NMR-Workshop on Particles in Nordic Urban Areas - Helsingör 7.November 2007

PM10 Health Effect Equivalent

New Approach to a Health Hazard Oriented PM-Characterization

A.Mayer / TTM

A.Mayer - TTM

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on Emission Reduction of IC-Engines

TTM is responsible on behalf of Swiss EPA and SUVA for

- VERT Verification of Particle Filter Systems
- Quality Control of Filter Retrofits in Switzerland

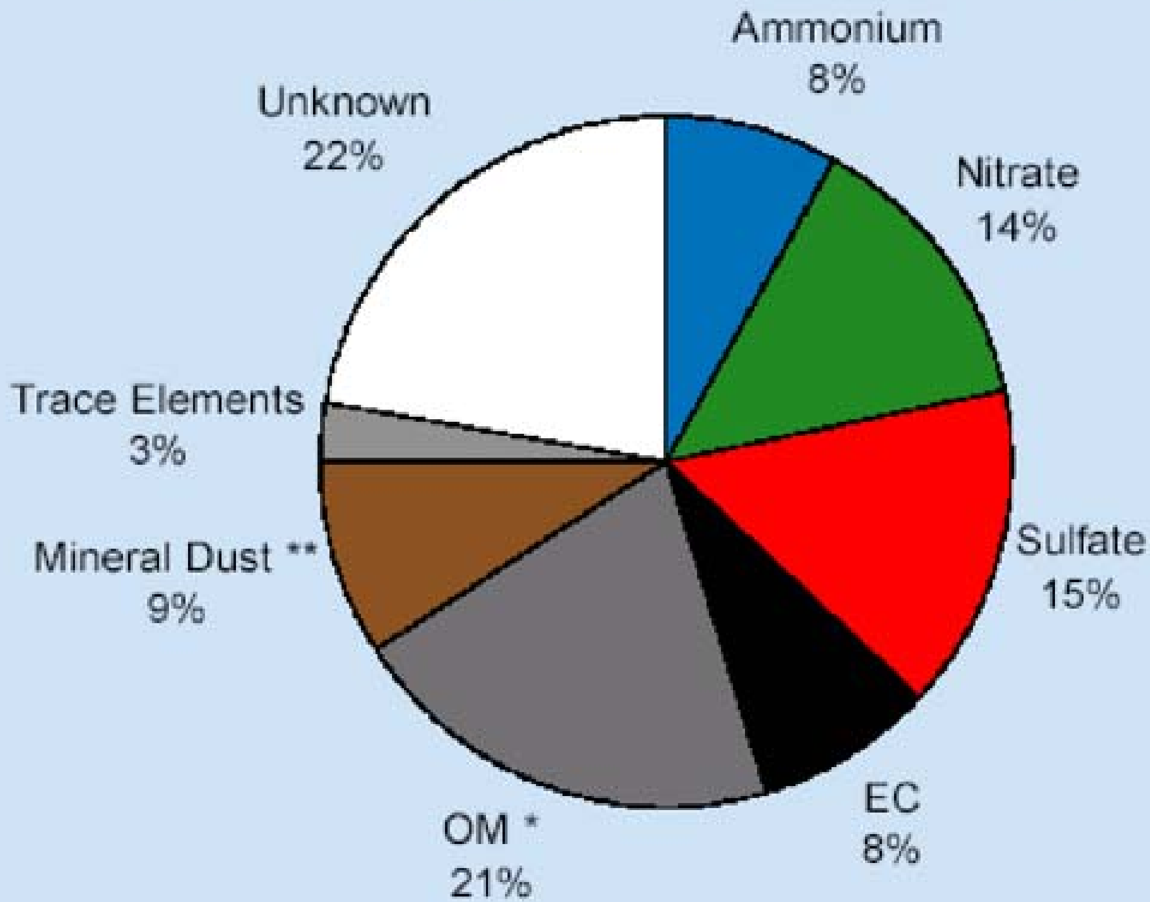
- Research and Development in International Projects
- Implementation of Emission Reduction Measures (Germany, Austria, Poland, Italy, California, Canada, Chile, Korea, Japan, Czechia ..),
- Organization of Seminars and Conferences
- 35 SAE-papers and 2 books published 2004/5 on “Elimination of Combustions Generated Particles”
- SAE-fellowship 2004
- Award of Swiss Cancer Ligue 2006

Ambient Air Pollution
is defined by law as PM10

PM 10 = overall mass of ambient aerosol below 10 µm

and here my Question:
Is it scientifically permitted to use the sheer mass of an unknown mix of substances (whether it is PM10 or PM2.5 or even PM1) as a **metric for human health hazard ?**

Chemische Zusammensetzung des Feinstaubs in Zürich (~50% sekundär!)

