The Abdus Salam
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Workshop on Aerosol Impact in the Environment: from Air Pollution to Climate Change

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Comparison of different real time measurements methods

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Workshop on Aerosol Impact in the Environment: from Air Pollution to Climate Change

The Limits of Aerosol Measurement

Comparison of different real time measurement methods: Gravimetric (BAM & TEOM), OPC, CPC, DMA, DMPS, SMPS™, APS, BC, OC: different suitability for different kind of environmental assessment

Ario A. Ruprecht [a] *, Cinzia De Marco[a] , Roberto Mazza[a] , Grisa Mocnik[b], Constantinos Sioutas[c], Dane Westerdahl[d], Giovanni Invernizzi [a] ,

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*** A.A. Ruprecht e-mail: info@tecanalysis.it**

However the tremendous increase of combustion processes for production of energy, transport, industry manufacturing etc. followed by the industrial revolution increased noticeably the pollution with heavy consequences on the environment as well as on the health of people.

The Aerosol is formed by solid or liquid particles of dimensions and morphology that allow them to remain suspended in the air after they are produced

Some are big enough to be visible as smoke or ashes, but other are so small to be visible only at the electronic microscope

The composition is very variable and is determined by their origin

The official measurement metric of the aerosol is the mass in $\mu g/m^3$ but the number of particles per liter or cc is also considered and used as a parameter in many scientific works

CLASSIFICATION OF PARTICULATE AEROSOL

TSP	Total Suspended Particles
PM_{10}	<= 10 micrometers (μm)
$PM_{2.5}$	<= 2.5 micrometers
PM_1	<= 1.0 micrometers
Ultrafine (UFP or UP)	<= 0.1 micrometers

Note: Normally in all Monitoring Stations operated by the Environmental Protection Agencies only the mass in $\mu g/m^3$ of PM_{10} and $PM_{2.5}$ is measured and used for epidemiological studies

But the measurement of the PM aerosol is not as easy as the measurements of other gaseous pollutants such as NOx, SO_2, CO, VOC, CO_2 etc. All these pollutants are well identified in their chemical and physical characteristics and also in their health effects

The measurement principles of these analyzers, based on UV, IR, chemiluminescence etc. can produce very accurate and precise values thanks to the possibility to be calibrated using gas cylinders with a known and certified concentration of gas to be measured

Unfortunately these procedures are not applicable to any PM measurements systems since it is not possible to have cylinders of known PM amount and composition

Consequently the only method to know the amount, the toxicity and carcinogenicity of the aerosol is collecting samples on special filters (usually teflon and/or quartz) and proceed with laboratory analysis.

But this procedure is complicated, time consuming and doesn't allow to have informations in real time

However in research projects as well as in the Monitoring Stations it is absolutely necessary to know immediately or in a short time the PM concentrations.

The different technologies that have been developed to measure the PM aerosol in real time are mainly:

Gravimetric automatic (BAM & TEOM), Optical Particle Counter (OPC), Condensation Particle Counter (CPC), Differential Mobility Analyzer (DMA) and Particle Sizer (DMPS), Scanning Mobility Particle Sizer (SMPS™), Aerodynamic Particle Sizer (APS).

Other technologies allow the measurements in real time also of some components of the PM such as the Black Carbon (BC) and the Organic Carbon (OC) in PM

Gravimetric manual system must be used as reference method for mass calibration of all other PM mass analyzers.

GRAVIMETRIC MANUAL

(Reference method)

The air to be measured is sampled by a pump at a known flow through a PM_{10} $PM_{2.5}$ or PM_1 inlet and a pre-weighted, temperature and humidity controlled filter for a programmed time where the particulate matter is accumulated. Mean of the sampling time as mass in $\mu g/m^3$ is determined from the increase in filter mass and volume of air sampled.

The method requires skilled technicians, adequate laboratory equipment and produce the results only after a few days.

However this is the only Reference Method to measure aerosol mass to which all other gravimetric automatic method must refer for calibration (Federal Reference Method in the U.S.A.)

GRAVIMETRIC AUTOMATIC

(Certified as Equivalent to Federal Reference Method)

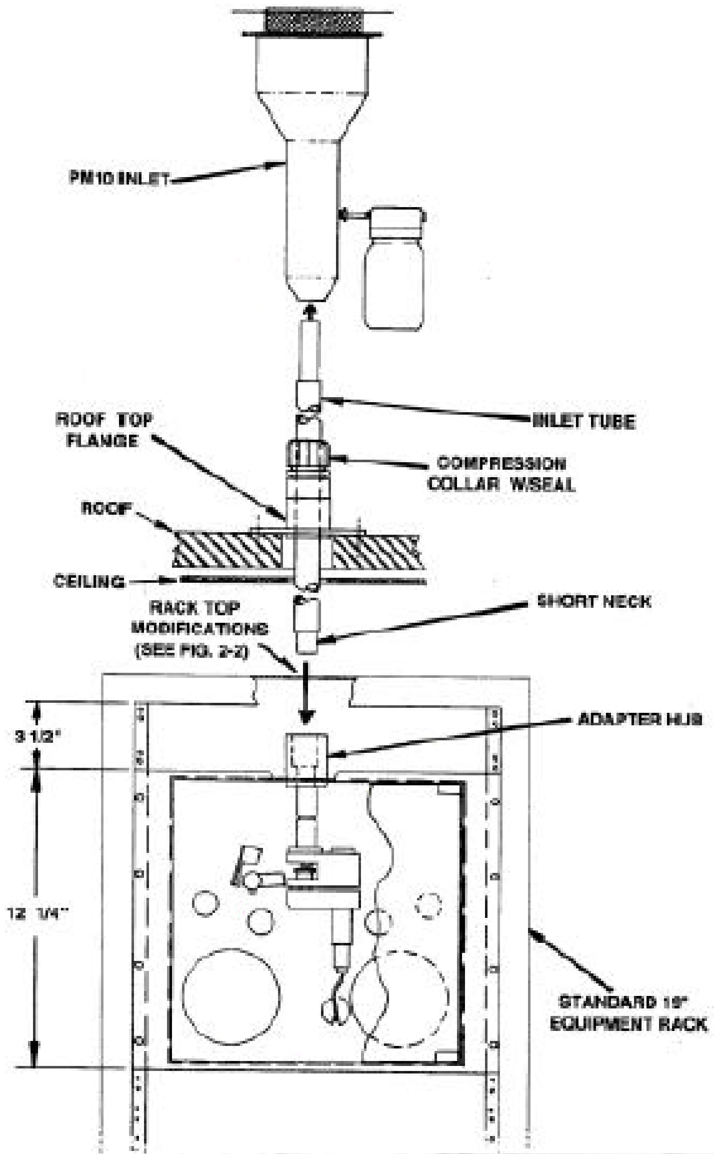
Gravimetric automatic systems are based on two principle of operation: the Beta Attenuation Monitors (BAM) and the Tapered Element Oscillating Microbalance (TEOM). Both systems are delivering the measurements in higly time resolved mass measurements.

The BAM uses beta ray attenuation to calculate collected particle mass concentrations in units of $\mu g/m^3$. A ^{14}C element (<60 µCi) emits a constant source of high-energy electrons, also known as beta particles. The beta rays are attenuated as they collide with particles collected on a filter tape. The decrease in signal detected by the BAM-1020 scintillation counter is inversely proportional to the mass loading on the filter tape.

The TEOM uses a tapered tube fixed on a rigid base, on the top of the narrow end of the tube is mounted a filter which accumulate the particulate. The natural frequency of oscillation of the tube changes as a function of the weight accumulated.

GRAVIMETRIC AUTOMATIC

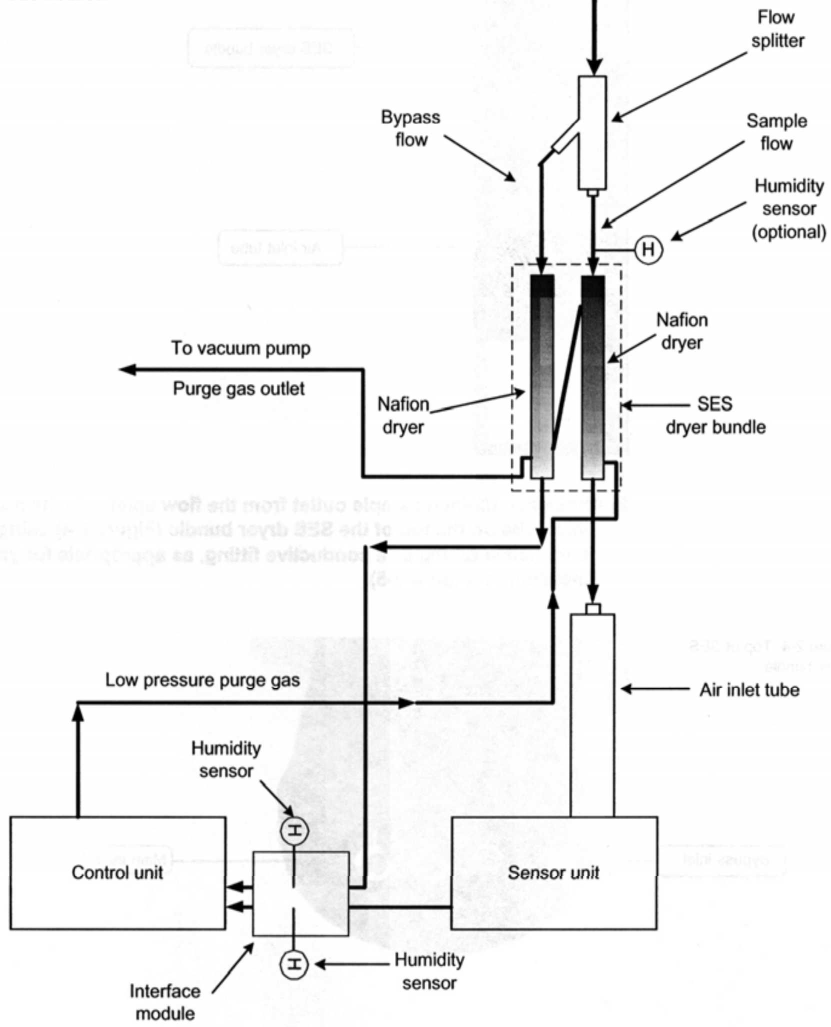
(BAM: certified as Equivalent to Federal Reference Method)



GRAVIMETRIC AUTOMATIC

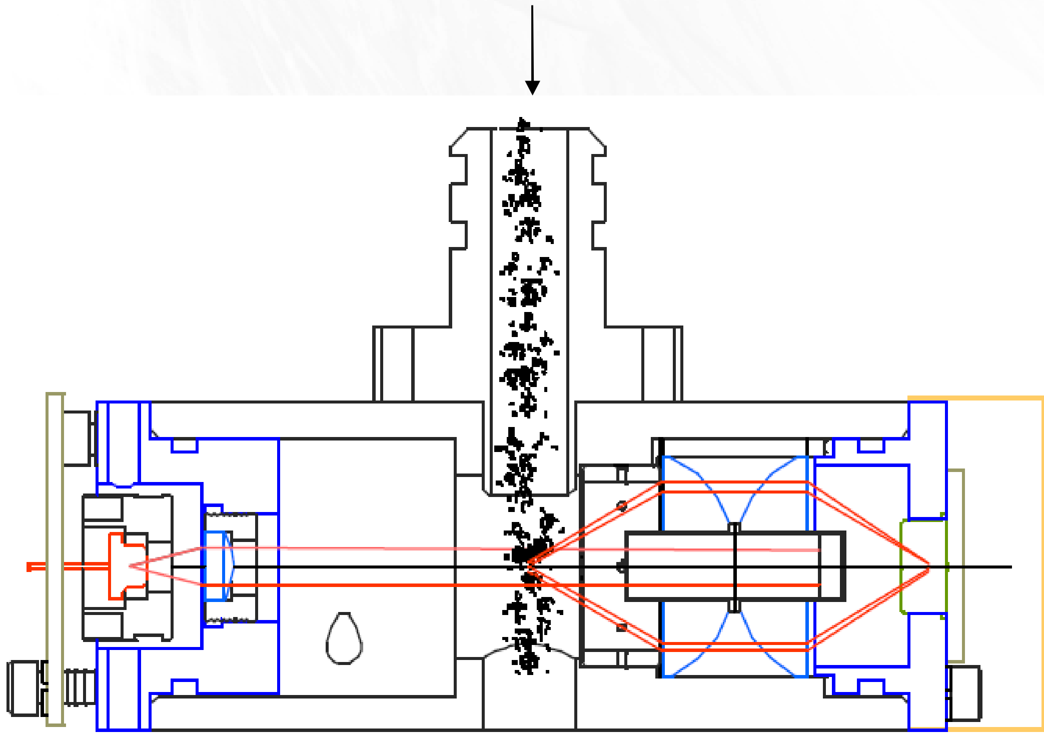
(TEOM: certified as Equivalent to Federal Reference Method)

Figure 2-5. Flow paths in a Series 1400a Monitor with the SES installed.



OPTICAL PARTICLE COUNTER

The basic principle of operation of the Optical particle Counter (OPC) is to measure the amount of light scattered by the particles as they are passing through a laser beam. Part of the scattered light is focused by a mirror/lens system to a photodetector and converted in a voltage pulse. The magnitude of the voltage is correlated with the particle size.



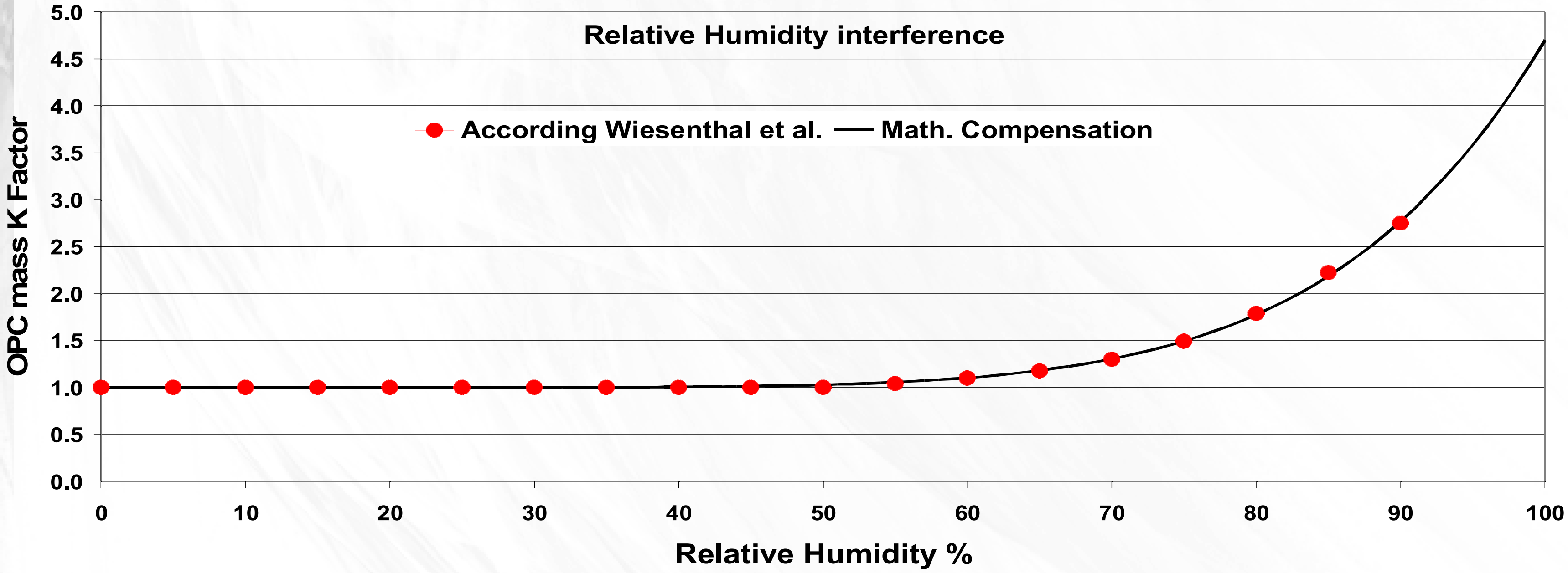
OPTICAL PARTICLE COUNTER

The measurement is possible with very fast sampling time (1 second) and is expressed in number of particles per liter or cc comprised within programmable size intervals, for instance number of particles between 0.3 and 1.0 μm. Multiple size channels ar also possible.

Some models also use mathematical equations for converting the number of particles in mass using a specific gravity factor that must be found only after calibration of each single instrument and for each aerosol type with a gravimetric system (manual or automatic).

All OPCs are unfortunately subject to heavy Relative Humidity interference above 50 % RH that must be eliminated by heating or drying the sample or mathematically compensated.

