UNIVERSITÀ DEGLI STUDI DI MILANO
DIPARTIMENTO DI FISICA

Optical properties of atmospheric aerosol: development of innovative instrumentation and modelling applications

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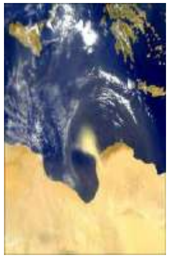
Assegnista di ricerca tipo A - Environmental Physics Group

co-authors:
Environmental Physics Group - R. Vecchi et al.
Instrumental Optics Laboratory Group - M. Potenza et al.

INFN Istituto Nazionale di Fisica Nucleare

Atmospheric aerosol and importance of its optical properties

Sources
(natural & anthropogenic)
Atmospheric processes

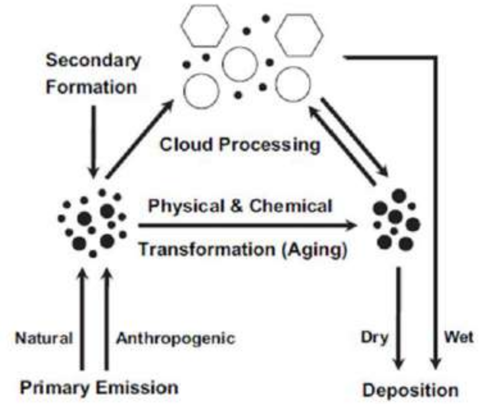


Fig. 23 Primary emissions, secondary formation, and atmospheric processing of natural and anthropogenic aerosols (Fuzzi et al., 2006; Pöschl, 2005).

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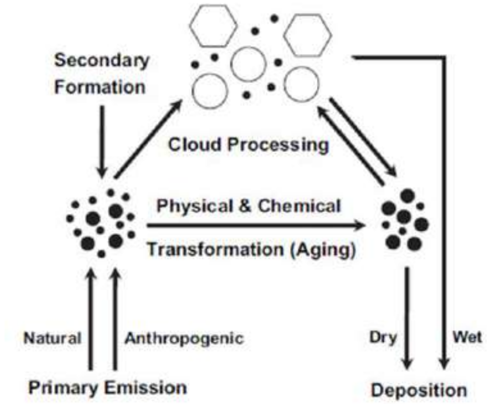

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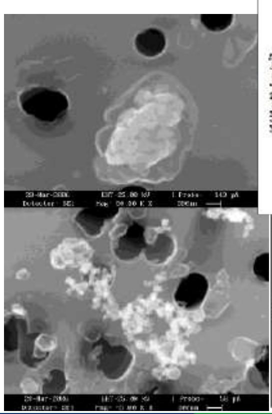
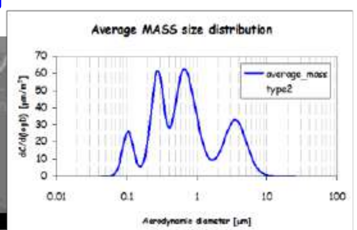
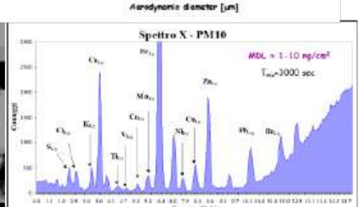
Aerosol size, composition & shape







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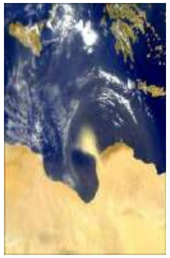

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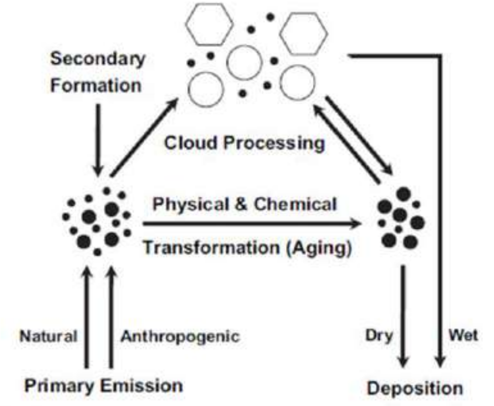

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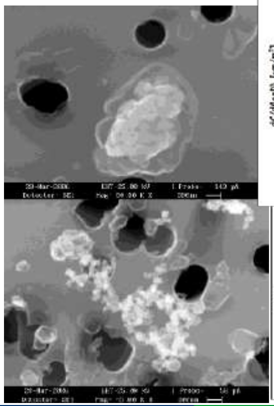
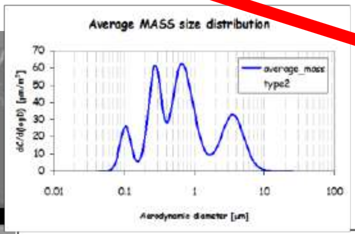
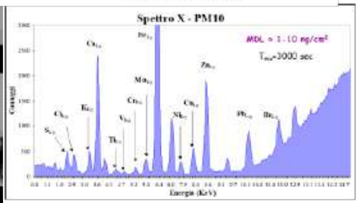
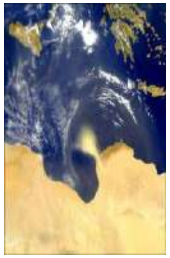






Effects
(local & global)

Atmospheric aerosol and importance of its optical properties



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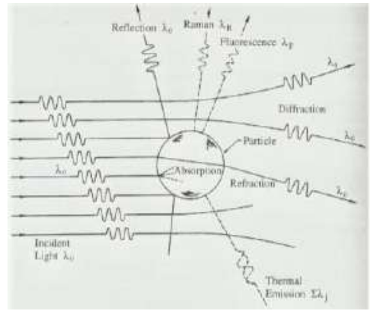

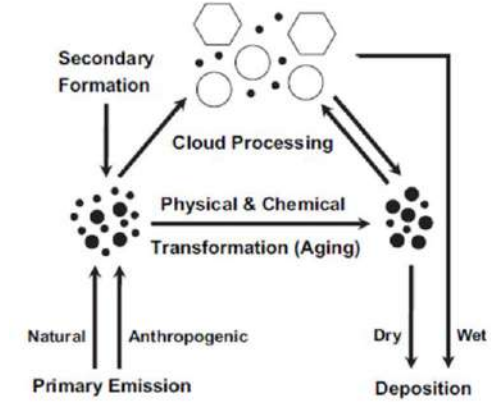

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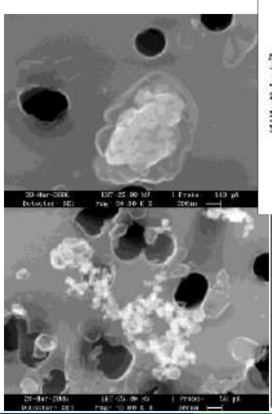

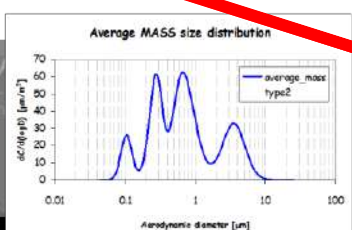

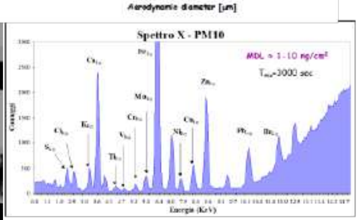

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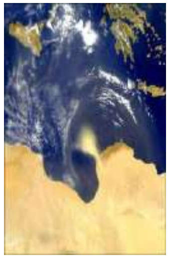

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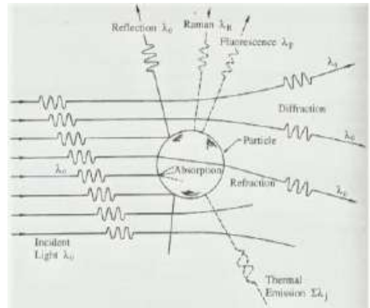

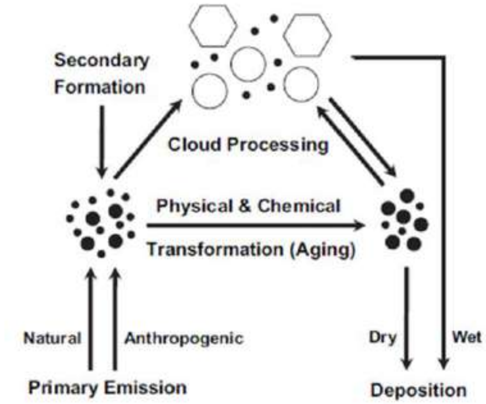

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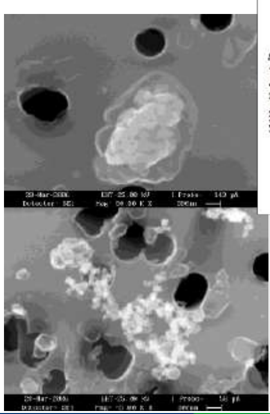
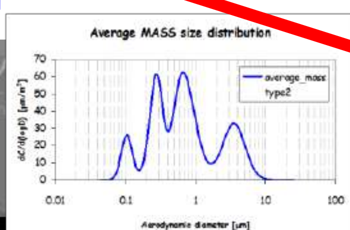
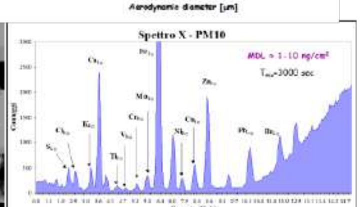
Effects on visibility & Earth Radiation balance







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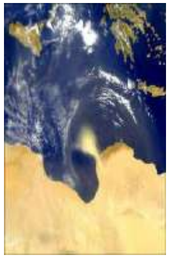

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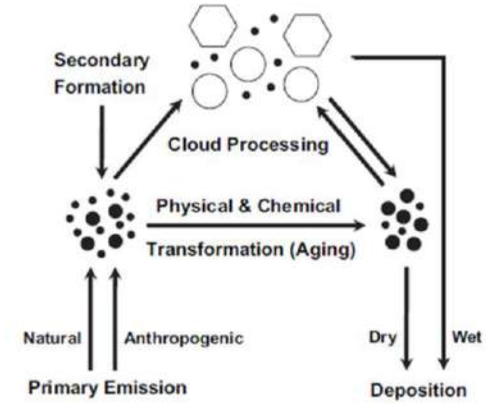

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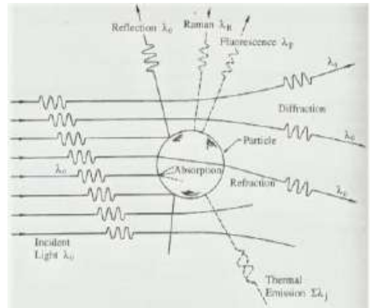

Source apportionment

Aerosol size, composition & shape

Particle scattering and absorption properties

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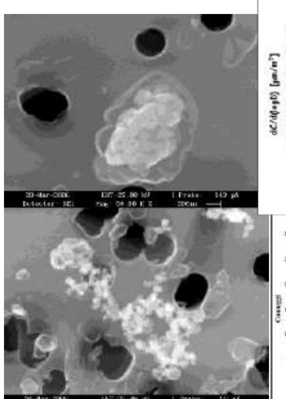
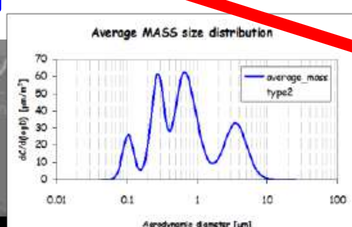
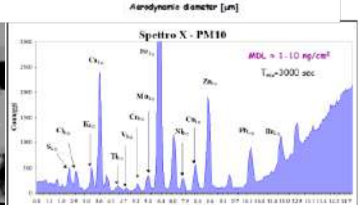








Anthropogenic contribution to Earth radiation balance

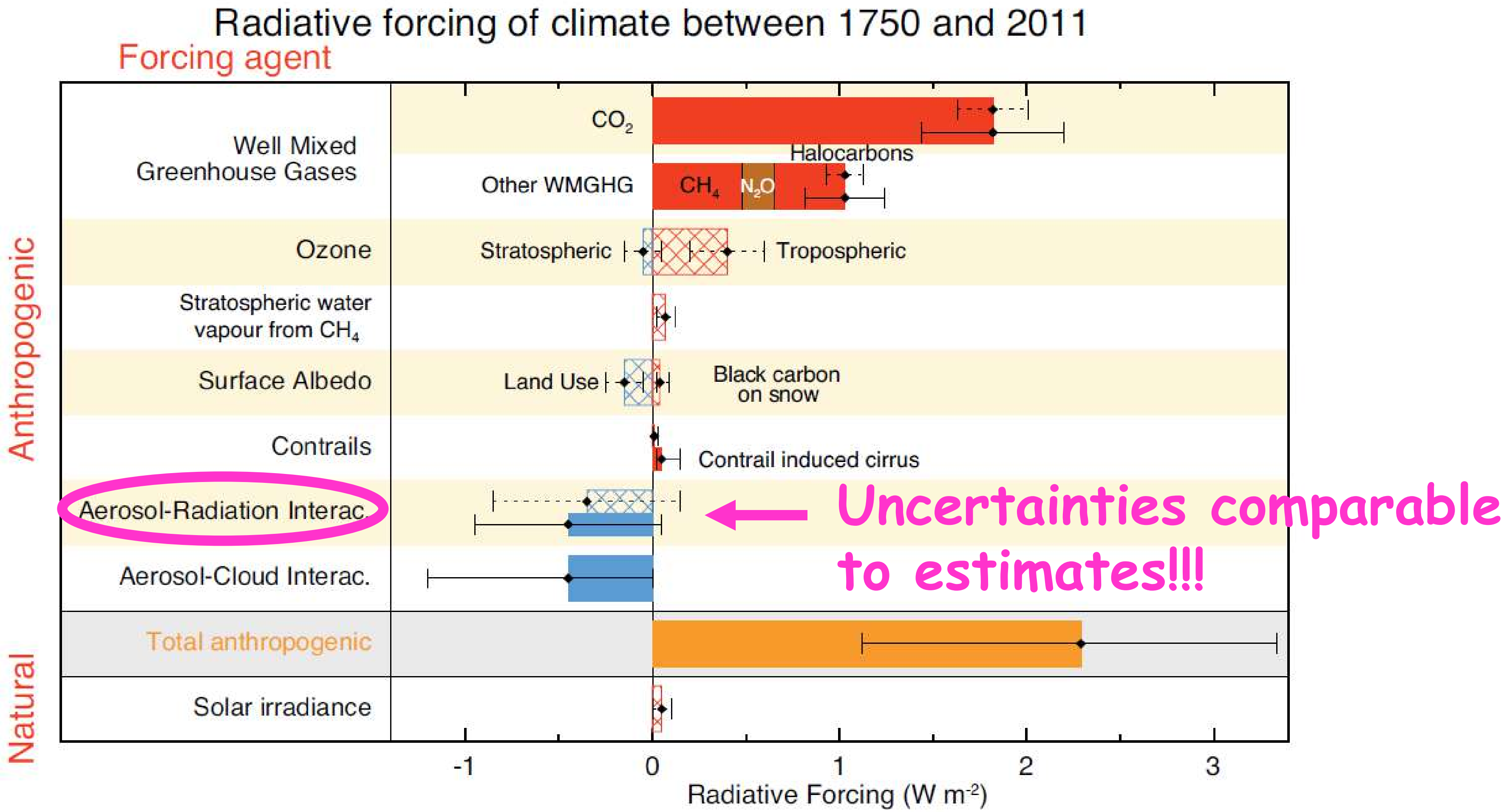


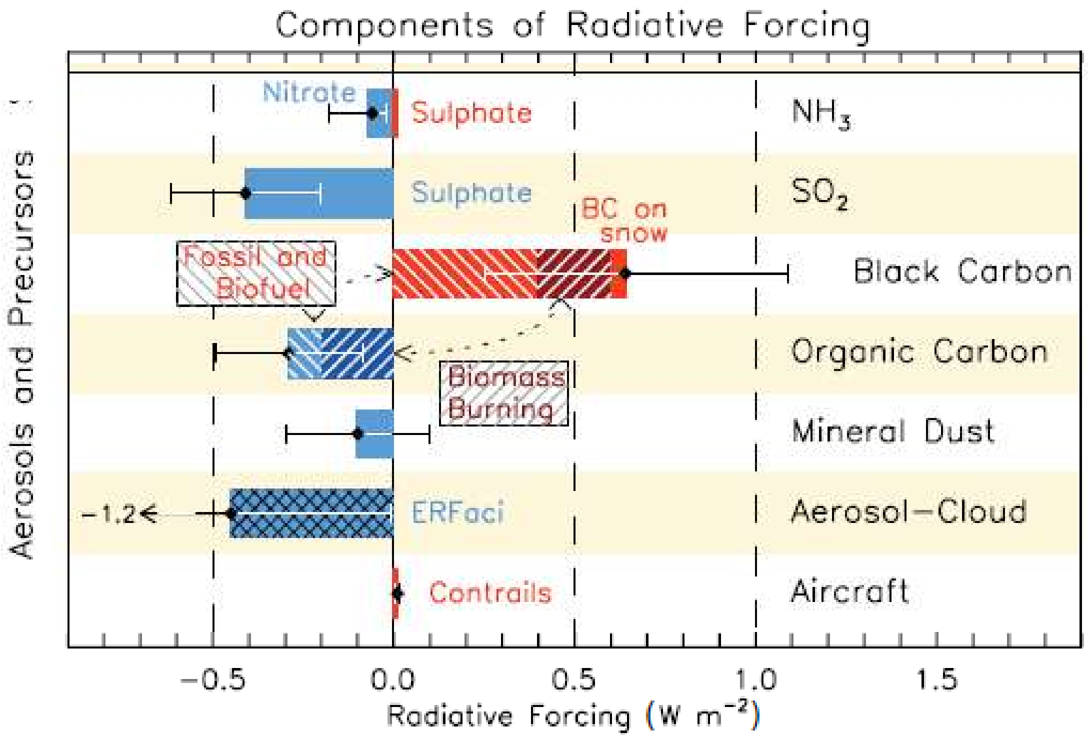
Figure 8.15 | Bar chart for RF (hatched) and ERF (solid) for the period 1750–2011, where the total ERF is derived from Figure 8.16. Uncertainties (5 to 95% confidence range) are given for RF (dotted lines) and ERF (solid lines).

IPCC, 2013

RF = net flux at tropopause

ERF = net flux at *top of atmosphere*

Impact of different aerosol components on Earth radiation balance

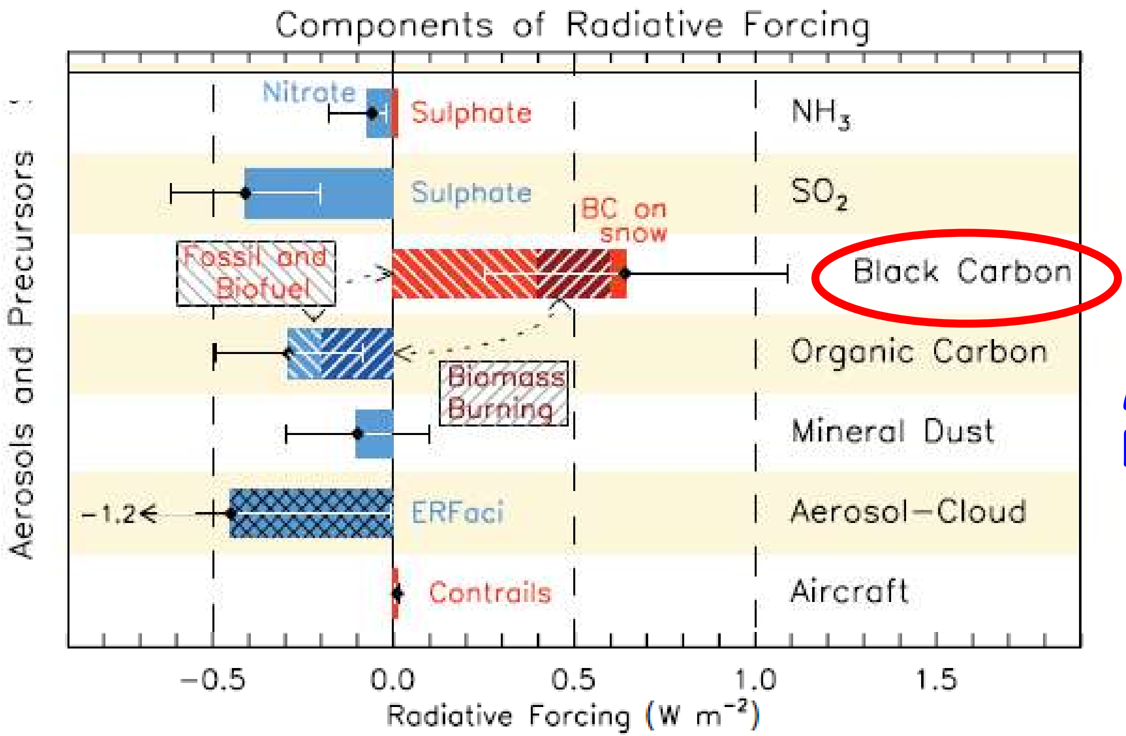


Adapted from IPCC, 2013

All particles SCATTER radiation!!!

Particles with non-zero imaginary part (k) of the refraction index ALSO ABSORB radiation.

Impact of different aerosol components on Earth radiation balance



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Main light - absorbing species: black carbon (BC)

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Main light absorbing species: Black and Brown carbon

Black Carbon (BC):
k(λ)=cost (about 0.7).

