4th International Workshop on Nanoparticle Emissions; Haifa 15th Siwan 5776

Physical and Chemical Properites of Ultrafine Particles

must be respected

to select and monitor

best available technology

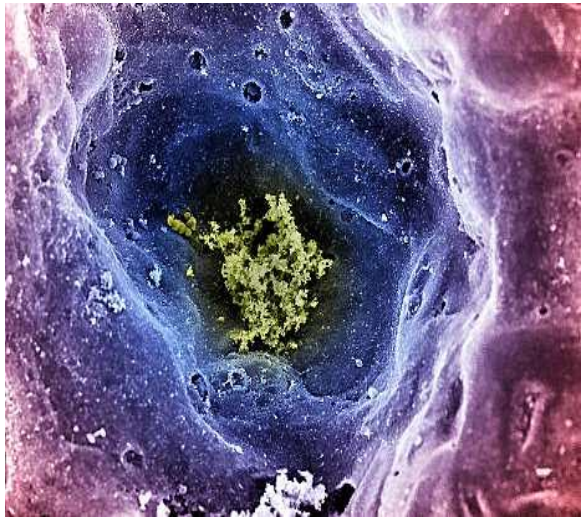
Andreas C.R. Mayer

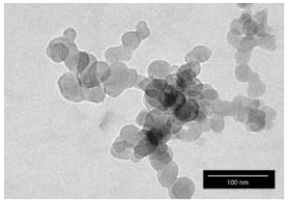
Why we need to question PM 2.5 [g/m^3]

- **PM2.5 does not respect physical and chemical properties of ultrafine particles in the breating air, wich must be regarded the Toxic Air Contaminant No1**
- But in **order to select and provide the best available mitigation technology w**e need to to define and classify the **main toxic air contaminants TOC** by physicochemical terms
- And we need to come up with a **health oriented monetary value** for these TAC ($/kg) to justify measures

Problem No. 1 – neglecting substance

what we breathe

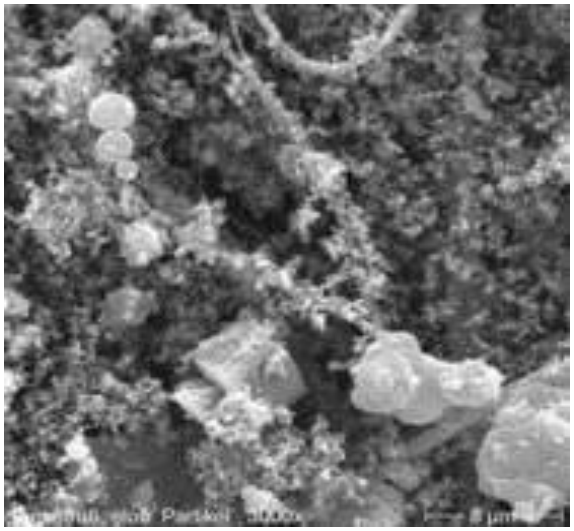




is an aerosol of very different particles

- solids and/or volatiles
- soluble and/or persistant
- highly toxic and/or harmless
- natural and/or industrial

what we measure with PM 2.5



is the overall mass of all particles collected on a filter during 24 hours

Irrespective of particle size

Irrespective of their substance

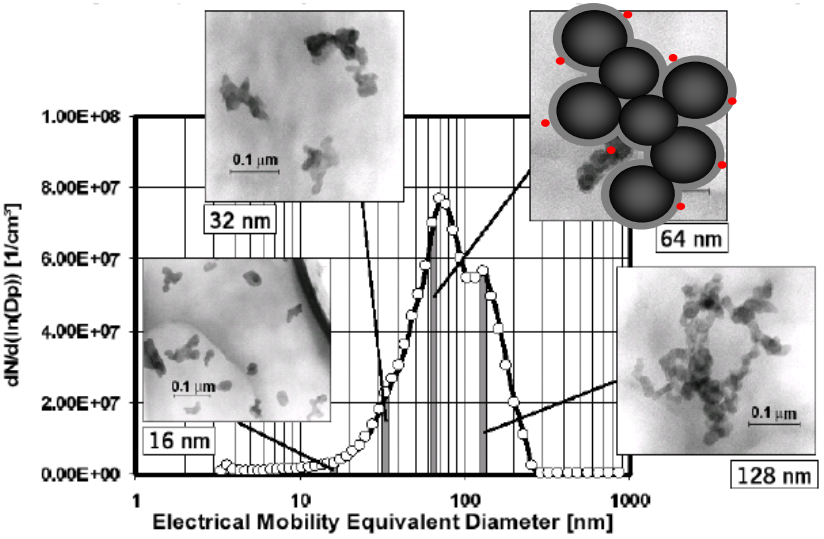
Irrespective of exposure dynamics

Is this simplification acceptable?

Comparing apples with oranges?

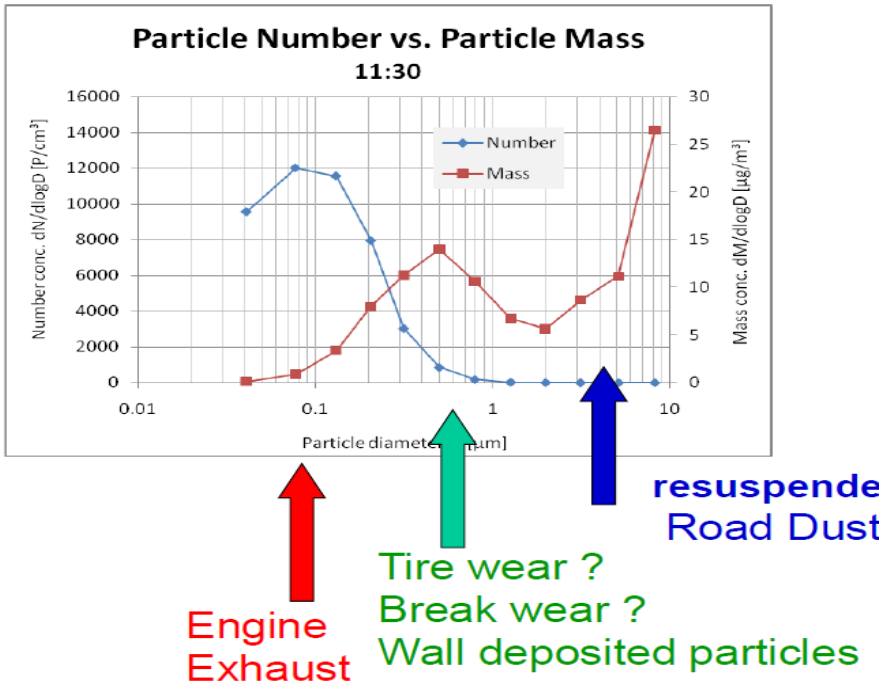
Problem No. 2 – neglecting size

what our Engines emit



Are solid core particles
in the size range of **< 100 nm**
covered by highly toxic PAH and
decorated be metal oxide particles
from lube oil and wear