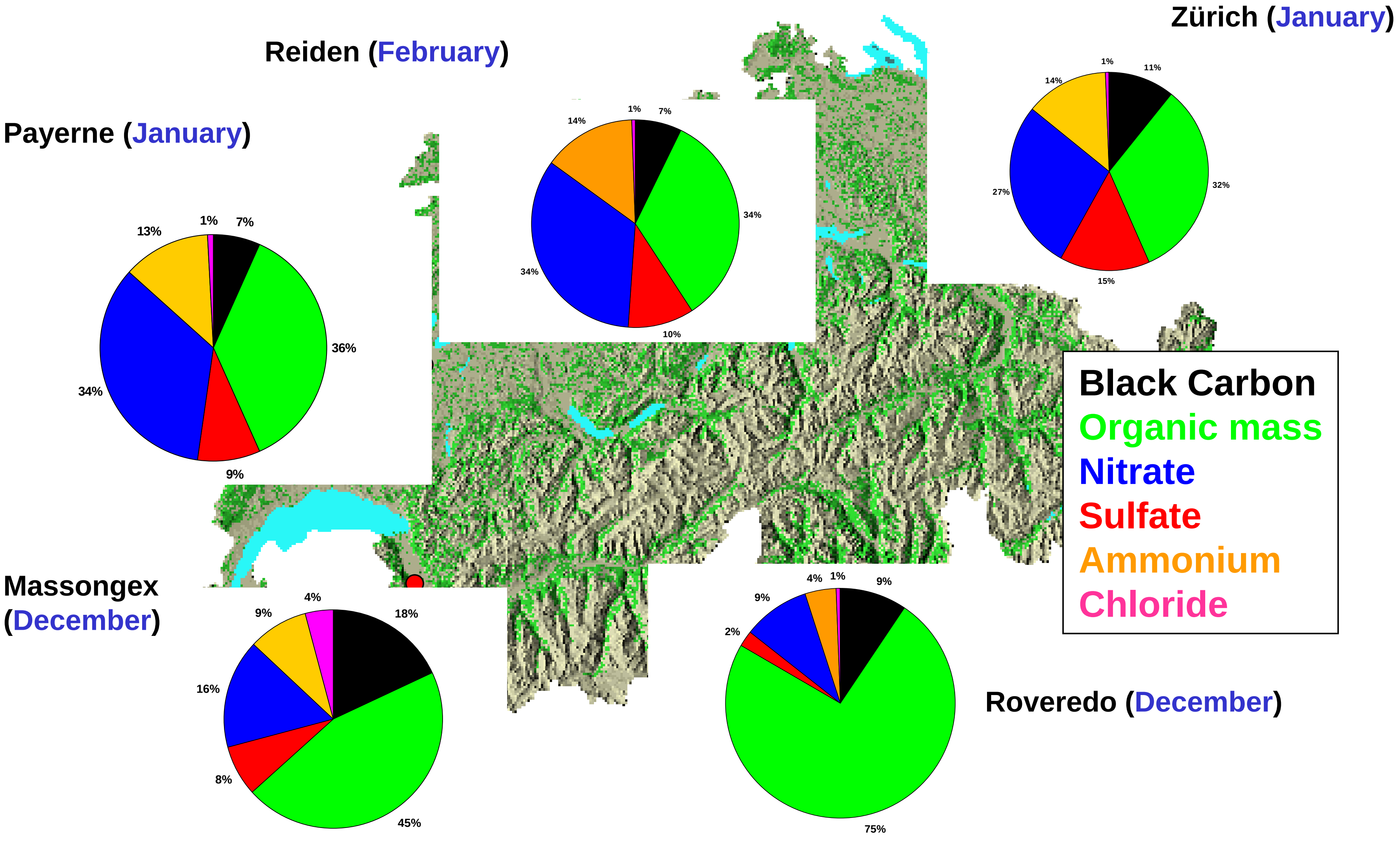


PM10
mean: 25.0μg/m

Hüglin et al., Atmos. Environ. 2005

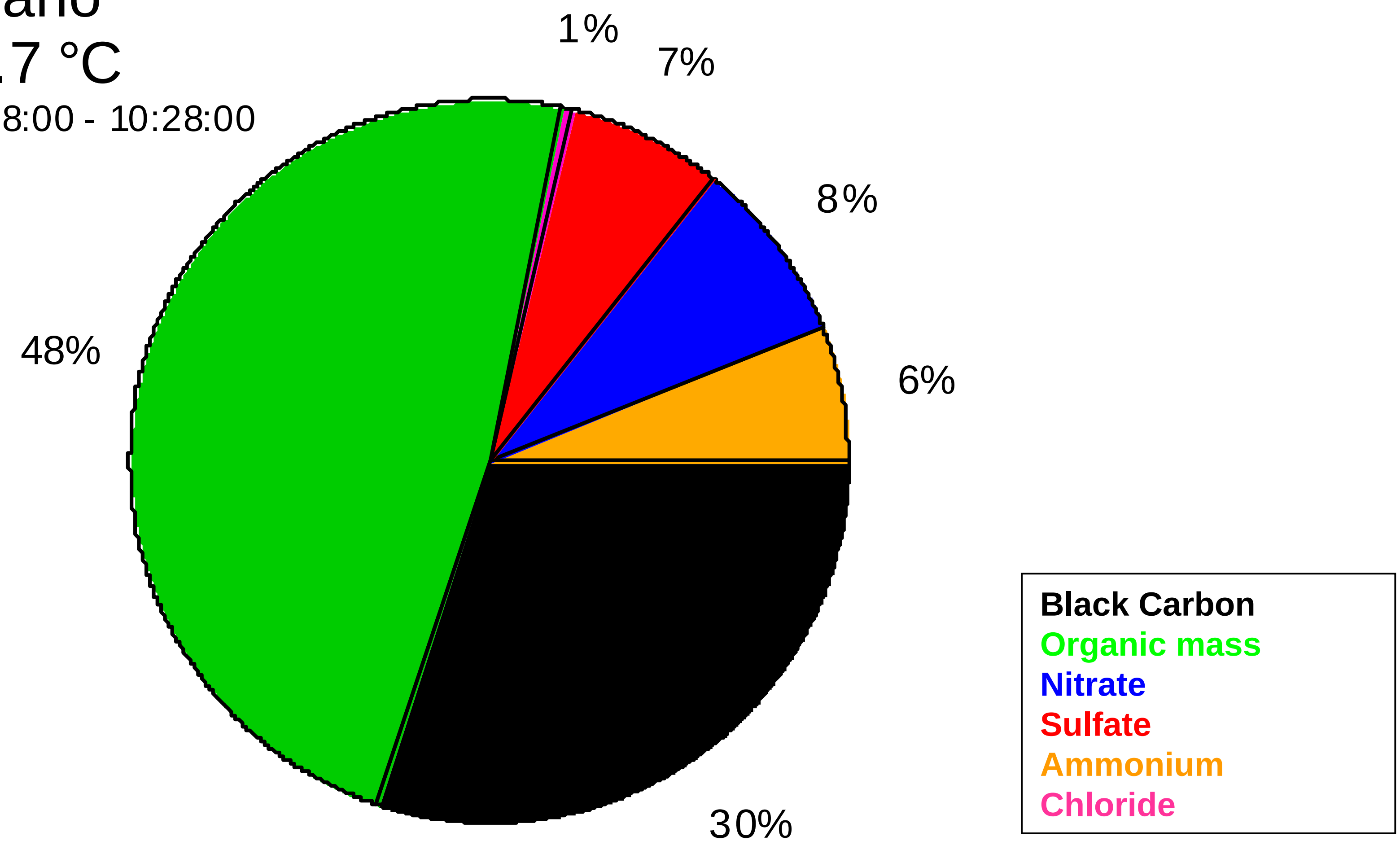
* OM = 1.4 · OC
** calculated from Al

Average CH-Compositions in Winter

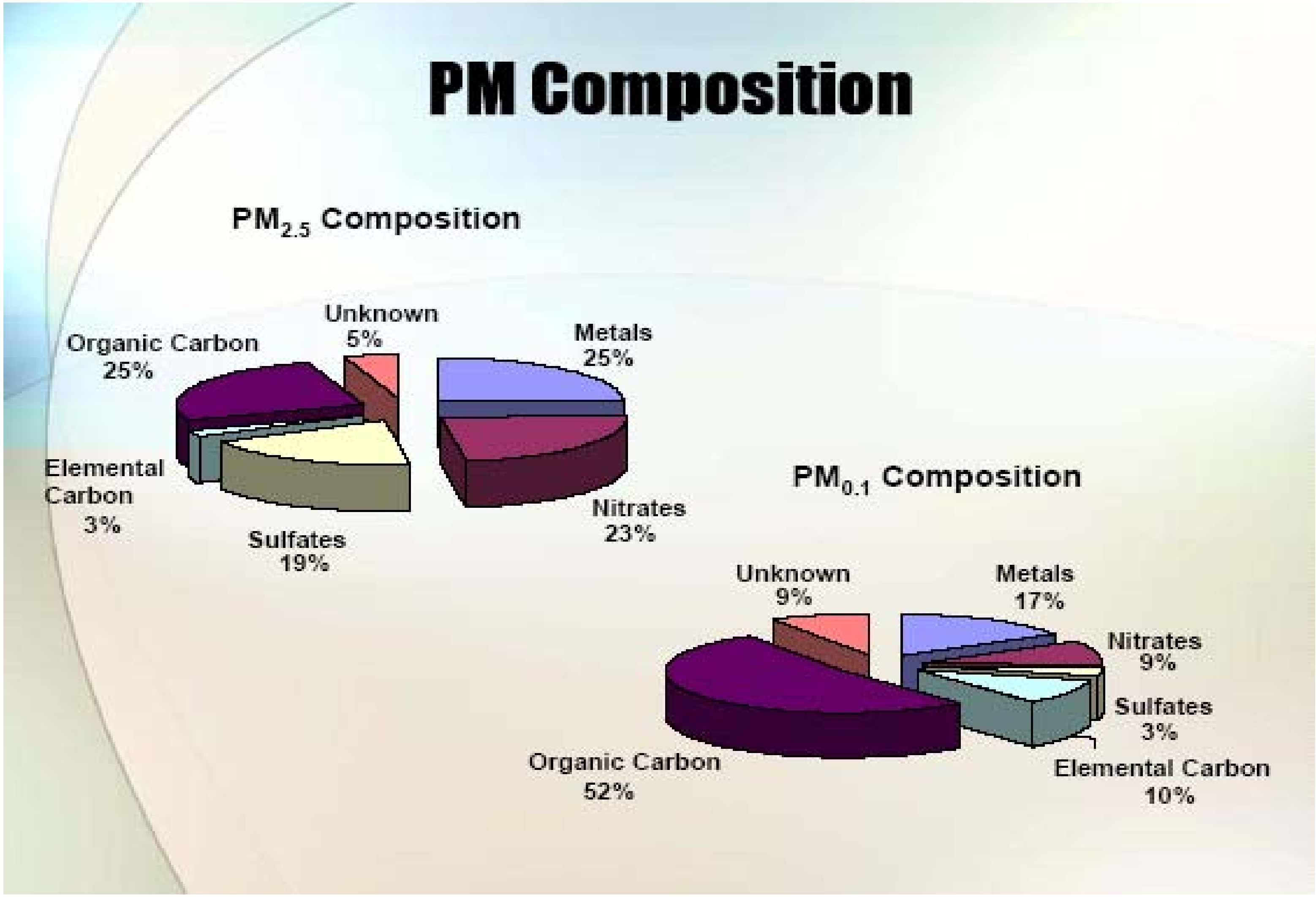


Milan 27.June 2007

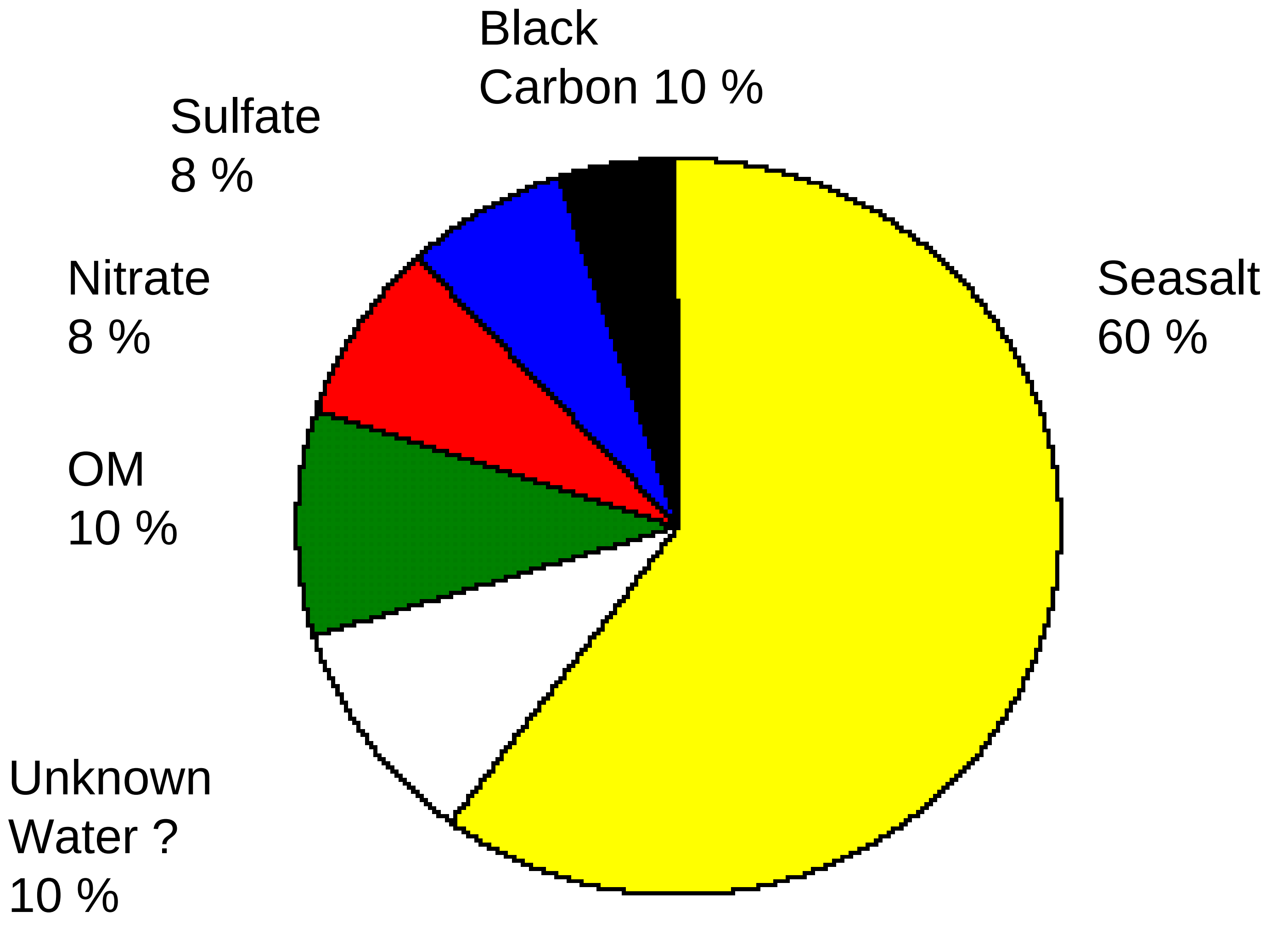
Milano
20.7 °C
06:08:00 - 10:28:00



Los Angeles (Froines 2006)



Honolulu / Hawai (artificial sample)



PM10 claims:

1 g Salt = 1 g Sand = 1 g Soot !

1 g = 1 g
yes, but with respect to any physical, chemical, biological effects we also must consider the properties of the substance

→ Something must be changed
or ....since we are in Prince Hamlet‘s hometown

Is 1 g Salt = 1 g Sand = 1 g Soot ?