For small particles
$b_{abs,BC}(\lambda)=\lambda^{-\alpha}$, $\alpha=1$

b_{abs}=aerosol absorption coefficient (Mm^{-1})

$$b_{abs}=\frac{\Sigma\,\sigma_{abs}}{V}$$

σ_{abs} → absorption cross section

V → volume in which particles are suspended

N.b. $e^{-b_{abs}x}$: fraction of light not absorbed in a path of length x

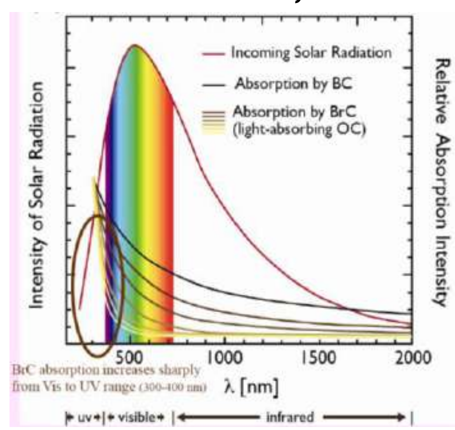
$b_{abs} \propto \lambda^{-\alpha}$ α=Ångström Absorption Coefficient

Main light absorbing species: Black and Brown carbon

Brown Carbon (BrC):
k(λ): strong λ-dependence
$k(\lambda)_{BrC} << k(\lambda)_{BC}$ in visible range,
BUT

$b_{abs,BrC}(\lambda) = \lambda^{-\alpha}$, $\alpha >> 1$

US EPA, Report to Congress on Black Carbon, 2012



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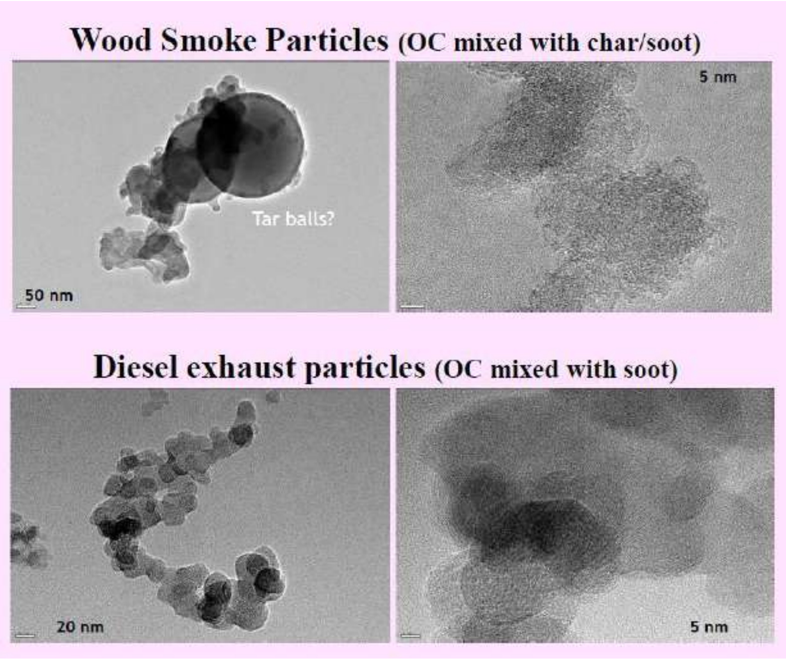
Impact of aerosol mixing on aerosol optical properties



Particle mixing influences particle absorption properties (generally enhancement)

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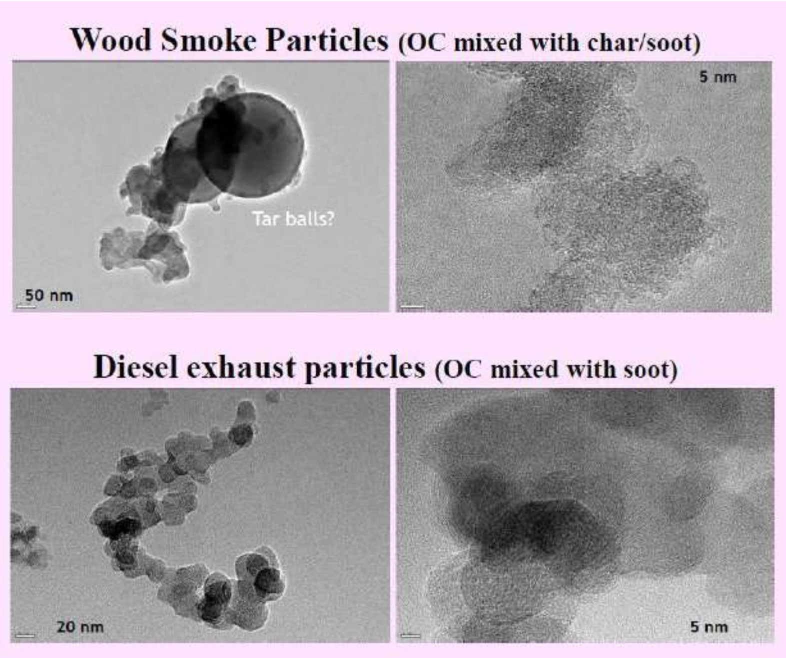


Particle mixing influences particle absorption properties (generally enhancement)

Models based on ideal schemes (e.g. core-shell): representativeness problem!!!

Lack & Cappa, Atmos. Chem. Phys. 2010

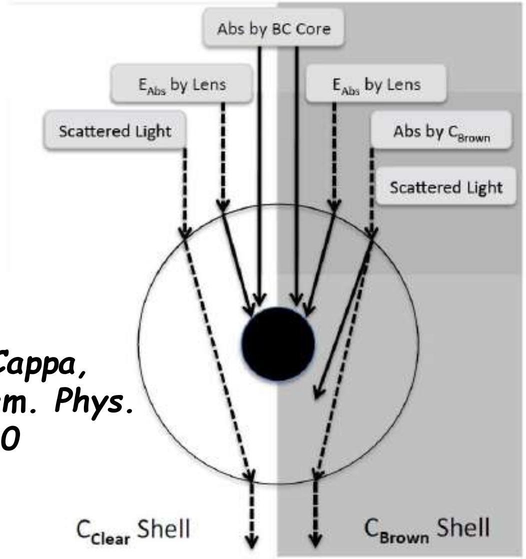
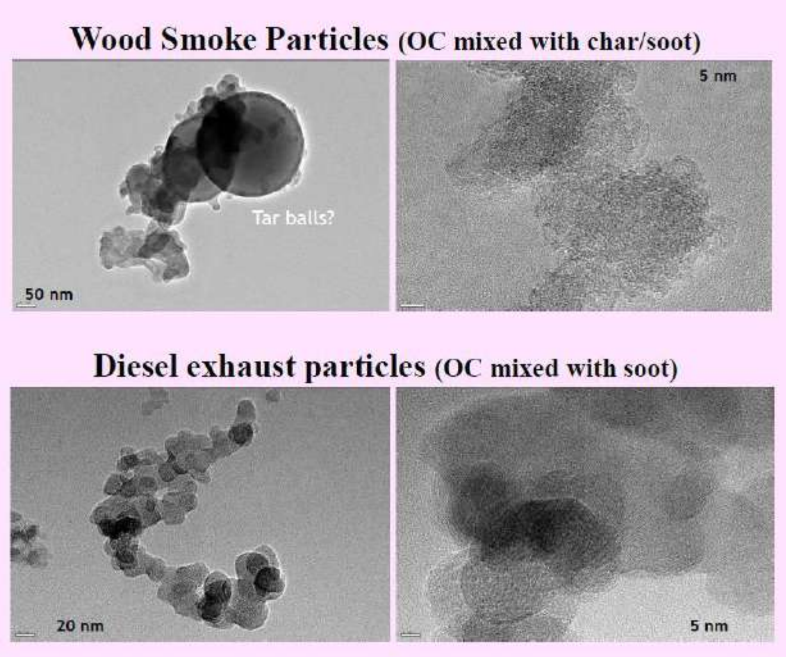


Fig. 1. Schematic of the effect of C_{Clear} and C_{Brown} shells on BC absorption.

Impact of aerosol mixing on aerosol optical properties



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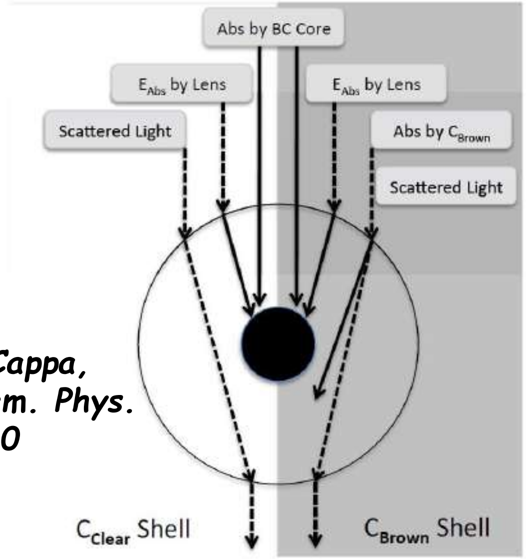

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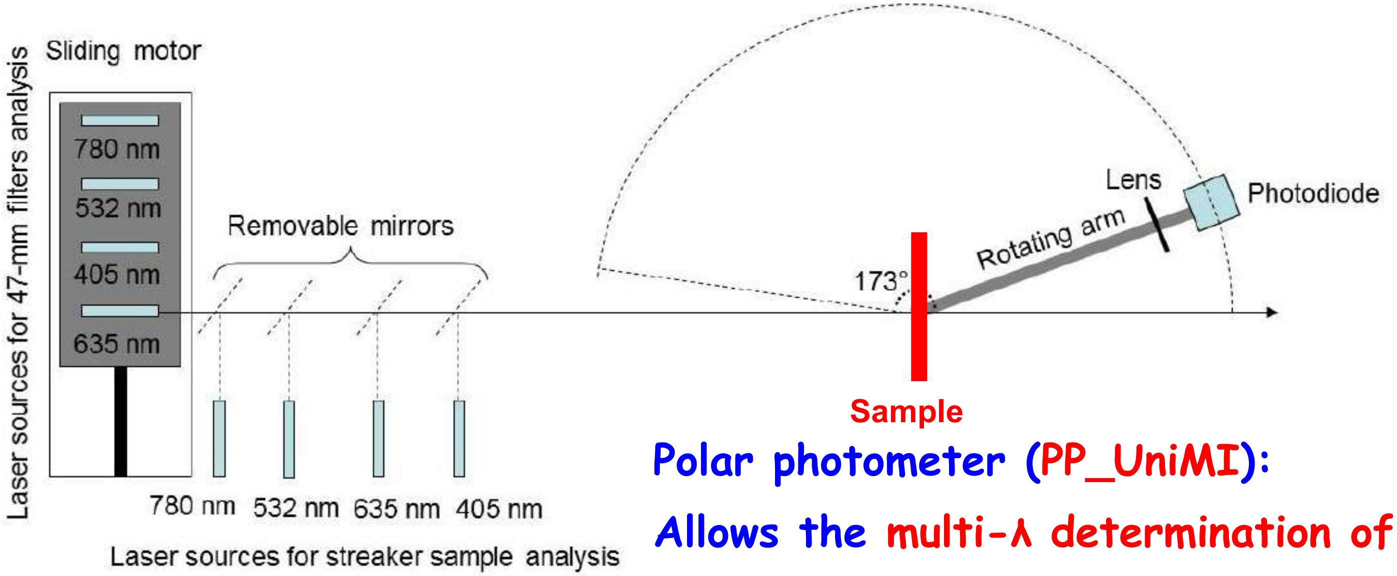
Importance of measurement of atmospheric aerosol optical properties with no sample pre-treatment (e.g. water extraction…)

PP_UniMI: what does it measure?

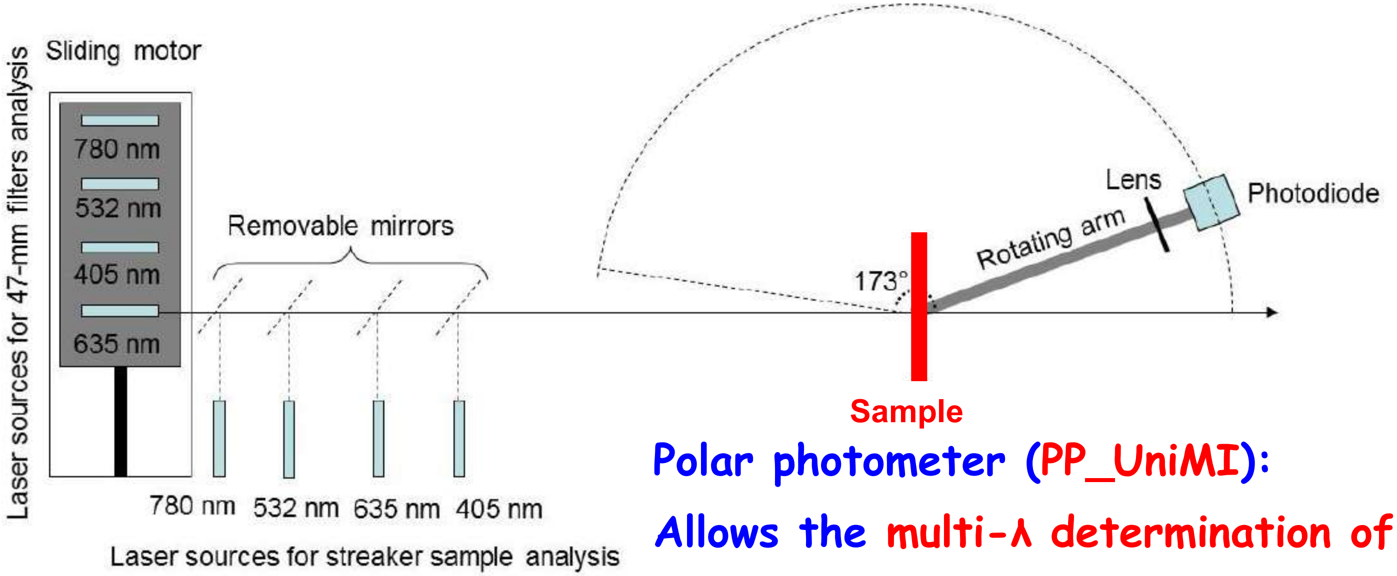


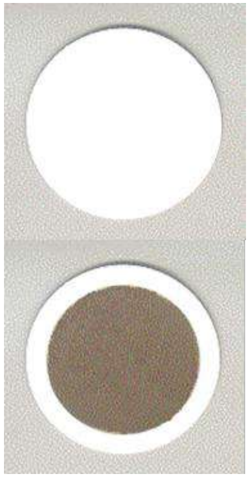
Polar photometer (PP_UniMI):

Allows the multi-λ determination of b_{abs} by measurements on aerosol samples collected on filter media

Vecchi et al, J. Aerosol Sci., 70 (2014)

PP_UniMI: what does it measures?





Blank filter

Loaded filter

Polar photometer (PP_UniMI):

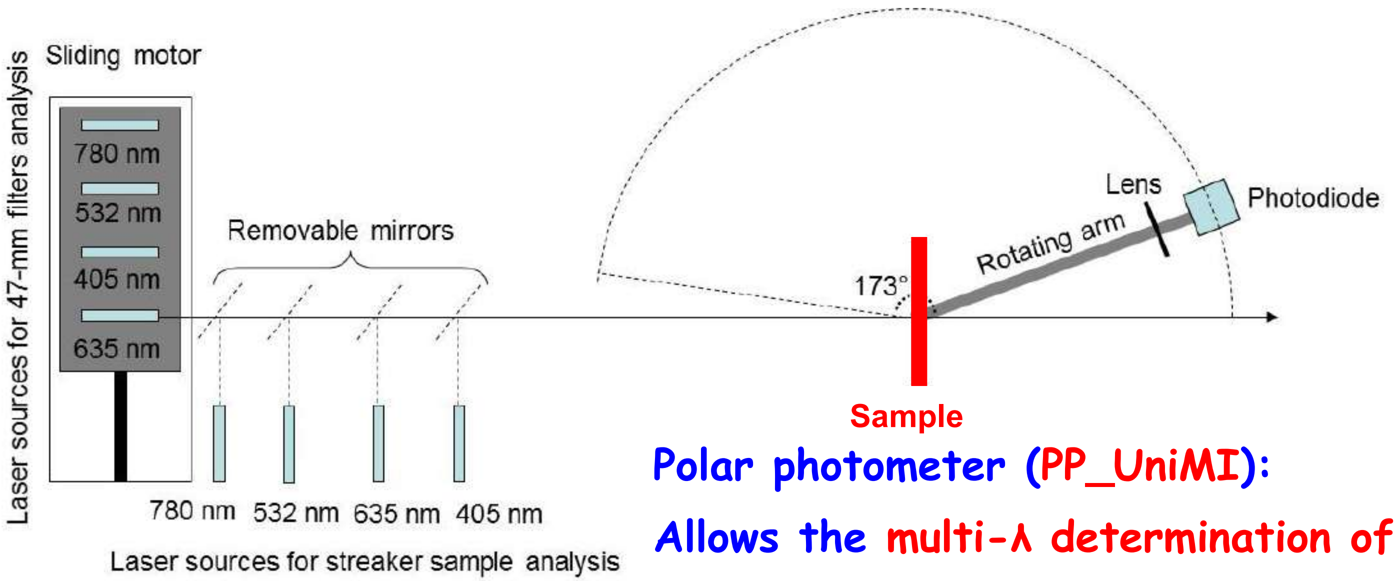
Allows the multi-λ determination of b_{abs} by measurements on aerosol samples collected on filter media

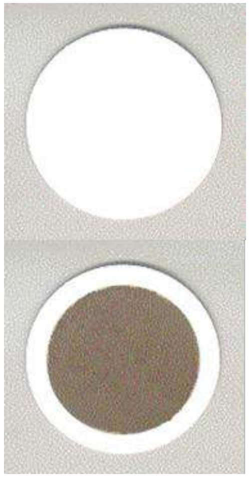
PP_UniMI is based on the measurement of the intensity distribution of the light diffused by filter before sampling (blank filter) and after aerosol collection (loaded filter).

Vecchi et al, J. Aerosol Sci., 70 (2014)

PP_UniMI: what does it measures?

@ Environmental Physics Group





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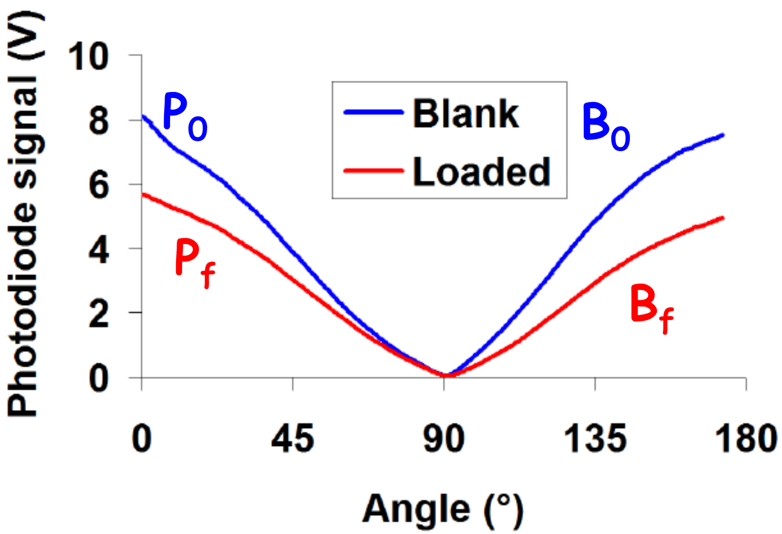
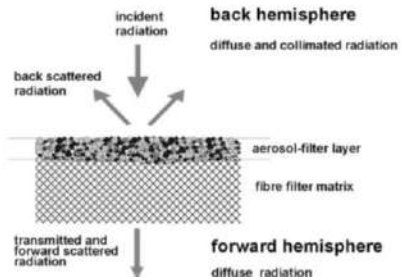


PP_UniMI is based on the measurement of the intensity distribution of the light diffused by filter before sampling (blank filter) and after aerosol collection (loaded filter).

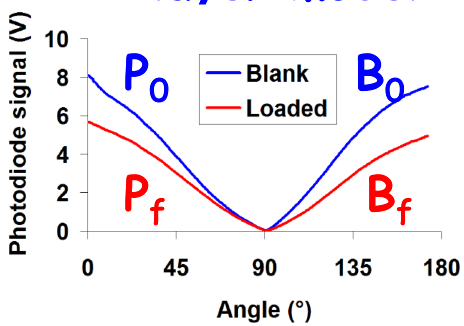
The integral signal measured in the front (P) and back (B) hemispheres for blank (0) and loaded filter are the inputs for b_{abs} determination

Vecchi et al, J. Aerosol Sci., 70 (2014)

PP_UniMI: basics for b_{abs} retrieval

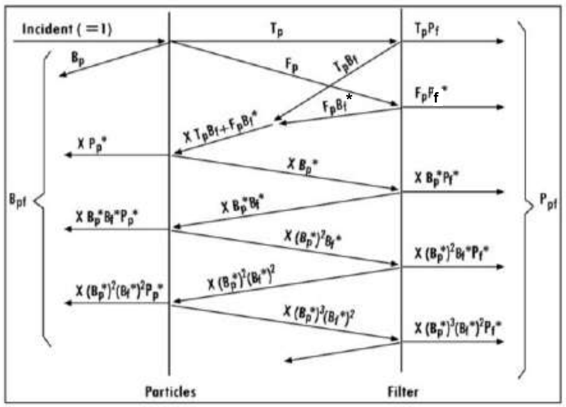


2-layer model



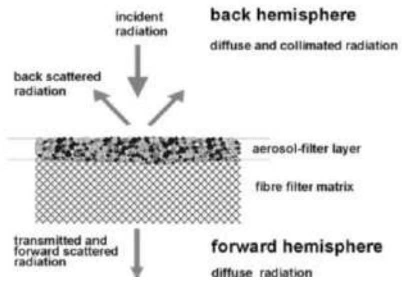
PP_UniMI: basics for b_{abs} retrieval

Adding method: considers all possible interactions between light, aerosol and filter.



