Measurement Techniques for Fine Particles in Ambient Air Possibilities and limitations for compliance measurements of regulated compounds

Robert Gehrig

[a] *Laboratory for Air Pollution/Environmental Technology, Empa, Dübendorf, Switzerland*

robert.gehrig@empa.ch

In Switzerland as well as in Europe the pollution of the ambient air with fine particles is limited in terms of maximum daily and yearly mass concentrations (PM10 and/or PM2.5). However, there has been concern whether these limit values are sufficient to adequately cover adverse health effects of fine particles. In particular ultrafine particles or some specific chemical constituents of the fine particle fraction might not be reflected sufficiently by the existing limit values. Additional metrics in addition to mass concentrations might be necessary in order to better address possible health effects of particulate air pollution.
Such metrics comprise e.g. number and surface concentrations of ultrafine particles as well as chemical constituents like carbonaceous compounds (soot, PAH) or metals.
An indispensable prerequisite for the inclusion of new metrics in routine measurement networks is the availability of reliable, practical and internationally harmonized measurement techniques. In particular the following conditions need to be met:

- Data internationally harmonized and comparable.
- Method traceable to an internationally agreed standard (certified reference material) or regular comparison with a defined reference method (e.g. manual gravimetry for PM).
- Method suitable for routine network operation; e.g. unattended and stable operation for at least 2 weeks and affordable maintenance.
- Sufficient time resolution.

There are good motivations to measure e.g. ultrafine particles in addition to mass concentrations because they are not covered by particle mass measurements. Also fresh combustion particles are found mainly in the ultrafine fraction. Such measurements would allow a better control of the effectiveness of emission reductions than mass concentrations.

Today instrumentation allowing measurements of number and surface concentrations of ultrafine particles with good time resolution are available. However, neither standard reference materials for calibration nor standardized methods are yet available. A CEN working group is attempting to standardize measurements of particle number concentrations in ambient air but this will still take some years.

The same is true for the measurement of carbonaceous particles (elemental carbon, black carbon). The standardization work of CEN is here somewhat more advanced and there is some hope for an agreed European standard within 1-2 years. It will most probably consist of a manual thermo-optical reference method for elemental and organic carbon(controlled stepwise burning with a defined temperature protocol of OC

and EC deposited on filters combined with an optical control/correction for charing.

In addition to the manual reference method, CEN will also give guidance for using automatic optical methods, in particular how to relate optical soot data to the reference method.

For the measurement of toxic constituents of fine particles (e.g. metals, polycyclic aromatic hydrocarbons) standardized methods are available. However, they require expensive manual analysis and suffer from very low time resolution.

Table 1 gives an overview of important particle parameters concerning the importance of the parameters, the availability of standardizes methods and time resolution.

Tab. 1: Overview of important particle parameters concerning the importance of the parameters, the availability of standardizes methods and time resolution

	Parameter is important?	Standardized measurement technique ready?	Time resolution
Mass concentrations	Yes	Yes	medium/high
Number concentrations	Yes	Not yet	high
Surface concentrations	Yes	Not yet	high
Carbonaceous particles	Yes	Soon?	medium/high
Metals	Yes	Yes	low
PAH	Yes	Yes	low

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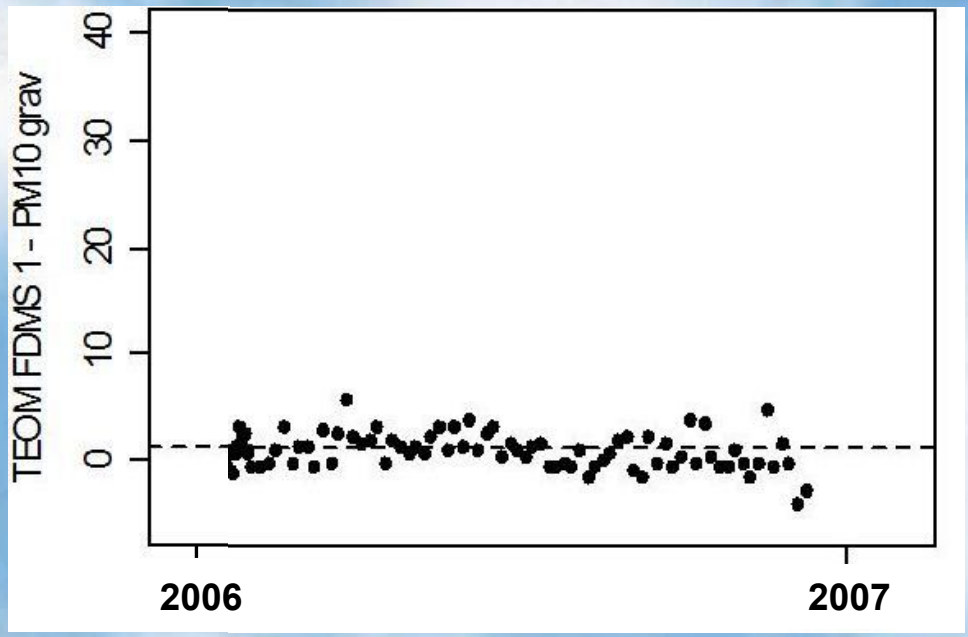
Empa Dübendorf

Air Pollution/Environmental Technology

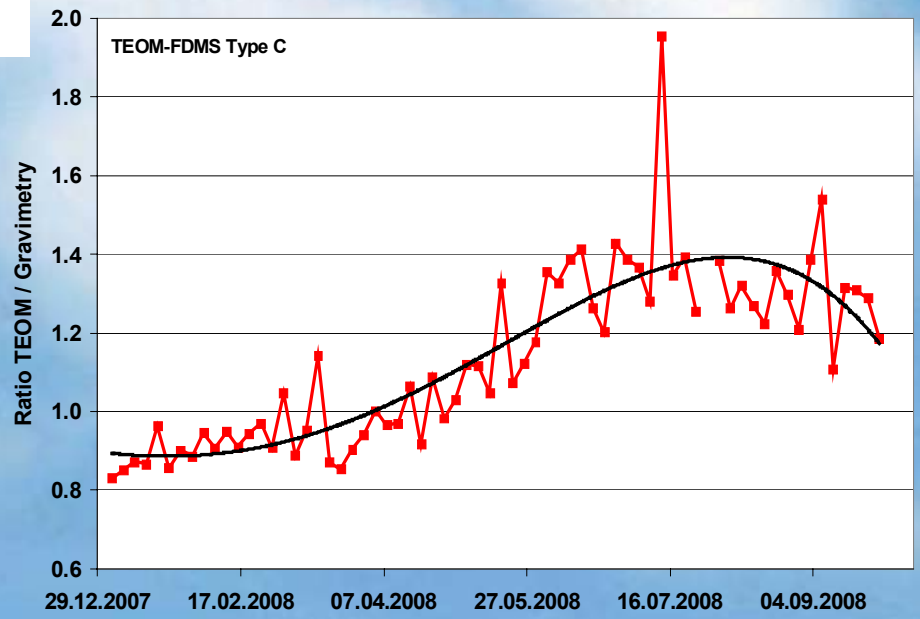
Compliance measurements of regulated pollutants: Essential requirements

- **Data internationally comparable.**
- **Method traceable to an internationally agreed standard (certified reference material) or regular comparison with a defined reference method (e.g. manual gravimetry for PM; EN 12341, EN 14907).**
- **Suitable for routine network operation; e.g.**
  - unattended and stable operation for at least 2 weeks
  - affordable maintenance.



PM Monitors

Monitor vs. Gravimetry



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Problem:

- Even a successful equivalence test does not ensure equivalence over longer time periods or at a different site.
- The relation between the monitor signal and the reference method can change without clear warning signals.

Crucial difference to many gaseous pollutants

- Gas monitors can be calibrated on-site with certified reference gases at regular intervals.
- No reference materials available for PM.

