Absorption Photometer - ITINERIS Training II

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Particle Light Absorption

- Absorption is the process by which the energy of a photon is taken up by another subject (here particles).
- In the atmosphere, light is absorbed by both, gas molecules and aerosol particles.
- Absorption by gases is usually weak compared to absorption by aerosol particles.
- The use of Absorption Photometers is:
  - to measure the particle light absorption coefficient
  - to estimate a corresponding particle mass concentration of Black Carbon, the mass absorption cross section (MAC) must be known.

Extinction Minus Scattering

Difference of Extinction Minus Scattering

The method “extinction minus scattering” is based on first principles of optics.

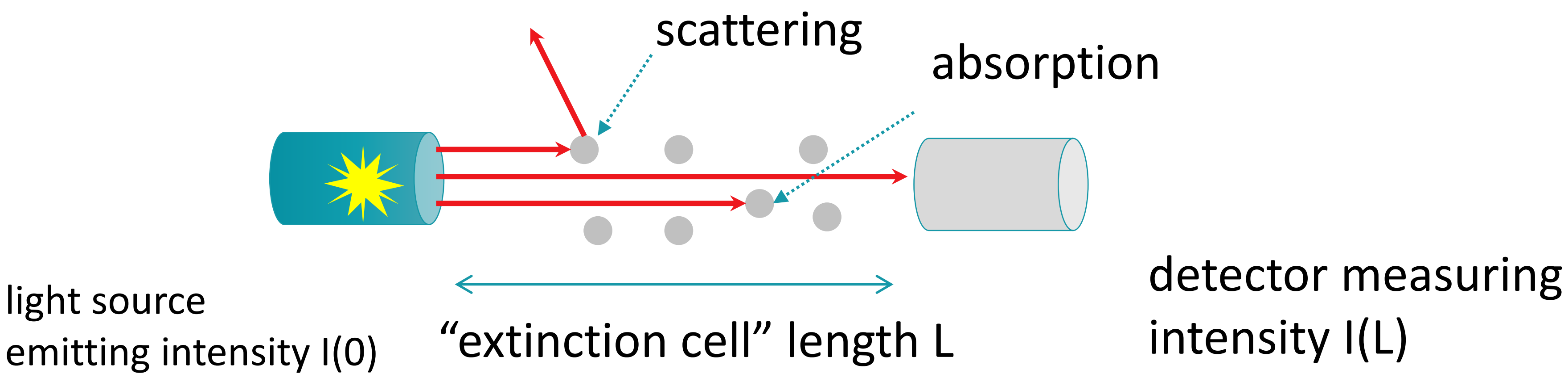
The basic equation is:

$$\sigma_{abs} = \sigma_{ext} - \sigma_{sca}$$

particle light extinction coefficient — particle light scattering coefficient

- Two concurrent measurements of the particle light extinction and scattering coefficients are needed.
- The instrument for measuring the particle light scattering coefficient is the Integrating nephelometers.
- This method is used a reference in the ACTRIS calibration laboratory.

Principle of Extinction Measurements



The extinction coefficient is derived from the Lambert-Beer law:

$$\frac{I(L)}{I(0)} = e^{-\sigma_{ext} \cdot L} \quad \Leftrightarrow \quad \sigma_{ext} = \frac{-\ln \frac{I(L)}{I(0)}}{L}$$

- The extinction coefficient is given in unit of 1/m.
- Measuring extinction at low aerosol particle concentrations requires cell lengths up to to several hundred meters.

Error propagation

- From the error propagation follows, that the uncertainty of the absorption coefficients is:

$$\Delta\sigma_{abs} = \sqrt{(\Delta\sigma_{ext})^2 + (\Delta\sigma_{sca})^2}$$

- The absolute uncertainty might be constant for all concentrations. It depends on the instrumental uncertainties of both instruments.

- The span between extinction and scattering changes with concentration and single scattering albedo.

