WP3- NA3: In-situ chemical, physical and optical properties of aerosols

Deliverable D3.16: Development of a standardized protocol for mw-AP measurements

Short description

During the reporting period a laboratory study for testing a reference system for determining the absorption coefficient at a single wavelength was tested. The reference absorption was determined by the difference of particle extinction coefficient and scattering coefficient (EC-SC). A series of tests were done to test the performance of this setup in a workshop at the World Calibration Center for Aerosol Physics at the Leibniz Institute for Tropospheric Research (TROPOS) in Leipzig Germany from Mar. 4 to 8, 2013.

This workshop was just the first approach towards the development of a standardized protocol for measurements of multi-wave-length particle light scattering absorption coefficients and a laboratory reference method.

Participants

Table: Participant list

ACTRIS scientific workshop for multi-wavelength absorption photometers			
March 4 - 8, 2013, WCCAP, TROPOS, Leipzig			
First name	**Family name**	**Institution**	**short form**
Drinovec	Luca	Aerosol d.o.o.	AEROSOL
Mogo	Sandra	Universidad de Valladolid	GOA-UVA
Mueller	Thomas	Leibniz Institute for Tropospheric Research	TROPOS
Titos	Gloria	Centro Andaluz de Medio Ambiente - Universidad de Granada	CEAMA
Tuch	Thomas	Leibniz Institute for Tropospheric Research	TROPOS
Virkkula	Aki	University Helsinki	UHEL
Vratolis	Stergios	National Centre for Scientific Research “Demokritos”	NCSR-D
Wiedensohler	Alfred	Leibniz Institute for Tropospheric Research	TROPOS

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1 Laboratory experiments

Laboratory experiments were performed in March 2013. At this stage, it was not possible to compare EC-SC to the absorption determined by another reference method, since no other reliable reference system was available. Therefore, the tests are limited to compare the extinction and the scattering coefficients for non-absorbing particles. The main difficulty is that scattering measurements done by integrating nephelometers, requiring a correction for the truncation error, which depends on particle number size distribution and particle composition. Two different methods for truncation correction were tested. Test measurements were done using ammonium sulfate and PSL particles.

Experiments with black particles were done to show the potential of using the EC-SC technique for calibrating filter based multi-wavelength absorption photometers. These experiments were done using mixtures of ammonium sulfate and Printex90 soot. The instruments, aerosol generation and the setup are described in the following chapter.

2 Setup

2.1 Extinction cell

The extinction cell is a Cavity Attenuated Phase Shift instrument (CAPS PM_{ex}, Aerodyne Research, MA, USA) with an operating wavelength of 530 nm. The nominal sensitivity is 0.25 Mm^{-1} (2σ) for 1 minute averaging time. The data recorded by the instrument need no instrument specific corrections. Temperature and pressure are measured for a correction of the extinction coefficient to standard temperature and pressure conditions.

2.2 Integrating Nephelometer

Two types of integrating nephelometers were used.

<u>TSI model 3565:</u>

Manufacturer:	TSI Inc., MN, USA
Wavelengths:	450, 550, 700 nm
Two operating modes:	total scattering & total/back- scattering
Truncation corrections:	Corrections using the Ångström scattering coefficient and based on Mie calculations are possible (see Anderson et al., 1996; Anderson and Ogren, 1998; Müller et al., 2011).

Aurora 4000:

Manufacturer:	Ecotech Pty Ltd, Knoxfield, Australia
Wavelengths:	450, 525, 635 nm
Operating modes:	'Polar mode': Scattering of light in up to 18 angular ranges. The angular ranges 0° - 180° and 90°-180° correspond to total and backscattering, respectively.
Truncation corrections:	Corrections using the Ångström scattering coefficient and based on Mie calculations are possible. Truncation correction for total and backscattering is the same as for Aurora3000 (c.f. Müller et al., 2011).

2.3 Test aerosols

Different test aerosol were used to characterize the setup and for first calibration experiments of absorption photometers.