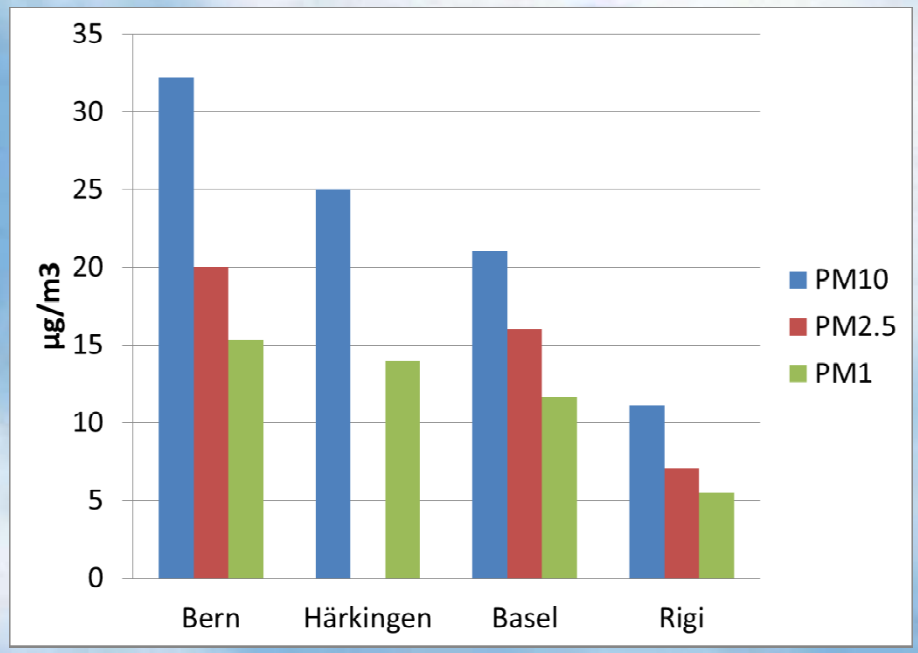
Additional metrics for fine particles in ambient air

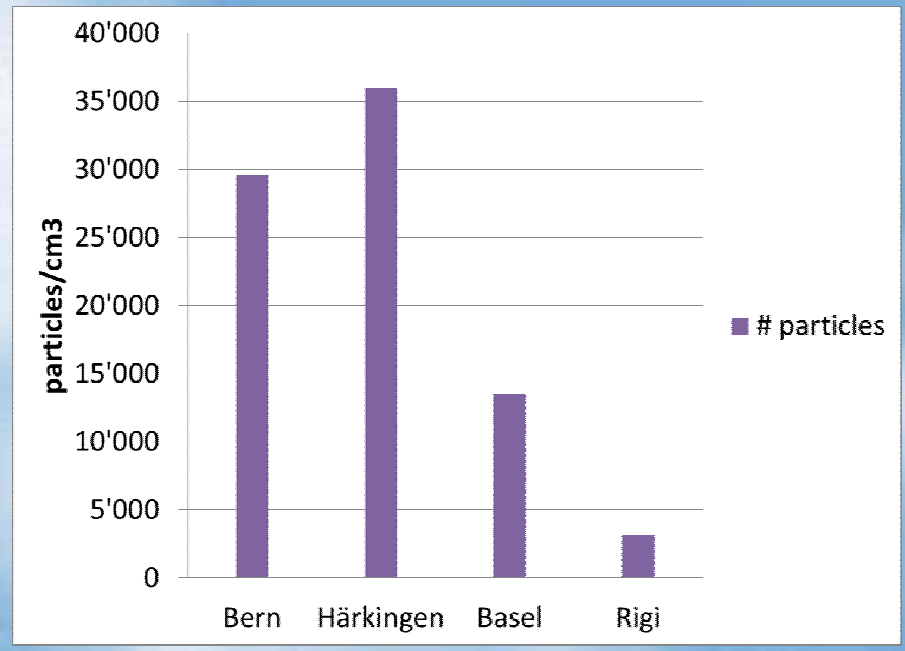
- Particle number and surface concentrations (ultrafine particles)
- Carbonaceous compounds (EC, OC, TC, BC, BS)
- Specific constituents: e.g. PAH, metals
- Other proxies: e.g. ROS, NO, NO_2 (not covered in this talk)

Motivation to measure ultrafine particles in ambient air

- **Not covered by particle mass measurements**
  (Mass of one 10µm particle = 1'000'000'000 10nm particles)
- **Fresh combustion particles (soot) are mainly in the ultrafine fraction**
- **Control of the effectiveness of emission reductions**
- **Specific health effects**

Mass and number concentrations (annual mean concentrations 2010)





Source: NABEL

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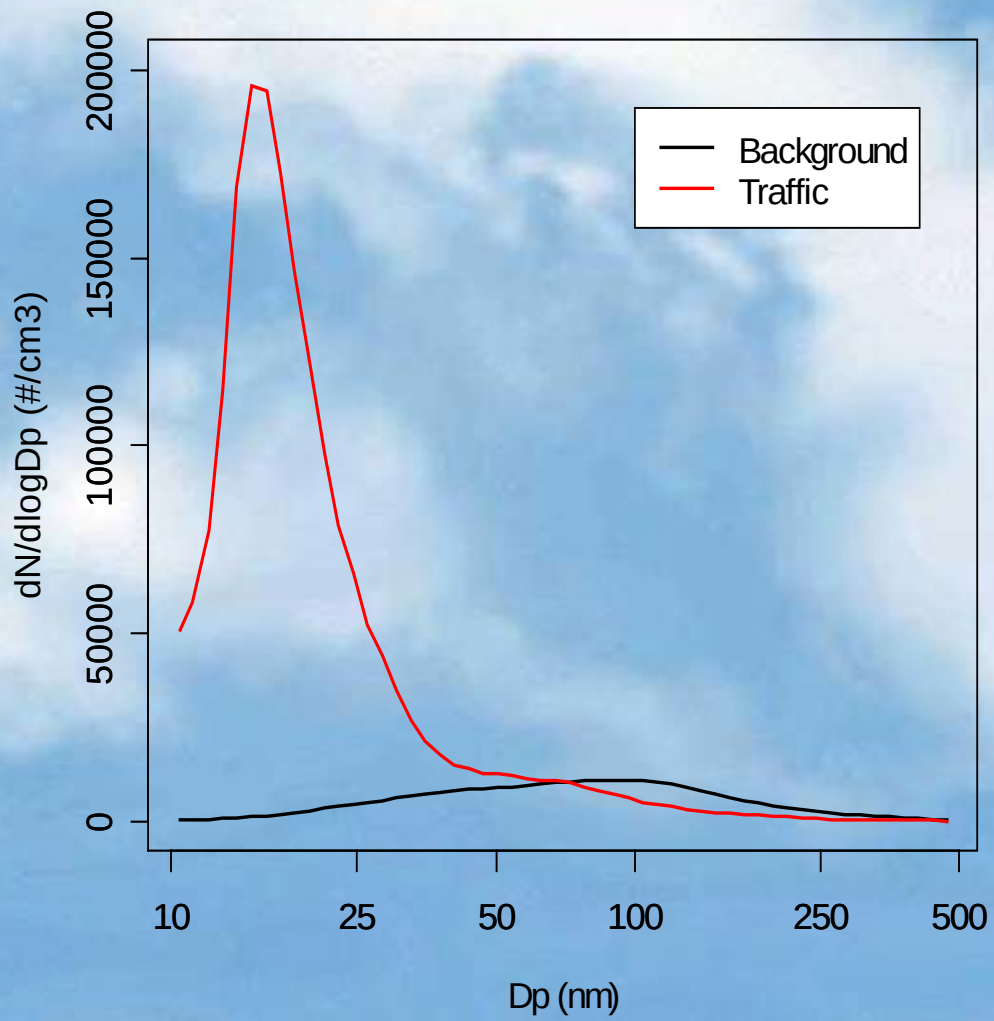
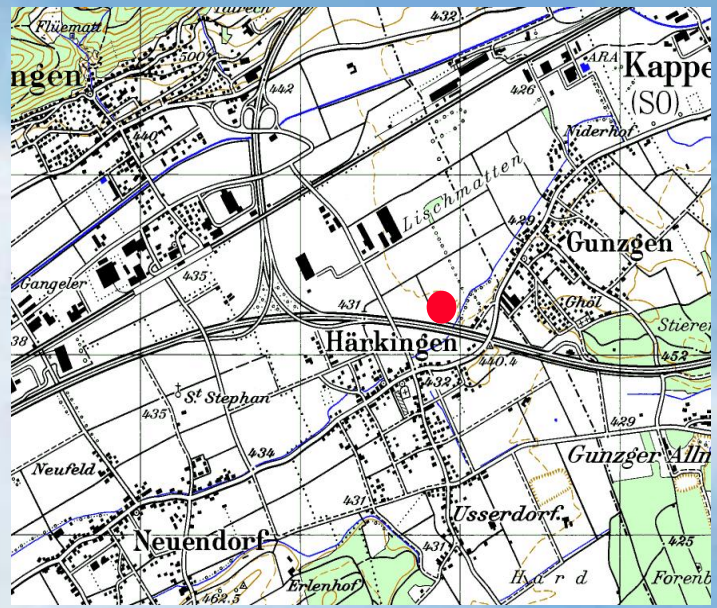
Typical particle size distribution at Härkingen