OPTICAL PARTICLE COUNTER



OPTICAL PARTICLE COUNTER

ADVANTAGES

They provide instantaneous informations, both in number of particles and in mass which is often very important for continuous monitoring and identification of the sources

Several models are portable or palm top and some also suitable for continuous operation in outdoor environments

DISADVANTAGES

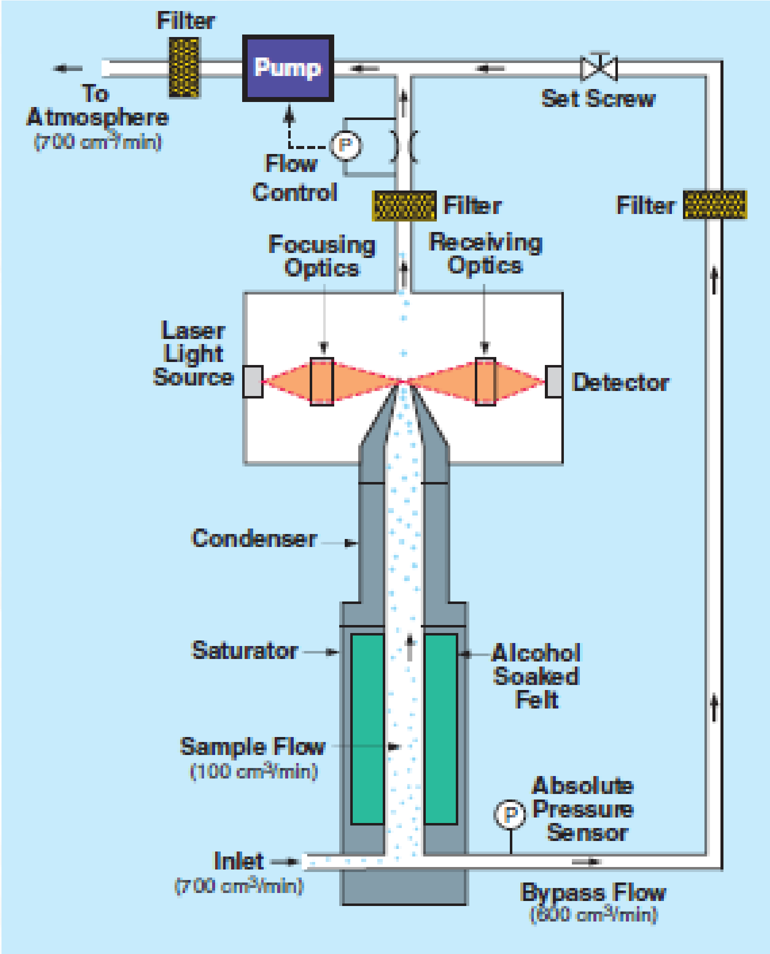
The particles properties such as shape, reflective index, morphology and chemical composition are normally unknown and in the real world very different from the ideal homogeneous sphere and this can lead to significant uncertainties in estimate both the number, size and/or mass of the aerosols.

The lower limit of measurement is about 300 nanometers in diameters since particles smalles are not big enough to produce a signal above noise level

CONDENSATION PARTICLE COUNTER

To solve the problem of the lower limit of 300 nanometer of the OPCs, the Condensation Particle Counters (CPC), operating on the same principle, add the function of growing the particles diameter by condensation in a supersaturated environment until they are sufficiently large to be detected optically above the noise level.

Different substances are used as condensing vapours:*n*-butil alcohol and water are the most common



CONDENSATION PARTICLE COUNTER

ADVANTAGES

CPCs can detect particles as small as 2.5 nm and are extraordinarily sensitive in detecting small amounts of aerosol mass.

Fast response to aerosol concentration changes

Insensitive to chemical composition of the aerosols due to very high supersaturation of the condensing vapours

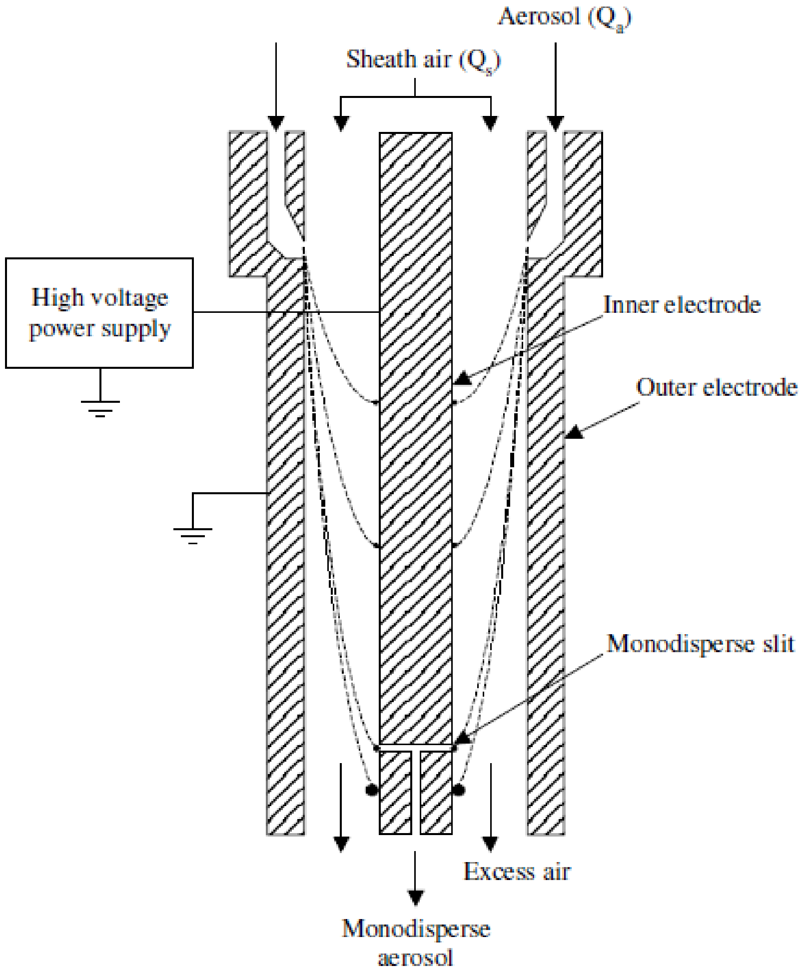
DISADVANTAGES

Possibility to optical floodings

Requires fine adjustments and not very suitable for continuous operation

DIFFERENTIAL MOBILITY ANALYZER

Principle of operation:the Differential Mobility Analyzer (DMA) can be described as an assembly of two concentrically cylindrical electrodes with an air gap between the walls. The sample, exposed to a stream of beta radiations in order to give to the particles a known electrical charge, enter from one end, pass through the annulus and exit the other end. An electric field is applied between the inner and outer electrodes. Particles having a specific electrical mobility exit with the monodisperse air flow through a small slit located at the bottom of the inner electrode.



DIFFERENTIAL MOBILITY ANALYZER

The DMA have been developed and are used because it is of fundamental importance to measure and classify the nanoparticles in the range from 2.5 to 1,000 nm in different fields: materials synthesis, biotechnology, semiconductor manufacturing, pharmaceutical products, nano-composites and ceramics, emission control, health effects etc.

The monodisperse aerosol, with a diameter that is a function of the differential voltages and other parameters, and coming out from the central tube may be directed to one CPC or to a Differential Mobility Particle Sizer (DMPS) or to Scanning Mobility Particle Sizer (SMPS™) to determine the particle concentrations and diameter distribution

These applications will be described in the next slides

DIFFERENTIAL MOBILITY PARTICLE SIZER

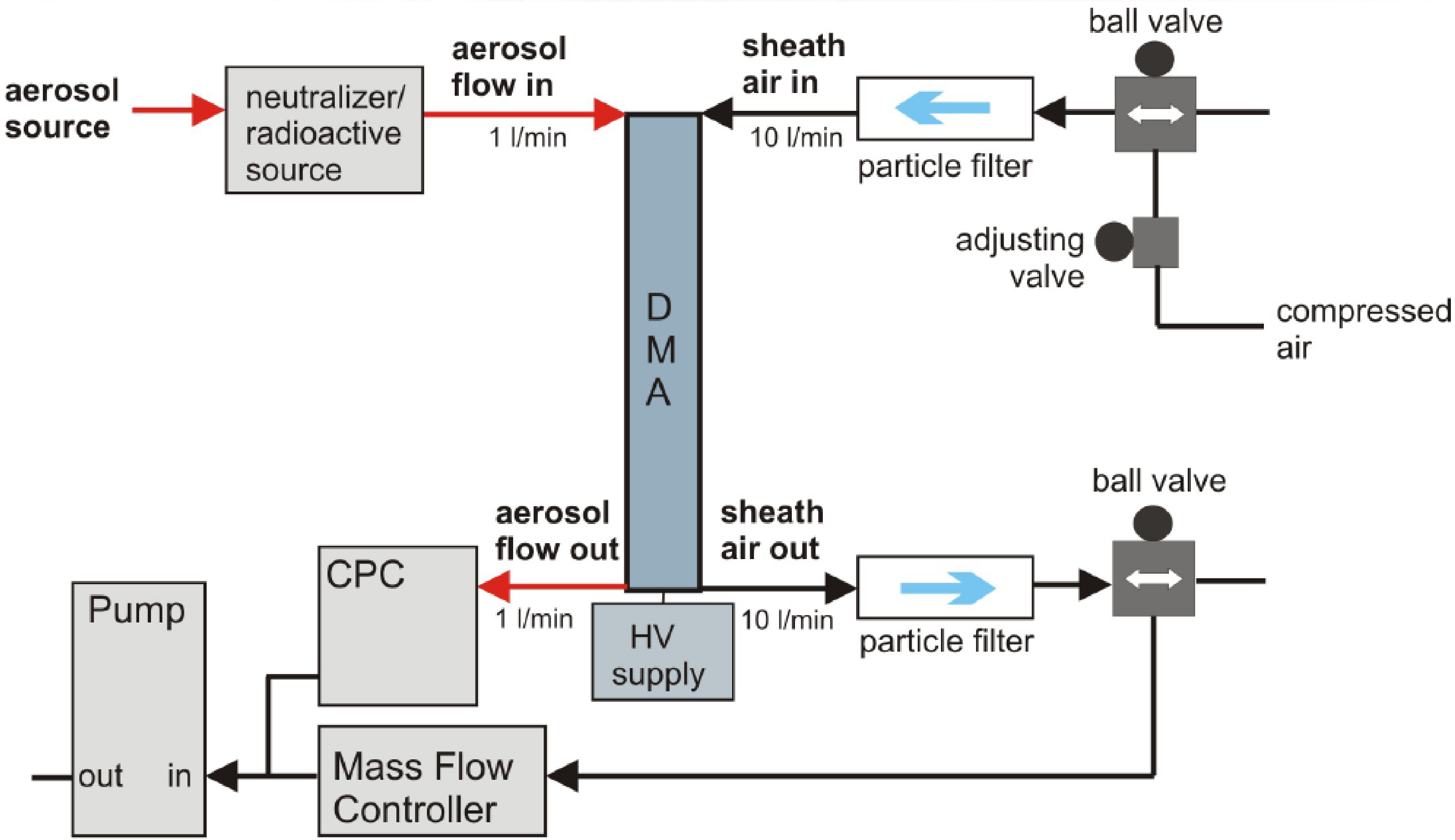
Differential Mobility Particle Sizer (DMPS) is an alternative to OPCs to measure submicrometric particle size distribution since all optical techniques cannot detect particles smaller than 300 nm and also are susceptible to errors in sizing due to changes in shape and refractive index

However DMPS cannot reach the same temporal resolution, typically 1 second response time, of the OPCs because of the time necessary to perform a complete scan

The scan is performed changing the electrode tube voltage both smoothly or in discrete steps

DIFFERENTIAL MOBILITY PARTICLE SIZER

Example of experimental setup



Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

SCANNING MOBILITY PARTICLE SIZER™

One of the most widespread system is the Scanning Mobility Particle Sizer (SMPS™)

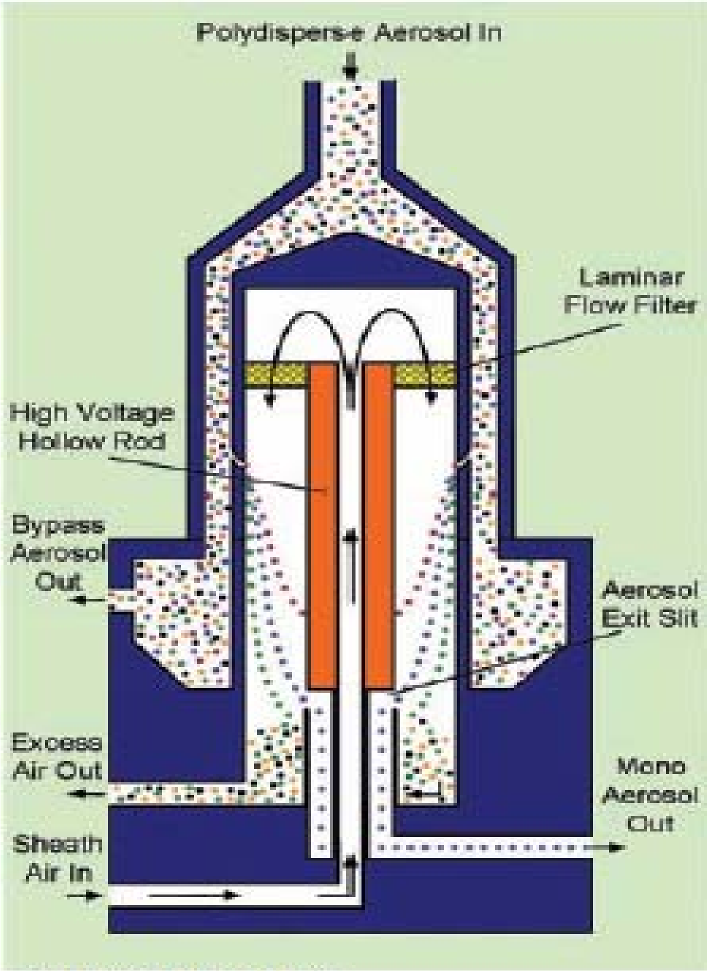
High resolution data: up to 167 particle sizes channels

Broad size range: from 2.5 to1,000 nm

Fast measurement scan

SCANNING MOBILITY PARTICLE SIZER™

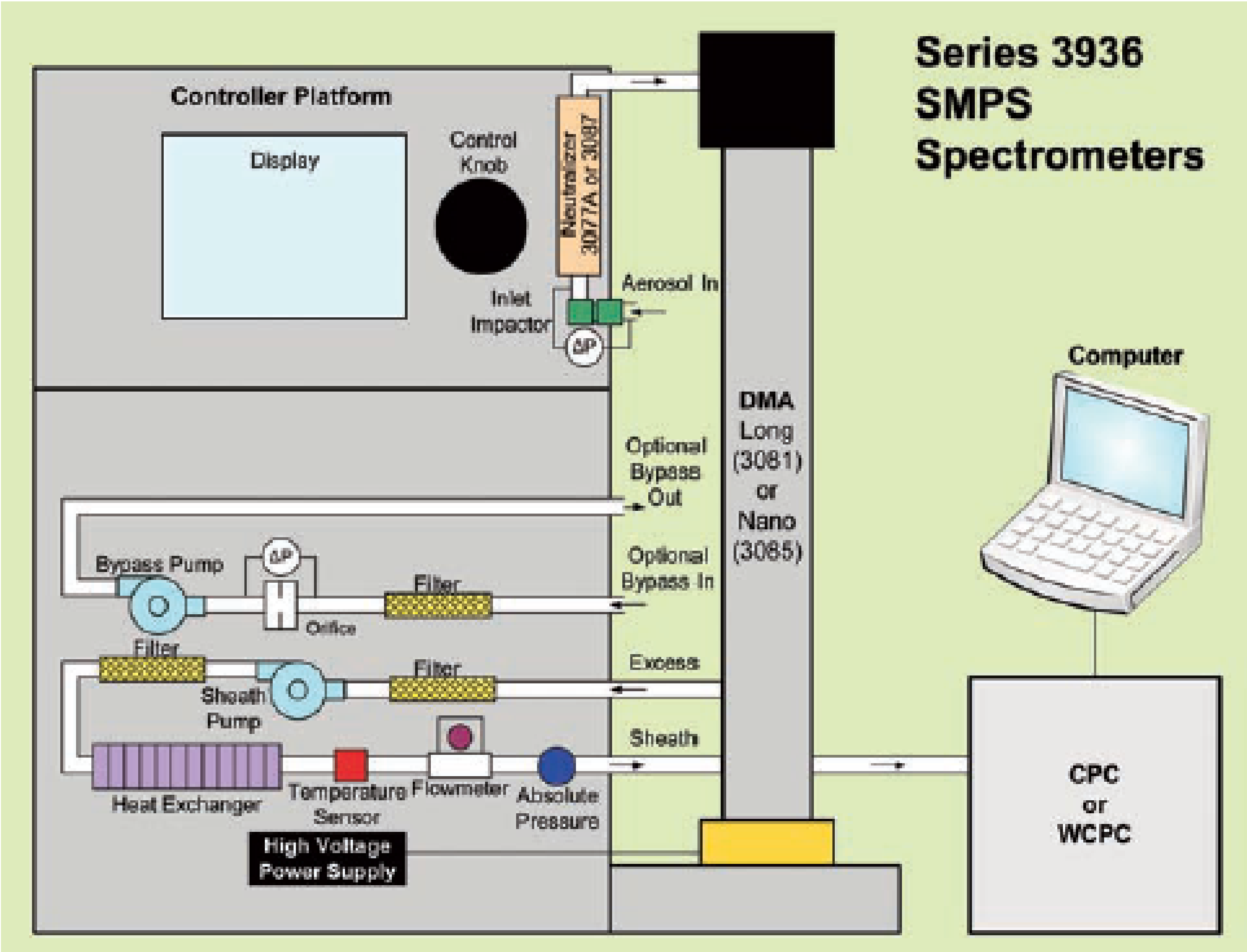
SMPS™ setup (*TSI*)