PSL:	Non-absorbing polystyrene spheres of diameter 350 nm generated with a nebulizer from a hydrosol.
Black:	Printex90 soot was aerosolized from solution using an atomizer
White:	Ammonium sulphate aerosolized from solution using an atomizer

It was ensured that the relative humidity of all test aerosols was low (<30%) by mixing it with dry air and further drying using diffusions dryers.

2.4 Filter-based absorption photometers

Filter-based absorption photometers used for this experiments were AE31, AE33 and PSAP. A detailed description of instrument and correction methods is not given, since the absorption photometers are not part of the EC-SC characterization. Details can be found in the literature and in the user manuals.

2.5 Mixing chamber

A mixing chamber with a volume of 0.5 m^3 was used for diluting the test aerosols and delivering it to the instrument. The chamber has two inlet ports for test aerosols and make up air. Up to eight outlet ports distribute the aerosol to the instruments with equal concentrations.

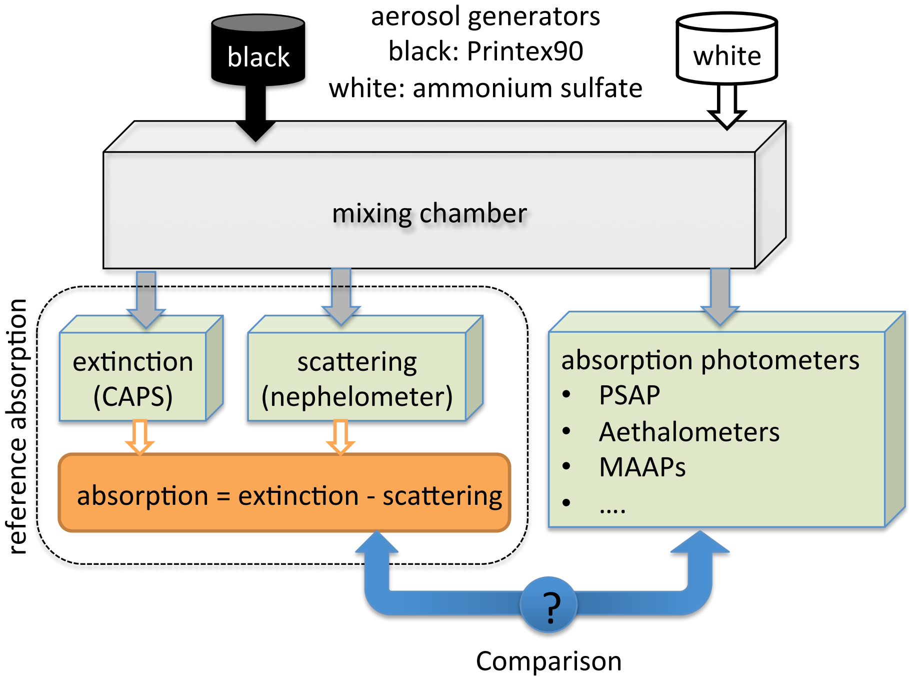

Figure 1: Experimental setup for experiments with ammonium sulfate and Printex90. Experimental runs with PSL were done with a similar setup, but without absorption photometers.

3 Experimental results

3.1 Noise characterization of Extinction cell

The noise of Aurora4000 depends on the configuration, meaning in how many angular ranges the scattering is measured. If total and backscattering are measured, the noise is expected to be similar to the noise of Aurora 3000. The noise (1σ) of Aurora 3000 and TSI model 3565 for the green wavelength are typically between 0.3 and 0.5 Mm^{-1} for one minute averaging time. For the present Aurora 4000 the noise was lower what is likely due to a less noisy photo multiplier. If the Aurora 4000 is operated in the polar mode with maximum 18 angular ranges, the noise amounts about 1 Mm^{-1} because of the shorter integration time for each angular range.

The noise for CAPS was measured using filtered air. The histogram distribution of noise is shown for averaging times of 3 and 60 seconds. Data for 60 seconds averaging time are calculated from the 3 seconds data using a moving average. In the shown case the median is shifted to negative values. This shift is caused by baseline drift. To avoid baseline drifts zero measurements should be done every 15 minutes for duration of 1 to 2 minutes. For laboratory conditions, a baseline drift within 15 minutes can be neglected. The overall performance of the CAPS agrees to the manufacturer specifications.

