Atmospheric aerosols

Pavel Mikuška

Institute of analytical chemistry AS CR, Brno

mikuska@iach.cz

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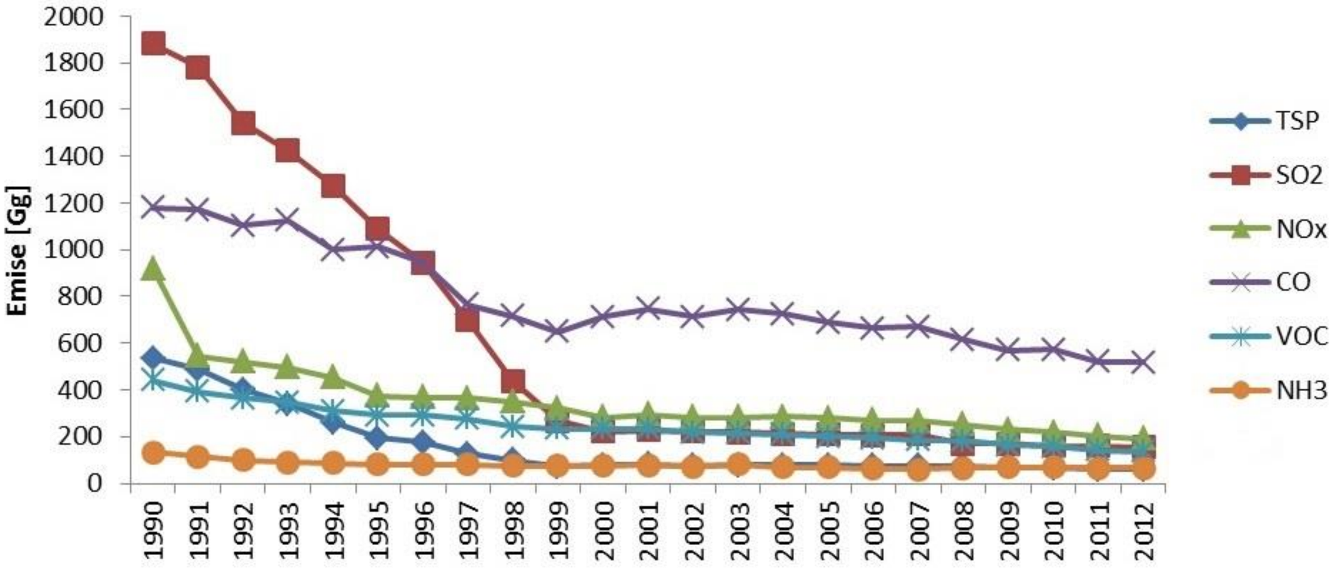
Program:

1. Atmospheric aerosol – definition, sources, deposition
2. Effect on human health and environment
3. Characterization of aerosols (size, shape, diameters, size distribution)
4. Specific types of aerosolů (nano-, bio-, indoor-aerosol)
5. Measurement of basic parameters (shape, size, concentration, …)
6. Chemical composition of aerosols (organics, metals, ions)
7. Air pollution by PM in the CR, limits
8. Positive application of aerosols
9. Literature

Main air pollutants:

- **SO_2**: 60.-80. of last century, power stations (brown coal)
- **NO_x**: 60.-80. of last century, power stations (brown coal)
  today – transportation (gasoline cars)
- **PM**: 60.-80. of last century, power stations+ industry
  today – transportation (diesel car) + residential combustion
- **O_3**: secondary pollutant, O_3 + PAN main components of photochemical smog

Today: **O_3 + PM**



Atmospheric AEROSOL

- „aerosol“ first used in 1920: "aero-" "air" + *sol*ution

- **Def.: dispersed system consisting of solid and liquid particles suspended in a gas (air)**

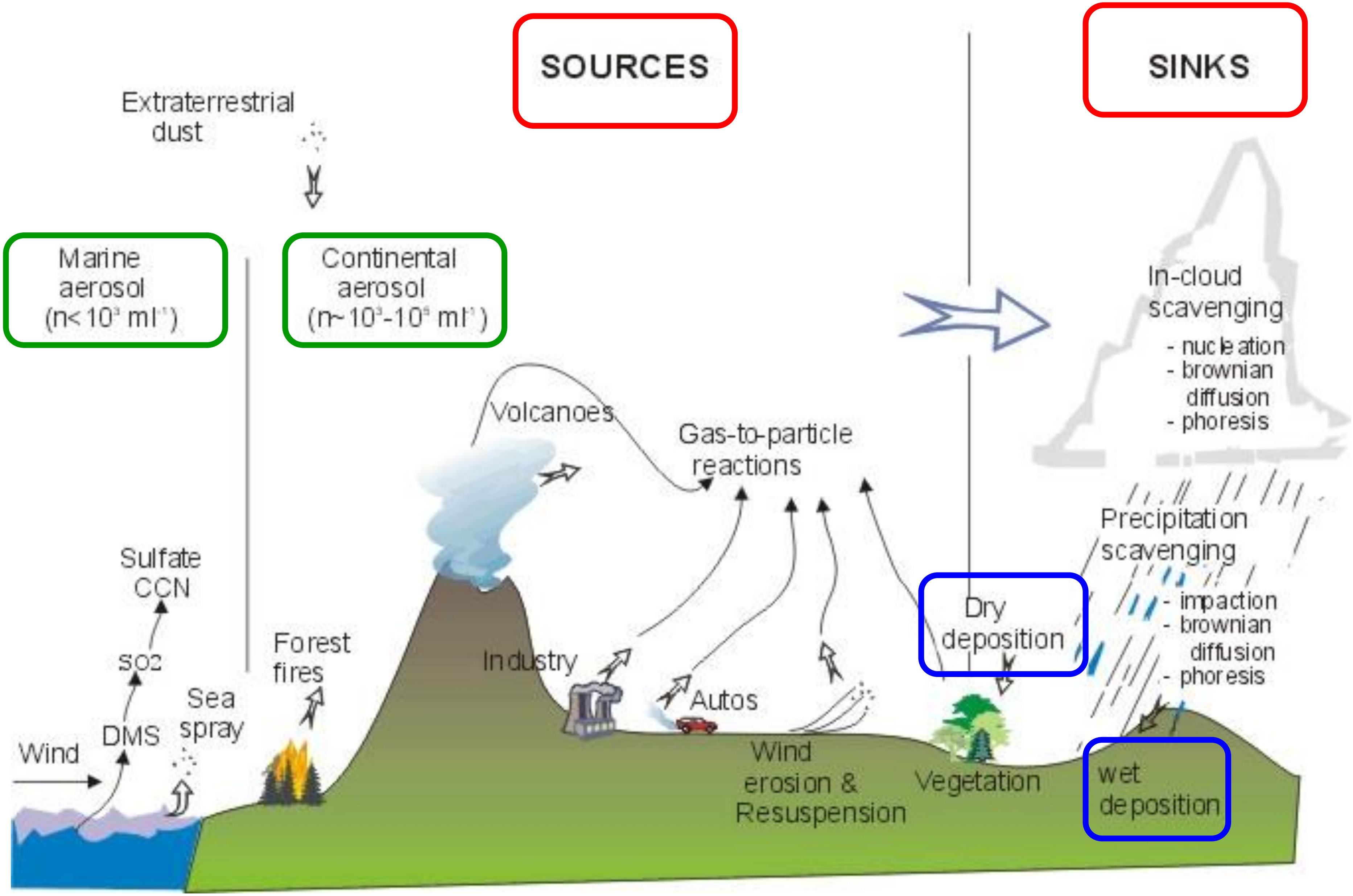
- **size range**: 1 nm – 100 µm

- **characterization:** diameter (nm, µm)
  mass concentration (µg/m^3, ng/m^3)
  number concentration (P/cm^3)

- **names of aerosols in specific size range:**

total suspended particles:	Σ all particles	(TSP)
coarse particles:	Da > 2.5 µm	
fine particles:	Da < 2.5 µm	(PM2.5)
submicrometer particles:	Da < 1 µm	(PM1)
ultrafine particles:	Da < 100 nm	(UFP)
nanoparticles:	Da < 50 / 100 nm	(NPs)

ATMOSPHERIC AEROSOL



SOURCES

SINKS

Extraterrestrial dust

Marine aerosol (n< 10^3 ml^{-1})

Continental aerosol (n~10^3-10^5 ml^{-1})

Volcanoes

Gas-to-particle reactions

In-cloud scavenging
- nucleation
- brownian diffusion
- phoresis

Precipitation scavenging
- impaction
- brownian diffusion
- phoresis

Sulfate CCN

SO2

DMS

Wind

Sea spray

Forest fires

Industry

Autos

Wind erosion & Resuspension

Vegetation

Dry deposition

wet deposition

Formation and sources of aerosols:

1)
- **primary sources**: direct emission from natural or anthropogenic sources
- **secondary sources**: formation in air by secondary reactions of gas precursors (gas-to-particle conversion, secondary oxidation)

2)
- **natural sources**: volcanic activity, sea aerosol, forest fires, mineral sources (soil erosion, desert dust), plant products (pollen, leaf detritus), bioaerosol
- **anthropogenic sources**:
  - combustion proceses: biomass, fossil fuels (coal, oil, …), traffic, …
  - industry activity: cement production, metallurgy (smelting ores and metals), power stations, steelworks, …
  - transport particles by wind from building areas, fields, …
  - agricultural activity
  - mining activity (quarry, …)

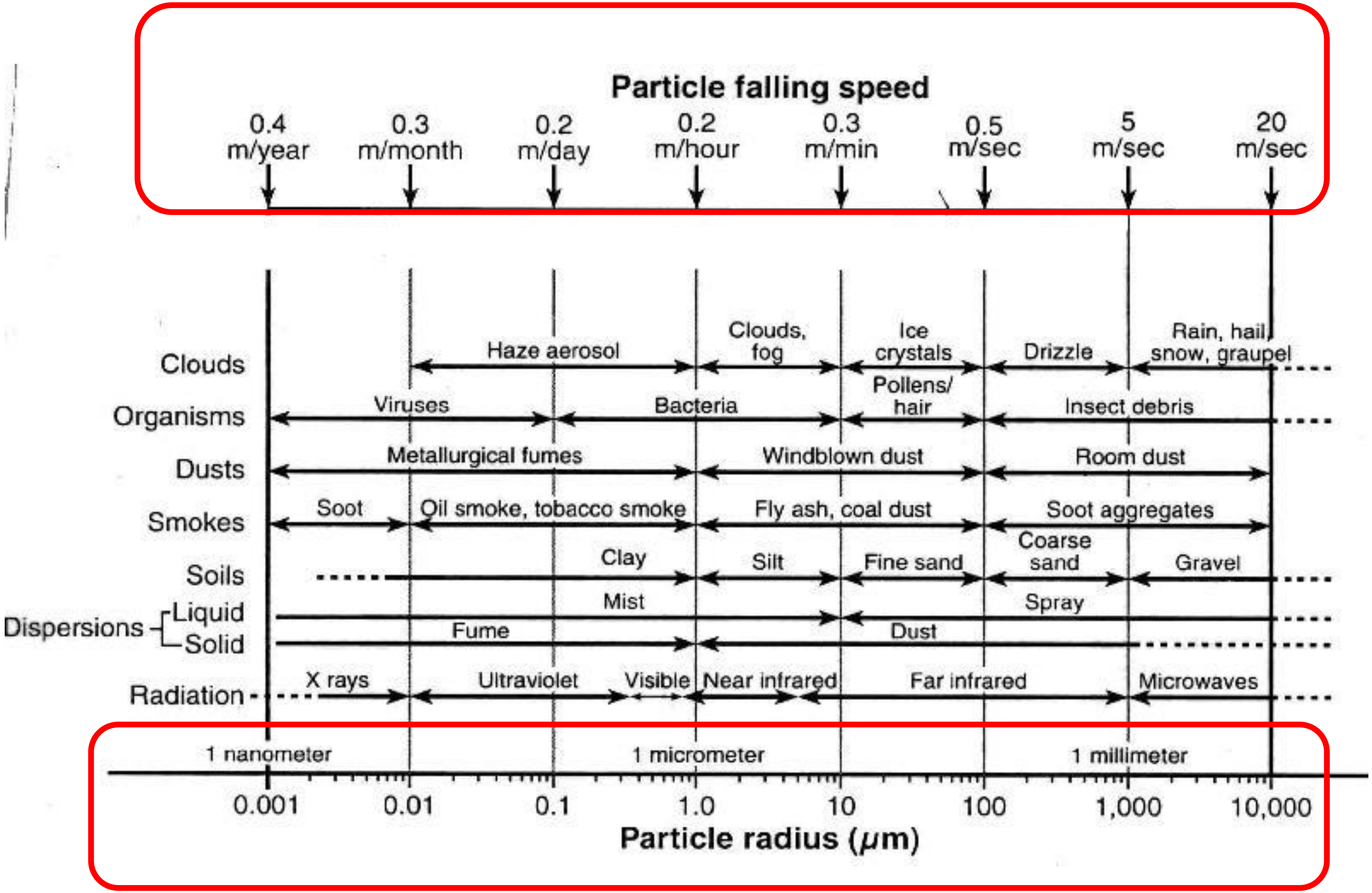
3)
- **fine aerosol**: reaction of gaseous precursors, nucleation, condensation reaction, combustion products (coal, biomass, traffic)
- **coarse aerosol**: earth crust material (particles of soil, weathered rock and minerals, resuspension, bioaerosol, emission of dust from industry and construction (cement, conveyor, …), volcanic activity, sea salt aerosol, desert dust

Specific aerosol types:

- Bioaerosol: aerosols of biological origin (viruses, bacteria, fungi, pollen, …)
- Cloud: visible aerosol with defined boundaries
- Dust: solid particle aerosol (> 0.5 µm) formed by mechanical disintegration of parent material (crushing, grinding)
- Fume: solid particle aerosol produced by the condensation of vapors or gaseous combustion products. Often clusters or chains of primary particles (< 0.05 µm)
- Haze: atmospheric aerosol that affects visibility
- Mist + Fog: liquid particle aerosol formed by condensation or atomization (1-200 µm)
- Spray: droplet aerosol formed by mechanical breakup of a liquid
- Smoke: visible aerosol formed by incomplete combustion; solid / liquid particles, mostly < 1 µm
- Smog: 1. general term for visible atmospheric pollution in certain areas. Term derived from words ***smo**ke* and *fo**g***
  2. London smog: winter, low temperature, fog, inversion, emissions from industry and coal combustion (SO_2, PM, …)
  3. photochemical smog: aerosol containig photochemical reaction products formed in atmosphere by action of sunlight on CHx and NOx (< 1 µm)

- ❑ Droplets – liquid particles
- ❑ Particulate Matter (PM) – solid particles or liquid droplets

Dry deposition:

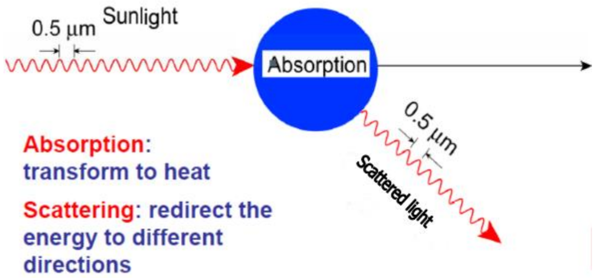


Effect of aerosols on environment:

- global climate ⇒ change in radiation balance of atmosphere
- visibility decrease
- acidification and eutrophication of soil and water resources
- surface for chemical reaction in atmosphere
- destruction of stratospheric ozone
- smog production

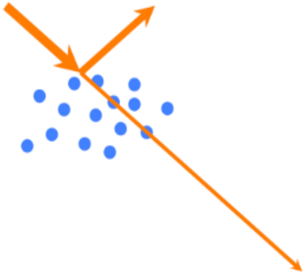
Effect of aerosols on the Earth's climate:

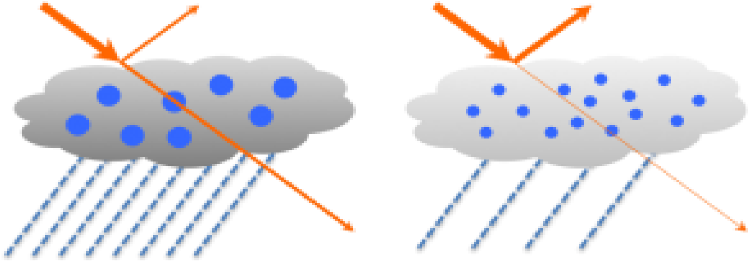
⇒ **change in the radiation balance of atmosphere**



Scattering, absorption = ∫ particle size, concentration,
chemical composition

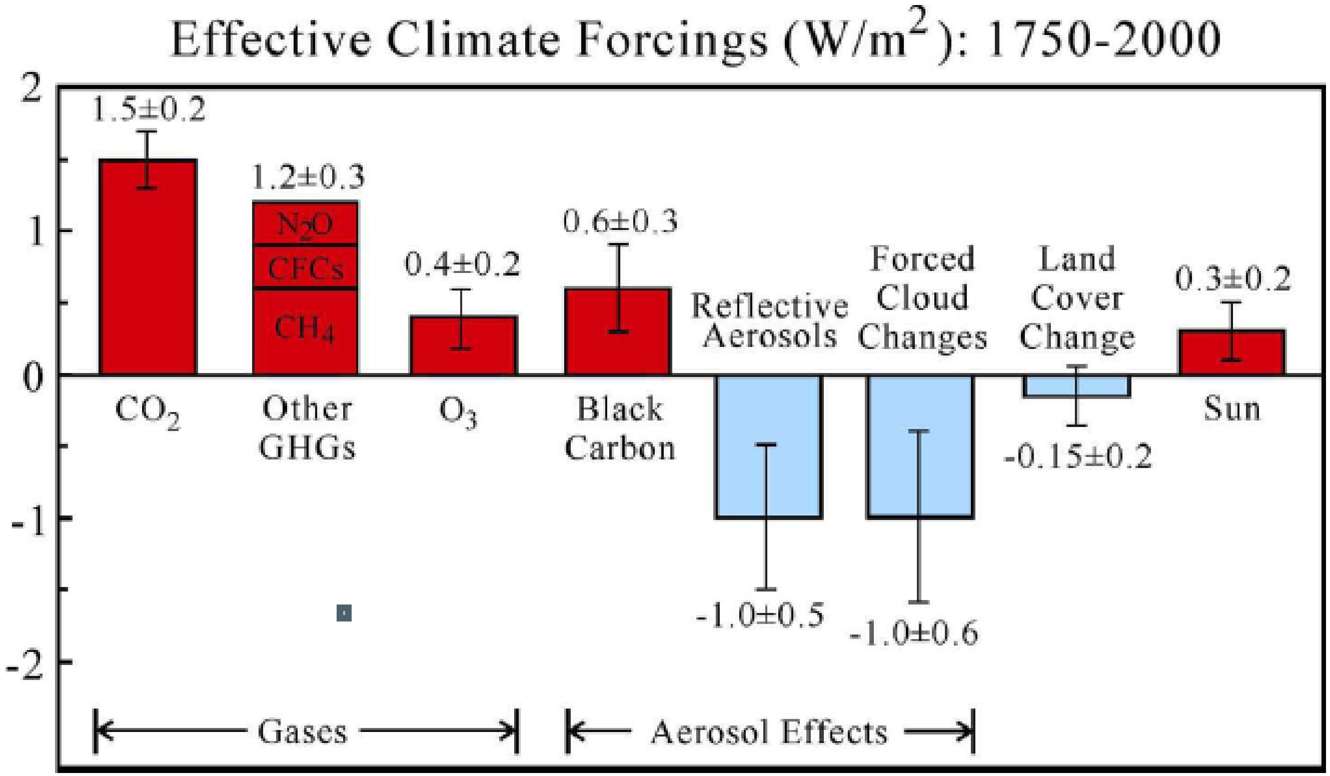
1) Direct Aerosol Effect: aerosol particles scatter radiation back to space or absorb sunlight, altering the amount of the sun’s energy that enters the Earth’s climate system, which has a cooling effect on the Earth’s energy balance (chemical composition vs size, larger particles scatter more light than smaller aerosol particles)





2) Indirect Aerosol Effect: aerosols acting as cloud droplet seeds influences both reflectivity of cloud (albedo) and its ability to produce precipitation

direct + indirect effect ⇒ Earth cooling („whitehouse effect“)



Climate forcing agents in the industrial era. “Effective” forcing accounts for “efficacy” of the forcing mechanism

Source: Hansen et al., JGR, **110**, D18104, 2005.

Contribution to total atmospheric absorption by aerosols (**warming effect**):

- brown carbon 19%
- black carbon 72%

Visibility reduction:

- visibility = ability of eye to distinguish the subject from surrounding background
- limited by dispersion of sun light on aerosol particles and molecules of air
- theoretically (PM ≈ 0 μg/m^3) ⇒ 340 km (→ dispersion of light by molecules of air)
- PM ≈ 10 μg/m^3 ⇒ visibility 30 - 40 km

Krkonoše from Hradec Králové (7.3.2011 after crossing the queue, 63 km, J. Strouhal)

Effect of aerosols on human health:

- wide range of health effects: increased mortality, cardiovascular, respiratory (astma), cancer, ...
- harmfulness of aerosols: deposition in organism (lung)
- **health effect = ∫ aerosol properties** (size, shape, concentration, composition, ….)
- „**All particles are equal but some particles are more equal**“ (Brunekreef, EAC, Zurich 2017)

  ⟶ all particles are toxic but some particle are more toxic !
- size: toxicity increases with decreasing size, … ⟶ UFP the most toxic
- shape: sphere, fibre, irregular, amorphous
- concentration: mass × number
- composition: BC, organic compounds (carcinogens), SOA, heavy metals → Cd, Pb, Ni, Tl, Hg, Ba, .., As

  organic compounds → PAHs, N-PAHs, PCBs, dioxines, …
- bioavailibility
- 2 different approaches:
  - epidemiological: exposure level (= delivered concentration), large populations
  - toxicological: mechanism of reaction, dose (delivered concentration retained in the tissue), mass conc. not useful, surface drives particle toxicity
- Europe in 2000: ≈ 370 000 inhabitants died due to air pollution by aerosols

  (= about 10times more than deaths due to traffic accidents)

1) **Meuse valley: 1.-5.12.1930**

- 5-day fog, T-inversion
- high conc. SO_2 (coal combustion)
- high conc. PM (H_2SO_4, …)
- 63 deads, 6 000 patients

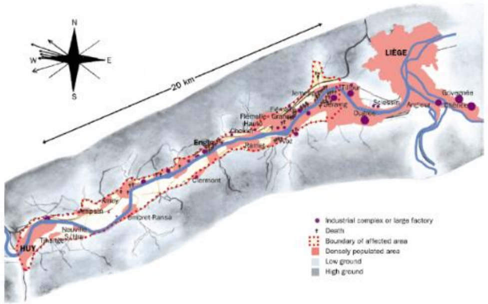


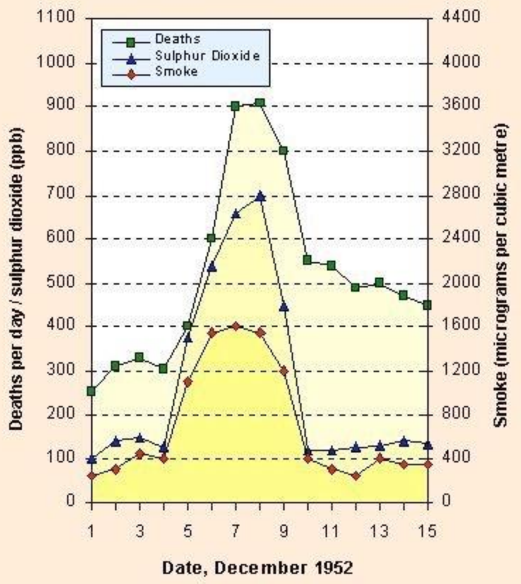
Figure 1: **Map of the Meuse Valley between Liège and Huy, indicating the fog-covered area and location of fatalities and factories**
Reproduced and modified from figure 1 of Firket and colleagues' report.[14]

2) **Donora (Pennsylvania): 26.-31.10.1948**

- fog, T-inversion
- high conc SO_2 and HF (steelworks, ceramic industry)
  $\Rightarrow$ high conc. PM (H_2SO_4, F^-, …)
- 20 deads, 7 000 patients

3) **London: December 1952**

- fog, low temperature (cca 0°C)
- T-inversion (from 5.11.)
  $\Rightarrow$ PM accumulation (coal combustion – industry, households)
- 7 December: visibility < **0.5 m !**
- **> 12 000 deads !**

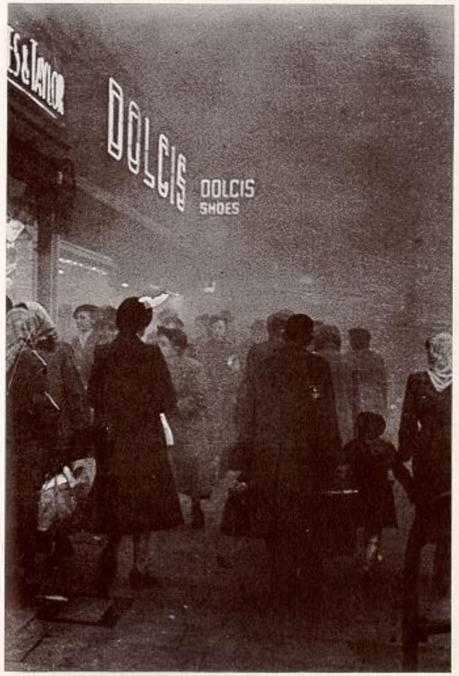


☐ Los Angeles, 50- 60s of 20th century
- **photochemical smog**

☐ **Today:** Peking, Delhi, Indonesia
Athens, Po Valley, Ostrava + South Silesia

cathedral St. Paul, 1903

London smog 1952



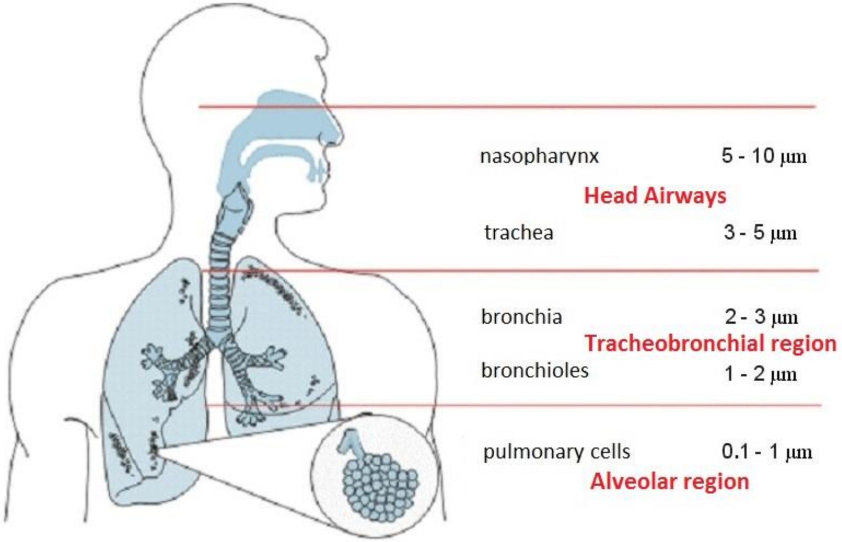
Particle deposition in respiratory tract:

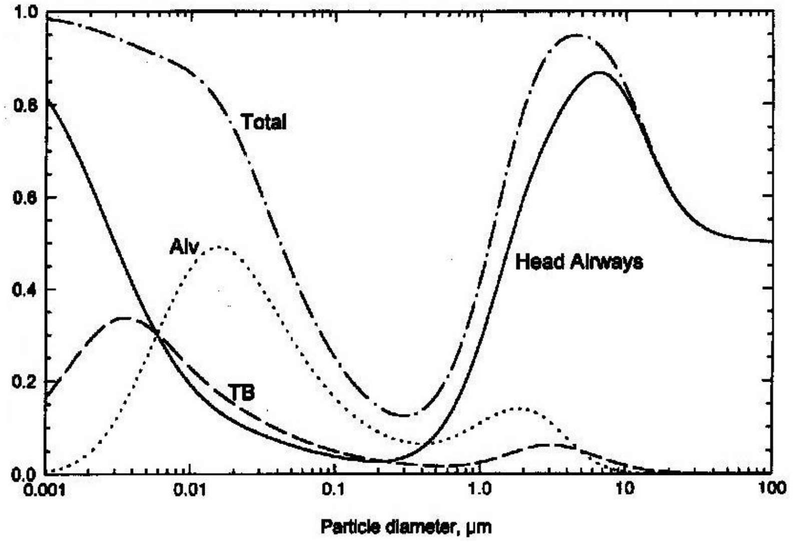
- Human respiratory tract is divided into 3 main regions:

  head airways, tracheobronchial region and alveolar region (pulmonary; gas-exchange)
- Particles must generally become deposited in respiratory tract to exert biological effects
- Particle separated according to penetration into respiratory regions:
  - Inhalable fraction: mass fraction of total airborne particles that enters body through nose and/or mouth during breathing
  - Thoracic fraction: mass fraction of inhaled particles penetrating beyond larynx (Da < 10 µm, PM10)
  - Respirable fraction: mass fraction of inhaled particles penetrating into alveolar region of lungs (Da < 4 µm, PM4): PM2.5 – particle penetration into bronchi