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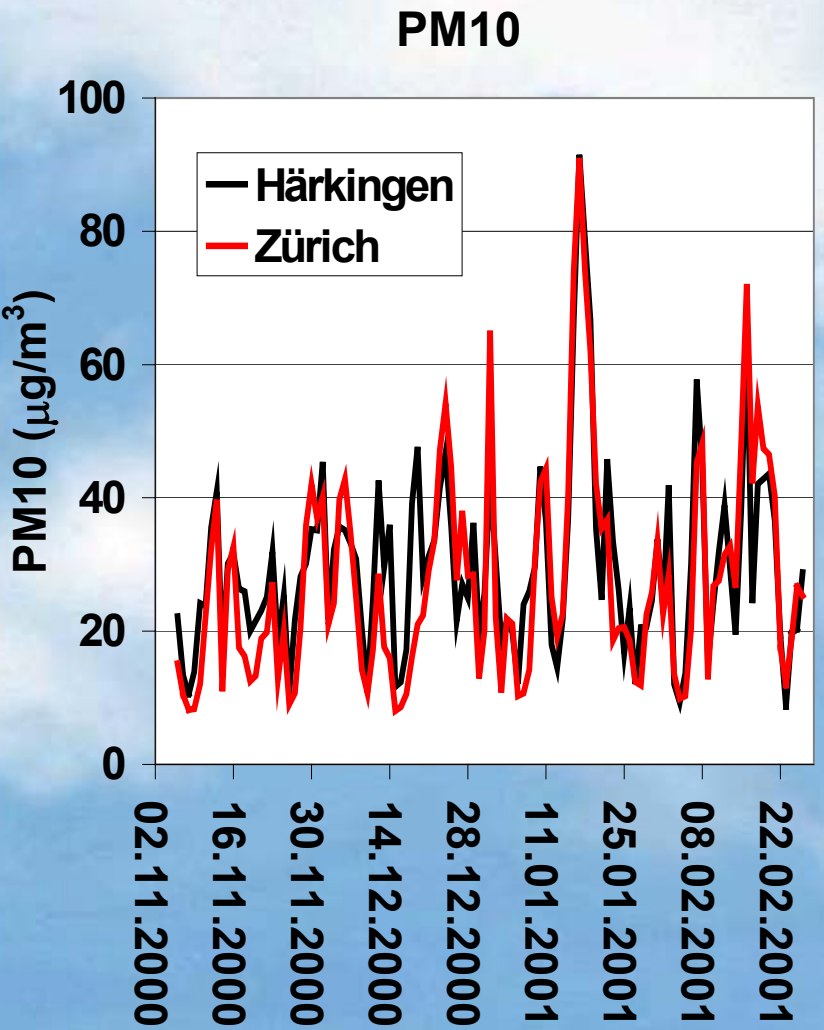
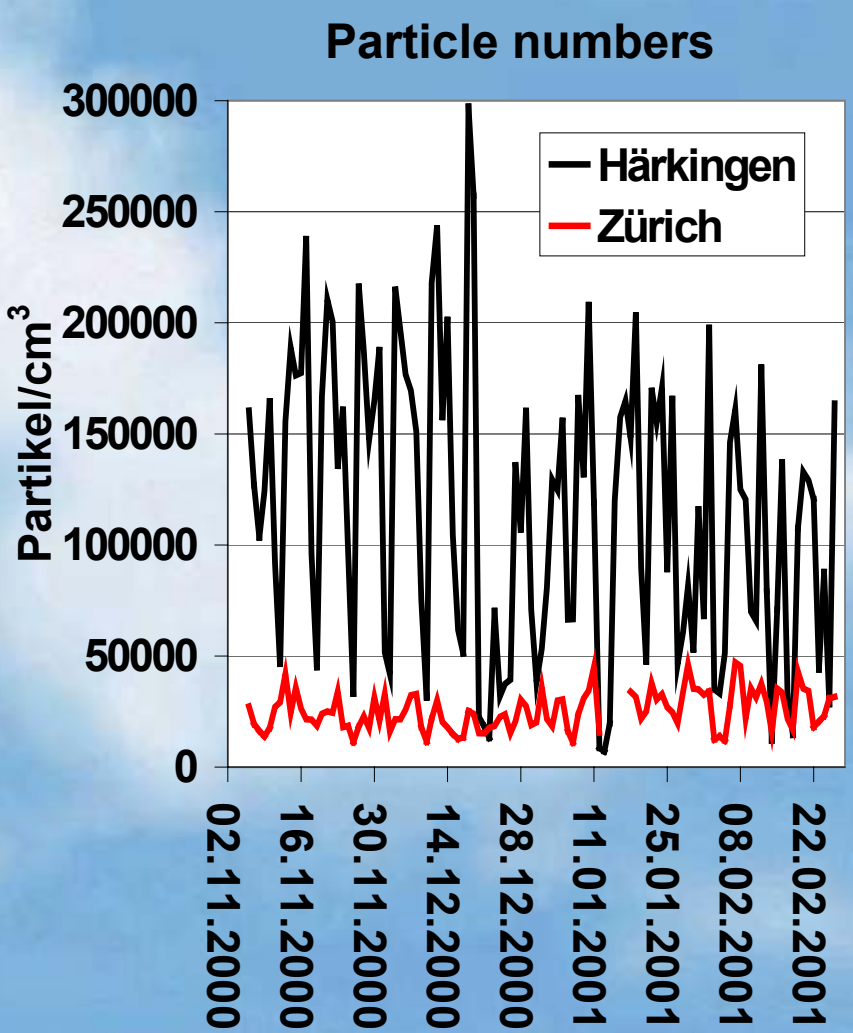
Particle numbers vs. PM10 concentrations