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

Examples

Low particle light extinction and scattering coefficients with 10% uncertainties

$$\sigma_{\text{ext}} = 20\frac{1}{\text{Mm}}$$

$$\Delta\sigma_{\text{ext}} = 2\frac{1}{\text{Mm}}$$

$$\sigma_{\text{sca}} = 18\frac{1}{\text{Mm}}$$

$$\Delta\sigma_{\text{sca}} = 1.8\frac{1}{\text{Mm}}$$

$$\Delta\sigma_{abs} = \sqrt{\left(2\frac{1}{\text{Mm}}\right)^2 + \left(1.8\frac{1}{\text{Mm}}\right)^2} = 2.7\frac{1}{\text{Mm}}$$

$$\sigma_{abs} = 20 - 18\frac{1}{\text{Mm}} = 2 \pm 2.7\frac{1}{\text{Mm}} \rightarrow 135\%$$

High particle light extinction and lower scattering coefficients with 5% uncertainties

$$\sigma_{\text{ext}} = 100\frac{1}{\text{Mm}}$$

$$\Delta\sigma_{\text{ext}} = 5\frac{1}{\text{Mm}}$$

$$\sigma_{\text{sca}} = 50\frac{1}{\text{Mm}}$$

$$\Delta\sigma_{\text{sca}} = 2.5\frac{1}{\text{Mm}}$$

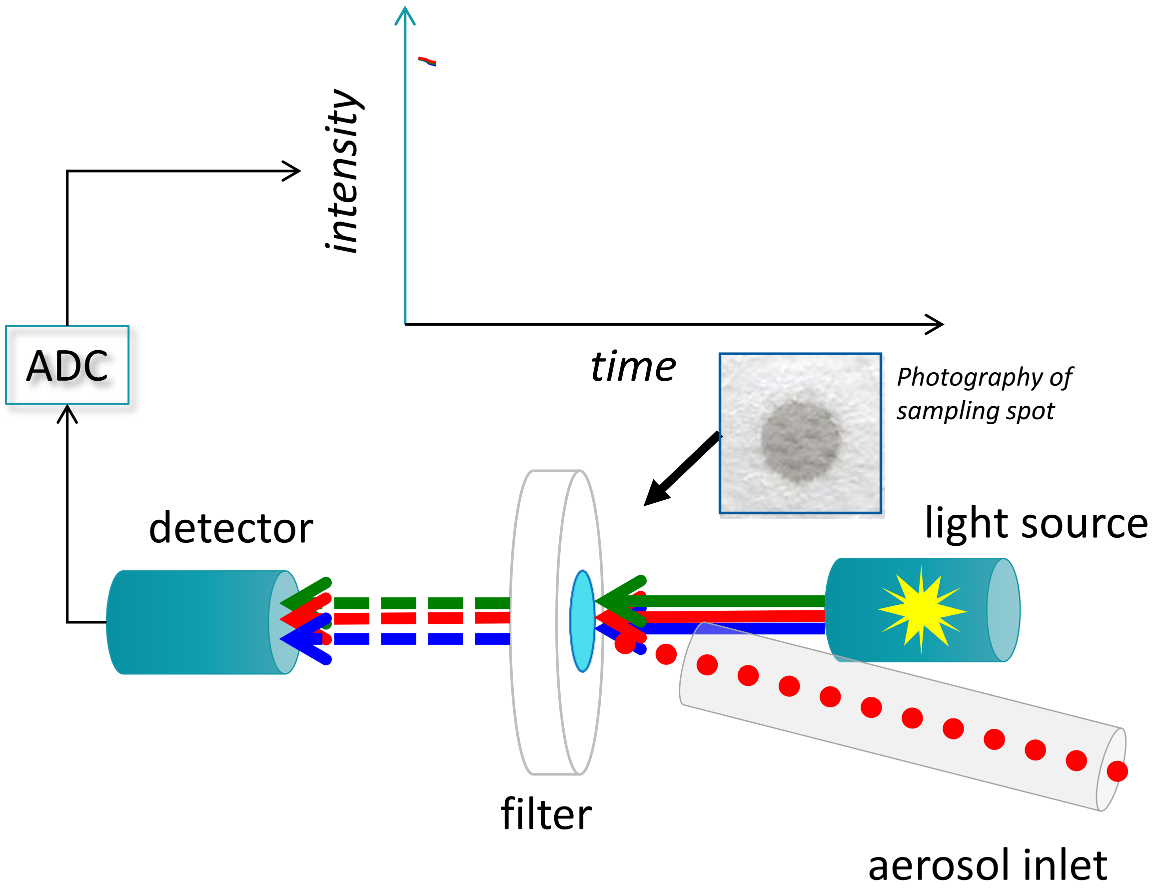
$$\Delta\sigma_{abs} = \sqrt{\left(5\frac{1}{\text{Mm}}\right)^2 + \left(2.5\frac{1}{\text{Mm}}\right)^2} = 5.6\frac{1}{\text{Mm}}$$

$$\sigma_{abs} = 100 - 50\frac{1}{\text{Mm}} = 50 \pm 5.6\frac{1}{\text{Mm}} \rightarrow 11\%$$