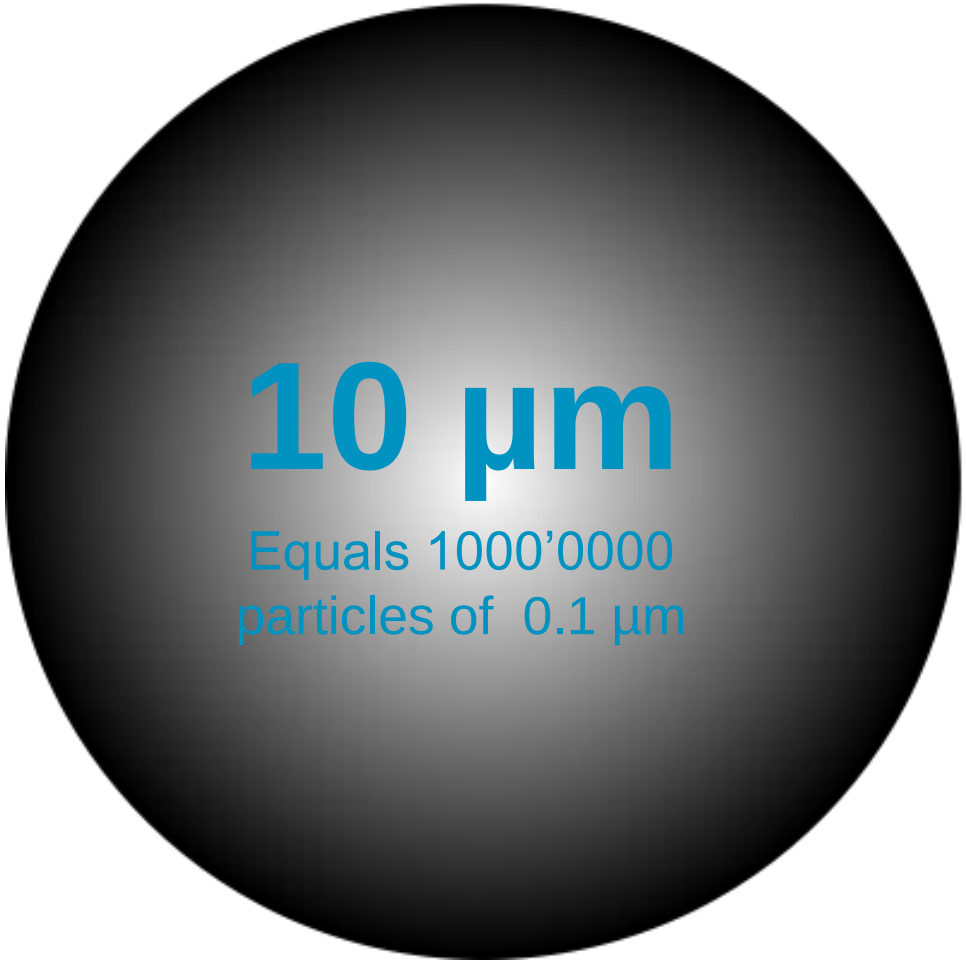
what we measure with PM 2.5

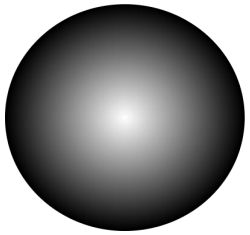


is the overall mass of all particles
dominated by dust **> 5000 nm**
Engine emissions are < 20%

Is this simplification acceptable?

Particle Mass vs. Size, Surface, Number

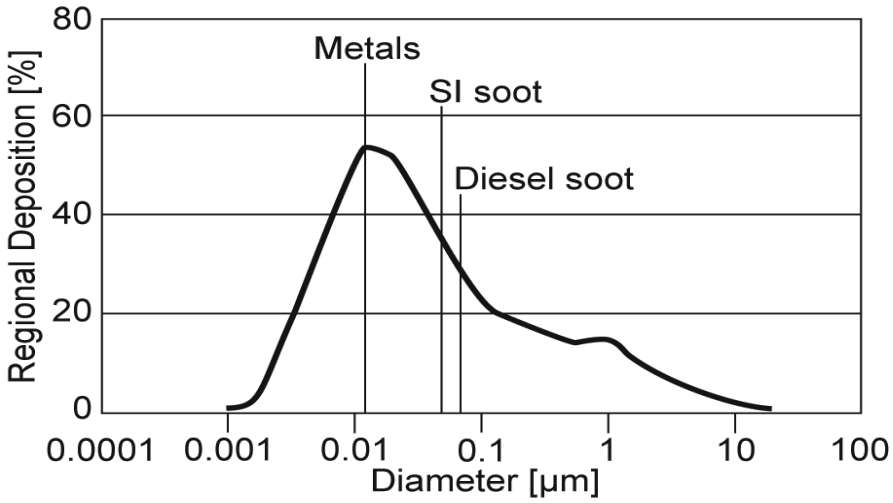




If a particle is soluble, then the total mass is the appropriate first metric of exposure; however, if it is insoluble, size and surface are more appropriate parameters (Oberdörster, EPA 2015)

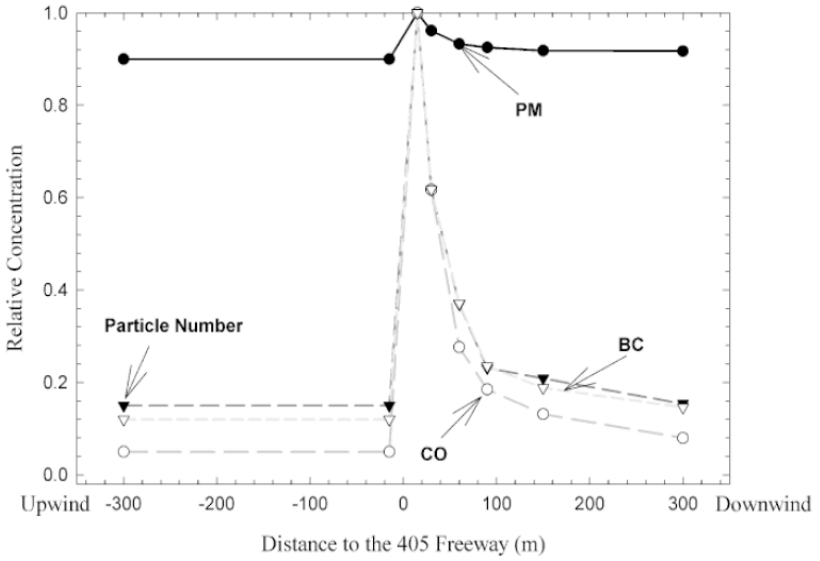
Problem No. 3 – neglecting source

what our engines emit



is exactly in the sensitive size range of the lungs to penetrate the membranes and enter into the blood stream

what we measure with PM 2.5



is neglecting engine emissions

does not notice the UFP from traffic

is no indicator for traffic emissions

Is this simplification acceptable?