Hänel et al, 1987

Relates the measured P_0, B_0, P_f, B_f to the properties of transmission and diffusion of the aerosol layer for collimated and diffused light (T_L, P_L, P_L^*, B_L, B_L^*)



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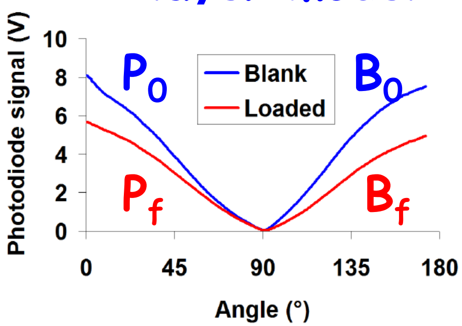

ω, τ

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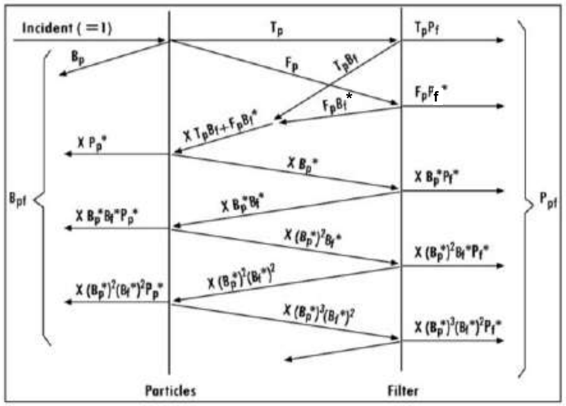

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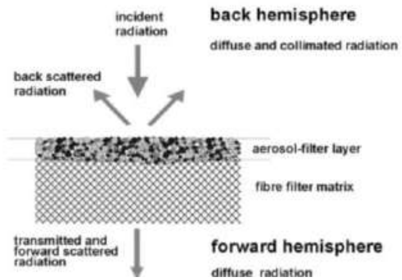

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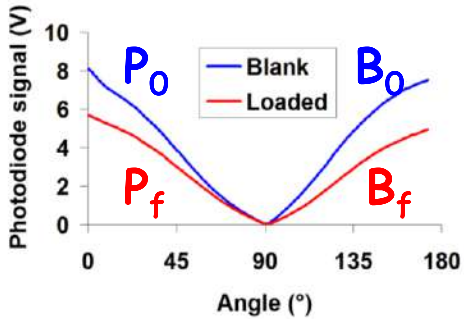
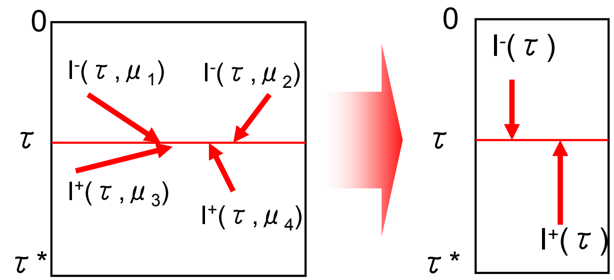


ω, τ

2-stream approximation (Coakley & Chylek et al., 1975) and assumption on the particle asymmetry factor g



Relates (T_L, P_L, P_L^*, B_L, B_L^*) to the single scattering albedo ω and the aerosol optical depth τ of the aerosol layer

$$\omega = \frac{\sigma_{scat}}{\sigma_{ext}}$$

Ratio of scattering and extinction cross sections

$\tau = -\ln T = -\ln (I/I_0)$

↓

transmittance

PP_UniMI: basics for b_{abs} retrieval

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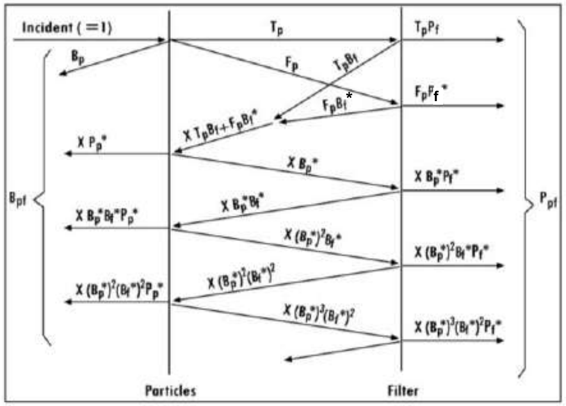

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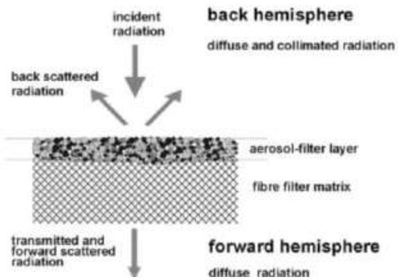

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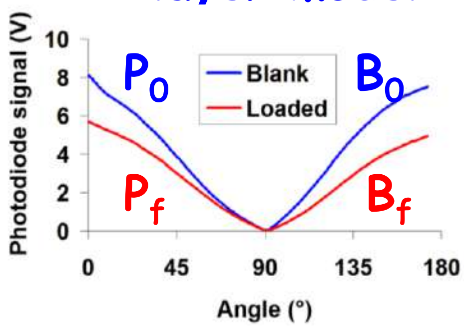


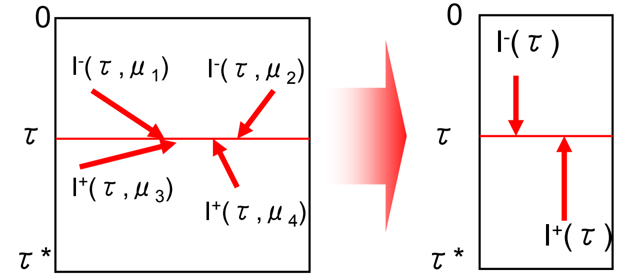
ω, τ

$ABS=(1-\omega)\cdot\tau$

considering sampling volume (V) & deposit area (A)

$$b_{abs}=ABS\ \frac{A}{V}$$

2-stream approximation (Coakley & Chylek et al., 1975) and assumption on the particle asymmetry factor g



Relates (T_L, P_L, P_L^*, B_L, B_L^*) to the single scattering albedo ω and the aerosol optical depth τ of the aerosol layer

$$\omega = \frac{\sigma_{scat}}{\sigma_{ext}}$$ Ratio of scattering and extinction cross sections

$\tau = -\ln T = -\ln(I/I_0)$

↓

transmittance

PP_UniMI: Implementation for 1-h resolved samples measurements

Polycarbonate filter
Thickness=10μm

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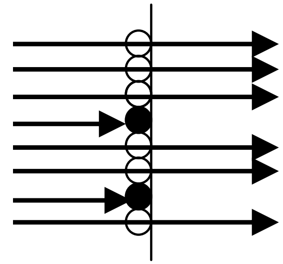
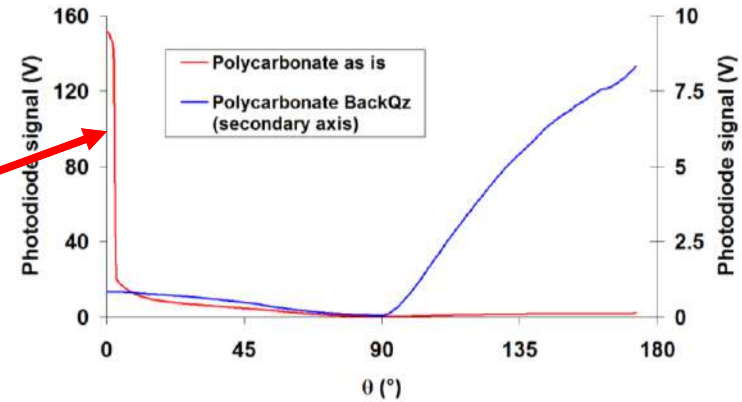
1.25 x 8 mm

Polycarbonate filter
Thickness=10μm

High fraction of transmitted light → Too low system sensitivity!

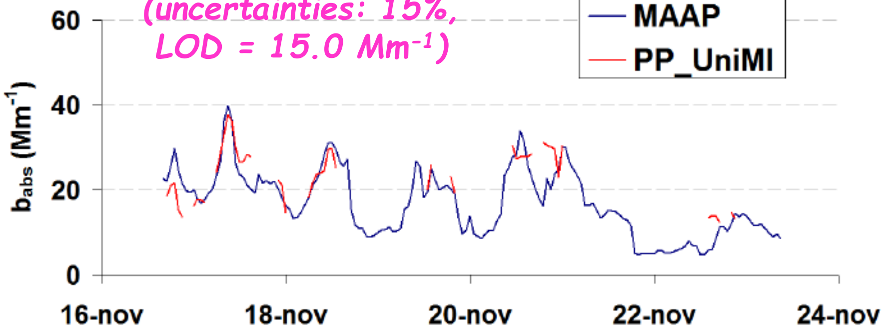
Polycarbonate filter





(uncertainties: 15%, LOD = 15.0 Mm^{-1})

Independent reference measurement (uncertainties: 13%)



MAAP= Multi-Angle Absorption Photometer

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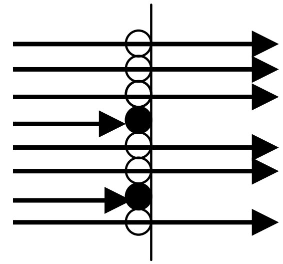
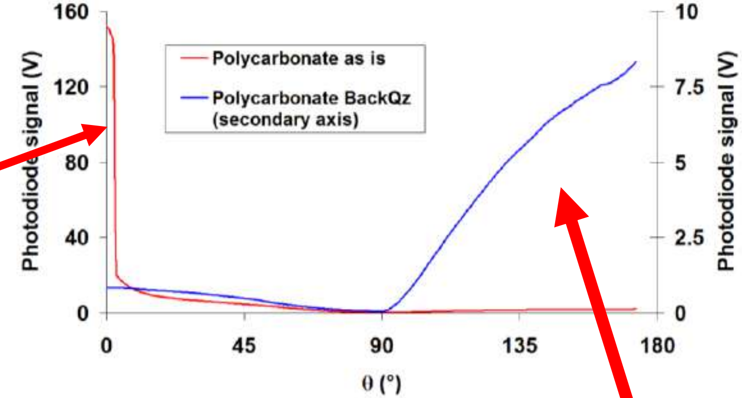
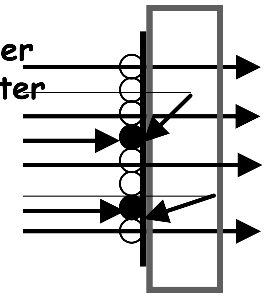




Polycarbonate filter + quartz fibre filter



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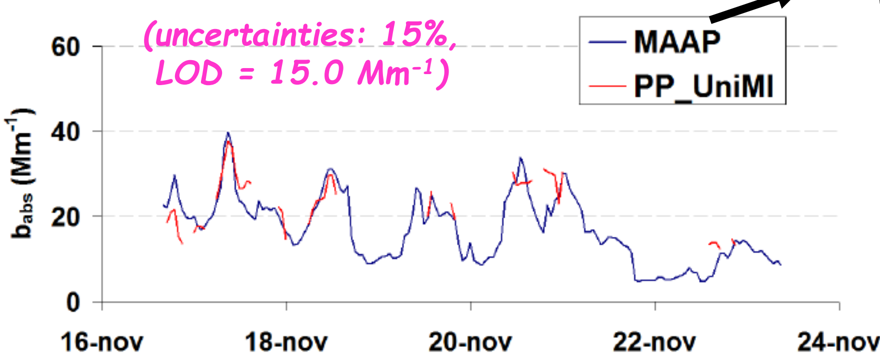

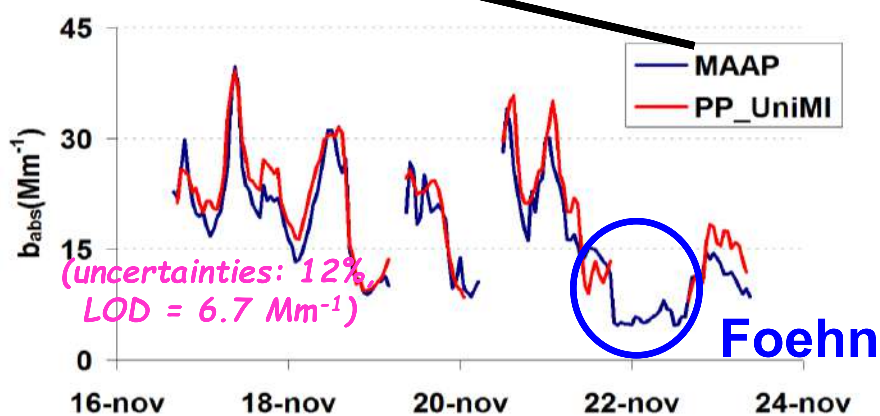

MAAP= Multi-Angle Absorption Photometer

Bernardoni et al., J. Aerosol Sci., 107 (2017)

SPES (Single Particle Extinction and Scattering)

@ Instrumental Optics Laboratory

Single Particle Extinction and Scattering (SPES): single particle device allowing to determine size and refractive index of particles suspended in air

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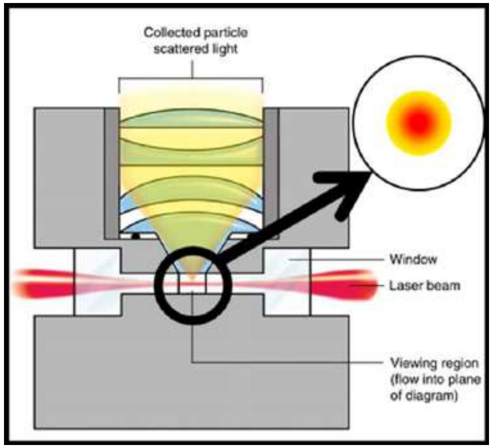
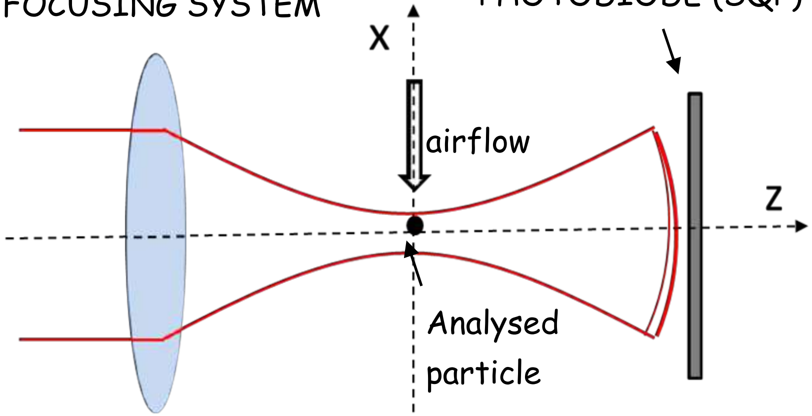
Single Particle Extinction and Scattering (SPES): single particle device allowing to determine size and refractive index of particles suspended in air

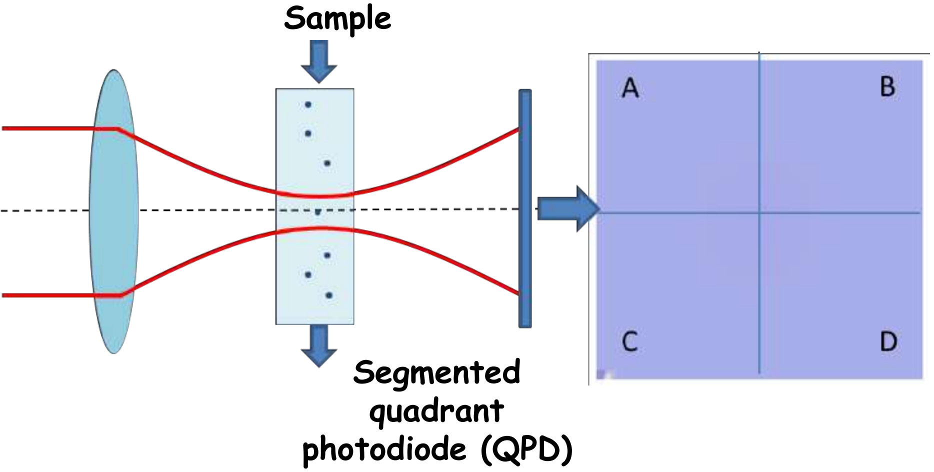
Traditional measurements: detection of INTENSITY of the scattered light to gain information on particle size OR monitoring attenuation of the beam.



SPES: measurement of extinction and scattering to gain information on the complex forward scattering amplitude S(0), which is related to particle polarizability (and thus to particle size and refractive index)



SPES: phenomenological description



While particle passes through the beam waist, incident and scattered fields combine.

Potenza et al., AIP Advances 5 (2015)

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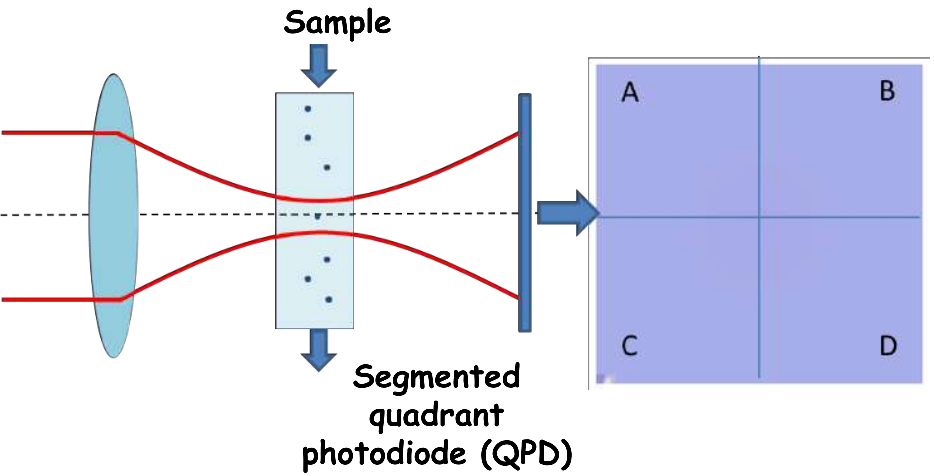
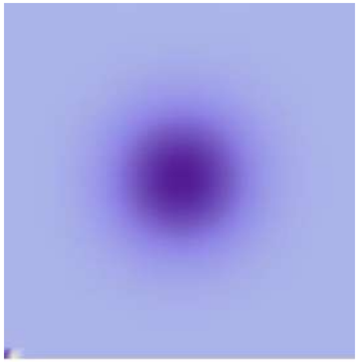


While particle passes through the beam waist, incident and scattered fields combine.

When particle is in the center of the beam: attenuation.



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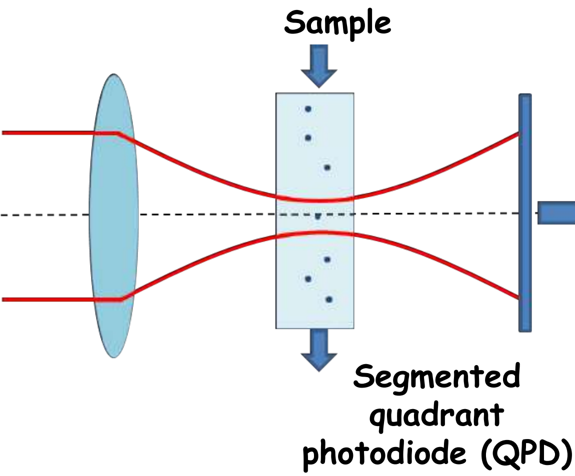

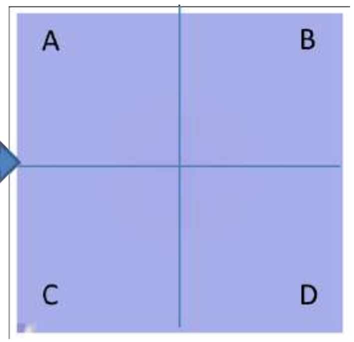

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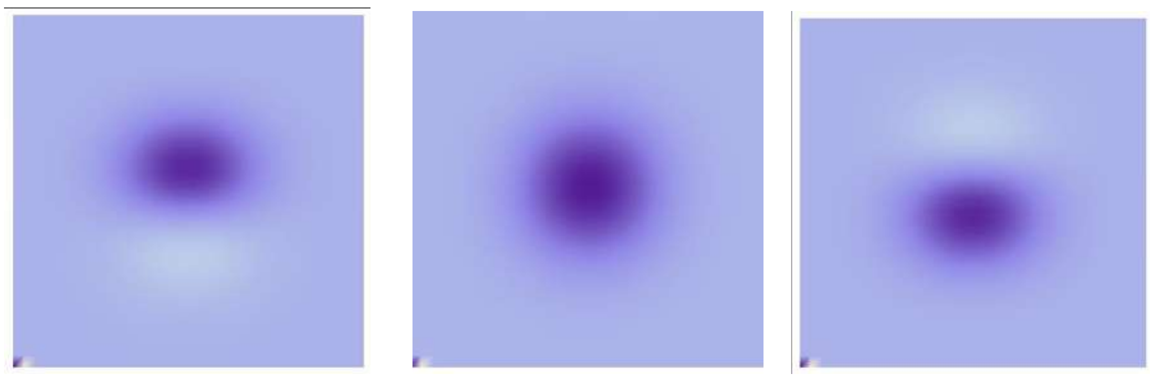
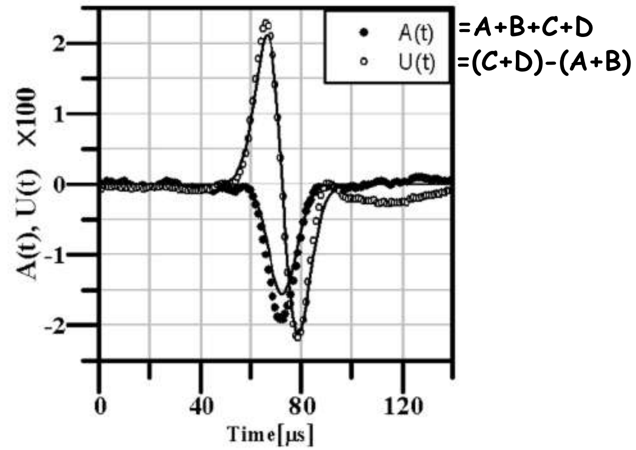
When out of the center: asymmetric interference figure is monitored by a QPD





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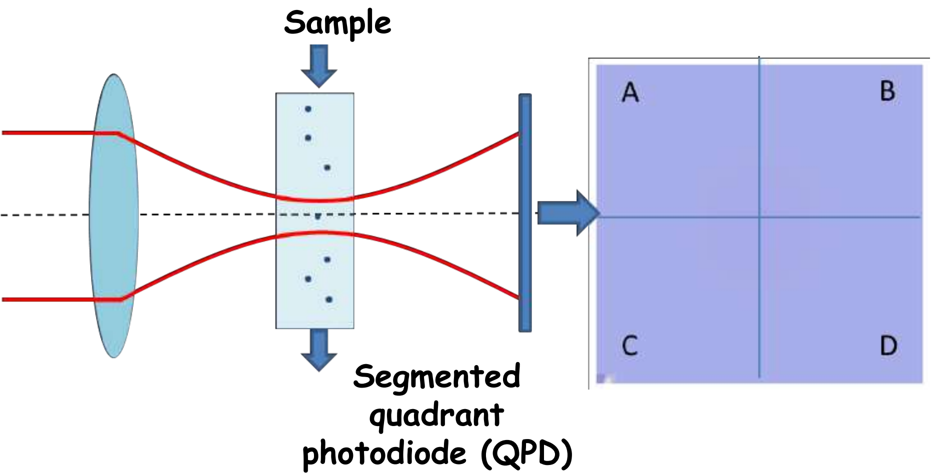