*US Patents 6, 230,572

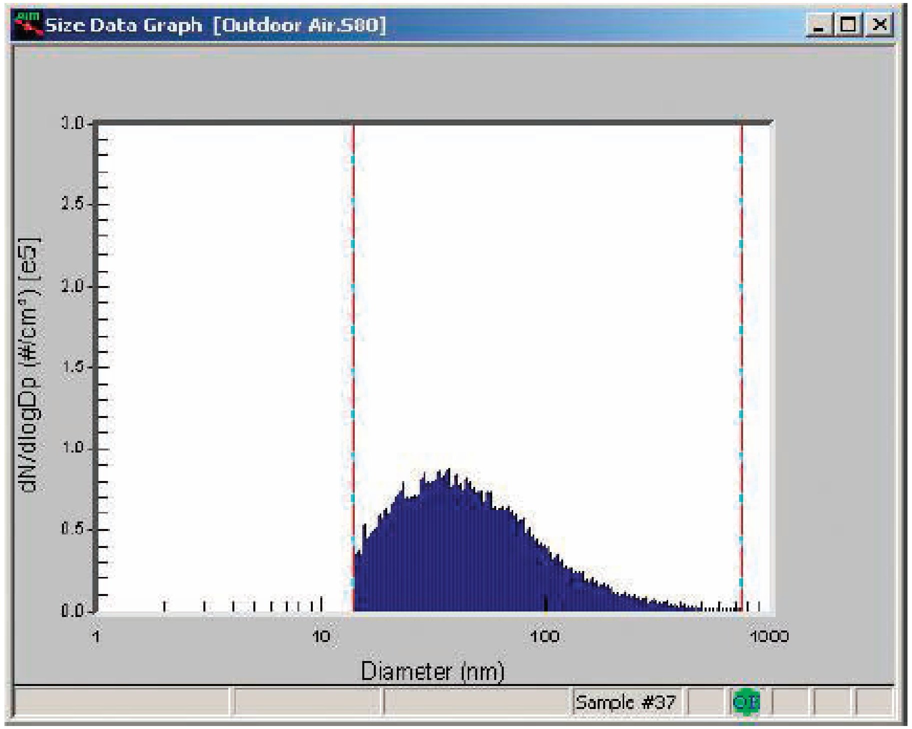
SCANNING MOBILITY PARTICLE SIZER™

SMPS™ setup (*TSI*)

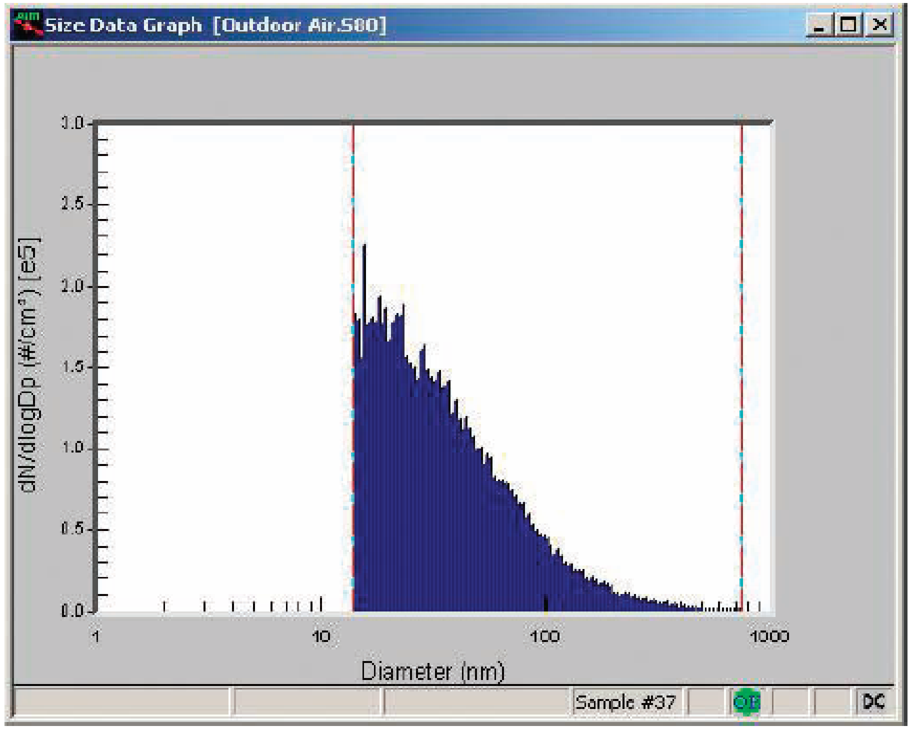


SCANNING MOBILITY PARTICLE SIZER™

Example of measurement of the SMPS™ (*TSI*)



Outdoor air measured with SMPS™ spectrometer *without* the diffusion loss correction.



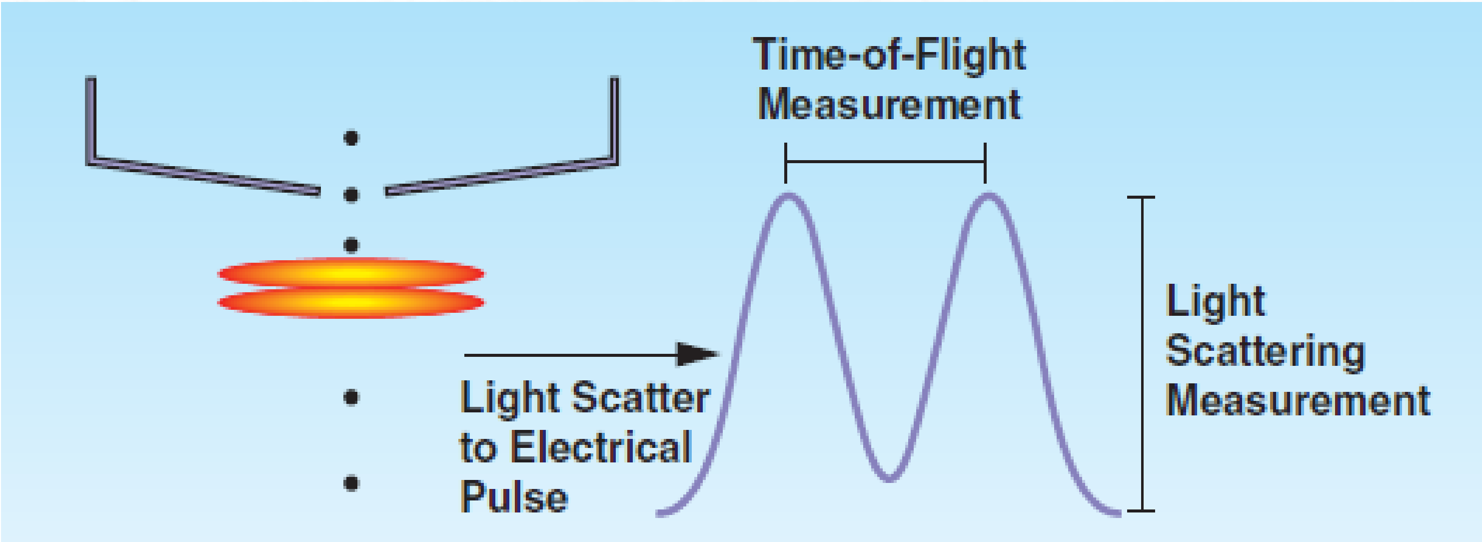
Outdoor air measured with SMPS™ spectrometer *with* diffusion loss correction.

AERODYNAMIC PARTICLE SIZER

A new technology is now available, based on a different principle of operation than that of the OPC, CPC or DMA, which may open new fields of research: the time-of-flight technique (*TSI Model 3321)*

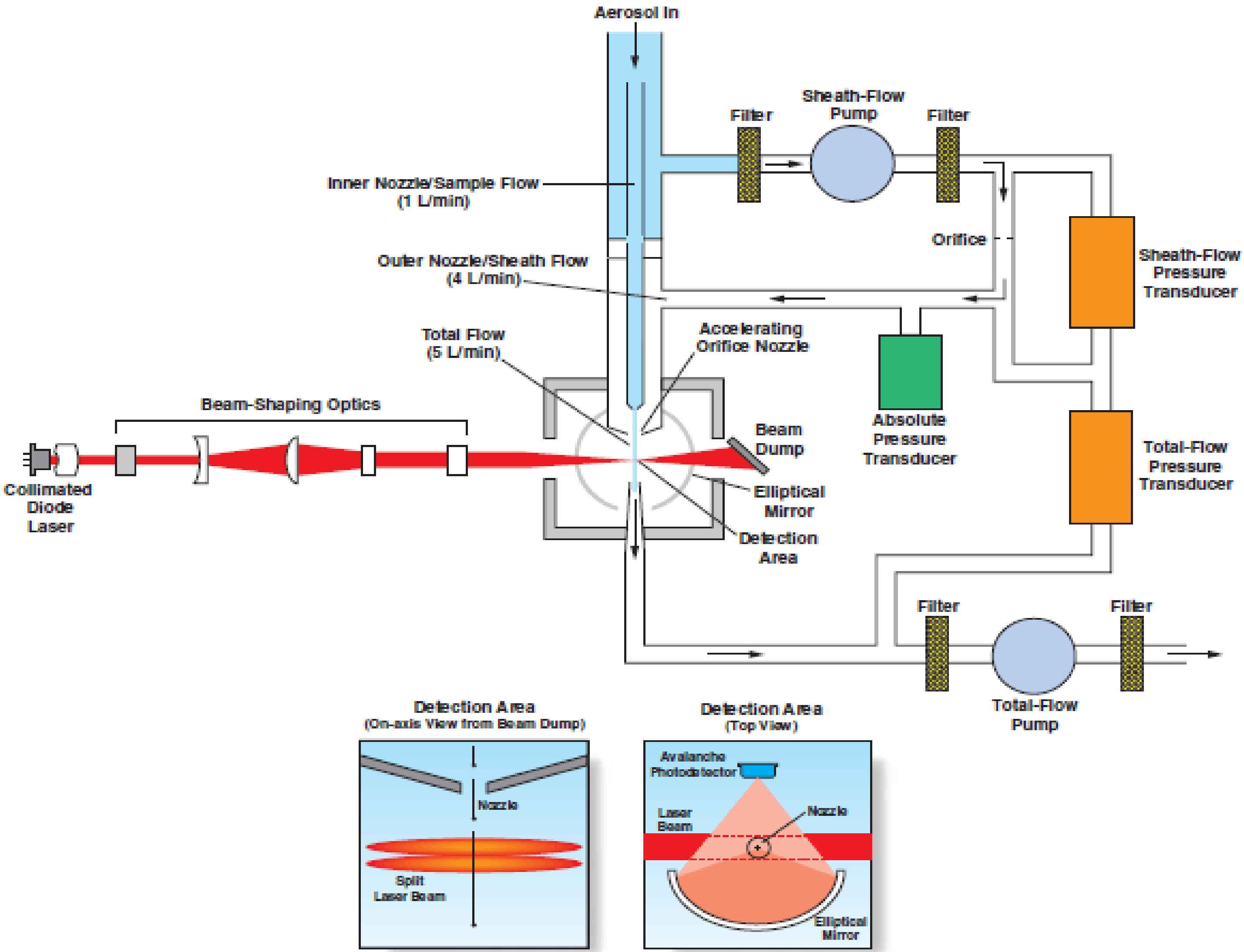
The principle of operation is similar to that of the OPCs, but with important changes: two overlapping laser beams, new optics and nozzle

AERODYNAMIC PARTICLE SIZER



AERODYNAMIC PARTICLE SIZER

TSI Model3321 schematic diagram



AERODYNAMIC PARTICLE SIZER

Aerodynamic diameter. The APS sizes particles in the range from 0.5 to 20 micrometers using the **time-of-flight technique** in real time

Because time-of-flight aerodynamic sizing accounts for particle shape and is unaffected by index of refraction or Mie scattering, it is superior to sizing by light scattering.

In addition, the monotonic response curve of the time-of-flight measurement ensures high-resolution sizing over the entire particle size range.

Relative light-scattering intensity. The APS detects particles from 0.37 to 20 micrometers using the light-scattering technique. While light-scattering intensity is not always a reliable indicator of particle size, it remains a parameter of interest.

The APS keeps this second measurement separate and distinct from aerodynamic size.

AERODYNAMIC PARTICLE SIZER

This is the only method capable of detecting coincidence (coincidence occurs when two particles are aligned when passing through the laser beam,)

The time between the crests provides aerodynamic particle size information. If more than one particle is in the viewing volume, more than two crests appear, and the APS logs this separately as a coincidence event

Converting light-scattering intensity to geometric size often produces inaccuracies when sizing particles of different shapes and refraction indices. The APS measures relative light-scattering intensity, but rather than use it to determine particle size, the APS logs this measurement as a separate parameter.

Light-scattering measurements can be made alone, in addition to aerodynamic diameter, or correlated to aerodynamic diameter on a particle-by-particle basis.

Thus, researchers are able to gain additional insights into aerosol composition.

BLACK AND ORGANIC CARBON

A step forward the possibility to analyze in real time the chemical composition of the PM is the measurement of the Black Carbon (BC) and the Organic Carbon (OC)

BC and OC are produced by incomplete combustion processes of any origin, forest fires, stove and open fires for domestic heating, vehicular emissions, thermal power stations etc. and are an empirical indicators of the precence of particle bound polycyclic aromatic hydrocarbons (pPAH), many of them classified as human carcinogens

BC shows a specific dynamics in diffusion as compared with other PM as shown in the next two slides which make this parameter particularly suitable for traffic proximity pollution measurements

BLACK AND ORGANIC CARBON

Zhu, Hinds, Kim and Sioutas, Journal Air Waste Management Association, 2002

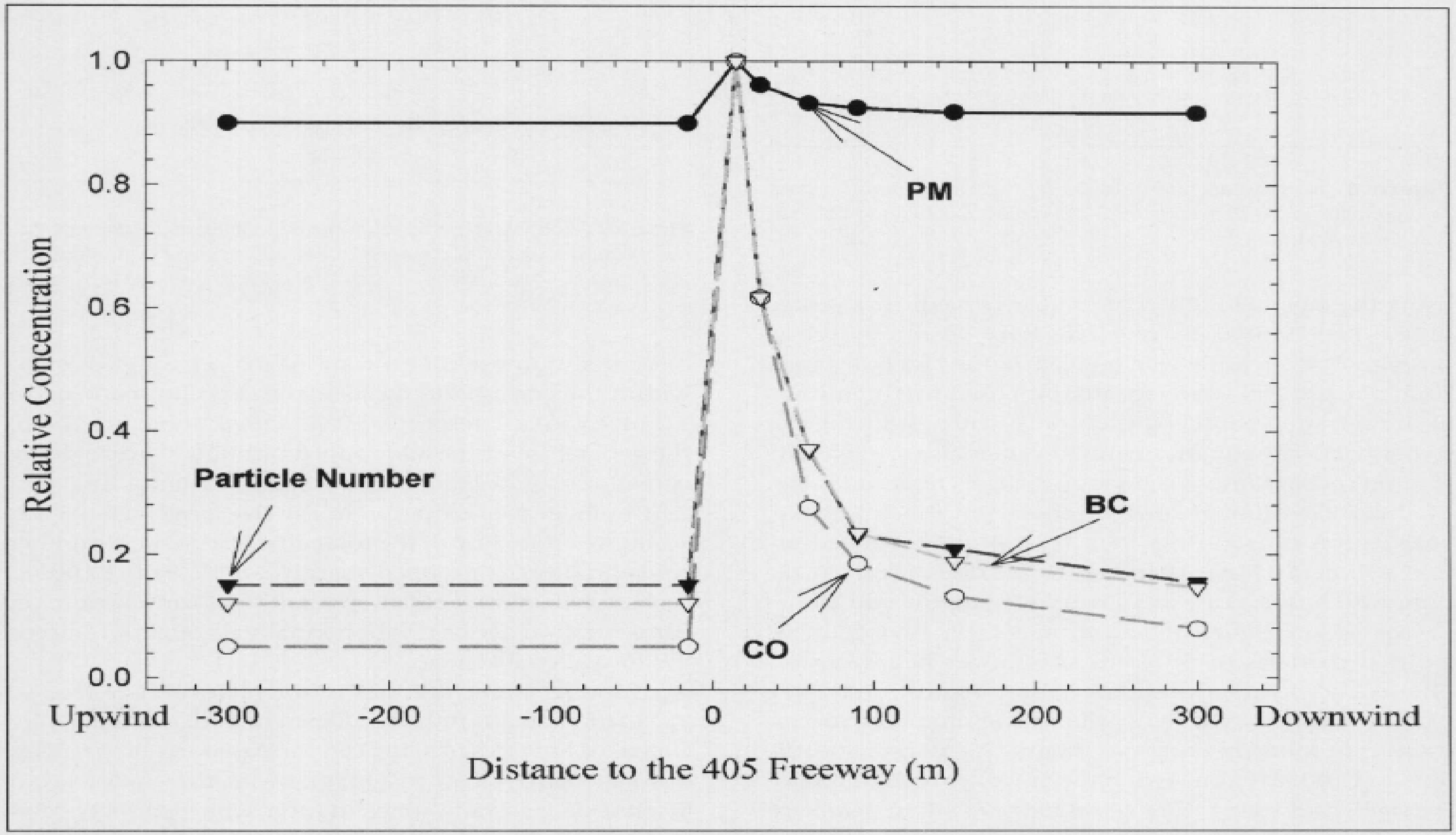


Figure 8. Relative mass, number, BC, and CO concentrations vs. downwind distance.