Filter-Based Absorption Photometers

Filter-Based Absorption Photometers

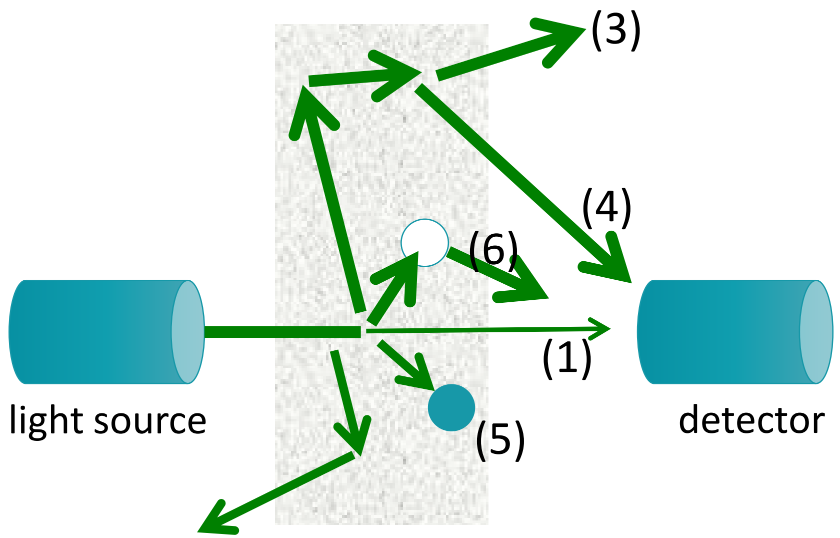
- A fibre filter is loaded with particles
- Transmitted intensity through system of particle and filter is measured
- Intensities for one or more wavelengths are recorded



Radiative transfer through a particle free filter

Light is scattered several times by the filter matrix

- very little light passes the filter without scattering
- light is scattered back
- light is scattered forward
- multiple scattered light reaches the detector



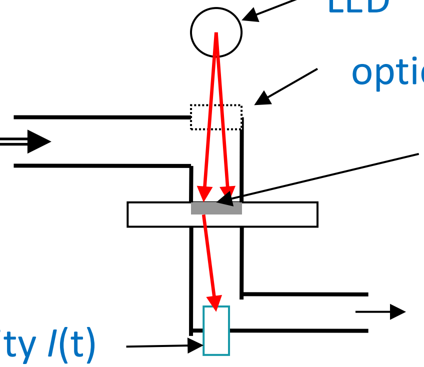
Radiative transfer through a particle loaded filter

Additional to scattering by the particle free filter matrix, light is scattered and absorbed by particles

- light is absorbed by particles
- light is scattered by particles (additionally to scattering by the filter)

- The light scattering by the filter fibres is one order of magnitudes larger than scattering by particles.
- Because of multiple scattering by the filter, the light path length inside the filter is larger than the filter thickness.
- The light absorbed by particles reduces light transmittance.
- The enhanced light path length causes a higher probability for a photon to be absorbed by particles.

Determining the Particle Light Absorption Coefficient: Filter-based Absorption Photometer



$I(0)$ = reference light intensity

$I(t)$ = measured light intensity

$$\tau = \frac{I(t)}{I(0)}$$ = transmittance

$$ATN = -\ln(\tau)$$ = attenuation

$$\mathrm{d}l = Q/A \, \mathrm{d}t$$ → column of air sucked through the filter

$$\sigma_{ATN}(l) = \frac{\mathrm{d}ATN(l)}{\mathrm{d}l}$$ combining →

$$\sigma_{ATN}(t) = \frac{Q}{A}\frac{\mathrm{d}ATN(t)}{\mathrm{d}t}$$ → attenuation coefficient

This is also attenuation coefficient →

$$\sigma_{ATN} = \mathrm{f}(sca, abs) = f_1 \cdot \sigma_{sca} + f_2 \cdot \sigma_{abs}$$

From this follows the absorption coefficient →

$$\sigma_{abs} \approx \frac{\sigma_{ATN} - f_1 \cdot \sigma_{sca}}{f_2}$$

Particle Soot Absorption Photometer

Loading Effect

- The loading effect in an absorption photometer refers to a reduction in the instrument's sensitivity due to the accumulation of aerosol particles on the filter over time.
- This effect can lead to an underestimation of light absorption and, consequently, an underestimation of the particle light absorption coefficient.