    PM1 – particle penetration into pulmonary cells

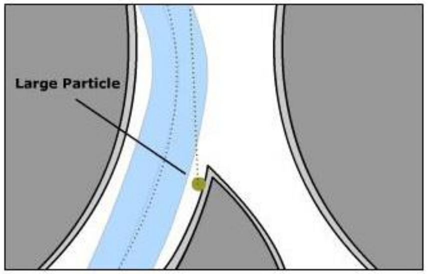
    NPs – particle penetration into blood



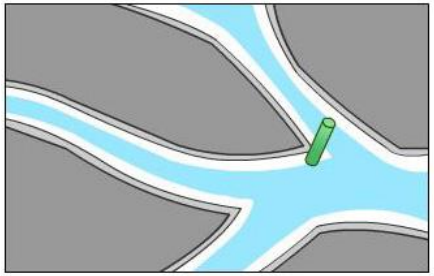


Particle deposition mechanisms in respiratory tract:

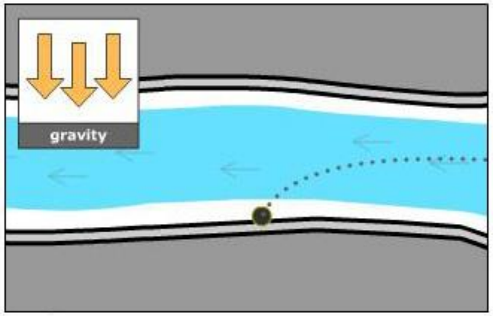
- Impaction: large particles at large velocity in curved pathway (bronchial region)



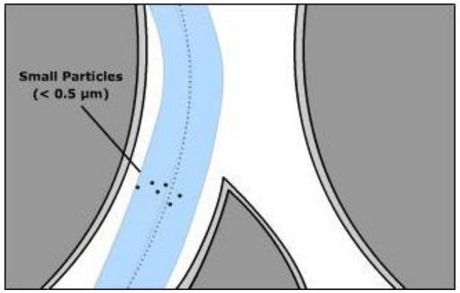
- Interception: long fibers in narrow airways



- Gravitational settling: large particles at low flow velocity and small airway dimension



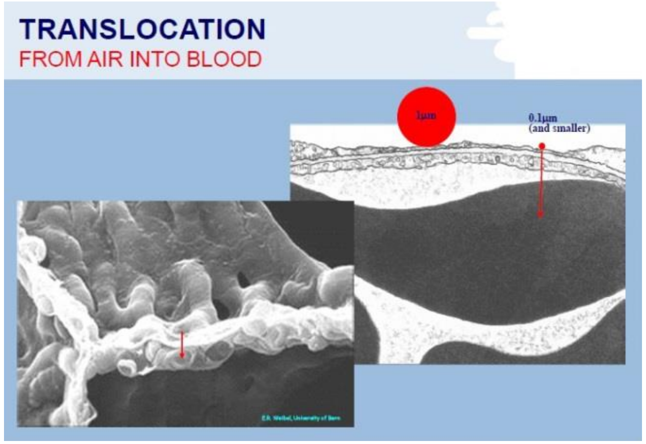
- Diffusion (Brown): small particles (< 0.5 μm) in small airways and long residence time (alveolar region)

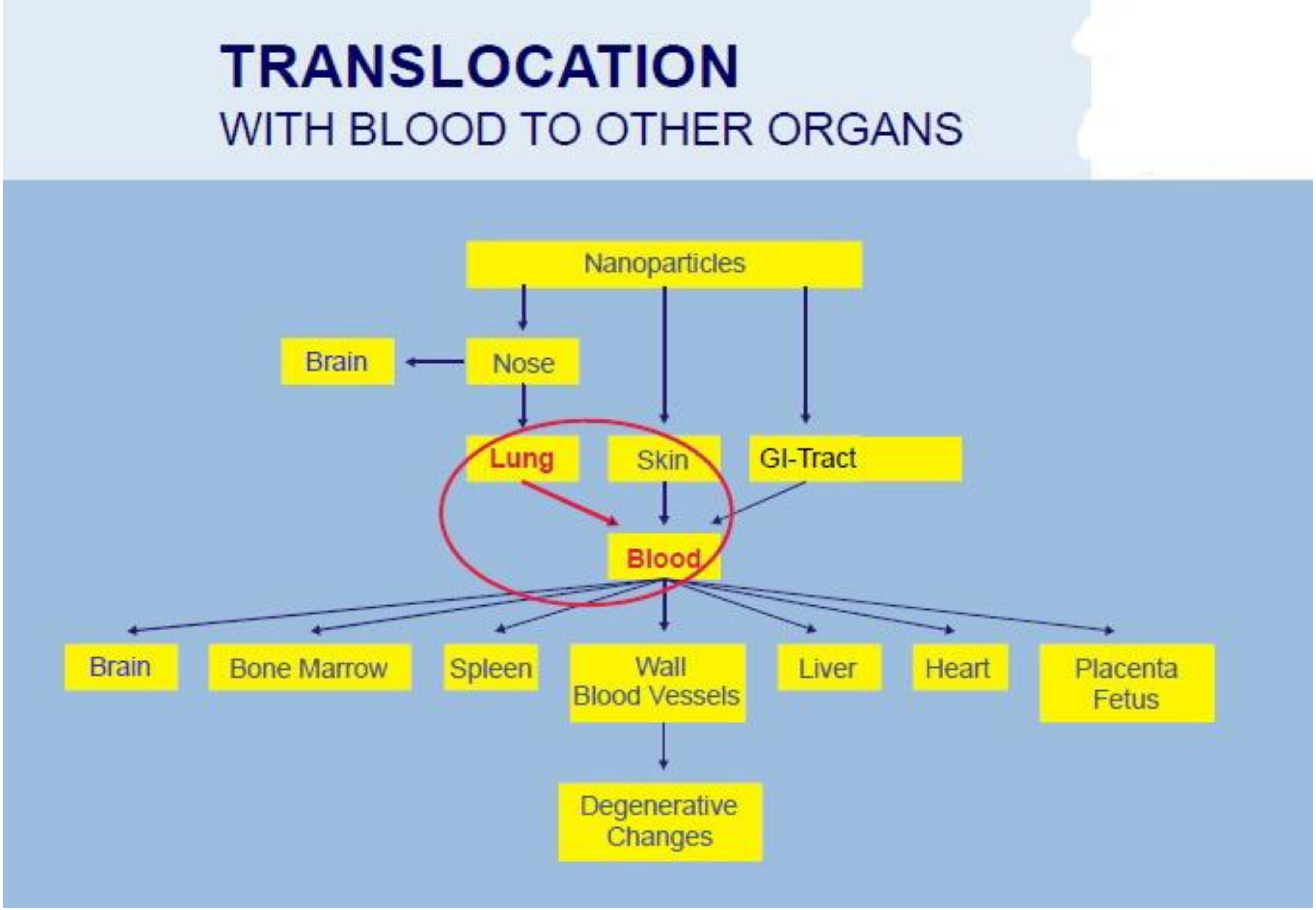


Nanoparticles (NPs): Da < 50 / 100 nm

- **nanomaterials** – at least 1 external dimension smaller than 100 nm
- **nanoparticles** – objects with all 3 external dimensions at the nanoscale (< 100 nm)
- **nanoclusters** – at least one external dimension smaller than 10 nm

- NPs sources:
  - natural (volcanic dusta, forest fires, …)
  - incidental byproducts of combustion processes (e.g., welding, diesel engines)
  - engineered nanoparticles: intentionally produced and designed with very specific properties (shape, size, surface properties and chemistry)
- different properties in comparison with the same material of large diameter (surface)
- surface area - biologically most relevant dose metric for NPs
- pathways of NPs entry into the body:
  - **inhalation** (mouth/nose → lungs, main route)
  - along olfactory nerv (directly to brain)
  - ingestion
  - skin (damaged)
  - food (gastrointestinal tract)
- serious health effects:
  - penetration through intercellular space into body → blood transport → accumulation in organs (brain, kidney, liver, …)
  - cardiovascular, neurodegenerative and carcinogenic effects
  - chronic breathing problems





TRANSLOCATION
WITH BLOOD TO OTHER ORGANS

Nanoparticles

Brain

Nose

Lung

Skin

GI-Tract

Blood

Brain

Bone Marrow

Spleen

Wall
Blood Vessels

Liver

Heart

Placenta
Fetus

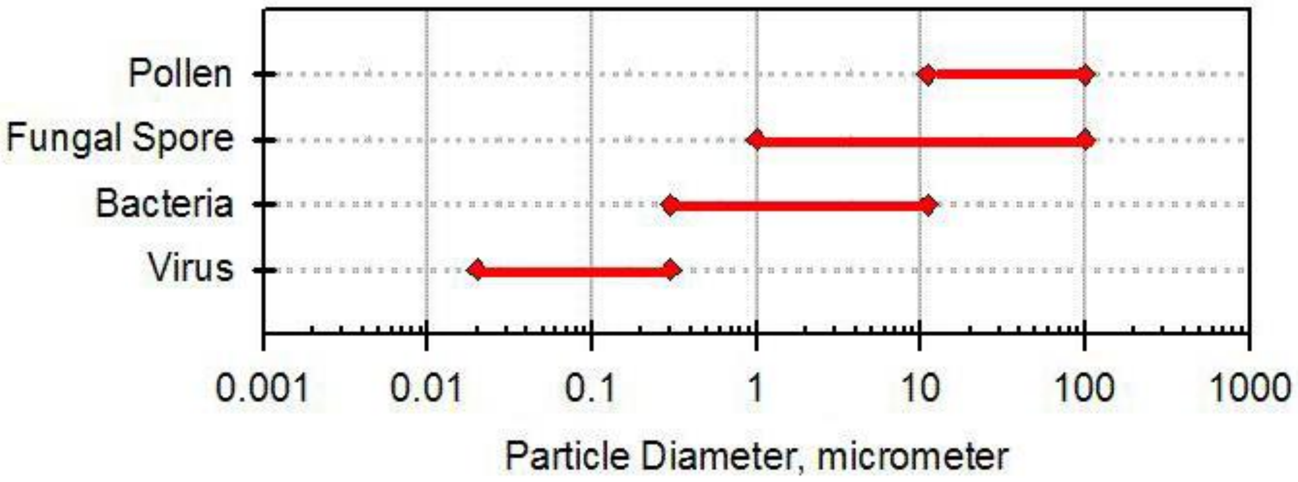
Degenerative
Changes

Gehr, BB workshop, Praha 2013

Bioaerosols: = aerosol of biological origin

- ☐ viruses
- ☐ viable organisms (they are reproduced): bacteria, fungi, mold, algae, yeast, …
- ☐ non-viable organisms (no reproduction): product of organisms (fungal spores, pollen), body parts of animals (hairs, skin, feathers), insects and plants

- size: 0.02 – 100 μm
- characteristic properties: size, viability, infectivity, allergenicity, toxicity, pharmacological activity
- importance: adverse health effects (allergy, illnesses, …, deaths)
  adverse social impacts (harvest damage, damage to cattle)



Radioaerosols:

- measurement of natural radioactivity: radiation protection
  mechanism of transport
  distribution of radionuclides in environment

- natural radioactivity: mainly Rn (^{220}Rn, ^{222}Rn) – gas (α)

  short-term products of Rn transformation bound to PM

- collection of air at filter, measurement of activity:

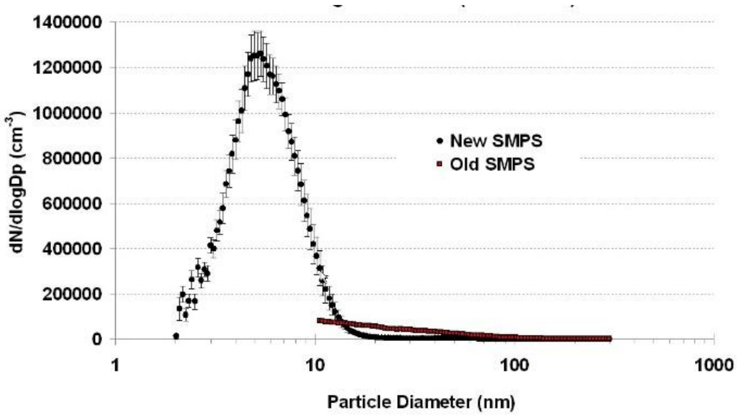
$$^{220}\mathrm{Rn} \longrightarrow {}^{212}\mathrm{Pb},\ {}^{212}\mathrm{Bi}$$

$$^{222}\mathrm{Rn} \longrightarrow {}^{218}\mathrm{Po},\ {}^{214}\mathrm{Pb},\ {}^{214}\mathrm{Bi}$$

- different half-lives of individual transformation products

Indoor aerosols:

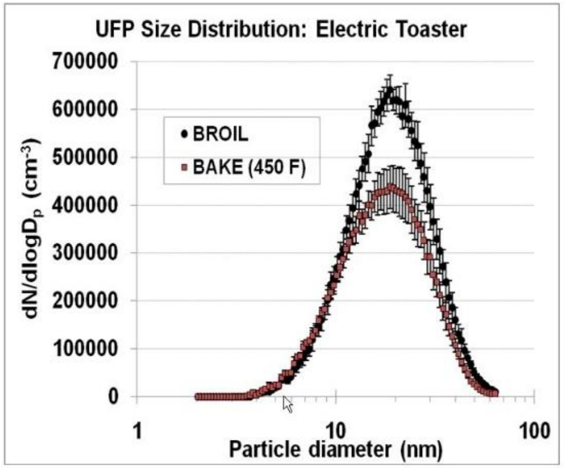
- 68 % time spent in indoor space

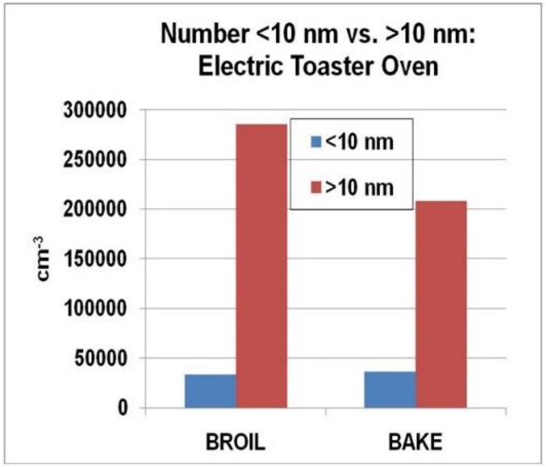


Gas stove

☐ **Indoor sources of aerosols**:

- cooking (main): 90% particles < 10 nm
- combustion: gas stove, fireplace, candles, aromatic sticks, …
- electrical equipments: stoves, tools, kitchen appliances, hair dryer
- smoking: cigarettes, pipes
- Laser / 3D printers
- home animal, plants
- building material: asbestos
- kitchen degreaser + cleaners
  (MEA, limonen, …)





☐ **Outdoor sources** : inward infiltration (penetration through window, door)

Characterization of atmospheric aerosols:

- **size** (diameter) ⇒ determines behaviour and properties
- **shape**
- **density**
- **concentration**: mass × number
  integral × size-resolved
- **chemical composition**
- toxicology analysis

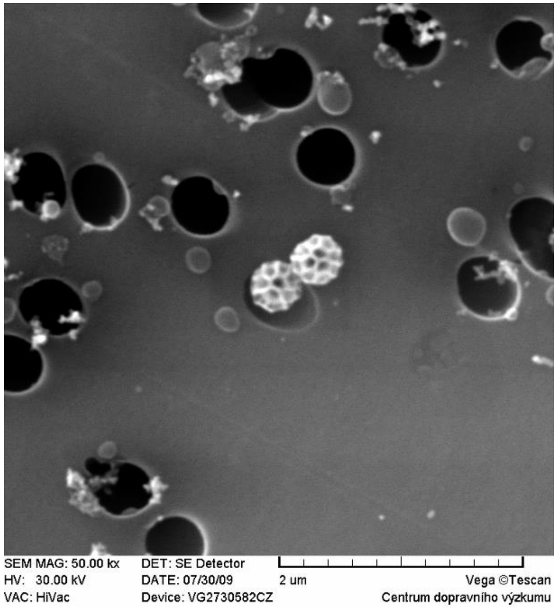
} evaluation / estimation of health risk / effects

- refractive index
- surface

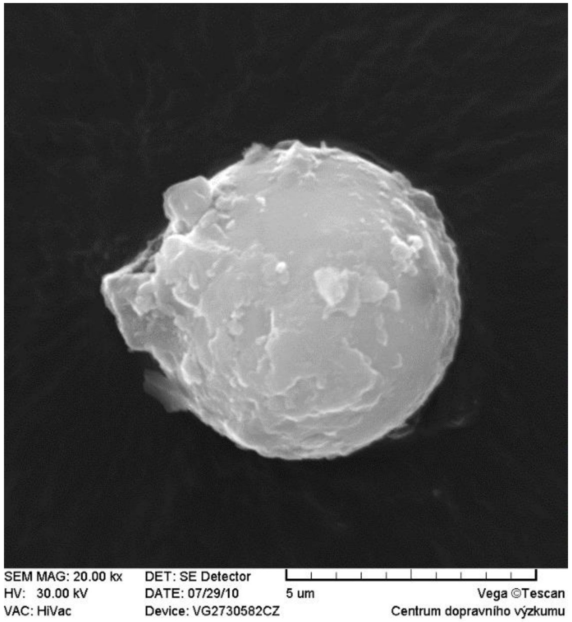
size + concentration ⇒ **size distribution**

Particle shape:

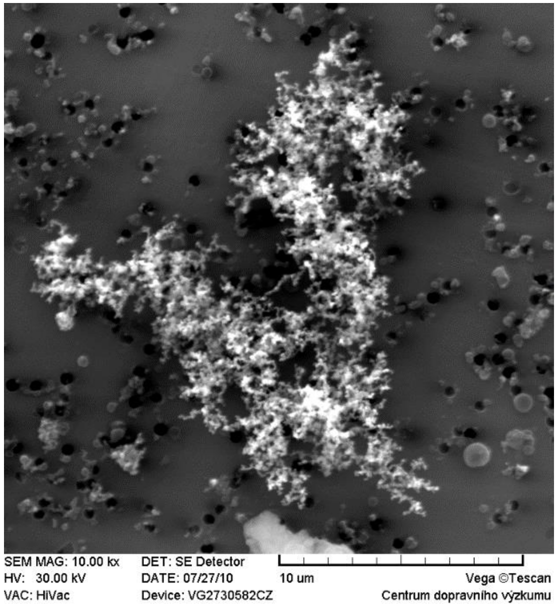
- spherical, fibrous, irregular, …
- collection PM on filters (polycarbonate filter)
- analysis individual particles with electron microscope ⇒
  simultaneously size, shape, chemical composition
- use: identification of emission sources
  estimation of health risk (fibres)



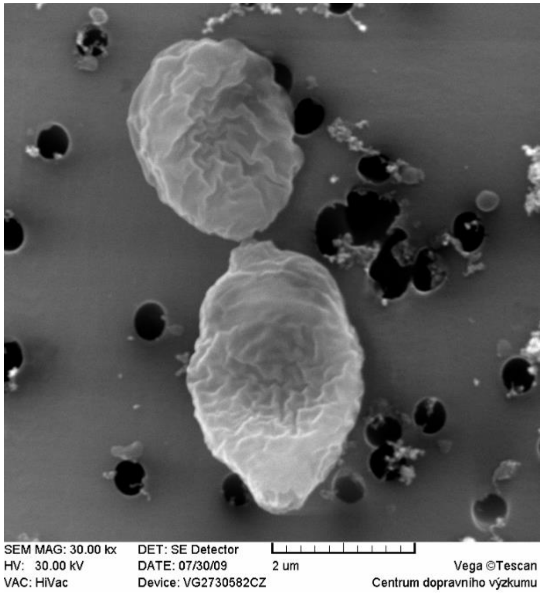
ash (Ostrava)



agreggates from traffic

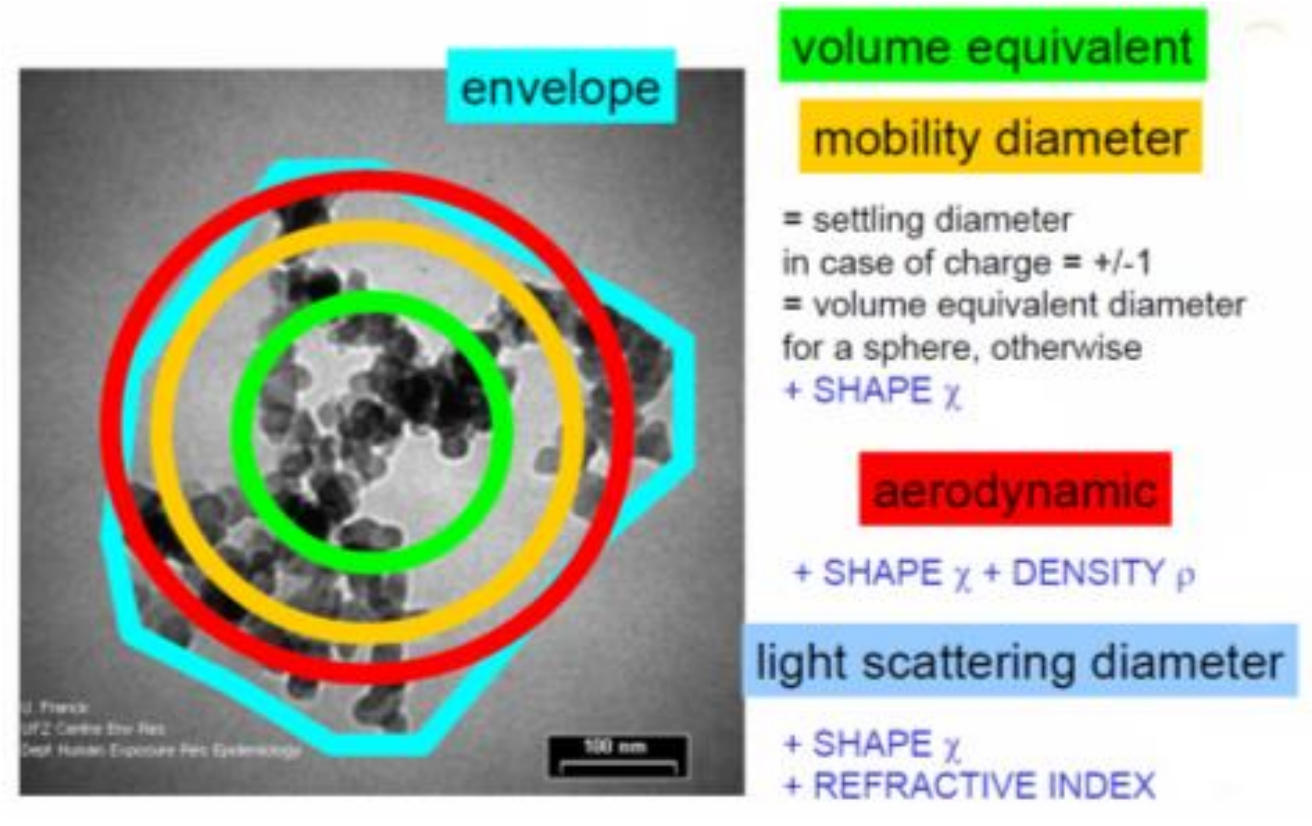


particles of biological origin



Particle diameter (D_p) ⇒ particle size

- unambiguous definition D_p: spherical particle
- particle with irregular shape → diameter of equivalent sphere
- **equivalent diameter**: dimeter of sphere with the same physical property as measured particle of irregular shape
- particle Ø defined according to measurement method ⇒ aerodynamic, optical, electromobility, Stokes, volume, geometric, …



= settling diameter
in case of charge = +/-1
= volume equivalent diameter
for a sphere, otherwise
+ SHAPE χ

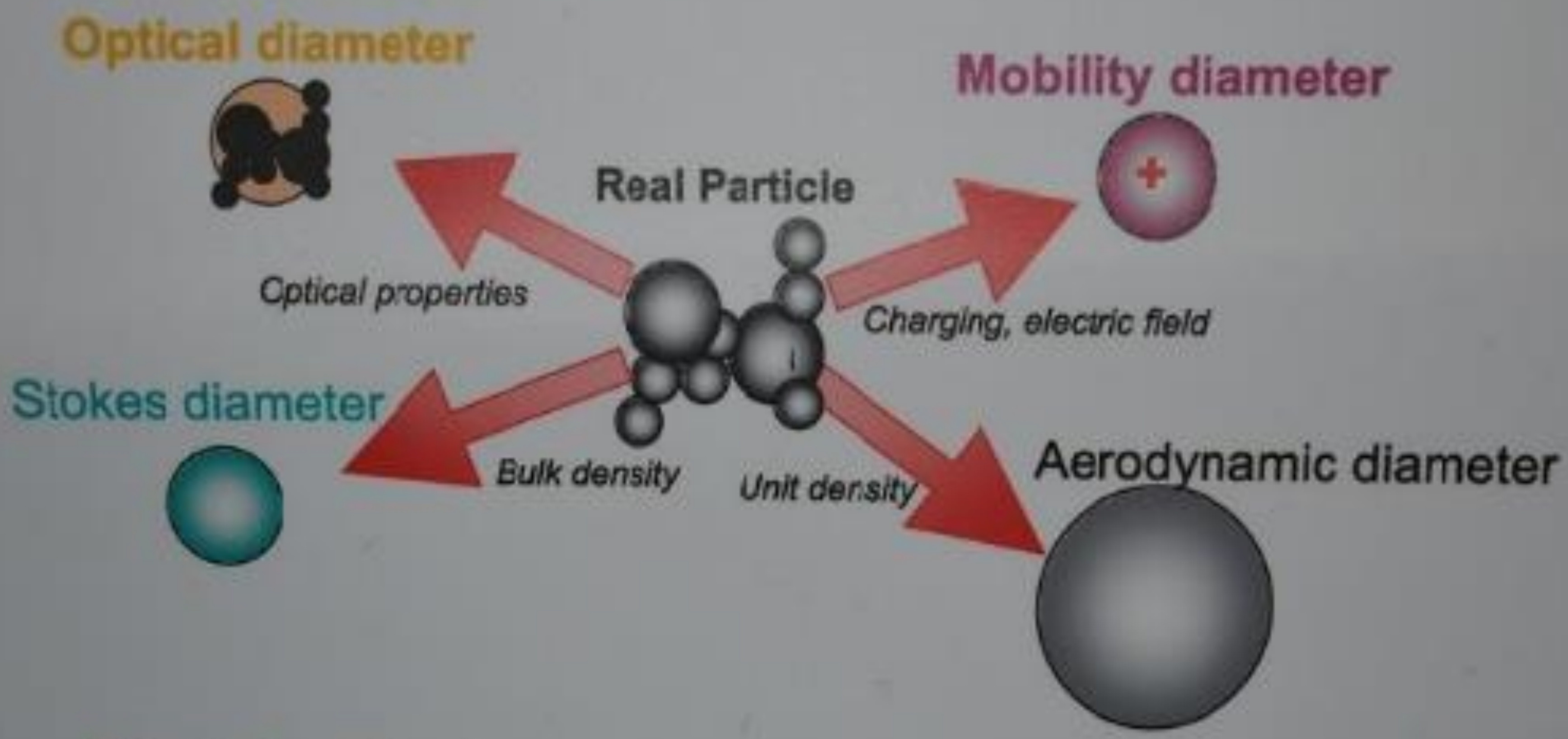
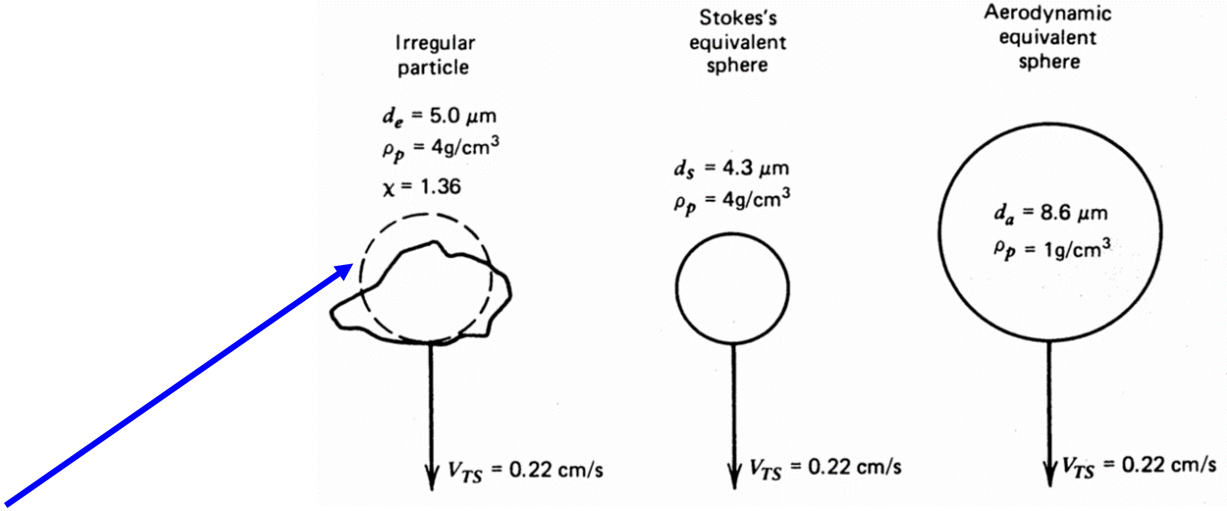


Fig. 1: Particle size concept, the diameter of particle varies depending on the measurement method.