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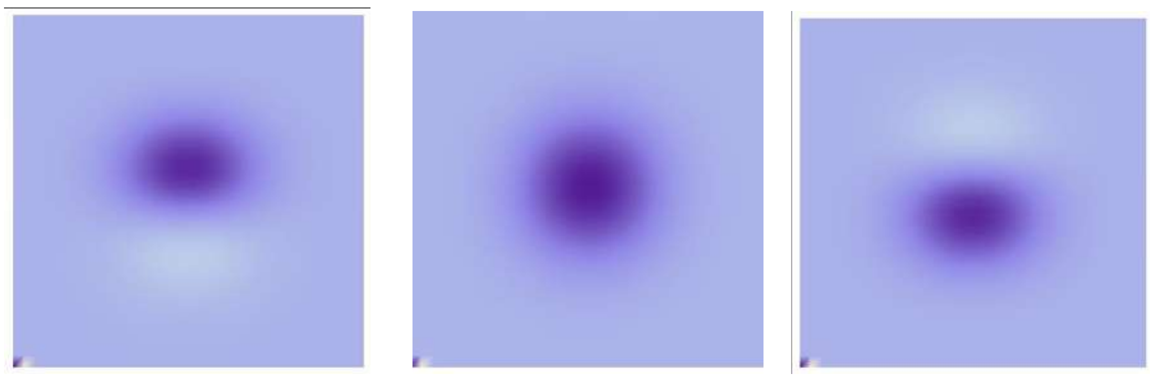
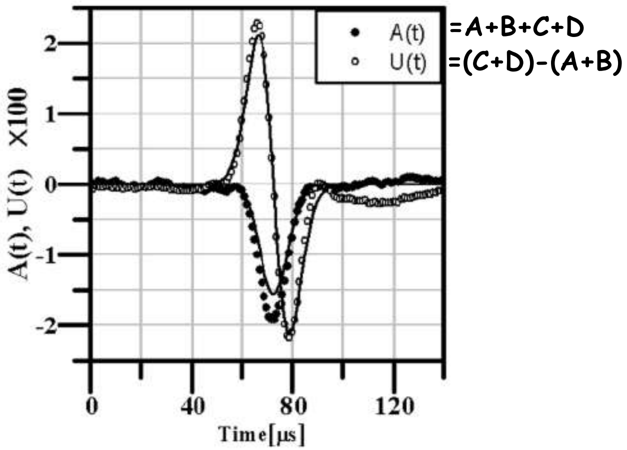




Attenuation: related to Re[S(0)] by Optical Theorem

Rayleigh regime

$$S(0) = ik^3\alpha + \frac{2}{3}k^6\alpha^2,$$

α=polarizability (related to refractive index & size)

k=2π/λ

Interference: related to |S(0)|

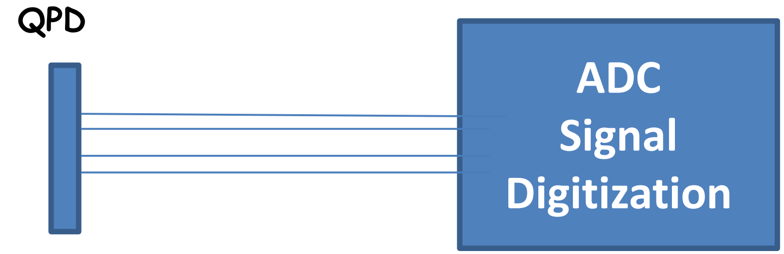
Potenza et al., AIP Advances 5 (2015)

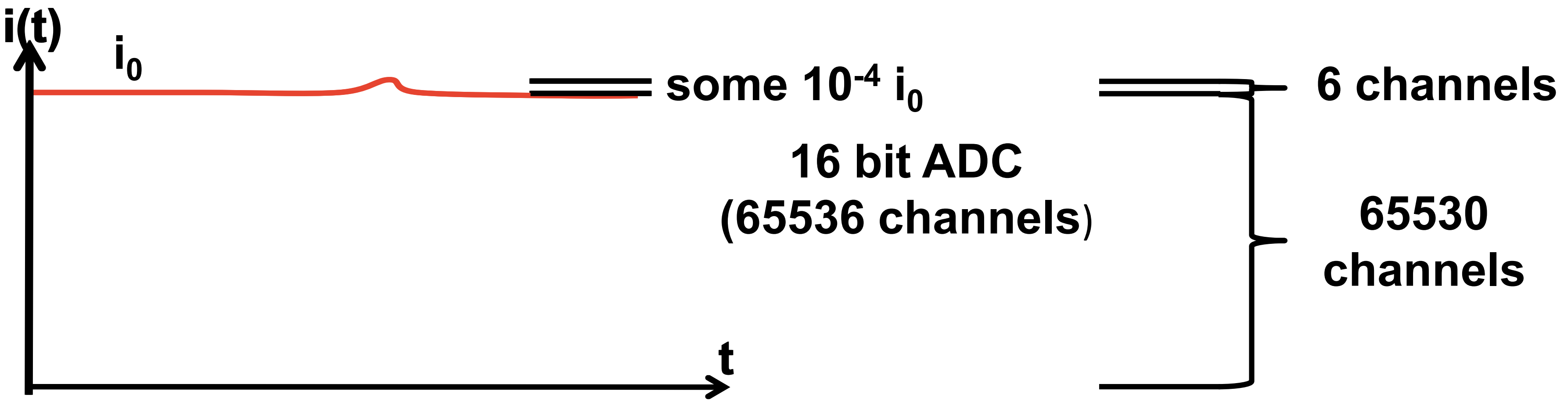
SPES: signal analysis

set up @ electronics group (A. Pullia)

Signal variation: $10^{-4} \cdot i_0$

Traditional electronics: low resolution for the signal of interest





slow, very low resolution

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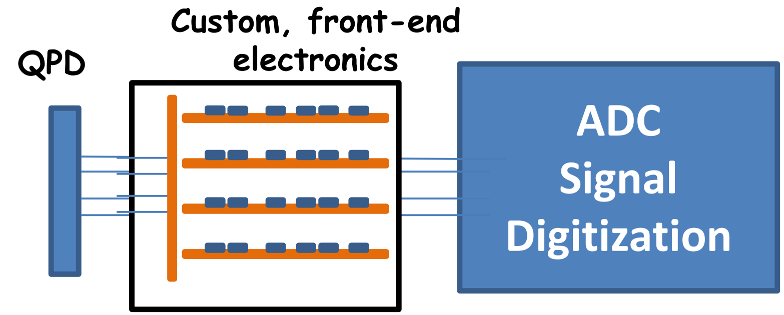


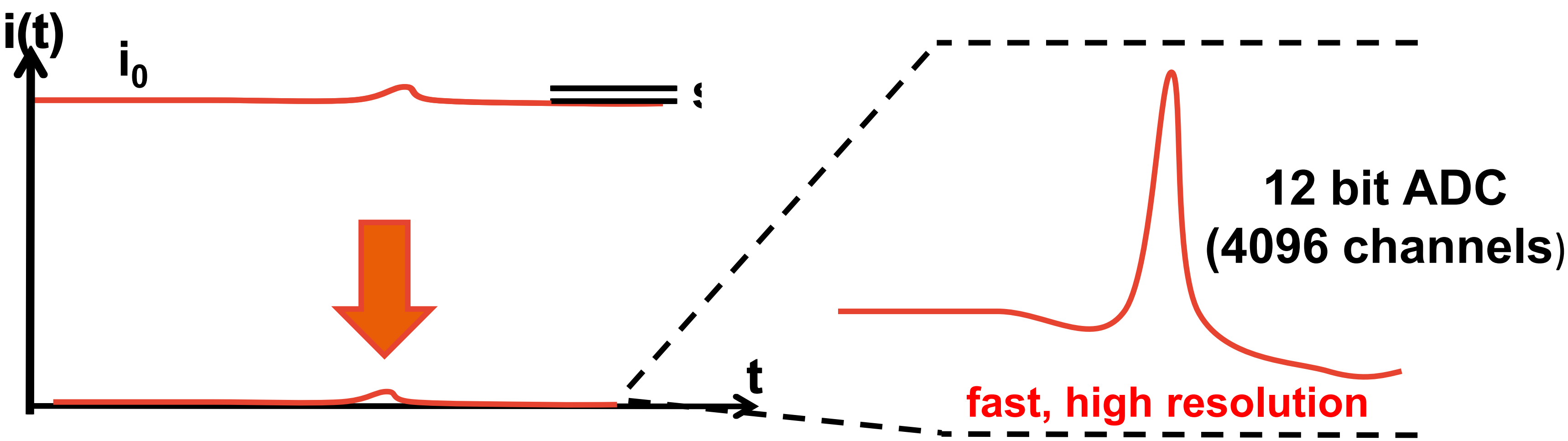
Signal variation: $10^{-4} \cdot i_0$

Traditional electronics: low resolution for the signal of interest

Custom, front end electronics

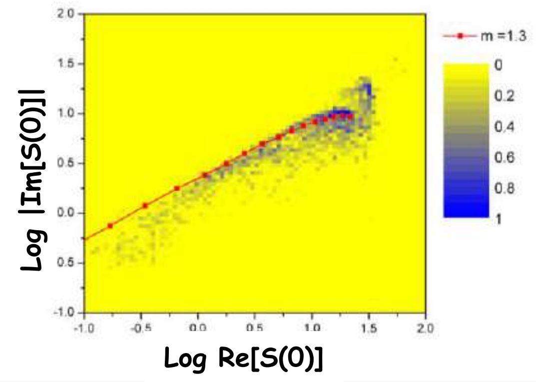
Slow signal by low pass filter with time constant (τ=250 μs) >> transit time: allows continuous monitoring of the intensity of the beam onto the sensor

Fast, zero average signal proportional to the fast intensity fluctuation due to particle passage



Pullia et al., Rev. Scient. Instr. 83 (2012)

SPES: examples of experimental results



Water droplets (expected as homogeneous spheres): **Good agreement of single measurement positioning in the complex plane to Mie prediction (including phase inversion, first time detected)**

Potenza et al. J. Nanopart. Res. (submitted)

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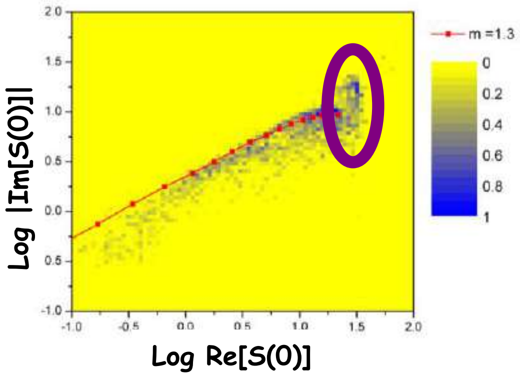

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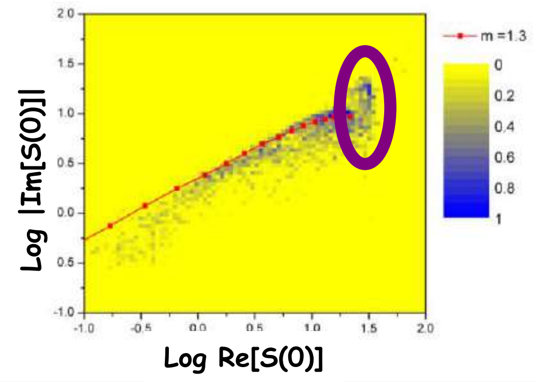

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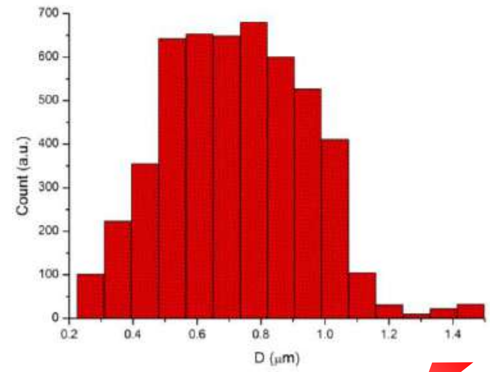

Statistical analysis of the data: more reliable information (e.g. m=1.32±0.01).

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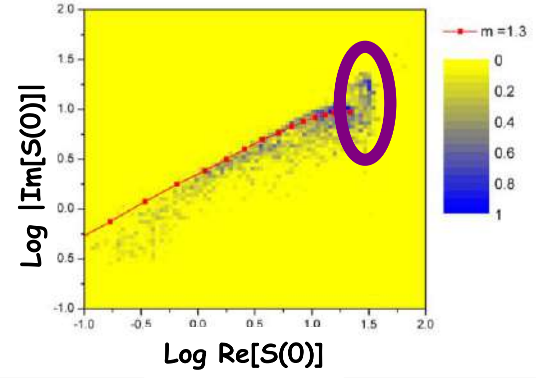

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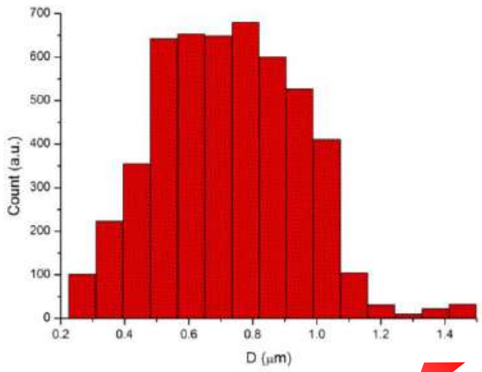

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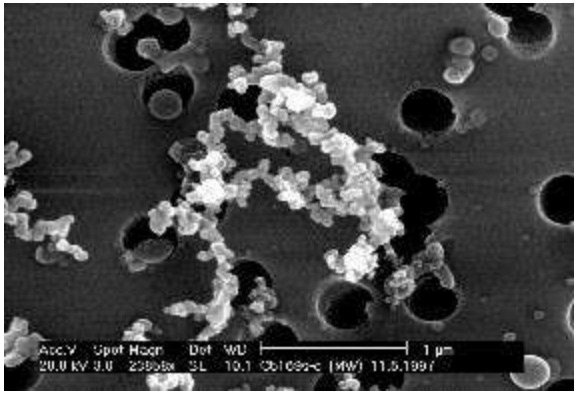
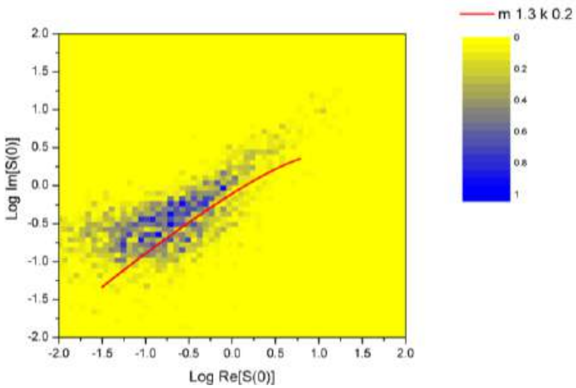
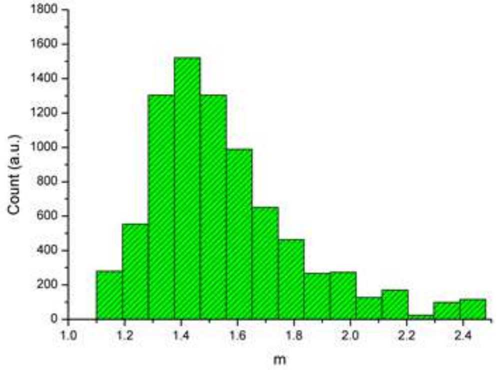






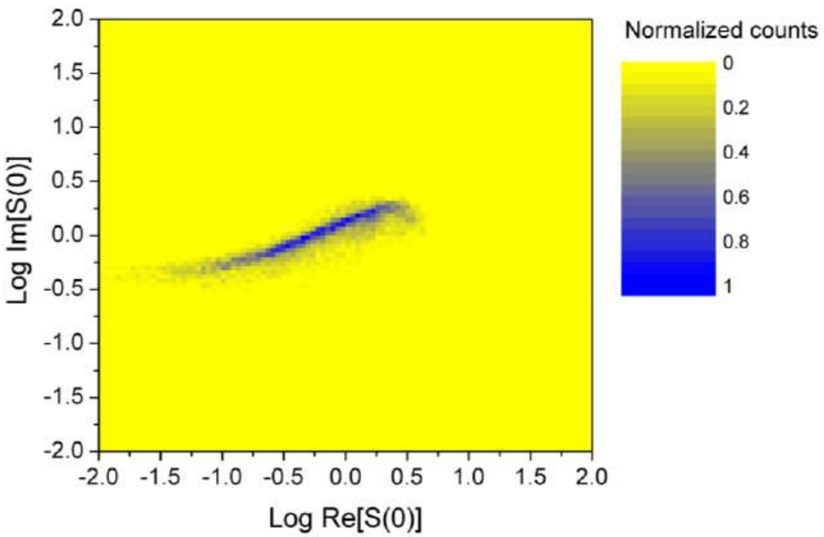
Soot (expected as non-homogeneous material with irregular shape):

This information is provided by SPES through a spread of particles in the complex plane and a very large distribution of retrieved refractive indices.

Potenza et al. J. Nanopart. Res. (submitted)

SPES and PP_UniMI to gain information on particle features

Pyrethrum smoke was analysed by SPES. Particles were then collected on filter medium and analysed by PP_UniMI



Information by SPES:

- Spherical, homogeneous particles (small spread of particles in the complex plain)
- k=0.1 (weakly absorbing) @ 640nm

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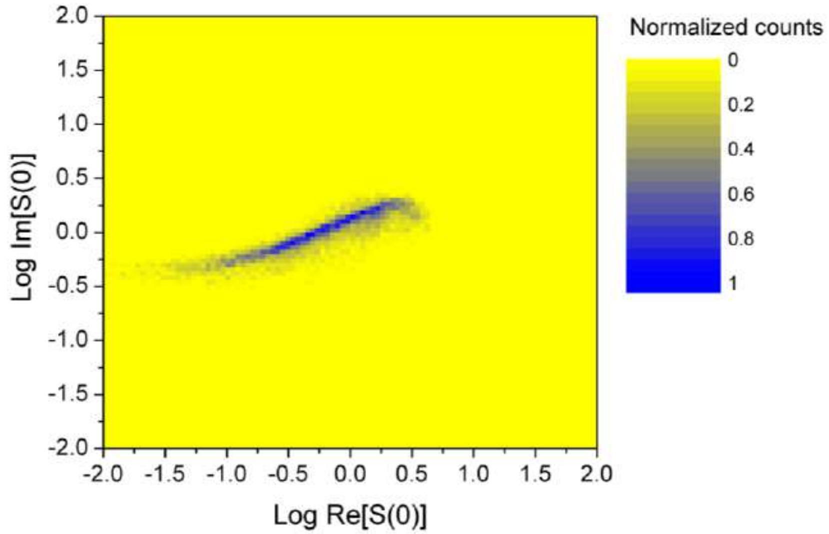

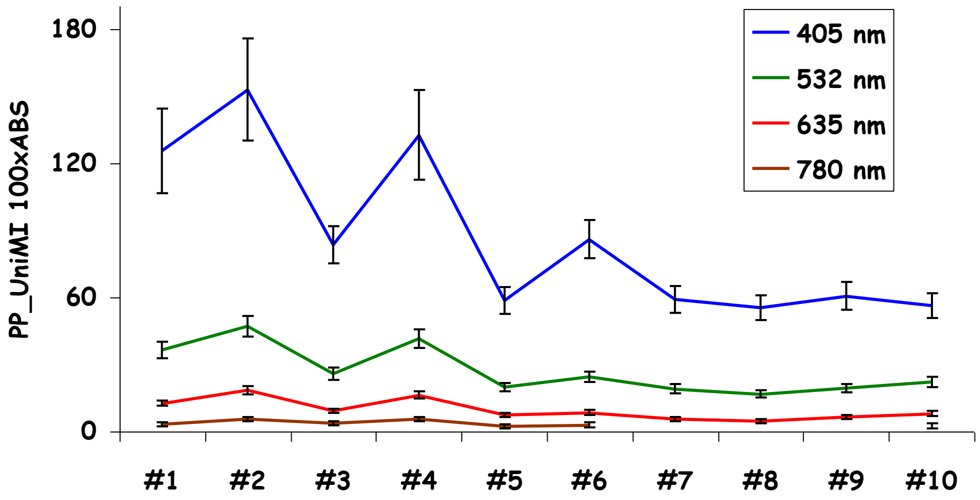

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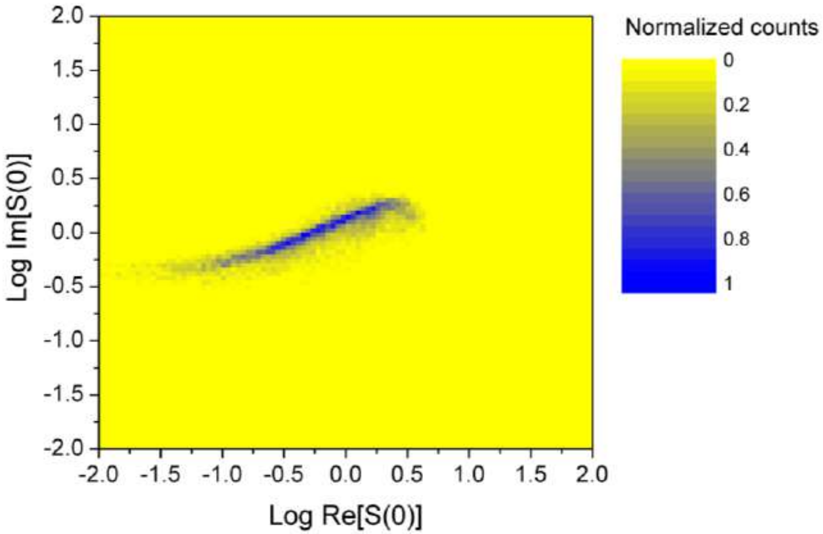

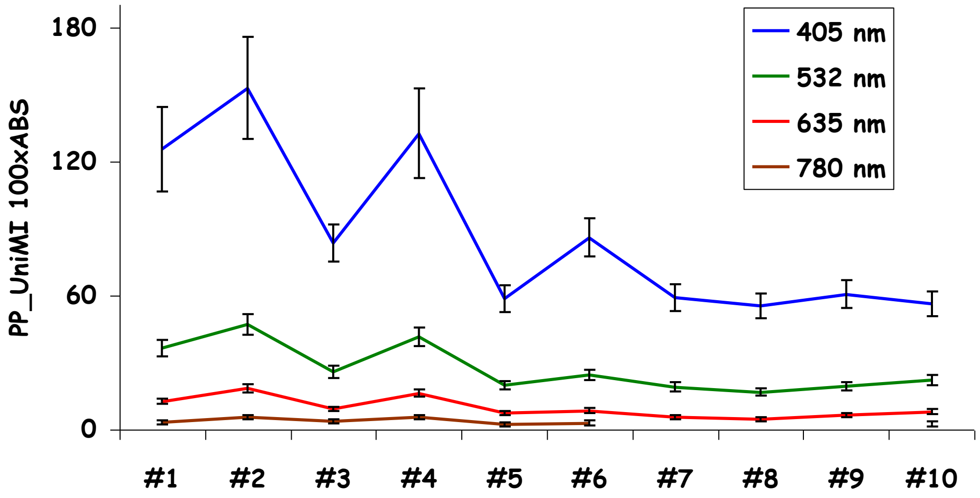

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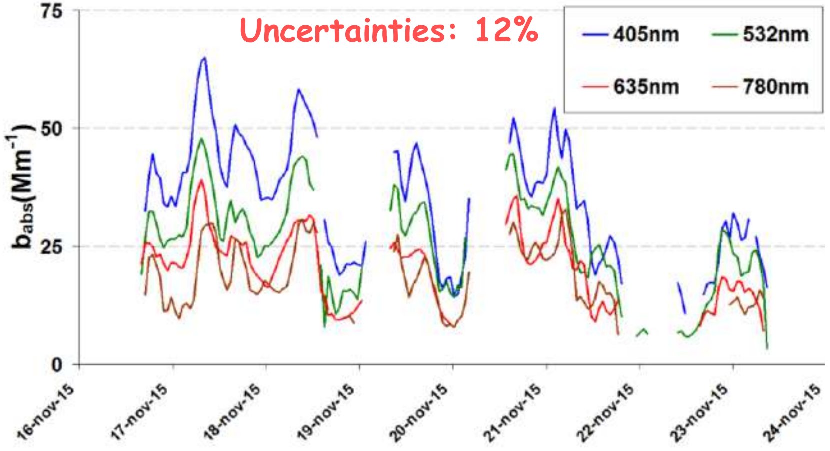
Possible emission of spherical BrC by pyrethrum !!!

