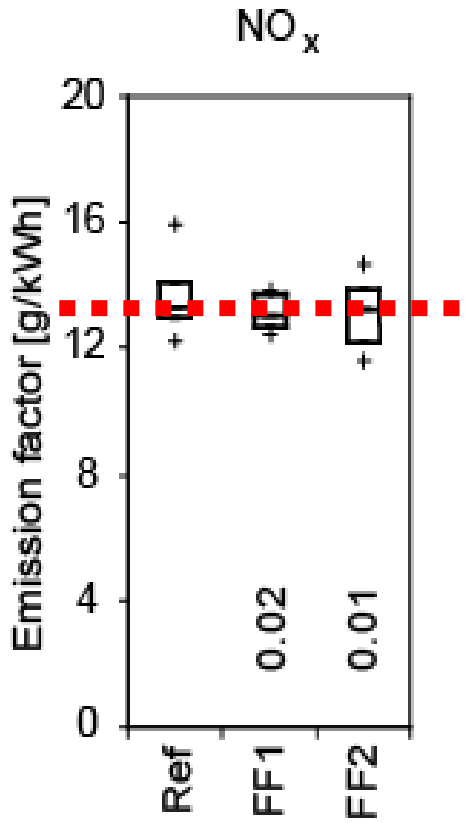
Development of diesel fleet without and with particle filter in CH



Nitrogen behavior in diesel particle filters

According to emission limits – NO EFFECT!

Nitrogen species (NOx, NO, NO2)



Heeb et al. Env. Sci. Tech. 2010, 44, 1078-1084.
Heeb et al. , Atm. Env. 2011, 45, 3203-3209.

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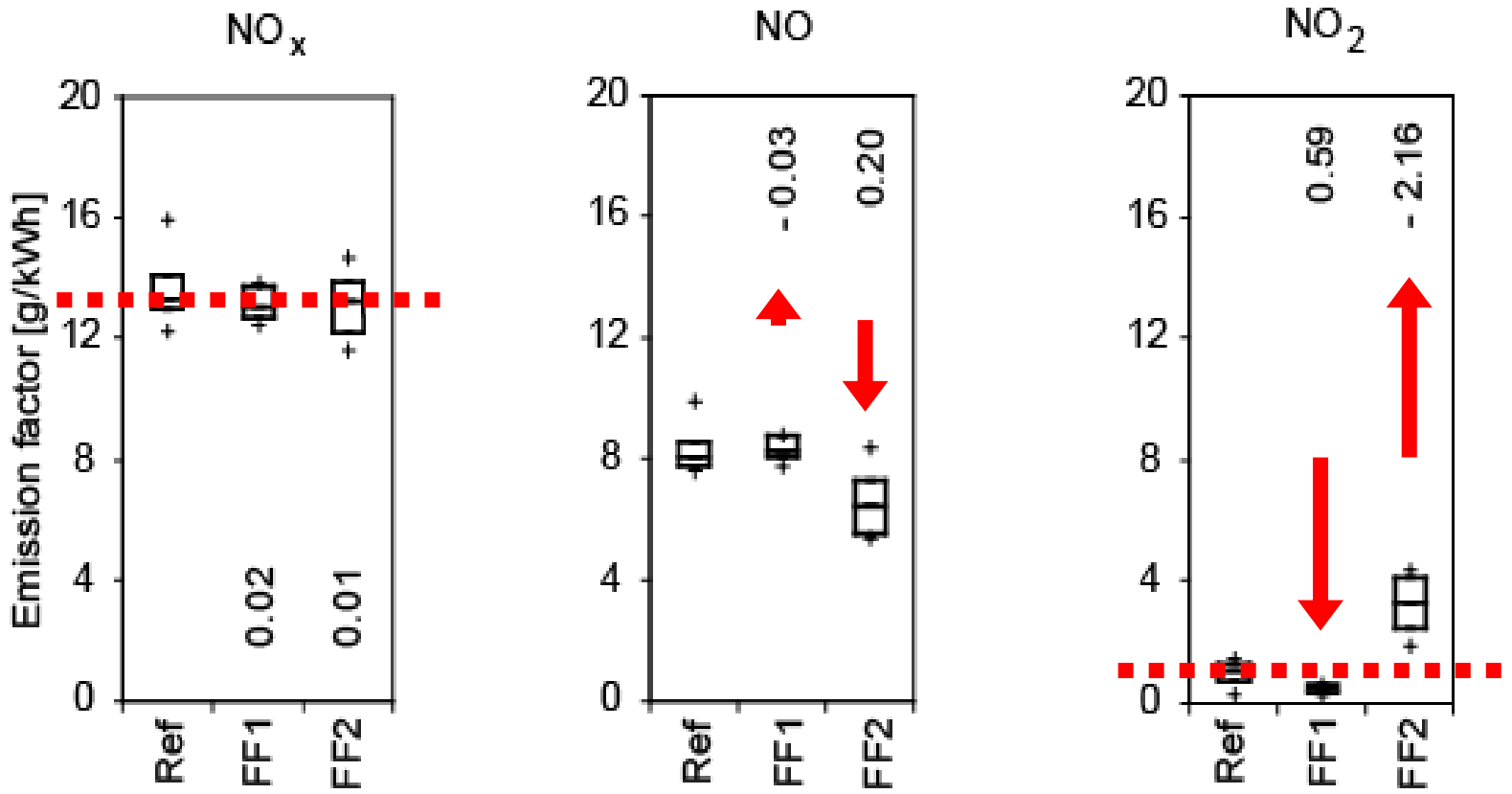
Nitrogen behavior in diesel particle filters