Important equivalent diameters of irregular particles:

- **Aerodynamic diameter (Da)**: diameter of sphere with unit density (1000 kg/m^3) and the same settling velocity as the irregular particle. Da determines particle behaviour in air (sedimentation, deposition in lungs, …)

- **Stokes diameter (Ds)**: diameter of sphere with the same density and the same settling velocity as the irregular particle.



- **Volume equivalent diameter:** diameter of spherical particles with the same volume and with the same settling velocity as the irregular particle.

  Corrections for other shapes: χ (dynamic shape factor): sphere 1.00; cube 1.08; quartz 1.6; fibre: 1.35 (5:1); 1.68 (10:1)

- **Equivalent mobility diameter:** diameter of spherical particles with the same mobility …

Size distribution of aerosol:

- simultaneous characterization of size and concentration of individual aerosol particles
- real aerosols: high concentration of particles
  impossible to characterize each particle separately
- size distribution (curve) ⇒ particle concentration as a function of particle diameter
  - concentration (number, mass, volume, surface) of particles in selected size interval
  - distribution is characterized by location and width of distribution

Locations of distribution curve:

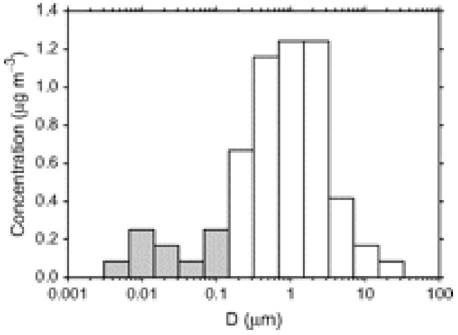
- **Mode**: particle diameter (D_p) with the highest frequency
- **Median:** D_p that divides frequency curve into equal areas
- **Mean** (arithmetic average, $\bar{d}_p$): D_p with arithmetic mean value
- **Geometric mean** (D_g): mean diameter on log-normal distribution curve

- **mode < median < mean**

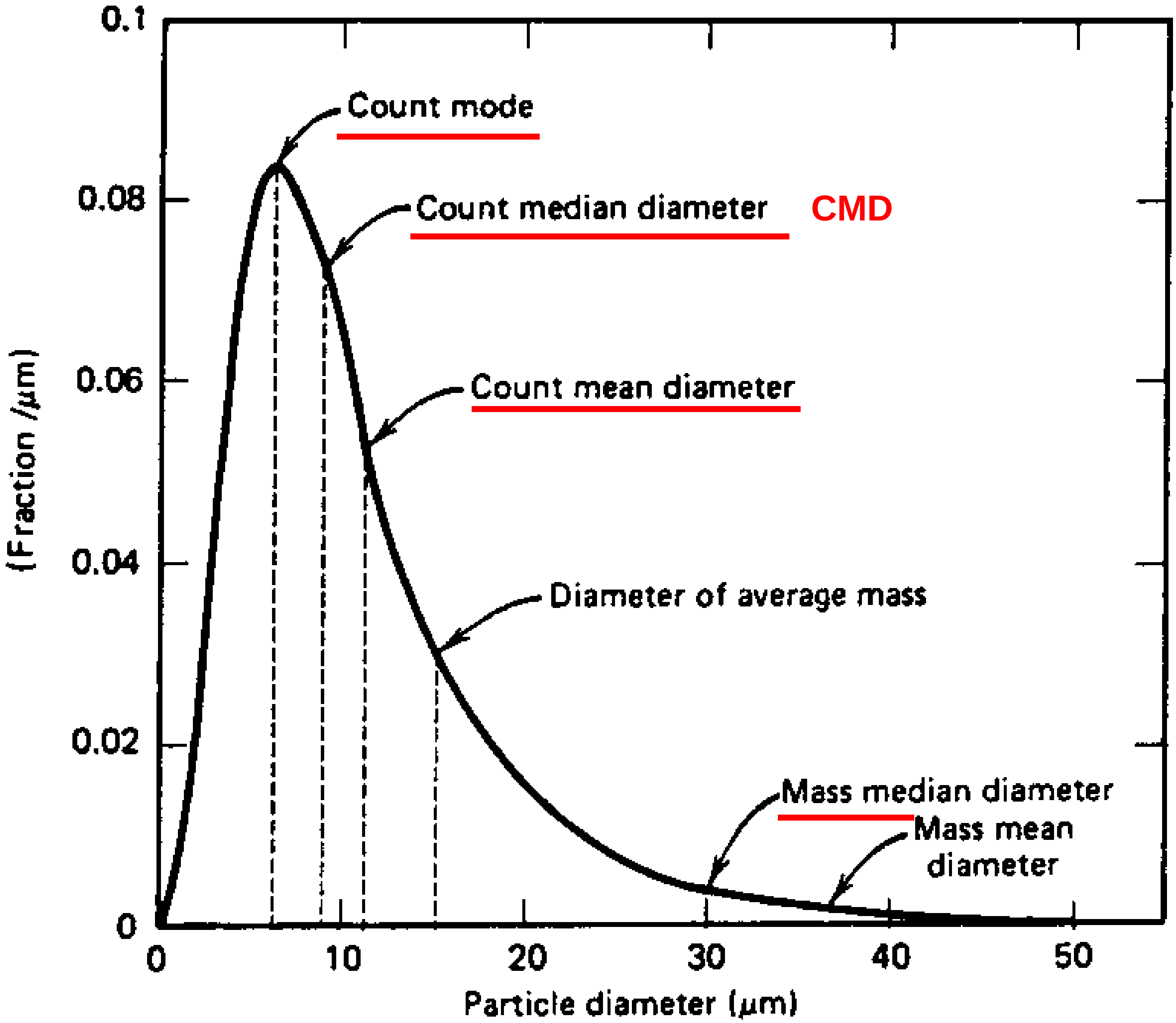
$$\bar{d}_p = \frac{\sum d}{N} = \frac{\sum n_i d_i}{N}$$

$$d_g = \left(\prod_{i=1}^{N} d_i \right)^{1/N} = (d_1 d_2 \ldots d_N)^{1/N}$$

$$\ln d_g = \frac{1}{N} \sum_{i=1}^{I} n_i \ln d_i$$



F = count number
(mass, volume)


Count mode
Count median diameter
CMD
Count mean diameter
Diameter of average mass
Mass median diameter
Mass mean diameter
(Fraction /μm)
0.1
0.08
0.06
0.04
0.02
0
0
10
20
30
40
50
Particle diameter (μm)

Monodisperse aerosol: very narrow range of particle sizes (mean = mode = median)

Polydisperse aerosol: wide range of particle sizes

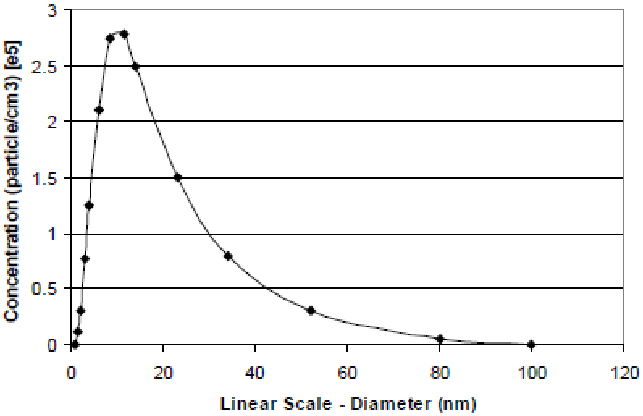
1) linear scale of sizes ⇒ Normal distribution

- unsymmetrical

$$f(d_p) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(d_p - \bar{d}_p)^2}{2\sigma^2}\right)$$

$$\sigma = \left(\frac{\sum n_i (d_i - \bar{d}_p)^2}{N-1}\right)^{1/2}$$

σ - standard deviation



2) logaritmic scale ⇒ Log-normal distribution

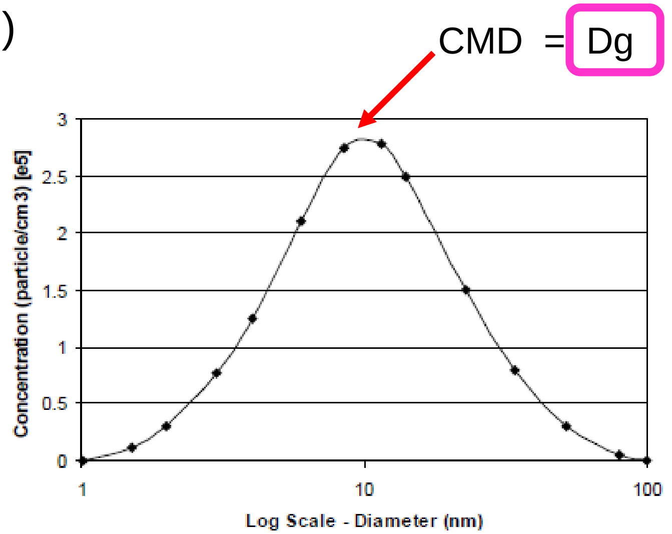
- normal distribution for log D (symmetrical shape)
- CMD = D_g

$$f(d_p) = \frac{1}{\ln\sigma_g\sqrt{2\pi}} \exp\left(-\frac{(\ln d_p - \ln CMD)^2}{2(\ln\sigma_g)^2}\right)$$

$$\ln\sigma_g = \left(\frac{\sum n_i (\ln d_i - \ln d_g)^2}{N-1}\right)^{1/2}$$

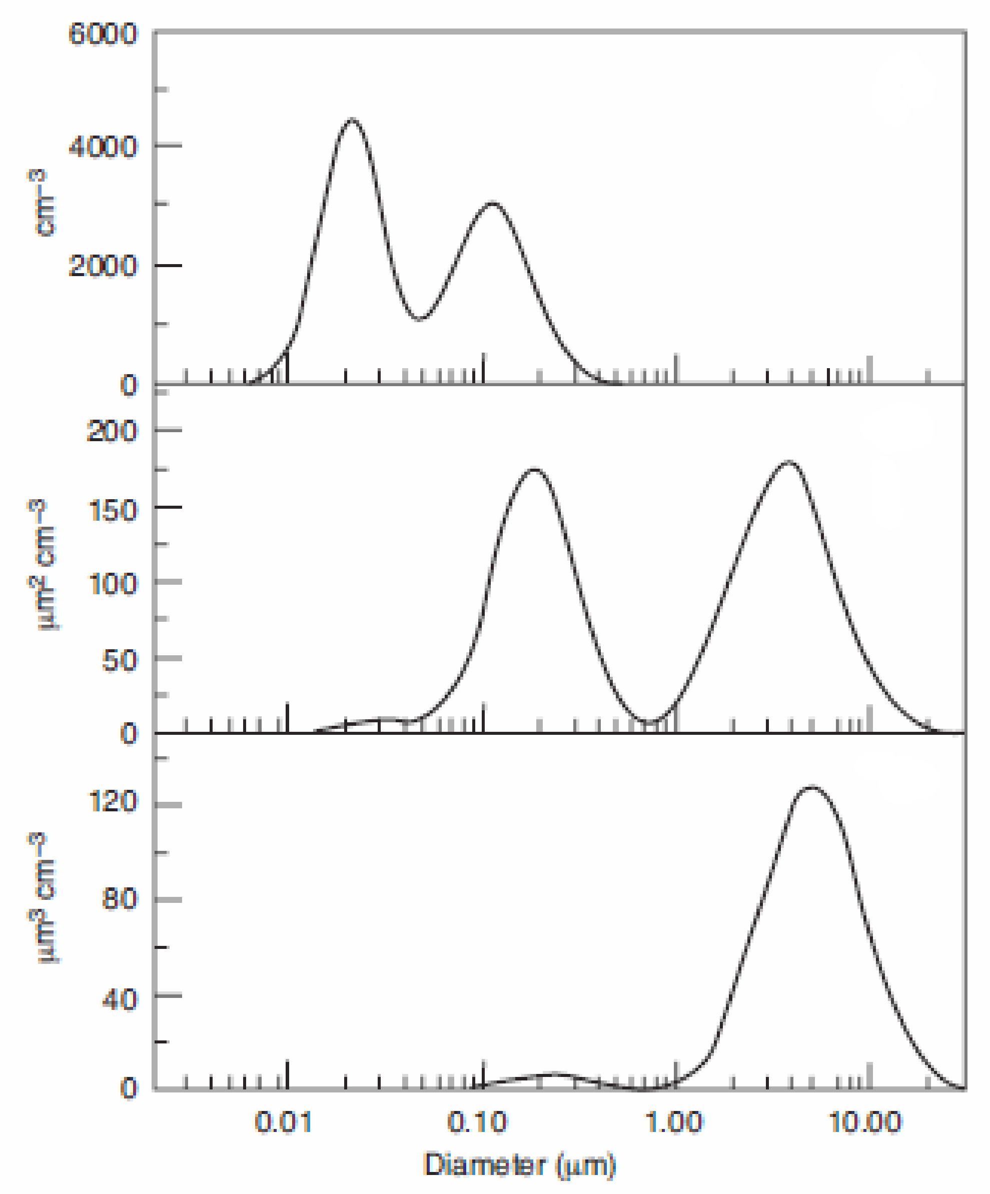
σ_g - **geometric standard deviation**

- monodisperse aerosol: $\sigma_g \leq 1.25$
- polydisperse aerosol: $\sigma_g \geq 1.25$


CMD = Dg

Log-normal distribution curves of ambient aerosol:

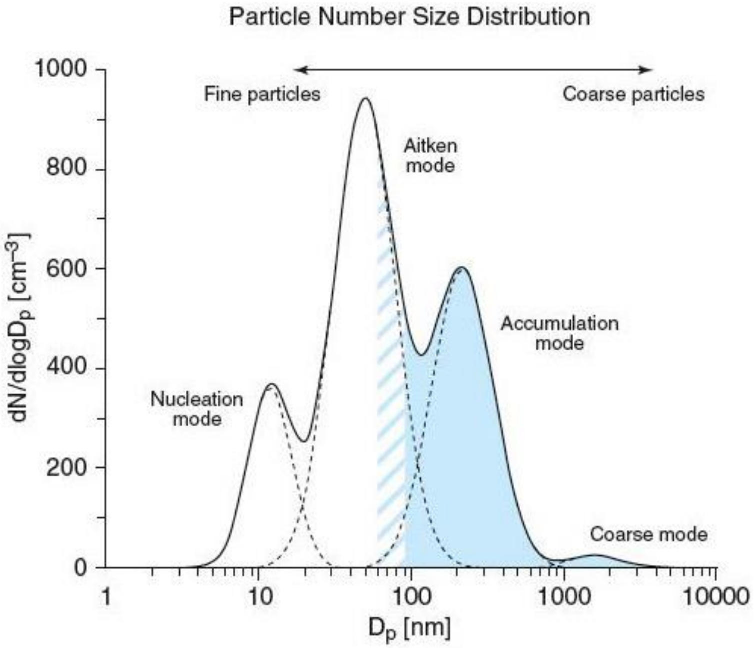
- weighted by N, S, M / V



- Number distribution
- Surface area distribution
- Volume / Mass distribution

Atmospheric aerosol: 4 - modal number size distribution

→ **different sources and composition particles**



- **Nucleation mode:** Dp < 20 nm, „lifespan“ ≈ 1 hod
  - origin: nucleation of gases → formation of new particles
  - composition: ions, organic compounds
- **Aitken mode:** 0.02 < Dp < 0.1 μm (UFP)
  - origin: emission from combustion processes, condensation of cooled gases after emission, coagulation of particles of nucleation mode
  - composition: EC, organic compounds, ions, metals
- **Accumulation mode:** 0.1 < Dp < 2.5 μm, „lifespan“ ≈ weeks
  - origin: coagulation of smaller particles, condensation of volatile compounds, reaction of gases
  - composition: sulphates, nitrates, NH_4^+, organic compounds, EC, metals
- **Coarse mode:** Dp > 2.5 μm, „lifespan“ ≈ hours - days
  - origin: resuspension, mechanic decomposition/erosion of material of earth's surface, emission from traffic and building, sea aerosol, …
  - composition: earth crust material (particles of soil, weathered rocks and minerals), bioaerosol, products of mechanic operation (milling, quarries, …) and traffic (abrasions of tires, cars, pavements, …), desert sand, sea aerosol, …

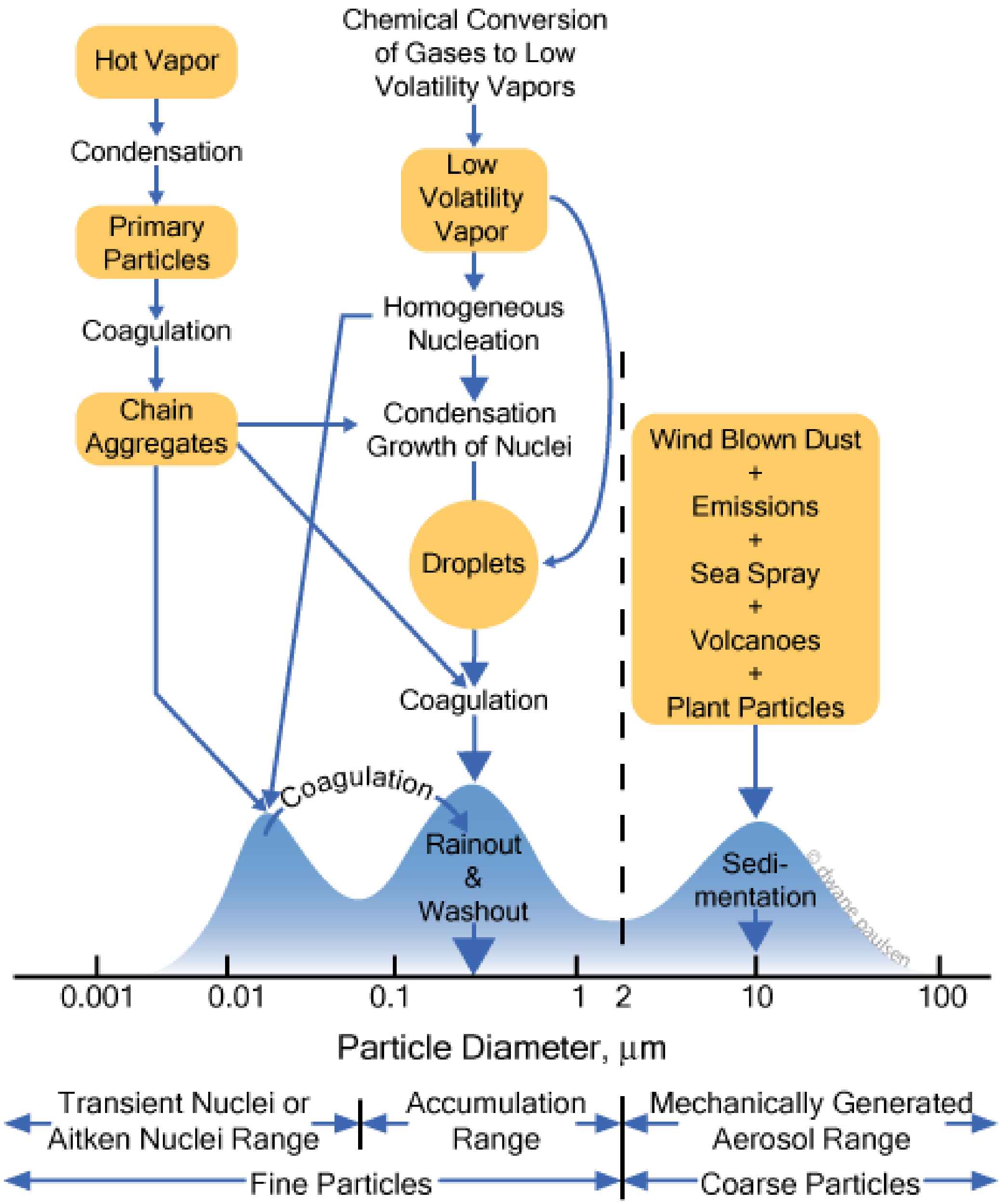
Fine aerosol = Nucleation + Aitken + Accumulation modes

4 ⇨ 3 - modal particle size distribution:

Σ Aitken + nucleation mode

nucleaction mode

3-modal distribution



Particle size: dependence of particle Ø on measurement method

- wide range (5 orders): 1 nm – 100 µm
- no universal method for all size range
- different measurement principles ⇒ different sizes pro the same particle

Diameter	**Dependence on:**	**Instrumentation**
aerodynamic	size, shape, density	APS, impactor
mobility	size, shape	SMPS, FMPS, EEPS
optical	size, shape, refractive index	OPC
geometric	size	electron microscopy
…		

APS, SMPS, OPC: **size + number concentration simultaneously**

⇒ **number size distribution**

Mobility diameter (D_{EM}):

SMPS Spectrometer = **S**canning **M**obility **P**article **S**izer

SMPS = impactor + neutralizer + DMA + CPC

1) **Impactor:** removal of particles $D_p > 1$ µm

2) **Neutralizer:** redistribution of electric charge of particles according to Boltzmann (^{85}Kr, ^{210}Po, ^{241}Am)

$$Z = \frac{n\,e\,C_c}{3\pi\,\mu\,D_p}$$

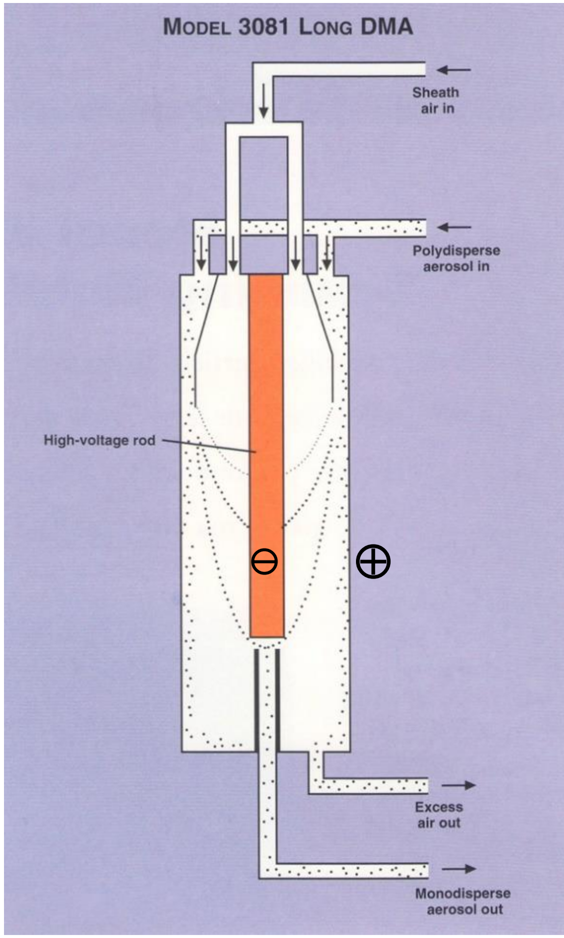
3) **DMA – Differential Mobility Analyser**

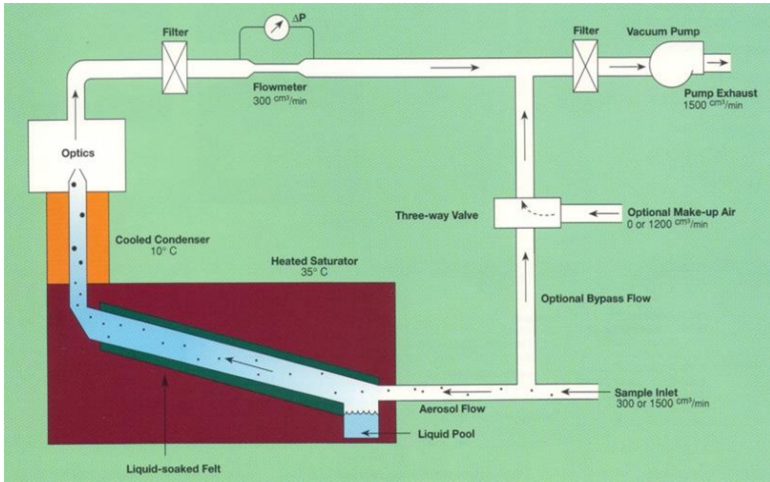
- classification of particles according to electric mobility (Z) into narrow size intervals depending on voltage difference between inner/outer electrodes → monodisperse aerosol at DMA output

- **$D_{EM} = f$ (shape, geometric size)**

4) **CPC – Condensation Particle Counter**

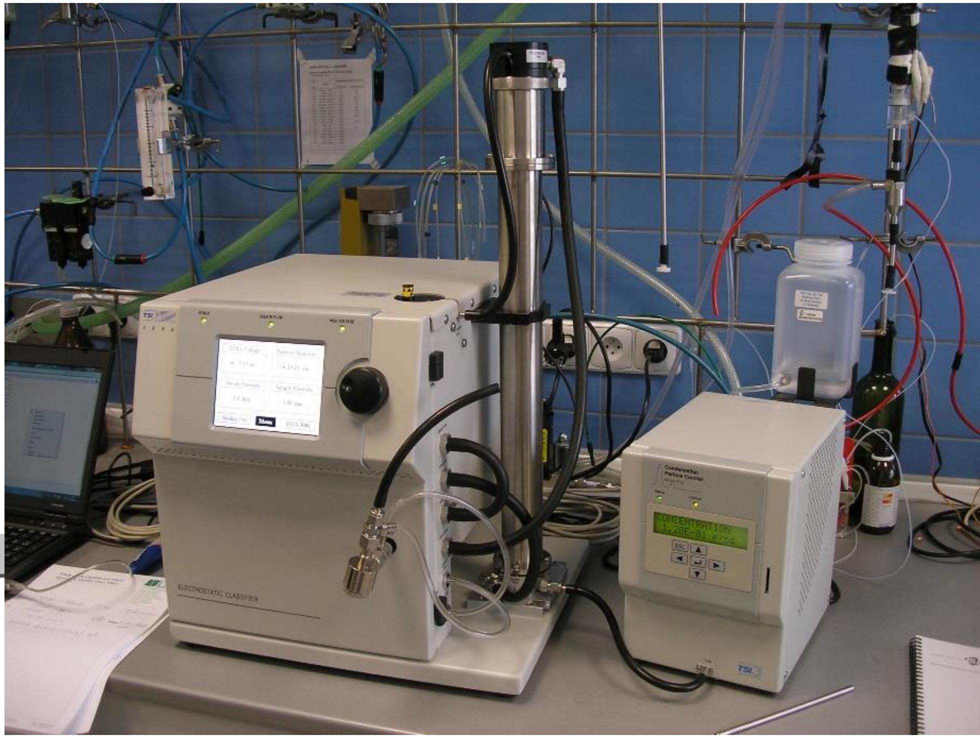
- detection of classified monodisperse particles
- saturation of air by vapor of n-BuOH (H_2O, isoPrOH) at increased T, condensation on particles after cooling, increase of particle size above 1 µm, optical detection (scattering of laser light)

