18. ETH-Conference on Combustion Generated Nanoparticles – Zürich June 2014

PM versus PN

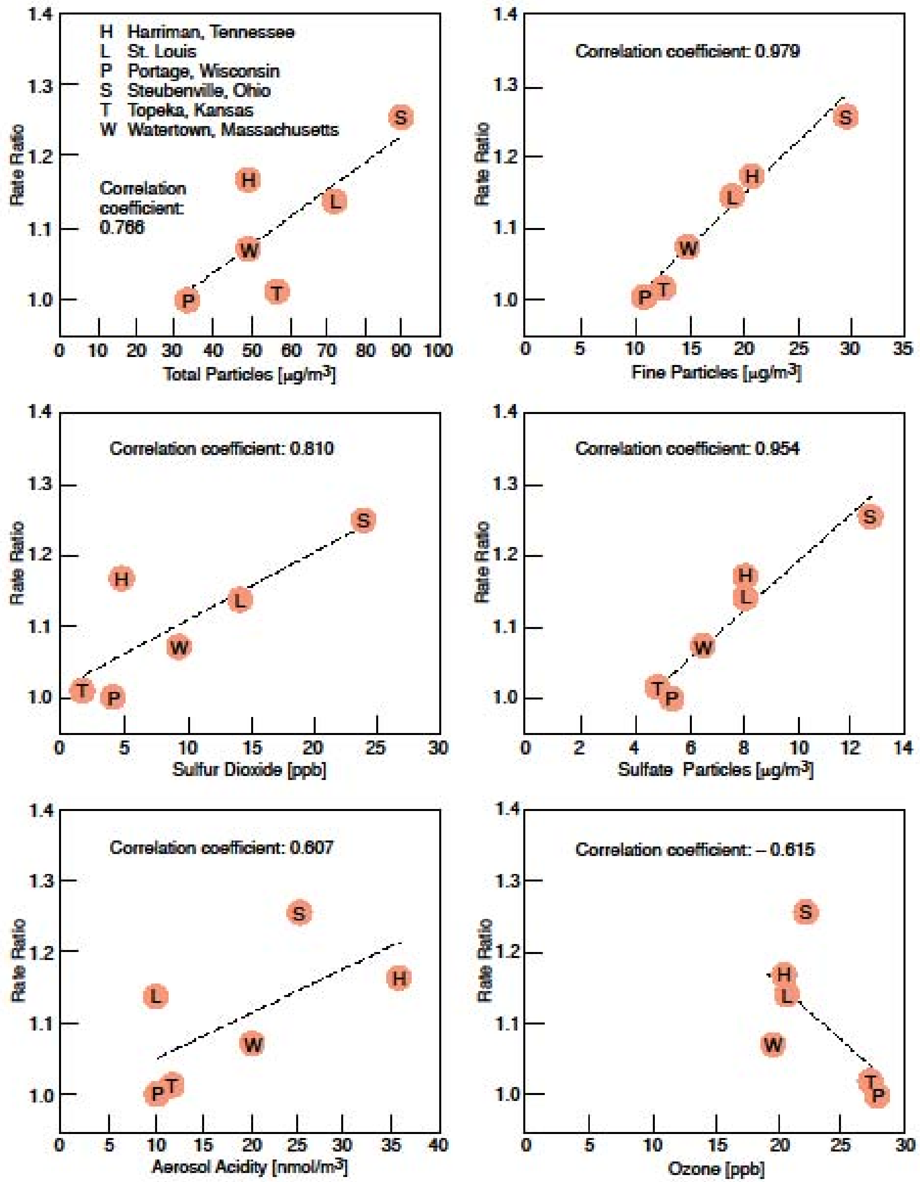
which Parameter describes the Toxic Air Contaminant emitted by CI and SI Engines better and should thus be used for Emissions Limits and AQ-Limits

Andreas C.R. Mayer

Which TOC correlates to Mortality ?

6-Cities-Study
USA 1978-93
15‘000 cases

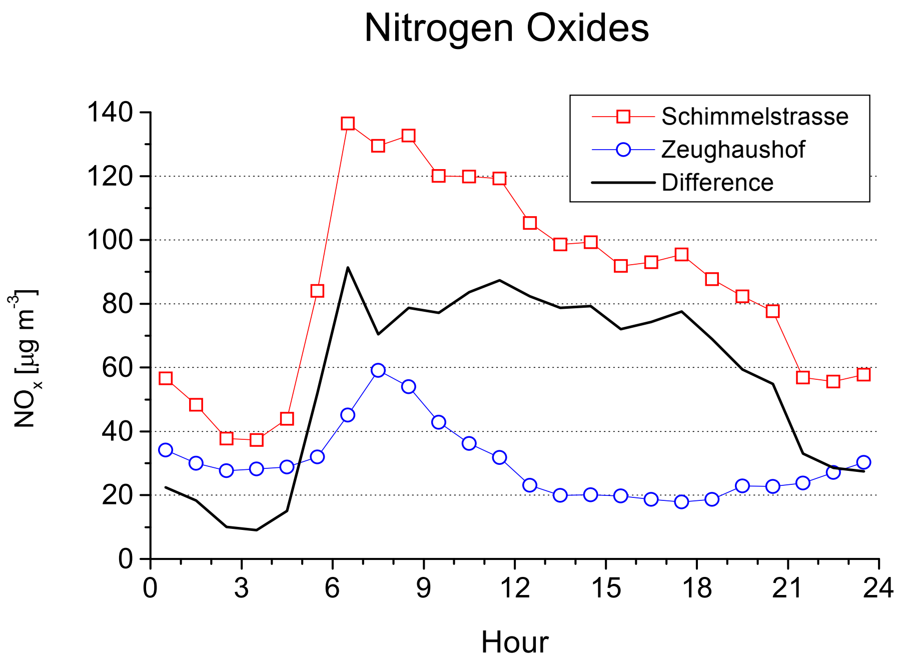
Correlation with fine particles only

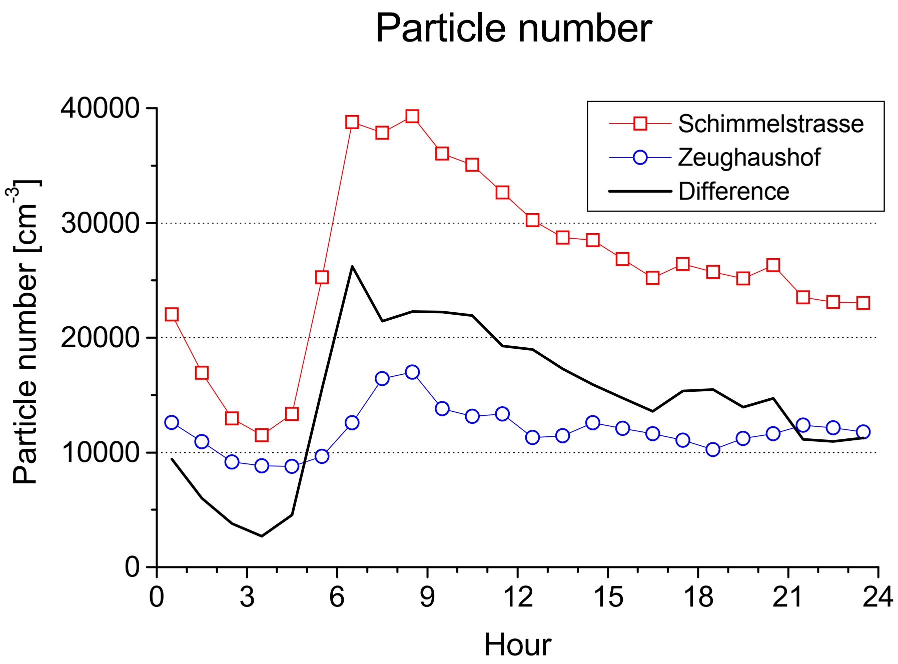


Source: Dockery NEJM 1993

Interpretation difficult: NOx or PNC ?