Potenza et al. J. Nanopart. Res. (submitted)

PP_UniMI as a tool for source apportionment

PP_UniMI output is a 4-λ aerosol b_{abs} temporal trend



Bernardoni et al., J. Aerosol Sci., 107 (2017)

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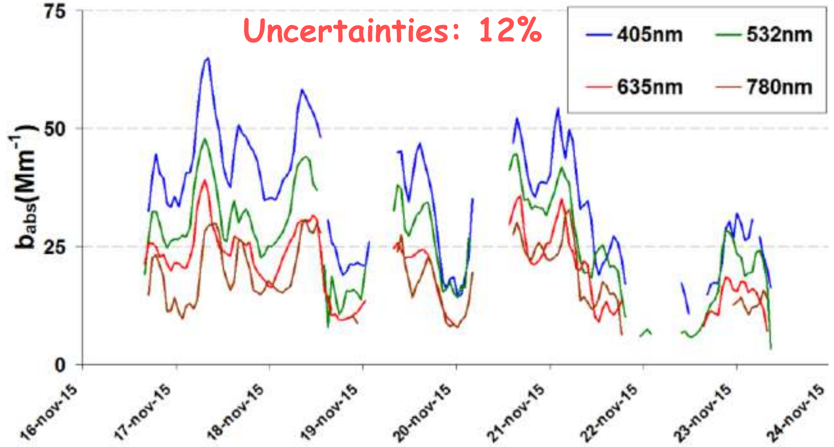

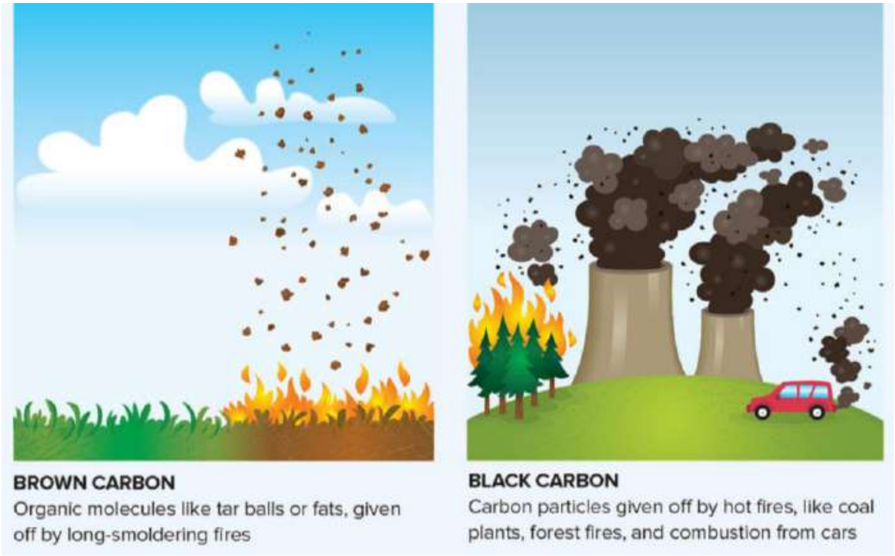

BC and BrC have not only different λ-dependence of their absorption properties, but also different (main) sources

BrC: mainly emitted by wood/biomass burning

BC: emitted by both fossil fuel combustion AND wood/biomass burning

Bernardoni et al., J. Aerosol Sci., 107 (2017)

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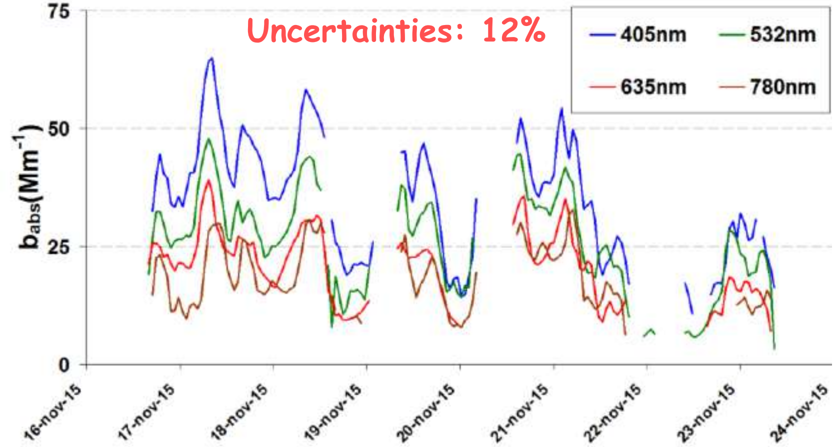

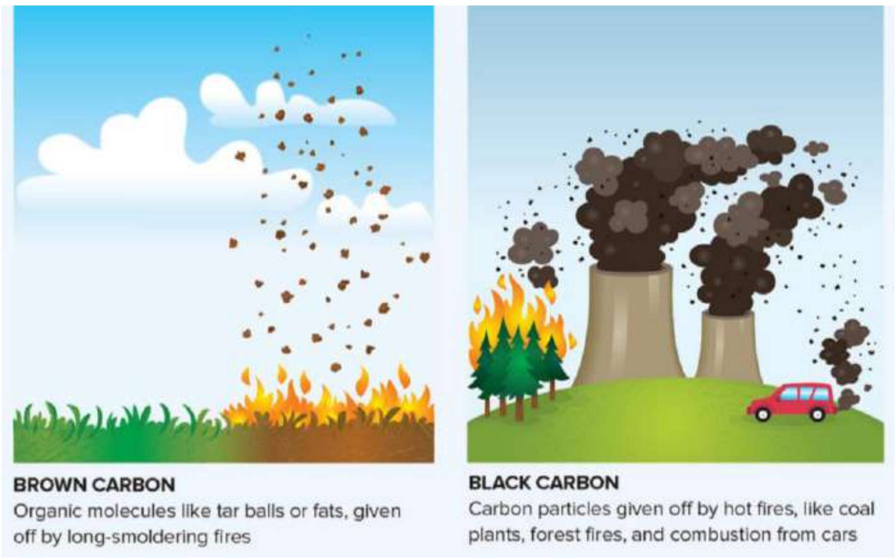

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POSSIBILITY TO PERFORM SOURCE-APPORTIONMENT STUDIES BY MULTI-λ ABSORPTION PROPERTIES MEASUREMENTS!!!

Bernardoni et al., J. Aerosol Sci., 107 (2017)

Optical apportionment methodologies

Aethalometer model

(source apportionment)

$$b_{abs}(\lambda)=b^{FF}_{abs}(\lambda)+b^{WB}_{abs}(\lambda)$$

$b^{FF}_{abs}(\lambda)\sim\lambda^{-\alpha_{FF}}$, $\alpha_{FF}=1$ (emit only BC)

? Range 1.6-3

$b^{WB}_{abs}(\lambda)\sim\lambda^{-\alpha_{WB}}$, $\alpha_{WB}=1.8$ (emits BC and BrC)

(Sandradewi et al., Env.Sci.Tech.,2008)

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MWAA (multi-wavelength absorption analyser model)
(source and component apportionment)

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Massabò et al., Atmos.Environ. (2015)

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Few literature information

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$$b_{abs}(\lambda) = \underbrace{\left[BC_{FF}\cdot\sigma_0^{BC}\right]}_{A'}\lambda^{-\alpha_{FF}} + \underbrace{\left[BC_{WB}\cdot\sigma_0^{BC} + BrC\cdot\sigma_0^{BrC}\right]}_{B'}\lambda^{-\alpha_{WB}}$$

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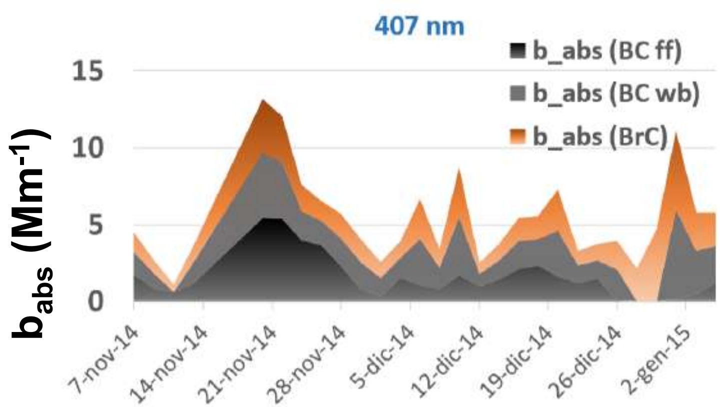
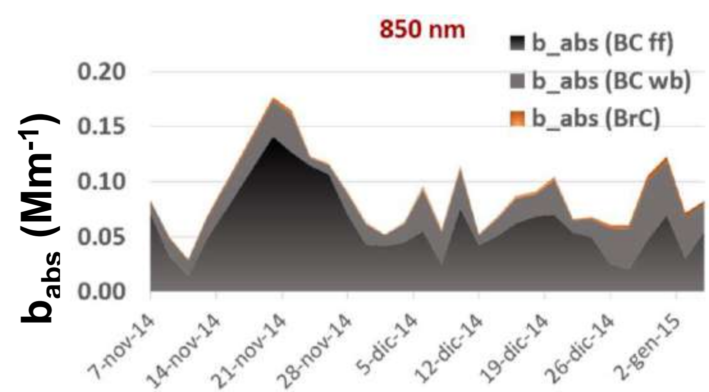
3.9 @ site highly impacted by WB

Much higher relative BrC contribution at 407nm than 850nm





Acknowledgements

The authors are grateful to:

INFN-Milan for funding (exp. MANIA, DEPOTMASS, TRACCIA)

Alberto Pullia & the group of electronics for the development of the front-end electronics for SPES

Francesco Cavaliere, Daniele Viganò & the team of the Mechanical Workshop of the Physics Department for technical support in PP_UniMI & SPES realisation

The Joint Research Center (JRC-Ispra) for allowing soot measurements by SPES

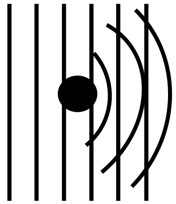
Thank you for kind attention!!

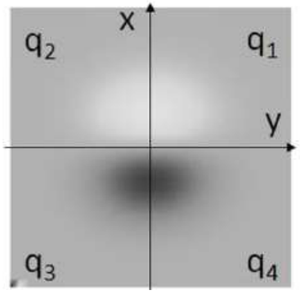
Further activities connected to the topics of the talk in the posters:

- Valentini et al., #50; Potenza et al., #35; Forello et al., #47

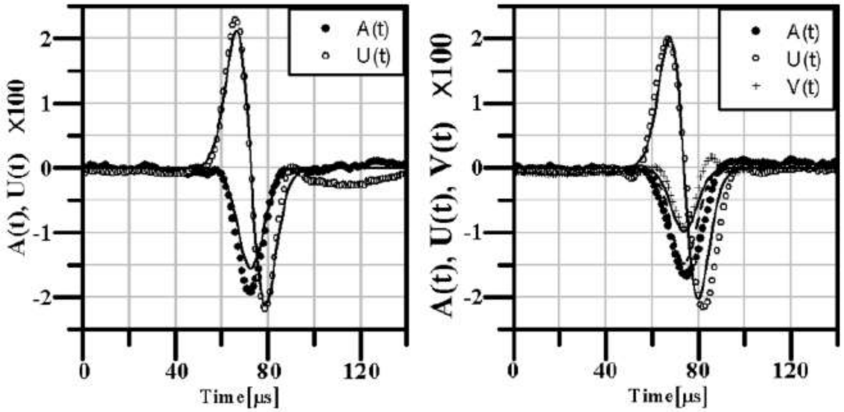
SPES: physical basis and data validation

Combination of the incident and the scattering fields lead to interference figure, which is monitored during particle movement through the beam waist





SQP allows measuring attenuation - due to scattering & absorption - of the incident beam A(t) and intensity asymmetry due to interference U(t), related to the dimensionless scattering amplitude S(0)=s(0)e$^{i\varphi}$ (thus to size & refractive index)



$$V(t) = -2\left(\frac{\lambda}{\pi w_0}\right)^2 s(0)\, e^{-2\xi^2(t)} e^{-2\eta^2} \sin\varphi\, \mathrm{erfi}\,\eta$$

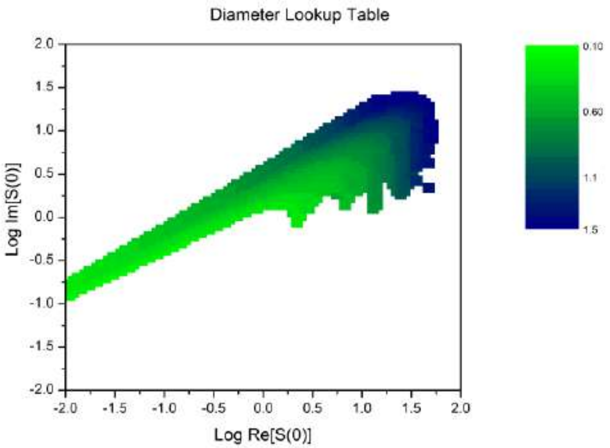
$$A(t) = 2\left(\frac{\lambda}{\pi w_0}\right)^2 \underline{s(0)}\, e^{-2\xi^2(t)} \underline{\cos\varphi}$$

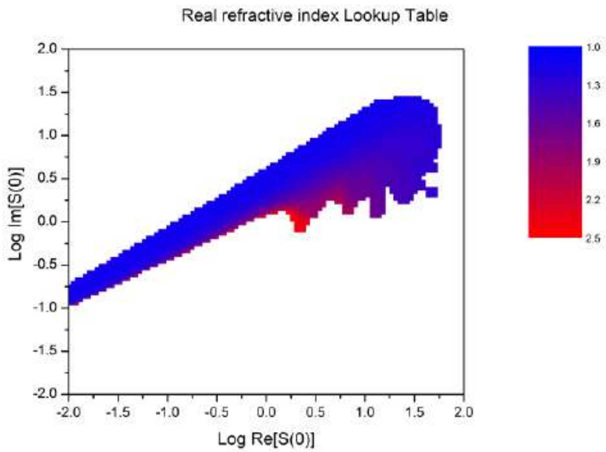
$$U(t) = -2\left(\frac{\lambda}{\pi w_0}\right)^2 \underline{s(0)}\, e^{-2\xi^2(t)} \underline{\sin\varphi}\, \mathrm{erfi}\,\xi(t)$$

Information on asymmetry of the signal in y-direction V(t) is indication of particle passage out of laser focus

➔ invalidation of the datum!!!

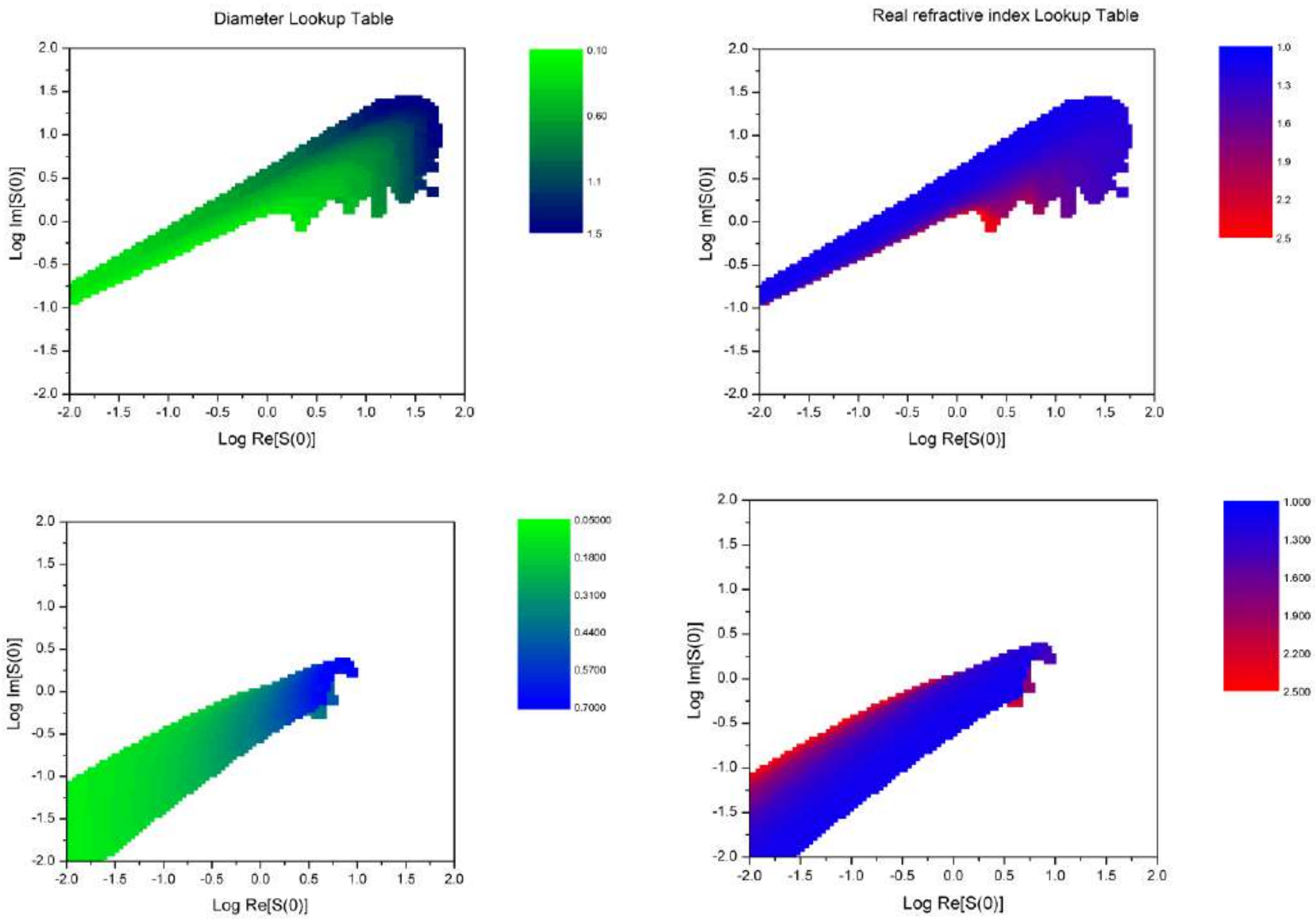
SPES: possibility to identify light-absorbing particles





Non absorbing particles (k=0)

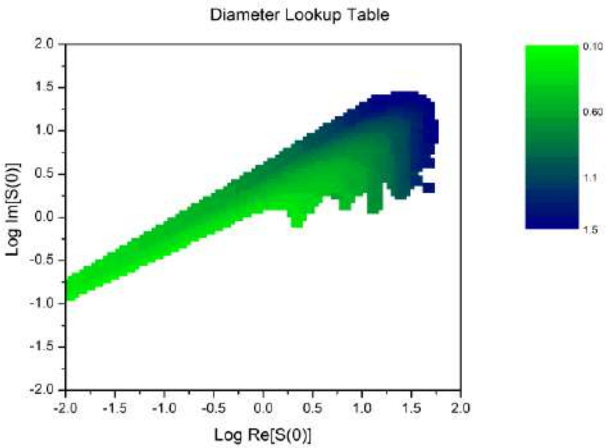
SPES: possibility to identify light-absorbing particles

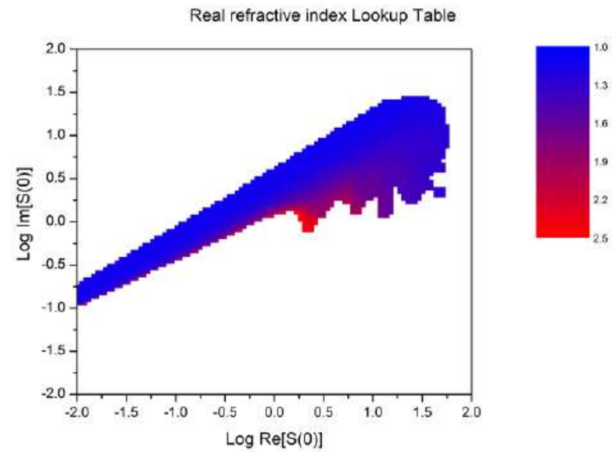


Non absorbing particles (k=0)

Absorbing particles (k=0.2)

SPES: possibility to identify light-absorbing particles





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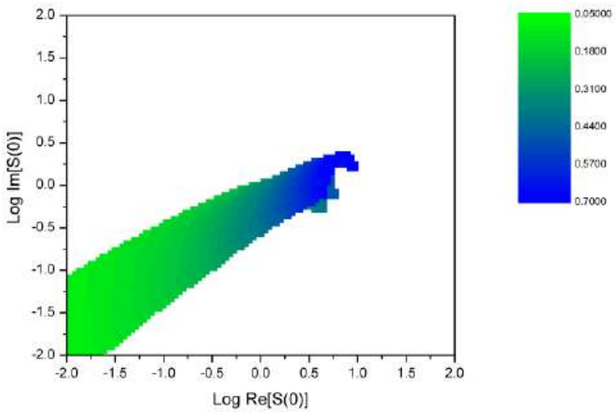

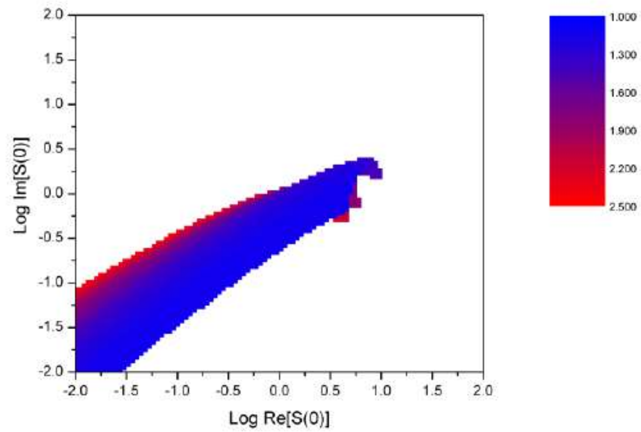

Absorbing particles (k=0.2)

Non absorbing particles and particles with significant imaginary part of the refractive index lay in different areas of the complex plane thus allowing their determination

IMPROVE algorithm: chemical extinction method

(see further details in the poster by Valentini S.)