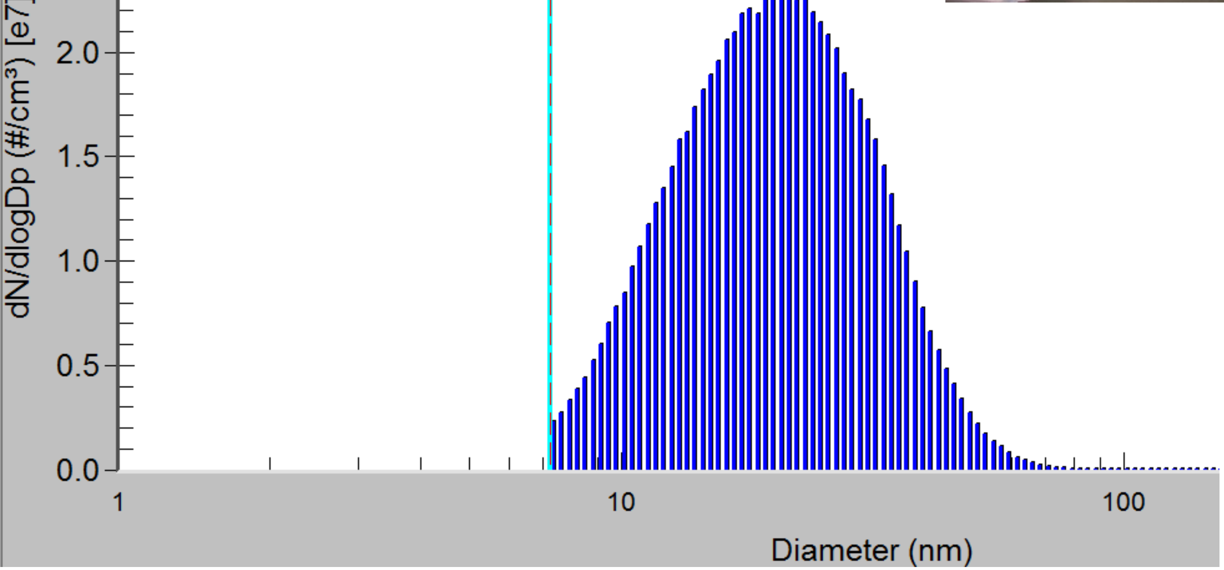




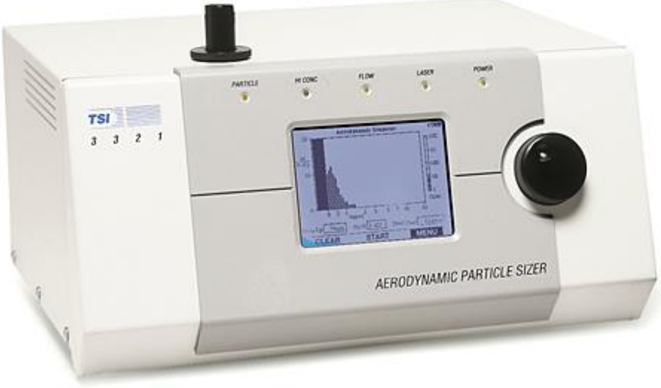
SMPS = Scanning Mobility Particle Sizer

- size range: 2.5 - 1000 nm
- concentration range: max. 2×10^8 P/cm^3
- resolution: max 167 size channels
- CPC: n-BuOH, isopropanol, H_2O
- electrometer: CPC alternative
  lower sensitivity





Aerodynamic diameter (Da):



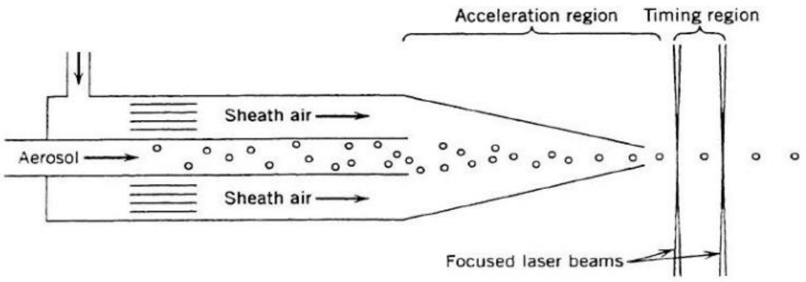
APS Spectrometer = **A**erodynamic **P**article **S**izer

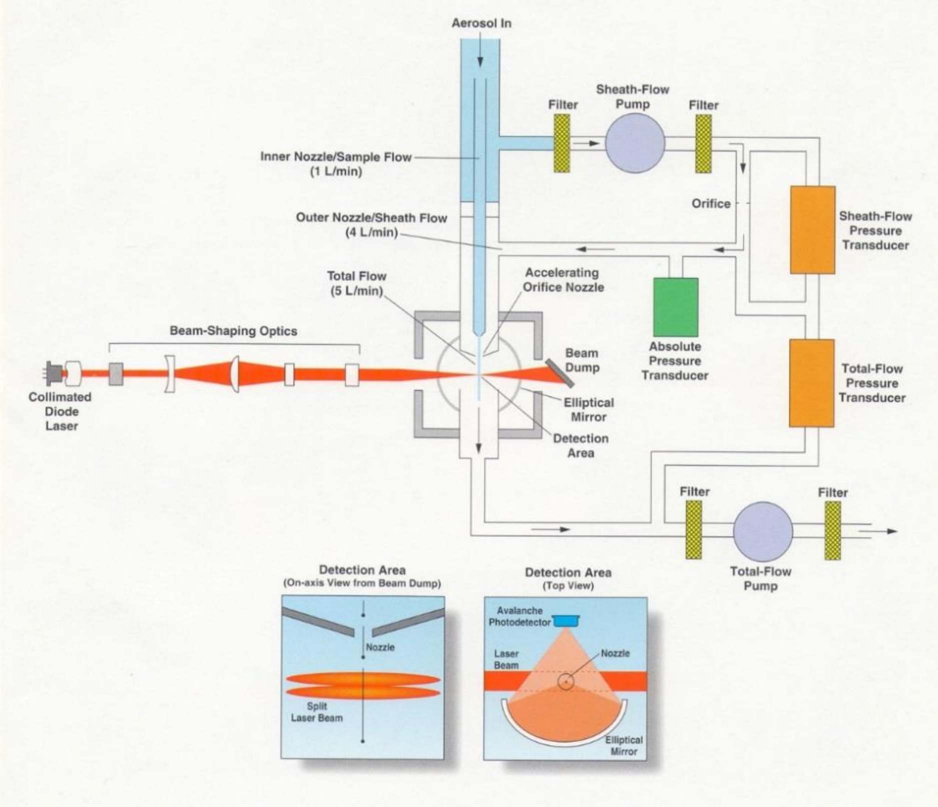
- measurement of flight time between 2 laser beams
- **$D_a = f$ (density, shape, size)**

→ $1\ g/cm^3$ → sphere

- study of deposition (lungs) and behaviour of particles in air (sedimentation)

- „**single-particle**“ detection
- size range D_a: 0.5 - 20 µm
- concentration range: max. $1 \times 10^3\ P/cm^3$
- resolution: 52 size channels

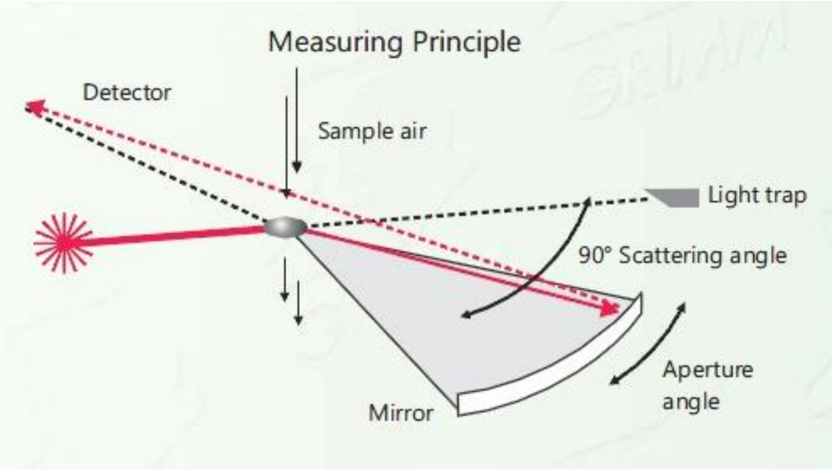




Optical diameter:

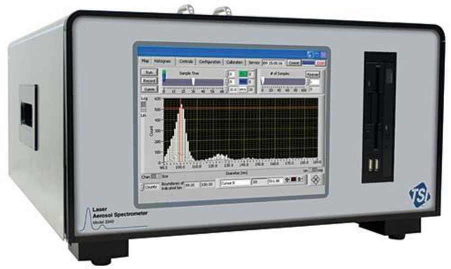
OPC = Optical Particle Counter

- light scattering on particle
- „**single particle**“ detection
- **D = *f* (size, shape, refractive index)**
- scatter angle → **particle size**
- intensity of scatter puls → **concentration**
- source: laser, white light (Palas)
- size range: 0.1 - 40 µm
- concentration range: max. 1×10^5 P/cm^3
- resolution: 52 size channels



Refractive index: $$m_P = \frac{v_{air}}{v_P} = x - iy$$

x – scatter, y - absorption



Number concentration of aerosols: P/cm^3

- measurement method determines:
  - measured size range
  - concentration range
  - particle diameter

Method	**Size range:**	**Concentration range** (P/cm^3)	Particle diameter
SMPS	1 – 1000 nm	$1 - 2 \times 10^8$	mobility
APS	0.5 – 20 μm	$1 - 1 \times 10^3$	aerodynamic
OPC	0.1- 40 μm	$1 - 1 \times 10^5$	optical

Mass concentration of aerosols: ng/m³, µg/m³

- measured mostly in defined size fraction (TSP, PM10, PM2.5, PM1)

1) discontinuous: sampling on filters (foils in impactors)

- integral method
- weighing filters or foils
- difference in mass of filters/foils before and after exposition
  - filters ⇒ 1-2 days equilibration in special weighing room (50%, 20°C)
  - static charge on filter/PM ⇒ charge removal
  - weighing filters on special microbalance (± 1 µg)
- reference method (nitrocellulose filters)
- low time resolution (~ 2 – 24 h)

2) continuous: on-line instrumentation

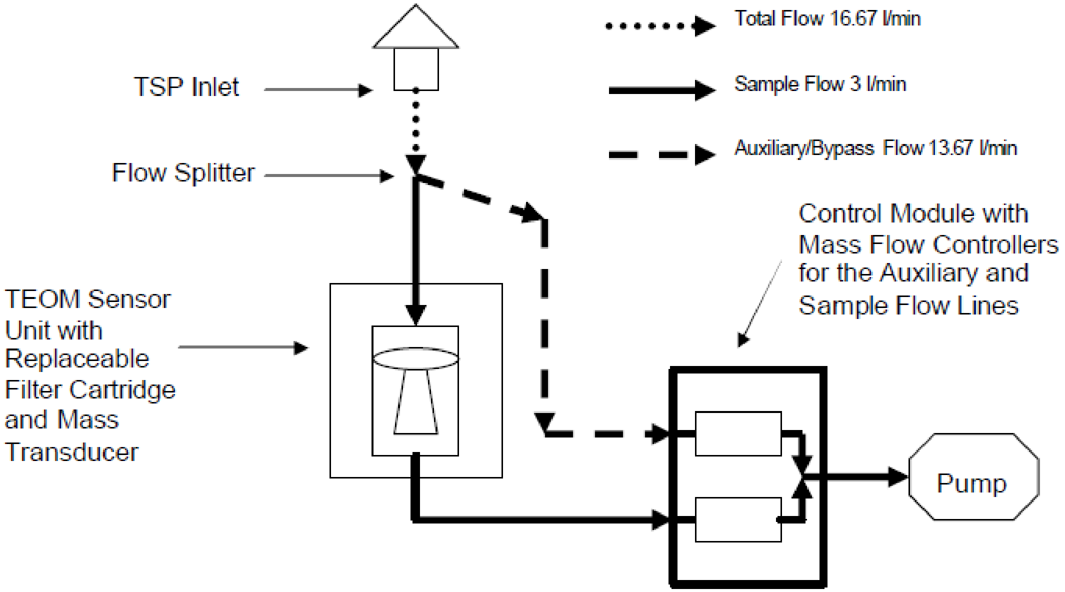
- high time resolution (1-min and less)
- oscilation microbalance (TEOM)
- radiometric method

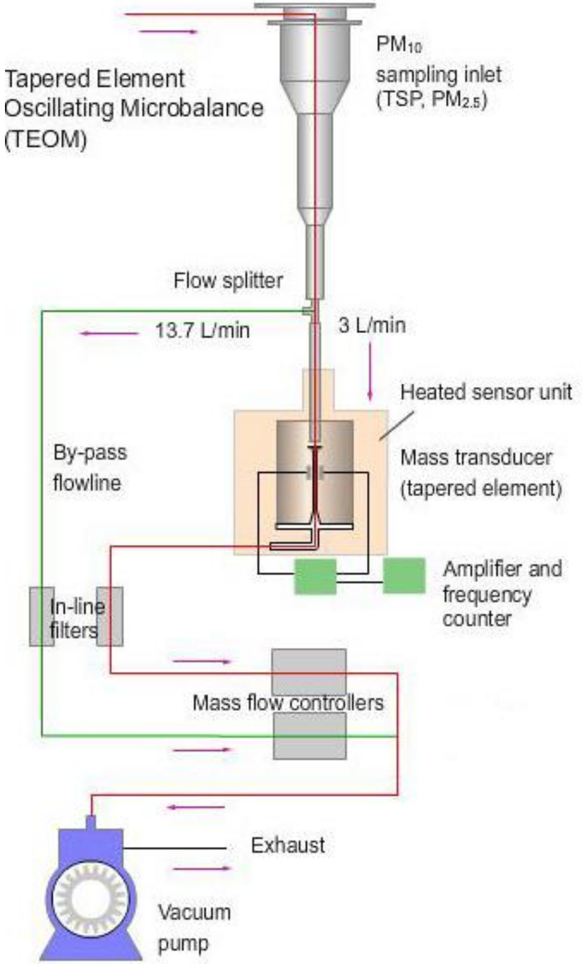
} **only 1 size fraction**

- optical spectrometer → **parallel 3 size fraction** (PM10, PM2.5, PM1)

TEOM = Tapered Element Oscillating Microbalance

- continuous on-line measurement of mass concentration
- collection of PM on filter placed on oscillating tube ⇒ oscillation frequences decreases with increasing mass of filter
- selection of analysed PM fraction according to inlet separator
- mass resolution: 0.1 µg/m^3 (5 min)



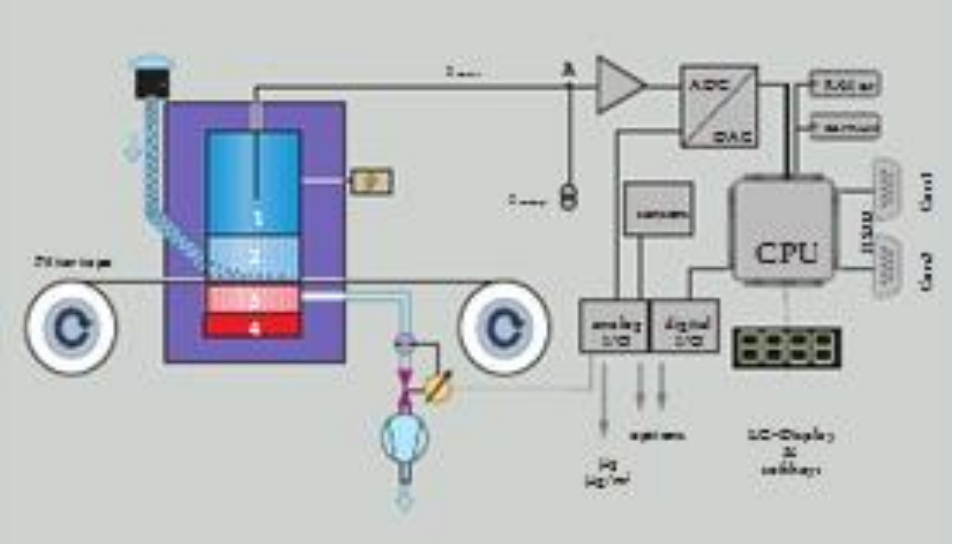


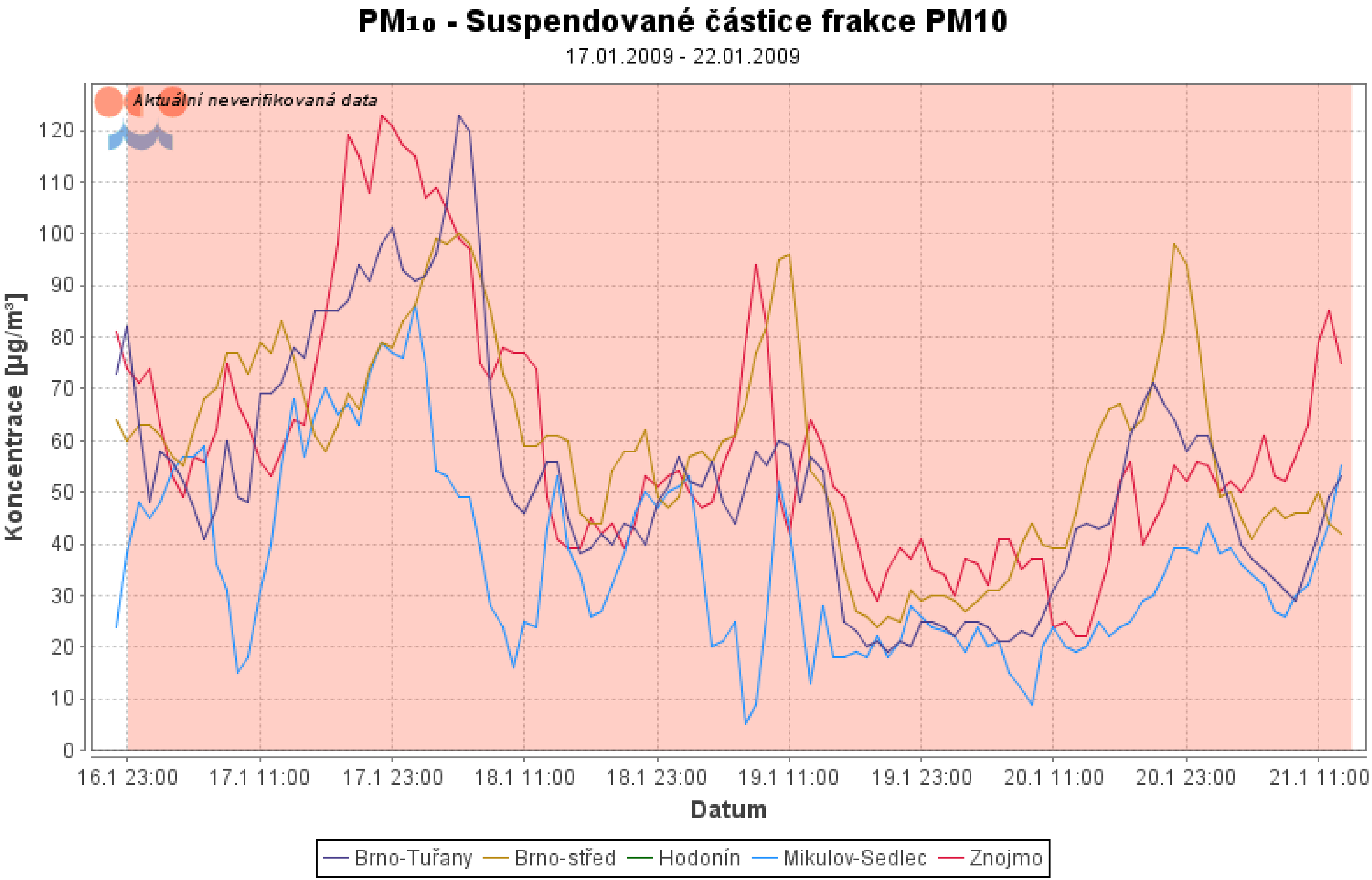
Radiometric method of mass concentration measurement:

„**beta attenuation**“

- semi-continuous measurement of mass concentration (time resolution 1 h)
- collection of aerosols on filters ⇒ measurement of β-radiation (^{14}C, ^{85}Kr) attenuation with Geiger-Müller counter
- selection of analysed PM fraction according to inlet separator
- mass resolution: 1 μg/m^3 (24 h)

  5 μg/m^3 (1 h)
- measurement of PM10 and PM2.5 in CHMI



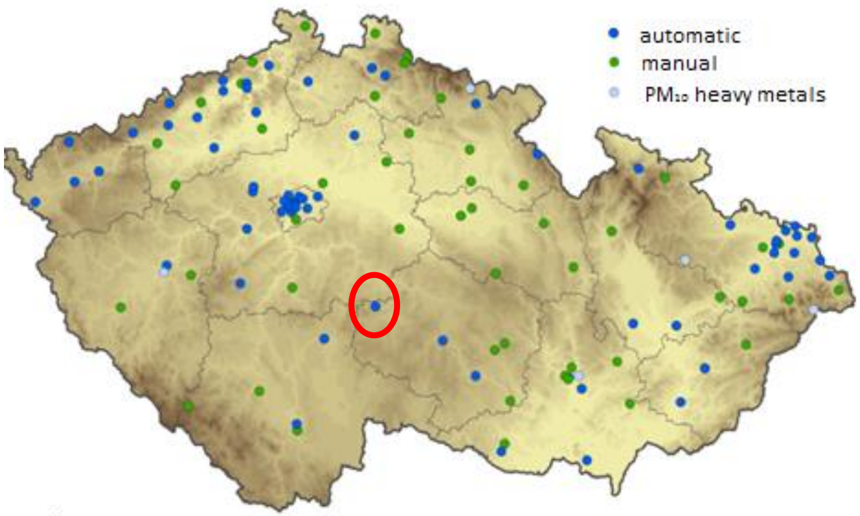


- Radiometric method („beta attenuation“)
- Daily limit PM10: 50 µg/m^3

AIM – automatic immision monitoring network (CHMI):

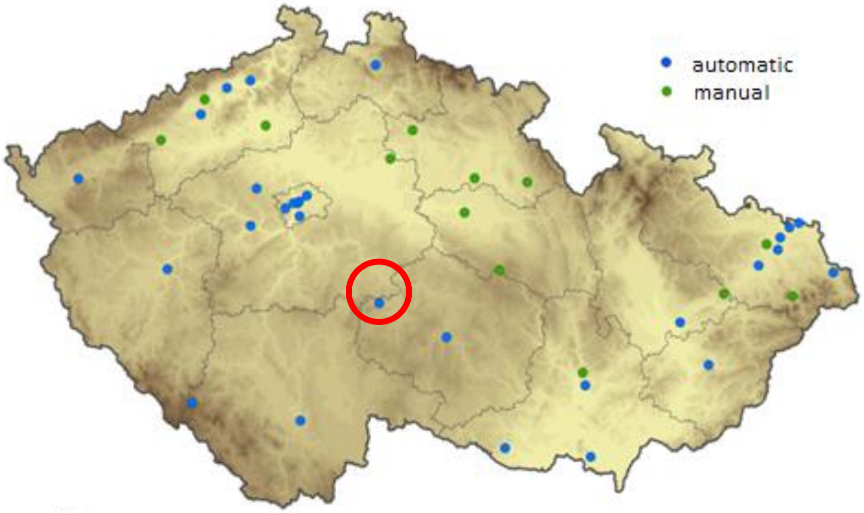
- measurement PM10 - from 1996
- measurement PM2.5 – from 2005

PM10



a)

PM2.5



b)

Station classification according to type: traffic, urban, rural, background

Váňa M., conference CAS 2013, Nový Smokovec

Aerosol toxicity:

Deposition of PM in lungs and subsequent release of bound harmful compounds

- particle size: Dp $<$ 10 μm ⇒ enter into respiratory tract
- particle shape: fibrous × spherical

  fibrous particles (asbestos) – cancerogenic effects
- particle components:
  - several compounds bound to PM toxic for body/organs ⇒ metals, organic compounds
  - solubility / bioavailability of components

a) organic compounds:

- PAHs: BaP – carcinogenic/mutagenic (WHO), estimation of health risk (cPAHs)

  cPAHs = 7 carcinogenic PAHs: benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene,
  benzo[*k*]fluoranthene, benzo[*a*]pyrene,
  dibenz[*a,h*]anthracene, indeno[1,2,3-*cd*]pyrene
- nitroPAHs
- PCBs
- PCDD/PCDFs, …

b) metals: Pb, Ni, Cr^{VI}, As, Cd, Hg (Be, Tl, Ba, Pt, …)

Analysis of chemical composition:

1. Aerosol sampling: continuous, semi-continuous, discontinuous
2. Sample treatment: extraction, derivatization, preconcentration
3. Sample analysis: organic compounds - GC, LC, IC, MALDI, …, AMS
   metals – PIXE, RTG, NAA, ICP, AAS, …
   ions - IC, CZE, FIA, AMS, …

❑ **continuous methods:**

- time resolution: seconds - min
- in-situ
- Aerosol Mass Spectrometer)

❑ **semi-continuous methods:**

- time resolution: min - hod
- continuous sampling
- on-line analysis (in-situ)
- limited mostly to water-soluble compounds (ions, DCA, NH_4^+, metals)

❑ **discontinuous methods:**

- time resolution: 2-24 hod
- aerosol collection on suitable medium (filters, foils)
- off-line analysis in laboratory

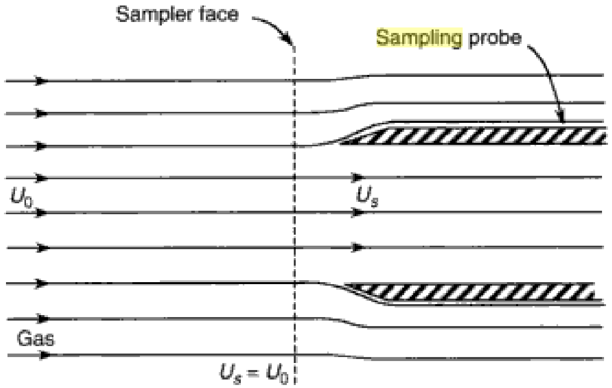
Aerosol sampling:

❑ **obtaining representative sample of aerosol**

- no change in chemical composition (elimination losses and deposition of PM)
- no change in particle distribution

❑ **Isokinetic sampling**:

- $U_{\text{inlet}} = U_{\text{streamline}}$
- same velocity of aerosol sample and air



❑ **Superisokinetic sampling**:

$U_{\text{inlet}} > U_{\text{streamline}}$

❑ **Subisokinetic sampling**:

$U_{\text{inlet}} < U_{\text{streamline}}$

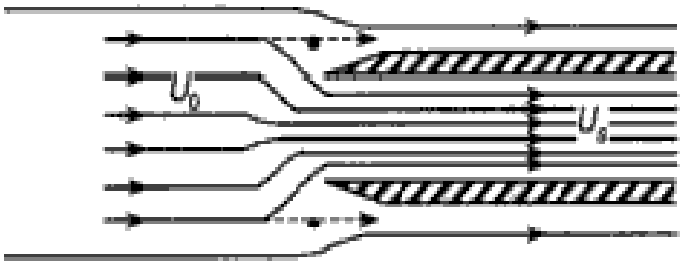
losses:

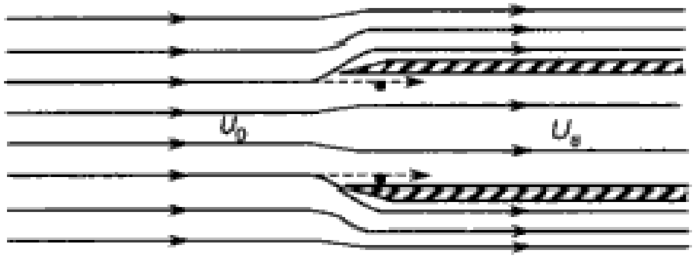
deposition,

turbulence,

coagulation,

…….