Measuring Black Carbon and Source Apportionment with Aethalometers

ICTP, 11 Aug 2011

Griša Močnik

Aerosol d.o.o.
grisa.mocnik@aerosol.si

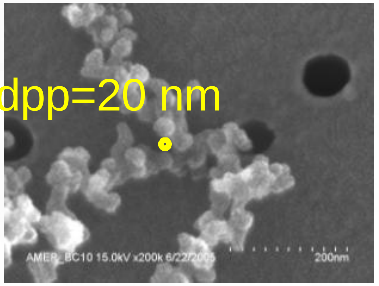
Aerosol Black Carbon

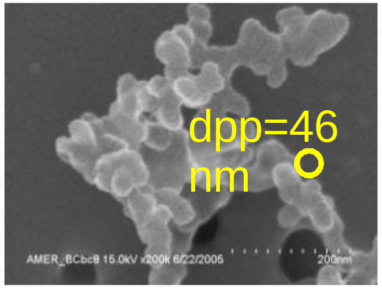
- BC is a product of incomplete **combustion**
- BC not automatically related to CO2 emission
- BC emissions can not be predicted:

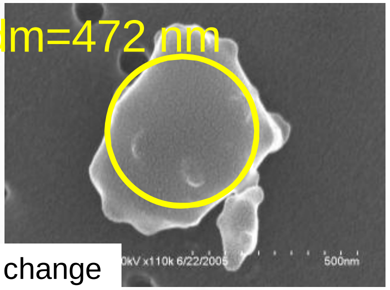
  must be measured

- BC particles from different sources can have different characteristics that produce different effects in the atmosphere:

  (Coal/Diesel/Biomass, USA/Asia/Europe)







Note change in scale

Advantages / Attributes of Optical Analysis

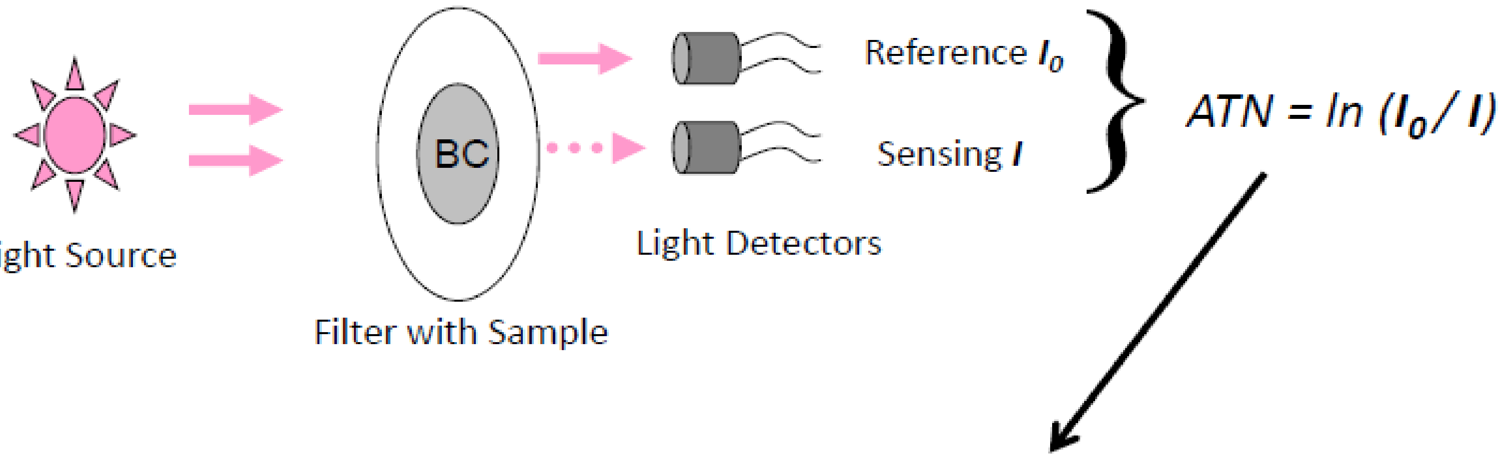
Typical **chemical speciation** time resolution – hours, **day**!

<u>Optical methods – minute!</u>

- Instantaneous
- Non-destructive
- Mobile / Portable
- Added dimension - *time*
- Added dimension – *wavelength*

Optical Analysis Method for Black Carbon

Optical Analysis Method for Black Carbon



$$b_{abs} \sim \Delta ATN$$

Optical absorption

Change of ATN from one measurement to the other

Aerosol

Analytical Instrument : Aethalometer™

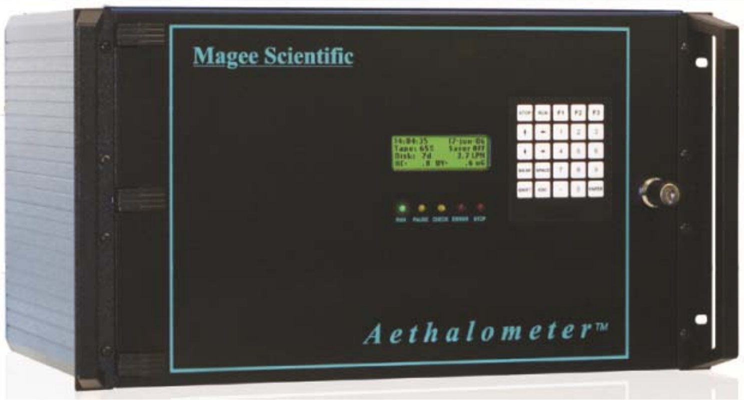
- Collect sample <u>**continuously**</u>.
- ***Optical absorption*** ~ change in attenuation (ATN).
- Measure optical absorption <u>continuously</u> :

  optical wavelengths from 370 nm to 950 nm.
- Convert ***optical absorption*** to ***concentration of BC:***

$$\boldsymbol{BC\ (t, \lambda) = babs\ (t, \lambda)\ /\ \square(\lambda)}$$

- Real-time data: 1 s / 1 min / **5 minutes**
  - <u>*Dynamical, real-time measurement, updated each period*</u>

Aethalometer – Continuous rack mount instruments



AE31 Spectrum – Ambient Air Quality Monitoring

- ✓ ***Seven wavelength (370, 470, 520, 590, 660, 880, and 950 nm)***
- ✓ ***Local source identification***
- ✓ ***Regional, Continental, Global Atmospheric studies***
- ✓ ***Particle size distribution, radiative transfer***
- ✓ ***Climate change, albedo, cloud modification***

EXAMPLES OF MEASUREMENTS

Our Environmental Research Laboratory (LARS) of SIMG, Italian College of GP's is making intensive use of several of the above tecnologies for temporal and spatial diffusion of aerosol pollution both in outdoor and indoor environments.

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Some of our works are shown in the next slides

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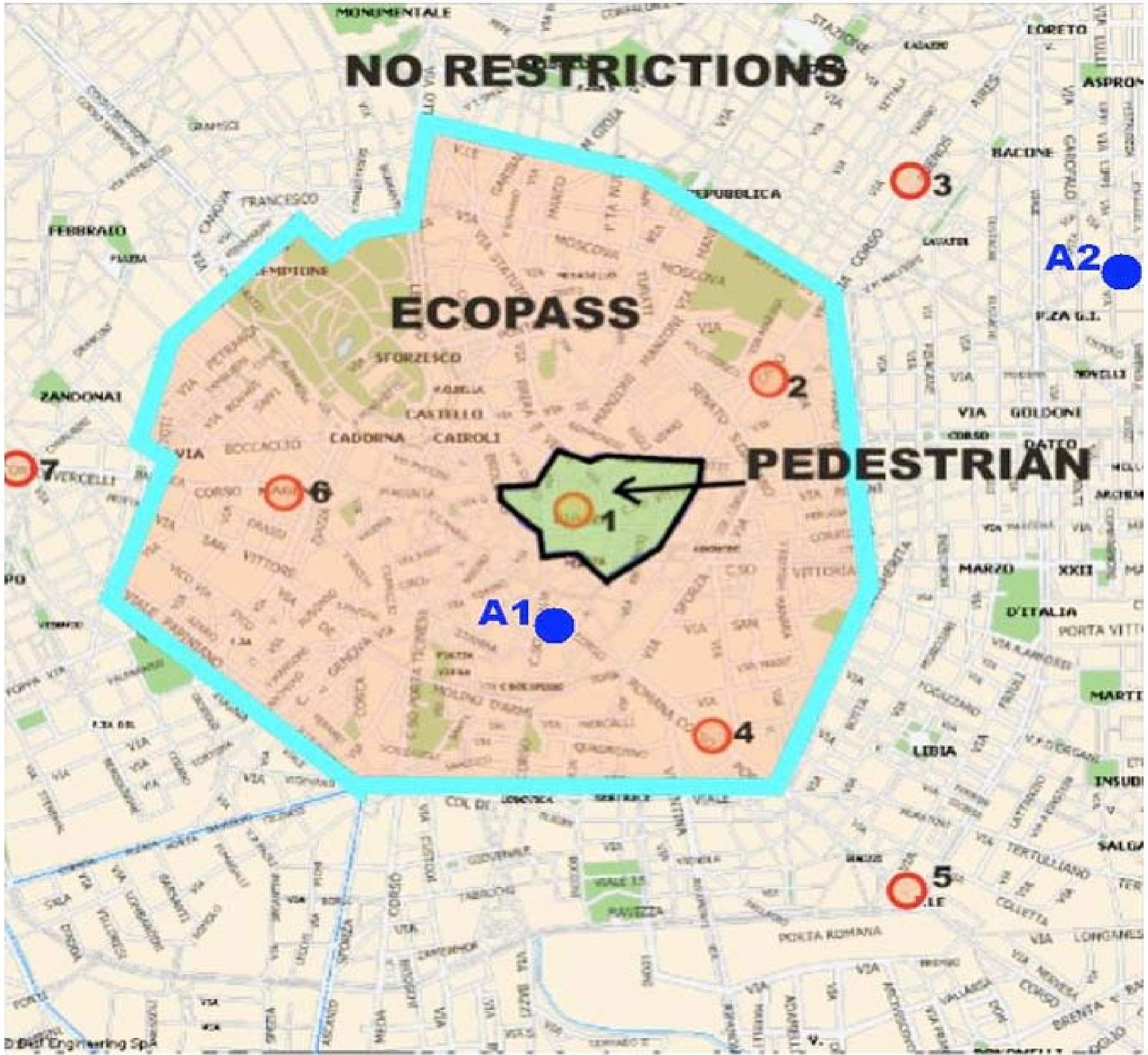
Measurement of black carbon (BC) concentration as an indicator of air quality benefits of traffic restriction policies within the ecopass zone in Milan, Italy



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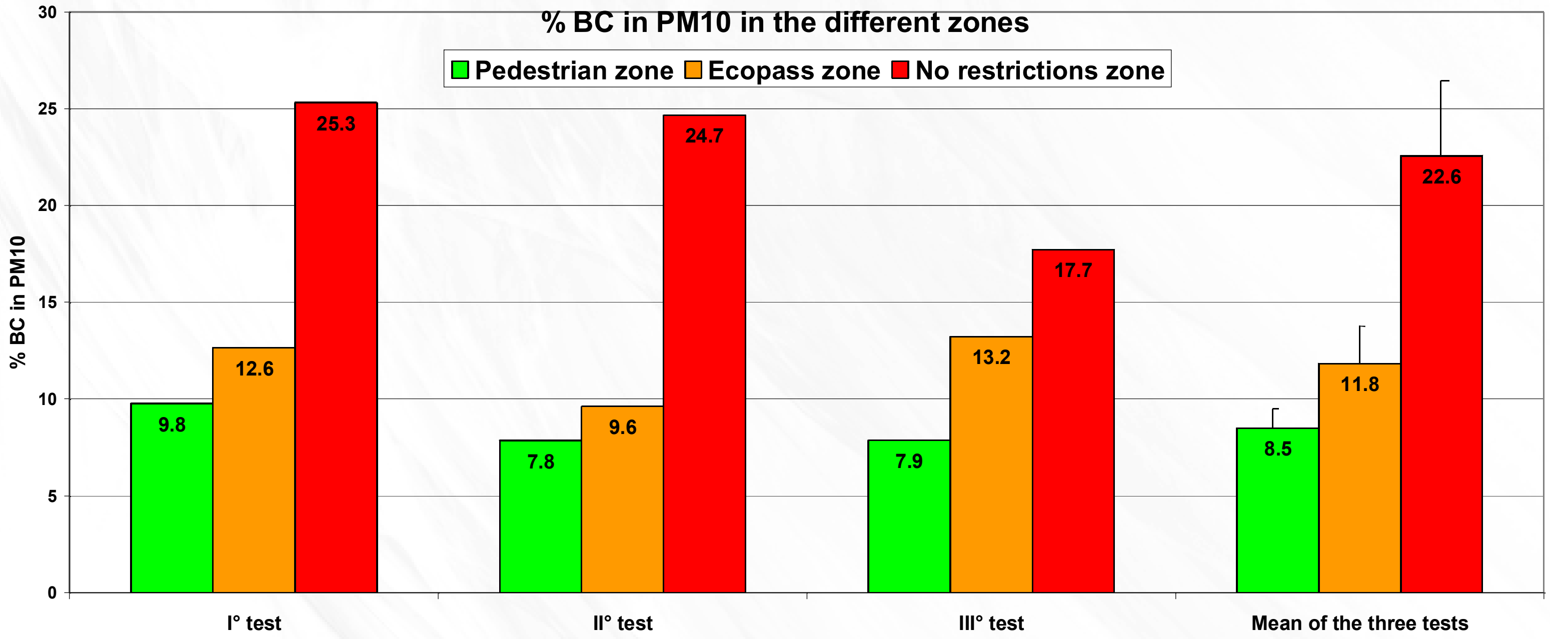

EXAMPLES OF MEASUREMENTS

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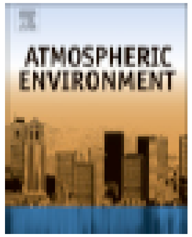


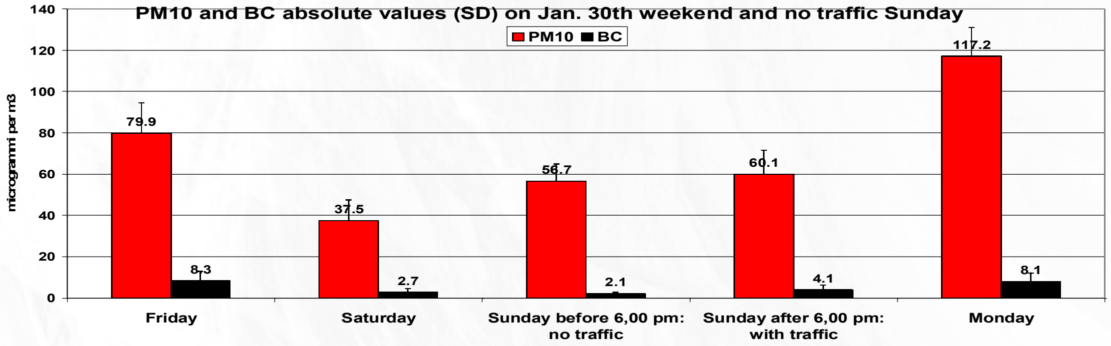
Measurement of black carbon concentration as an indicator of air quality benefits of traffic restriction policies within the ecopass zone in Milan, Italy

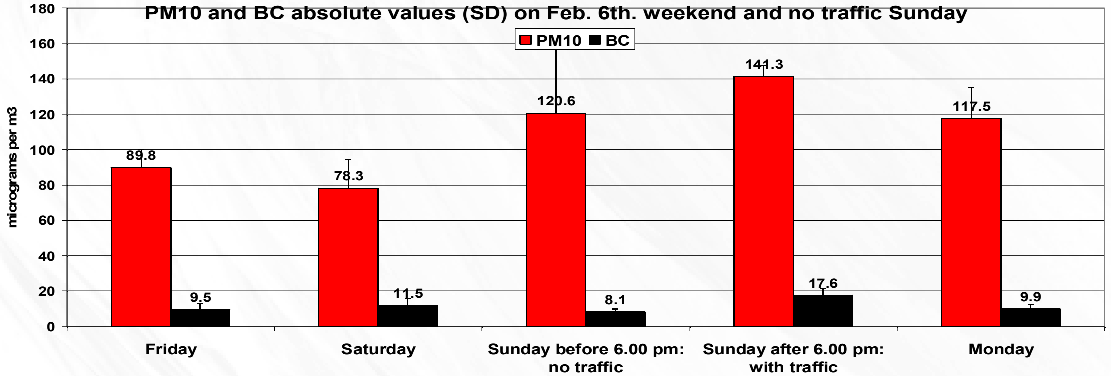
Giovanni Invernizzi [a,*], Ario Ruprecht [a], Roberto Mazza [b], Cinzia De Marco [b], Griša Močnik [c], Costantinos Sioutas [d], Dane Westerdahl [e]

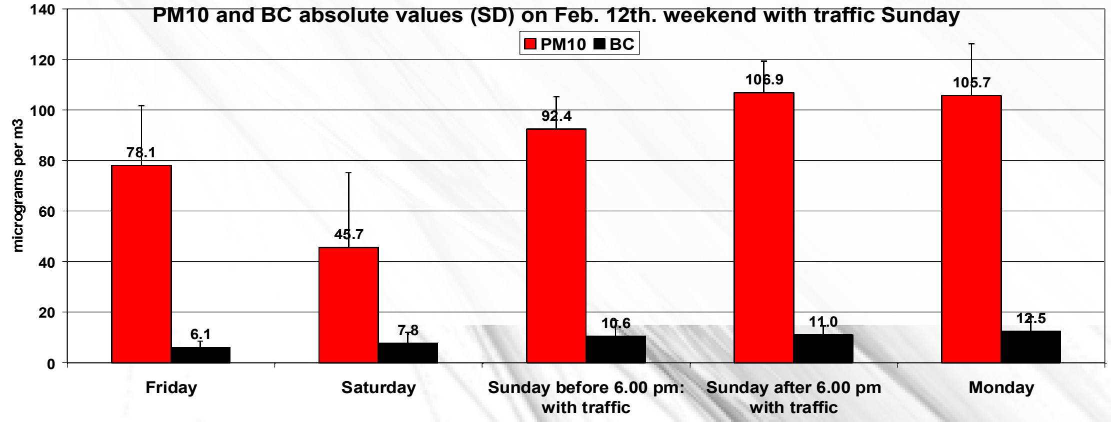
[a] LARS, Environmental Research Laboratory SIMG-Italian College GPs, ISDE-International Doctors for the Environment, Milan, Italy
[b] Istituto Nazionale dei Tumori, Milan, Italy
[c] Aerosol d.o.o., Ljubljana, Slovenia
[d] University of Southern California, Los Angeles, CA, USA
[e] Cornell University, Ithaca, NY, USA