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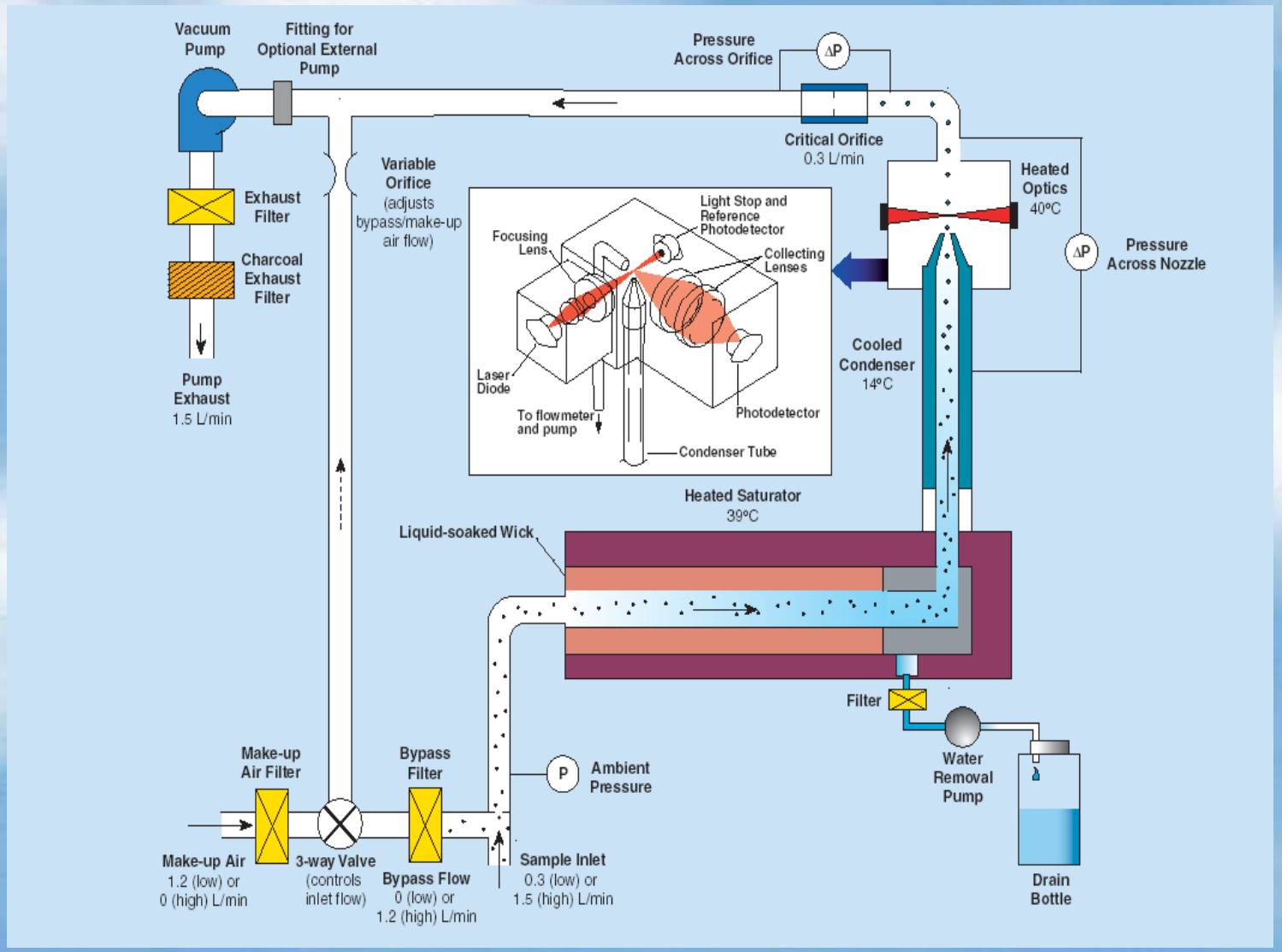
Condensation particle counter (CPC)



d > 3nm; large measurement range (1-10^7 particles per cm^3)

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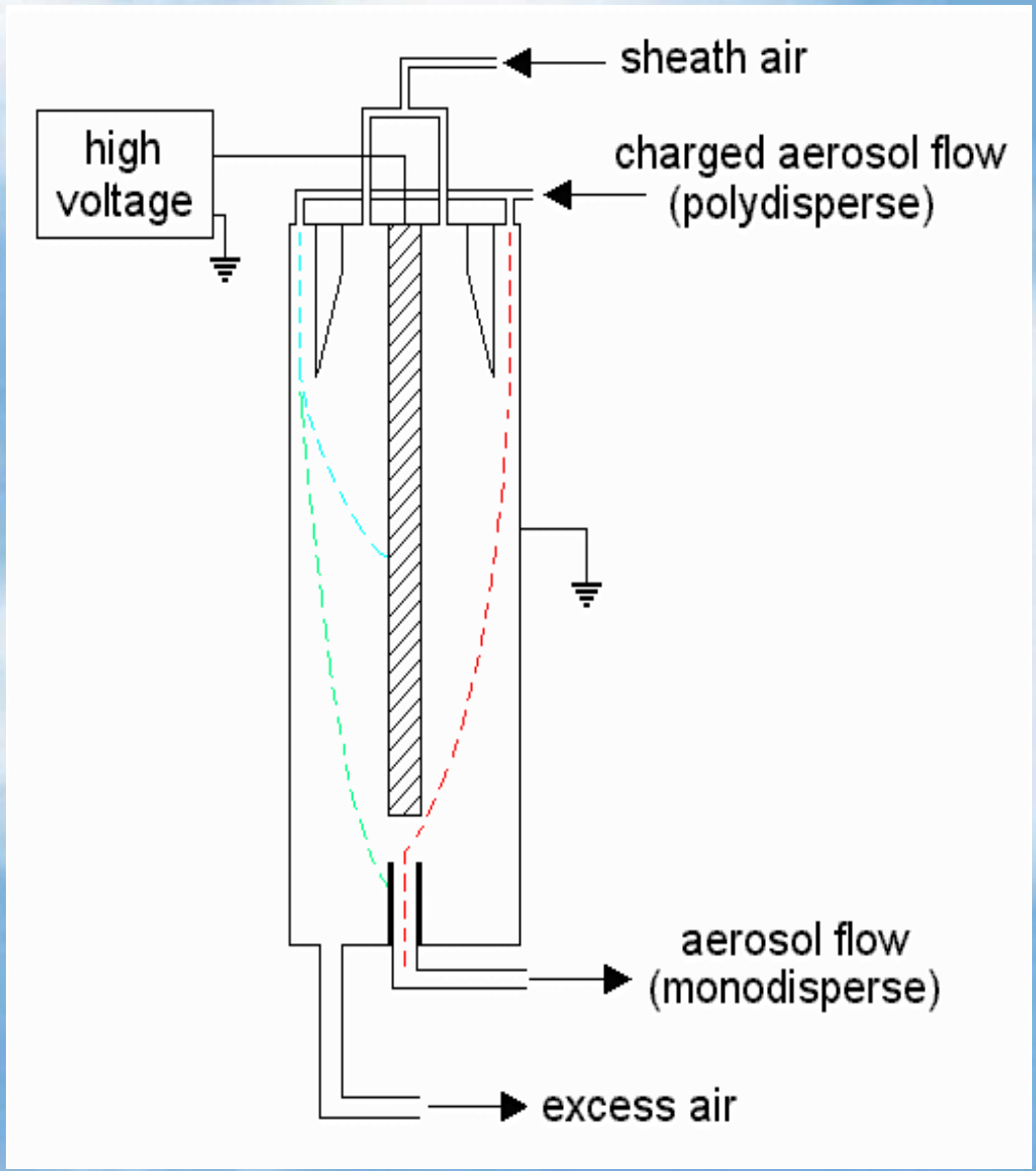
Classification – Differential Mobility Analyzer (DMA)



d = 7 nm to 500 nm

Size distribution when combined with a CPC

= SMPS (Scanning mobility particle sizer)

Particle number concentrations

- Instrumentation available (CPC, DMA, SMPS etc.)
- High time resolution (hourly values or shorter)
- No standard reference materials for calibration available
- Standardized methods not yet available
- CEN TC 264/WG 32: Attempt to standardize measurements of particle number concentrations in ambient air