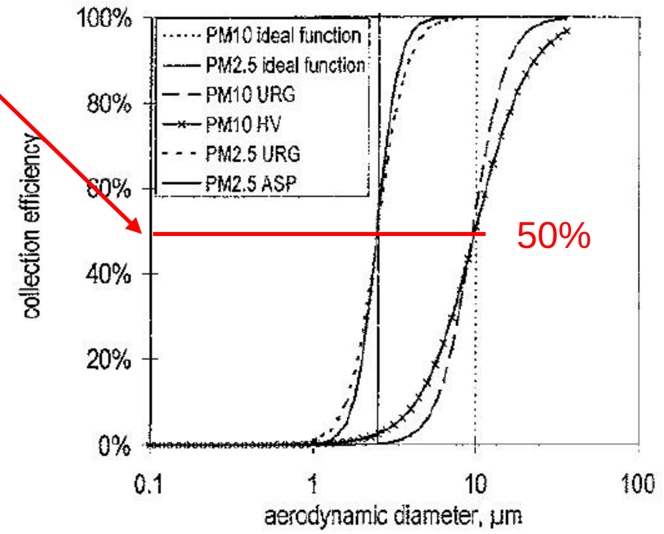


Size selective inlets:

- selection of sampled particle fraction
- removing of particles with $D_p > D_{p50}$ from sampled air stream
- **PMX** $\Rightarrow$ **X** = „cut-point“ diameter (D_{p50}) $\Rightarrow$ PM10, PM2.5, PM1, …)
- **X (D_{p50})** determines size fraction sampled with 50% efficiency (PMX)

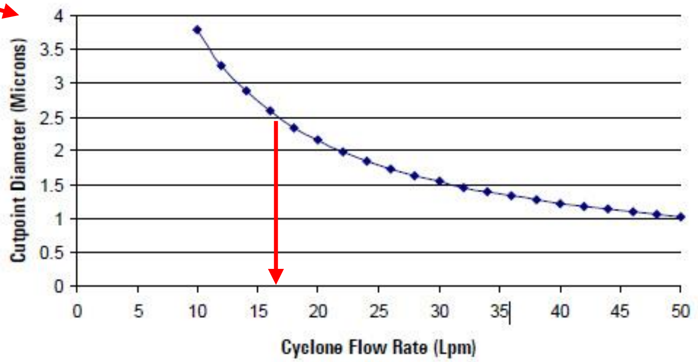
  $D_p > X$ $\Rightarrow$ particle removal (collection in inlet)

  $D_p < X$ $\Rightarrow$ particle penetration through inlet into sampler



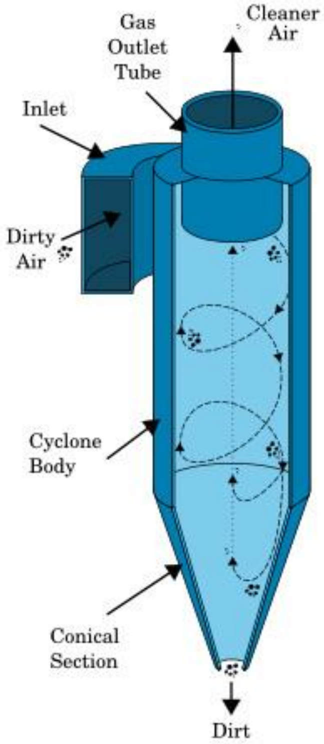
- PMx = f (sample flow rate) from sampled air stream
- principle inertial classification:
  - ☐ impactor
  - ☐ cyclone

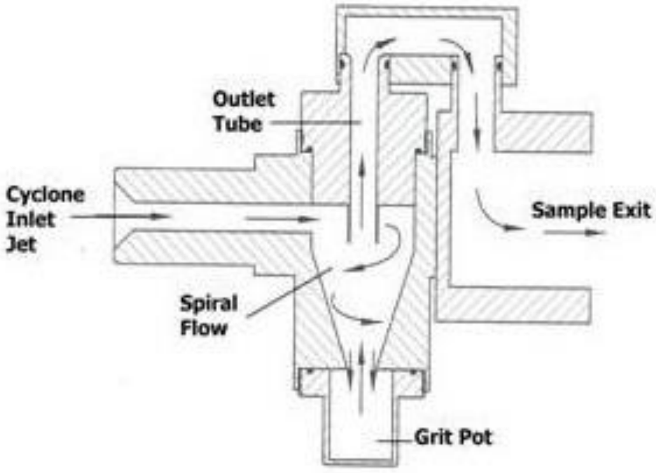
  designed for specific cut-point diameter and sample flow rate



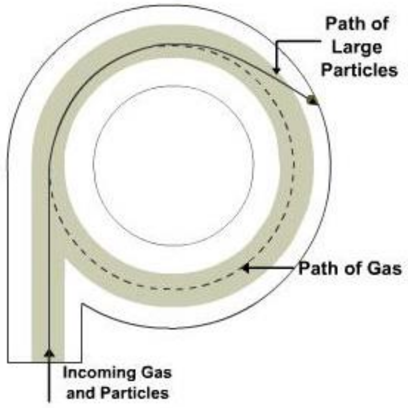
Size selective inlet: 1. cyclone

- particle separation based on principle of inertia
- larger particles with a higher inertia cannot follow the path and impact on the cyclone wall while gases and lighter particles have less inertia and exit cyclone through outlet tube
- no reliable theory for cut-off point calculation
- cut-off are not as sharp as in impactors
- long-term operation without maintenance
- collection of much larger quantity of particles than impactor





BGI Sharp Cut Cyclone
(SCC)



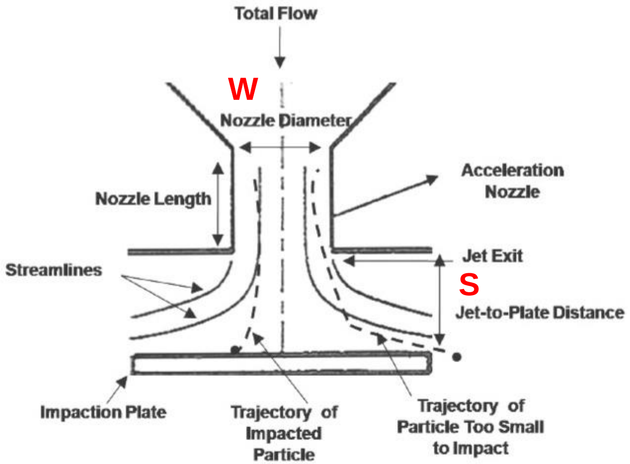
Size selective inlet: 2. impactor

- particle separation based on principle of impaction of PM on impaction plate in front of jet nozzle
- calculation of collection efficiency → **Stk** (Stokes number)
- cut-off (d_{p50}) = $\sqrt{Stk}$

Stk_{50} = 0.24 (circular nozzle)

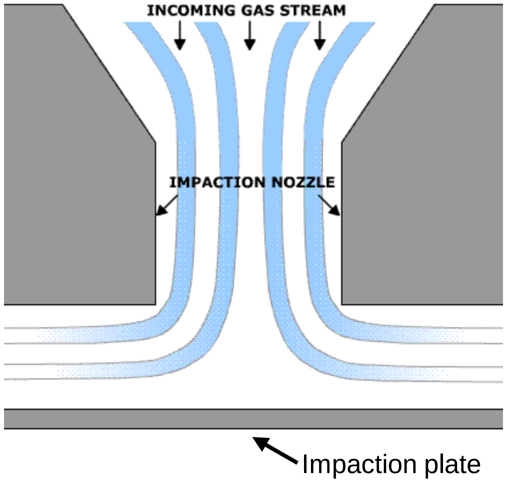
= 0.59 (rectangular nozzle)

- particles with Stk > Stk_{50} are collected

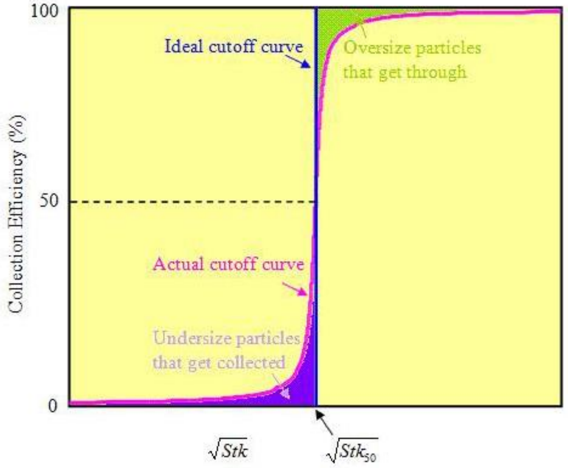


$$Stk = \frac{\rho_p d_p^2 U C_c}{9\eta W} \approx \frac{S}{W}$$

S – stopping distance
Cc – slip correction factor
W – nozzle diameter (width)
U – velocity



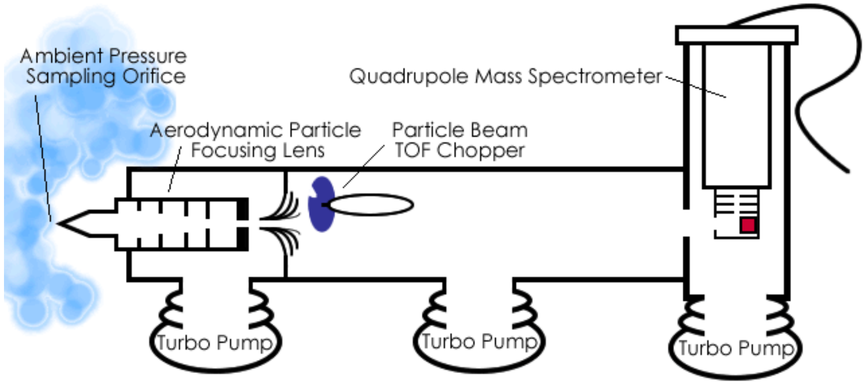
actual and ideal impactor cutoff curves

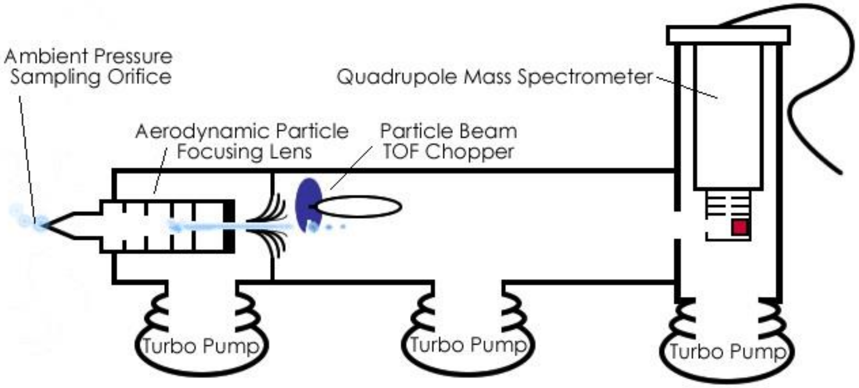


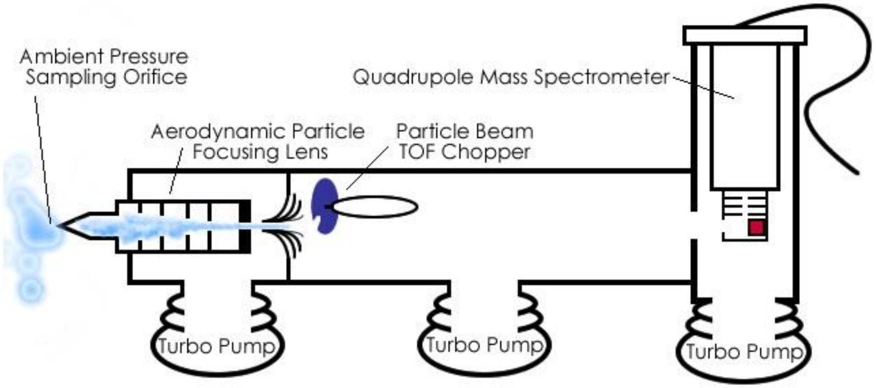
inlet PM2.5 + PM10

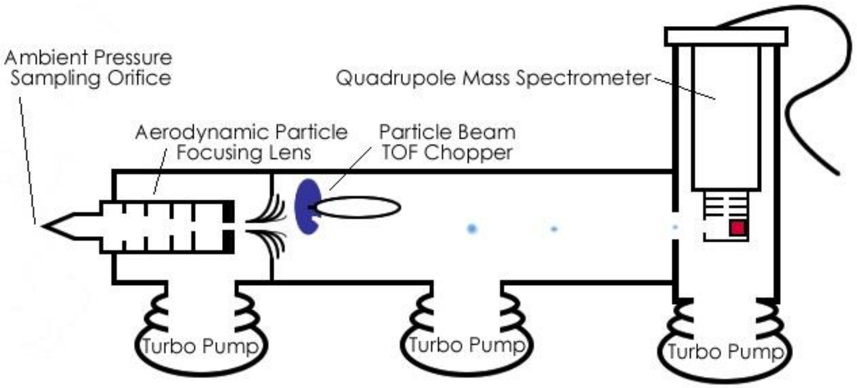
Continuous analysis of chemical composition of aerosols:

- **Aerosol Mass Spectrometer**
- **continuous sampling + on-line MS analysis of particles in real time**





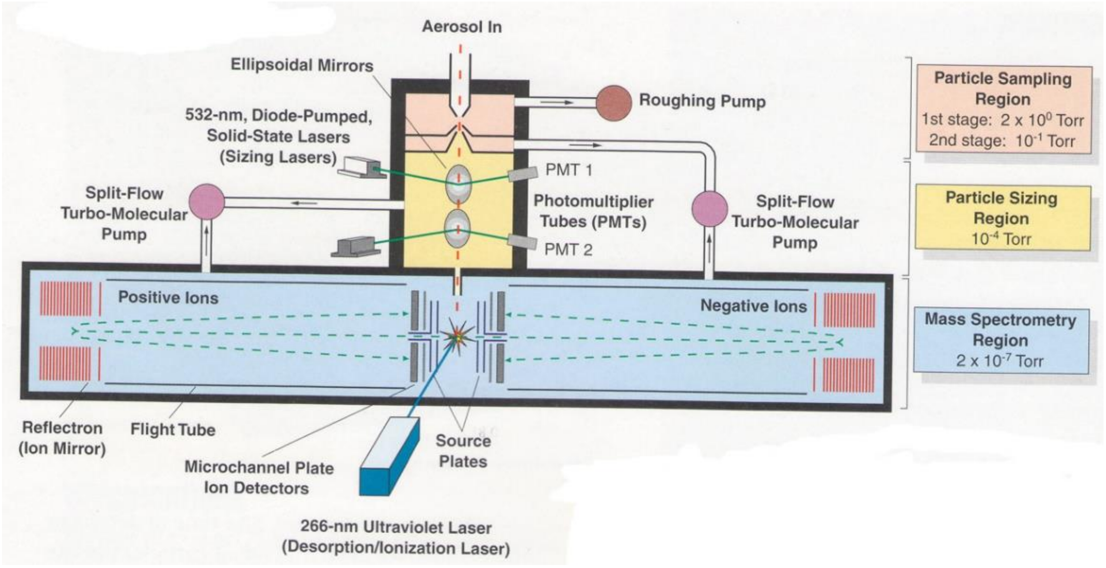


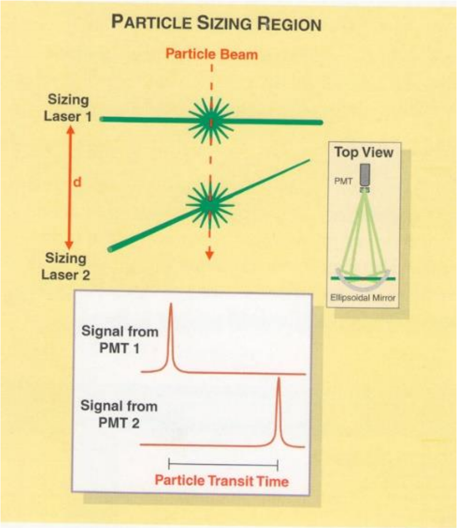


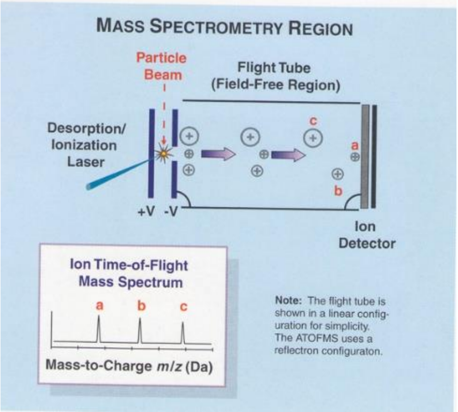
Aerosol Time of Flight Mass Spectrometer:

❑ **continuous sampling + on-line analysis in real time**

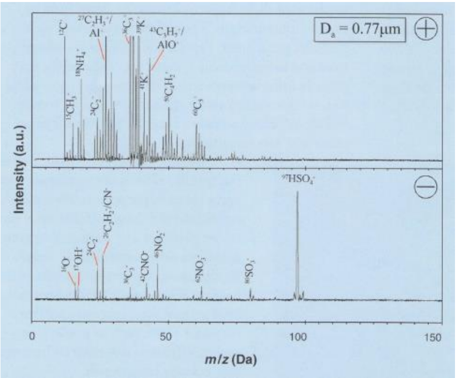
- size and chemical composition of individual particles in real time
- size range: 30 – 1000 (3000) nm
- qualitative analysis:
  - sufficient for inorganic ions, metals
  - insufficient for identification of organic compounds
- quantitative analysis: questionable
- problematic field application (high weight)





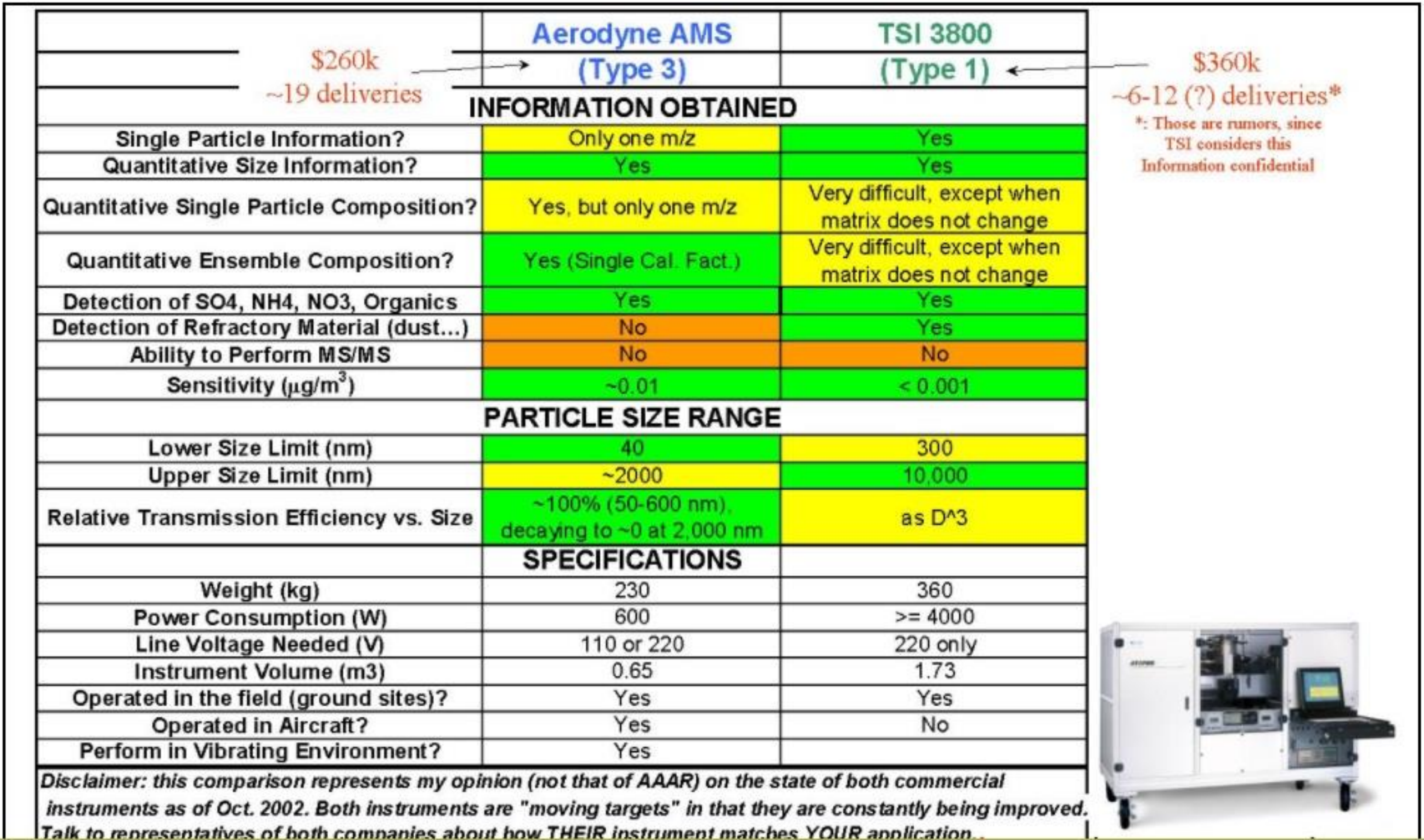


Note: The flight tube is shown in a linear configuration for simplicity. The ATOFMS uses a reflectron configuraton.



Commercial AMSs comparison:

- **Aerodyne AMS** (Aerodyne)
- ATOFMS = **Aerosol Time of Flight Mass Spectrometer** (TSI, model 3800)



$260k
~19 deliveries

$360k
~6-12 (?) deliveries*
*: Those are rumors, since TSI considers this Information confidential

	Aerodyne AMS (Type 3)	TSI 3800 (Type 1)
	INFORMATION OBTAINED	
Single Particle Information?	Only one m/z	Yes
Quantitative Size Information?	Yes	Yes
Quantitative Single Particle Composition?	Yes, but only one m/z	Very difficult, except when matrix does not change
Quantitative Ensemble Composition?	Yes (Single Cal. Fact.)	Very difficult, except when matrix does not change
Detection of SO4, NH4, NO3, Organics	Yes	Yes
Detection of Refractory Material (dust...)	No	Yes
Ability to Perform MS/MS	No	No
Sensitivity (µg/m^3)	~0.01	< 0.001
	PARTICLE SIZE RANGE	
Lower Size Limit (nm)	40	300
Upper Size Limit (nm)	~2000	10,000
Relative Transmission Efficiency vs. Size	~100% (50-600 nm), decaying to ~0 at 2,000 nm	as D^3
	SPECIFICATIONS	
Weight (kg)	230	360
Power Consumption (W)	600	>= 4000
Line Voltage Needed (V)	110 or 220	220 only
Instrument Volume (m3)	0.65	1.73
Operated in the field (ground sites)?	Yes	Yes
Operated in Aircraft?	Yes	No
Perform in Vibrating Environment?	Yes	

Disclaimer: this comparison represents my opinion (not that of AAAR) on the state of both commercial instruments as of Oct. 2002. Both instruments are "moving targets" in that they are constantly being improved. Talk to representatives of both companies about how THEIR instrument matches YOUR application..

Black – Brown – Elemental – Soot – Organic – Inorganic Carbon

- **Soot**: A black, blackish or brown substance formed by combustion, present in atmosphere as fine particles, or adhering to sides of chimney or pipe conveying smoke
- **Soot carbon** (**Csoot**): carbon particles with morphological and chemical properties typical of soot particles from combustion: aggregates of spherules made of graphene layers, consisting almost purely of carbon, with minor amounts of bound heteroelements (H, O)
- **Black carbon** (**BC**) originates from combustion processes (coal, wood, traffic), responsible for absorption of visible sunlight and warms atmosphere. BC is generally used when optical methods are applied for its determination
- **Elemental carbon** (**EC**): fraction of carbon oxidized in combustion analysis above a certain temperature threshold, and only in presence of oxygen-containing atmosphere
- "BC" and "EC" are used as synonyms for Csoot

  BC × EC: different measurement methods
- **Brown carbon** (**BrC**; light-absorbing organic carbon): class of organic carbon, light brownish color, absorbs strongly in the ultraviolet wavelengths and less significantly in VIS. Includes tar materials from smoldering fires or coal combustion or biomass burning
- **Organic carbon** (**OC**): carbon in organic compounds (primary emissions from sources)
- **Secondary organic carbon** (**SOC**): C in organic compounds formed secondary in atmosphere
- **Total carbon** (**TC**): TC = OC + EC
- **Inorganic carbon** (**IC**): carbon in inorganic carbonates

Aethalometer

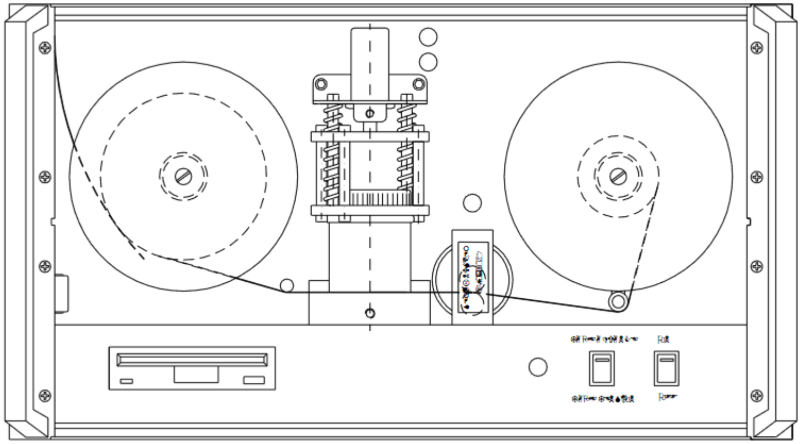
- optical method of continuous detection of BC and BrC concentration

- **BC** = Black Carbon , **BrC** = Brown Carbon

- principle:
  - ○ continuous collection PM on qurtz filter
  - ○ attenuation of IR (880 nm) across filter is proportional to **BC** concentration
  - ○ attenuation of VIS (520 nm) is proportional to **BrC** concentration
  - ○ attenuation of UV (370 nm) is proportional to aromatic compounds

Model AE33:

- attenuation of transmitted light at wavelengths of **370**, 470, **520**, 590, 660, **880** and 950 nm
- detection limit (1 hour): <0.005 μg/m^3
- range: <0.01 to >100 μg/m^3 BC
- resolution: 0.001 μg/m^3

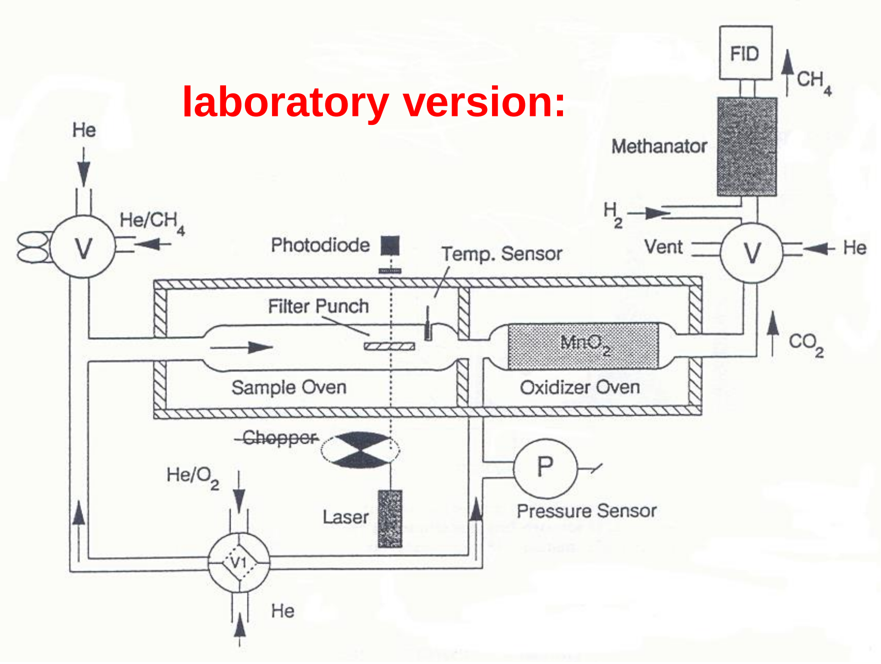


f. Magee Scientific

EC-OC analyser: thermal-optical transmission method (TOT)

f. SunSet Laboratory

laboratory version:



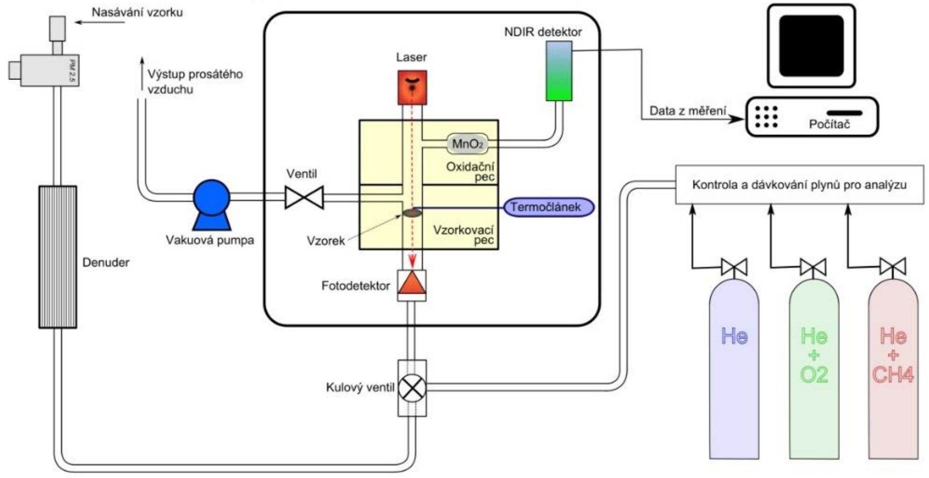
- direct analysis without derivatization
- collection PM on quartz filters
- laboratory version: off-line filter treatment