we need equivalent metrics for emission source and the TAC target

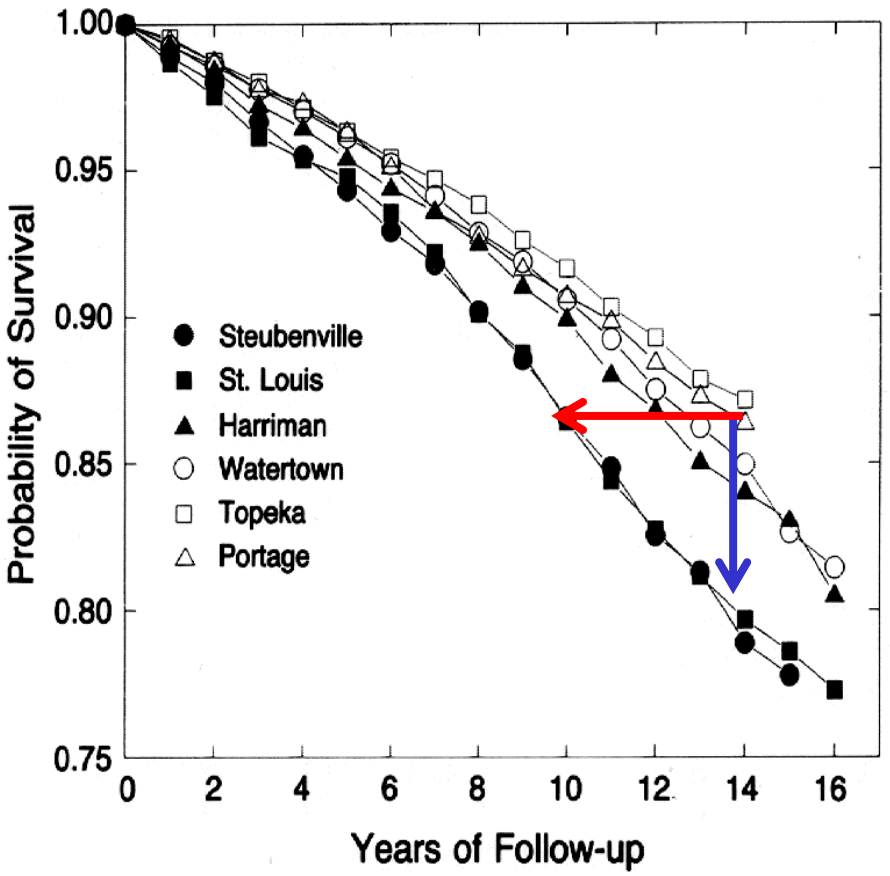
How to link
Air Pollution to Public Health?
→ by Epidemiology
based on mass PM10 or PM2.5

Epidemiologic evidence needs 20 years of consistant observation and comes always too late.
Preventive measures are needed for public health.

Dough Dockery ETH-NPC 2011

1973-1993 “Six Cities Mortality Study”

- Random sample of 8411 adults in six cities
  - Dirty: *Steubenville, OH & St. Louis, MI*
  - Moderate: *Watertown, MA & Harriman, TN*
  - Clean: *Topeka, KS & Portage, WI*
- Enrolled 1974-77
- 14-16 years of mortality follow-up



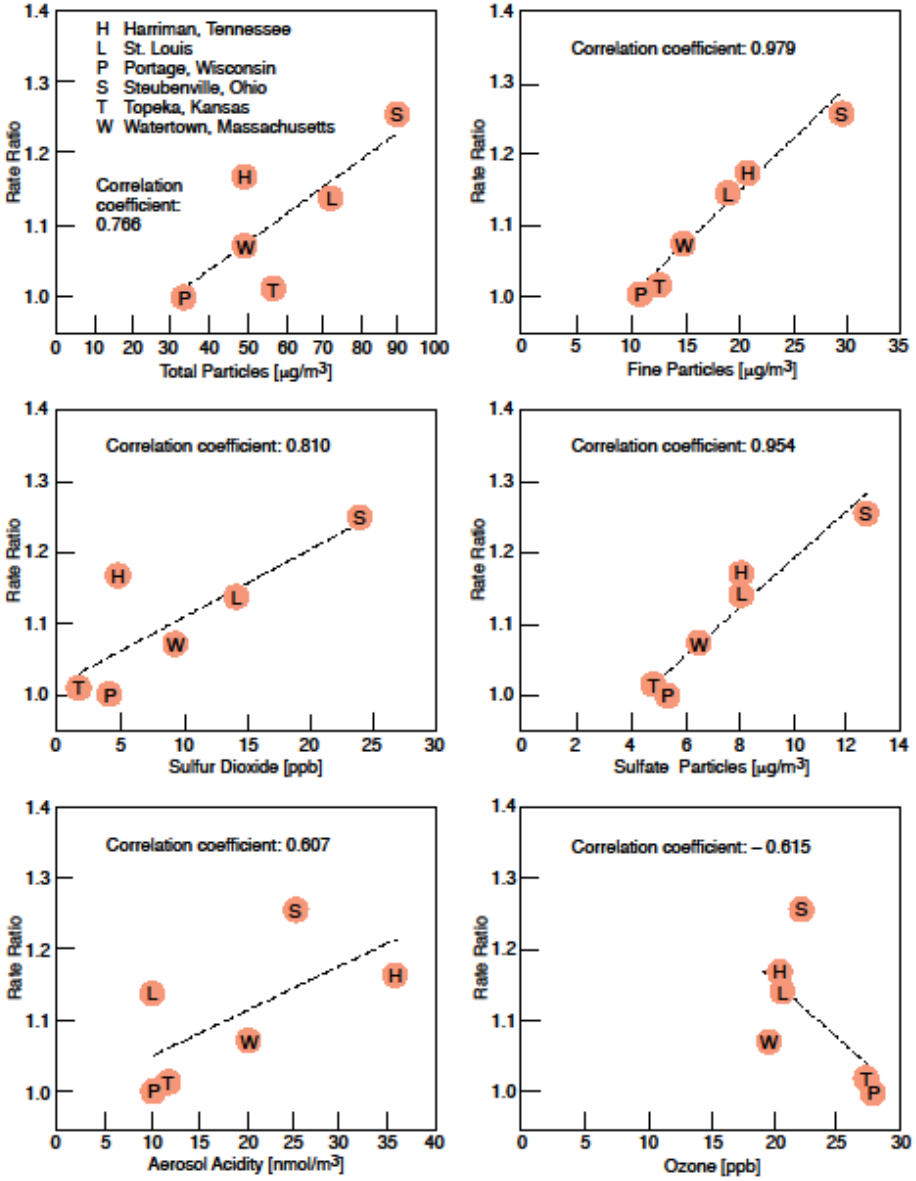
Dockery et al, NEJM 1993;329:1753

Statistics:

which TAC correlates best with mortality ?