Exhaust emission measurements (PMP) and ambient air measurements (Input to discussion of Theses D10 and E4)

Exhaust emissions:

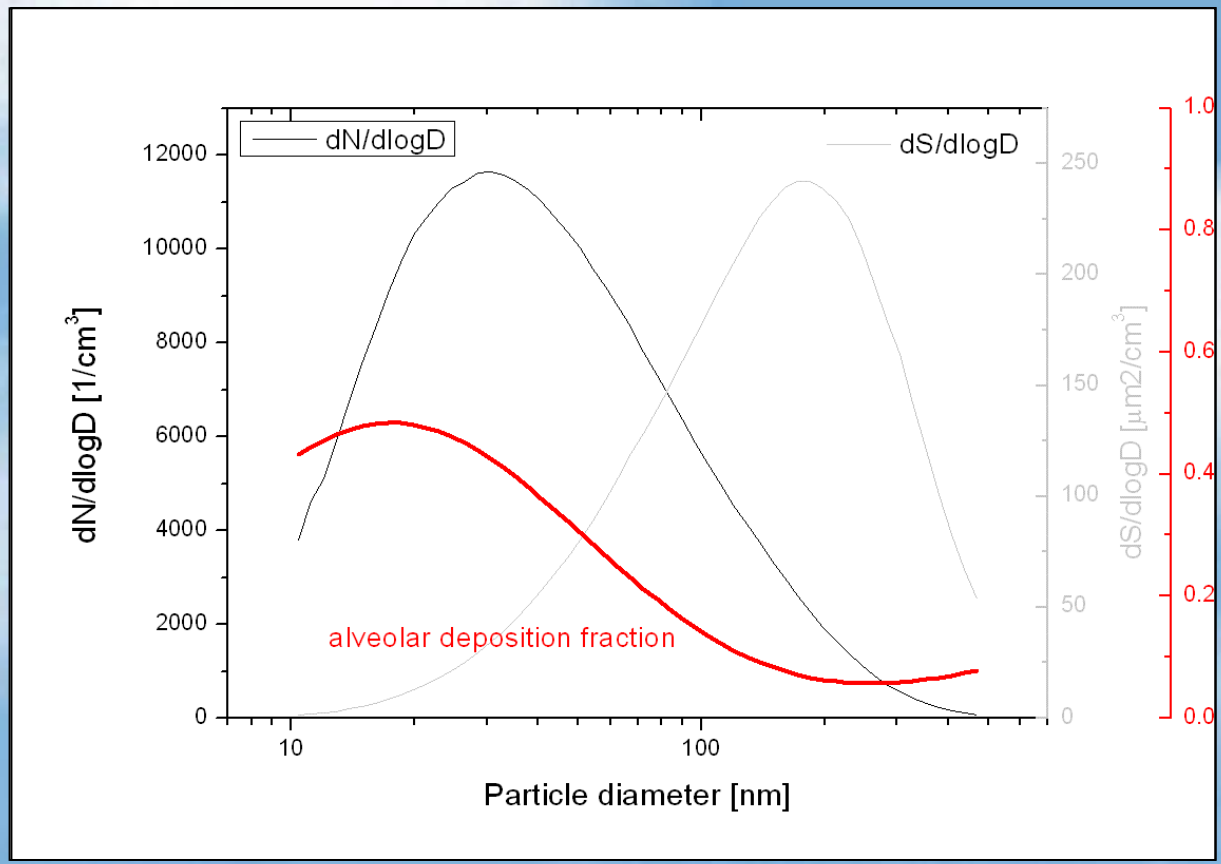
- Counting solid particles < 23nm after dilution, heating and evaporation of volatile material.
- Adequate for hot exhaust gases: Representative capture of solid particles alone, avoiding condensates.

Ambient air:

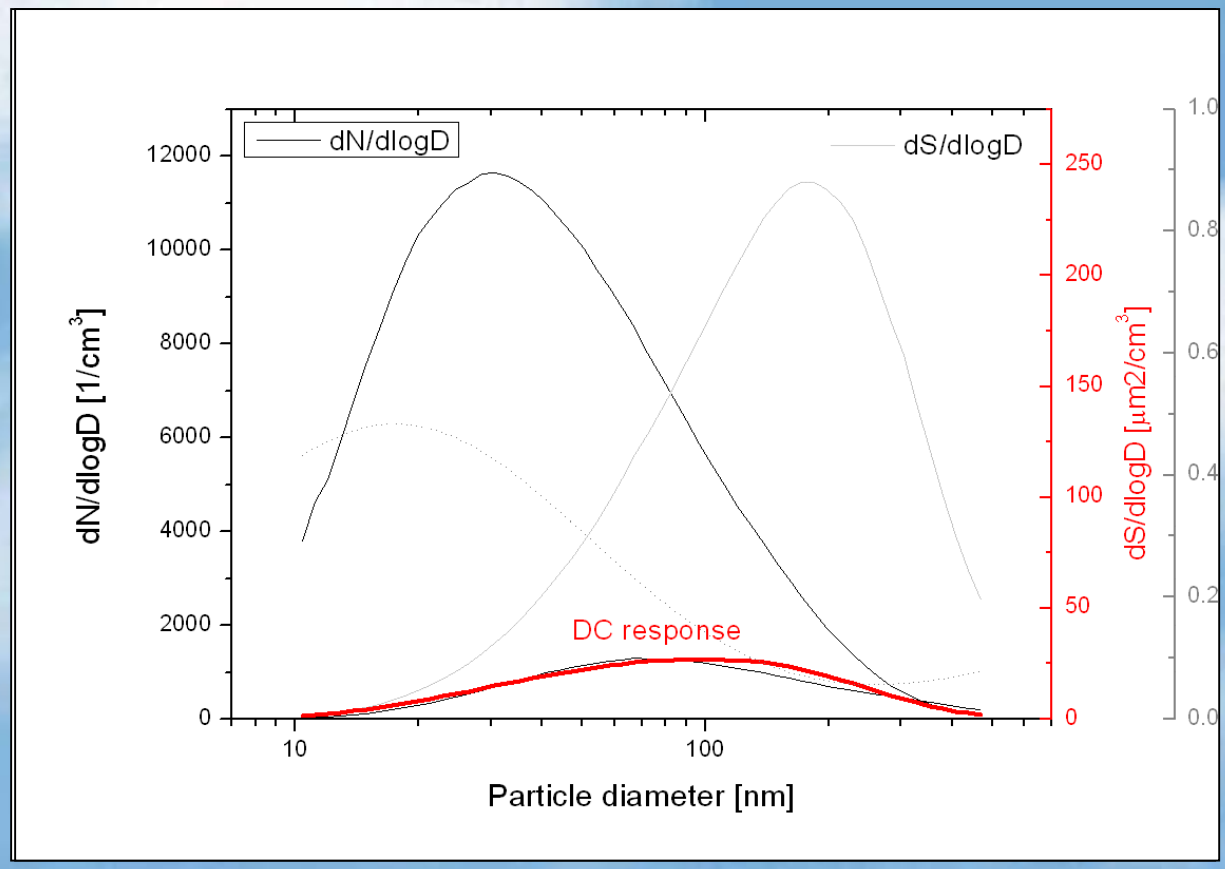
- Broad variety of primary and secondary ultrafine particles.
- PMP method could be used, but cut at 23 nm and heating would neglect possibly important parts of the ambient ultrafine particles.

Particle surface concentrations

Average SMPS data for 2008 (NABEL)



Lung-deposited surface area (LDSA) and diffusion charging (DC)



LDSA and DC response to average Zürich aerosol
(Martin Fierz, FHNW)

Terminology of carbonaceous particles

- **Elemental carbon (EC):**
  Amount of elemental carbon in particles.

- **Organic carbon (OC):**
  Amount of organically bound carbon in particles.