Causes of the Loading Effect:

- Increased Multiple Scattering: As more particles accumulate on the filter, they can scatter more light, altering the effective absorption measurement.
- Filter Saturation: The filter's optical properties change as it gets loaded with particles, reducing its ability to transmit light correctly.
- Shadowing Effect: Newly deposited particles may experience less light exposure due to the presence of previously accumulated particles, leading to a reduced apparent absorption.

Particle Soot Absorption Photometer (PSAP) – not produced anymore

- The absorption needs to be calibrated because of
  - the increased sensitivity (light path length enhancement) to particle absorption
  - The remaining cross sensitivity to particle scattering
  - The dependence on the transmission τ is called loading effect.
- Calibration of this type of absorption photometers (Bond, 1999):

$$\sigma_{abs} = \frac{\sigma_{atn}}{1.317\,\tau + 0.886} - 0.016\,\sigma_{sca}$$

- For an unloaded filter (τ=1).
- The sensitivity to absorption is increased by a factor of 2.18.
- For τ=0.5 → the sensitivity drops to 1.54

- The sensitivity to scattering is approx. 1.6 %.
- We need to correct for the particle light scattering coefficient.

Multi-Angle Absorption Photometer

Multi Angle Absorption Photometer (MAAP) – not produced anymore

- The MAAP is another instrument with a build in loading correction.
- Intensities are measured in forward and in backward direction.

Wavelength correction:

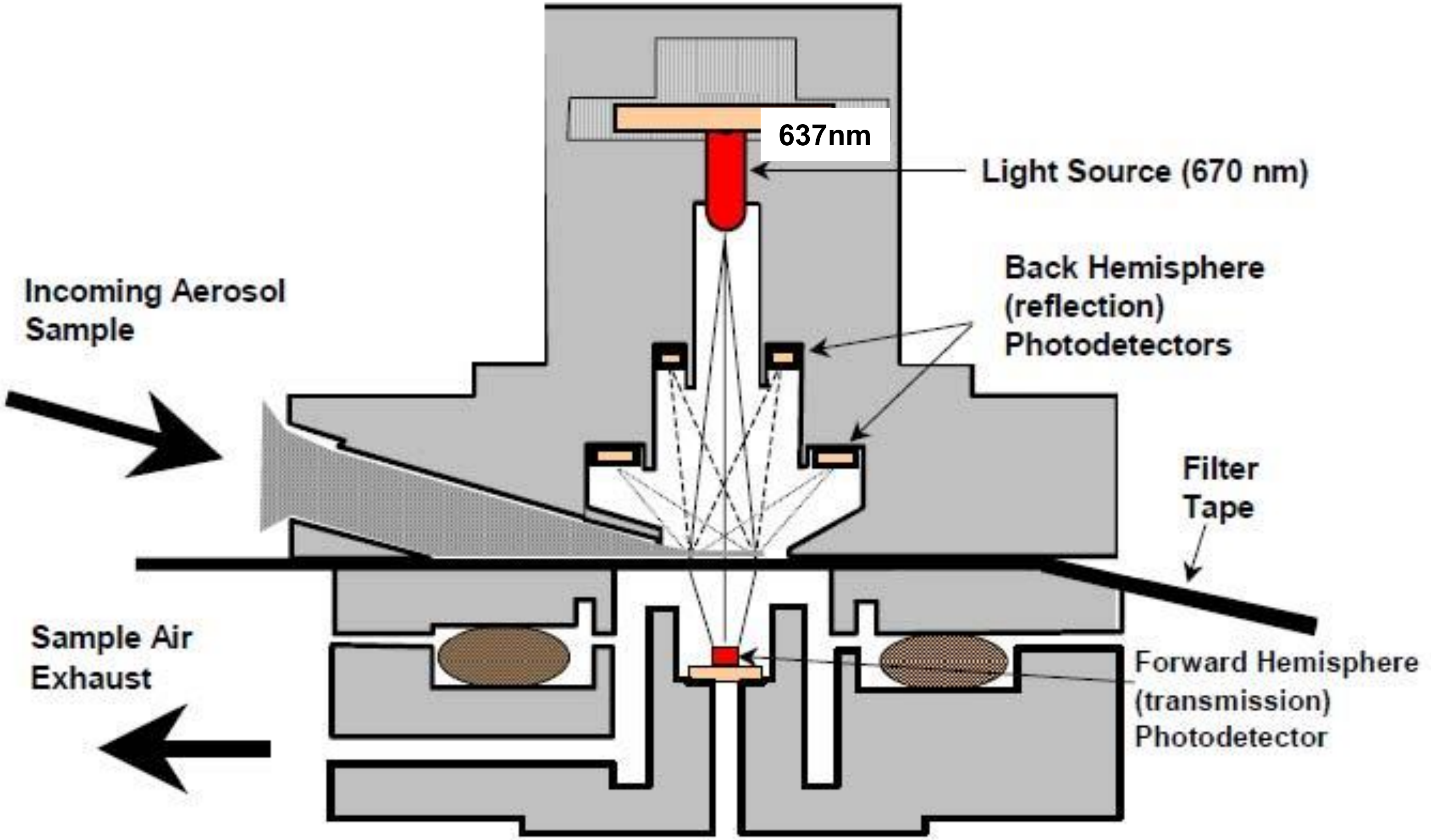
$$1.05 = \frac{670\text{nm}}{637\text{nm}}$$