Rosengarten Studie Imhoff SAE 2008-01-0336

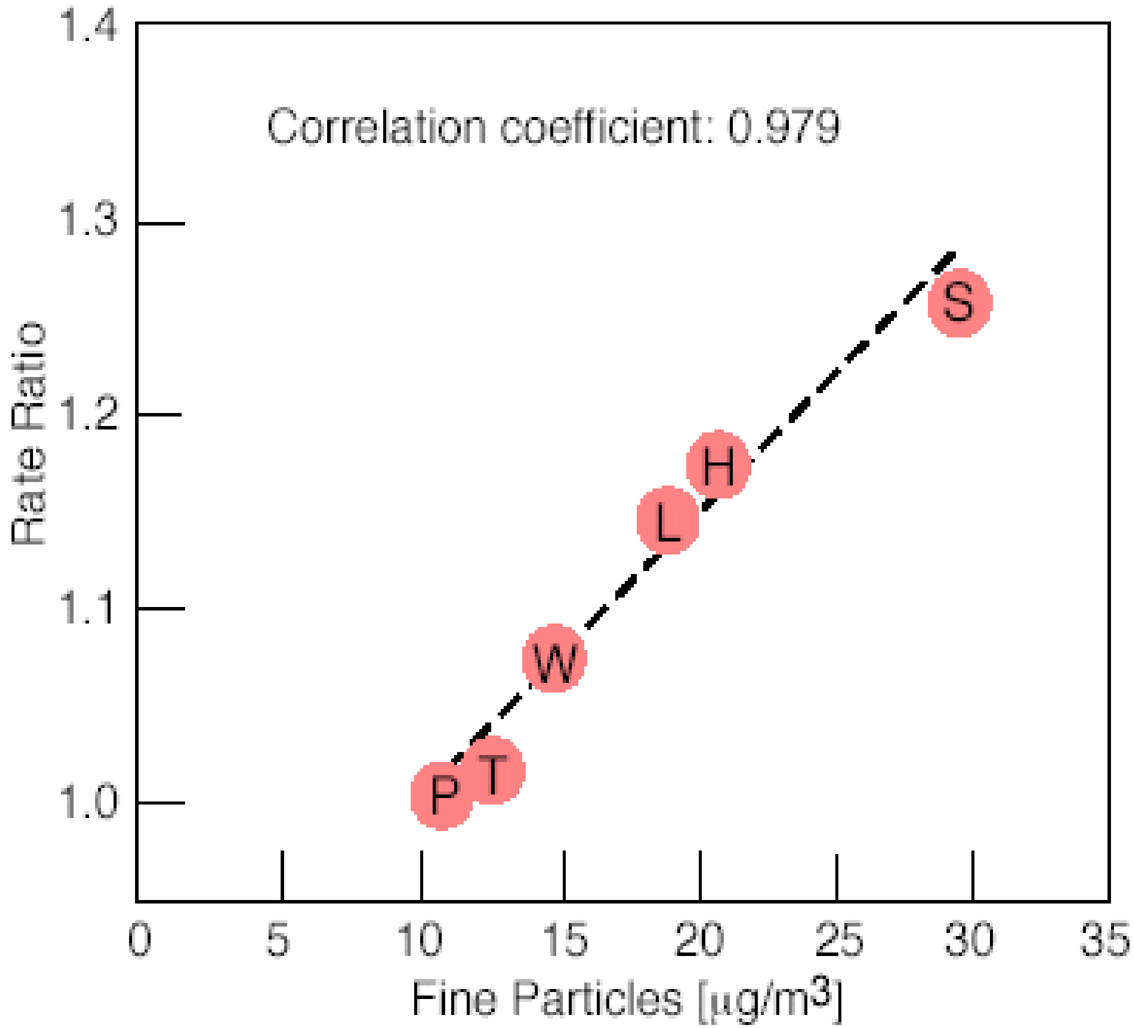




NO2 was always measured in epi-demiological studies PNC not – «maybe health effects attributed to NO2 in the past result from PNC» Neuberger, Vienna April 2014

Long Term Effects

Mortality due to PM 2.5 quantified



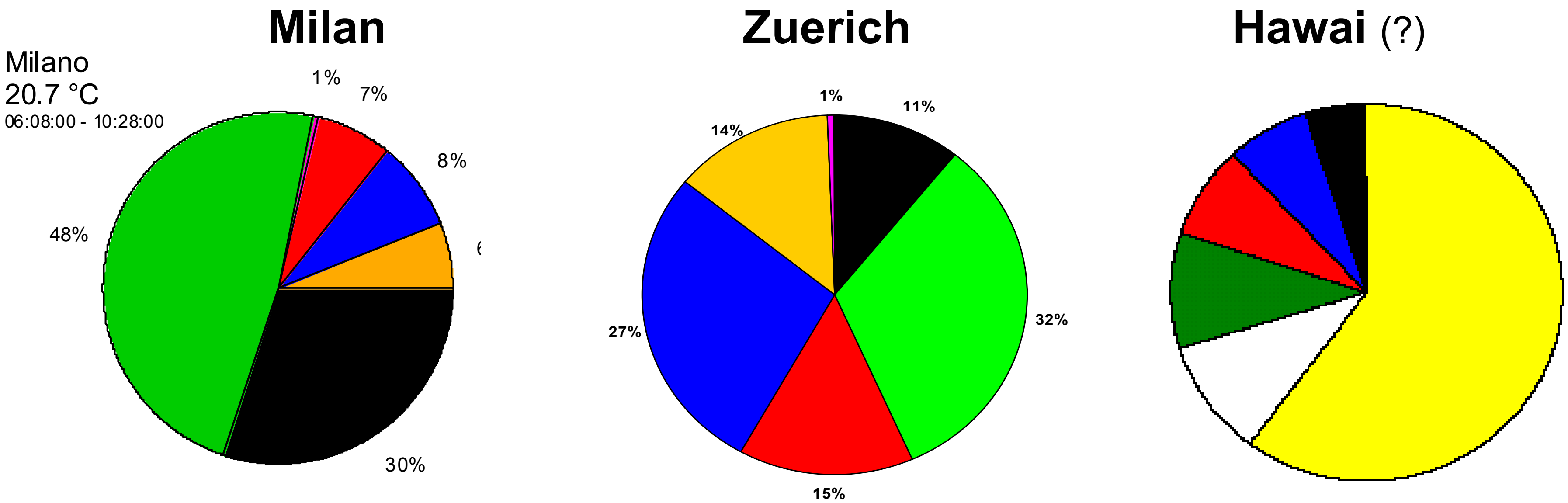
This does not mean that PM2.5 <u>is the toxic substance</u>, but only means, that PM2.5 <u>contains a toxic substance</u>

→ so we need to find the culprit to draw right conclusions

What is PM2.5 - Mass [mg/m3] of what ?

mix of unspecified substances – which is the toxic one ?

what represents the engine emission ?