- **Total carbon (TC):**
  EC + OC

- **Black carbon (BC):**
  Metric derived from light absorption of particles deposited on a filter.

- **Black smoke (BS):**
  Metric derived from light reflection of particles deposited on a filter.

Carbonaceous Particles

Thermo-optical methods (EC, OC):

Controlled stepwise burning (defined temperature protocol) of OC and EC deposited on filters, optical control/correction for charing. (EUSAAR2, NIOSH, IMPROVE)

- **Mostly performed as manual method (analysis in the lab)**
- **Medium time resolution (daily values)**

Optical methods (BC, BS):

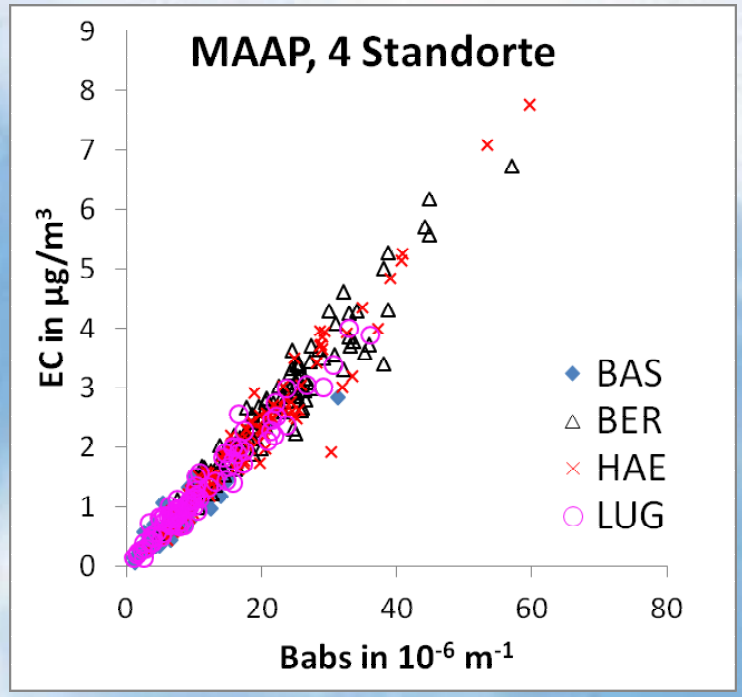
Light absorption (BC) or light reflection (BS) by particles deposited on filters

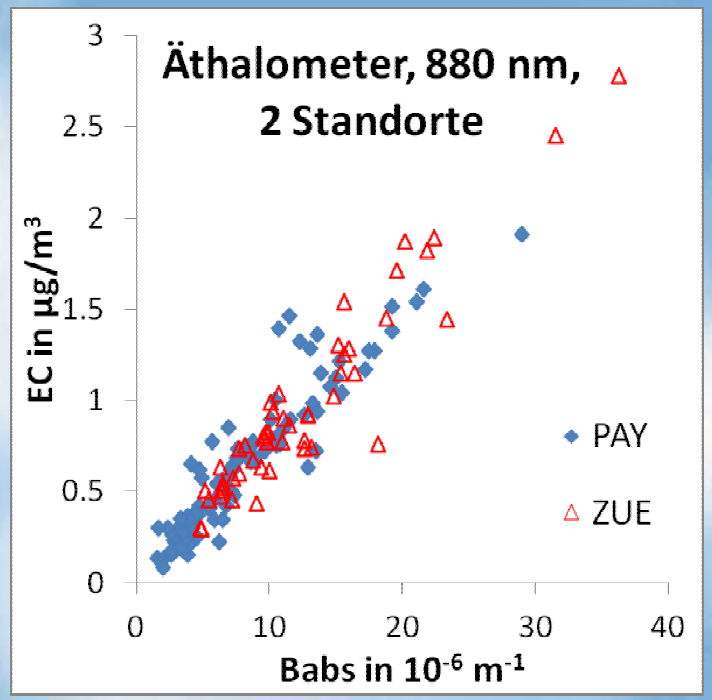
- **Aethalometer, MAAP, reflectometer etc.**
- **High time resolution (hourly values or shorter)**

Carbonaceous particles (CEN TC 264/WG35)

- Standard reference method for EC and OC measurements near to completion (Thermo-optical method, EUSAR2 protocol).
- Technical Report already available (CEN/TR 16243:2011).
- Guidance for using optical methods. How to relate optical data (BC, BS) to reference EC.

Comparison of EC with BC (NABEL)





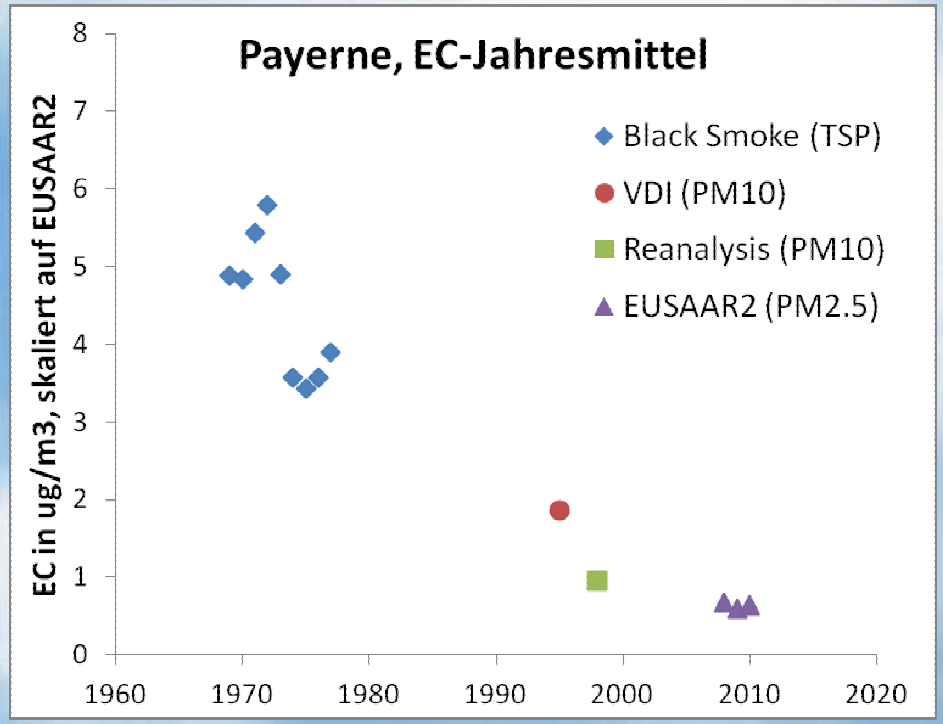
Empirical factor range (NABEL):

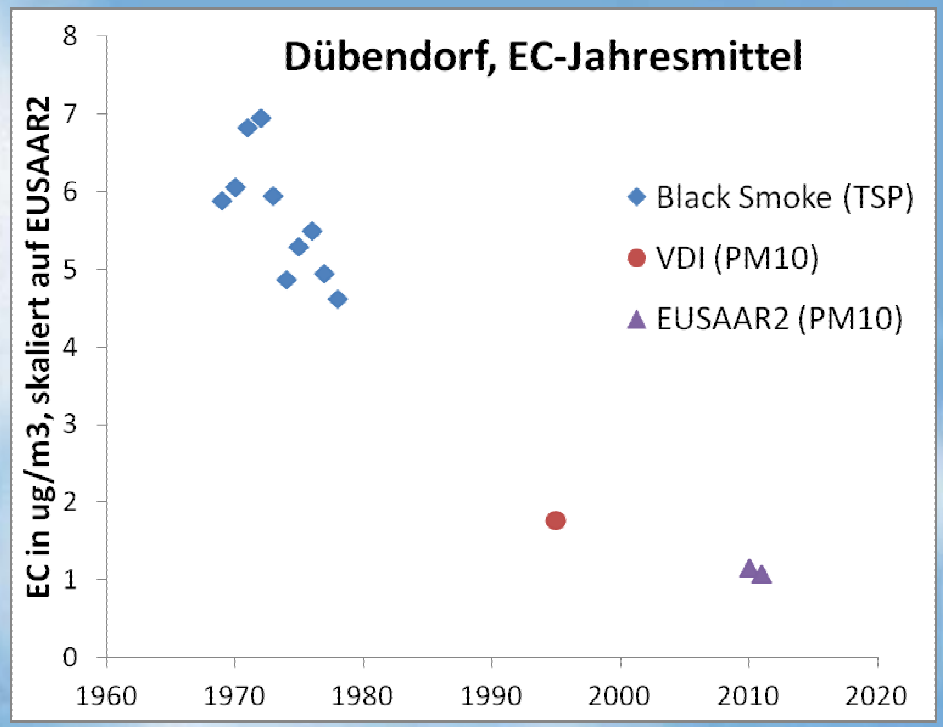
σ_{MAAP} = 8.0 – 9.6 m^2/g

$\sigma_{Äthalometer}$ = 12.1 – 12.9 m^2/g

Variability over time and different sites.