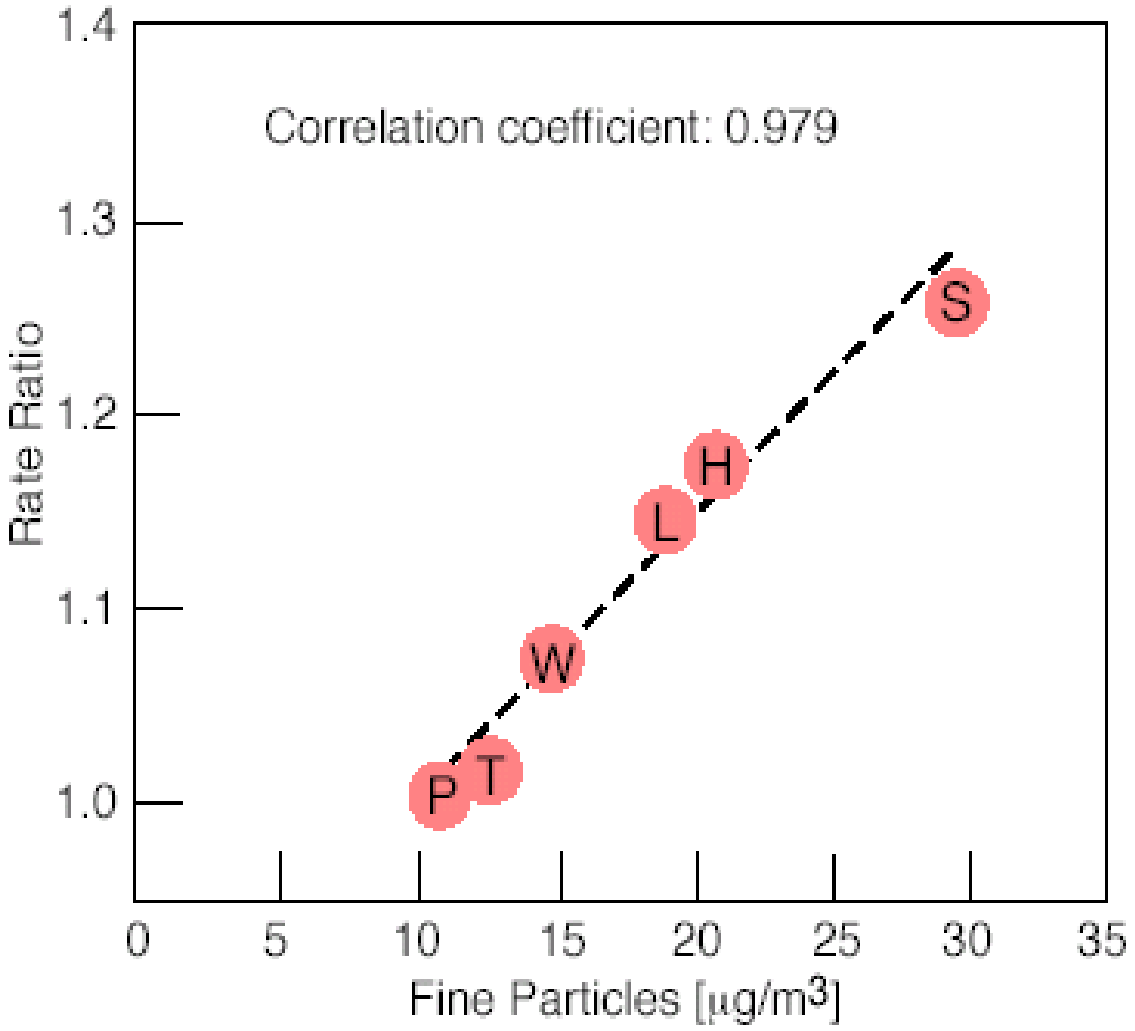
6-Cities-Study
USA 1978-93 observed
8'400 test persons

→ Finding
statistic significant
correlation
only with fine particles



Source: Dockery NEJM 1993

Dose/Effect for Mortality due to PM 2.5



This does not mean that PM2.5 is the toxic substance,

but only means, that PM2.5 contains a toxic substance

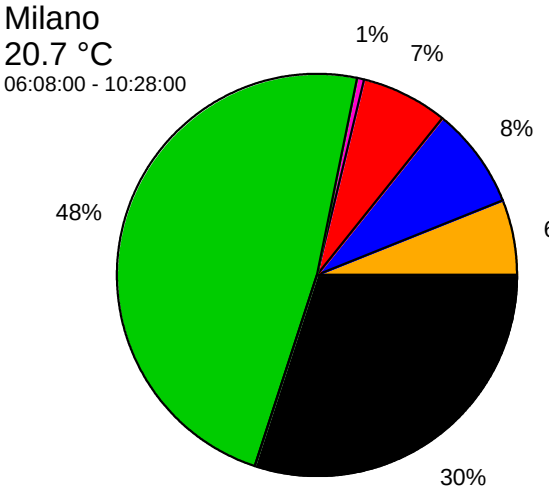
→ so we need to find the culprit to draw right conclusions

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

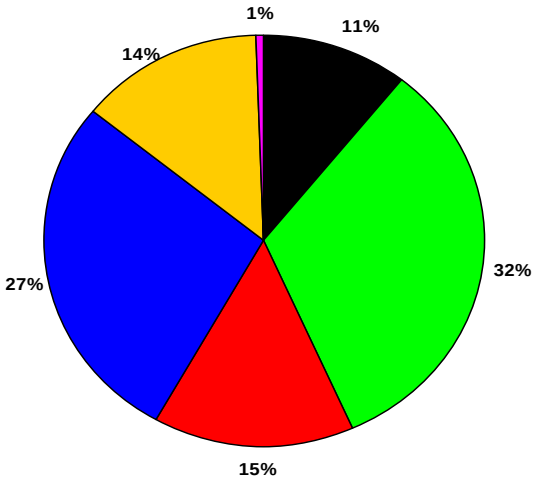
mix of unspecified substances – which is the toxic one ?

what represents the engine emission ?

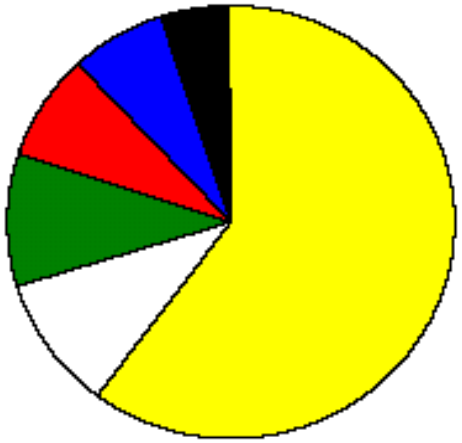
Milan



Zuerich



Hawaii (?)



PM2.5 [µg/m^3] **identical Mass**

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

Black Carbon	**1-5**
Organic mass	**1-4**
Nitrate	**1-4**
Sulfate	**1-2**
Ammonium	**1-3**
Chloride (Salt)	**1-100**

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*

Which Substance makes PM2.5 toxic?