PM2.5 [μg/m^3] identical Mass

But these 3 situations can definitely not represent same air pollution = toxicity

Black Carbon
Organic mass
Nitrate
Sulfate
Ammonium
Chloride

If we do not know which Size and Substance is the Toxic Element

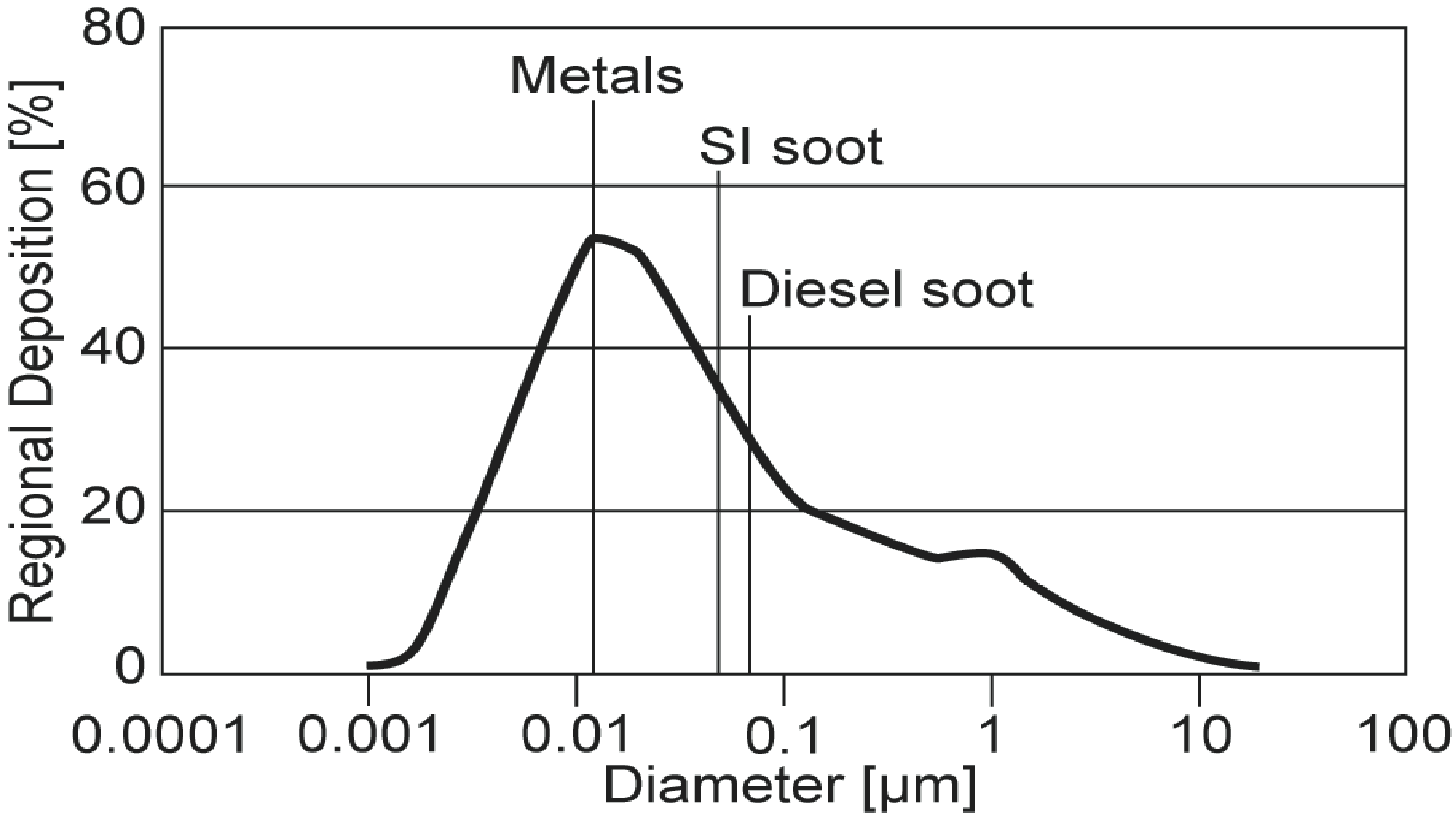
- *we can not identify the responsible sources*
- *we can not determine the countermeasures*
- *we can not justify to spend money*
- *we can not control the success*

Best example is Berlin LEZ, where traffic emissions were reduced by 50 % but PM10 by < 5 %

Which Substance in PM2.5 ?

Health Effect Equivalence Analysis HEQ, a tool to answer this question. Simplified Example:

Toxicity -Parameters	Sulfates Nitrates	Mineral Dust	Solid Nano-Particles
invasive (mobility) penetrate membranes ?	☹ 1	☺ < 0.1	☹ 1
Insoluble Solids ?	☺ 0.01	☹ 1	☹ 1
persistant collected and stored ?	☺ 0.01	☹ 1	☹ 1
carcinogen mutagene, genotoxic ?	☺ 0.01	☺ 0.01	☹ 1



The Lung is an open door for ultrafine particles

Histological Research

of lungs compartments from 50 yeary old autopsies

Electron microscopic analyses revealed the dominance of retained soot and a surfeit of other particle types. A variety of metal-bearing particle types were found in all compartments, but Pb, Zn, and SnZn types appeared the least biopersistent. The results support the acute toxicologic importance of ultrafine carbonaceous and metal PM. *Key words:* 1952 London smog, autopsy, lung

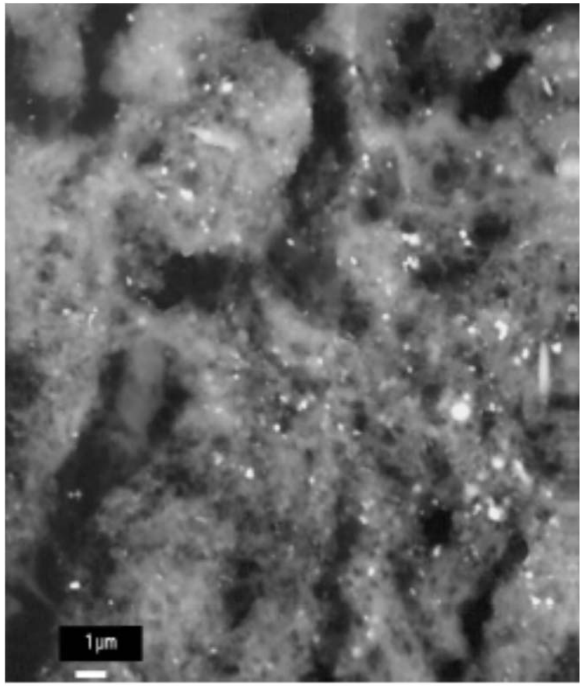


Figure 2. BE micrograph of section of airway aggregate from case 2 revealing abundant submicrometer inorganic (bright) particles.