Indicative trend of EC concentrations (NABEL)





Source: R. Weber (BAFU):
Normalized to EUSAAR 2 (Quincey et al., Atmospheric Environment 45, 3528 (2011))

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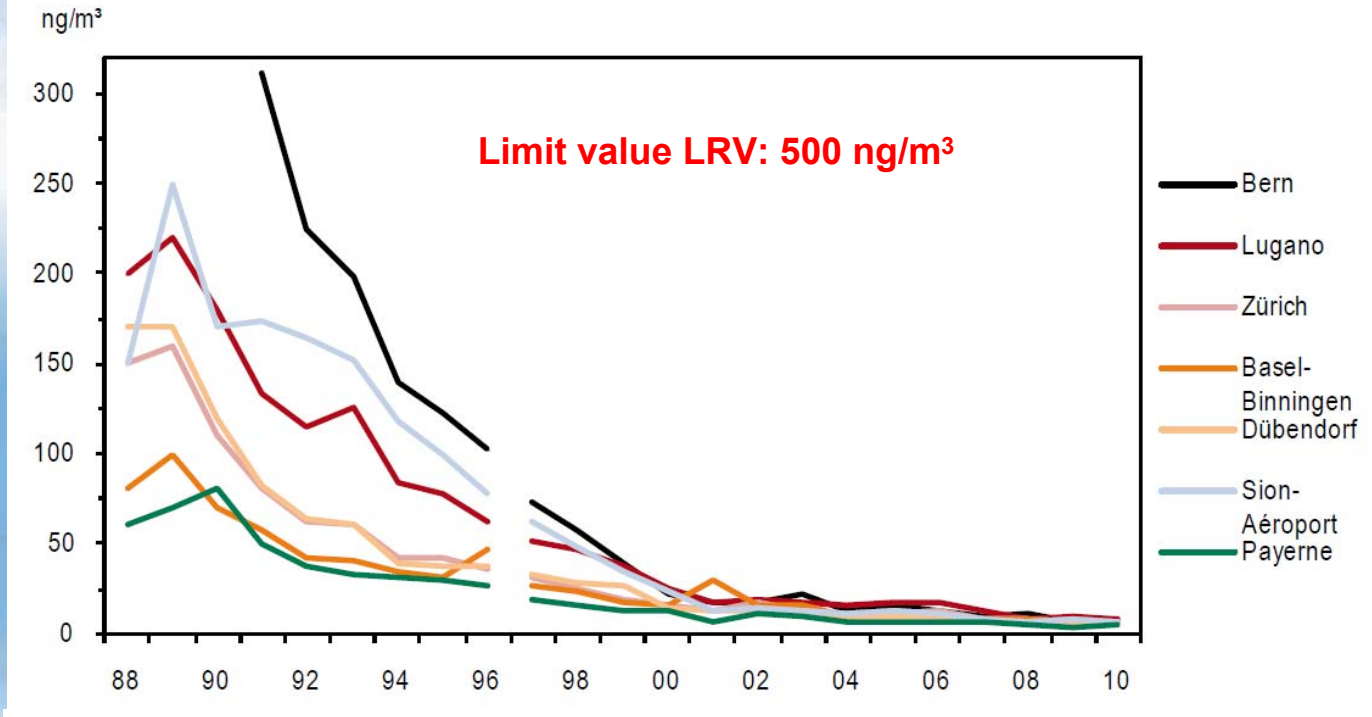
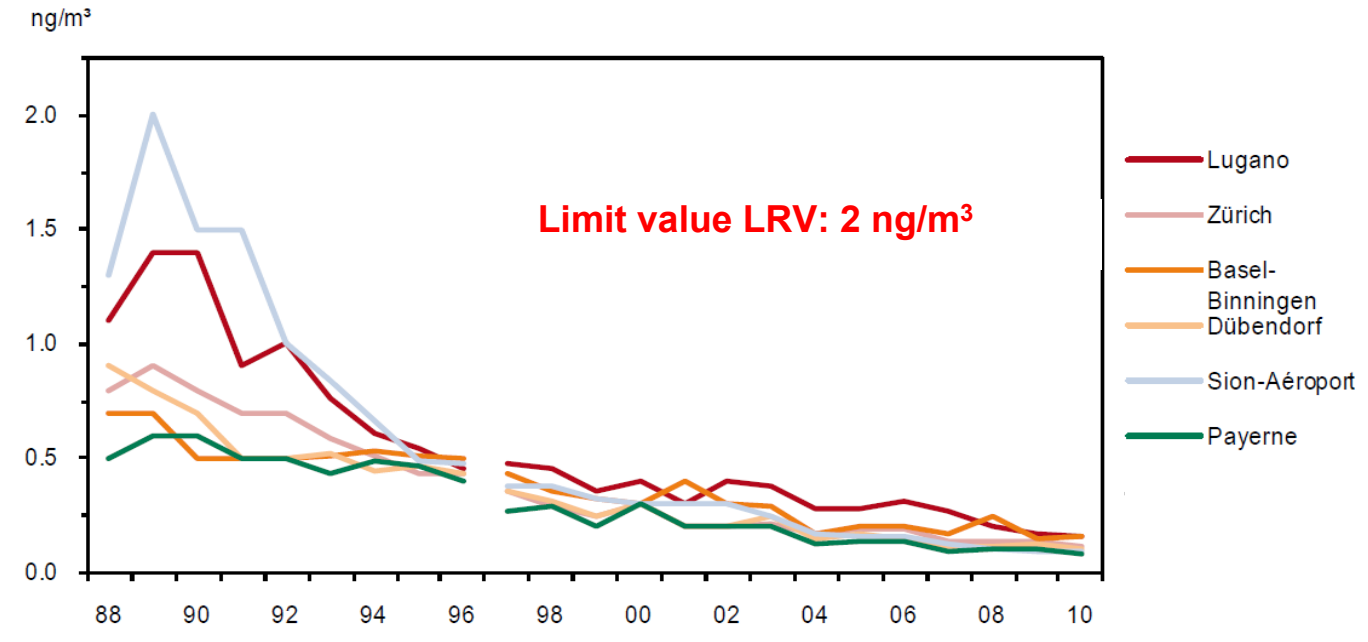
Metals

- Standardized methods available for total metal content in PM (EN 14’902) but not specifically for ultrafine metal particles.
- Requires expensive manual analysis (sampling on filters, laboratory analysis).
- Low time resolution.
- Annual limit values for Pb and Cd (Switzerland) and Pb, Cd, Ni and As (EU).
- On-line XRF monitors under development, but not yet realistic (and too expensive) for routine monitoring.