Simplified Example

Toxicity -Parameters	Sulfates Nitrates	Mineral Dust	Solid Nano-Particles
invasive (mobility) can penetrate membranes	☹ 1	☺ < 0.1	☹ 1
Insoluble or dissolved in water ?	☺ 0.01	☹ 1	☹ 1
persistant or metabolized ?	☺ 0.01	☹ 1	☹ 1
carcinogen mutagene, genotoxic ?	☺ 0.01	☺ 0.01	☹ 1

PM 2.5 Critical Substance Classes?

- **Organic and Elemental Carbon**:
  - EC (fine, coarse)
  - OM / OC (overlap with pPAH)

  Hydrocarbons
  - pPAH
- **Inorganics**:
  - NH4+
  - NO3-
  - SO4-
- **Metals and Metaloxides** :
  - transition metals (all; overlap with individual metal oxides)
  - FeO
  - MgO
  - CaO
  - precious metals (all; maybe individual: Pt, Pd, Rh)
- **Minerals**:
  - mineral dust (silicates, incl. Al, Mg, ...

Weighing by Toxicity Contribution → HEQ

along the way of the particle entering the organism

process	parameters	quantify
Location of aerosol deposition	Diffusion	**Size,**
		Hygroscopicity
Contact with body surface	Solubility in water…	**1/Solubility**
	... in Mucus, Surfactants?	Lipophility
Translocation	Cell membrane penetration; Phagocytosis	**Size**
Interaction	Overall Toxicity	**MAK (Threshold)**
	Bioavailability	?
	Cytotoxicity	?
	Mutagenicity	?
	Carcinogenicity	?
Excretion	Biopersistence	**Decay Time**

→Health Equivalent Index HEQ

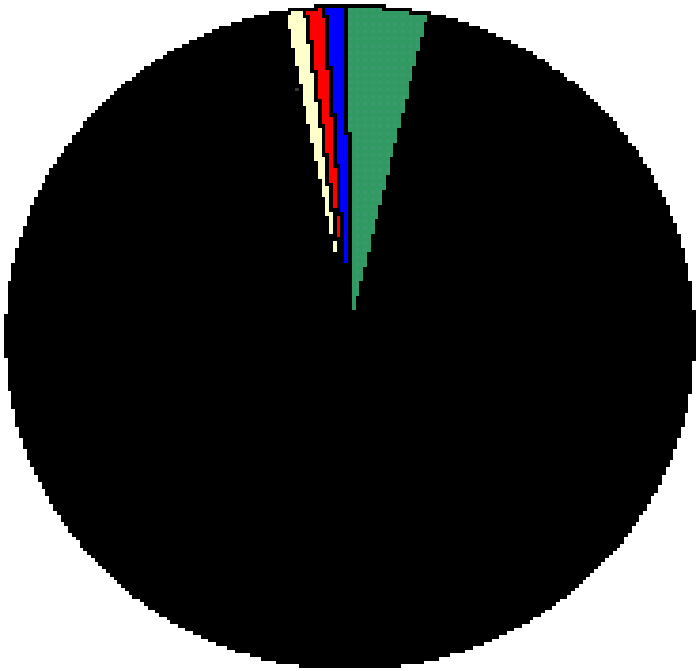
PM-HEQ of a typical PM 2.5 - sample

PM10-HEQ Influence Factors *Example*

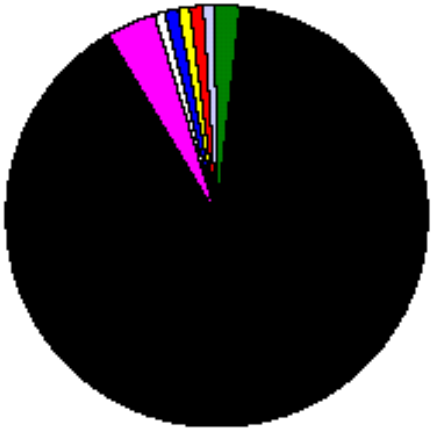
PM10-Compounds	EC < 500 nm	EC > 500 nm	Metals Minerals > 500 nm	Metals <100 nm	Sea Salt	OM	Benz(a) Pyren	Ammonia	Nitrate	Sulfate	Water
Mass %	15	2	10	2	15	20	0.01	10	10	10	6
Solubility	1	1	1	1	0.001	0.2	1	0.01	0.01	0.1	0.0001
Mobility	1	0.1	0.1	1	1	1	1	1	1	1	1
Toxicity	1	0.1	0.1	10	0.01	0.1	50	0.1	0.1	0.1	0.001
HEQ -Index	1	0.01	0.01	10	0.00001	0.02	50	0.001	0.001	0.01	0.000001
PM10-HEQ	15	0.02	0.1	20	0.00015	0.4	0.5	0.01	0.01	0.1	0.000006

Resulting PM10-HEQ

Milan



Zürich



Hawaii

Do we only have Epidemiology by particle mass PM10 or PM2.5

No

since 2012 we have >10 studies comparing epidemiologic results based on mass PM and number PN