1 g = 1 g

Yes but with respect to any physical, chemical, biological effects we also must consider the properties of the substance

„something is rotten in the state of Denmark„

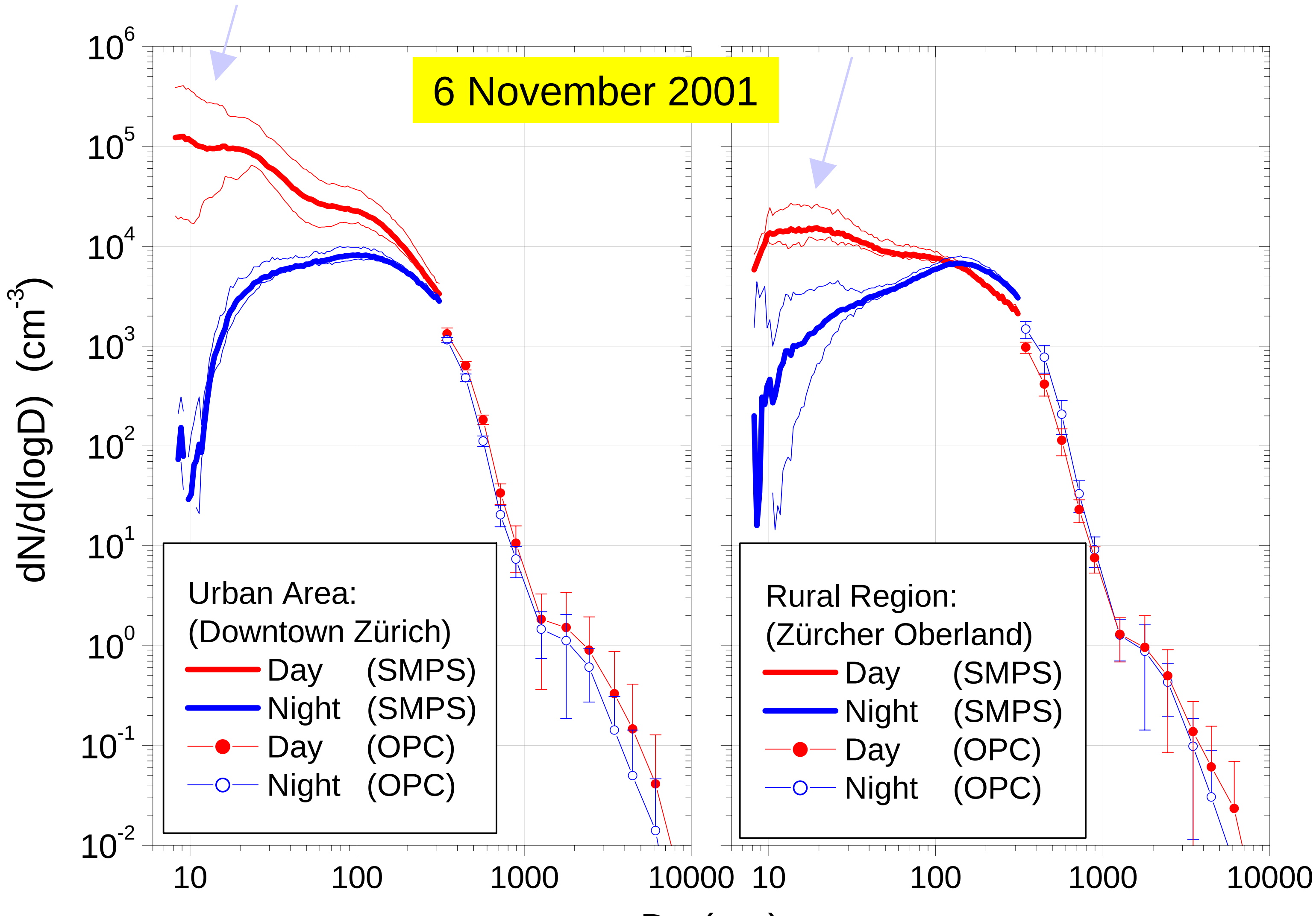
and not only in Denmark

Which physical and chemical properties make a particle more or less dangerous for human health ?

1.

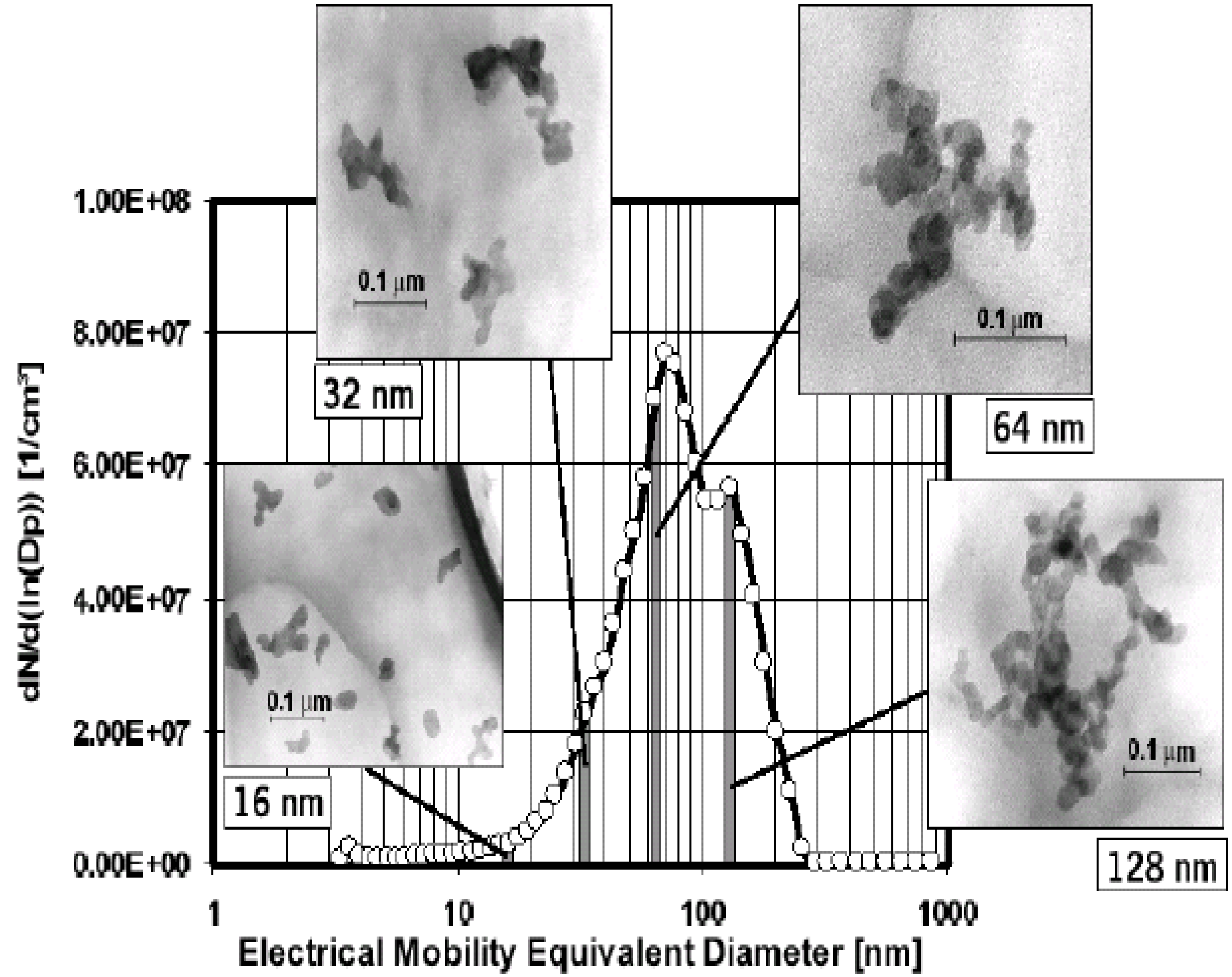
Can we neglect the Influence of the Particle Size and its Mobility ?

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



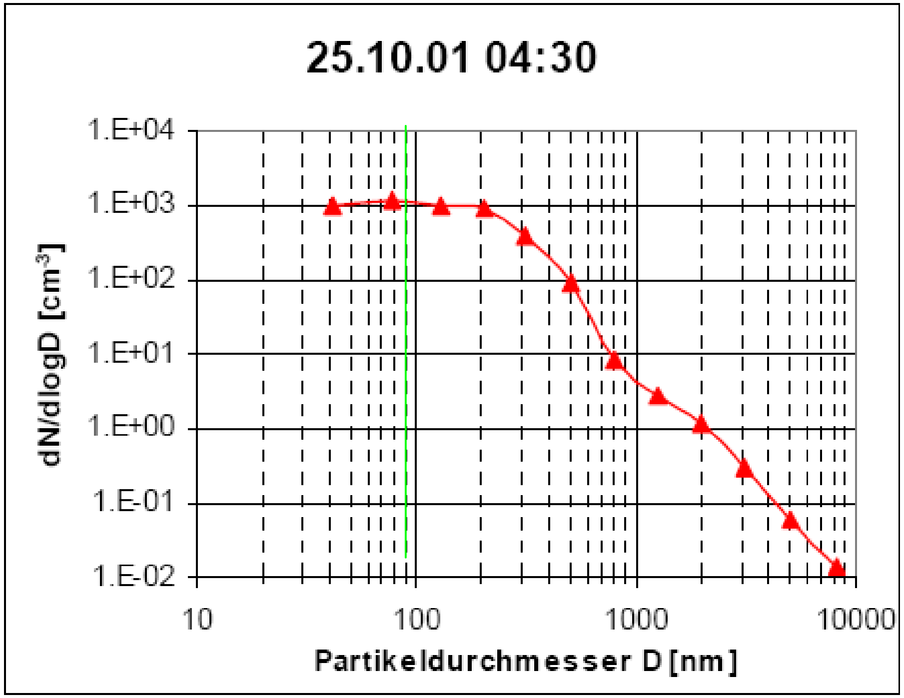
Bukowiecki et al., Atmospheric Environment, 2002