Absorptioncoefficient:

$$\sigma_{abs-MAAP} = eBC_{raw-MAAP} \cdot 6.6 \cdot 1.05$$

Harmonized eBC:

$$eBC_{corr-MAAP} = \frac{\sigma_{abs-MAAP}}{10}$$



Petzold et al. 2004 JAS 421-441

Advantages of a Multi-Angle Absorption Photometer (MAAP)

- Unlike traditional absorption photometers, which suffer from filter-based loading effects, the MAAP corrects for these artifacts in real time by measuring scattered and transmitted light at multiple angles.
- MAAP incorporates multi-angle detectors to measure both absorption and scattering of aerosol particles.
- This allows for a more direct calculation of the particle light absorption coefficient, reducing uncertainties caused by assumptions about filter-based scattering effects.
- Traditional single-angle instruments (e.g., Aethalometers) rely on empirical correction factors to estimate the absorption coefficient, whereas MAAP directly measures the particle light absorption with fewer assumptions.
- MAAP applies real-time corrections for multiple scattering within the filter matrix, eliminating the need for post-processing correction factors.
- Because MAAP accounts for light scattering at multiple angles, it is less affected by changes in aerosol composition, shape, or coatings, which can introduce errors in other photometers.

Aethalometer

Aethalometer AE33/AE36

- The aethalometer AE33 is a further development of the AE31.
- The main feature is the dual spot technology to compensate for loading effects.

The particle light absorption coefficient is calculated by

$$\sigma_{abs} = \frac{\mathrm{d}OD(t)}{\mathrm{d}t}$$

with an empirically determined loading function of the form:

$$ATN = \frac{1}{k}\left(1 - e^{-k \cdot OD}\right)$$

The compensation parameter *k* is determined by the dual spot technology.

Aethalometer AE33/AE36 dual spot compensation

Two spots are loaded simultaneously with different aerosol flows Q_1 and Q_2, respectively. Therefore, one spot has a higher loading than the other spot.