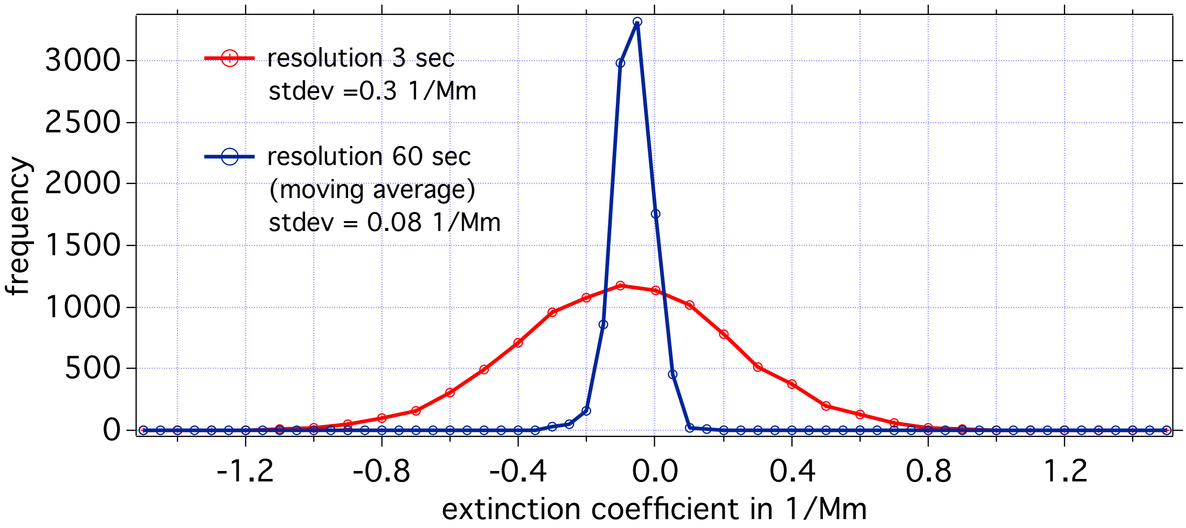

Figure 2: Histogram of noise of CAPS measured using filtered air.

3.2 Comparison of CAPS and integrating nephelometer using non-absorbing PSL spheres

PSL spheres of size 350 nm were aerosolized using a nebulizer. Beside particle light extinction and scattering coefficients, also the particle number size distribution was measured using a mobility particle size spectrometer (reference instrument of the WCCAP). The particle number size distribution consisted of two modes, the main mode at 350 nm and a second mode consisting of clusters of PSL spheres. The clusters appear at larger of about 410 nm. The ratio of particle number concentrations in the two modes was about 23:1. Mie scattering calculations used for simulating the truncation error of Aurora4000 resulted in a truncation correction factor of C_{TS}=1.06. An estimation of the truncation correction factor using the measured scattering Ångström exponent of 1.54 (measured at wavelengths 450 and 525 nm) results to values of C_{TS}=1.11. Figure 3 shows the time series and correlation plot of extinction and truncation corrected (C_{TS}=1.11) scattering coefficients. CAPS and integrating nephelometer agree well. The difference is about 2%, what can be explained by calibration uncertainties of the integrating nephelometer, which is typically in the order of 3% and by the differences of the truncation correction methods.