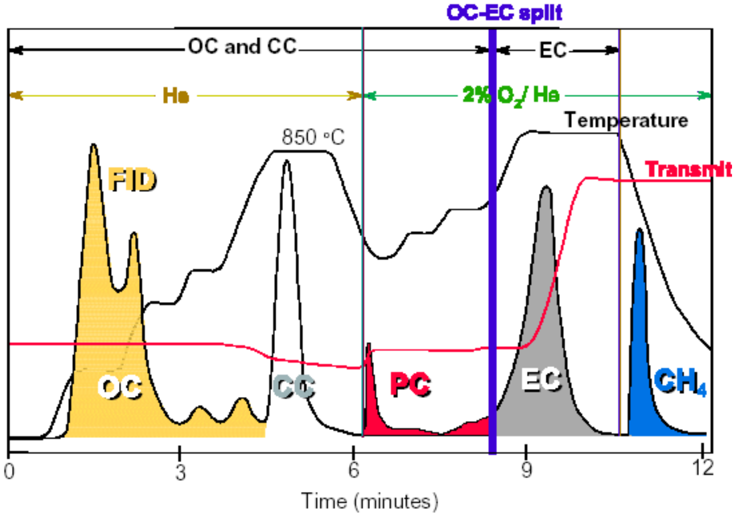
  EC-OC → CO_2 → CH_4 → **FID**

- field version: on-line filter treatment

  EC-OC → CO_2 → **IR**

„field“ version:





CC – carbonate

PC – pyrolytic carbon

Semi-continuous analysis of chemical composition:

- ☐ **continuous collection of PM into liquid and subsequent on-line analysis** (FIA, LC, IC, …)

- ☐ **advantages**:
  - collection of PM from air directly into liquid (H_2O)
  - elimination of errors resulting from manual treatment of filters
  - quick detection (FIA – CL / FL) → short time resolutiom (s – min)

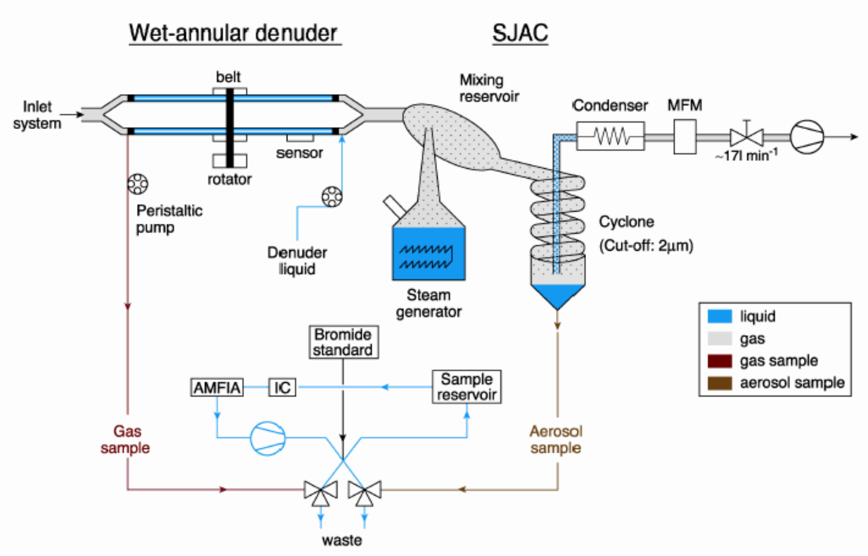
- ☐ **disadvantages**:
  - size of small particles has to be first increased to be collected
  - limited only to water–soluble aerosol components: ions, NH_4^+, metals, several organic compounds (DCA, saccharides)
  - **interference**: positive ⇒ collection gaseous pollutants into water (HNO_3, NO_2, NH_3, PAHs, …)
    → eliminated by **diffusion denuder**
    negative ⇒ losses of volatile compounds by evaporation in oversaturated environment (PAHs, NH_4NO_3)
  - on-line detection requires fast and sensitive instrumentation

- ☐ continuous collectors → 2 different principles:
  - condensation of supersaturated water steam on particles
  - Venturi scrubber

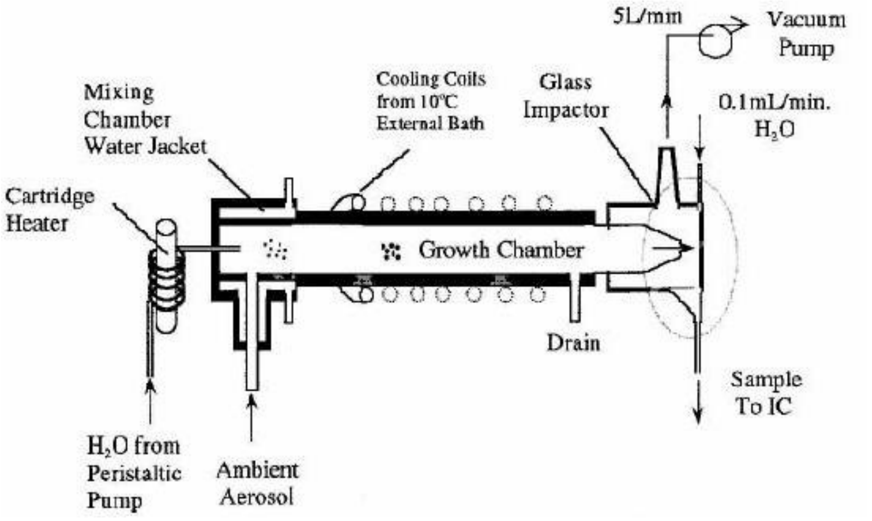
Continuous collectors: 1) condensation type

- condensation of supersaturated water steam on aerosol particles
- turbulent mixing of analysed air with water steam (100° C) → adiabatic cooling → water steam supersaturation → **steam condensation** → **particle size increase** → collection of enlarged particles into H_20
- 100 % CE for Dp > 10 nm
- disadvantages: SVOC losses, NO_2 interference

SJAC: Steam-Jet Aerosol Collector

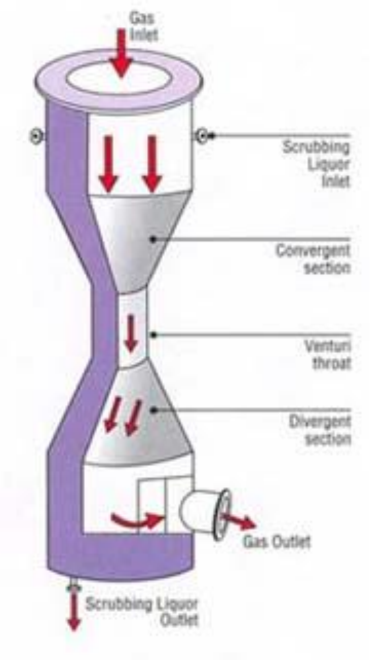


PILS: Particle-Into-Liquid Sampler

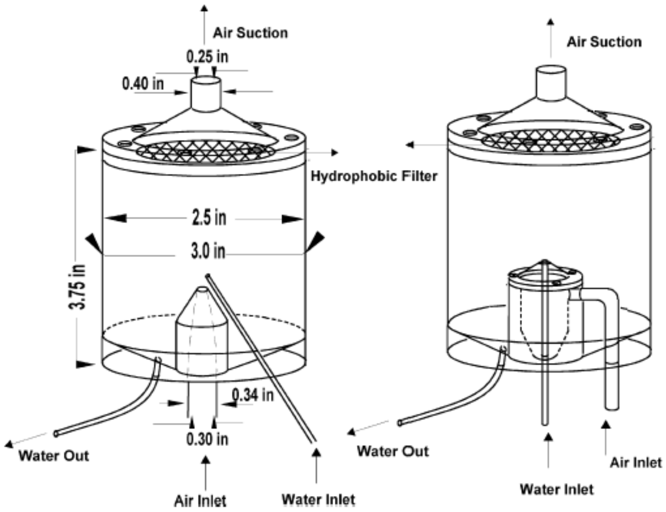


Continuous collector: 2) Venturi scrubber

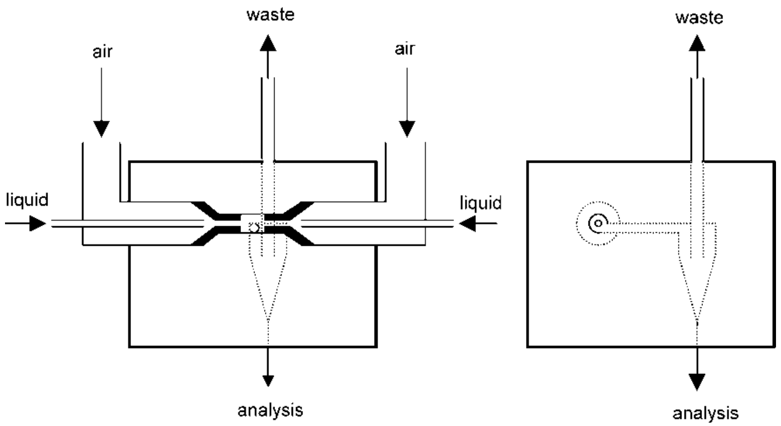
- Venturi scrubber: efficient way for removing of particles from air stream
- turbulent mixing of air and absorption liquid in Venturi throat, increased velocity of air, atomisation of water, mutual collisions of particles and water droplets, particles are collected into water droplets
- 100 % CE for Dp > 0.3 µm



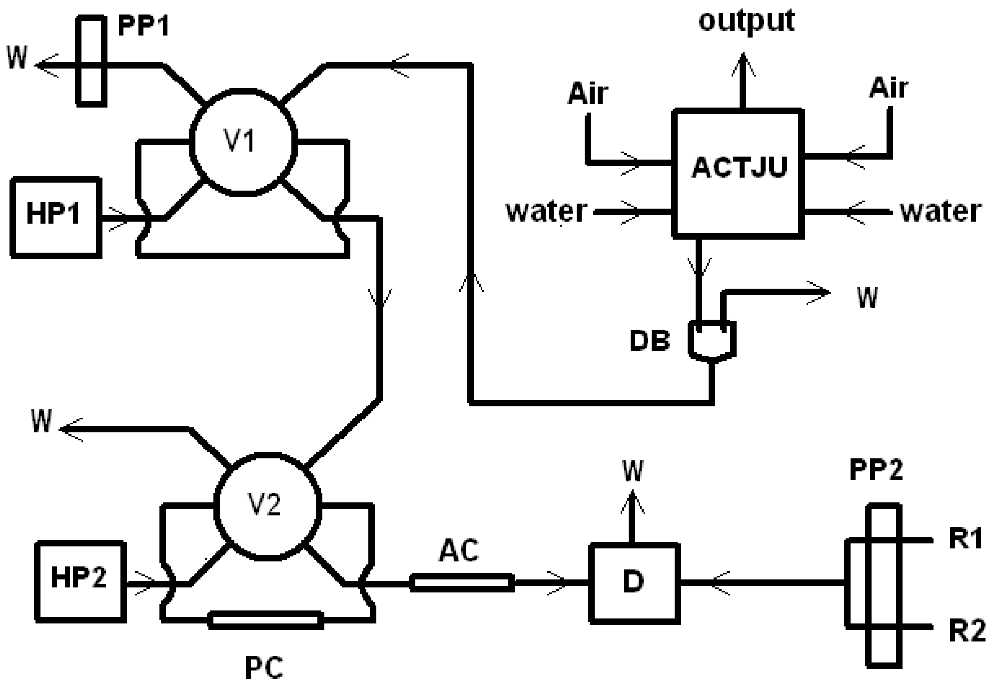
VPC: Venturi Particle Collector

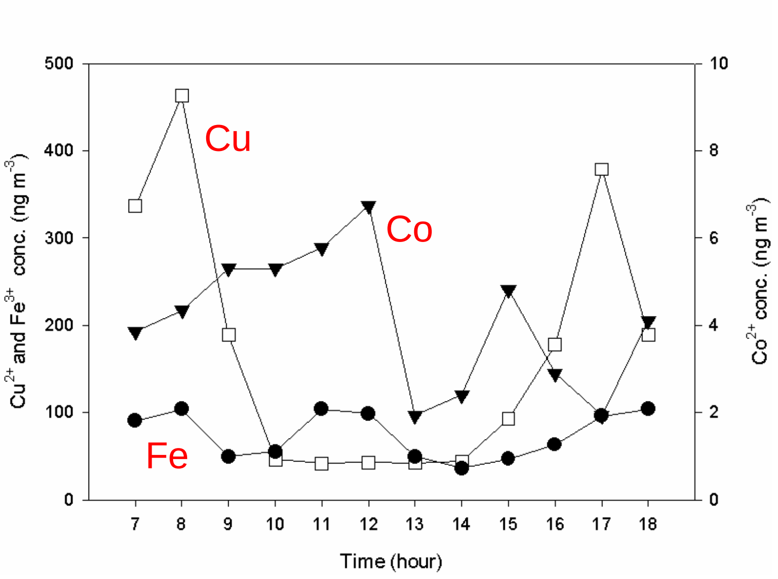


ACTJU: Aerosol Counterflow Two-Jets Unit



Semi-continuous determination of metals in PM:





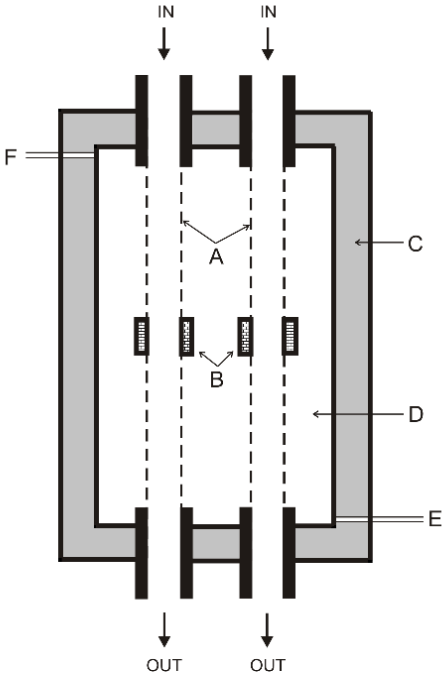
PP - peristaltic pump, D - detector, W - waste,
V - injection valve, HP - high-pressure pump,
DB - debubbler, PC - preconcentration column,
AC - analytical column, R1, R2 - reagents

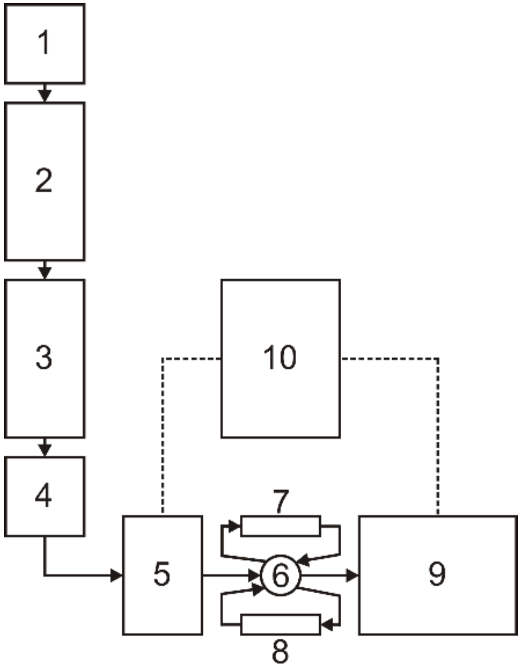
Absorption liquid – H_2O

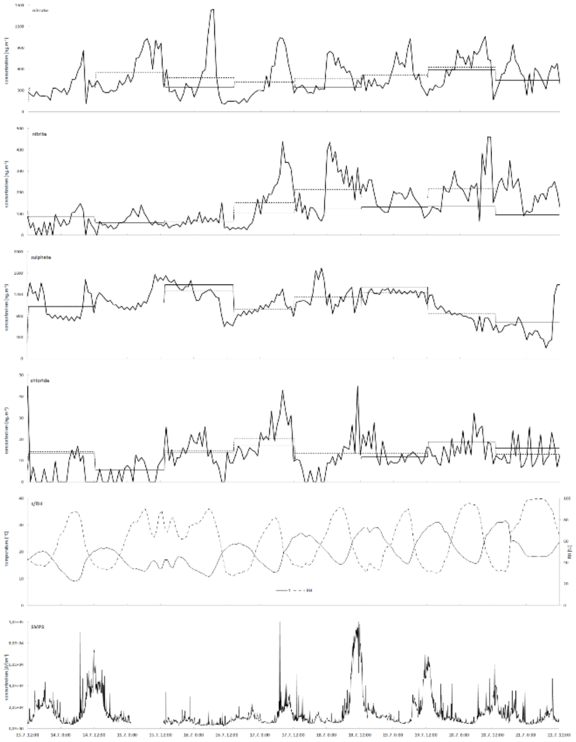
CL detection: luminol + H_2O_2

Time resolution - 30 min

Semi-continuous determination of ions and DCAs in PM:







Absorption liquid – H_2O
Time resolution - 60 min

1 – cyclone inlet, 2 – annular diffusion denuder, 3 – Condensation Growth Unit, 4 – ACTJU, 5 – piston pump, 6 – 10-way injection valve, 7 – preconcentration column No. 1, 8 – preconcentration column No. 2, 9 – IC, 10 – computer

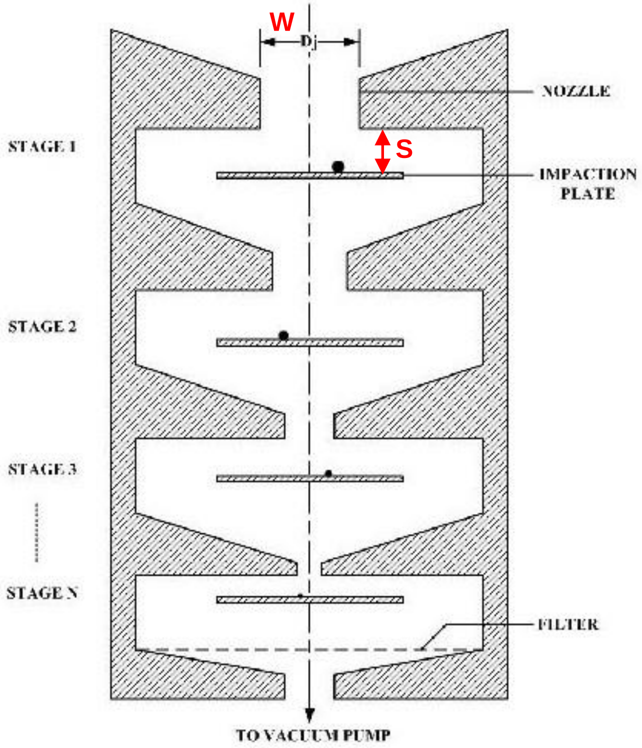
Discontinuous analysis of chemical composition:

- ❑ **sampling aerosols on filters / foils + off-line analysis in laboratory**
- ❑ the most frequent method for determination of chemical composition
- ❑ **sampling medium:**
  - ➢ filters → only 1 size fraction of aerosols (PM1, PM2.5, PM10, TSP)
    → size selective inlets: impactor, cyclone
  - ➢ foils in cascade impactors → several size fraction simultaneously ⇒ size resolved chemical composition
- ❑ advantages:
  - ➢ collection of sufficient amount of sample → analysis of different groups of compounds
- ❑ disadvantages:
  - ➢ off-line analysis of aerosol components in laboratory
  - ➢ long time of sampling
  - ➢ results averaged over time
  - ➢ sampling artefacts (over-/under- estimation of aerosol component concentration):
    1. positive (adsorption of gases, organic vapors or SVOC on collected particles/filter)
    2. negative (losses due to volatility of compounds bound to collected particles (NH_4NO_3, PAHs, …)
    3. change in composition of collected particles (reaction with NO_2 or oxidants (O_3, OH, …)
  - ➢ possible contamination during manual processing or transport
  - ➢ particle size distortion (particle losses in inlet or between plates of cascade impactor)

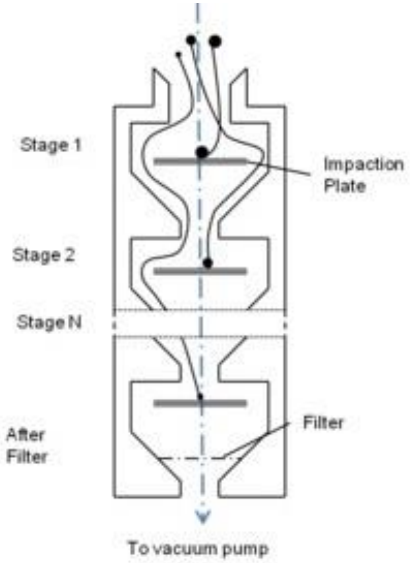
Sampling PM on cascade impactors:

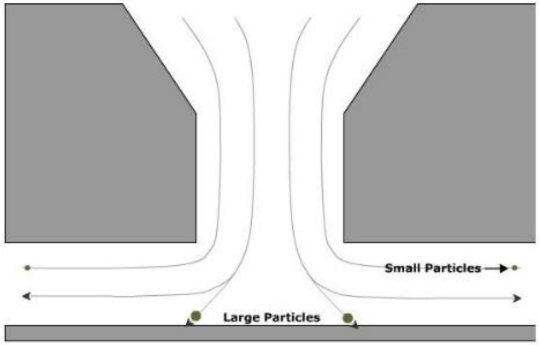
- classification of particles into several sizes according to aerodynamic diameter
- collection of particles on principle of inertial impaction:
  - mass concentration and chemical composition in several size fraction simultaneously (size resolved composition)
  - number concentration PM → „electrical“ impactor
- **cascade impactor:** 3 - 13 plates + „back-up“filter
- separation particles in size range 10 nm - 18 µm
- low plates – small amount of samples
- sampling medium: 1. foils (Al, Tedlar)

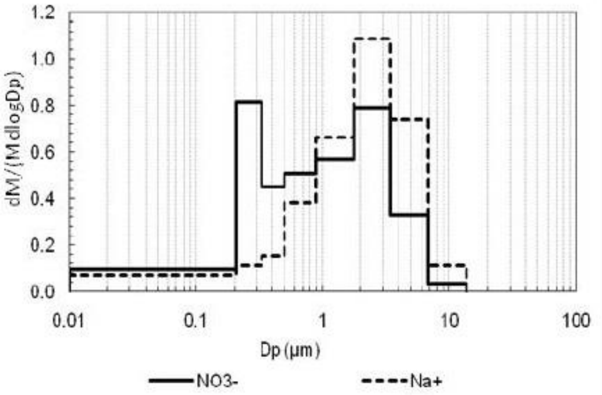
  2. filter (Nucleopore, Zefluor)
- foils covered with inert grease (Apiezon, silicone) to prevent particle bouncing and transfers to next plate



Gradual decrease of W, S and D_{p50}:







Cascade impactors used for mass + chemical composition:

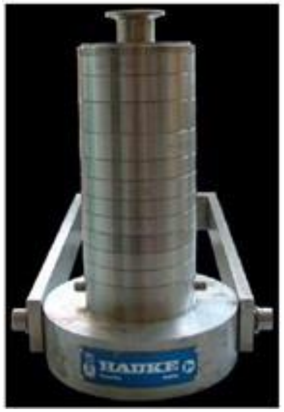
- Berner low pressure: 10 plates, 25 LPM, 26 nm – 6.8 µm
- Moudi (rotating): 13 plates, 30 LPM, 10 nm - 18 µm
- Dekati low pressure: 13 plates, 30 LPM, 30 nm – 10 µm
- Andersen: 8 plates
- Sioutas personal: 3 plates, 9 LPM

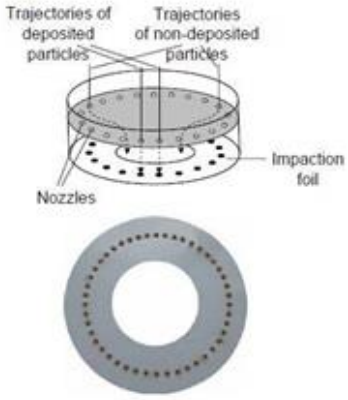
Moudi:

Parameters of Berner LPI:

Stage	D_{Nozzle} (mm)	$No_{Nozzles}$	$S_{Jet\text{-}to\text{-}Plate}$ (mm)	Re_{Nozzle}	P_{up} (kPa)	Stk_{50}	D_{50} (µm)
1	0.289	262	0.99	461	17.74	0.198	0.026
2	0.315	127	0.95	872	29.90	0.213	0.062
3	0.343	65	0.74	1565	47.34	0.234	0.110
4	0.426	25	1.01	3275	77.19	0.235	0.173
5	0.531	16	1.24	4106	95.23	0.204	0.262
6	0.686	16	1.70	3178	100.47	0.194	0.460
7	0.711	46	2.28	1066	101.11	0.190	0.890
8	1.210	33	2.96	874	101.26	0.202	1.770
9	2.180	20	3.48	800	101.30	0.202	3.400
10	5.150	6	5.98	1129	101.32	0.190	6.800
preimpactor	14.60	1	-	-	101.32	0.200	13.70

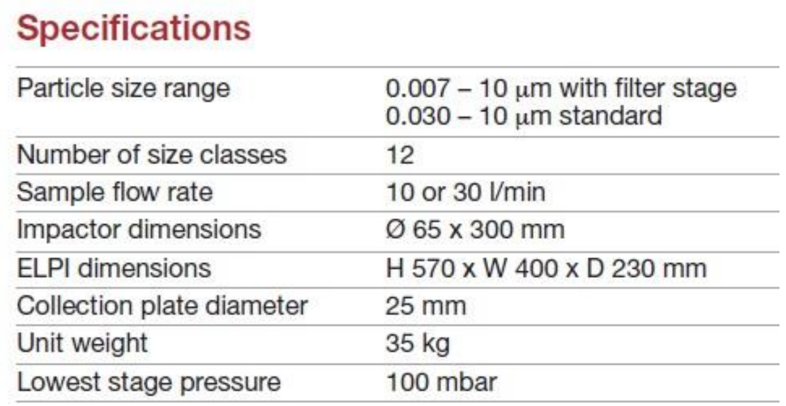
Berner Low Pressure Cascade Impactor





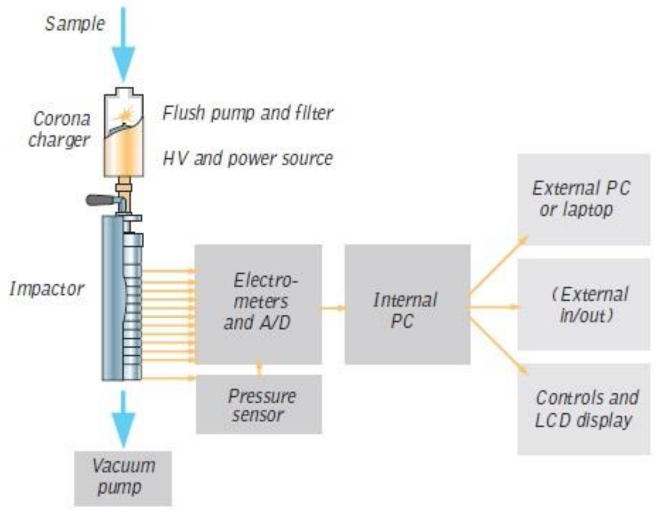
Electrical Low Pressure Impactor (ELPI, Dekati)

- measurement of real-time particle size distribution and number concentration (7 nm – 10 µm)
- principle:
  - particle charging in a unipolar corona charger
  - size classification of particles in a cascade impactor according to aerodynamic diameter
  - electrical detection of electric charge carried by particles into each impactor stage