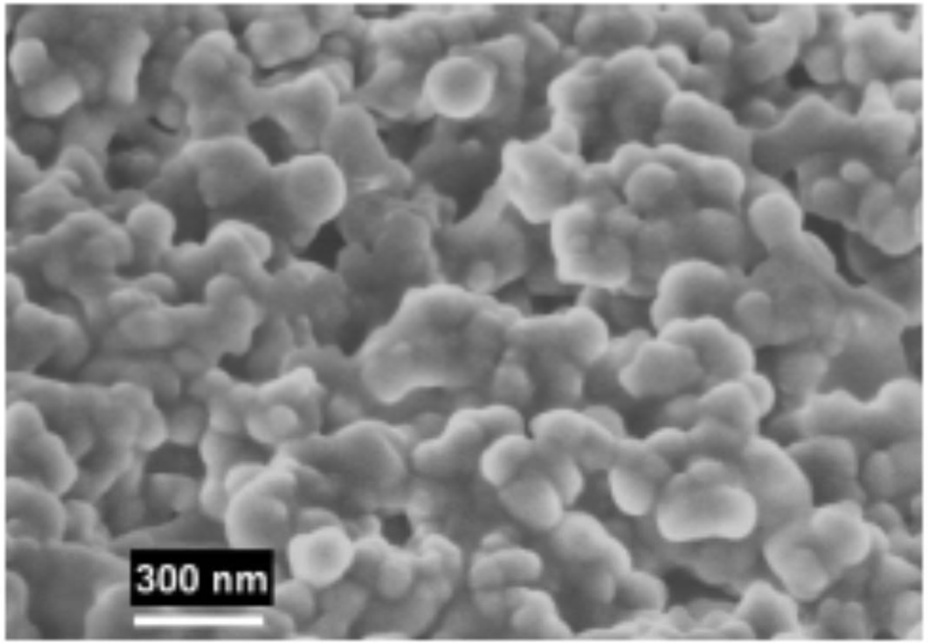


Figure 3. High-magnification field emission scanning electron micrograph of airway aggregate from case 2 showing ultrafine PM structure.

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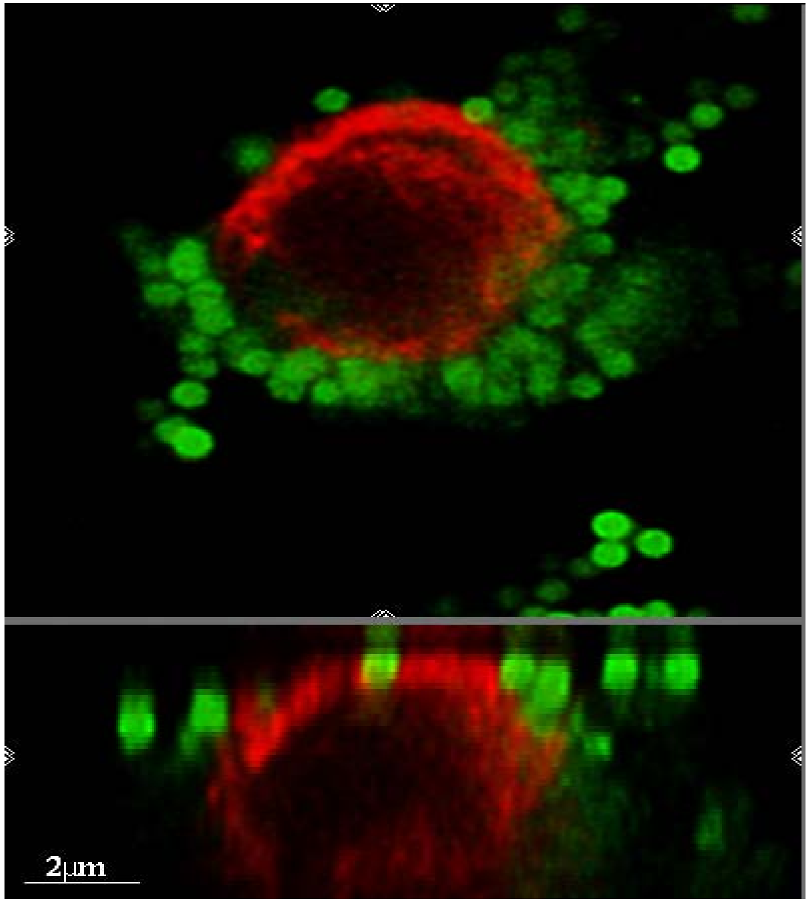
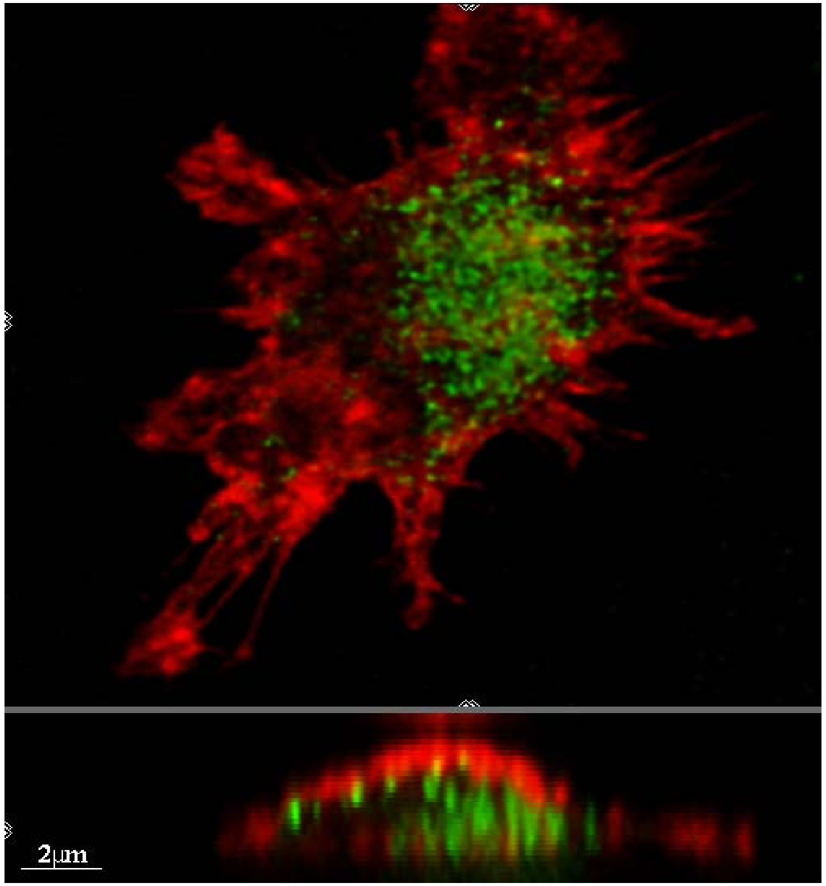
Particle Size Penetrating Membranes