2 types of filter families, one which reduces NO_2 and the second forms NO_2!

Nitrogen species (NOx, NO, NO2)



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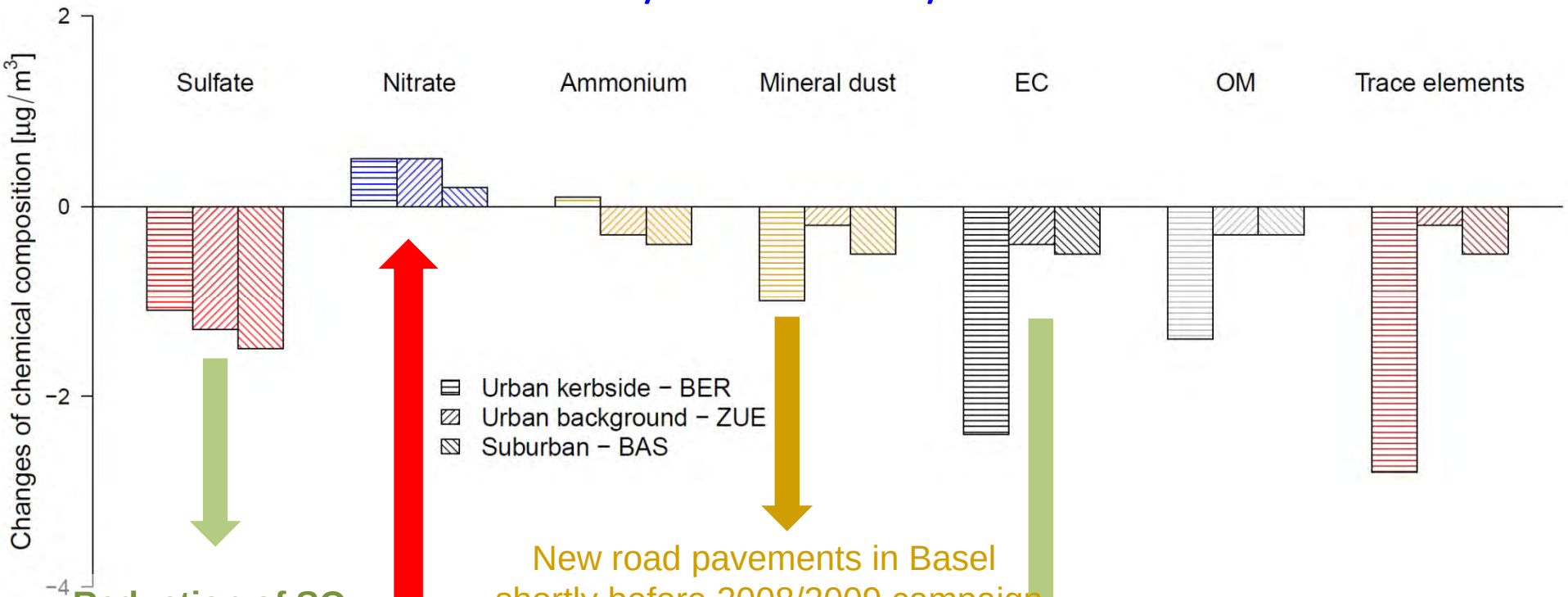
1998/1999 - 2008/2009



Reduction of SO_2 emission regulations e.g. less S in fuel

Exchange of SO_2 by NO_x species DeNovo-formation of NO_2 in some DPF types

New road pavements in Basel shortly before 2008/2009 campaign Reduction of re-suspension of mineral and road dust.