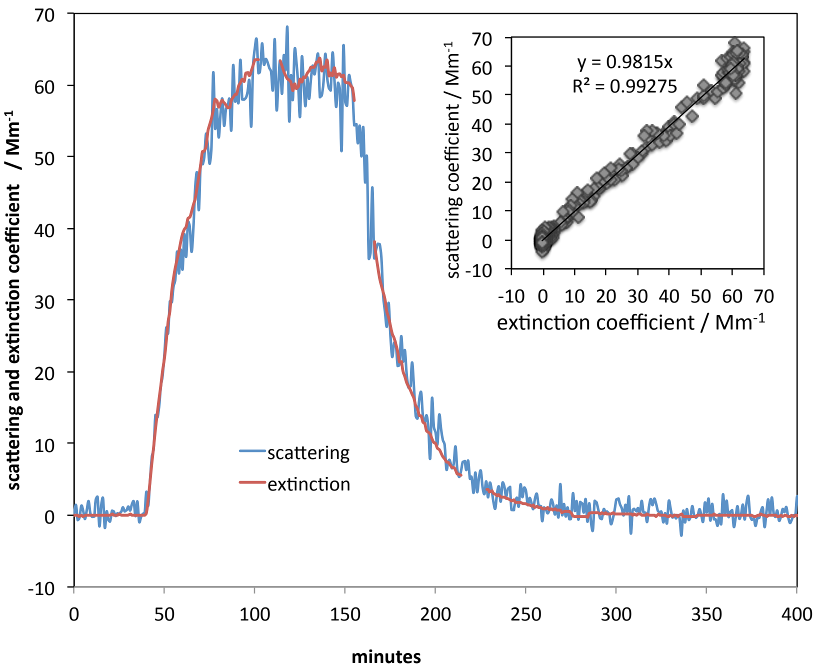

Figure 3: Time series of extinction coefficient and the truncation-corrected particle light scattering coefficient for 350 nm PSL particles. The averaging times of Aurora4000 and CAPS are 1 minute.

3.3 Comparison of CAPS and integrating nephelometer using ammonium sulfate

Particle light scattering coefficients determined from integrating nephelometers of types Aurora 4000 and TSI model 3565 were compared to extinction coefficients measured with CAPS. The test aerosol was ammonium sulphate. The truncation errors were corrected using Ångström parameterizations (Müller et al., 2011). Results are shown in Fig. 4. The averaging time for all instruments was 1 minute. The Aurora 4000 was operated in the polar mode with 18 angular ranges. Therefore the noise is higher compared to TSI 3565. The correlation lines of TSI3565 vs. CAPS and Aurora4000 vs. CAPS were forced through the origin. The slopes indicate, that the Aurora 4000 measures 0.7% lower values compared to CAPS with an uncertainty (95% confidence) of 1.9%. The TSI 3565 measures 1.7% lower values with an uncertainty of less than 1%. Uncertainties can occur due to uncertainties of the truncation correction and the integrating nephelometer calibration. The uncertainty of calibration constants typically amounts less than 3% for the green wavelength. In this respect the comparison of integrating nephelometers and CAPS was successful.