1000 nm
Polystyrene Particles



78 nm
Polystyrene Particles

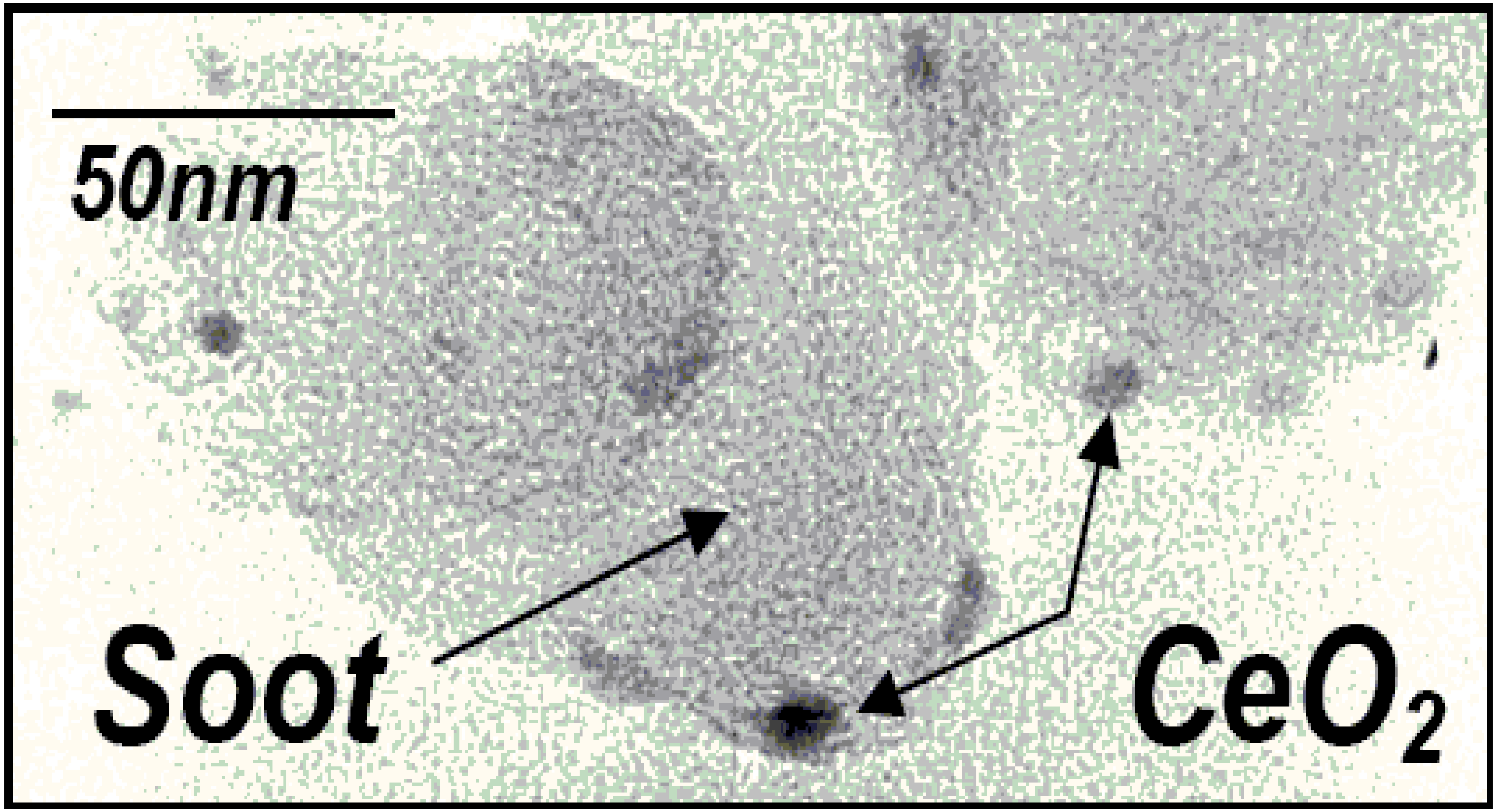


Laser Scanning Microscopy

B. Rothen-Rutishauser, University Berne

Cerium Oxide FBC on Soot Particles

source:Rhodia

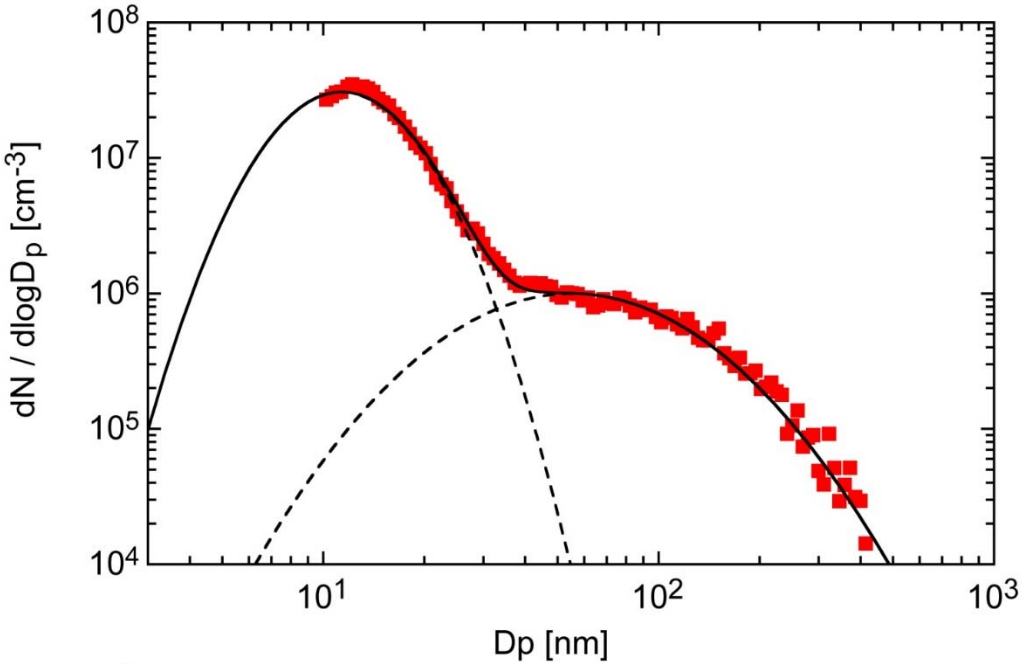


Partikel Emission of ICE

Diesel

Russpeak: 80 nm; 10^6

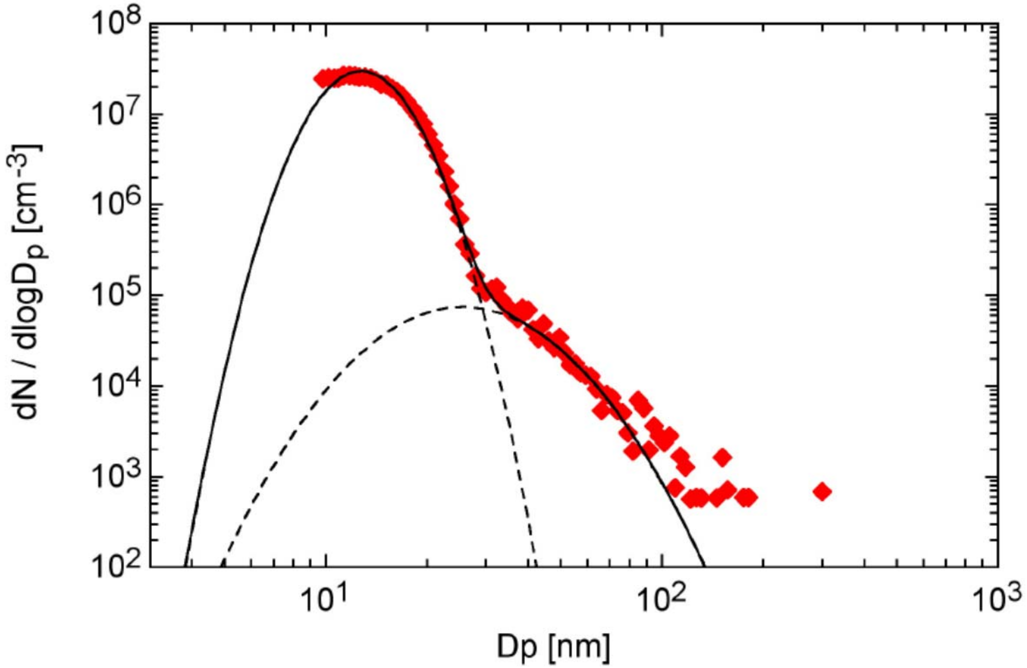
Aschepeak: 10 nm; 10^7



Petrol

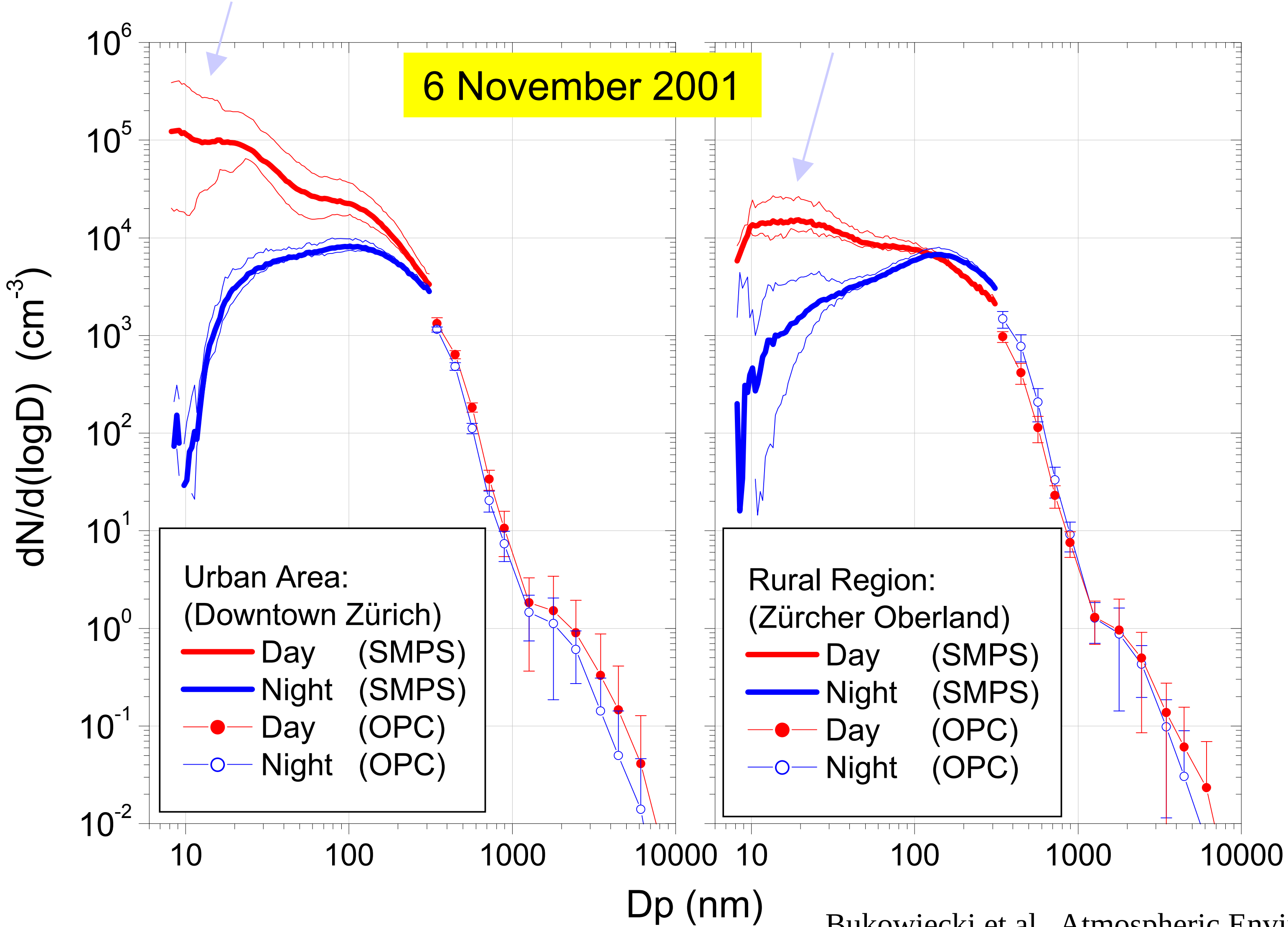
Russpeak: 40 nm; 10^5

Aschepeak: 10 nm; 10^7



Soot and Ash Peaks

Aerosol Number/Size – Distribution
City (Zürich) and Coutry (Zürcher Oberland)



Bukowiecki et al., Atmospheric Environment, 2002

Health Effect for PNC and Mass PM 2.5

Short Term Cardiovacular Mortality (CVD) – Katsuyanni ETH-NPC 2012

Original Data

Study	City, Year	**CVD [%] per PN P/cm3**		CVD - PM 2.5 **per 10 µg/m3**
Atkinson	London 2010	2.2/10166		0 - 0.5 %
Stolzel	Erfurt 2007	3.1/9748		0 - 1.5 %
Breitner	Beijing 2011	7.3 / 6250		NA
Branis	Prag 2010	1.1/1000		0 - 0.4
Forastiere	Rom 2006	7.6/27790		0.1- 3.1 %
Kettunen	Helsinki 2012	8.5/4979		2.1 - 23 %
Average				3.1 %