Lead in PM10



Cadmium in PM10



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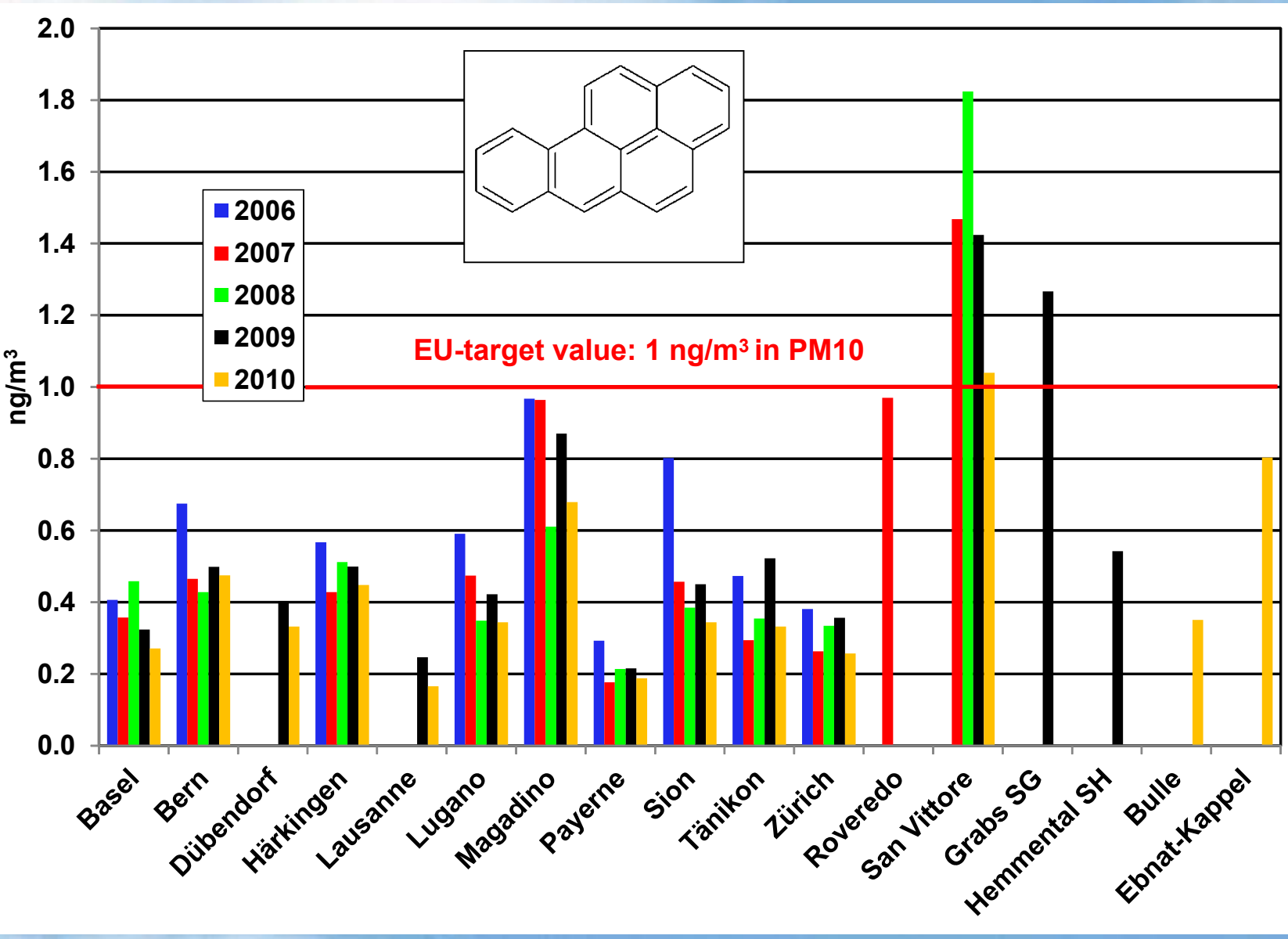
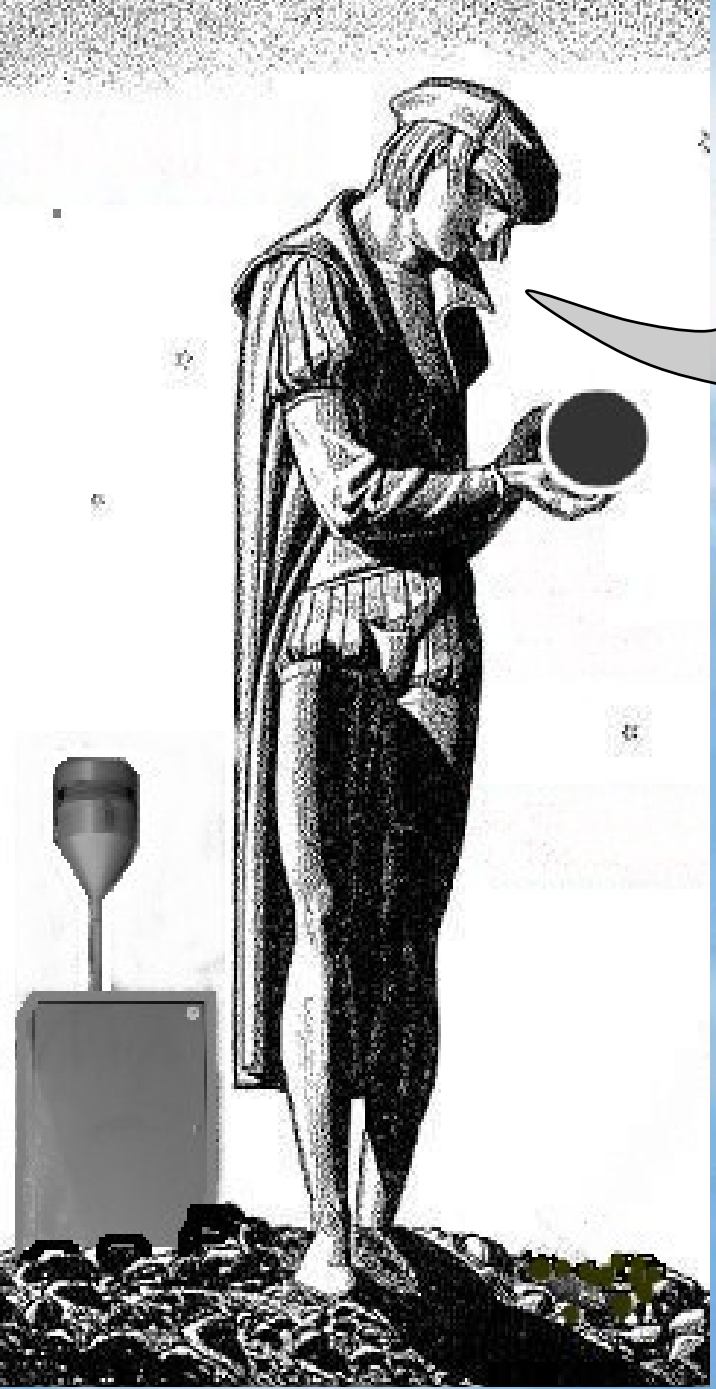
Polycyclic aromatic hydrocarbons (PAH)

- Standardized methods available (EN 15’549).
- Requires expensive manual analysis (sampling on filters, laboratory analysis).
- Low time resolution.
- EU annual target value for benzo(a)pyrene and minimum measurement requirements for some additional PAHs.

Benzo(a)pyren in PM10 (2006 – 2010)





And yet, to me, what is this quintessence of dust?

(Hamlet: Act II, Scene 2)

Summary

	Important?	Standardized measurement technique ready?	Time resolution
Mass concentrations	Yes	Yes	medium/high
Number concentrations	Yes	Not yet	high
Surface concentrations	Yes	Not yet	high
EC, BC	Yes	Soon?	medium/high
Metals	Yes	Yes	low
PAH	Yes	Yes	low