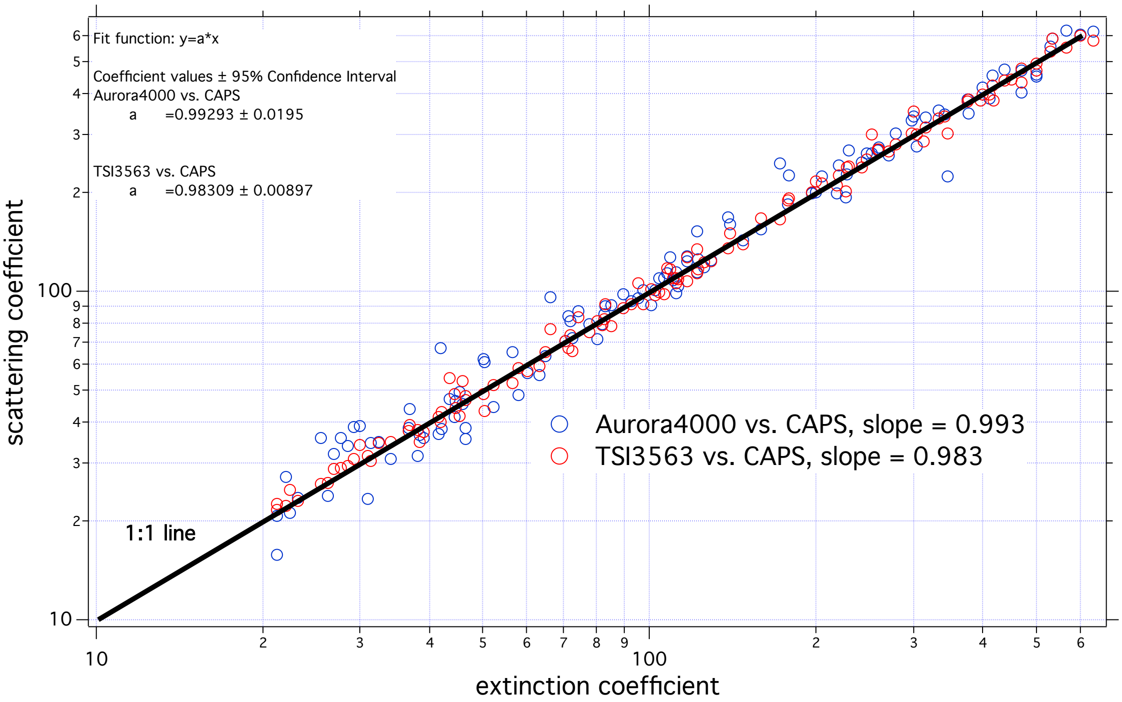

Figure 4: Comparison of the truncation-corrected particle light scattering coefficients and the particle light extinction coefficients for non-absorbing ammonium sulfate particles.

A main result from these experiments is that integrating nephelometer and extinction cell agree within the calibration uncertainty of the integrating nephelometers. Since the 'reference absorption' is defined as the difference of extinction and scattering, the instruments should be matched. That means, that the comparison results with white particles are used to compensate for systematic calibration errors and partly for systematic errors of the truncation correction of integrating nephelometers. Uncertainties of the truncation correction can not be fully compensated, since the truncation depends on particle number size distribution and particle composition. One task for the future is to find the best aerosol (composition, size) for matching CAPS and integrating nephelometer.

3.4 Uncertainty of EC-SC

The particle extinction coefficient determined by CAPS can be written by

$$\sigma_{ext}^{CAPS} = \varepsilon_{baseline} + \varepsilon_{noise} + c_{ext} \cdot \sigma_{p,ext} ,$$

with the baseline drift $\varepsilon_{baseline}$, the noise ε_{noise}, a calibration constant c_{ext} and the particle light extinction coefficient $\sigma_{p,ext}$. With a 15 minute intervals between baseline measurement, no drift was observed ($\Delta\varepsilon_{baseline}$=0), and the standard deviation of noise amounts $\Delta\varepsilon_{noise}$=0.08 Mm^{-1} for one minute averaging time. According to Petzold et. al (2012) the calibration constant can be set to unity (c_{ext}=1 and Δc_{ext}=0) after a new determination of the effective path length of CAPS. The uncertainty of extinction coefficient reduces to:

$$\Delta\sigma_{ext}^{CAPS} = \Delta\varepsilon_{noise}\,.$$

Similarly the scattering is given by

$$\sigma_{sca}^{neph} = \xi_{zero} + \xi_{noise} + c_{sca}\cdot\sigma_{p,sca} + \xi_{trunc}\cdot\sigma_{p,sca}\,,$$

with zero drift ξ_{zero}, noise ξ_{noise}, calibration constant c_{sca}, and truncation correction ξ_{trunc}. Within 15 minutes intervals no zero drift was observed ($\Delta\xi_{zero}$=0). The noise for integrating nephelometers in total/backscatter mode is about $\Delta\xi_{noise}$=0.3 Mm^{-1}. The calibration uncertainty is about Δc_{sca} =0.03. Comments on the difficulty of estimating the errors of the truncation correction were given in the previous section. The error of integrating nephelometers then is

$$\Delta\sigma_{sca}^{neph} = \sqrt{\left(\Delta\xi_{noise}\right)^2 + \left(\Delta c_{sca}\right)^2\cdot\sigma_{p,sca} + \left(\Delta\xi_{trunc}\right)^2\cdot\sigma_{p,sca}}\,.$$

Combining the uncertainties of CAPS and integrating nephelometer, the overall uncertainty for EC-SC is

$$\Delta\sigma_{abs}^{EC-SC} = \sqrt{\left(\Delta\varepsilon_{noise}\right)^2 + \left(\Delta\xi_{noise}\right)^2 + \left(\Delta c_{sca}\right)^2\cdot\sigma_{p,sca} + \left(\Delta\xi_{trunc}\right)^2\cdot\sigma_{p,sca}}\,.$$