Information on aerosol chemical composition and size distribution

(carried out @ Environmental Physics group)

Air quality, source apportionment, and health effect studies,

BUT ALSO

Aerosol extinction coefficient and visibility estimates

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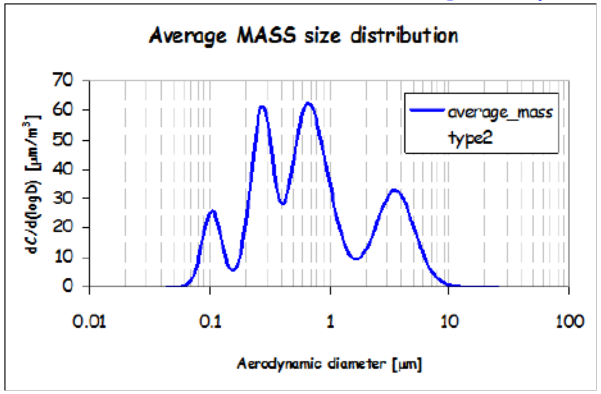

Aerosol size distribution

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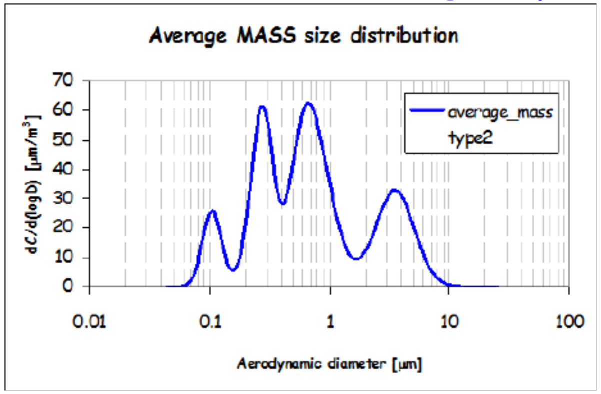

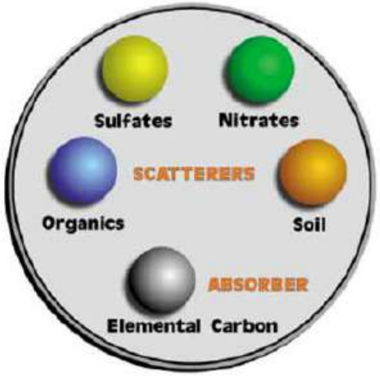

Aerosol size distribution

Aerosol composition

(density, complex refractive index)

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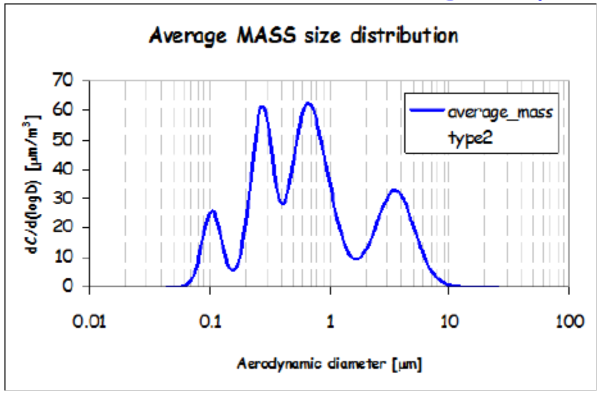

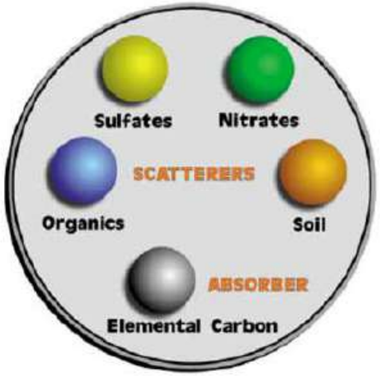

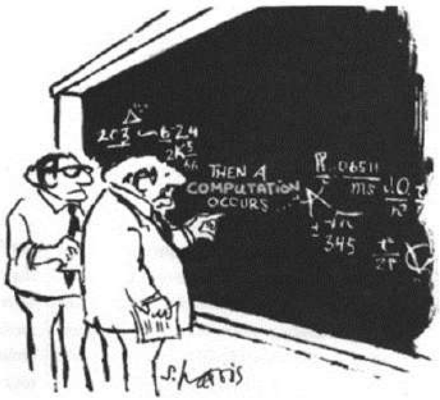

Aerosol size distribution

Aerosol composition
(density, complex refractive index)

Algorithm for solving
Mie equations

IMPROVE algorithm: chemical extinction method

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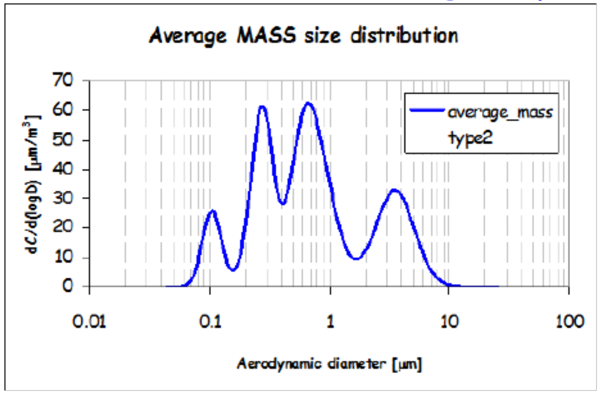

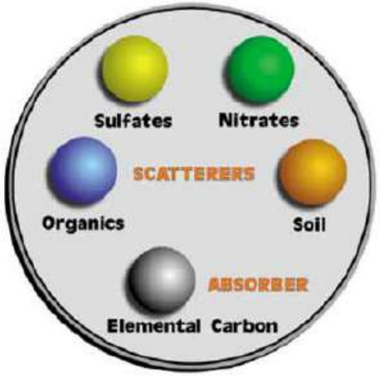

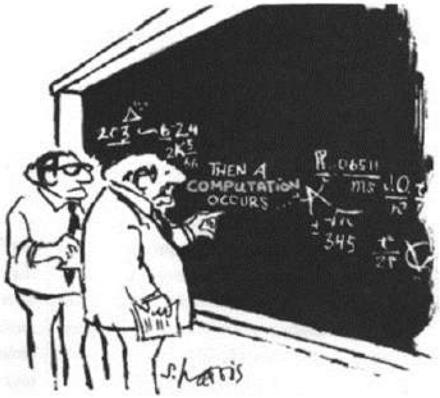

Aerosol size distribution

Aerosol composition
(density, complex refractive index)

Algorithm for solving Mie equations

Estimate of extinction coefficient and (by Koeschmieder equation) visual range

Dati ARPA Lombardia
Immagini tratte dalla presentazione del Dott. Lazzarini
Giornate della sostenibilità focus ambiente – 21/03/14

Misure di proprietà di assorbimento dell'aerosol

Influenza del *mixing* sulle proprietà di assorbimento del campione

Necessità di eseguire misure sul campione non pre-trattato.

Strumento aggiuntivo per ogni sito di interesse!

Necessitano correzione per *multiple scattering*

In aria on-line

Su filtro on-line

Su filtro, off-line

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Fotoacustico (possibile perdita di semivolatili per riscaldamento, anche con impatto su misura per perdita energia come calore latente; solo di recente sviluppo multi-λ);

SP2 (single particle soot photometer, può dare info su massa assorbente e mixing 1! λ)

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Multi-Angle Absorption Photometer (1! λ; misura radiazione trasmessa e retrodiffusa per valutare proprietà assorbimento)

Aethalometer/Particle-Soot absorption photometer (multi-λ, ma solo misure di trasmittanza: richiede ulteriore correzione per scattering del campione!)

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Misure di proprietà di assorbimento dell'aerosol su filtro

VANTAGGI:

- Ricavare informazioni da campioni raccolti durante le campagne di misura per la caratterizzazione fisico-chimica;

-eseguire indagini retrospettive su campioni correttamente conservati

Misure di proprietà di assorbimento dell'aerosol su filtro

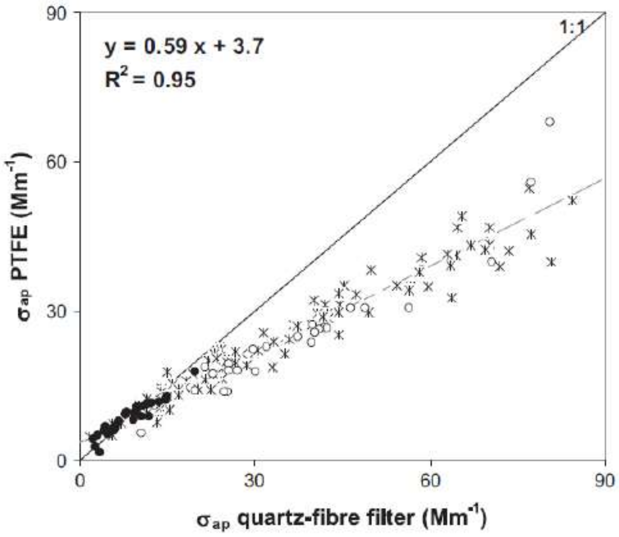
VANTAGGI:

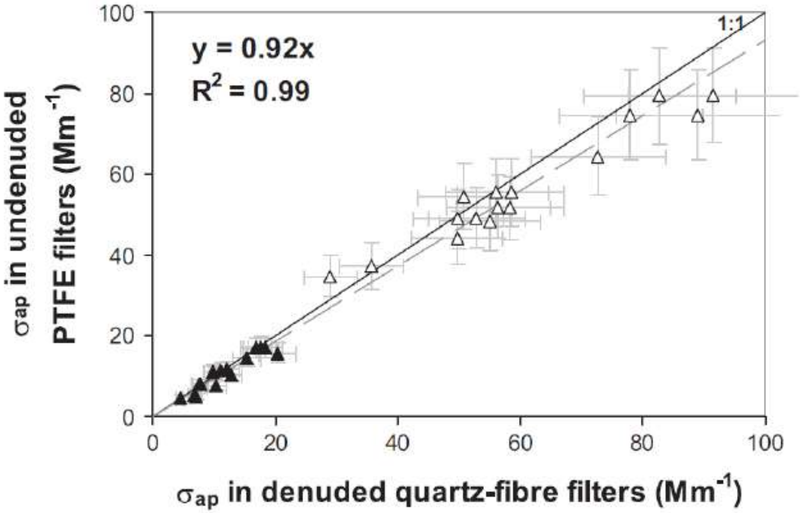
- Ricavare informazioni da campioni raccolti durante le campagne di misura per la caratterizzazione fisico-chimica;
-eseguire indagini retrospettive su campioni correttamente conservati

SVANTAGGI:

- Artefatti di campionamento o altre condizioni ambientali, per alcune tipologie di filtro, hanno possibile impatto sulle misure

Vecchi et al., 2014





Misure di proprietà di assorbimento dell'aerosol campionato ad elevata risoluzione temporale

1.25 x 8 mm

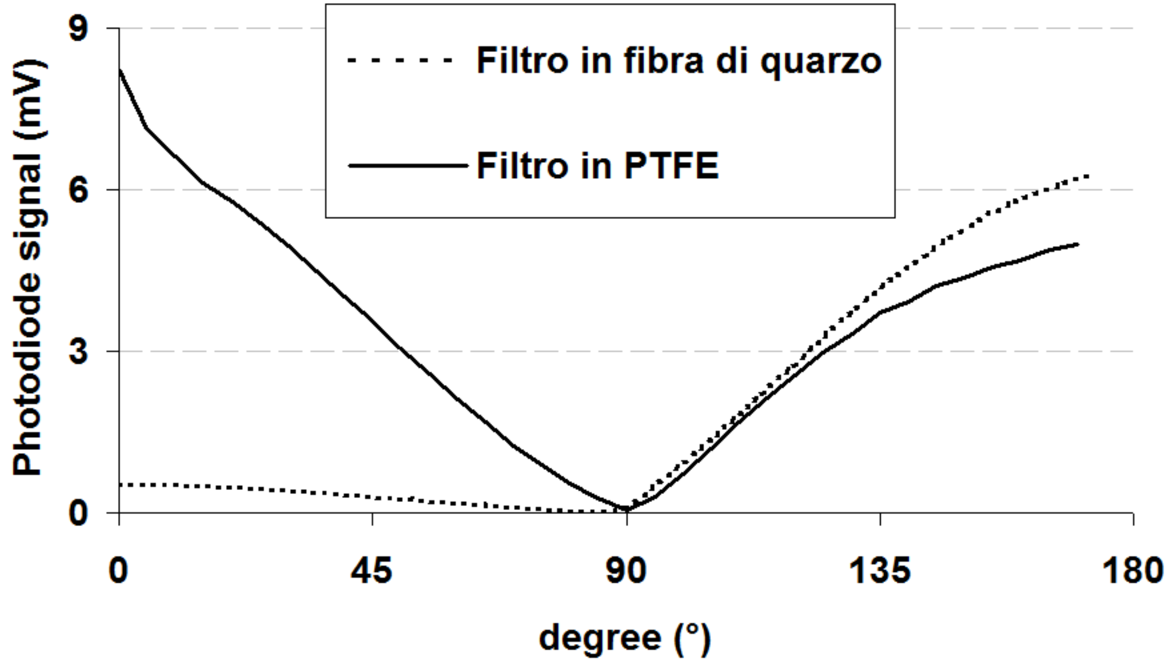
Particolare interesse per misure su campioni raccolti su filtro ad elevata risoluzione temporale.

Finora solo caratterizzazione elementale (Na-Pb, tecnica PIXE).

Misure di assorbimento → *source apportionment* con metodi applicati direttamente alle proprietà ottiche o, dopo valutazione di BC attraverso opportuno MAC (v. poi) e fornire un ulteriore *marker* utile per *source apportionment* da informazioni sulla massa delle diverse componenti chimiche.

Il fotometro polare. Andamenti di luce misurati

FILTRI BIANCHI

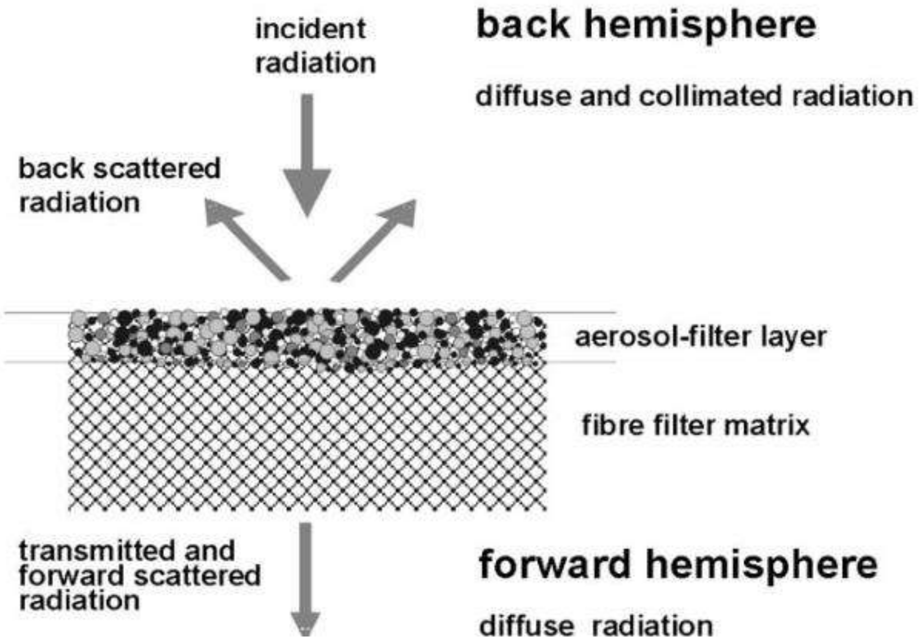


Distribuzione di luce

- Aerosol raccolto
- Supporto filtrante → Es. Trasmissione dominante per filtri sottili

→ Modello di trasferimento radiativo per ricavare ABS

Il modello di trasferimento radiativo: step 1: schema a 2 layer



Schema di trasferimento radiativo a 2 layer

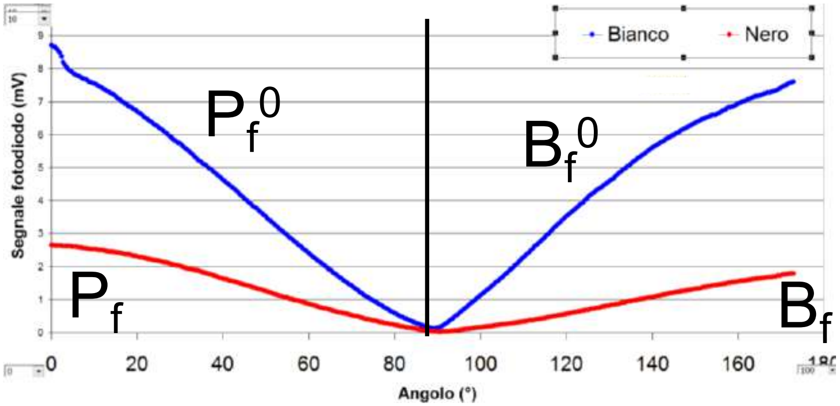
Filtri a membrana

Filtri in fibra (vetro o quarzo)

Layer 1: aerosol
Layer 2: filtro

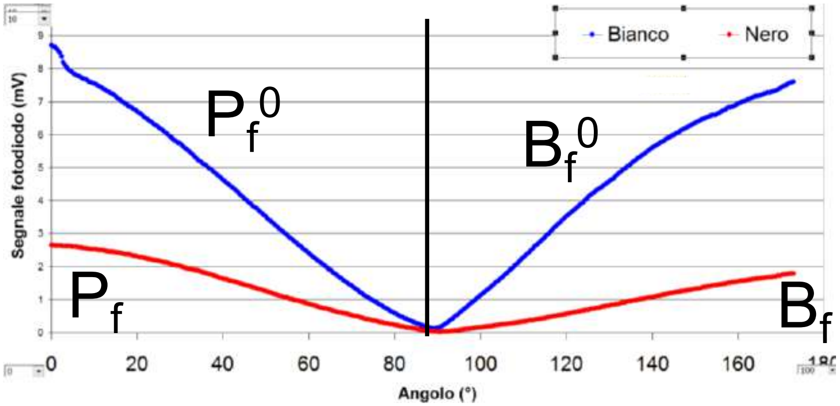
Layer 1: aerosol + filtro
Layer 2: filtro

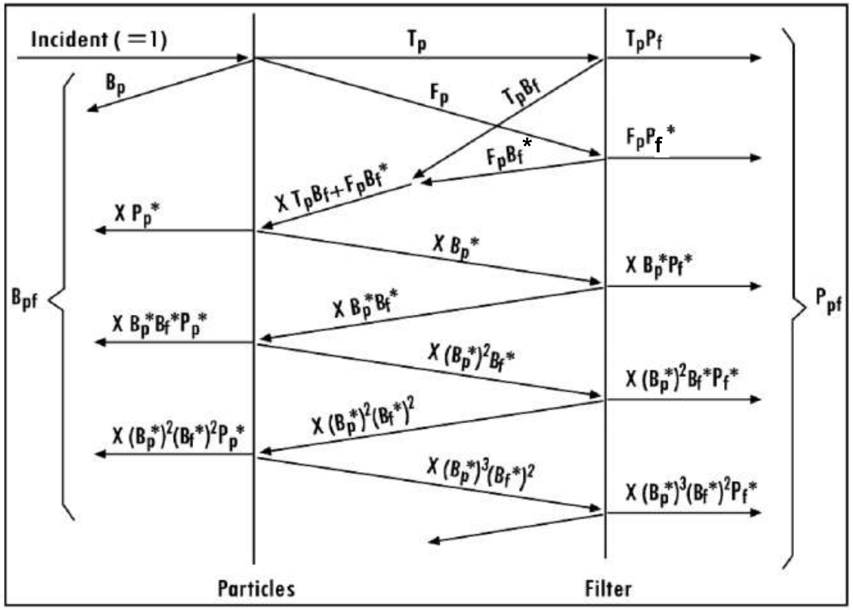
Il modello di trasferimento radiativo: step 2: adding method



Adding method: lega le misure delle frazioni di luce nei due emisferi su filtro bianco e carico alle proprietà di trasmissione/diffusione del layer di particelle e del filtro separatamente.

Il modello di trasferimento radiativo: step 2: adding method





Hänel et al, 1987

Adding method: lega le misure delle frazioni di luce nei due emisferi su filtro bianco e carico alle proprietà di trasmissione/diffusione del layer di particelle e del filtro separatamente.

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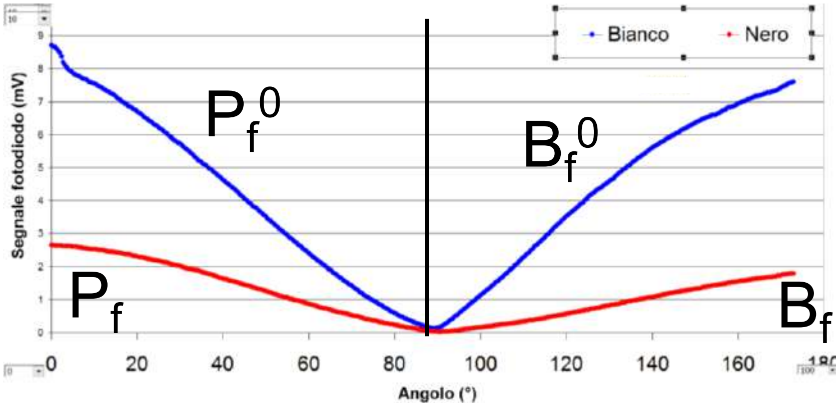
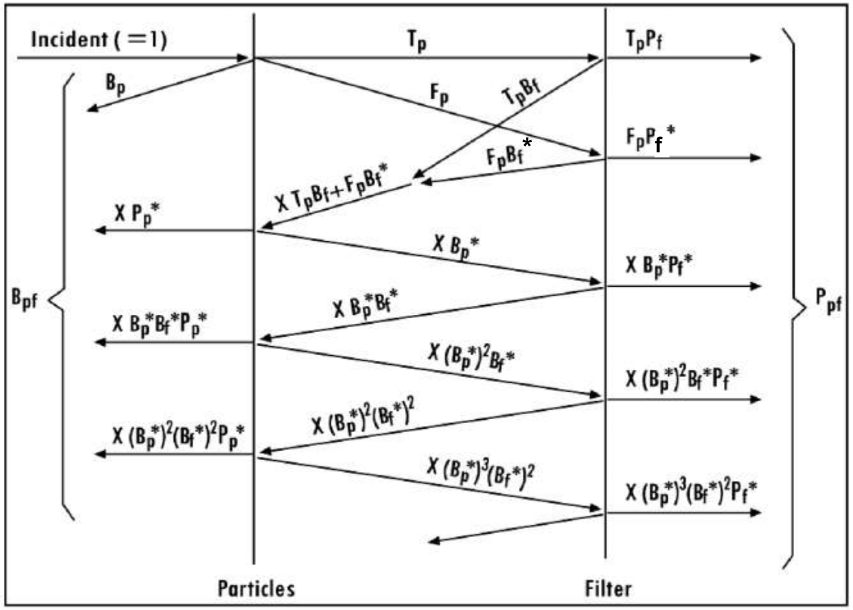




Hänel et al, 1987

Adding method: lega le misure delle frazioni di luce nei due emisferi su filtro bianco e carico alle proprietà di trasmissione/diffusione del layer di particelle e del filtro separatamente.