Meta-Study Katsouyanni ETH-NPC 2012

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)–Katsouyanni ETH-NPC 2012

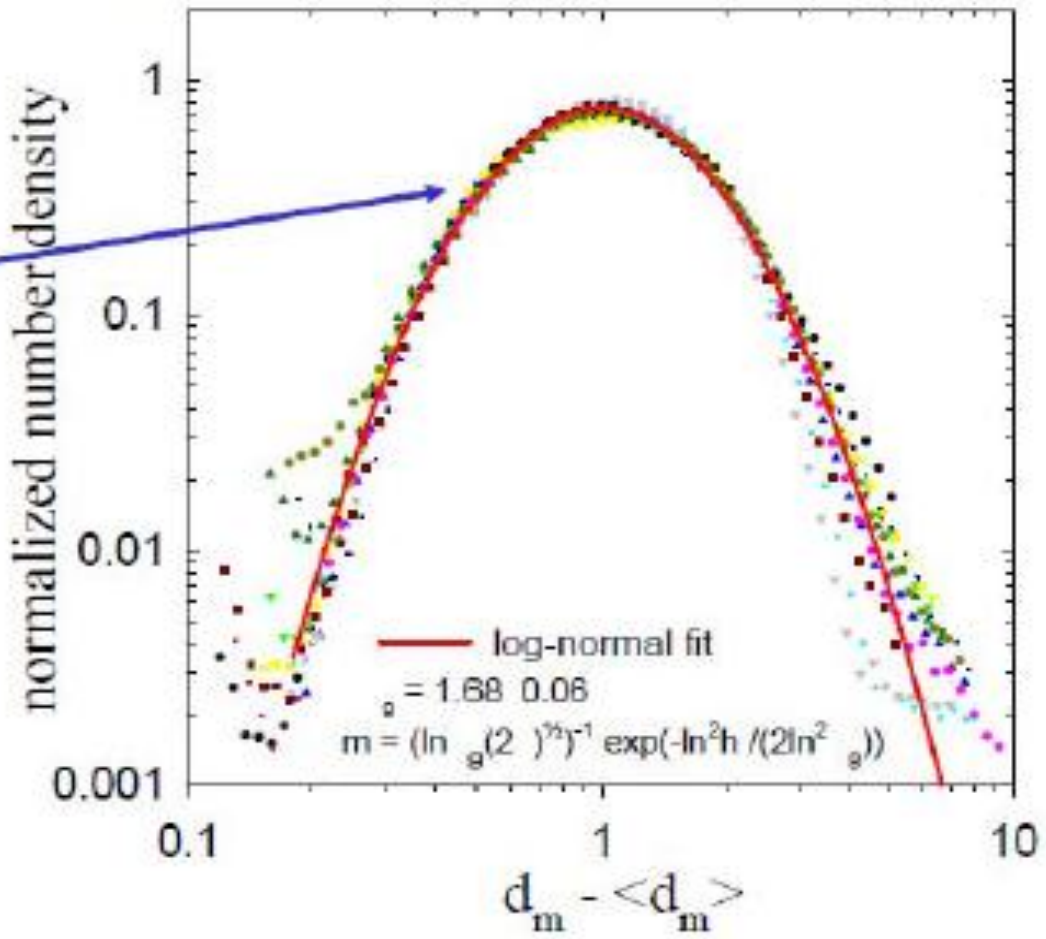
normalized to 10'000 P/cc

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 5×10^{11} #/km → PM mass must be < 1 mg/km



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

Health Effect for PNC and Mass PM 2.5

Short Term Cardiovacular Mortality (CVD) – Katsuyanni 2012

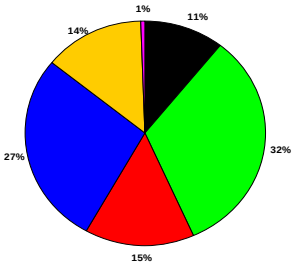
comparing mass (PNC) to mass (PM2.5)

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 x 10^{-16} g/P / 10‘000 P/cm3 = 3.2 µg/m3

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 20 %
- concluding soot particles are the main toxic



→**MHI of soot is 2'000 €/kg soot**

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

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

UNIVERSITY OF BIRMINGHAM

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.**

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

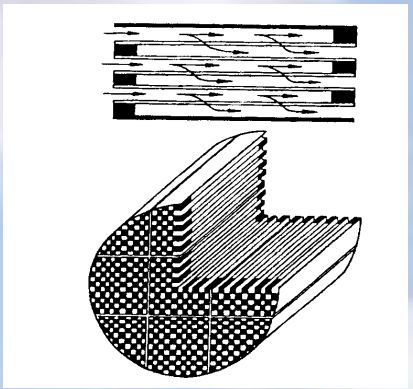
→ BAT-particle filters

→ 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.



DPF

reduces PM, PN

and if catalysed CO, HC, PAH

operated with FBC also NO2

and with SCR-coating even NO2

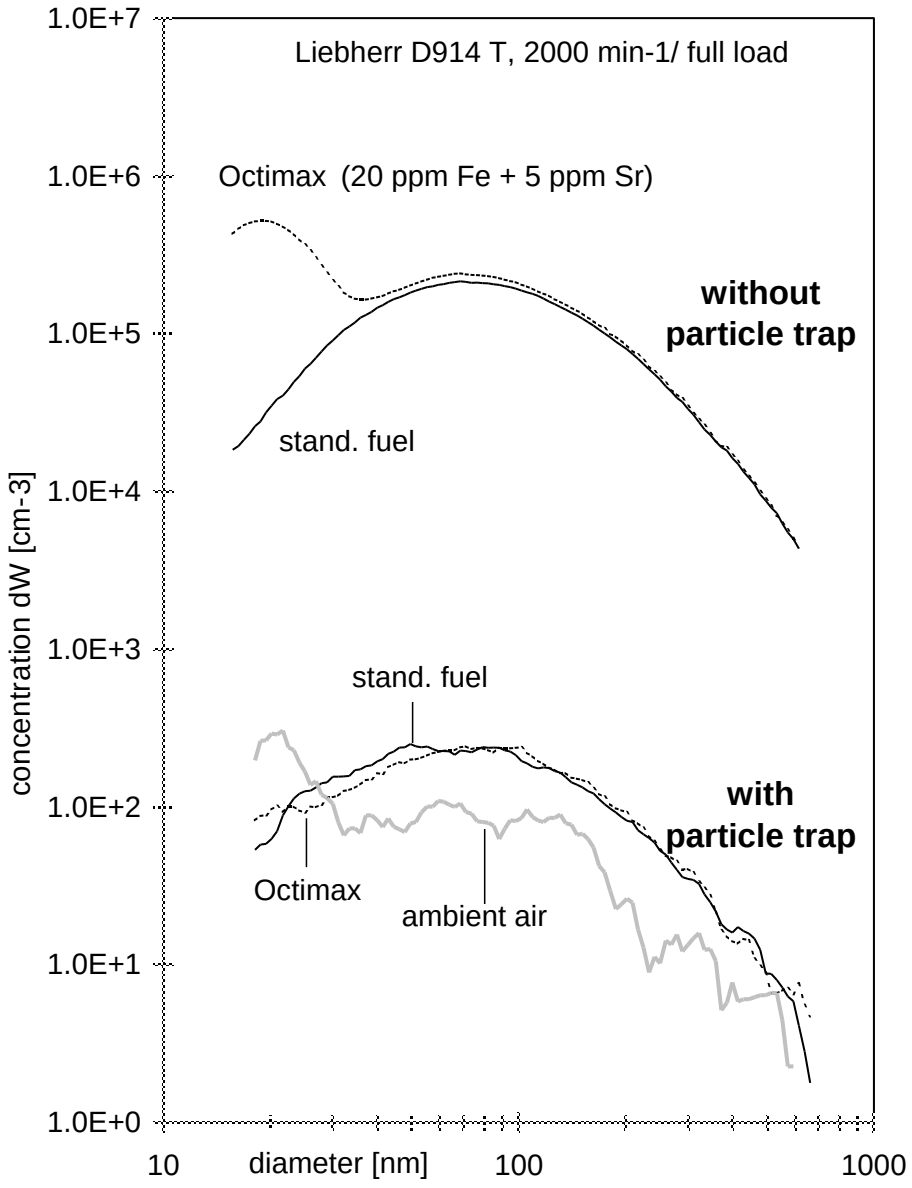
but can also be a Chemical Reactor ?

with extremely long residence time

BAT is Filtration

Filtration achieves 99.9 % on every engine as long as SV is below the limit. Only VERT certified DPF shall be used

99.9 % means
0,01 mg/kWh



Implementation of Particle Filters

20 years – 45’000 Retrofits in CH

500’000 Retrofits worldwide

100’000’000 DPF OE first fit

Efficiency > 99% - 10-2500 nm

no manipulation, no tempering, no-defeat devices

SUCCESS CONTROL

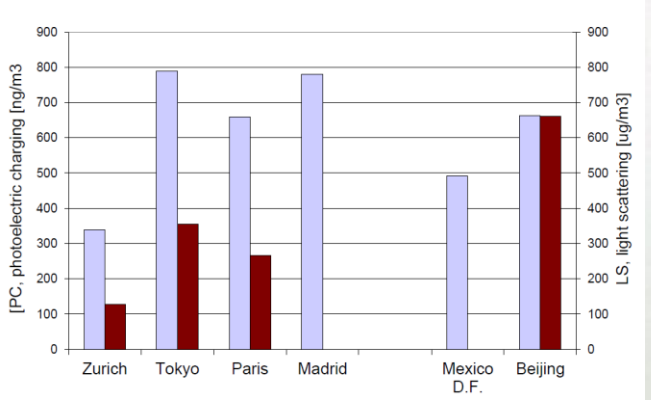
How to monitor air quality when introducing particle filters in the Low Emission Zone of Haifa

PM 2.5 [g/m^3] ?
or PN [1/cc] ?
or both ?