Health Effect for PNC and Mass PM 2.5

Short Term Cardiovacular Mortality (CVD) – Katsuyanni ETH-NPC 2012

normalized to 10’000 P/cc

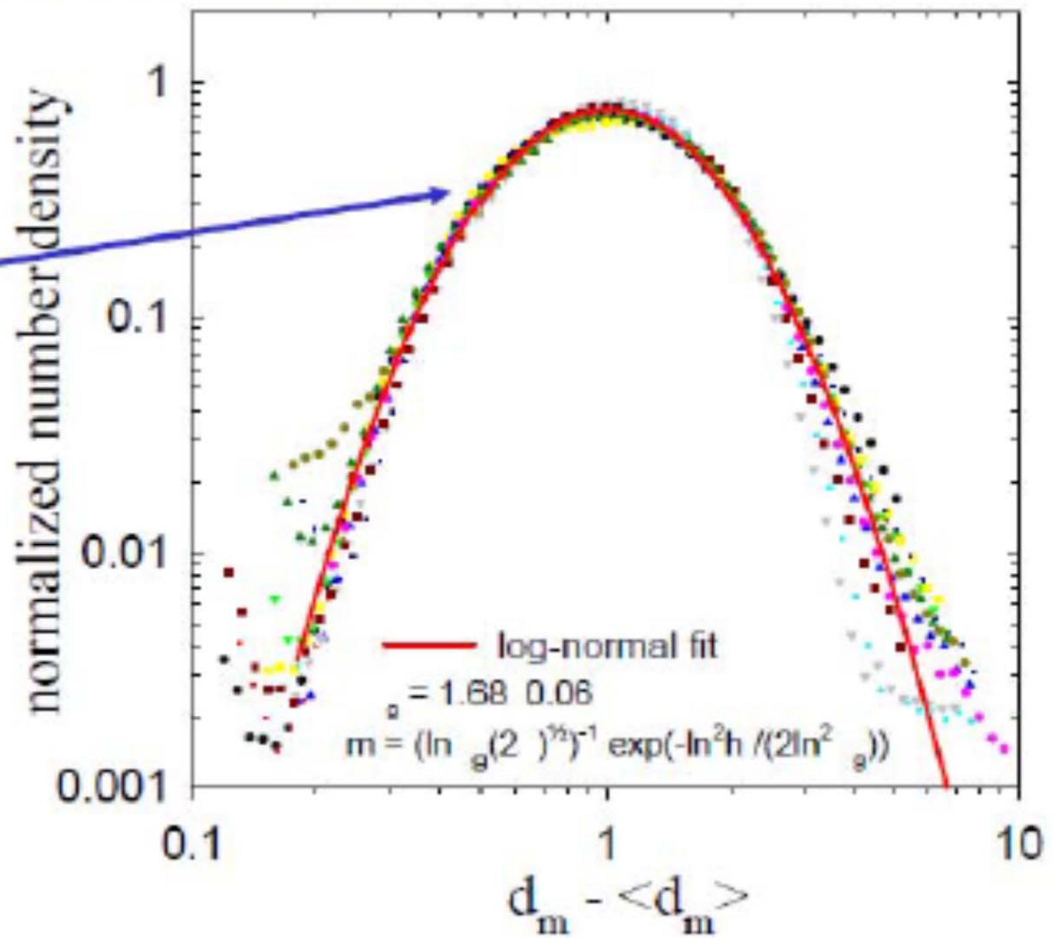
Study	City, Year		CVD - PNC per **10‘000 P/cm3**	CVD - PM 2.5 **per 10 µg/m3**
Atkinson	London 2010		2.2 %	0 - 0.5 %
Stolzel	Erfurt 2007		3.2 %	0 - 1.5 %
Breitner	Beijing 2011		11.7 %	NA
Branis	Prag 2010		11 %	0 - 0.4
Forastiere	Rom 2006		2.7 %	0.1- 3.1 %
Kettunen	Helsinki 2012		17.%	2.1 - 23 %
Average			7.9 %	3.1 %

Calculate Particle Mass from N and d

following the Maricq-Algorithm,

respecting size statistics, fractal dimension and density

- PMP method removes nuclei particles
- Remaining solid particles follow lognormal distribution with 2 free parameters
  - Number
  - Mean diameter
- Mean diameter between ~40 – 80 nm
- To fulfill number standard of $5x10^{11}$ #/km → PM mass must be < 1 mg/km



$$\text{Mass} = N\ \pi/6\ \rho_0\ d_0^{(3-df)}\ \mu_g^{df}\ \exp(df^2\ (\ln\sigma_g)^2/2)$$

Health Effect for PNC and Mass PM 2.5

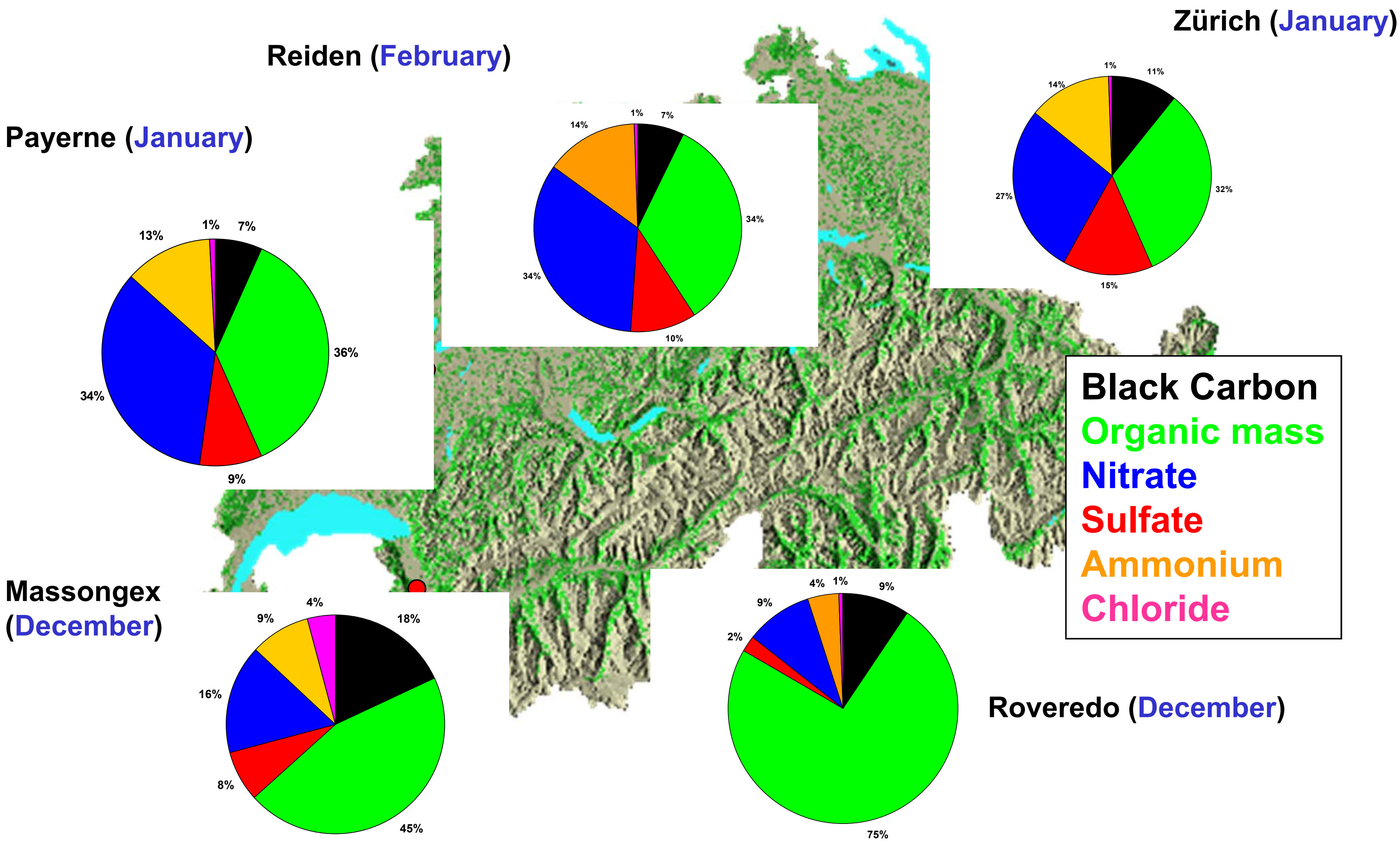
Short Term Cardiovacular Mortality (CVD) – Katsuyanni 2012

comparing mass (PNC) to mass (PM2.5)

Study	City, Year		CVD -PNC per **10 µg/m3**	CVD - PM 2.5 **per 10 µg/m3**
Atkinson	London 2010		6.8 %	0 - 0.5 %
Stolzel	Erfurt 2007		9.9 %	0 - 1.5 %
Breitner	Beijing 2011		36.5 %	NA
Branis	Prag 2010		34.1 %	0 - 0.4
Forastiere	Rom, 2006		8.4 %	0.1- 3.1 %
Kettunen	Helsinki 2012		52.7 %	2.1 - 23 %
Average			24.7 %	3.1 %

Assumption: Particles 70 nm, Density:1, mass 3.2×10^{-16} g/P / 10‘000 P/cm3 = 3.2 µg/m3

Average CH-Compositions in Winter



What does this mean for Monetary Health Impact MHI ?