$$ATN_1 = \frac{1}{k}\left(1 - e^{-k \cdot OD_1}\right)$$

$$ATN_2 = \frac{1}{k}\left(1 - e^{-k \cdot OD_2}\right)$$

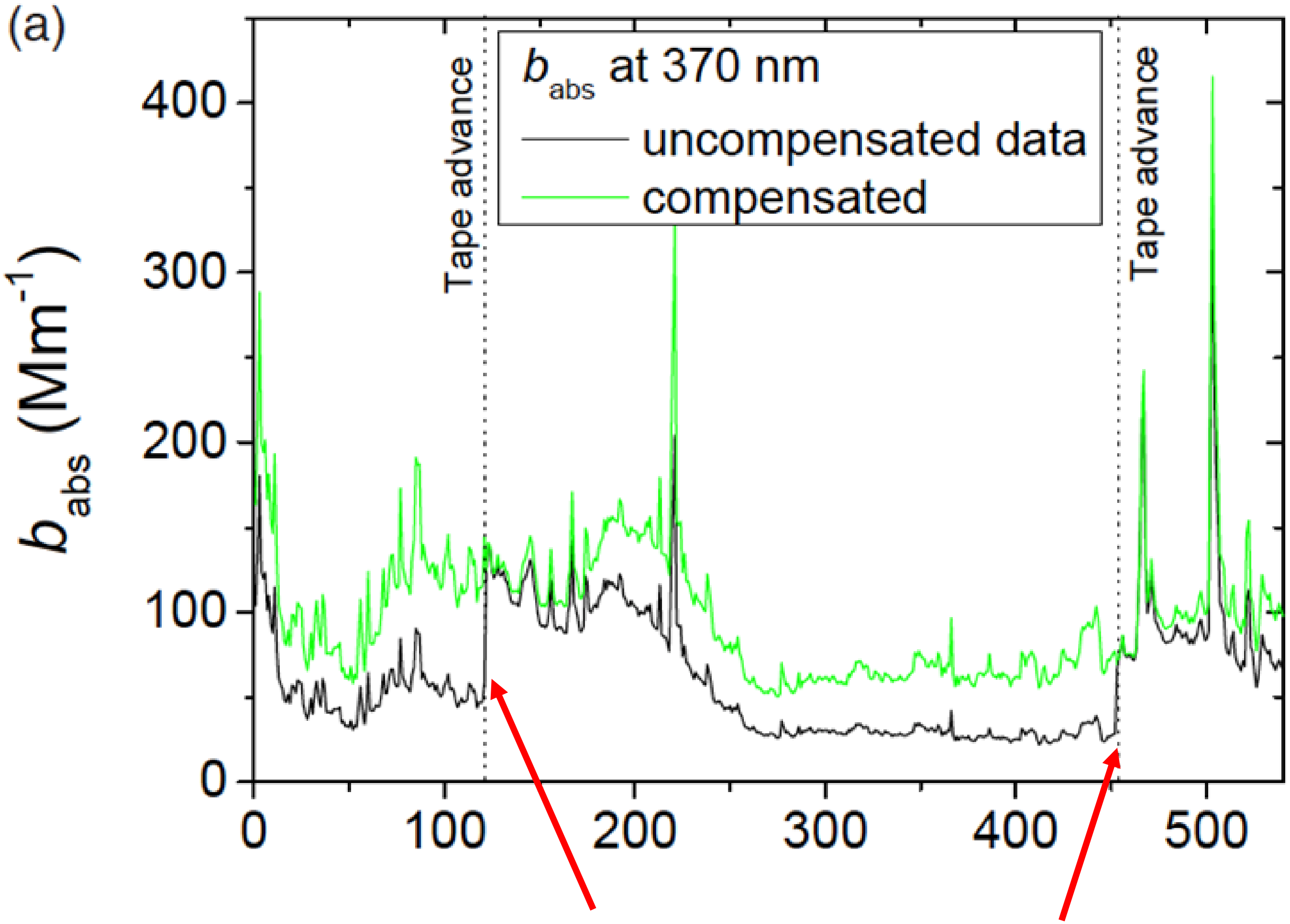
ATN_1 and ATN_2 are measured while k, OD_1 and OD_2 are unknown.

There is one more information! The ratio of the optical depth equals the flow ratio:

$$\frac{Q_1}{Q_2} = \frac{OD_1}{OD_2}$$

Combining the information from two spots, a compensation for the loading effect can be derived while collecting particles and taking data.

Aethalometer AE33/AE36 dual spot compensation



Without compensation: Jump in time series occurs, when changing to a new, unloaded spot.

Drinovec, et al., 2015.

Aethalometer AE33/AE36 Harmonization Factor

Observations in the field and in the laboratory showed that the sensitivity to light absorption varies depending on the aerosol type compared to other techniques.