Specifications

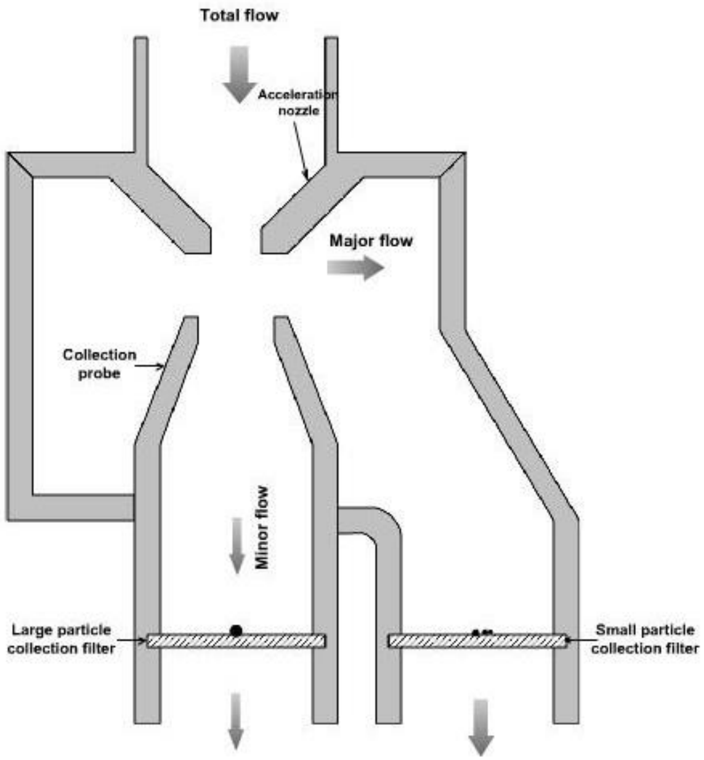
Particle size range	0.007 – 10 µm with filter stage 0.030 – 10 µm standard
Number of size classes	12
Sample flow rate	10 or 30 l/min
Impactor dimensions	Ø 65 x 300 mm
ELPI dimensions	H 570 x W 400 x D 230 mm
Collection plate diameter	25 mm
Unit weight	35 kg
Lowest stage pressure	100 mbar

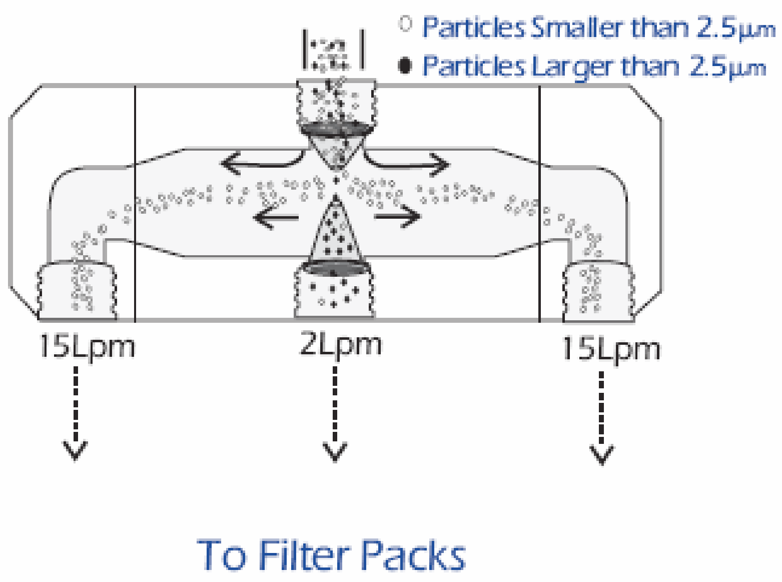


Stage	Di [µm]	Number max [1/cm³]
13		
12	8,4	2,0E+04
11	5,3	2,0E+04
10	3,2	4,5E+04
9	2	8,8E+04
8	1,3	1,6E+05
7	0,81	2,9E+05
6	0,51	5,4E+05
5	0,33	9,8E+05
4	0,21	1,7E+06
3	0,14	3,1E+06
2	0,081	6,1E+06
1	0,042	1,4E+07
Filter stage	0,014	6,9E+07

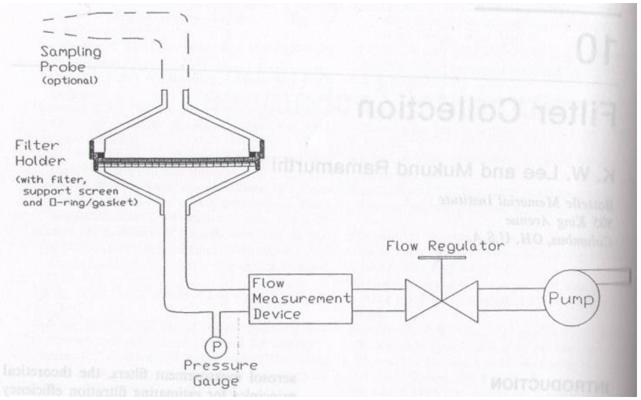
Virtual Impactor

- impaction plate is replaced with collection probe
- particles with sufficient inertia are thrown into collection probe. These particles remain airborne and are carried by minor air flow into filter.
- smaller particles are carried radially away from jet axis by major air flow, avoid collection probe and are collected on another filter
- particles larger than and smaller than cut-off diameter are collected on separate filters





Sampling on filters:



Samplers:

- high-volume (30-60 m³/h: Digitel (filters **150 mm**), …
- medium-volume (3-6 m³/h): Leckel, Derenda
- low-volume (1 m³/h): Leckel, home-made

} filters **47 mm**

NILU filter (47 mm) holder

inlet PM2.5

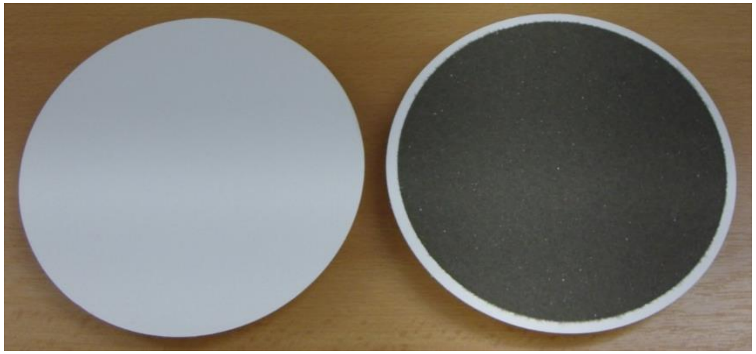
PM1 inlet

Digitel DHA-80

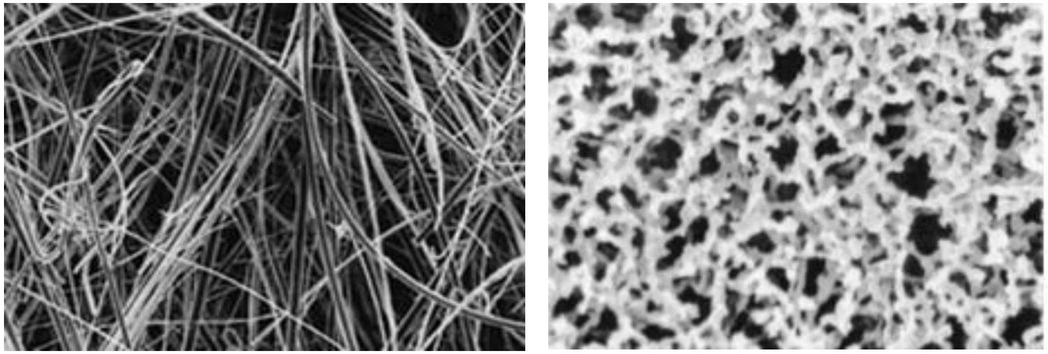
inlet PM2.5

Filters:

- 100 % collection efficiency (Dp ≈ 0.3 μm)
- choice of filter type according to analysed compounds:
  - **fibrous** (quartz, QMA) - porosity 70-99%, low flow resistance, Ø fibre 1-100 μm
    - **analysis of organic compounds (ions, metals)** bound to PM
  - **membrane**: porosity 50-90%, higher flow resistance
    - cellulose esters (nitrate/acetate-cellulose) → **analysis of metals**
    - Teflon (Zefluor, Teflo) → **analysis of ions**
    - polycarbonate → **determination of particle shape** (SEM, TEM)
- shape and size of filters: circular (Ø 25; 37; 47; 150 mm)
  rectangular (250 × 200 mm)
- dependence on air humidity → equilibration at const t/RH before weighing (24-48 hod)



clean and exposed QMA (PM2.5, 24 h, 720 m^3)

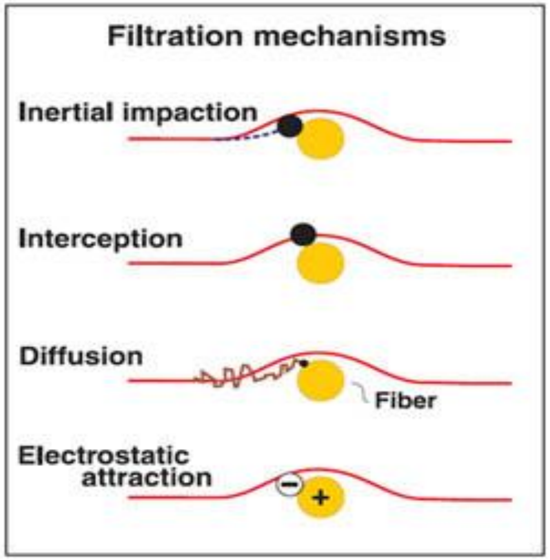


quartz and membrane filter under microscope

Efficiency of PM collection on filters:

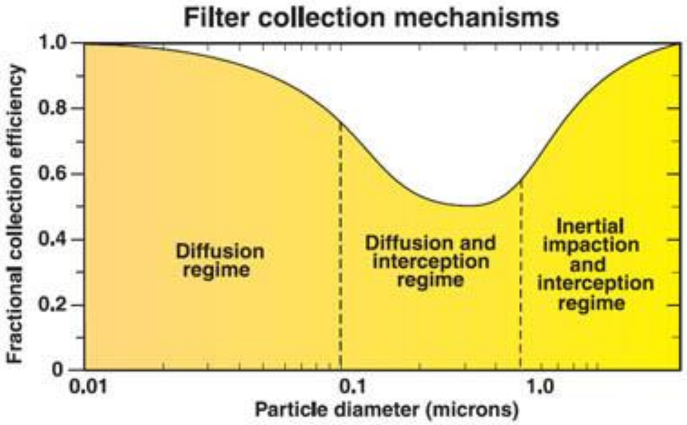
Mechanisms of PM collection on filters / deposition in lungs:

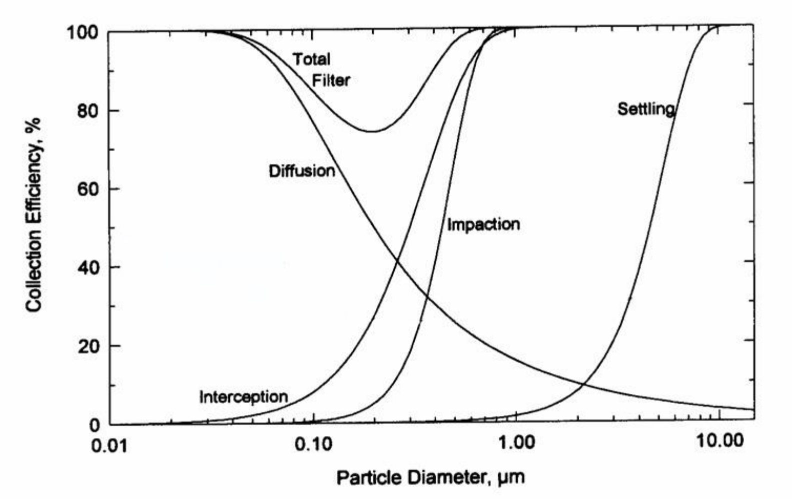
- inertial impaction
- interception
- diffusion (Brown)
- electrostatic deposition
- gravitational settling



Efficiency of filters:

- *f*: ➢ filter type (filter thickness, diameter of pores/fibres, …)
  - ➢ particle diameter
  - ➢ flow rate of sample through filter
  - ➢ filtration mechanism
- minimum filtration efficiency for particles with $D_a \approx 0.3$ μm (the most penetrating particle size !)





Discontinuous analysis of chemical composition:

1. collection of PM on filters or foils
2. direct on-line filter analysis: OC/EC: field analyser
   BC: aethalometer
   metals: RTG, NAA, PIXE, …, LAS, LIBS, …
3. off-line filter/foils analysis:
   - ☐ filter treatment:
     - ➢ before sampling: - filter cleaning – only for QMA (500°C, min. 10 h)
       - equilibration at constant T/RH (20°C / 50%)
       - removal of static charge
       - weighing of filter on sensitive microbalance (± 1 μg)
     - ➢ after sampling: - equilibration, removal static charge, weighing
       - extraction: water – ultrasonic extraction
         organic solvents: MeOH, DCM, acetone, hexane, …
         ultrasonic / Soxhlet / ASE / PSE
       - decomposition: HNO_3, HF, …
   - ☐ extract treatment: extract preconcentration: solvent evaporation
     extract fractionation: silicagel/alumina + solvents with increased polarity
     extract derivatization: low volatility or thermally unstable compounds
   - ☐ extract analysis: organic compounds: GC-MS/FID, LC-MS, HPLC, IC, MALDI, …
     OC/EC: laboratory analyser
     metals: ICP-MS, AAS, RTG, OES, …
     ions: IC, CZE, FIA, LC, ….

Chemical composition of aerosols:

- ❑ variable
- ❑ dependent on particle size, time and place of sampling (different emission sources)
- ❑ use: identification of emission sources of PM

  estimation/evaluation of health risk PM
- ❑ fine × coarse aerosol
- ❑ PM10, PM2.5, PM1, UFP
- ❑ water-soluble × water-insoluble
- ❑ **primary PM components:** compounds emitted directly from source

  secondary PM components: compounds formed secondary in atmosphere
  - ○ reaction of gaseous precursors (SO_2, NO_2, … → H_2SO_4, HNO_3)
  - ○ oxidation of VOCs, reaction with NO_2, …
  - ○ photolysis of organic compounds, …

Chemical composition of atmospheric aerosols:

1) **inorganic compounds**: ♦ primary emission: metals, insoluble minerals, …
♦ secondary formation: nitrates, sulphates, NH_4^+, …

2) **organic compounds**:

- ➢ primary: EC, polar (acids, saccharides,...) and nonpolar (PAHs, alkanes, …)
- ➢ secondary: oxo-, nitro-, … derivates, dicarboxylic acids, …
- ➢ HULIS (HUmic-LIke Substances)

3) **water:** mainly PM2.5 particles are mostly hygroscopic, water content increases with RH
(RH > 80%: H_20 usually forms more than ½ PM2.5 mass)

❑ **SIA**: NH_4NO_3, $(NH_4)_2SO_4$, NH_4Cl, …
SOA: secondary organic aerosol (DCAs, oxo/nitro-derivates, …)

❑ carbon in PM: „**carbonaceous fraction** of aerosols“: EC + OC (+ carbonates)

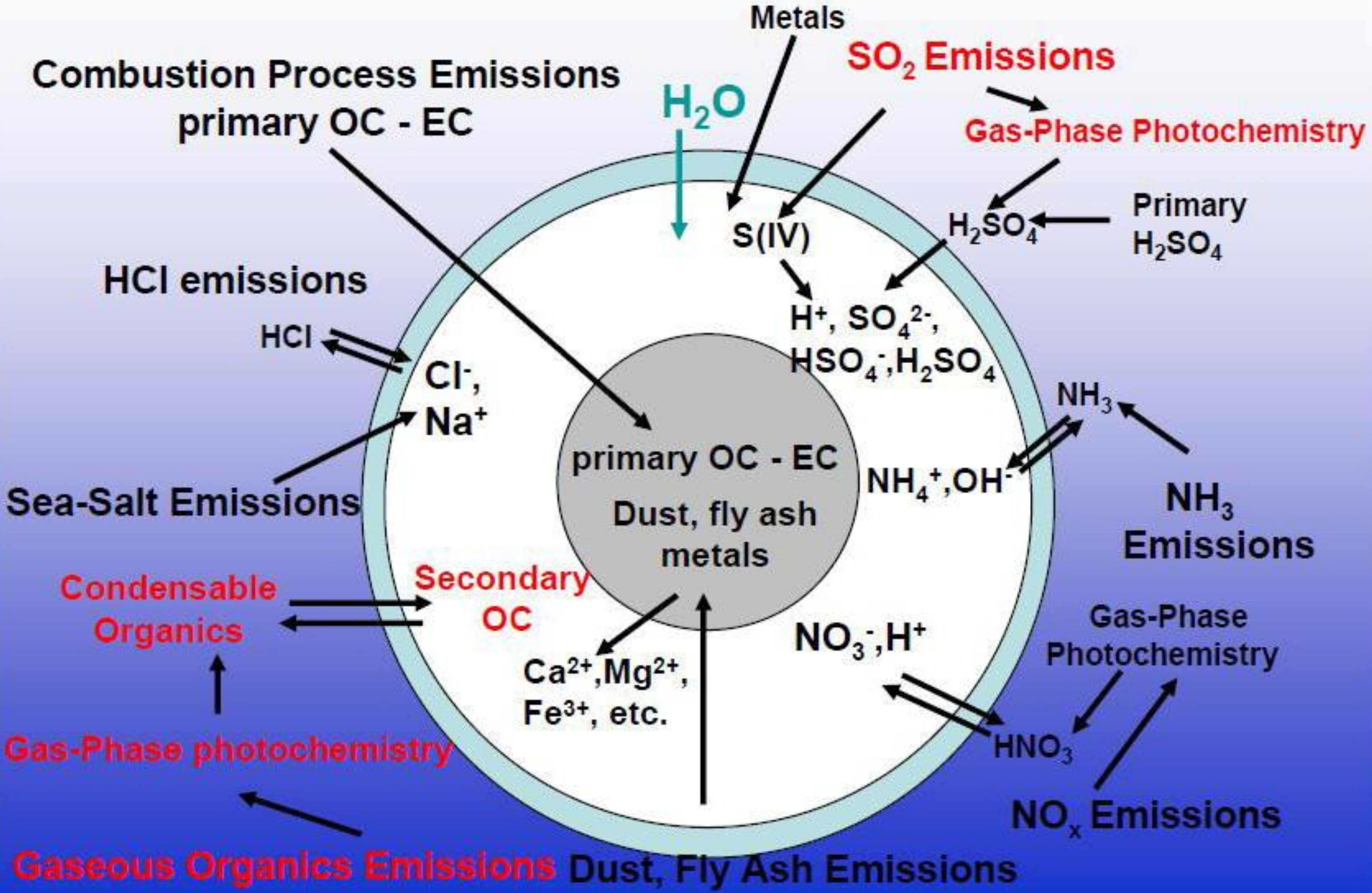
- **EC**: elementary carbon (≈ BC, soot)
- **OC**: organic carbon, ∑ C in organic compounds in PM

} OC + EC form 25-75% PM mass,
OC + EC = TC, **TC** - total carbon

- **WSOC**: **w**ater **s**oluble **o**rganic **c**ompounds
- **WNSOC**: **w**ater **n**on-**s**oluble **o**rganic **c**ompounds

❑ **HULIS:** group of WSOC with high molecular weight (200-600 Da) accounting up to 72% of WSOC mass. HULIS are comprised of hydrophobic aliphatic and aromatic compounds containing different polar functional groups (hydroxyl, carboxyl and carbonyl). Due to complexity and chemical diversity (hundreds of individual substances), chemical characterization is still relatively poor. Primary and secondary origin.

Chemical composition



Metals

SO_2 Emissions

Combustion Process Emissions
primary OC - EC

H_2O

Gas-Phase Photochemistry

H_2SO_4

Primary
H_2SO_4

S(IV)

HCl emissions

H^+, SO_4^{2-},
HSO_4^-,H_2SO_4

HCl

Cl^-,
Na^+

NH_3

primary OC - EC

NH_4^+,OH^-

Sea-Salt Emissions

Dust, fly ash
metals

NH_3
Emissions

Condensable
Organics

Secondary
OC

NO_3^-,H^+

Gas-Phase
Photochemistry

Ca^{2+},Mg^{2+},
Fe^{3+}, etc.

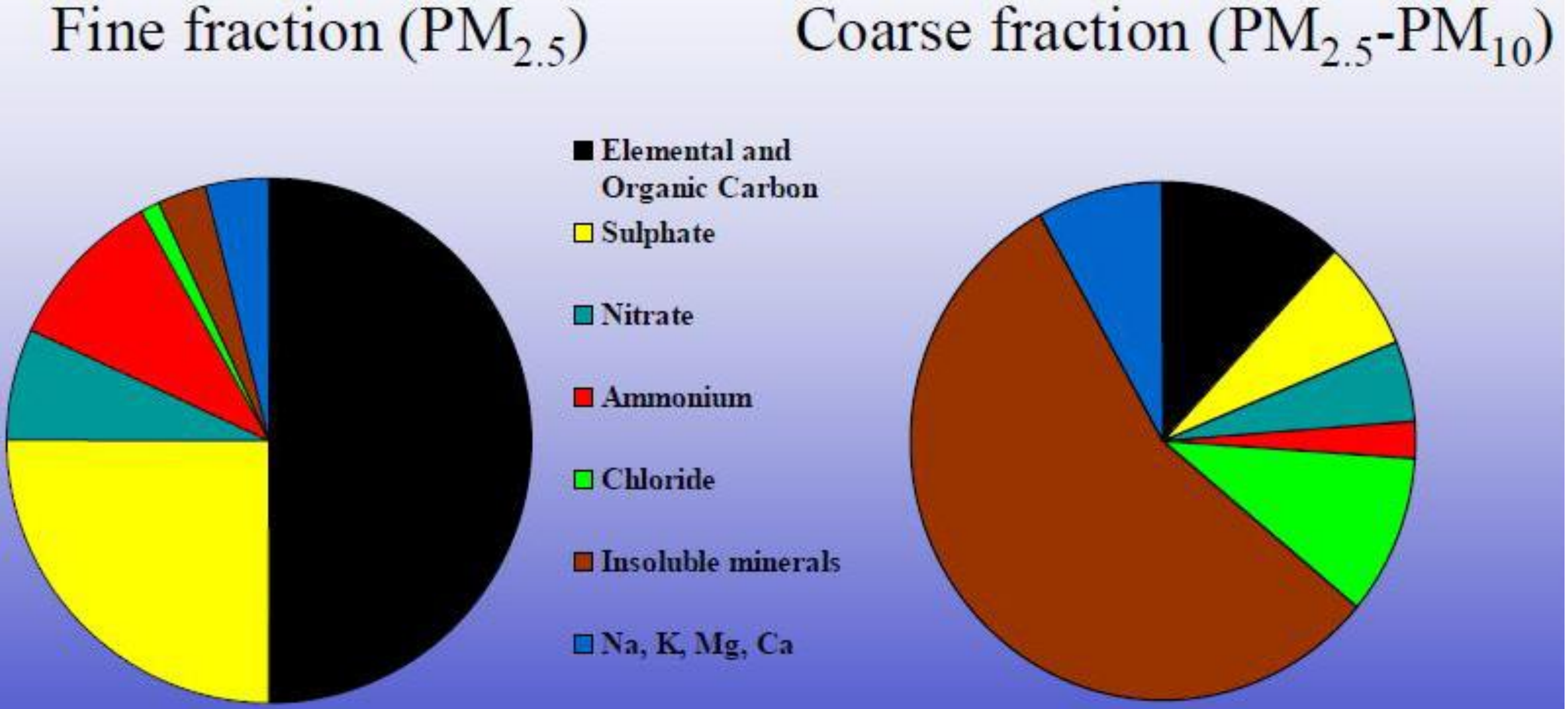
HNO_3

Gas-Phase photochemistry

NO_x Emissions

Gaseous Organics Emissions Dust, Fly Ash Emissions

Chemical composition : an example of its dependence on aerosol size



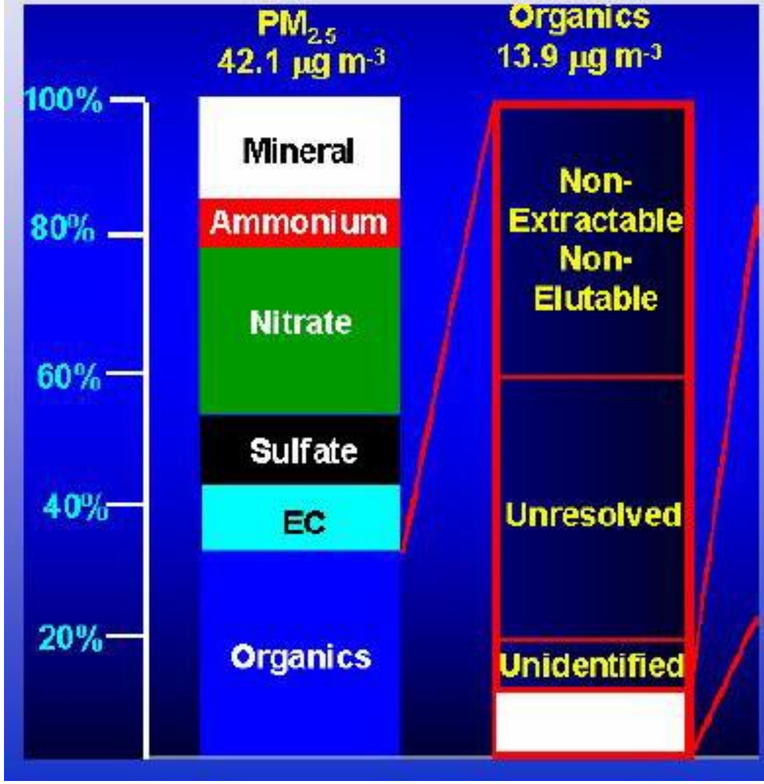
Fine fraction ($PM_{2.5}$)

Coarse fraction ($PM_{2.5}$-PM_{10})

Field campaign in UK, 1997

Organic Compounds (OC)

- Man made : combustion processes + SOA from VOC
- Natural : SOA from biogenic VOC
- Complex mixture of 1000’s of compounds



Only 10% identified with $n_C > 20$ (semi & nonvolatile):

n-Alkanes

n-Alkanoic acids

Polycyclic aromatic compounds (e.g. Polycyclic Aromatic Hydrocarbons, PAH)

- Unresolved (UCM): rozvětvené cyklické a nenasycené CHx (emise z dopravy)
- Non-Extractable/Non-Elutable: HULIS, …

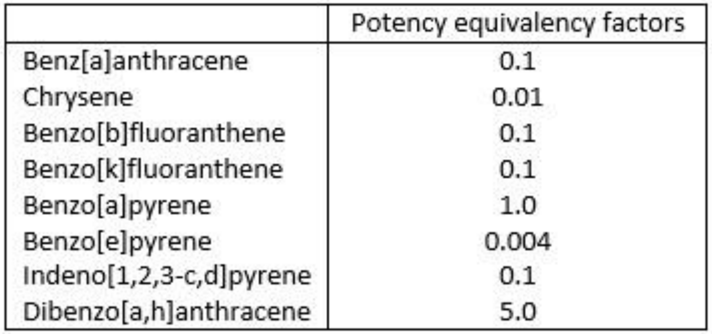
Organic compounds analysed in PM collected on filters + indicated sources:

- ❑ compounds important due to health effects ⇒ evaluation of health risk
  (PAHs, nitroPAHs, PCBs, dioxines, …)
- ❑ **molecular markers** ⇒ unique identification of emission sources
  - ➢ monosaccharide anhydrides: biomass combustion
  - ➢ resin acids + retene: softwood combustion
  - ➢ methoxyphenols: wood combustion (soft- and hard-wood)
  - ➢ saccharides: monosaccharides: wood combustion, plant
    disaccharides: plant (pollen, …), microorganisms
    polyols: fingal spores, bacteria, soil microorganisms
  - ➢ alkanes: traffic, coal combustion, biological sources (plant metabolites)
  - ➢ acyclic isoprenoids: traffic, biogenic sources
  - ➢ hopanes: coal combustion, traffic
  - ➢ steranes: traffic
  - ➢ picene: coal combustion
  - ➢ triphenylbenzene: plastic material combustion
  - ➢ 1-nitropyrene: diesel
  - ➢ oxo/nitro-PAHs: SOA
  - ➢ dicarboxylic acids: traffic, SOA
  - ➢ higher monocarboxylic acids (C_{16}, C_{18}) + cholesterol: cooking
- ❑ other: OC-EC, HULIS, …

Polycyclic aromatic hydrocarbons:

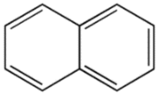
16 priority PAHs

carcinogenic PAHs ——

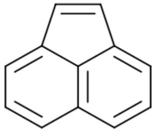


	Potency equivalency factors
Benz[a]anthracene	0.1
Chrysene	0.01
Benzo[b]fluoranthene	0.1
Benzo[k]fluoranthene	0.1
Benzo[a]pyrene	1.0
Benzo[e]pyrene	0.004
Indeno[1,2,3-c,d]pyrene	0.1
Dibenzo[a,h]anthracene	5.0