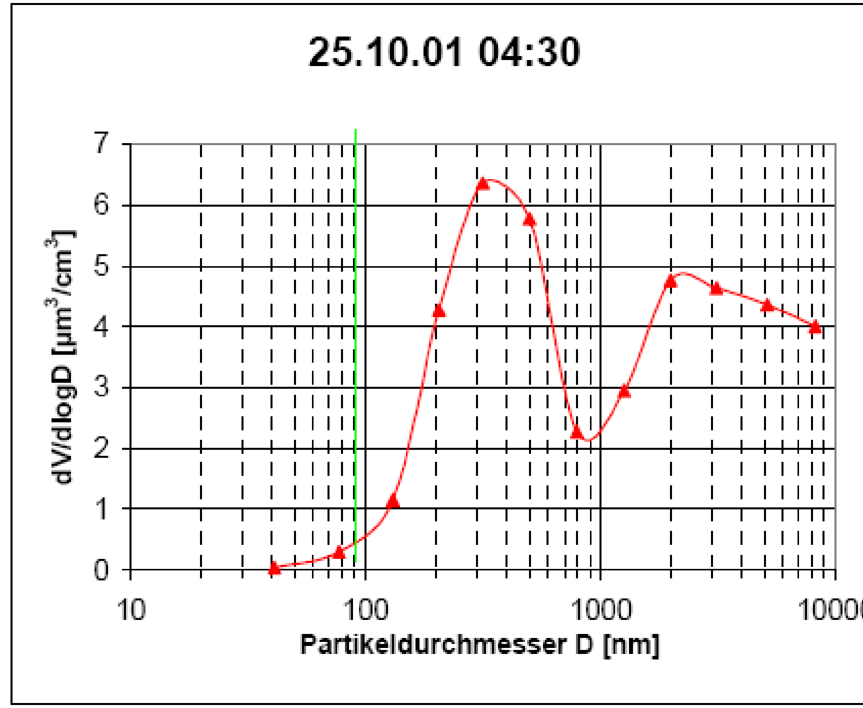
Diesel Particles



Quelle: METZ, BMW

Number- and Mass-Distribution





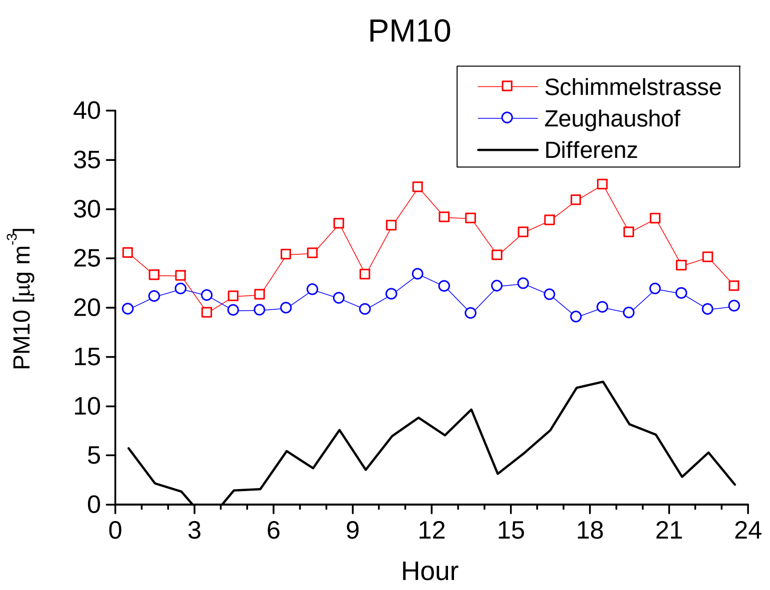
Anzahl

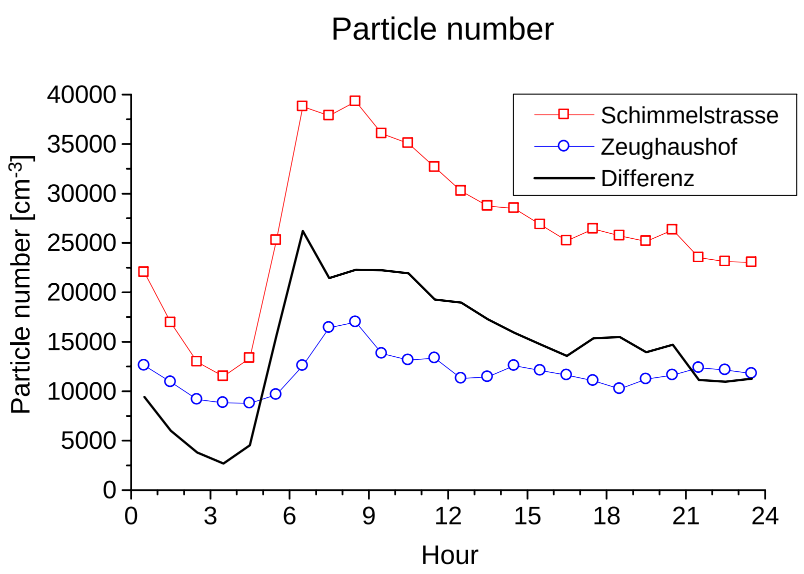
PSI, UVEK 2003

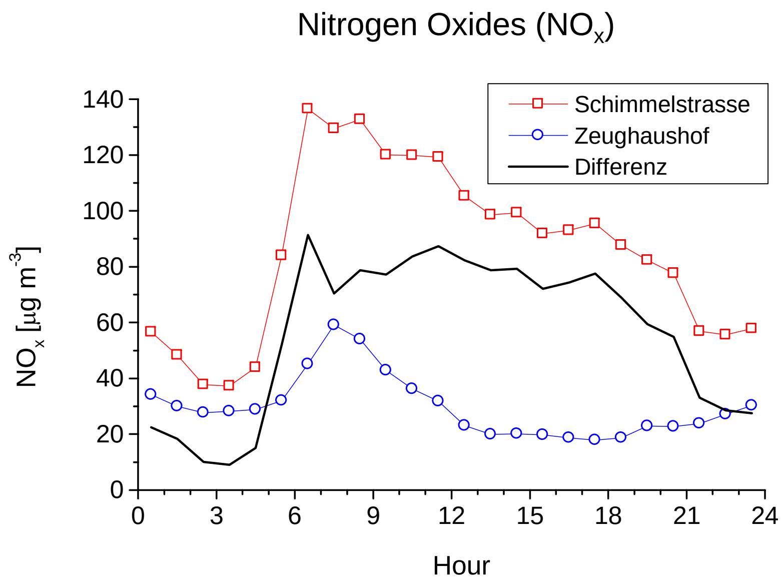
Volumen, Masse

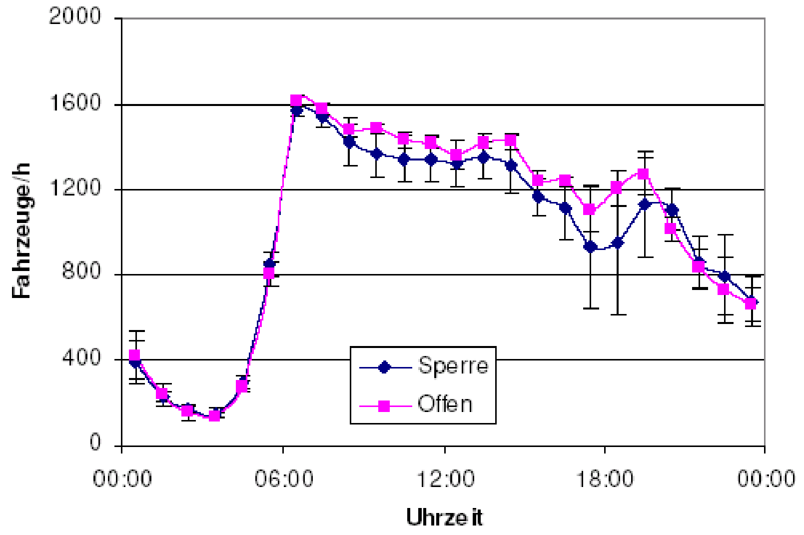
Volumen bzw. Masse der Aerosolpartikel wird durch die Partikel über 100nm bestimmt, die Anzahl durch die feinen und ultrafeinen Partikel