Complicating factors are:

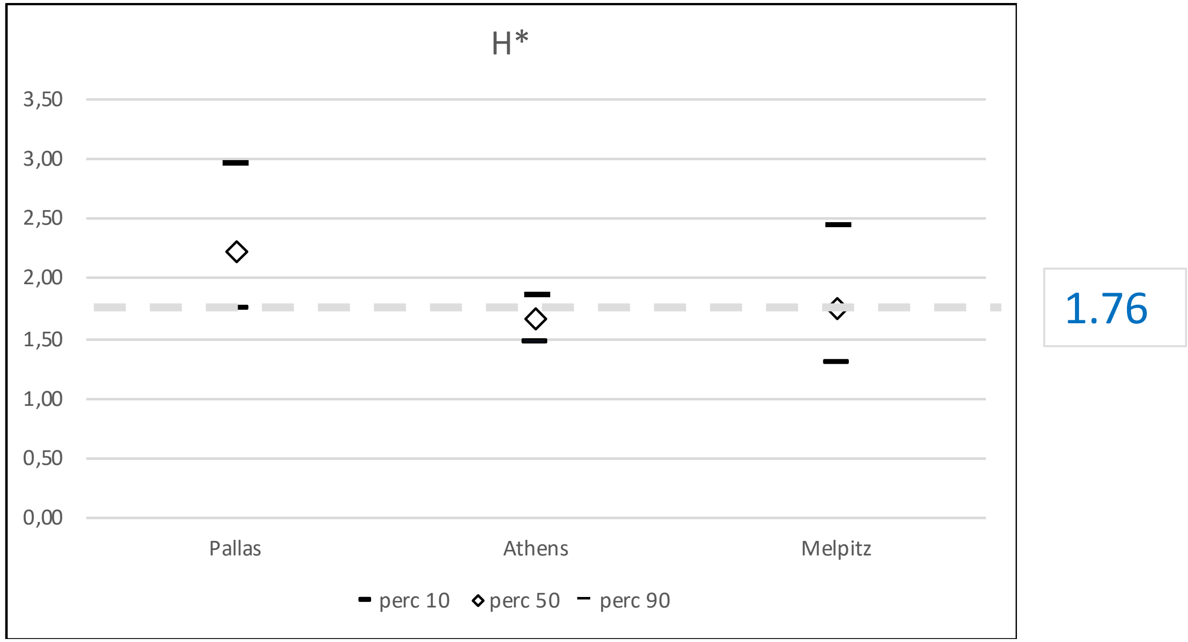
- Aethalometer reports an equivalent soot concentration.
- Filter types, and thus calibration factors, have changed.
- Comparison devices at stations are also filter-based instruments, which can show similar problems, but to a lesser extend.

The solution was to introduce a harmonization factor.

MAAP was chosen as the field 'reference' for this purpose and using long-term parallel measurement to the AE33

Summary of H* values

	hours	perc. 10	perc. 50	perc. 90
Pallas	589	1.75	2.23	2.97
Athens	1637	1.47	1.66	1.86
Melpitz	7607	1.29	1.74	2.44
Average		1.50	1.88	2.43
Time-weighted average		1.34	**1.76**	2.38



MAAP: Harmonized Absorption Coefficient and eBC Mass Concentration

$$\sigma_{abs-MAAP} = eBC_{raw-MAAP} \cdot 6.6 \cdot 1.05$$

$$1.05 = \frac{670\text{nm}}{637\text{nm}}$$

$$eBC_{corr-MAAP} = \frac{\sigma_{abs-MAAP}}{10}$$

Aethalometer AE33/AE36: Harmonized Absorption Coefficient and eBC Mass Concentration

The internal C value for the latest recommended filter tape is 1.39 (M8060).

$$\sigma_{abs-raw-AE} = \frac{\sigma_{ATN-raw-AE}}{C}$$

$$C = 1.39$$

The harmonization factor is then:

$$H^{*} = \frac{\sigma_{abs-raw-AE}}{\sigma_{corr-MAAP}} = 1.76$$

From this, the harmonized absorption coefficient and eBC mass concentration can be calculated:

$$eBC(880)_{harm-AE} = \frac{BC(880)_{raw-AE}}{1.76}$$

$$\sigma_{abs-harm-AE} = \frac{BC(\lambda)\cdot MAC(\lambda)}{1.76}$$