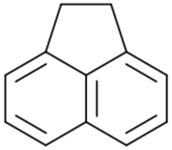
1. **Naphthalene**



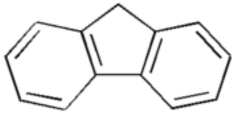
2. **Acenaphthylene**



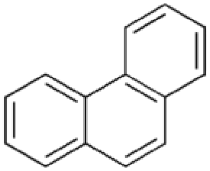
3. **Acenaphthene**



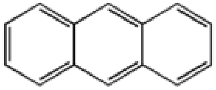
4. **Fluorene**



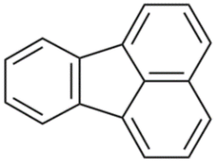
5. **Phenanthrene**



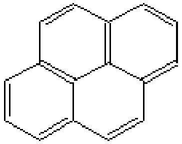
6. **Anthracene**



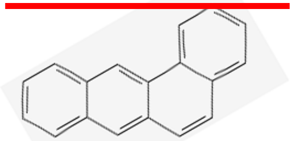
7. **Fluoranthene**



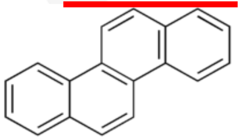
8. **Pyrene**



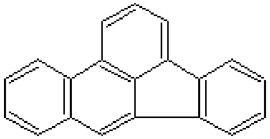
9. **Benz[a]anthracene**



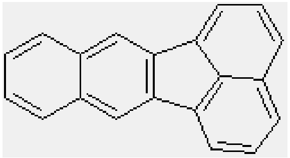
10. **Chrysene**



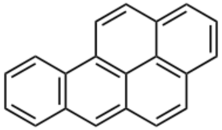
11. **Benzo[b]fluoranthene**



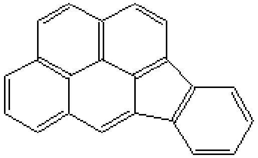
12. **Benzo[k]fluoranthene**



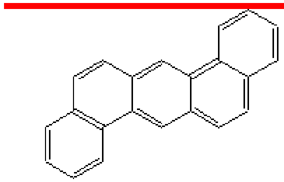
13. **Benzo[a]pyrene**



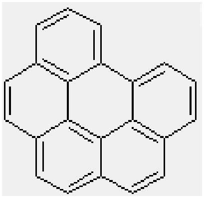
14. **Indeno[1,2,3-cd]pyrene**



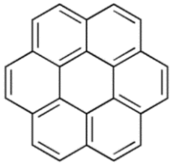
15. **Dibenzo[a,h]anthracene**



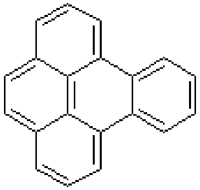
16. **Benzo[ghi]perylene**



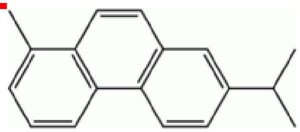
Coronene



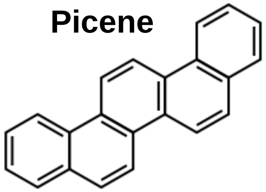
Benzo[e]pyrene



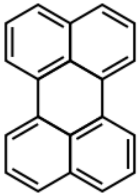
Retene



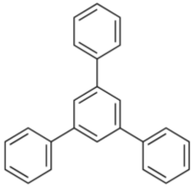
Picene

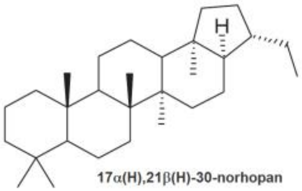


Perylene

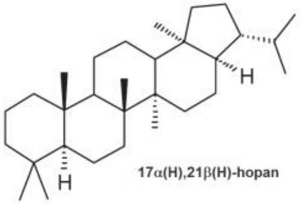


Triphenylbenzene

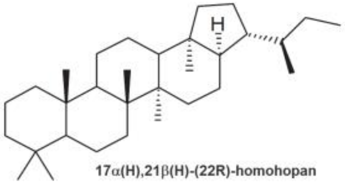




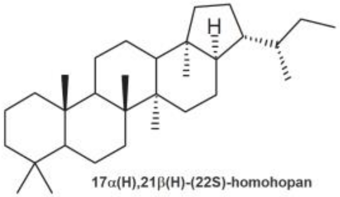
17α(H),21β(H)-30-norhopan



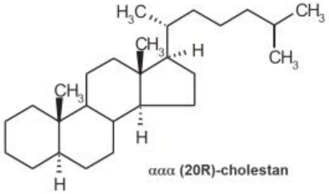
17α(H),21β(H)-hopan



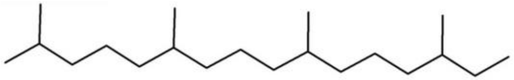
17α(H),21β(H)-(22R)-homohopan



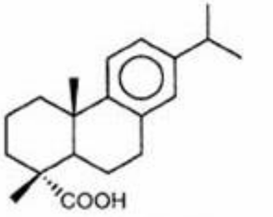
17α(H),21β(H)-(22S)-homohopan



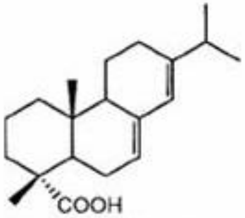
ααα (20R)-cholestan



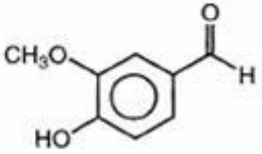
Pristane: $C_{19}H_{40}$, Phytane: $C_{20}H_{42}$



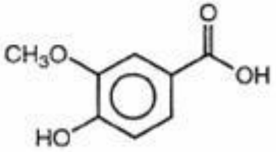
Kyselina dehydroabietová



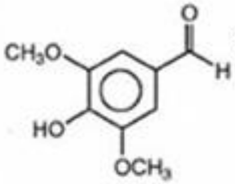
Kyselina abietová



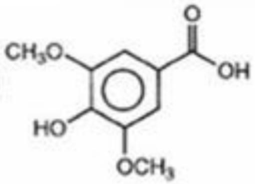
Vanilin



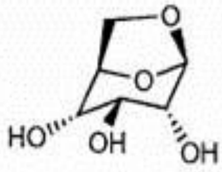
Kyselina vanilová



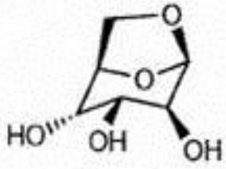
Syringaldehyd



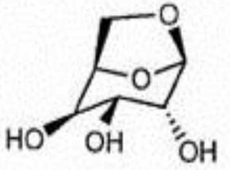
Kyselina syringová



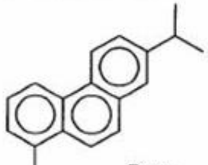
Levoglucosan



Mannosan



Galactosan



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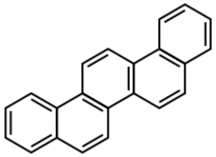
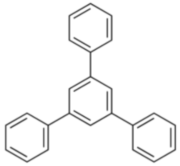
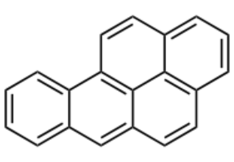


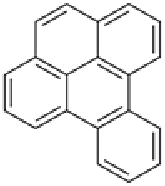
picene



triphenylbenzene



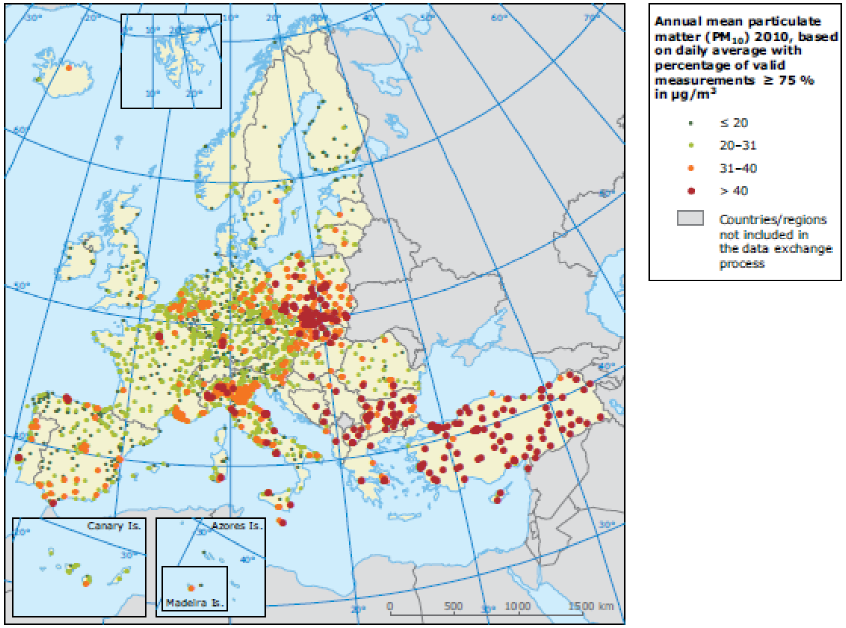
BaP



BeP

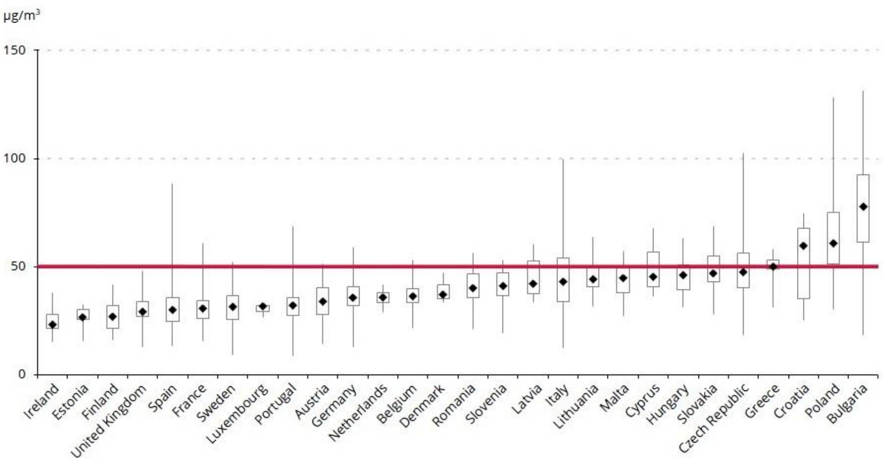
PM10 in Europe

Map 2.1 **Annual mean concentrations of PM_{10} in 2010**

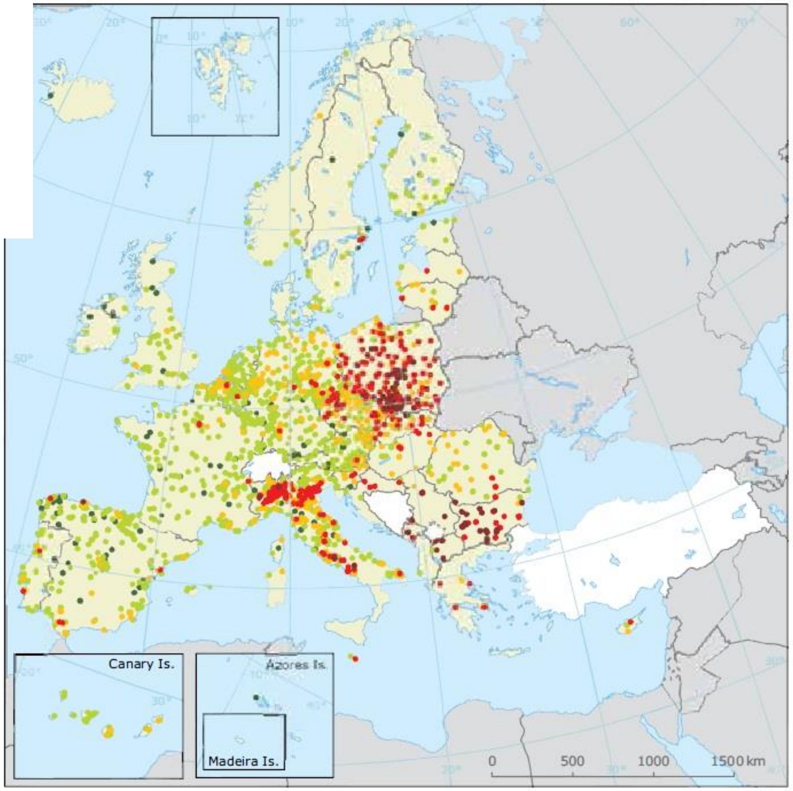


EEA report 2012

Figure 4.1 **PM_{10} concentrations in relation to the daily limit value in 2014 in the EU-28**



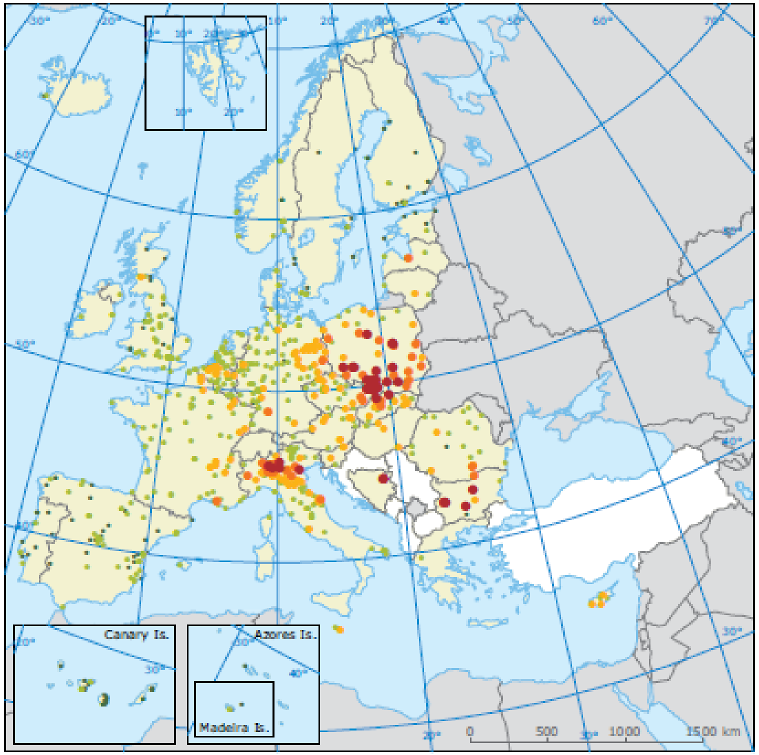
p 4.1 **Concentrations of PM_{10} in 2014**



EEA report 2016

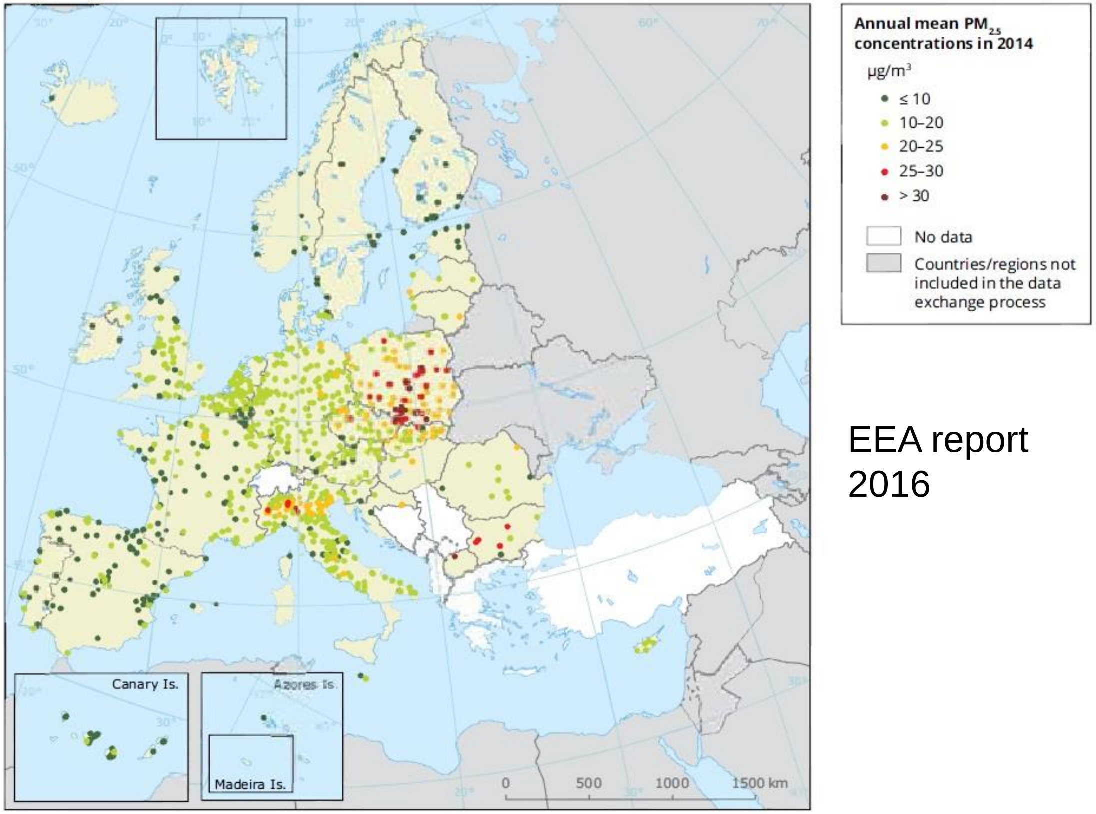
PM2.5 in Europe

Map 2.2 **Annual mean concentrations of $PM_{2.5}$ in 2010**



EEA report 2012

Map 4.2 **Concentrations of $PM_{2.5}$ in 2014**



EEA report 2016

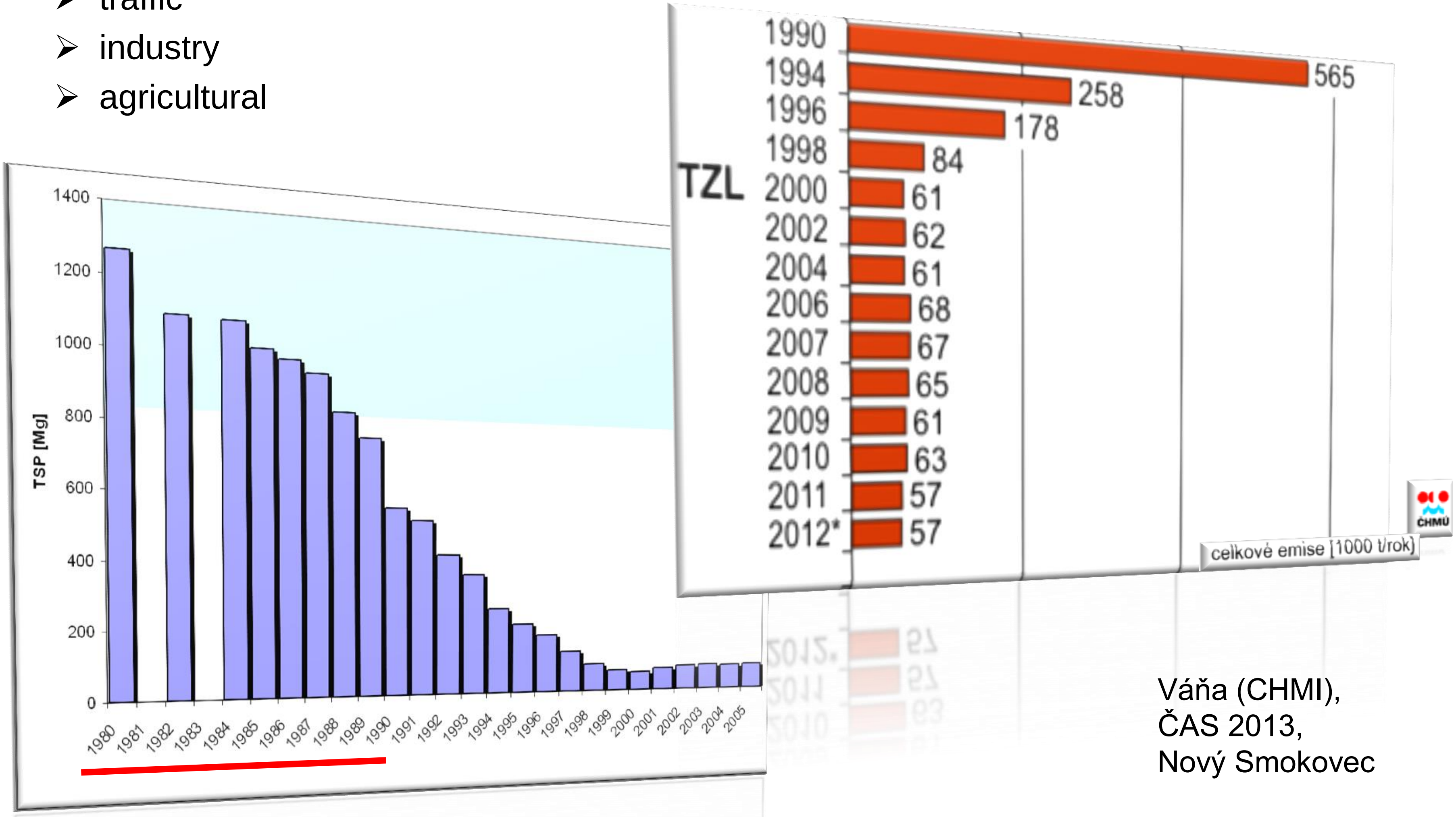
TSP concentration + dust emission: trend in CR

Main sources of PM:

- coal combustion
- biomass (wood) burning

} residential heating

- traffic
- industry
- agricultural

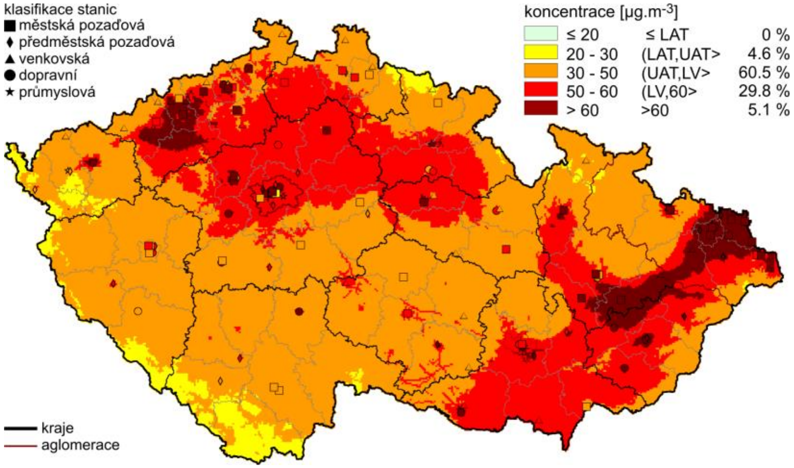


Váňa (CHMI),
ČAS 2013,
Nový Smokovec

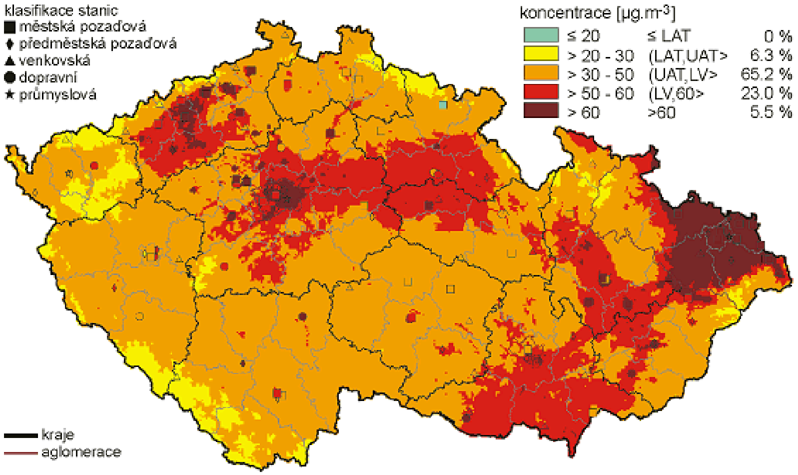
Field of 36. highest 24-hod concentration PM10 in CR (CHMI):

⇒ effect of meteorological situation on PM10

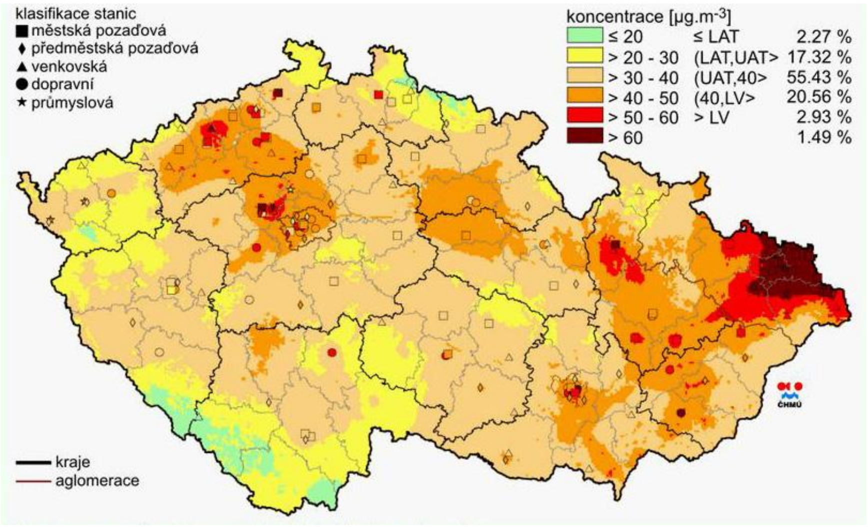
2005



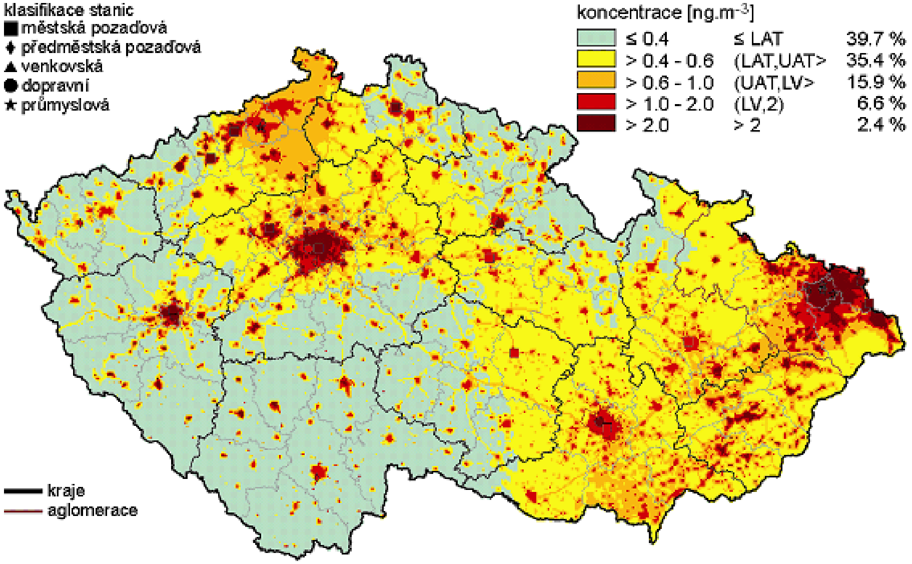
2007



2009



Annual average concentration of benzo(a)pyrene in 2007



Positive use of aerosols:

- ☐ **Speleotherapy** ⇒ inhalation of speleoaerosols (cave aerosols) in selected caves (Sloupsko-Šošůvské caves), specific clima with constant temperature and high humidity, metals in aerosols: Ca, Mg, K, Na, Cl, Fe, … → **treatment of asthma**
- ☐ **Inhalation aerosols**:

  - application of therapeutic aerosols for targeted dosing of aerosols into patient lungs → aerosols as carrier of drug → **treatment of allergy**

  - treatment of cystic fibrosis (disruption of chloride cellular transport): transport of genetically modified virus to lungs

- ☐ **Elimination of CO_2 increase in atmosphere**: transport sulphate aerosols into low stratosphere (5% contribution of sulphur into aircraft fuel)

Literature:

1) W.C. Hinds: Aerosol Technology. Properties, Behaviour, and Measurement of Airborne Particles (Wiley, 1982)

2) K. Willeke, P.A. Baron: Aerosol Measurement. Principles, Techniques, and Applications (Nostrand Reinhold, 1993)

3) P.C. Reist: Aerosol Science and Technology (McGraw-Hill, 1993)

4) C.N. Davies: Aerosol Science (Academic Press, 1966)

5) I. Colbeck: Environmental Chemistry of Aerosols (Blackwell Publishing, 2008)

6) K.R. Spurný: Analytical Chemistry of Aerosols (CRC Pres, 1999)