Average Diurnal Traffic and Emissions

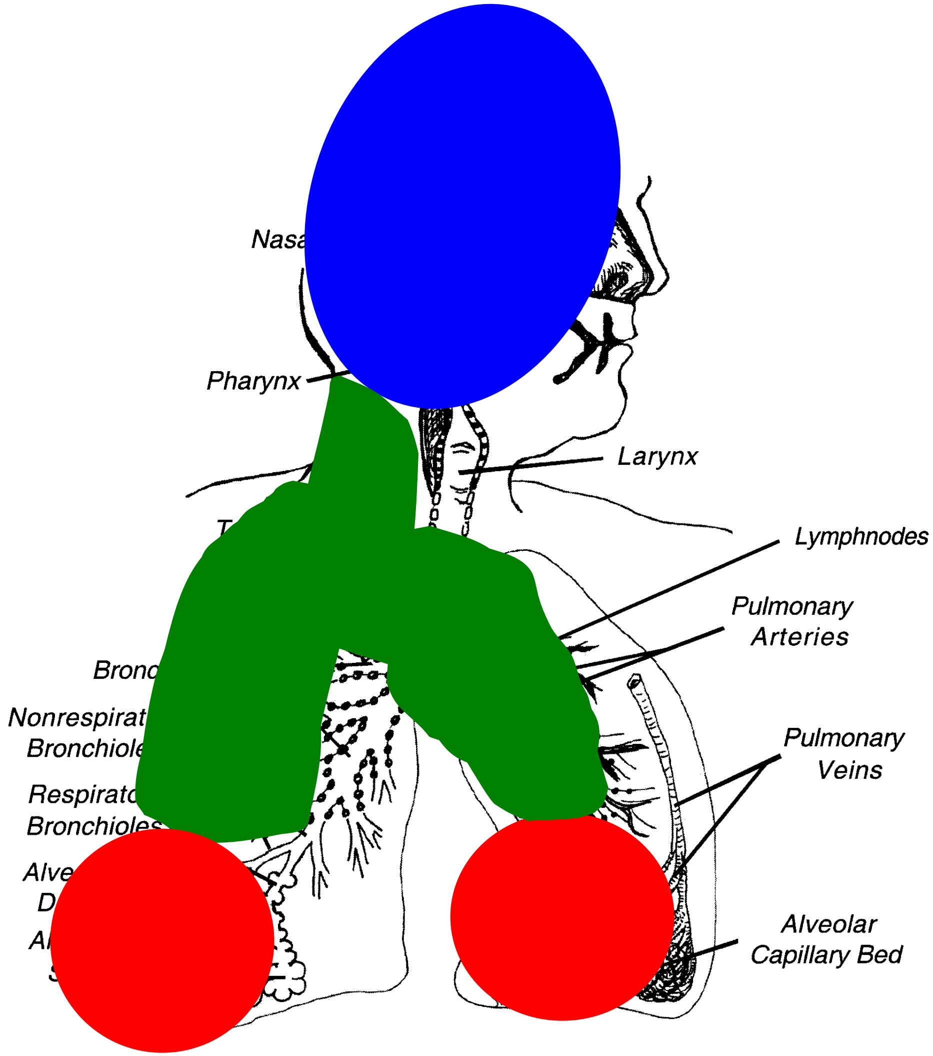


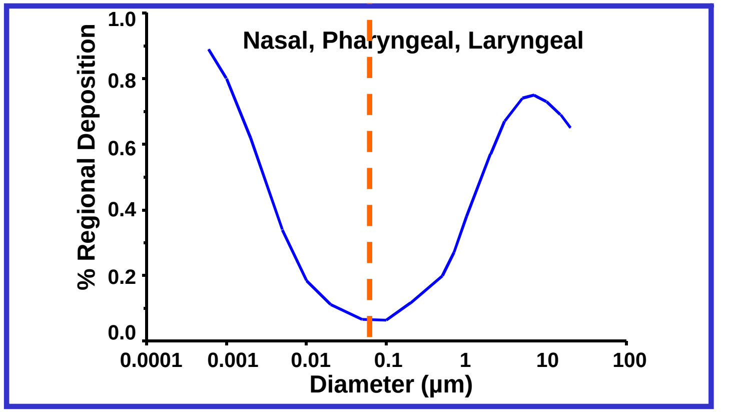


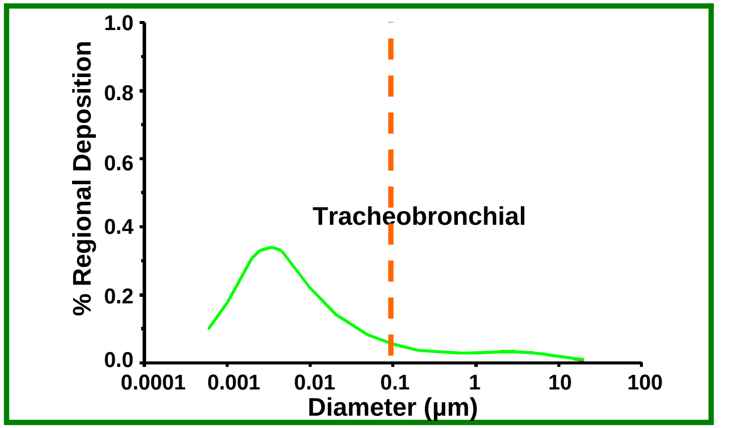




Fractional Deposition of Inhaled Particles (Oberdörster)







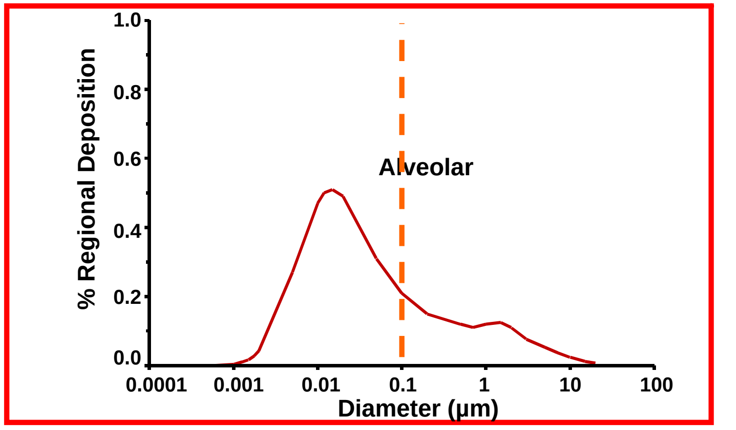
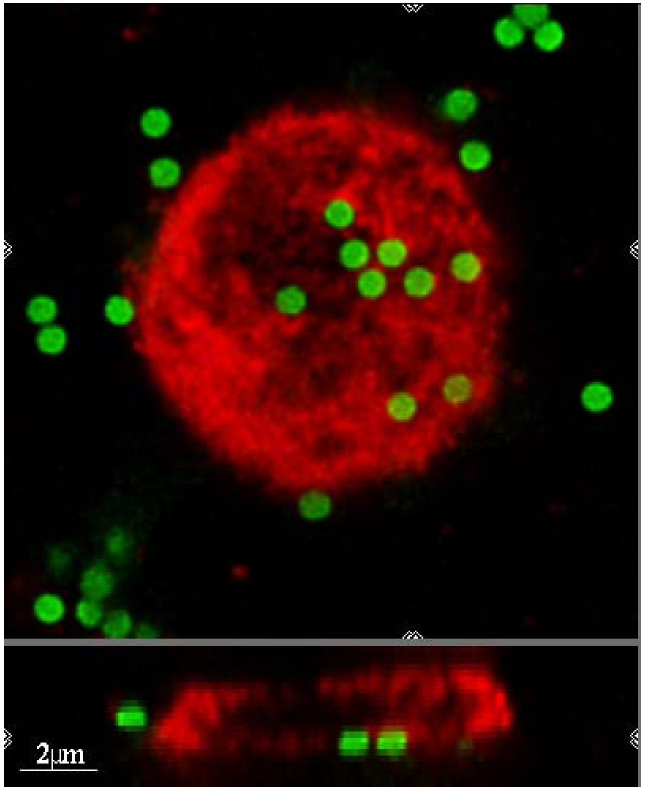
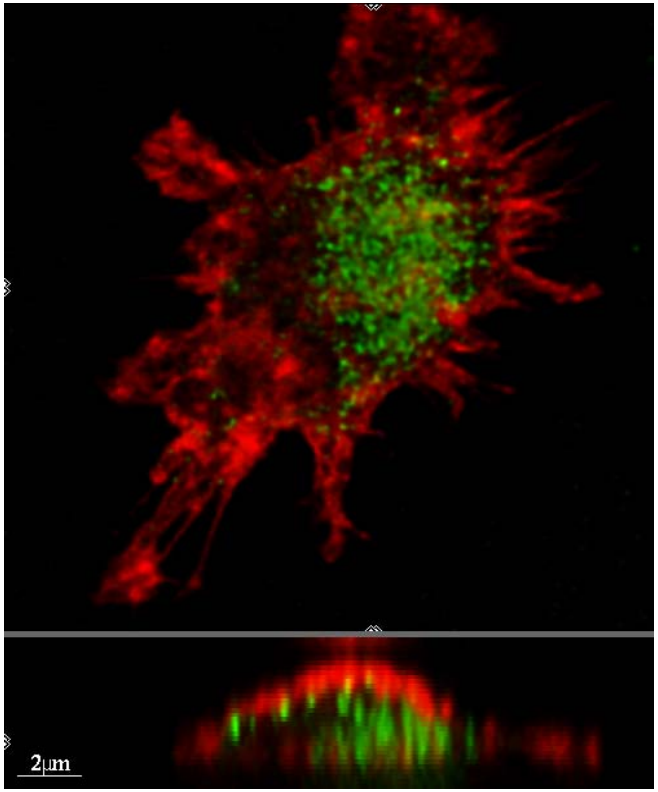


Figure courtesy of J.Harkema

Macrophages *in vitro*: Laser Scanning Microscopy



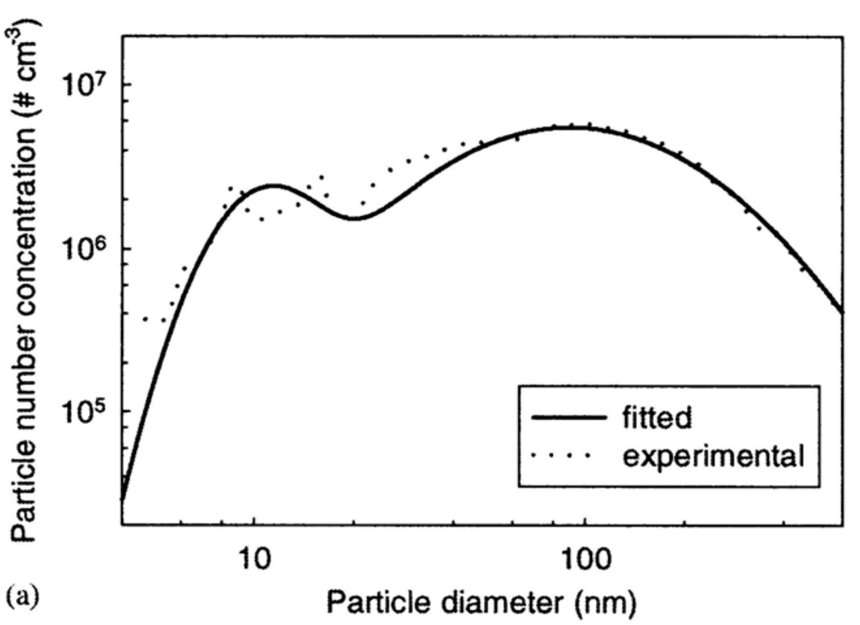
1-µm
Polystyrene particles



78-nm
Polystyrene particles

B. Rothen-Rutishauser
In: Geiser et al., EHP
(in press)


Zimmer et al., 2002


Particle number concentration (# cm^{3})
10^{7}
10^{6}
10^{5}
10
100
fitted
experimental
Particle diameter (nm)