Confidence it good, Control is better, Lenin 1922

PM or PN ?

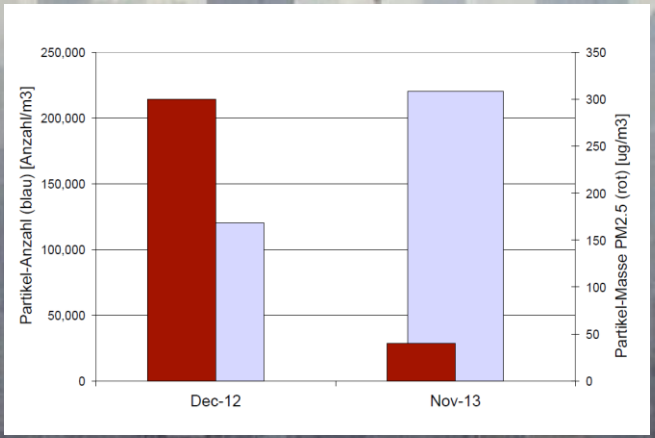
Scavenging



2004 Siegmann, Kasper

Measurements in Beijing:

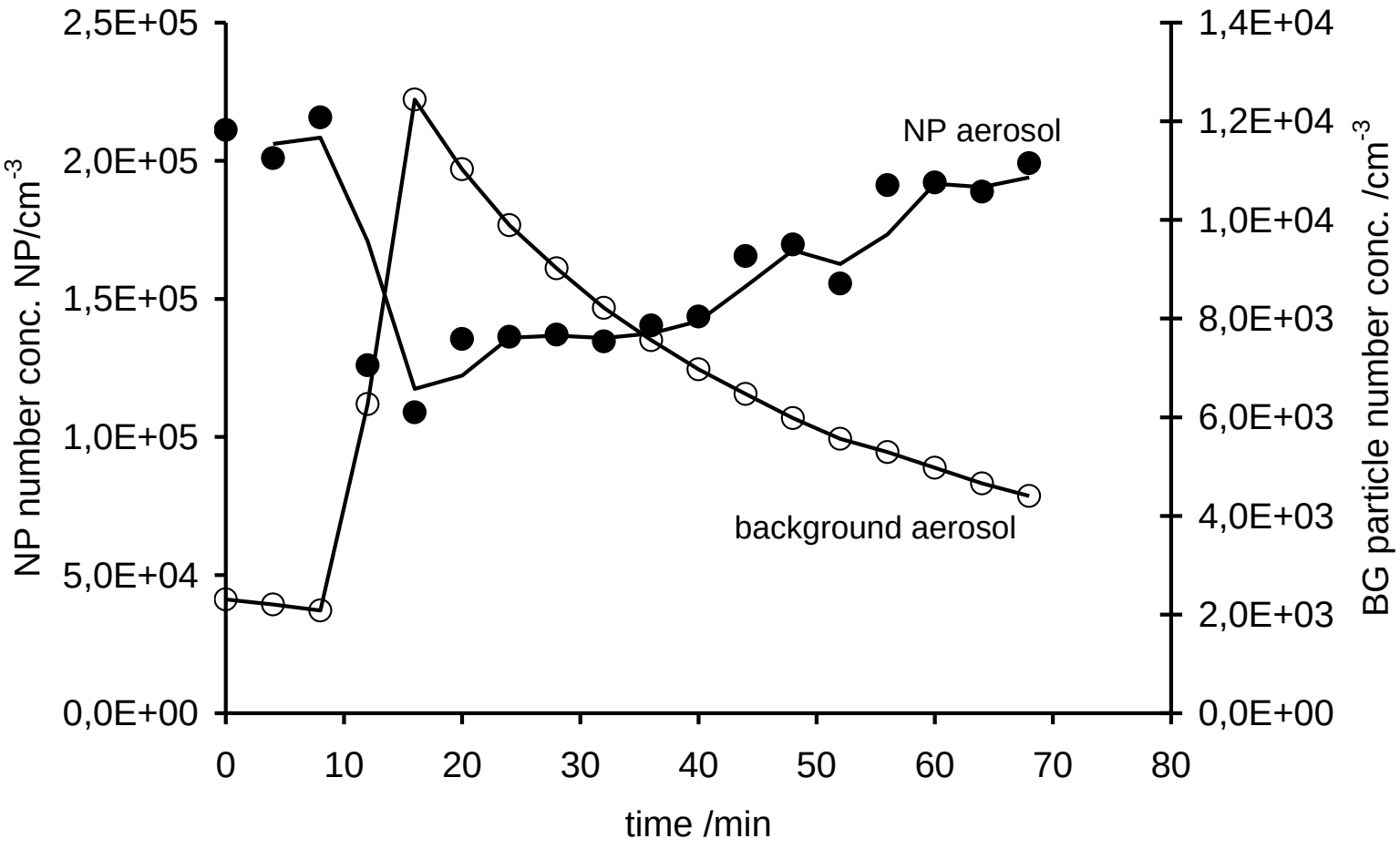
120.000 p/cm³ at PM2.5>300µg/m³
200.000 p/cm³ at PM2.5<50µg/m³



2012/13 Mayer

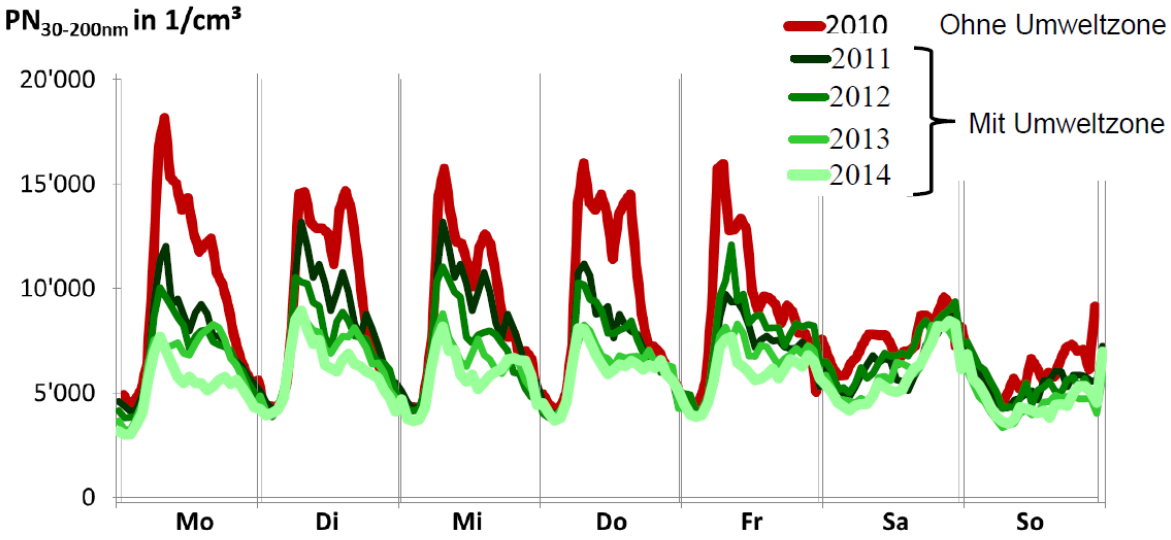
Apparent disconnect between number concentrations and PM concentrations in Amospheres