Reduction of EC emissions Euro vehicle standards changes of fleet, DPF for diesel vehicles, DPF mandatory for construction machinery

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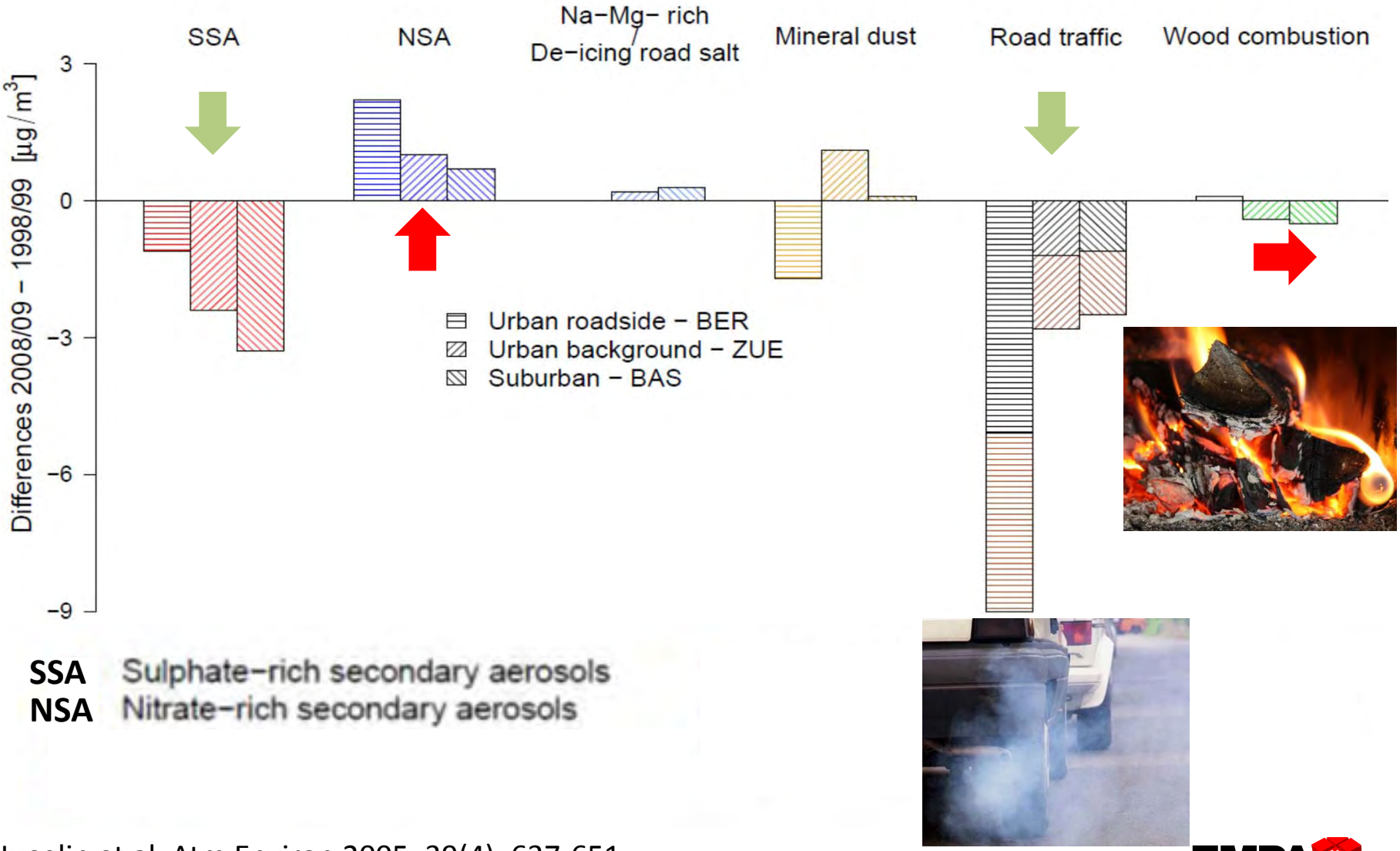
Changes of average source contributions in PM10
(1998/1999 – 2008/2009)



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Acknowledgements

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A. Fischer

N. Heeb

R. Gehrig

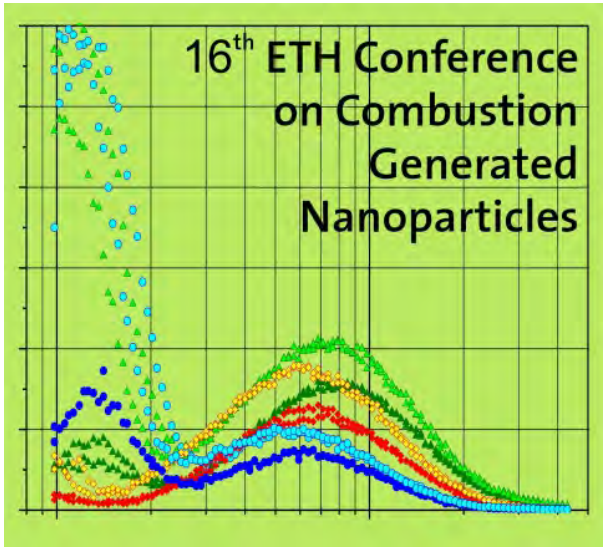
C. Hueglin

Thank you for your attention

16th ETH-Conference on Combustion Generated Nanoparticles

June 24. - 27 , 2012 Zurich, CH

*www.lav.**ethz**.ch/nanoparticle_conf/*



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