(a)

and this is not new at all

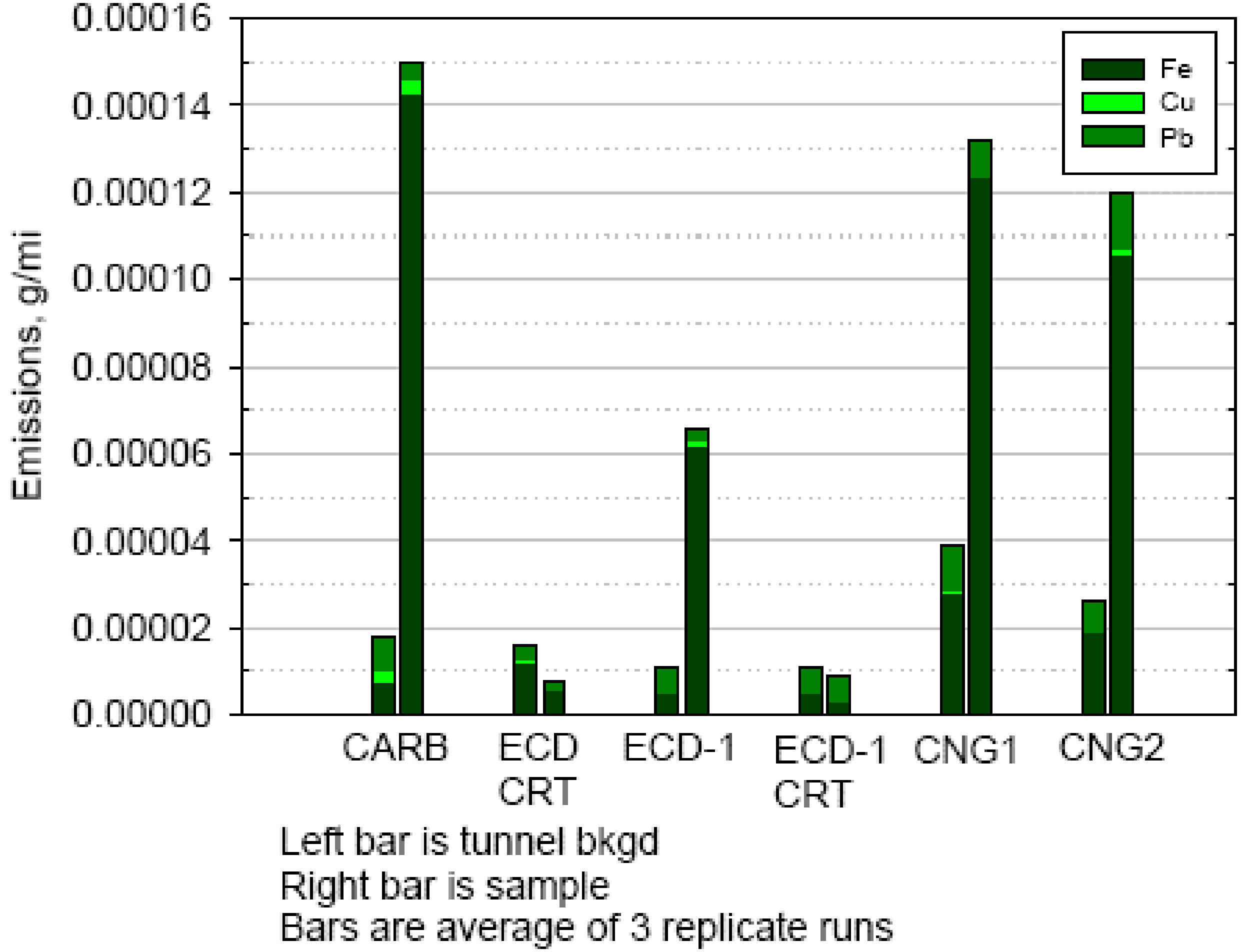
- *Lambrechts: measurement of particles size 1916 performed*
- *Staub 1936: importance of particles < 0.5 µm emphasized*
- *Pneumoconiosis Conference at Johannesburg 1959:*
  - agreement on size, number concentration, surface
  - importance of particles below 0.4 µm
- *DIN EN 481: 1993*
- *BIA (MAK-Lieferung 1998): particle size 10-200 nm*
- *VERT 1998: 20-300 nm*

2. Can we neglect the different chemical properties of the particle substances ?

pollutant	threshold concentration [µg/m³]	inverse thres-hold conc. [per µg/m³]	unit risk [per pg/m³]
Particulate matter	5	0.200	
Solid particulate matter	3.5	0.286	100.00
NO2	40	0.025	
Ethylbenzene	1000	0.001	
Formaldehyde	10	0.100	0.27
Acetaldehyde	300	0.003	2.20
Platinum	0.015	66.667	
Benzene			9.20
Benzo[a]pyrene			70'000.00
1,3-butadiene			4.50

Table 1: Threshold concentration, inverse threshold concentration, and unit risk values from UBA (1999).

CNG/Diesel: Particle Samples analysed for Engine Wear Elements



Quelle: West Virginia University

3. Can we neglect the influence of solubility ?

***Soot particles** are insoluble*

and most metal oxides are nearly insoluble

→ *remain solid particles even after penetrated into blood or brain; local concentration remains high;*

→ *HE is defined by the local number concentration*

3. ***Can we neglect the influence of solubility ?***

Nitrates, Sulfates*, Ammonium, Seasalt have a high to very high solubility in water, even higher due to continuous clearing*

→ *local concentration disappears quickly by dilution;*

→ *HE is defined by the overal mass concentration (per kg bodyweight)*

3. Can we neglect the influence of solubility ?

***Organic Matter OM** may also be dissolved quite quickly in the liquid layers covering the upper airways due to surfactant and continuous clearing*

→ *local concentration disappears quickly by dilution;*

→*HE is defined by the overal mass concentration (per kg bodyweight)*

and this is not new at all

- *BIA (MAK-Lieferung 1998) requires: „only insoluble particles shall be included"*
- *VERT 1998 defines: „Feststoffpartikel 20-300 nm"*
- *ECE-PMP 2004: volatiles to be separated by heat treatment at 300 °C and dilution*
- *MAK 1970: dust and smoke contain solid particles only, fog contains liquid phase, aerosol is the general term containing both phases*

Conclusion

- ***Particle Size matters***
- ***Particle Substance matters***
- ***Particle Solubility matters***

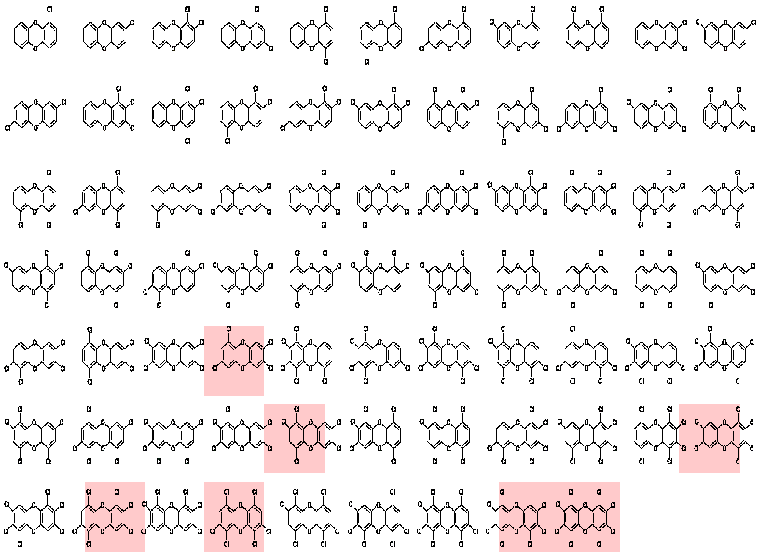
Why not weighing the effects

of different substances included in PM10 before using it as a parameter for the health hazard

weighing is a well established approach

TEQ Sum to weigth the Influence of 75 Isomeres in a Dioxin Sample

PCDD: only 7 out of 75 isomeres are highly toxic



Toxizitätsäquivalente DIOXINE

	BGA[30]	NATO (I-TEF)[31]
2,3,7,8-Cl_4DD	1	1
1,2,3,7,8-Cl_5DD	0,1	0,5
2,3,7,8-subst. Cl_6DD	0,1	0,1
1234678-Cl_7DD	0,01	0,01
Cl_8DD	0,001	0,001
2,3,7,8-Cl_4DF	0,1	0,1
2,3,4,7,8-Cl_5DF	0,01	0,05
2,3,7,8-subst. Cl_6DF	0,01	0,01
2,3,7,8-subst. Cl_7DF	0,01	0,01
andere Cl_7DF	0,001	0
Cl_8DF	0,001	0,001
andere PCDD und PCDF	0,01	0

Source: N. Heeb, EMPA (2005)
Haus der Technik, München

TEQ Sum to weigh the influence
of PAH compounds in a PAH sample

Messtelle	*Siedepunkt*	*TEF*
Fluoranthen	*384*	*0.001*
Pyren	*364*	*0.001*
Benz(a)anthracen	*435*	*0.1*
Chrysen	*441*	*0.01*
Benzo(b)fluoranthen	*481*	*0.1*
Benzo(j)fluoranthen	*481*	*0.1*
Benzo(k)fluoranthen	*481*	*0.1*
Benzo(a)pyren	*496*	*1*
Indeno(1,2,3,cd)pyren	*534*	*0.1*
Dibenzo(ah)anthracen	*535*	*1*
Benzo(ghi)perylen	*542*	*0.01*

Source: Nisbet and Lagoy 1992

*Why not put a **Number***

on each PM10 compound for

- *influence of size*
- *Influence of solubility*
- *Influence of substance toxicity*

PM10 Substance Classes

- **Carbon**:
  - EC (fine, coarse)
  - OM / OC (overlap with pPAH)
  - pPAH
- **Inorganics**:
  - NH_4^+
  - NO_3^-
  - SO_4^-
- **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, ...

Source: M.Kasper, ETH-NPC 2007

Toxicity Contributors

along the way of the particle entering the organisme

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

HEQ Index Value

Source: M.Kasper, ETH-NPC 2007

How can we numerically address the relative importance of each of these properties characterizing elements of toxicity ?

- *size*
- *solubility*
- *overall toxicity*

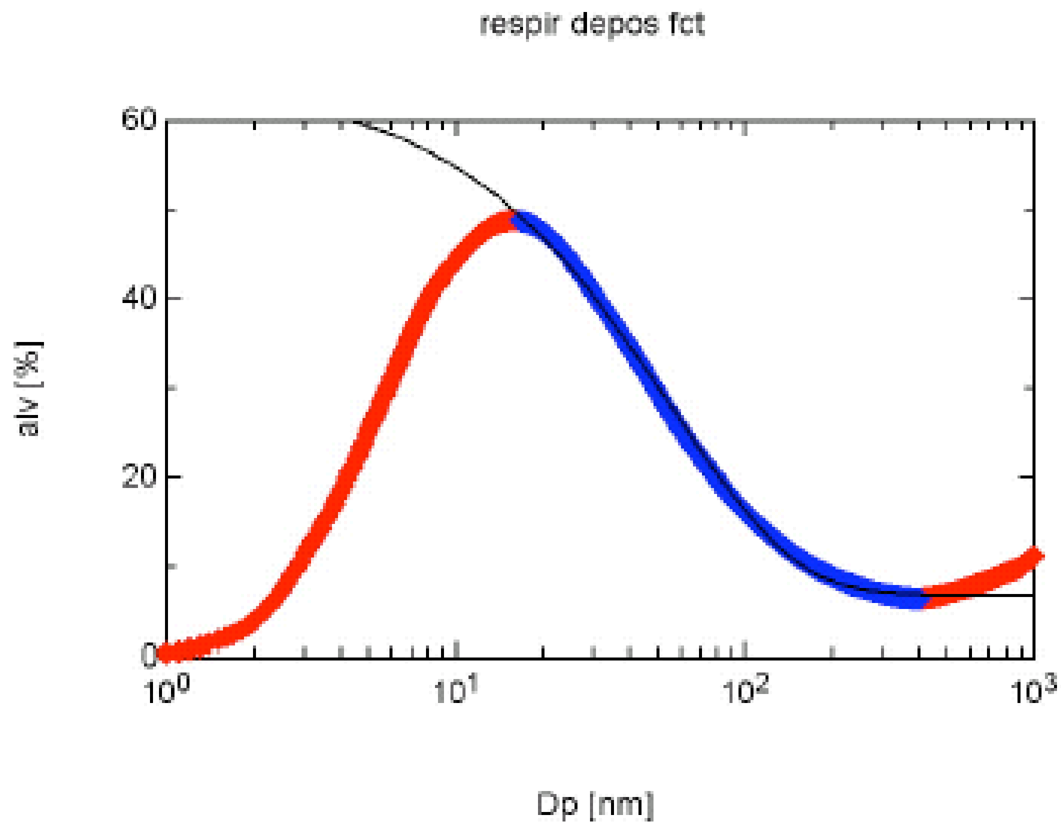
1.