EXAMPLES OF MEASUREMENTS

Results of monitoring campaign about the impact of no-traffic Sunday's on atmospheric pollution: a scientific breaking news for the City of Milan







EXAMPLES OF MEASUREMENTS

Influence of Outdoor Smoking on Outdoor Urban Pollution PM and Black Carbon Concentration Measurement at Fixed Monitoring Stations over a Typical Summer Weekend in the Pedestrian Brera Historical District of Milan, Italy

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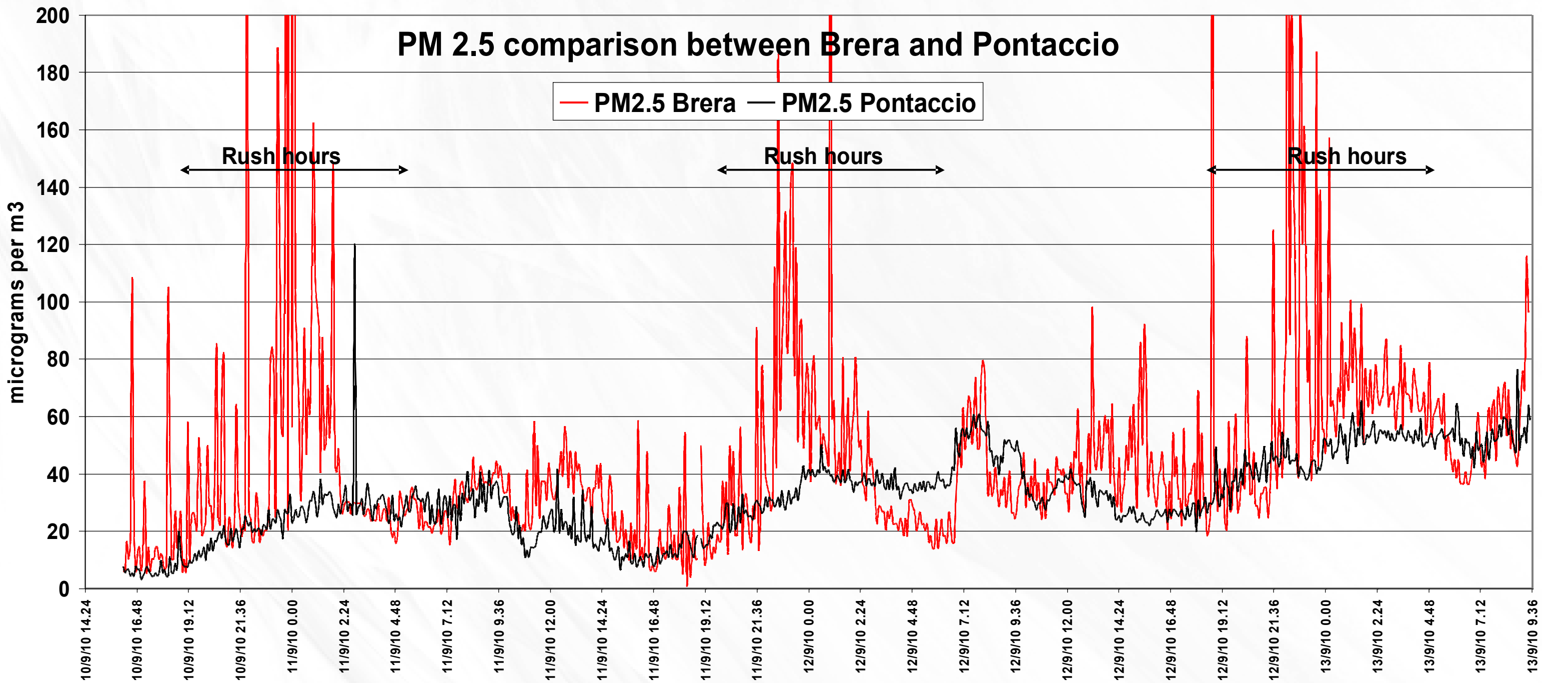

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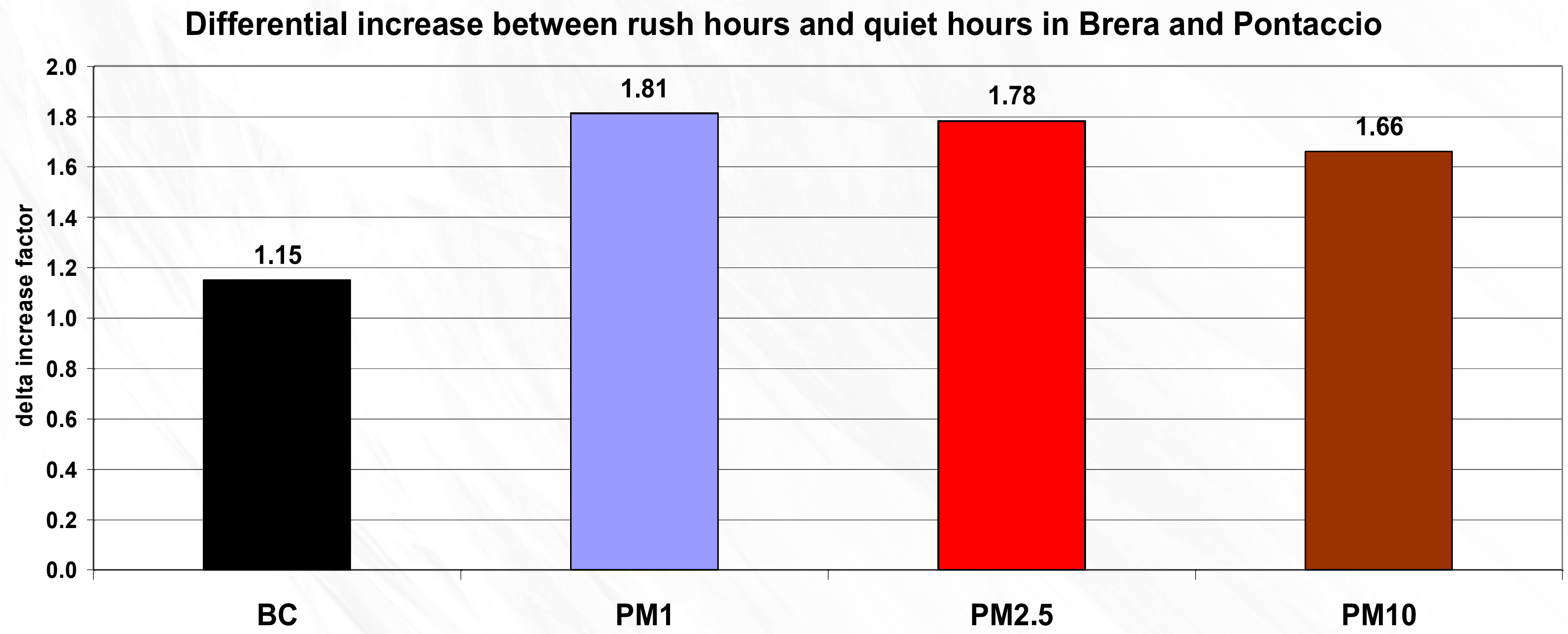

Nicotine was detected only in the pedestrian but not in the open to traffic street

EXAMPLES OF MEASUREMENTS

Influence of Outdoor Smoking on PM and Black Carbon (BC) Concentration Measurement during a soccer game in the Meazza Stadium of Milan, Italy

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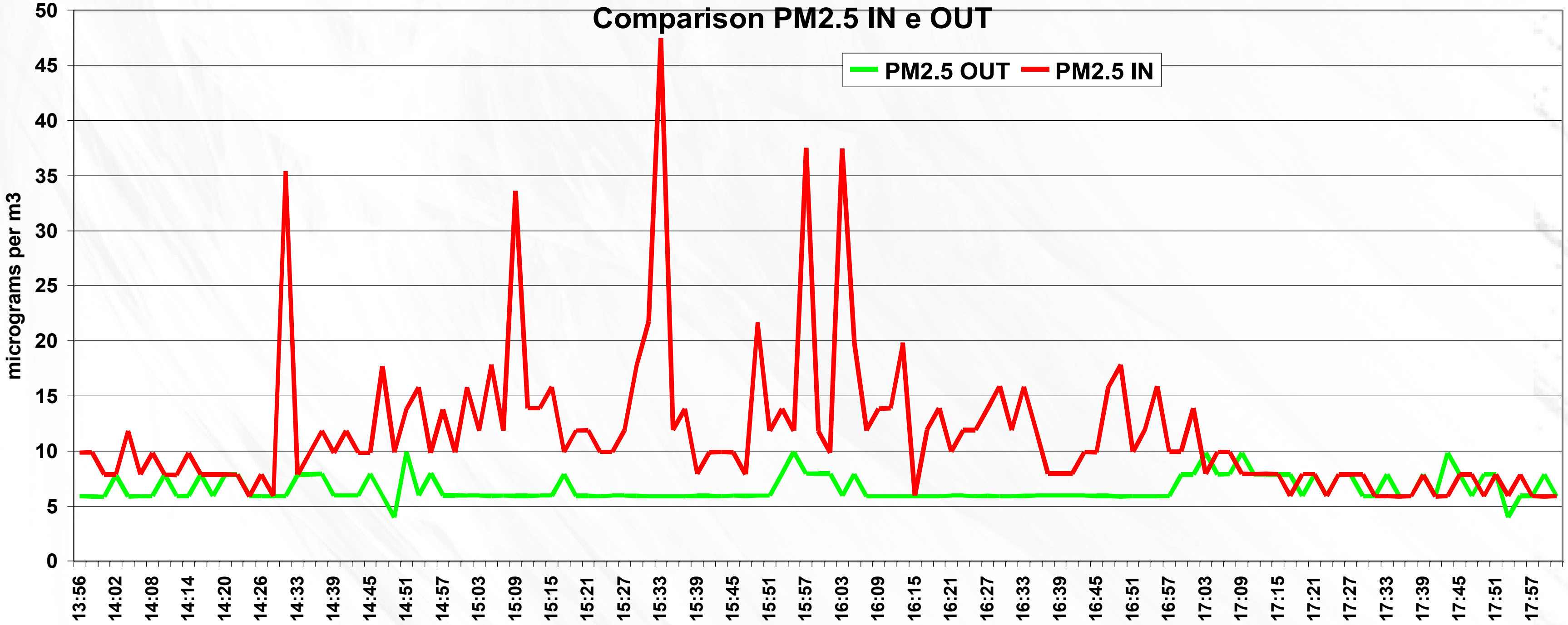

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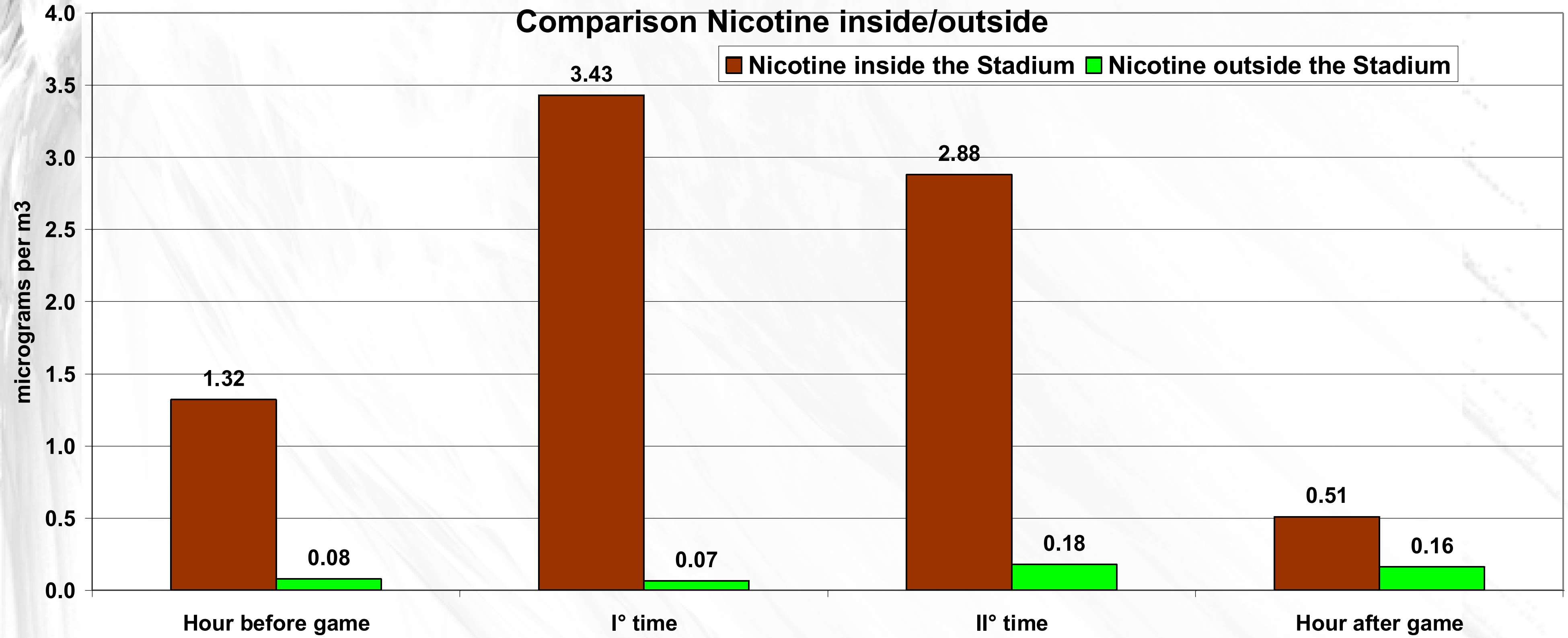
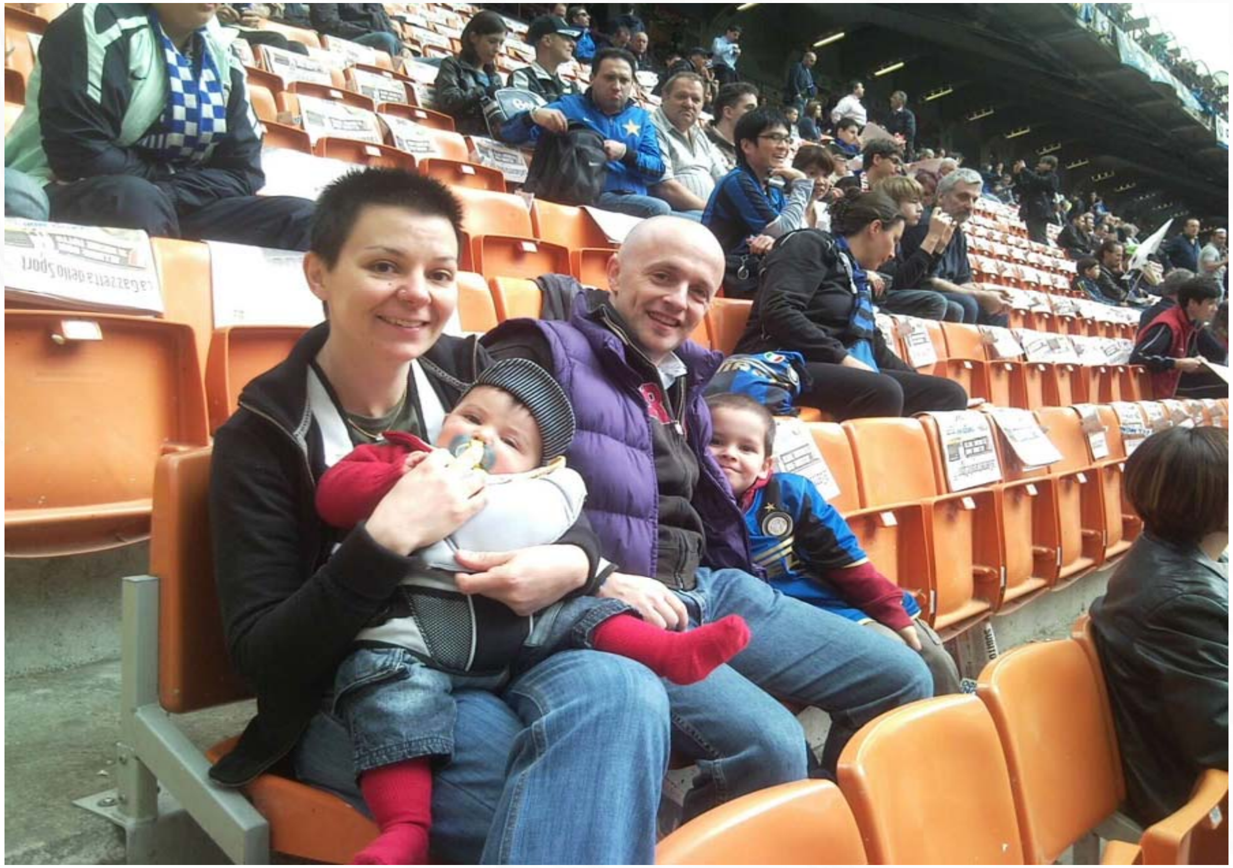