After matching the integrating nephelometer to CAPS using white particles the calibration error can be omitted (Δc_{sca} =0). If the truncation and the error of the truncation correction for non-absorbing for white and black/grey particles are similar also the error of truncation correction can be omitted. For this special case the uncertainty of EC-SC amounts

$$\Delta\sigma_{abs}^{EC-SC} = \sqrt{\left(\Delta\varepsilon_{noise}\right)^2 + \left(\Delta\xi_{noise}\right)^2}\,.$$

This equation describes the uncertainty for the best case. The more realistic case with particle size and composition depending truncation error needs to be further investigated.

After some reformulations the relative error as function of the single scattering albedo can be derived. Results are in Figure 5 for the best case and for an assumed remaining error (error of truncation correction or mismatch of CAPS and integrating nephelometer) of 2% of the scattering coefficient.

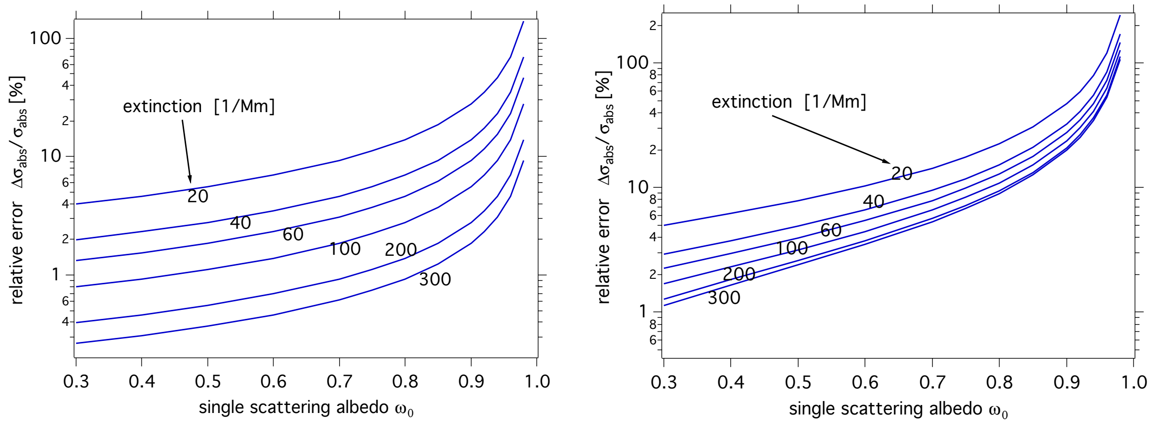

Figure 5: Relative error (1σ) of particle light absorption coefficient derived from the method extinction minus scattering. The relative error is plotted versus the single scattering albedo for different levels of extinction. The left plot shows the best case when truncation and calibration uncertainties cancels out. The right plot is for the case of a remaining error of 2% of the scattering coefficient.

The errors discussion of EC-SC can be summarized by

- The uncertainty in the best case is dominated by the noise of integrating nephelometer and CAPS. The noise can be reduced by long averaging times.
- It is important to match integrating nephelometer and extinction cell. The aerosol used for matching the instruments should be chosen to have similar truncation errors as the black or grey aerosol under investigation. Similar truncation errors imply that the phase functions of the white (matching aerosol) and black/grey are similar. This point needs to be investigated in more detail.
- The systematic errors of truncation correction are not well understood.

3.5 Preliminary calibrations experiments for filter-based absorption photometers

A series of experiments was conducted with black particles. Some of the main results are summarized in this section. The focus of experiments was to investigate particle size effects for filter-based absorption photometers. The size effect is still under debate, since it was found that Aethalometer of type AE31 require an aerosol type dependent correction factor. It suspected that the correction factor corresponds to particle size.

Black particles were generated with nebulizer. Different particle sizes have been selected from the broad particle size distribution using DMA. The volume mean diameters were determined of the particle volume size distribution measured by the reference mobility particle size spectrometer and are given below.