Size

We propose to use
Alveolar Deposition Probability - normalized

- *Diesel Soot 20-300 nm = 1*
- *Metal Oxide Partikel 20-300 nm = 1*
- *Fine mineral dust 2-3 µm = 0.1*
- *resuspended agglomerated dust < 0.1*

Alveolar Deposition of traffic related Particles



Source: M.Kasper (2006) , ME

2.
Solubility

We propose to use 1/ solubility (water) - normalized

- *Diesel Soot: 1 (insoluble)*
- *Metal Oxide Partikel : 1*
- *Mineral Dust : 1*
- *OM (PAH): 1 [1)]*
- *Nitrates: 0.01*
- *Sulfates: 0.1*
- *Sea Salt: 0.001*

[1)] *We assume that OM-solubility will be much higher in actual airways because of surfactents and also due to the rapid clearing process*

3.

Toxicity

We propose to use 1/MAK - normalized

- *Diesel Soot = 1*
- *Coarse Metal Oxide Particles = 0.1*
- *Ultrafine Metal Particles = 1 (- 10 Stoeger)*
- *Nitrates = 0.1 (?)*
- *Sulfates = 0.1*
- *PAH Benz(a)pyren = 50*
- *Mineral Dust = 0.1*
- *Sea Salt = 0.01 (no MAK)*
- *Water = 0.001 (no MAK)*

Alternatively Unit Risk-factors could be used or weighing factors by CML (Heijungs 1992), WHO, IARC, OEHHA, HEI, EPA, UBA

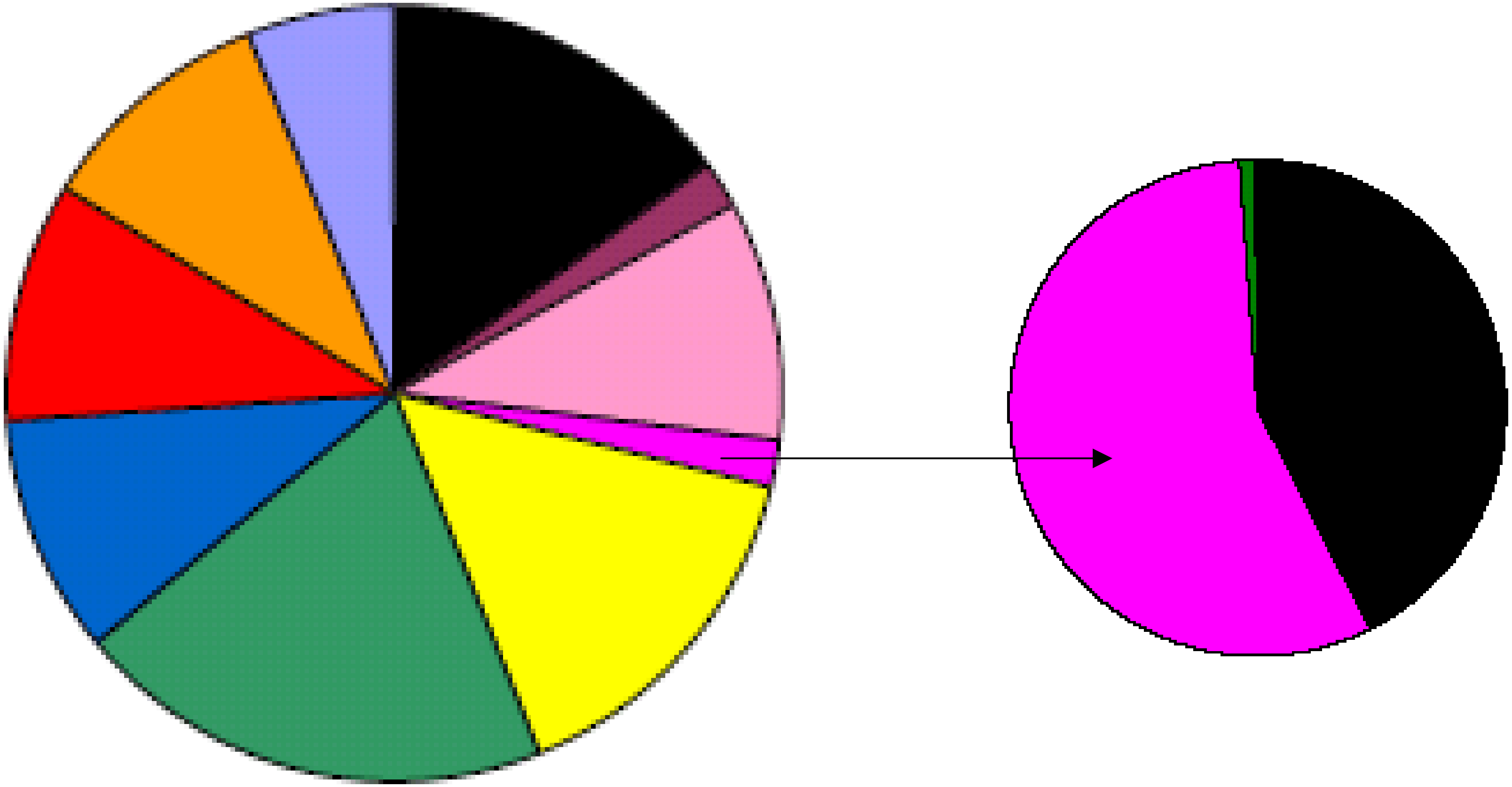
Just an Example

PM10-HEQ Influence Factors *Example*

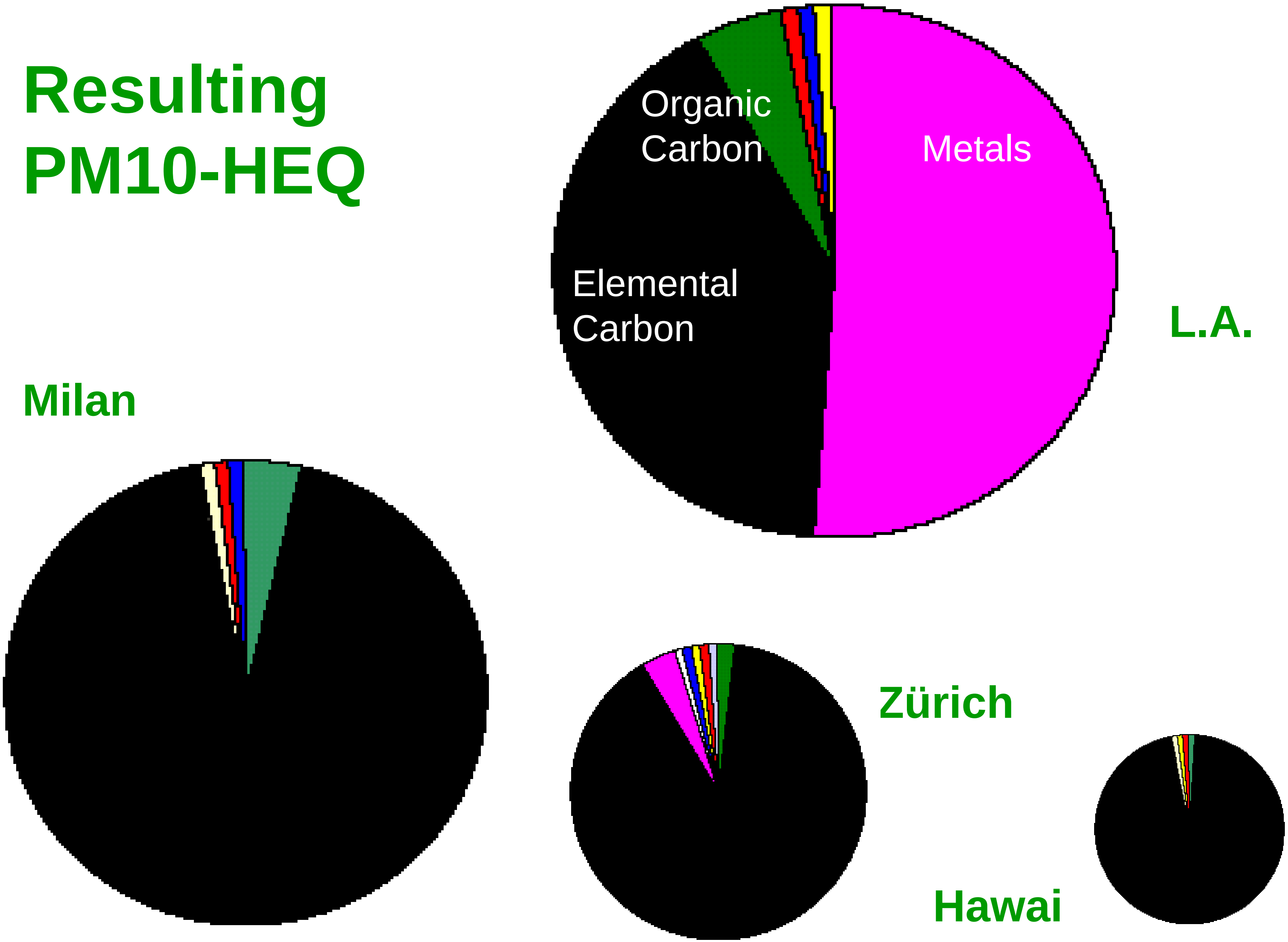
PM10-Compounds	EC < 500 nm	EC > 500 nm	Metals Minerals > 500 nm	Metals <100 nm	Sea Salt	OM	Benz(a) Pyren	Ammonia	Nitrate	Sulfate	Water
Mass %	15	2	10	2	15	20	0.01	10	10	10	6
Solubility	1	1	1	1	0.001	0.2	1	0.01	0.01	0.1	0.0001
Mobility	1	0.1	0.1	1	1	1	1	1	1	1	1
Toxicity	1	0.1	0.1	10	0.01	0.1	50	0.1	0.1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