EXAMPLES OF MEASUREMENTS

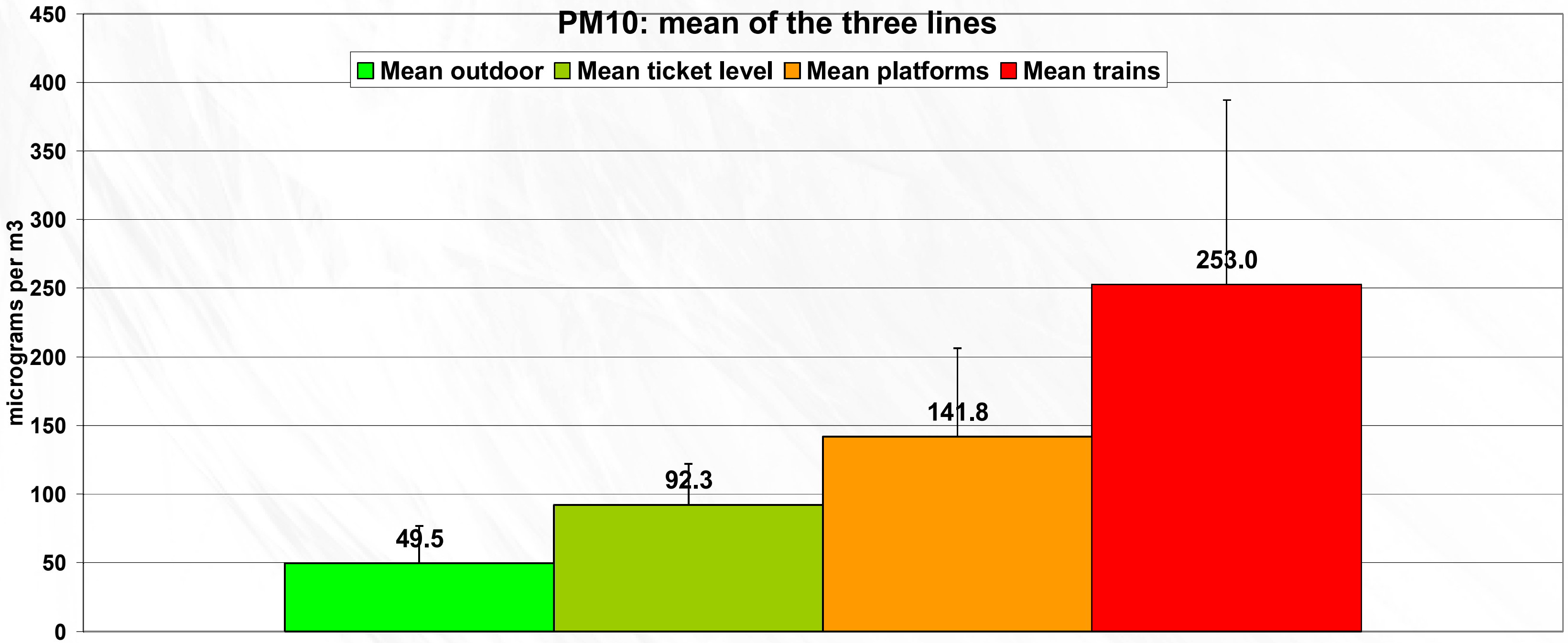
Influence of Outdoor Smoking on PM and Black Carbon (BC) Concentration
Measurement during a soccer game in the Meazza Stadium of Milan, Italy

IS THE STADIUM A SAFE PLACE FOR CHILDREN?



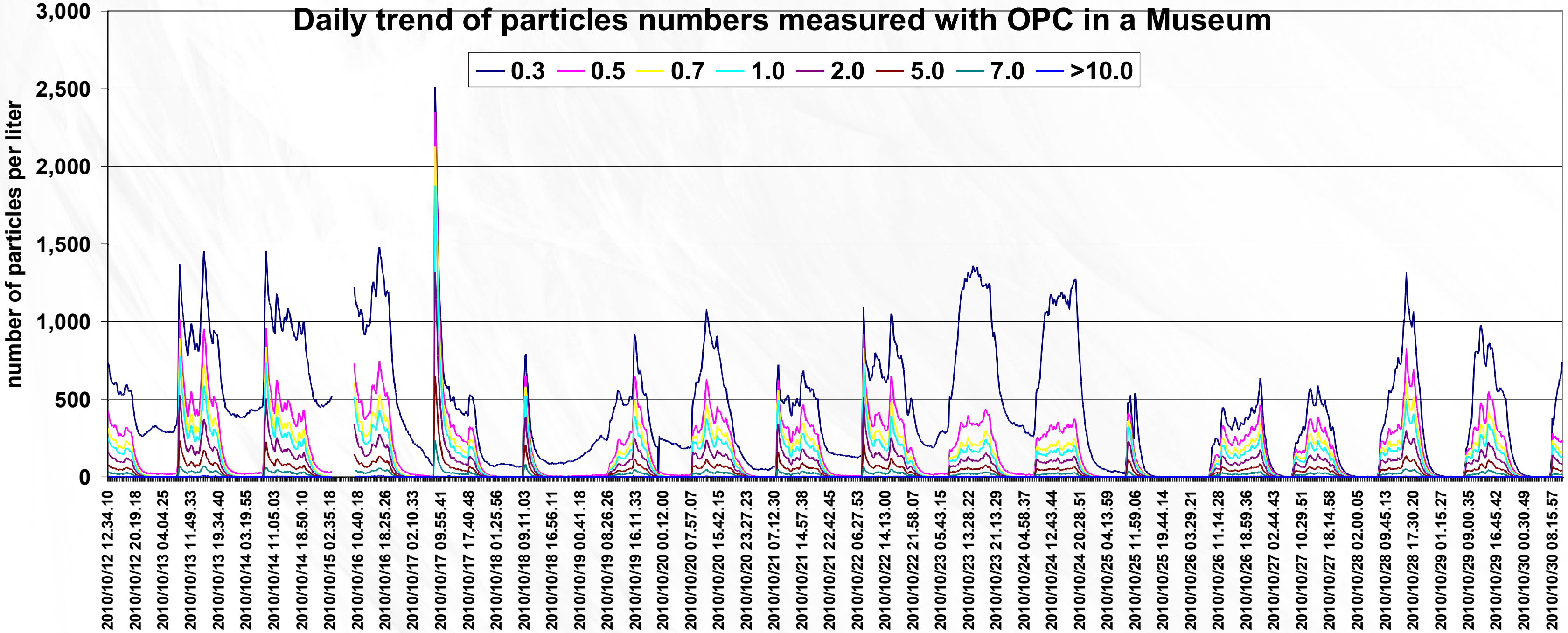
EXAMPLES OF MEASUREMENTS

Measurements of Particulate Matter (PM) pollution in the Subway System of the City of Milan, Italy



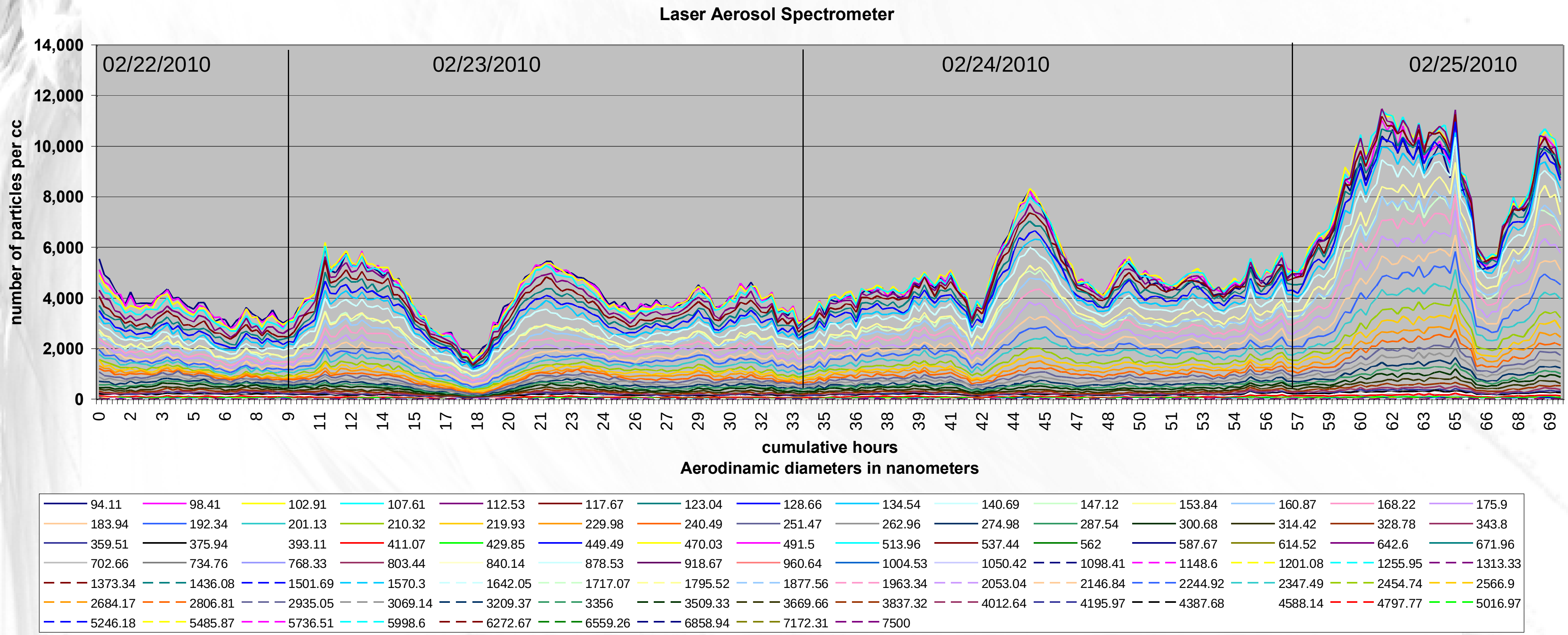
EXAMPLES OF MEASUREMENTS

Measurements of number of particles in a Museum using 8 channels OPC (0.3; 0.3; 0.5; 0.7; 1.0; 2.0; 5.0; 7.0; >10.0



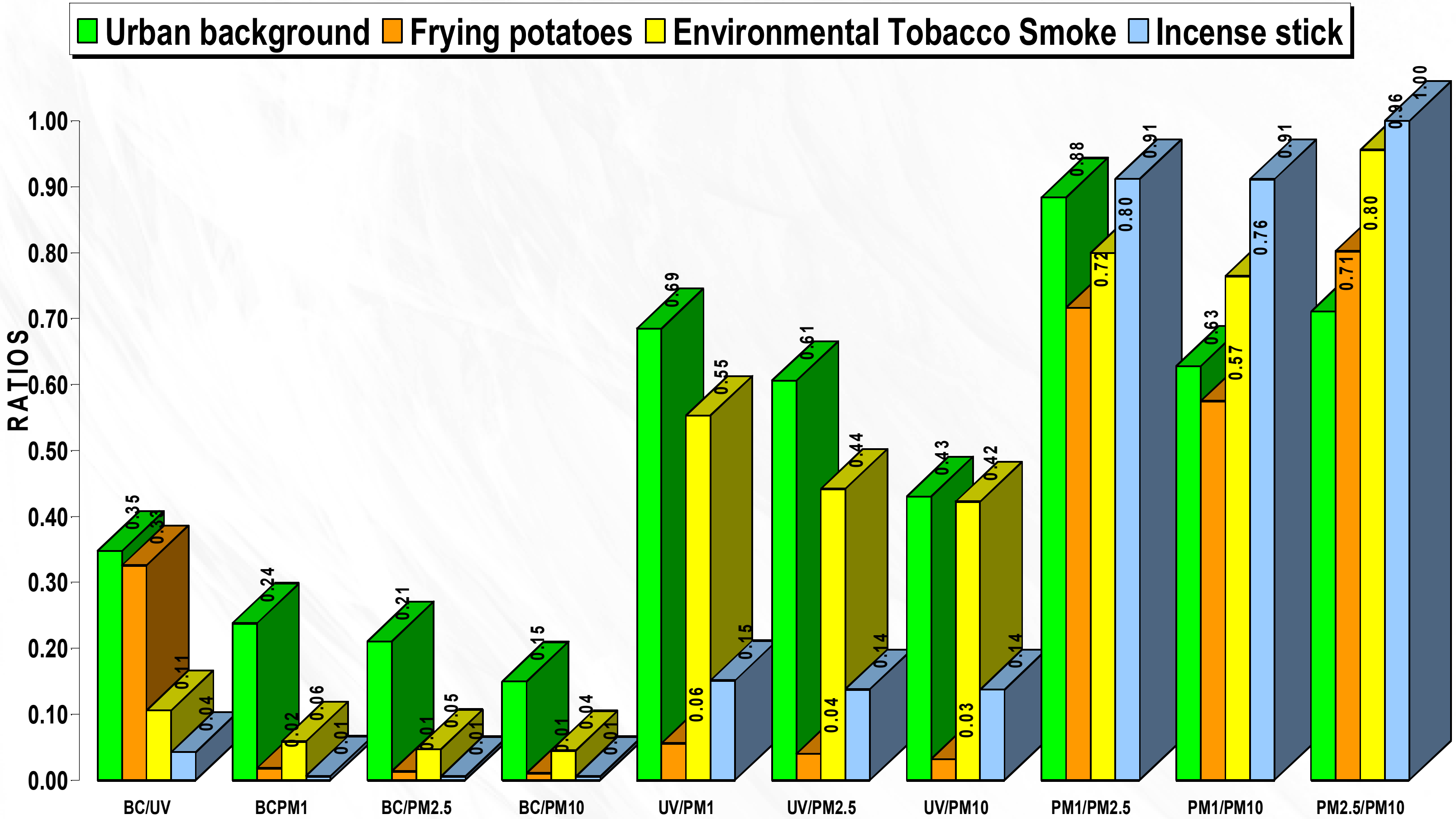
EXAMPLES OF MEASUREMENTS

Measurements of number of particles in a Museum using the 99 channels (from90 to 7,500 nanometers) APS Model ATS 3321



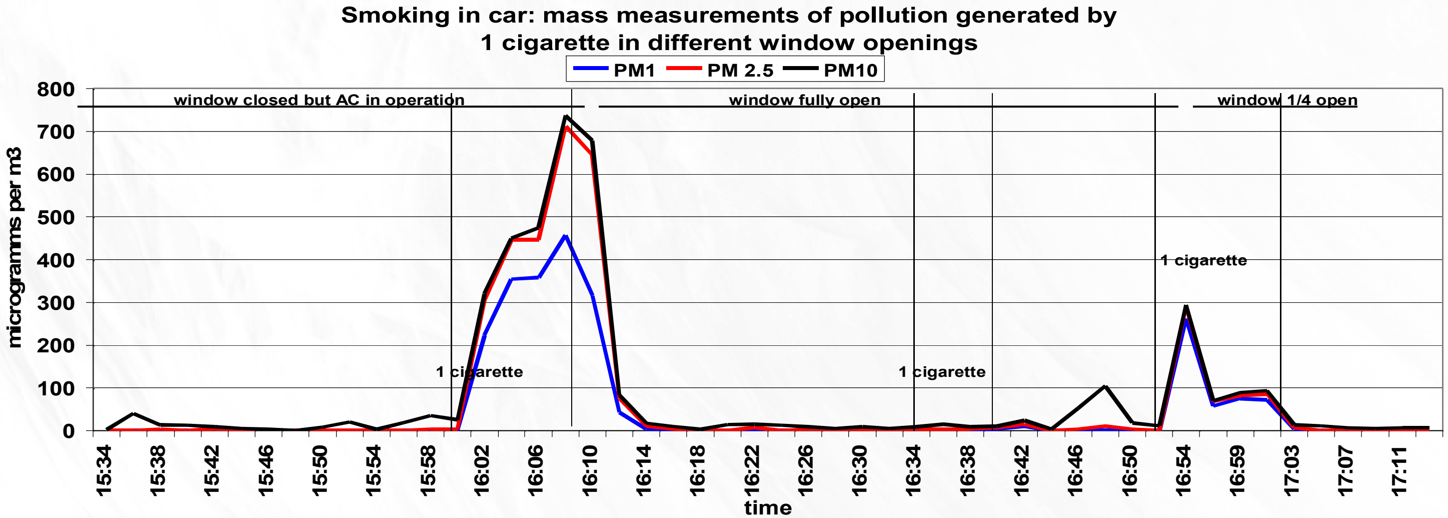
EXAMPLES OF MEASUREMENTS

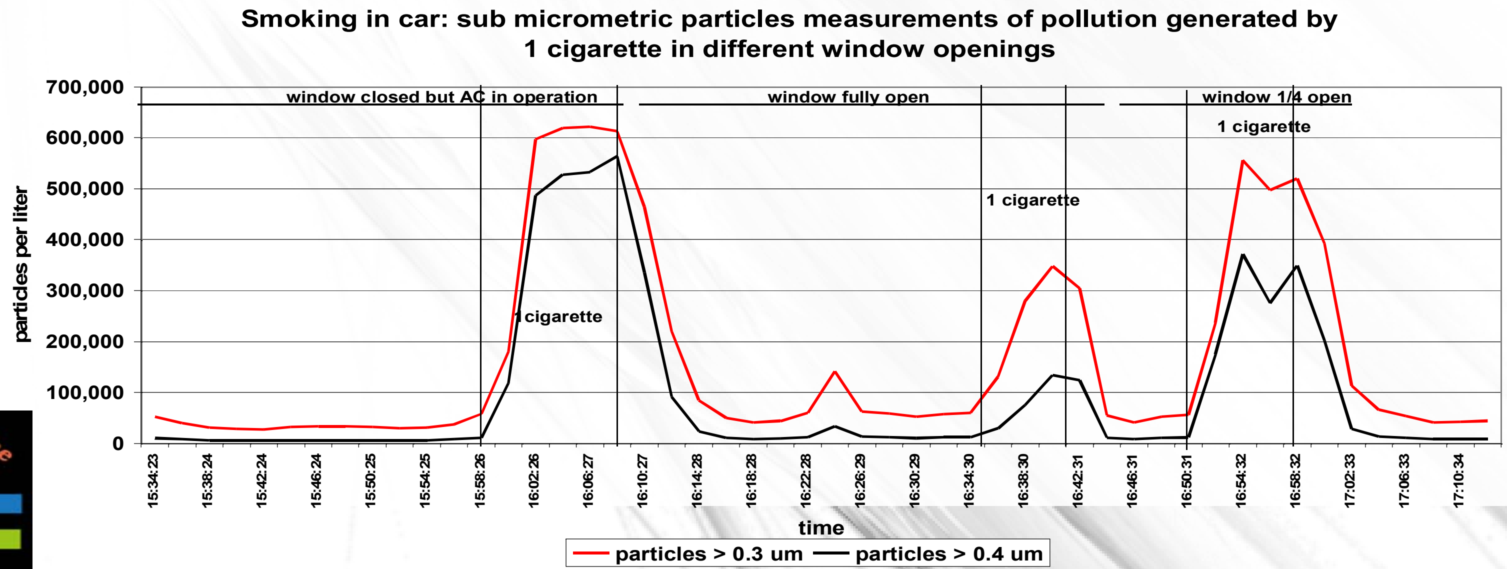
In search of a real time ETS "fingerprint": preliminary characterization of real time PM mass and composition profile in smokes from different sources: cigarette, incense sticks, potato frying, and urban pollution