T_L=trasmittanza del layer

F_L= frazione di luce parallela incidente diffusa nell'emisfero in avanti dal layer

B_L= frazione di luce parallela incidente diffusa nell'emisfero indietro dal layer

P_L*= frazione di luce diffusa dal filtro che il layer ri-diffonde nell'emisfero avanti

B_L*= frazione di luce diffusa dal filtro che il layer ri-diffonde nell'emisfero indietro

$$\frac{P_F}{P_F^{(0)}} = \frac{T_L + F_L}{1 - B_L^* B_M},$$

$$\frac{B_F}{B_F^{(0)}} = P_L^* \frac{T_L + F_L}{1 - B_L^* B_M} + \frac{B_L}{B_M}.$$

5 incognite

Il modello di trasferimento radiativo: step 3: two-stream approximation

F_L
P_L^*
B_L
B_L^*

⟷ Two stream approximation models (Coakley & Chylek et al., 1975)

ω (single scattering albedo)
τ_{ext} (ln T_L, spessore ottico)

Il modello di trasferimento radiativo: step 3: two-stream approximation

F_L
P_L^*
B_L
B_L^*

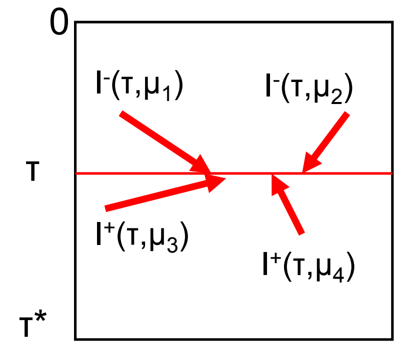
Two stream approximation models
(Coakley & Chylek et al., 1975)

ω (single scattering albedo)
τ_{ext} (ln T_L, spessore ottico)

$$\mu \frac{dI^{(0)}(\tau,\mu)}{d\tau} = I^{(0)}(\tau,\mu) - \frac{1}{2}\int_{-1}^{1} d\mu' p^{(0)}(\mu,\mu') I^{(0)}(\tau,\mu')$$

Equazione di trasferimento radiativo per un' “atmosfera” diffondente e assorbente a piani paralleli.

Si scompone in:
$I^+(\tau,\mu)=I(\tau,\mu)$ e $I^-(\tau,\mu)= I(\tau,-\mu)$ per $0\leq\mu\leq1$.



Il modello di trasferimento radiativo: step 3: two-stream approximation

F_L
P_L^*
B_L
B_L^*

Two stream approximation models
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ω (single scattering albedo)
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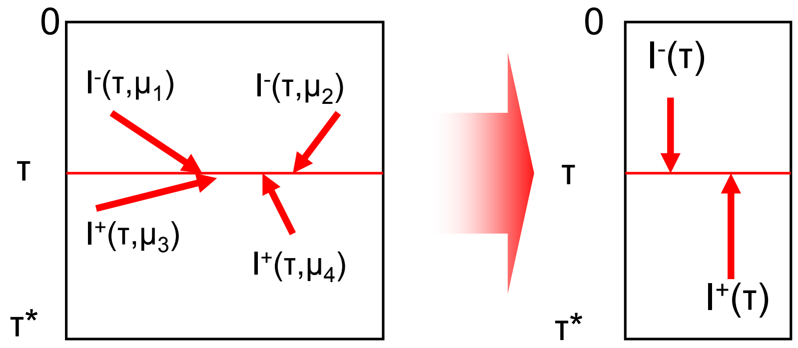
La *two stream approximation* prevede che:
$I^+(\tau,\mu)= I^+(\tau)$ e $I^-(\tau,\mu)= I^-(\tau)$ (si introducono intensità "effettive" dipendenti dall'emisfero).



Il modello di trasferimento radiativo: step 3: two-stream approximation

F_L
P_L^*
B_L
B_L^*

Two stream approximation models
(Coakley & Chylek et al., 1975)

ω (single scattering albedo)
τ_{ext} (In T_L, spessore ottico)

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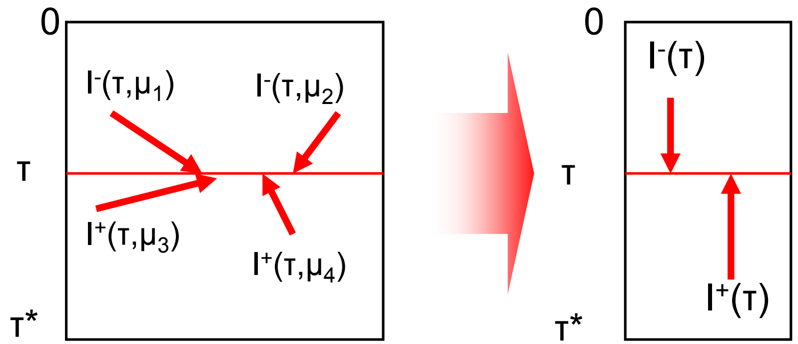

Condizioni al contorno per sorgente di luce esterna (fascio parallelo)

$I^-(\tau=0)=I_0$

$I^+(\tau=\tau^*)=0$

Condizioni al contorno per sorgente di luce interna (diffusa):

$I^-(\tau=0)=0$

$I^+(\tau=\tau^*)=0$

Two stream approximation: risultati

F_L
P_L^*
B_L
B_L^*

Two stream approximation models
(Coakley & Chylek et al., 1975)

ω (single scattering albedo)
τ_{ext} (ln T_L, spessore ottico)

Per i termini di luce diffusa:

$$B_L^* = \frac{b\left(1 - T_L^{2\sqrt{B}}\right)}{\sqrt{B} + a + (\sqrt{B} - a)\, T_L^{2\sqrt{B}}},$$

$$P_L^* = \frac{1}{2\sqrt{B}}\left[\left(\sqrt{B} - a + B_L^* b\right) T_L^{-\sqrt{B}} + (\sqrt{B} + a - B_L^* b) T_L^{\sqrt{B}}\right],$$

$$a = 2[1 - \omega_L(1 - \beta_L^*)],\ b = 2\,\omega_L \beta_L^*,\ B = a^2 - b^2.$$

Per i termini legati alla luce incidente parallela:

$$B_L = \frac{c - \frac{p_1}{1+\sqrt{B}} - \left(c - \frac{p_1}{1-\sqrt{B}}\right) T_L^{2\sqrt{B}} - 2\,\frac{p_1\sqrt{B}}{1-B}\, T_L^{1+\sqrt{B}}}{\sqrt{B} + a + (\sqrt{B} - a)\, T_L^{2\sqrt{B}}},$$

$$F_L = \frac{1}{2\sqrt{B}}\left[\left(d + B_L b + \frac{p_2}{1+\sqrt{B}}\right) T_L^{-\sqrt{B}} - \left(d + B_L b + \frac{p_2}{1-\sqrt{B}}\right) T_L^{\sqrt{B}}\right] + \frac{p_2}{1-B}\, T_L,$$

$$c = \omega_L \beta_L,\ d = \omega_L(1 - \beta_L),\ p_1 = c - ac - bd,\ p_2 = -ad - bc - d.$$

Two stream approximation: risultati

F_L
P_L^*
B_L
B_L^*

Two stream approximation models (Coakley & Chylek et al., 1975)

ω (single scattering albedo)
τ_{ext} (ln T_L, spessore ottico)

Per i termini di luce diffusa:

$$B_L^* = \frac{b\left(1 - T_L^{2\sqrt{B}}\right)}{\sqrt{B} + a + (\sqrt{B} - a)\, T_L^{2\sqrt{B}}},$$

$$P_L^* = \frac{1}{2\sqrt{B}} \left[\left(\sqrt{B} - a + B_L^* b\right) T_L^{-\sqrt{B}} + (\sqrt{B} + a - B_L^* b) T_L^{\sqrt{B}}\right],$$

$$a = 2[1 - \omega_L(1 - \beta_L^*)],\ b = 2\omega_L \beta_L^*,\ B = a^2 - b^2.$$

Per i termini legati alla luce incidente parallela:

$$B_L = \frac{c - \frac{p_1}{1+\sqrt{B}} - \left(c - \frac{p_1}{1-\sqrt{B}}\right) T_L^{2\sqrt{B}} - 2\,\frac{p_1\sqrt{B}}{1-B}\, T_L^{1+\sqrt{B}}}{\sqrt{B} + a + (\sqrt{B} - a)\, T_L^{2\sqrt{B}}},$$

$$F_L = \frac{1}{2\sqrt{B}} \left[\left(d + B_L b + \frac{p_2}{1+\sqrt{B}}\right) T_L^{-\sqrt{B}} - \left(d + B_L b + \frac{p_2}{1-\sqrt{B}}\right) T_L^{\sqrt{B}}\right] + \frac{p_2}{1-B} T_L,$$

$$c = \omega_L \beta_L,\ d = \omega_L(1 - \beta_L),\ p_1 = c - ac - bd,\ p_2 = -ad - bc - d.$$

$$\beta_L = \frac{1}{2}\left[1 - g - \frac{4}{25}\left(1 - \frac{|1-2g|}{8} - \frac{7}{8}(1-2g)^2\right)\right.$$

$$\beta_L^* = \frac{1}{2}\left[1 - \frac{g}{4}(3 + g^{3+2g^3})\right],$$

Dove β_L e β^*_L sono le frazioni di luce retrodiffusa rispetto al totale di luce incidente collimata e diffusa e sono legate al parametro di asimmetria g (assunzione: g=0.65 per particelle atmosferiche).

$$g = \frac{1}{2}\frac{\int_0^\pi \cos\theta\ F(\theta)\sin\theta\ d\theta}{\int_0^\pi F(\theta)\sin\theta\ d\theta} = \frac{1}{2}\int_0^\pi \cos\theta\, P(\theta)\sin\theta\ d\theta$$

Intensità diffusa ad angolo θ

Funzione di fase

Il modello di trasferimento radiativo: step 4: calcolo di ABS

Data l'assunzione su g (e quindi note βe β^*), le uniche 2 incognite nell'espressione ottenuta con l'adding method rimangono ω e la trasmittanza del layer di particelle T_L.

$$\frac{P_F}{P_F^{(0)}} = \frac{T_L + F_L}{1 - B_L^* B_M},$$

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$$ABS = (1-\omega)^* \tau_L$$

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Considerando l'area del deposito e il volume campionato → coefficiente di assorbimento dell'aerosol in aria:

$$\sigma_{ap} = ABS \frac{A}{V} = b_{ABS}$$

RISULTATI

Caratterizzazione del sistema: short- and long-term stability

Stabilità del laser valutata da misure a 0° (mediante utilizzo di opportuno attenuatore)

λ	VARIABILITA' INTRA-GIORNALIERA MEDIA (dev.st rel)	STATISTICHE A LUNGO TERMINE (dev.st rel)
405 nm	0.7%	3.9%
532 nm	2.8%	8.8%
635 nm	0.6%	1.0%
780 nm	0.5%	1.0%

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Problema variabilità intra-giornaliera 532 nm.
N.b. problema dovrebbe ridursi con nuovo set-up per filtri da 47 mm, perchè campione irraggiato senza passaggio attraverso specchio.

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Incluso nelle incertezze sperimental

Info utilizzate per correzione dato pre-elaborazione dati: misura su filtro bianco corrette attraverso rapporto $I_{dayBlack}/I_{dayWhite}$

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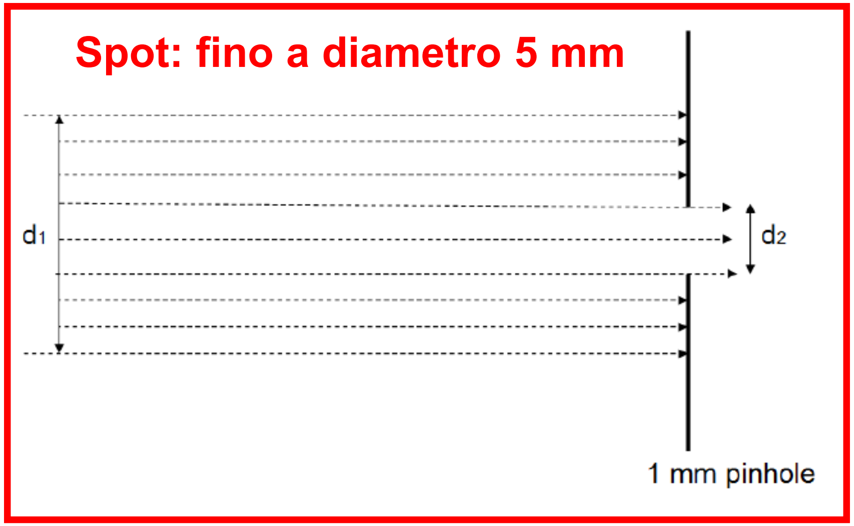
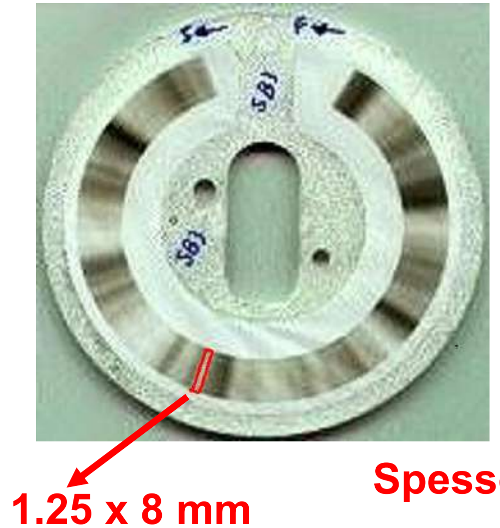
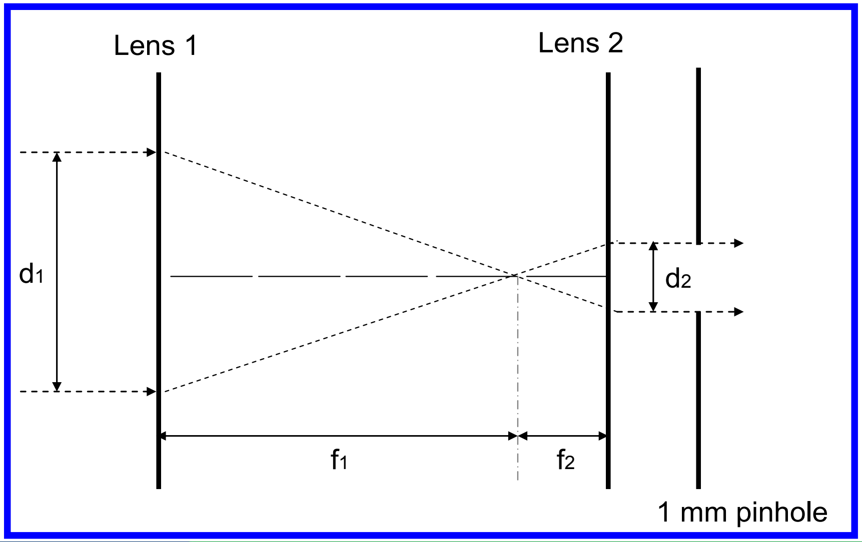
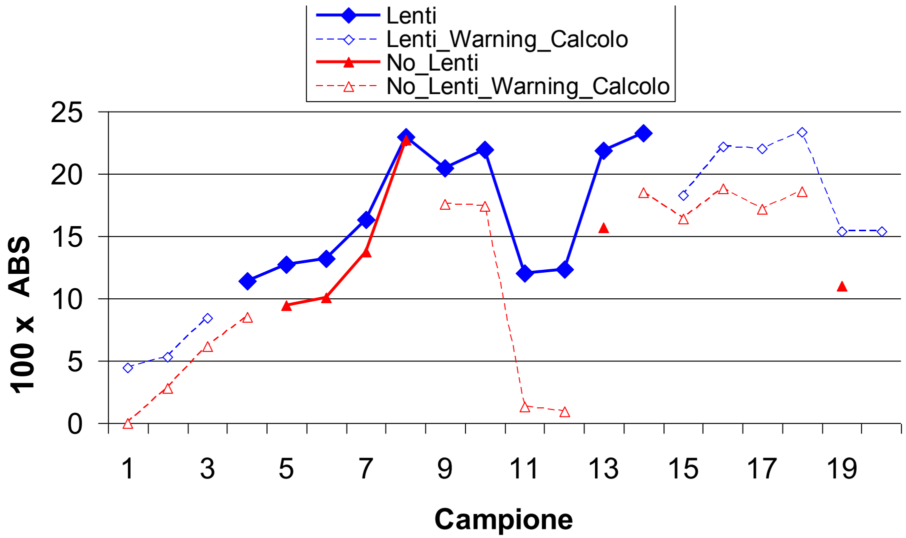
Sviluppo del set-up per le misure ad elevata risoluzione temporale: collimazione mediante lenti





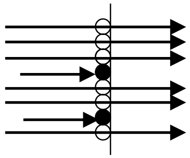
Spessore=10μm

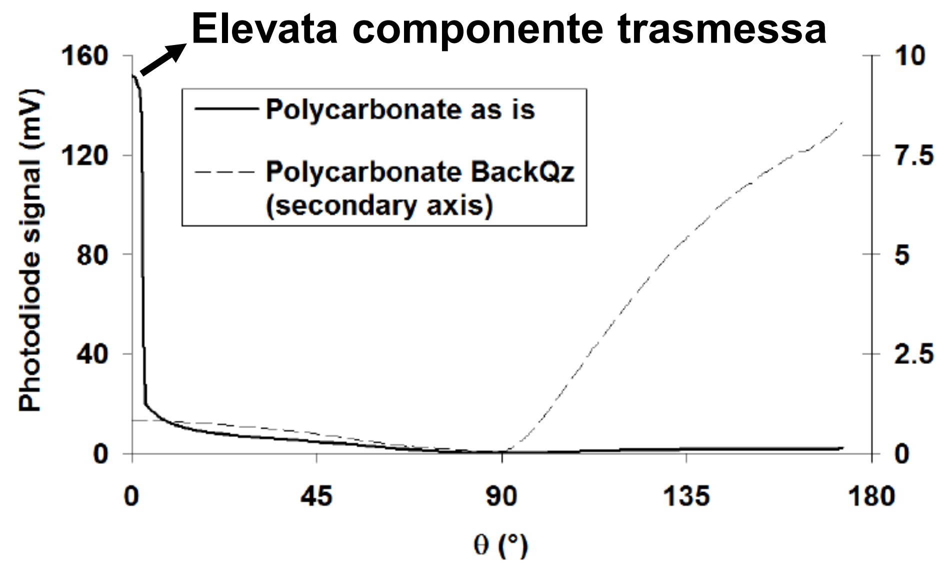




Sviluppo del set-up per le misure ad elevata risoluzione temporale: amplificazione dell'assorbimento utilizzando multiple scattering campione - filtro

Filtro in policarbonato





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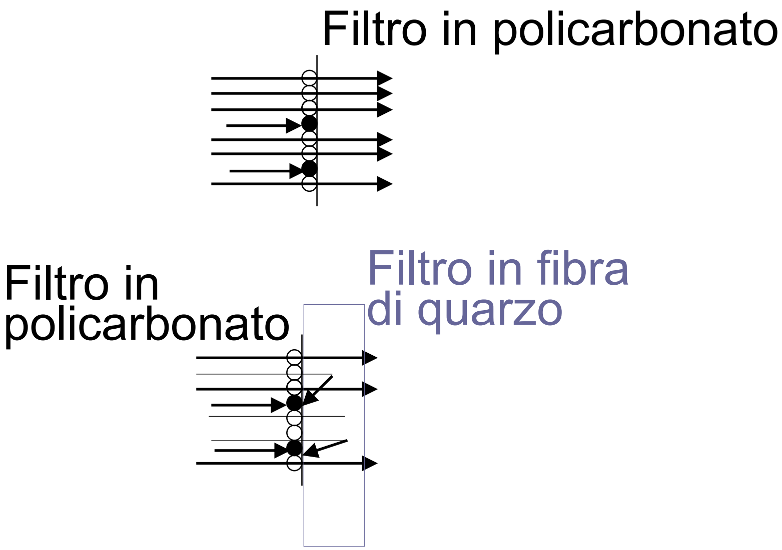