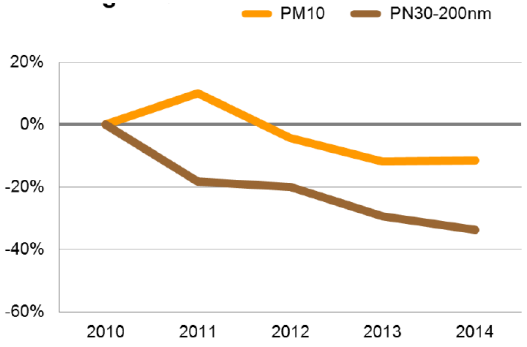
SCAVENGING: Coagulation of ultrafine aerosol with larger Background Particles in the atmosphere – a lab experiment – by Seippenbusch KIT

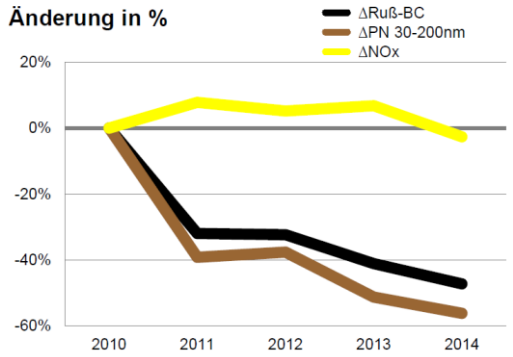


PM and PN can be anticorrelated

Low Emission Zones – Leizig, Berlin

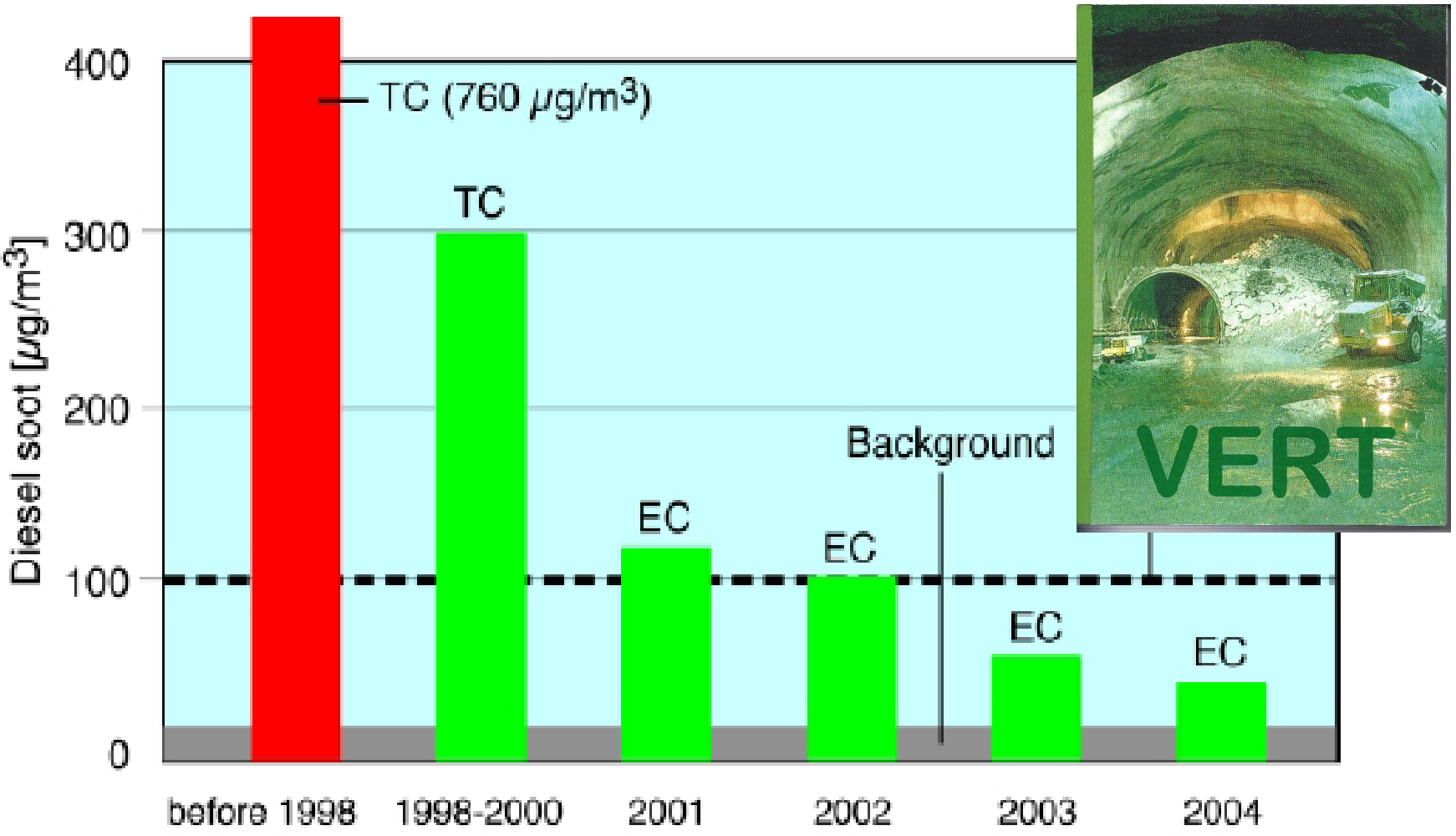






Only Particle Number PN can be used as success

→ PN, BC – Monitoring required from start of Haifa LEZ



How we cleaned Swiss tunneling sites

Conclusion

- Cleaning car exhaust not reflected by PM 2.5
- Toxicity is not correctly reflected by PM 2.5
- Health Conclusions based on PM 2.5 are misleading
- Policies based on PM 2.5 will fail

→Air Quality Monitoring of the Haifa LEZ must be by PN and BC complementing PM2.5

see new EU-Standard CEN/TS 16976

Harmonizing number concentration measurements of ultrafine particles in atmospheric aerosol