EXAMPLES OF MEASUREMENTS

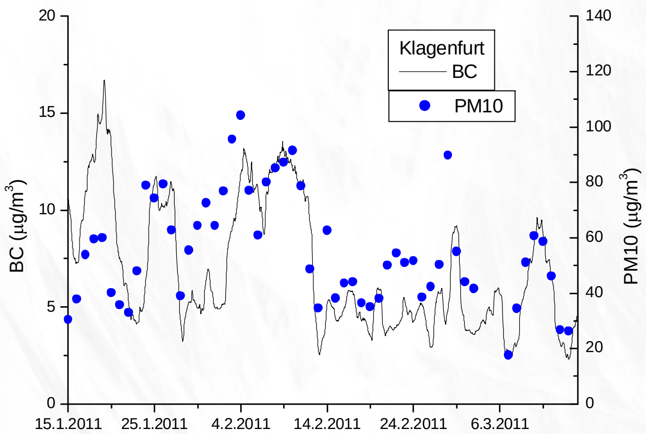
Smoking in car: mass measurements and sub micrometric particles pollution generated by 1 cigarette in different window openings

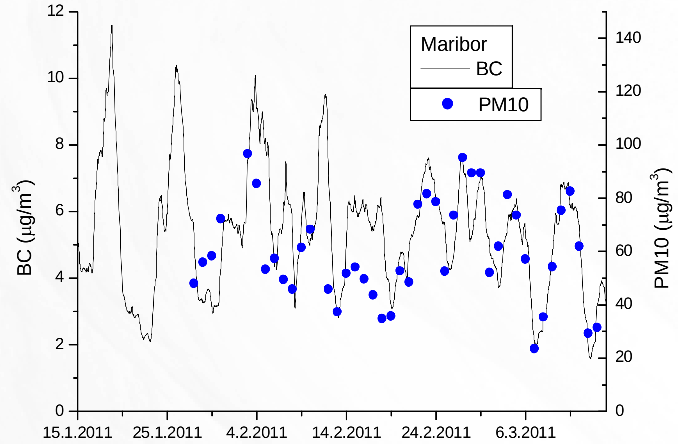


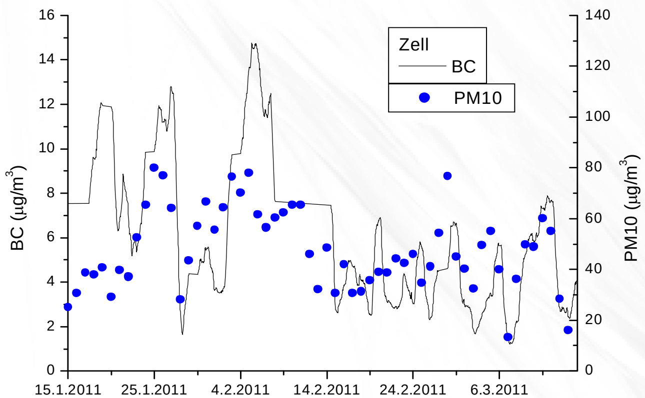


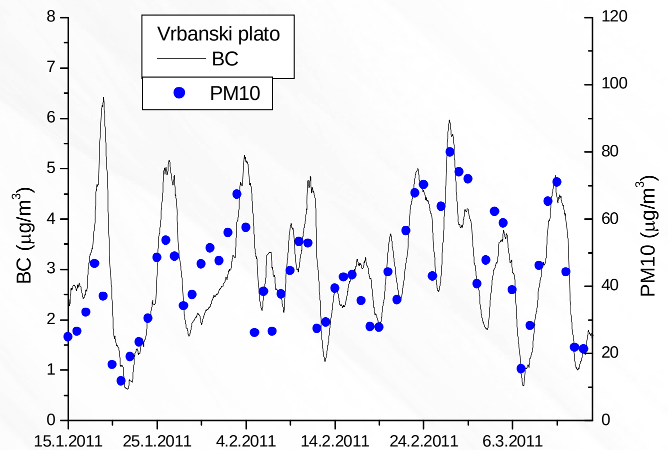
EXAMPLES OF MEASUREMENTS

BC and PM_{10} correlations in different locations









BC time-series

EXAMPLES OF MEASUREMENTS

Renewable fuels: wood

- wood/biomass is a **sustainable fuel** – trees recycle CO2
- burning biomass is and has been a **major energy source**
- various combustion regimes: high-efficiency distric heating ovens – individual wood-stoves
- possible extreme emissions of PM – up to 40% of PM is woodsmoke (Caseiro 2009) , 20% in Paris center (Favez 2009)!

EXAMPLES OF MEASUREMENTS

Wood-smoke vs. diesel

- measure attenuation with the Aethalometer: UV-IR
- calculate absorption coefficient *babs (λ)*
- for completely **black sample**: *babs ~1/λ*
- woodsmoke contains aromatic substances – increased absorption: more at **lower wavelengths**!

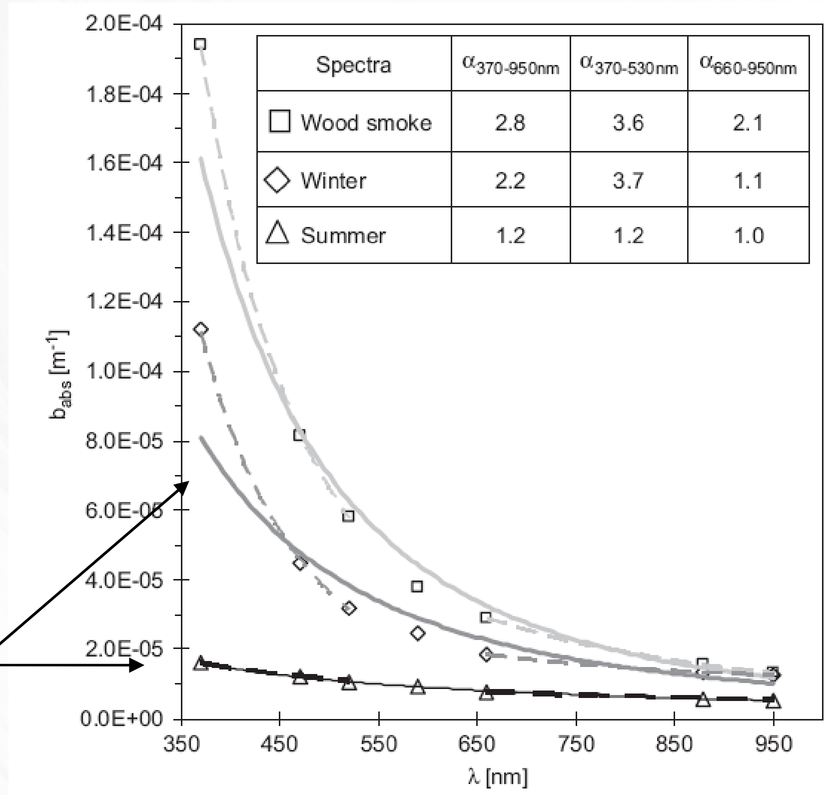
EXAMPLES OF MEASUREMENTS

Wood-smoke vs. diesel – 7 wavelengths

- measure attenuation with the Aethalometer
- absorption coefficient - *babs*
- for pure black carbon: *babs ~1/λ*
- generalize **Angstrom exponent**: ***babs ~1/λα***