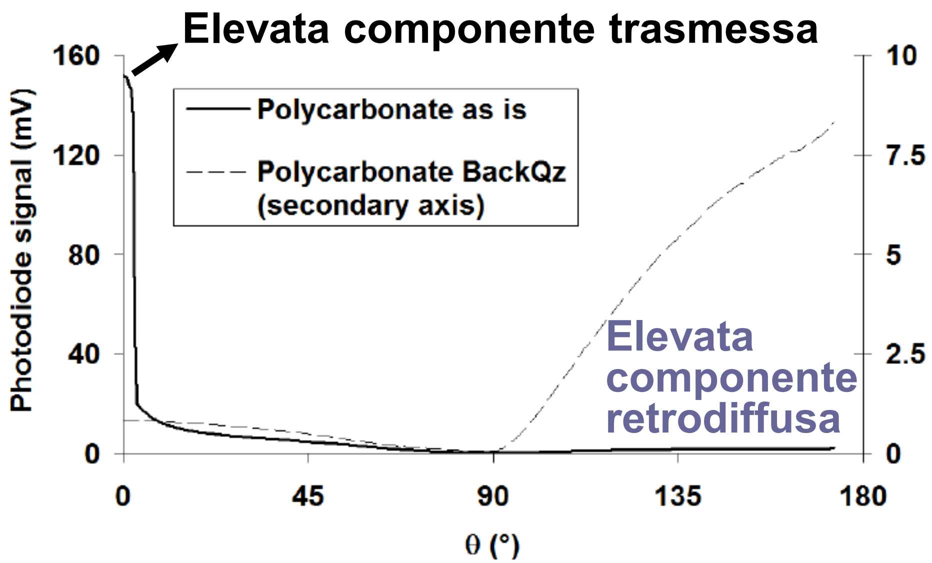

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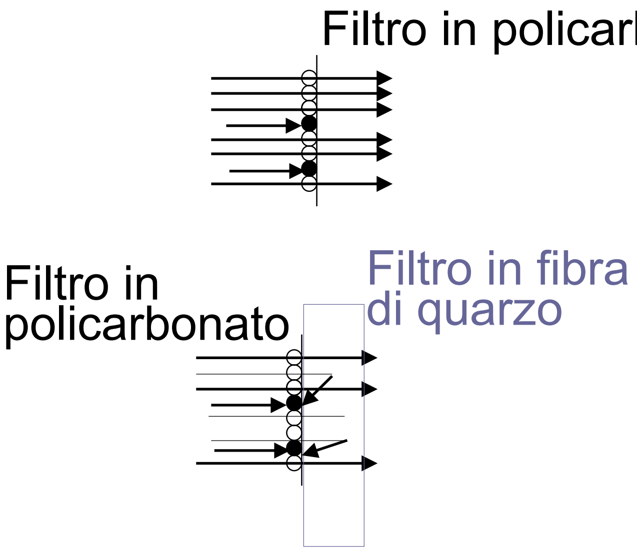
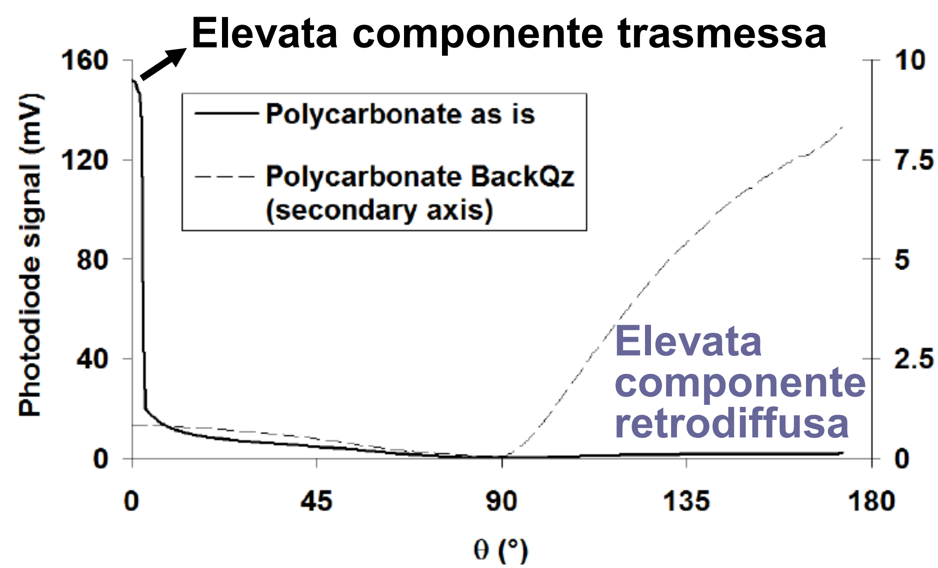


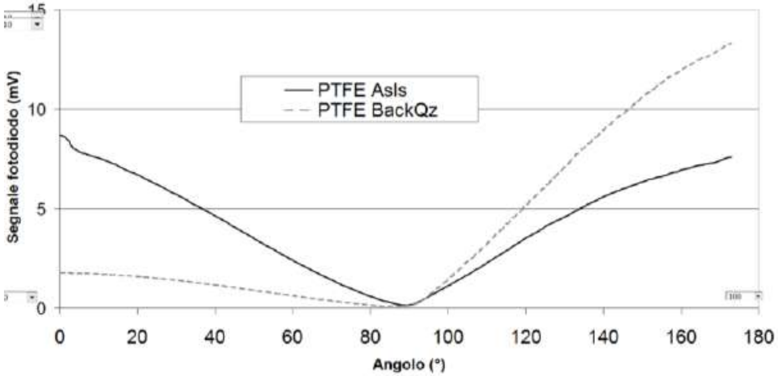


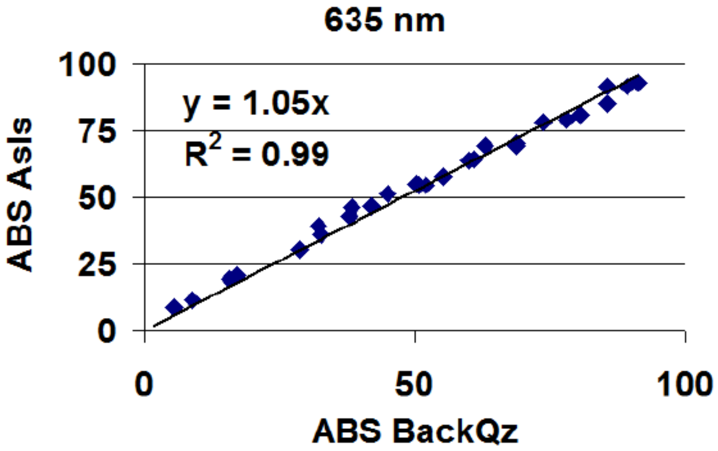
Utilizzo di un filtro in fibra appoggiato al filtro in policarbonato ⇒ aumento della componente retrodiffusa ⇒ aumento della probabilità di interazione tra fascio incidente e materiale assorbente

AUMENTO DELLA SENSIBILITA' DELLO STRUMENTO!!!

Risultati filtro as-is vs. filtro + back qz

Check 1: utilizzo filtri in **PTFE** (spessore 40μm, permettono di ottenere risultati affidabili anche con il filtro as-is)





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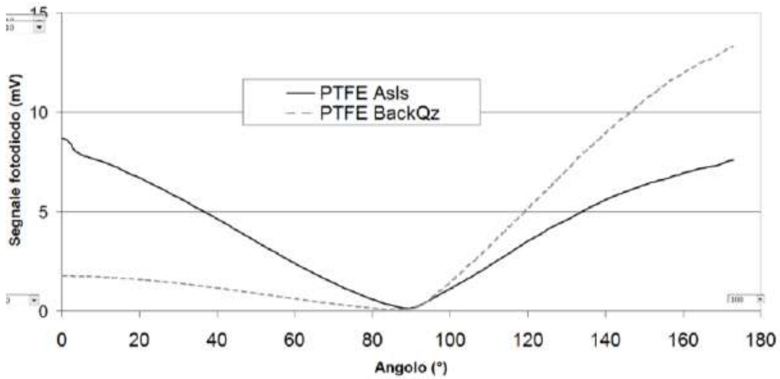
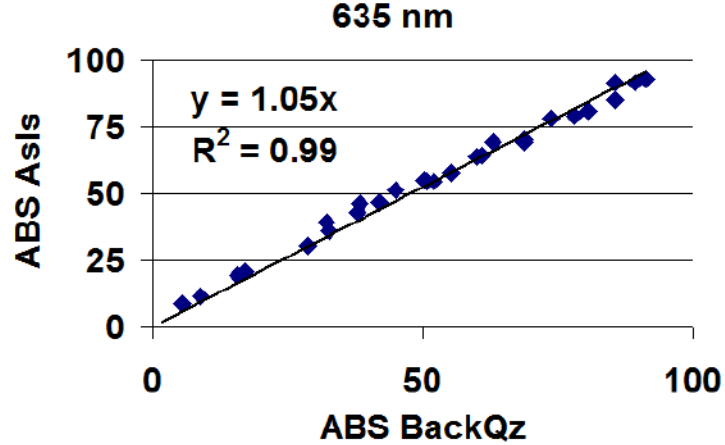
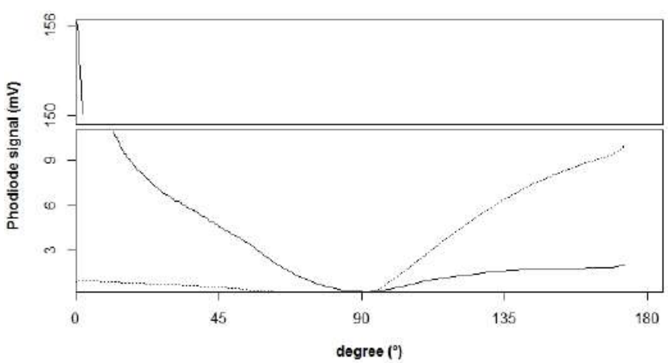
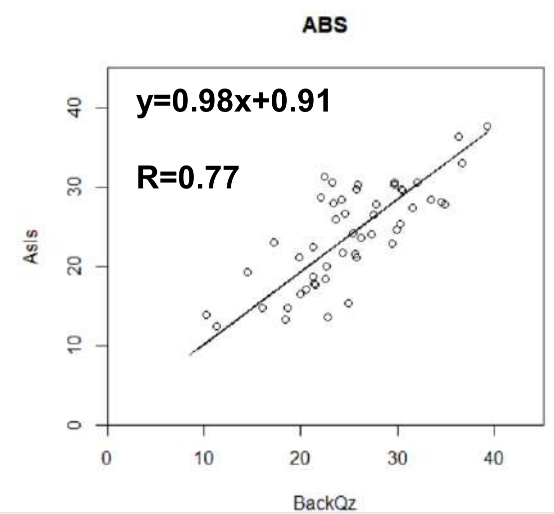




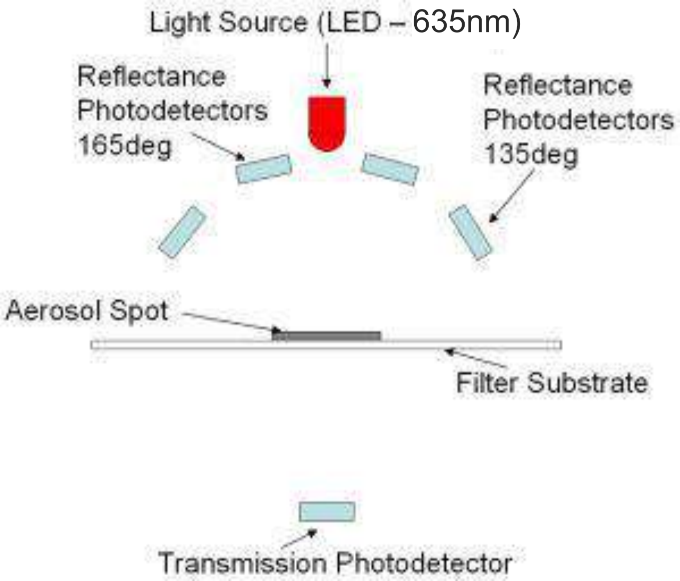
Check 2: aerosol campionato con HR temporale su policarbonato (spessore 10µm)





N.b. con analisi as-is disponibili solo 44% dei valori misurati con filtro in quarzo back!!!

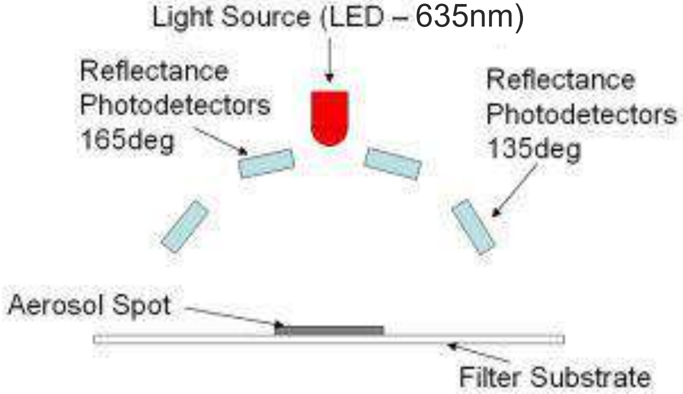
Strumento di riferimento (Multi-Angle Absorption Photometer), λ = 635 nm



Strumento di riferimento (Multi-Angle Absorption Photometer), λ = 635 nm

Ricostruisce distribuzione emisfero indietro come somma di diffusione Lambertiana e riflessione quasi-speculare (gaussiana)

$$S(\theta) \propto \left(\alpha \cos(\theta - \pi) + (1 - \alpha) \exp\left[-\frac{1}{2} \frac{(\theta - \pi)^2}{\rho^2}\right]\right)$$



Ricostruisce distribuzione in avanti assumendo diffusore Lambertiano

$$S(\theta) \propto \cos\theta.$$

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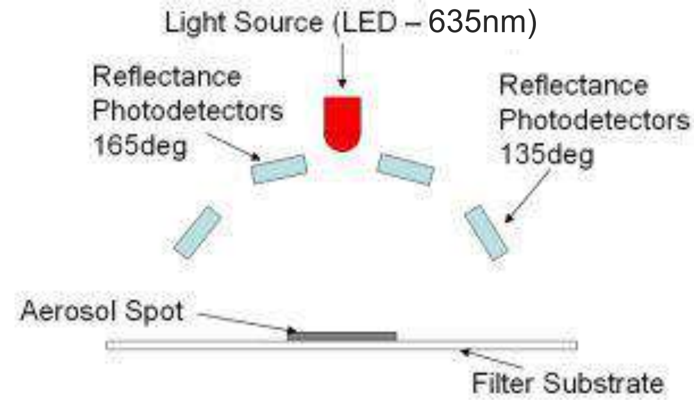

Ricostruisce distribuzione in avanti assumendo diffusore Lambertiano

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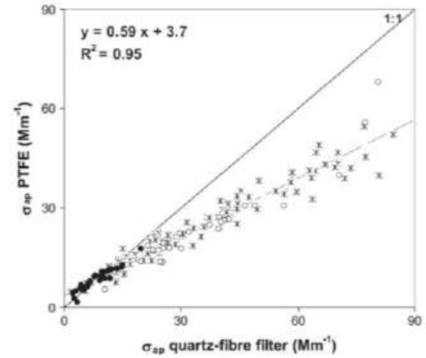
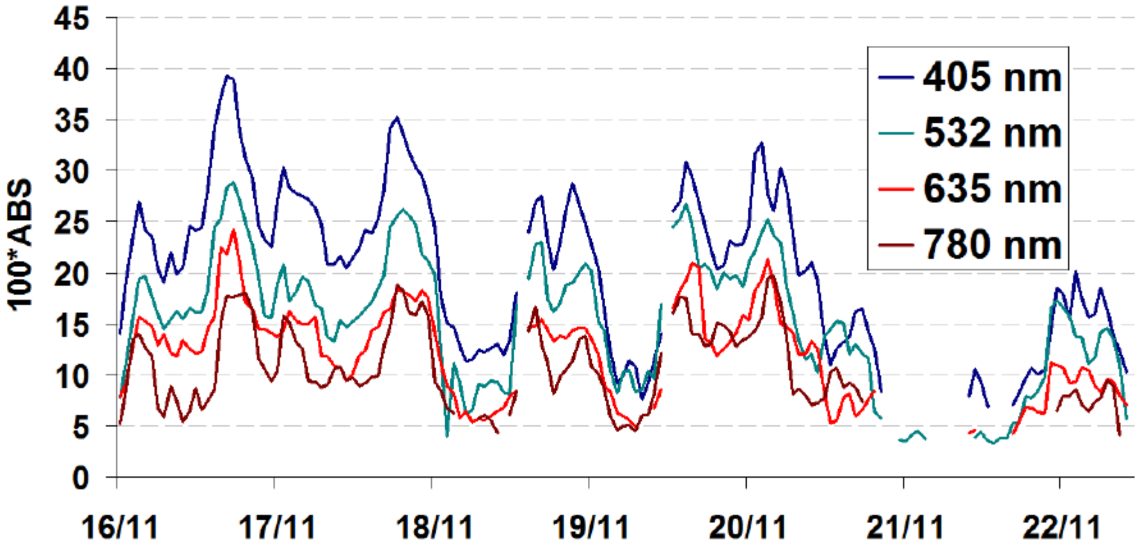
Misura ad elevata risoluzione temporale su filtro in fibra di quarzo ➔ suscettibile di effetti di amplificazione legati ad artefatti di campionamento, quindi le misure sono state corrette seguendo Vecchi et al, 2014

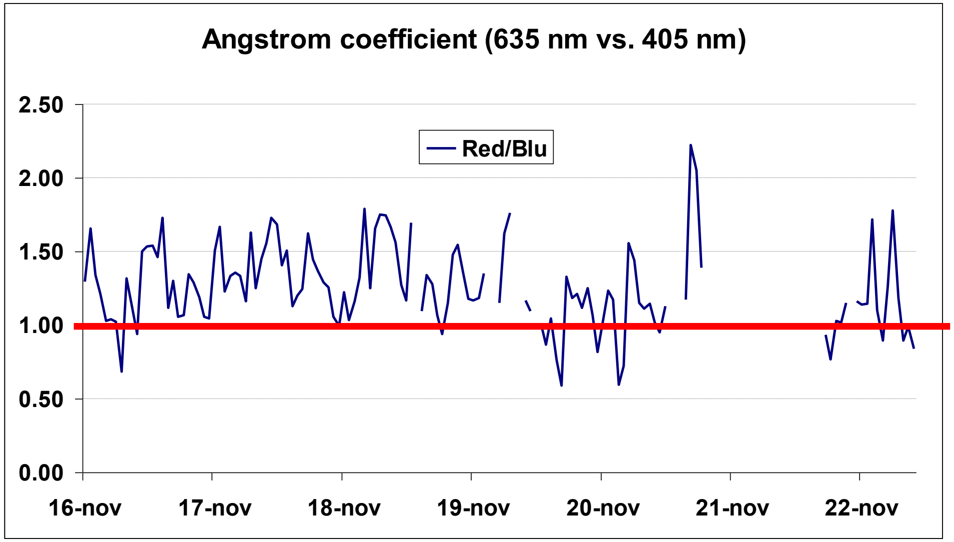


Misure su streaker sampler a più lunghezze d'onda



Esempio di misure a 4-λa risoluzione oraria

N.b: passaggio a BC/BrC richiede conoscenza di mass absorption coefficient (critico! V. prospettive)



Coefficiente di Ångström:

$$\alpha = -\frac{\ln(ABS(\lambda_1)/ABS(\lambda_2))}{\ln(\lambda_1/\lambda_2)}$$

α=1: valore atteso per BC puro (in letteratura considerato marker di combustione di combustibili fossili

MWAA (Multi-wavelength absorption analyser) model

Si basa su scrittura dello spessore ottico di assorbimento in funzione di componenti chimiche o sorgenti

$$b_{abs}(\lambda) = b_{abs}{}^{BC}(\lambda) + b_{abs}{}^{BrC}(\lambda)$$

$$b_{abs}(\lambda) = b_{abs,FF}(\lambda) + b_{abs,WB}(\lambda)$$

Massabò et al., 2015

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Viene esplicitato il legame funzionale con la lunghezza d'onda attraverso esponenti di assorbimento di Angstrom legati alle componenti chimiche o alle sorgenti.

$$b_{abs}(\lambda) = \underbrace{\left[(BC_{FF} + BC_{WB}) \cdot \sigma_0^{BC}\right]}_{A} \lambda^{-\alpha_{BC}} + \underbrace{\left[BrC \cdot \sigma_0^{BrC}\right]}_{B} \lambda^{-\alpha_{BrC}}$$

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Massabò et al., 2015

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Massabò et al., 2015

IPOTESI

a) Wood burning come unica sorgente di BrC;

b) BC_{FF} and BC_{WB} hanno lo stesso AAE (α_{BC}), indipendentemente dalla sorgente;

c) BC e BrC hanno diverse dipendenze spettrali, cioè diversi AAE (α_{BC} e α_{BrC}, rispettivamente);

d) La combustione di combustibili fossili non produce BrC, quindi $\alpha_{FF} = \alpha_{BC} = 1 \pm 0.1$

e) $\alpha_{WB} = 1.8$ (stimato da confronto con stime del contributo da legna ottenute indipendentemente da misure di ^{14}C).

MWAA (Multi-wavelength absorption analyser) model

Si basa su scrittura dello spessore ottico di assorbimento in funzione di componenti chimiche o sorgenti

$$b_{abs}(\lambda) = b_{abs}{}^{BC}(\lambda) + b_{abs}{}^{BrC}(\lambda) \qquad b_{abs}(\lambda) = b_{abs,FF}(\lambda) + b_{abs,WB}(\lambda)$$

Viene esplicitato il legame funzionale con la lunghezza d'onda attraverso esponenti di assorbimento di Angstrom legati alle componenti chimiche o alle sorgenti.

$$b_{abs}(\lambda) = \underbrace{\left[(BC_{FF} + BC_{WB}) \cdot \sigma_0^{BC}\right]}_{A} \lambda^{-\alpha_{BC}} + \underbrace{\left[BrC \cdot \sigma_0^{BrC}\right]}_{B} \lambda^{-\alpha_{BrC}}$$

$$b_{abs}(\lambda) = \underbrace{\left[BC_{FF} \cdot \sigma_0^{BC}\right]}_{A'} \lambda^{-\alpha_{FF}} + \underbrace{\left[BC_{WB} \cdot \sigma_0^{BC} + BrC \cdot \sigma_0^{BrC}\right]}_{B'} \lambda^{-\alpha_{WB}}$$

Massabò et al., 2015

IPOTESI

a) Wood burning come unica sorgente di BrC;

b) BC_{FF} and BC_{WB} hanno lo stesso AAE (α_{BC}), indipendentemente dalla sorgente;

c) BC e BrC hanno diverse dipendenze spettrali, cioè diversi AAE (α_{BC} e α_{BrC}, rispettivamente);

d) La combustione di combustibili fossili non produce BrC, quindi $\alpha_{FF} = \alpha_{BC} = 1 \pm 0.1$

e) $\alpha_{WB} = 1.8$ (stimato da confronto con stime del contributo da legna ottenute indipendentemente da misure di ^{14}C).

SOLUZIONE

Il programma di minimizzazione esegue fitting separati delle precedenti equazioni, utilizzando le misure di b_{abs} multi-λ per ottenere A, B, A', B' e α_{BrC} per ogni campione

source apportionment di b_{abs}

$$\begin{cases} b_{abs,WB}{}^{BC}(\lambda) = (A - A')\lambda^{-\alpha_{BC}} \\ b_{abs,FF}{}^{BC}(\lambda) = A'\lambda^{-\alpha_{BC}} \\ b_{abs}{}^{BrC}(\lambda) = B\lambda^{-\alpha_{BrC}} \end{cases}$$