- assuming MHI is 400 €/kg PM10 (Swiss Data)
- assuming exhaust soot content of PM2.5 is 15 %
- concluding soot particles are the main toxic

→**MHI of soot is 3’200 €/kg soot**

→Benefit/Cost-Ratio of a emission measure eliminating soot will be > 20

→Health Cost and B/C-Ratio must be based on PNC

VERT 1996

Based on this physiological and toxicological findings (mostly from occupational health, see Johannesburg convention 1952) a first definition was proposed

„Solid, insoluble particles in the mobility size range of 10-500 nm“

→development of new instrumentation
→ BAT-particle filters
→ start of the ETH-NPC

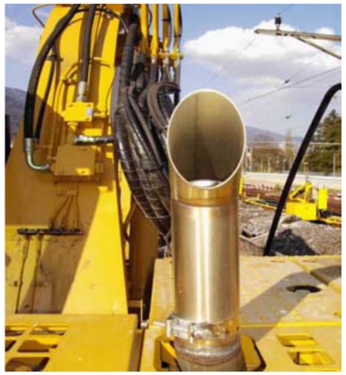
Conclusion on European Level

EU CO-Decision (Art.12, Rec.15 - 2008)

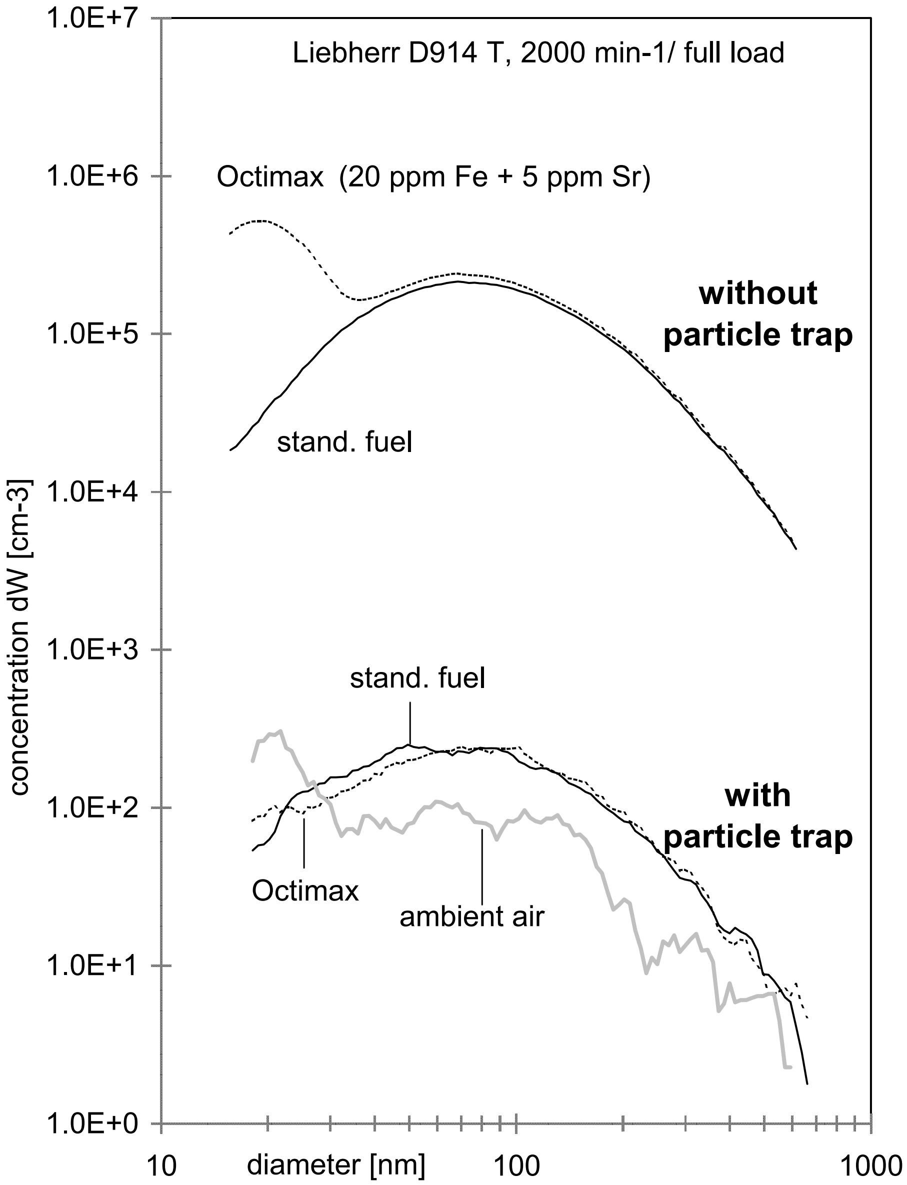
- In order to achieve these environmental objectives it is appropriate to indicate that particle number limits are likely to reflect the highest level of performance with particle filters using best available technology
- .. the commission shall introduce particle number based limit values at a level appropriate to the technologies actually being used.

BAT is Filtration downstream Engine

Filtration achieves 99.99 % on every engine as long as SV is below the limit.
<u>One</u> VERT test is sufficient
Duplication avoided



99.99 % means
0,001 mg/kWh



Directive 1999/30/CE for AQ

EU limit values for PM10 and NO_2		
averaging period	limit value	attainment period
24 h	50 µg/m^3 PM $_{10}$ 35 exceedances/year	1 Jan. 2005
1 year	40 µg/m^3 PM $_{10}$	1 Jan. 2005
24 h	50 µg/m^3 PM $_{10}$ 7 exceedances/year	1 Jan. 2010*
1 year	20 µg/m^3 PM $_{10}$	1 Jan. 2010*
1 h	200 µg/m^3 NO_2 18 exceedances/year	1 Jan. 2010
1 year	40 µg/m^3 NO_2	1 Jan. 2010

* **indicative limit values**, to be reviewed by the EU Commission

These values are those being elaborated in 1997 by a WHO working group and well-known as the WHO-AQG (Air Quality Guidelines of World Health Organization).

Switzerland 1998:

PM 10 24h: 50 µg(m3 / 1 x pa
1 year 20 µg/m3
NO2: 1h 100 µg/m3
1 year 30 µg/m3

Ambient Air Limit Values Monitoring and Control

- Ambient Air Limit Values still PM10 resp. PM2.5
- not respecting impact of size or substance

→ Cleaning car exhaust not reflected by ambient air metrics
→ Toxicity is not correctly reflected by ambient air metrics
→ Epidemiologic conclusions are misleading
→ Policies based on mass (PM10 or PM2.5) will fail

Regulatory and Air Quality Implications of Setting Particle Number Standards

Roy M. Harrison
University of Birmingham and
National Centre for Atmospheric Science

Conclusions

- **It would be possible to use the results of studies such as Atkinson et al. (2010) and Stolzel et al. (2007) to set air quality standards for (traffic generated) particles by number.**

Messages and Conclusions

1. PM is not sufficient to address health effects
2. PM is not sufficient to define BAT emission control
3. PM criteria are misleading for filter selection
4. PN instrumentation is available
5. PN is undispensible to link emission to air quality
6. **AQ must replace or complement PM by PN**
7. **Metrics in Emission and AQ must be coherent**