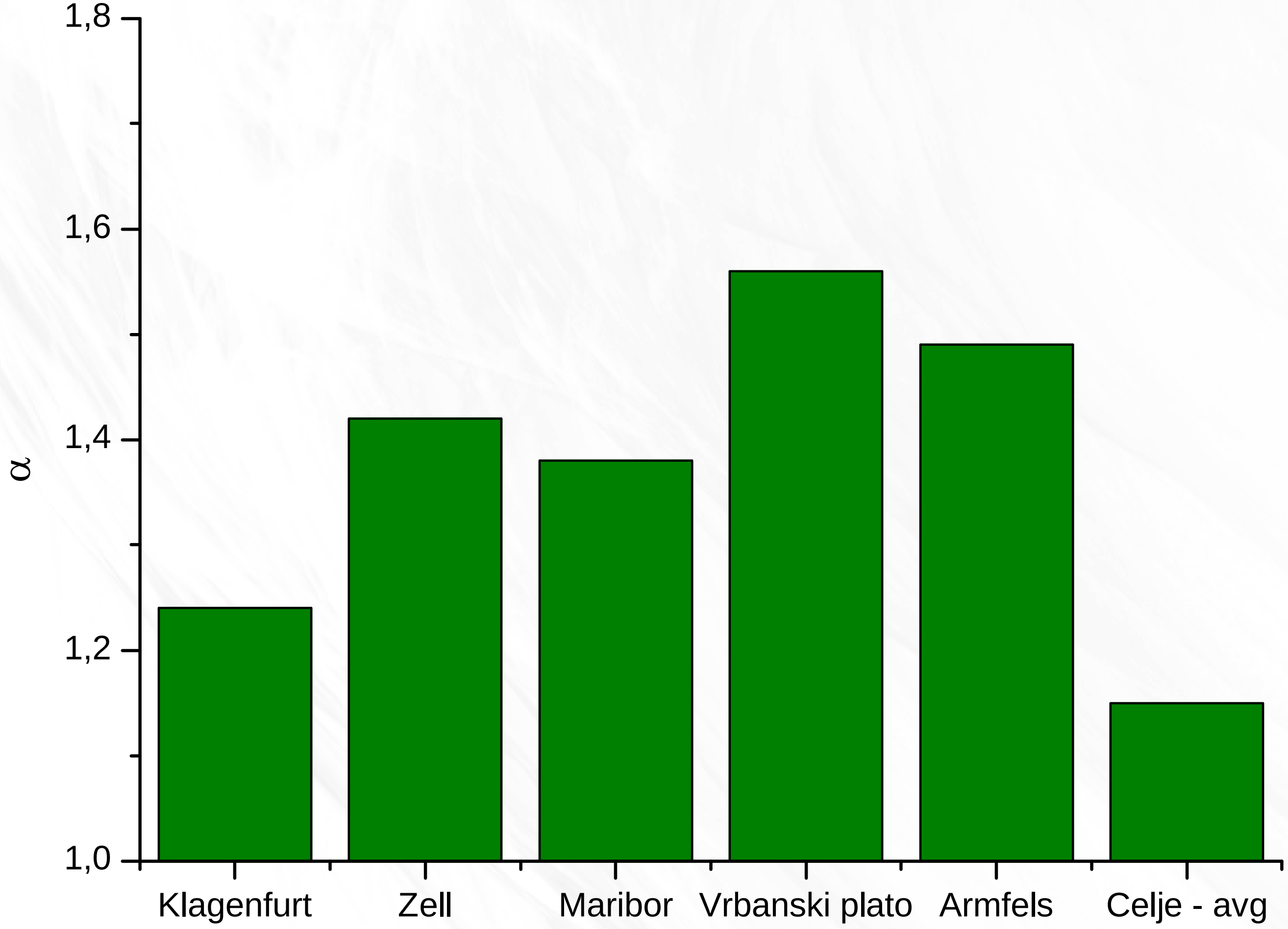
diesel: $\alpha \approx 1$

wood-smoke: $\alpha \approx 2$ and higher



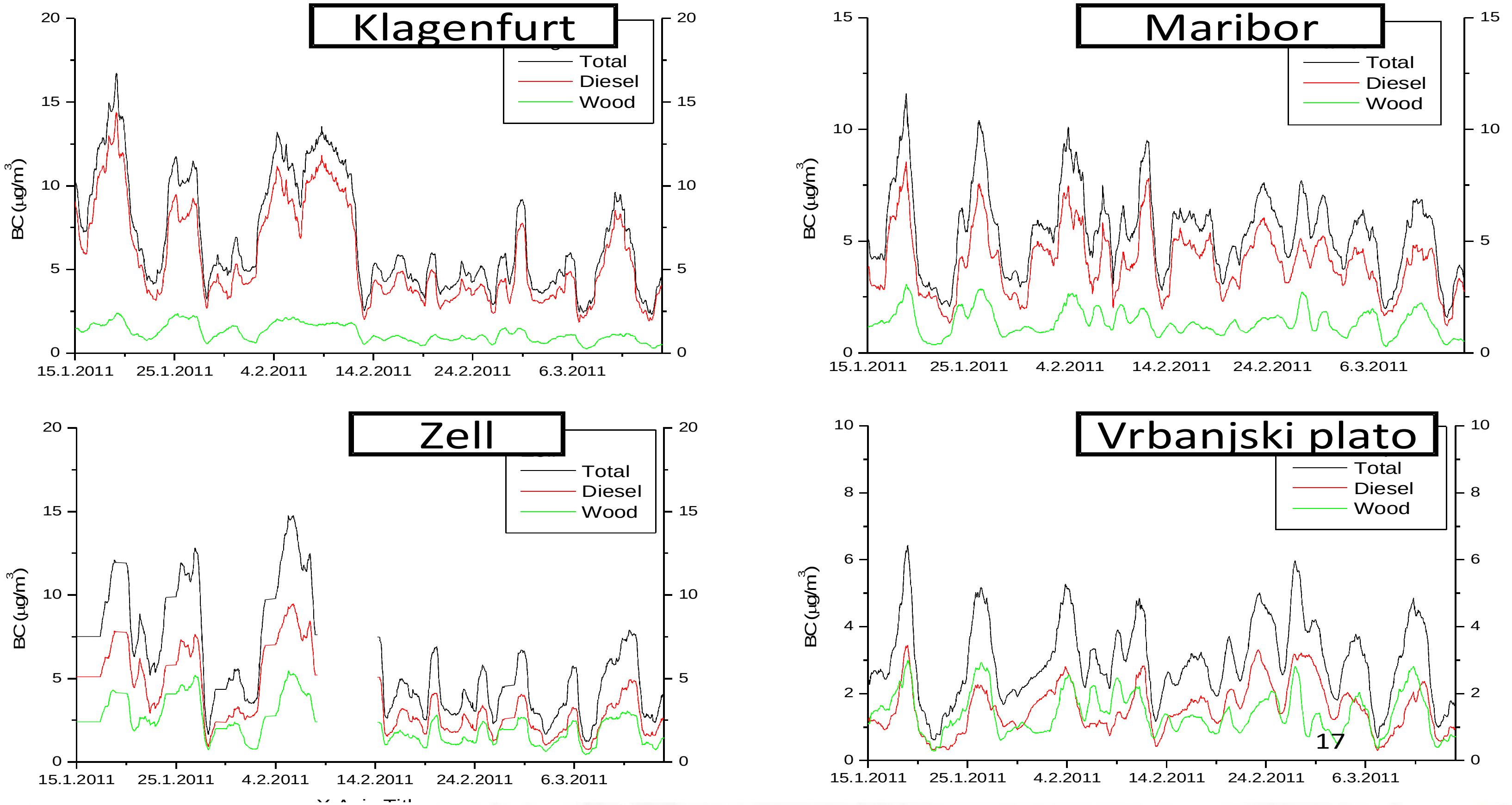
EXAMPLES OF MEASUREMENTS

Angstrom exponent



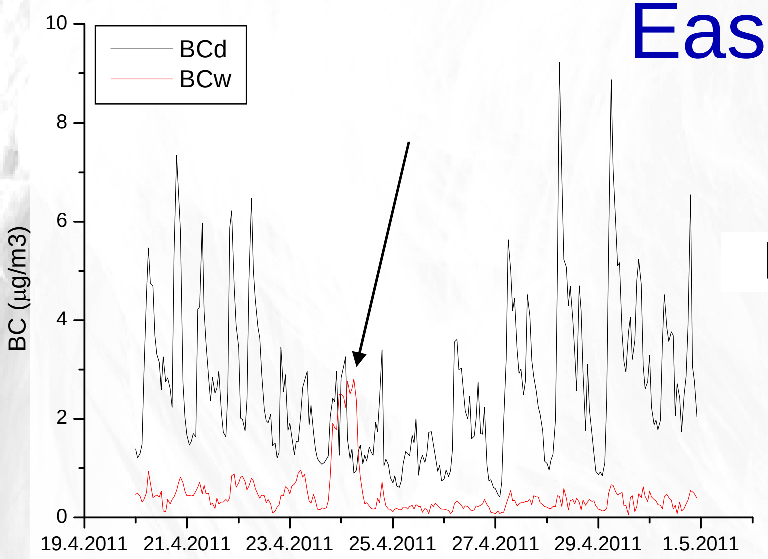
EXAMPLES OF MEASUREMENTS

BC_{ff}, BC_{wb} time series

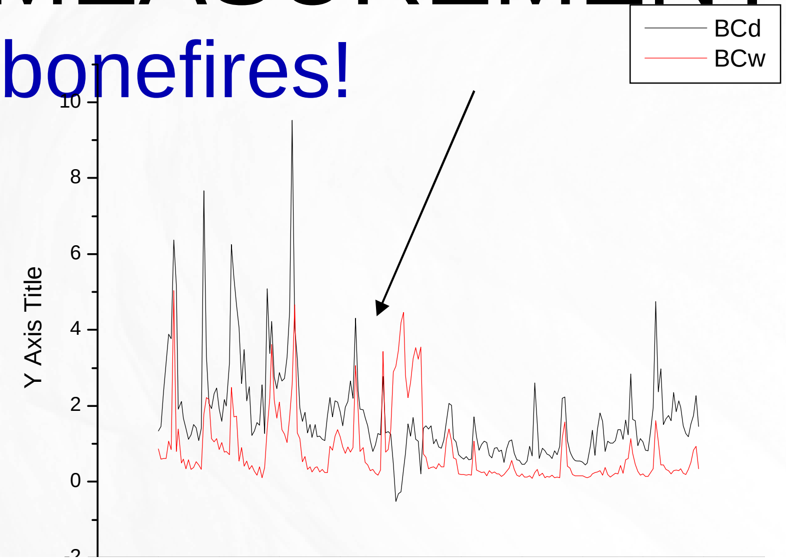


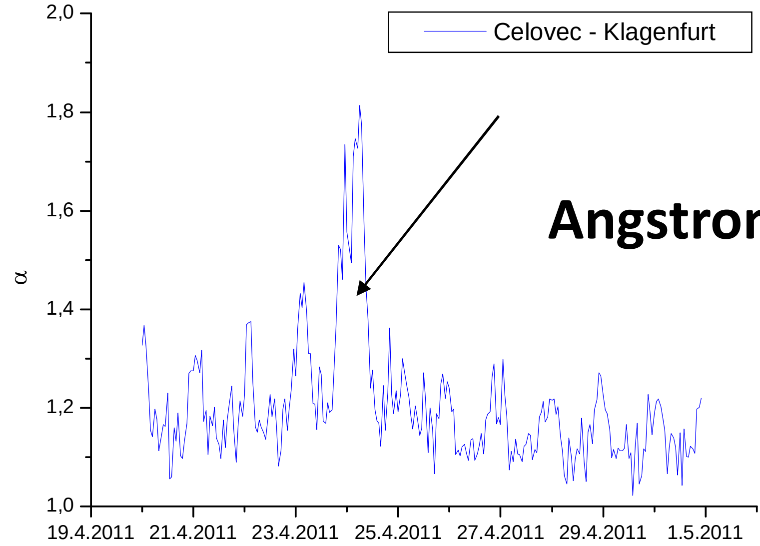
EXAMPLES OF MEASUREMENTS

Easter bonefires!

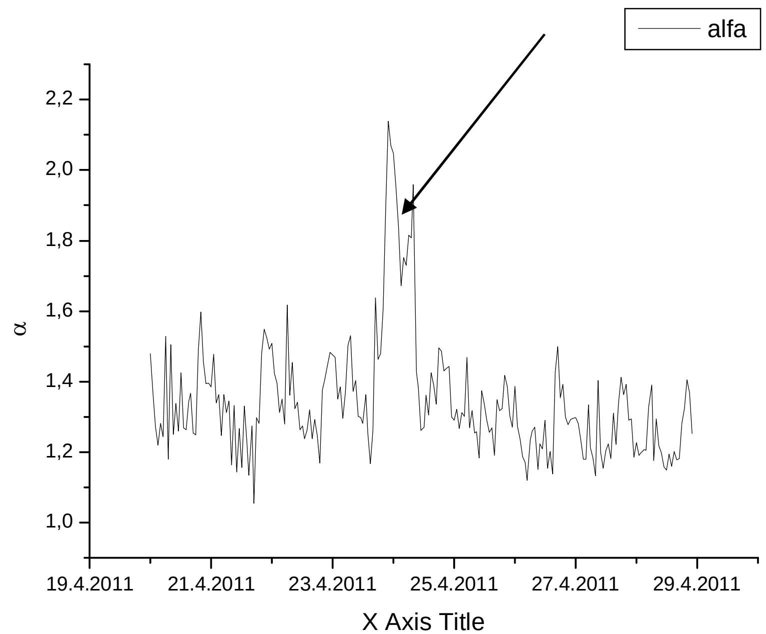


BC

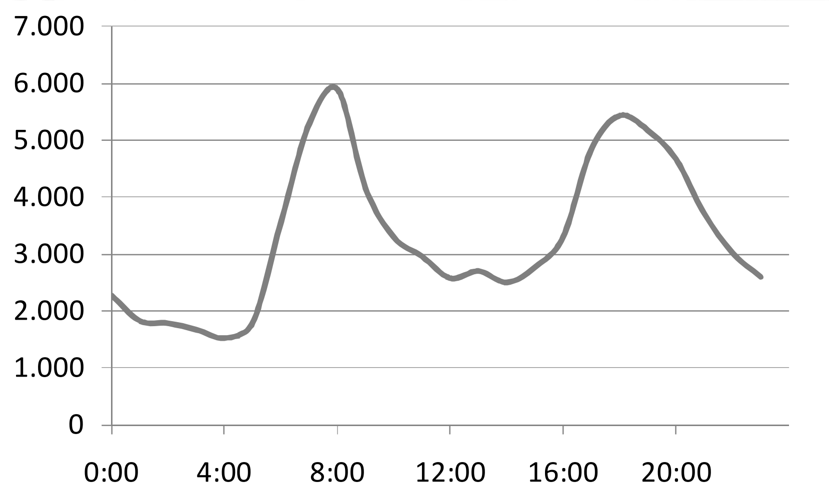




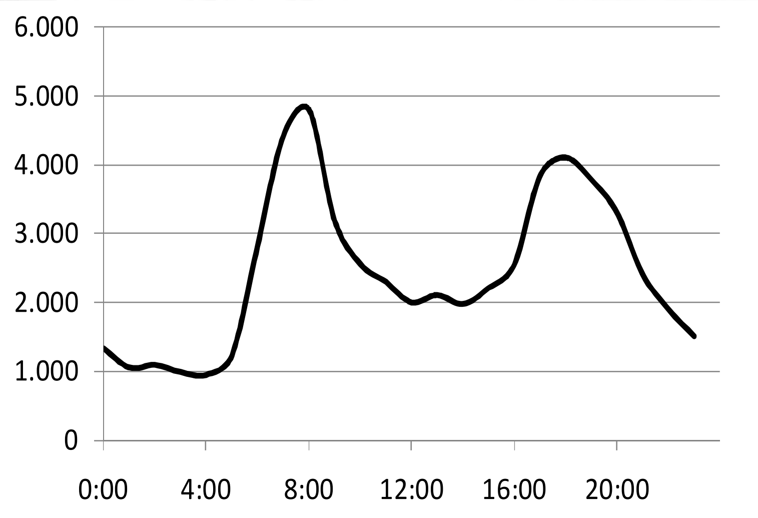
Angstrom exp

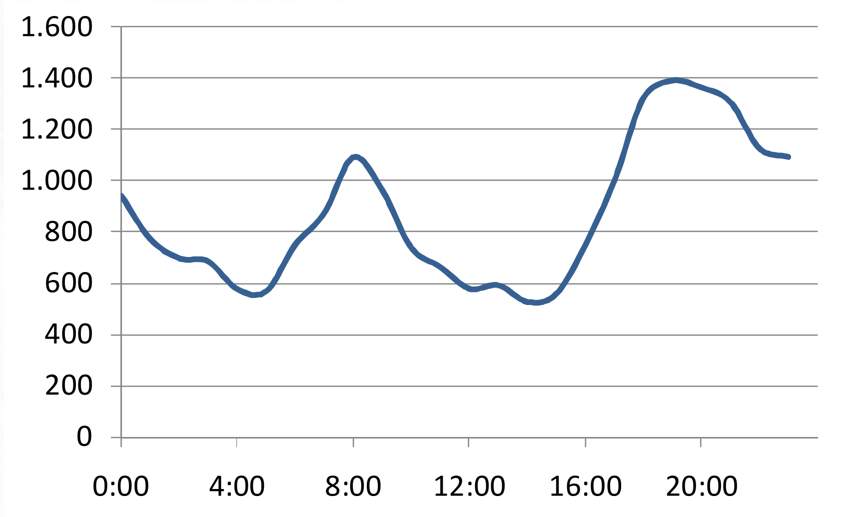


EXAMPLES OF MEASUREMENTS

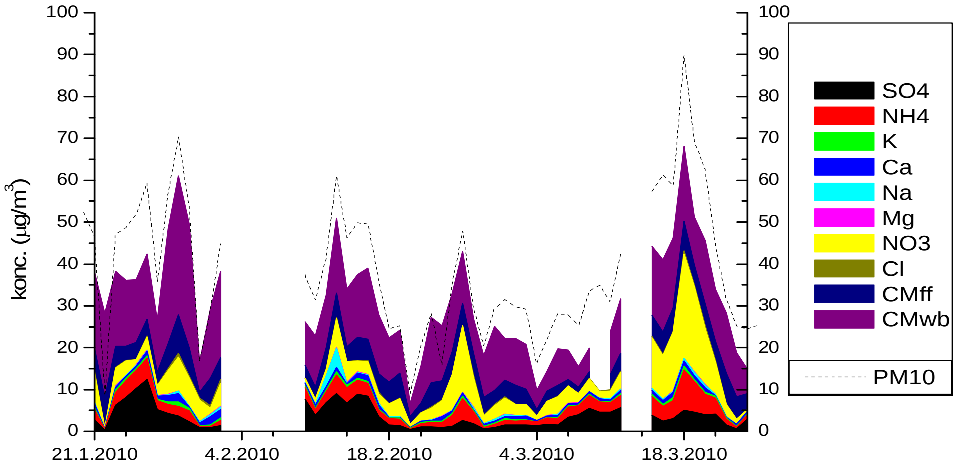


BCff, BCwb diurnal



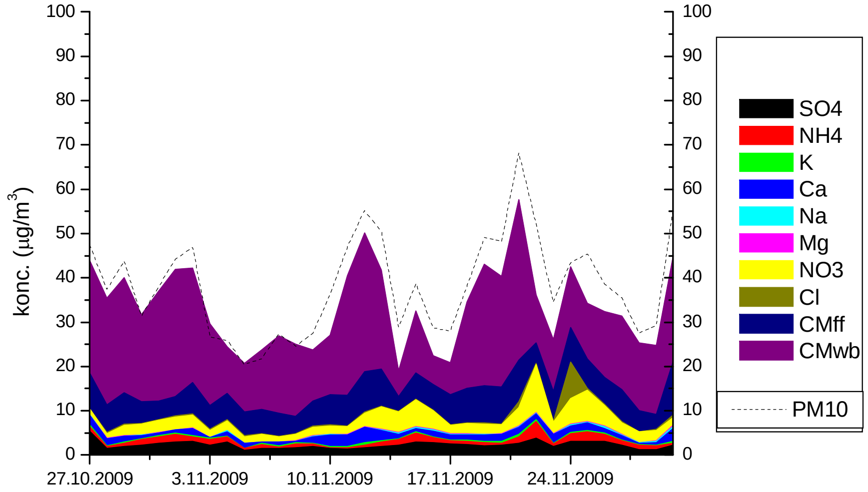


EXAMPLES OF MEASUREMENTS



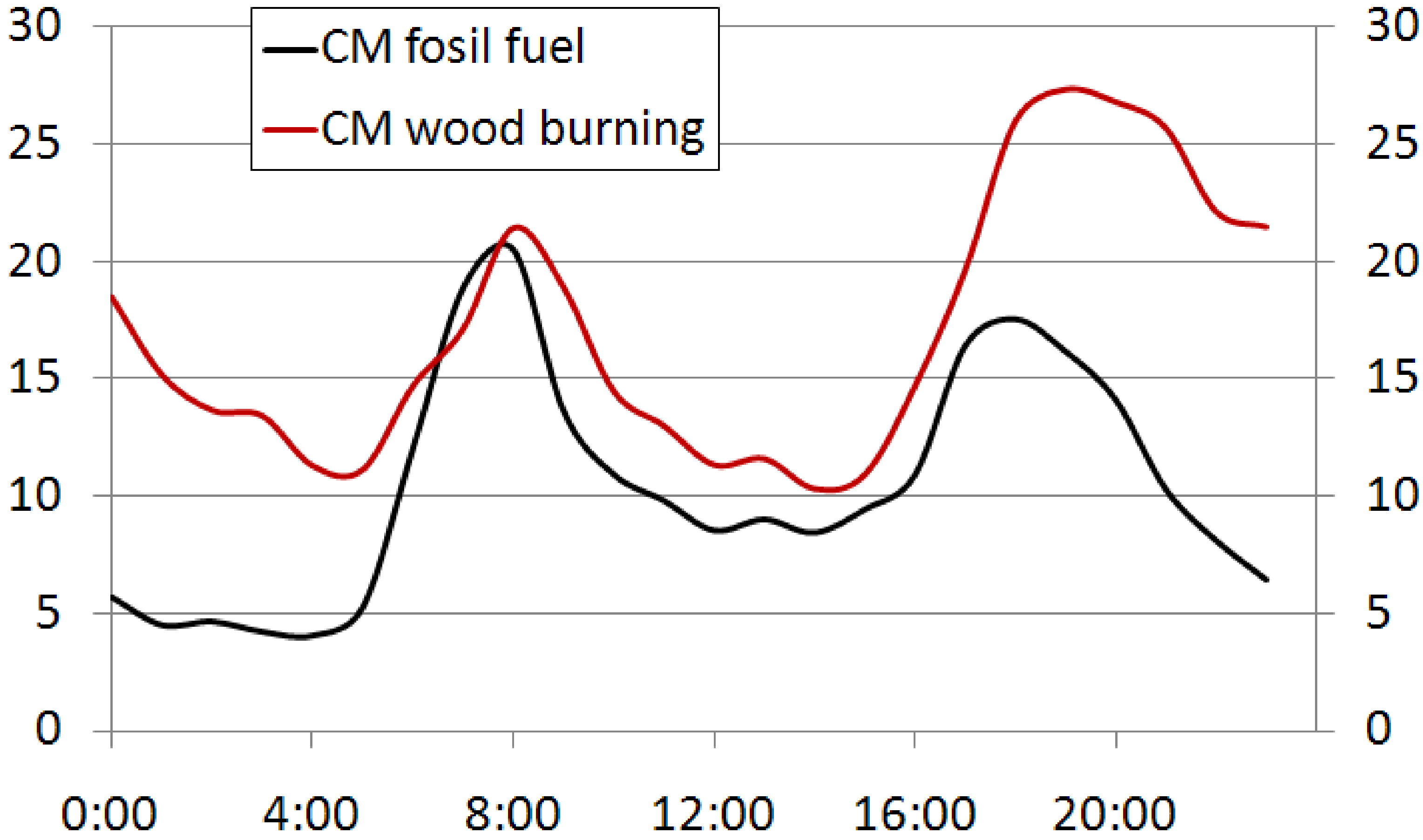
Chemical filter analysis - ARSO

Wood smoke is a major air pollution component!



EXAMPLES OF MEASUREMENTS

CMff, CMwb – **example** from Nova Gorica



EXAMPLES OF MEASUREMENTS

Conclusions of BC examples

- we can measure **fossil fuel** and **wood-smoke Black Carbon** with the Aethalometer: less BC from wb than ff
- time resolution is **5 min**
- we can investigate **time evolution** of BC and wood-smoke during the day
- Quantitative wood-smoke and diesel exhaust determination – use 24 h TC calibration, Aethalometer -> high time resolution
- See POSTER: **Influence of biomass combusiton on air quality in two pre-Alpine towns with different geographical settings**

CONCLUSION 1

Generally the gravimetric manual and automatic (BAMs & TEOMs) are employed as certified mass maesurements in Monitoring Station operated by Environmental Protection Agencies while the portable and fixed OPCs are employed in real time researches of outdoor and indoor temporal and spatial diffusion of the aerosols

All other technologies (CPCs, DMA, DMPS, SMPS and APS) are mainly employed in research programs

Generally in many research programs, the described different technologies are used toghether with laboratory chemical analysis for better source apportionement

All these systems can supply extremely accurate informations in number of particles and/or in mass in real time but unfortunately none can give any information about the chemical composition, toxicity and/or carcinogenicity of the aerosols

CONCLUSION 2

However BC, OC and PM simultaneous measurements allows the calculation of the percent BC/OC in PM_{10}, $PM_{2.5}$ and PM_1

CONCLUSION 2

BC, OC and PM simultaneous measurements allows the calculation of the percent BC/OC in PM_{10}, $PM_{2.5}$ and PM_1

BC is a valuable additional air quality indicator to evaluate the health risks of air quality dominated by primary combustion particles and should be considered as an additional indicator of adverse health effects of airborne particles compared to PM_{10} and $PM_{2.5}$ (Janssen NA *et al.* Environmental Health Perspectives 2011)

BLACK AND ORGANIC CARBON

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Black Carbon as an Additional Indicator of the Adverse Health Effects of Airborne Particles Compared to PM_{10} and $PM_{2.5}$

Nicole AH Janssen, Gerard Hoek, Milena Simic-Lawson, Paul Fischer, Leendert van Bree, Harry ten Brink, Menno Keuken, Richard W Atkinson, H Ross Anderson, Bert Brunekreef, Flemming R Cassee

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