Example: only BC and metals remain important

PM10 PM10-HEQ

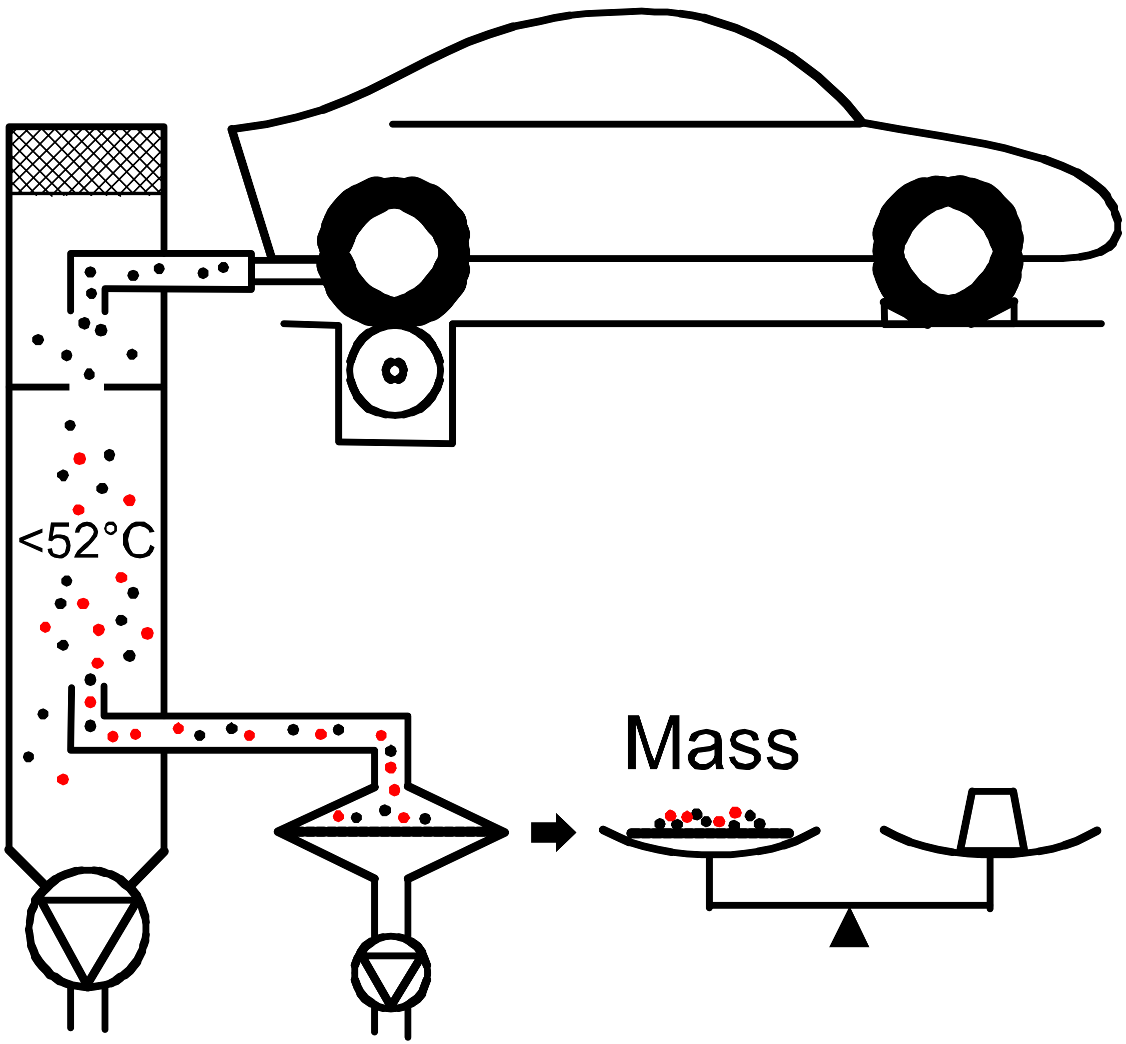


Resulting PM10-HEQ

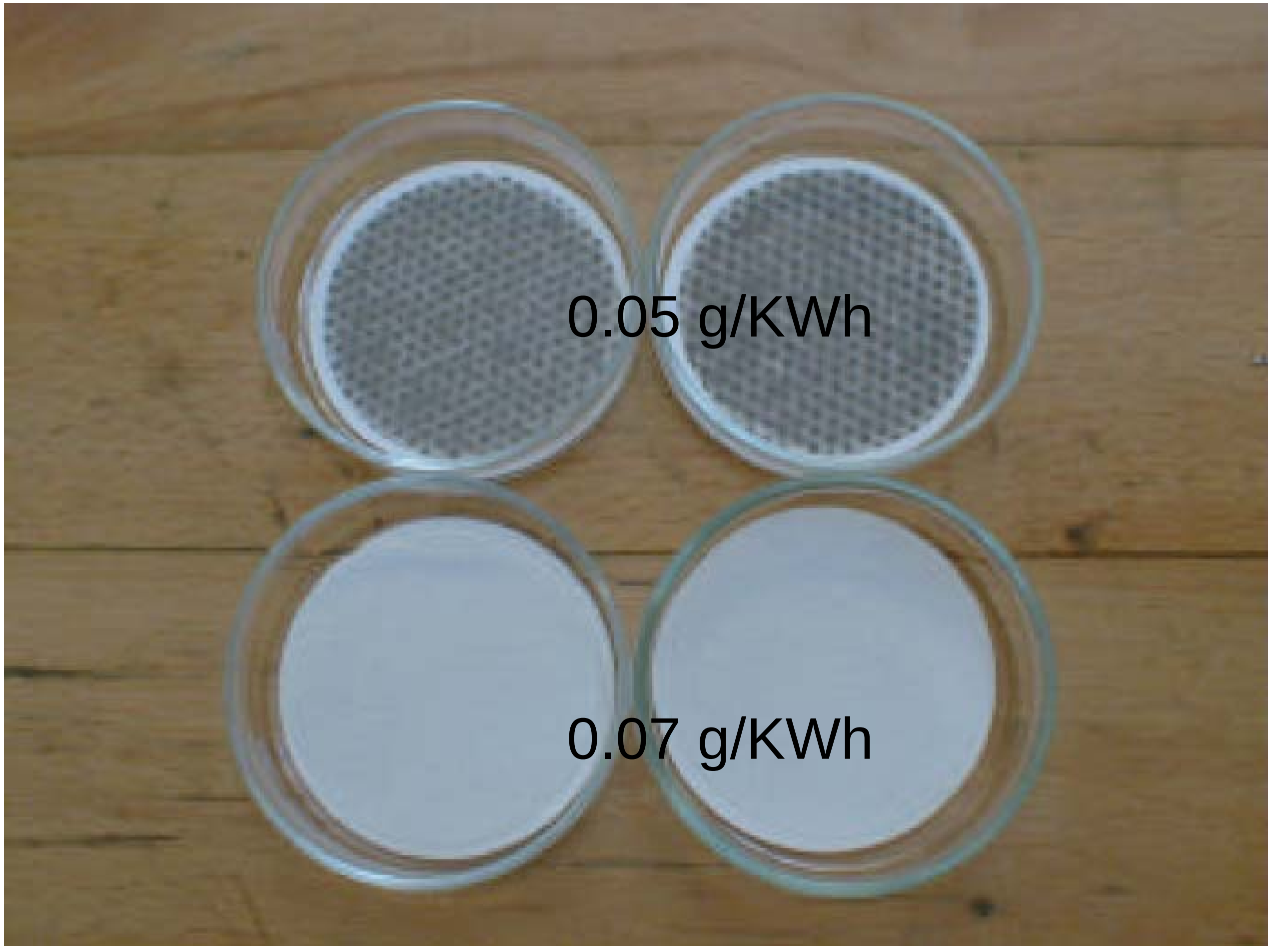


And why not use the same approach for tailpipe emissions ?

Measurement of Particle Mass PM at
tailpipe acc. to legal procedure



Particulate Mass Samples
upstream and downstream of a Bus Particle Filter



Hansen, Jensen, Ezerman (2001) Report 270-1-0019, Engine Technique Aarhus

And why not use the same approach for occupational health ?

Priority for Particle Elimination based on Occupational Health Limit Values

	Gases				Aerosols	
mg/Nm^3	CO	NO	NO_2	SO_2	**PM = EC + OC**	H_2SO_4
Emissions	1000	2700	300	100	**250**	25
Limit Values						
• Switzerland	33	30	6	5	**0.1 (EC)**	1
• Germany					**0.1 (EC)**	
• EC-Target			<0.6			
• MSHA 2007					**0.16 (EC)**	
Required Dilution	> 28	> 90	>50 (500)	> 20	**> 2500**	> 25

Summary

- **PM10 (2.5, 1.0) is a misleading metric to characterize the Health Hasard of Air Pollution**
- **PM10 composition must be weighed to form a Health Effect Equivalent PM10-HEQ**
- **This is just a beginning –** …………………….. please take it as a trans-disciplinary proposal
- **A scientific group has been formed in Switzerland with**
  - **Prof.P.Gehr – Institute of Lung Anatomy / Uni Bern**
  - **Prof.H.Burtscher - Aerosol Research University Windisch**
  - **Dr.Chr. Leuenberger and Dr. Heeb, EMPA, Chemists**
  - **Dr.M Kasper, Aerosol Physicist and Dr.M.Schmitz, Biologist**
- **Scientific Contributions are very welcome**

Further Information by TTM

- **Nanoparticle Conference ETH Zürich**
  www.nanoparticles.ethz.ch
- **Particle Filter Seminar HDT**
  www.hdt.de
- **VERT Filter List**
  www.buwal-umwelt.ch
- **Database 4500 DPF in Switzerland**
  www.akpf.org
- **Book on DPF published 2005 by EXPERT**
  www.expert.de
- **30 SAE-Papers and many other technical publications**