Table: volume median diameters of experimental runs.

run	**volume mean diameter / µm**
#1	0.178
#2	0.208
#3	0.243
#4	0.31
#5	0.151

Figs. 6 to 8 show particle light absorption coefficients measured with PSAP, AE31 and AE33 versus the reference absorption method. The reference absorption was EC-SC, whereas the particle light scattering coefficient was taken from the TS3565 integrating nephelometers. The truncation error was corrected using the scattering Ångström parameterization and the particle light scattering coefficient was adjusted to 532 nm using the scattering Ångström exponent.

Data from PSAP were corrected using the Bond correction (Bond et al. 1999). Data for Aethalometers are converted from BC concentration to attenuation coefficients. Conversion factors for AE31 and AE33 are 28.1 m^2/g and 13.2 m^2/m, respectively. The different conversion factors results from a new data processing scheme of AE33 using dual spot measurements and a different filter type.

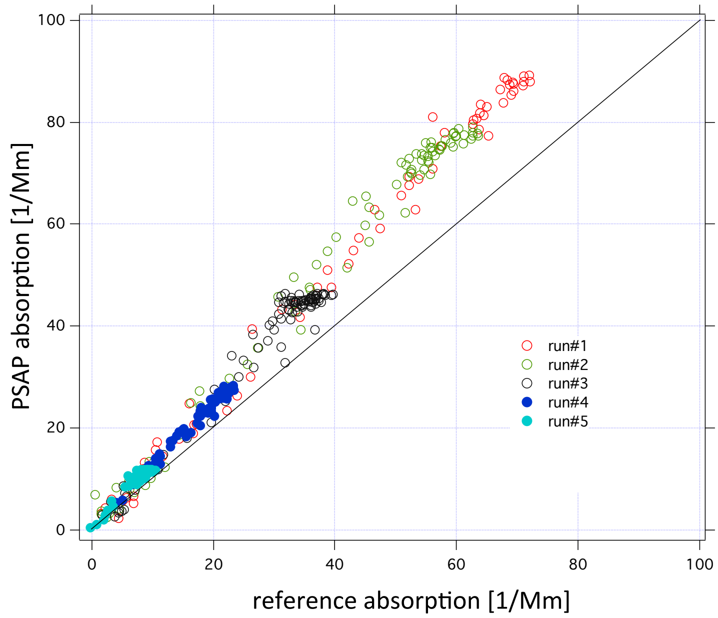

Figure 6: Absorption coefficients from PSAP versus reference absorption.

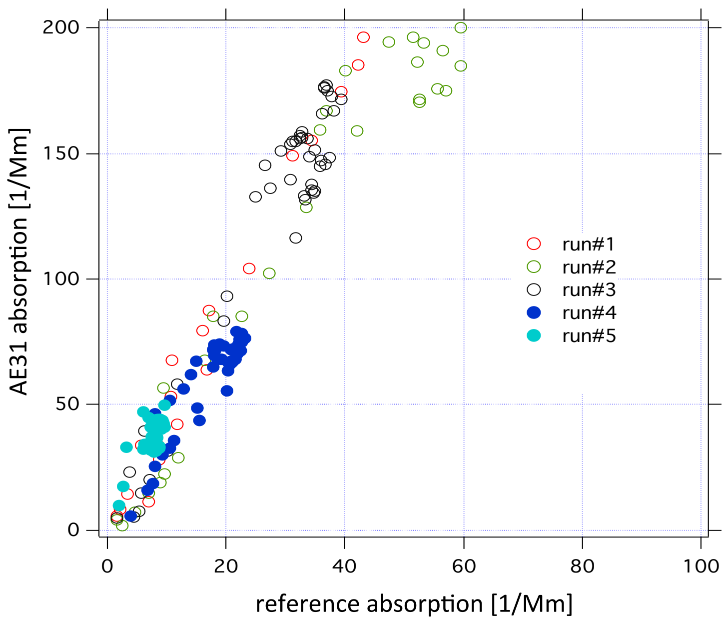

Figure 7: Attenuation coefficient from AE31 versus reference absorption.

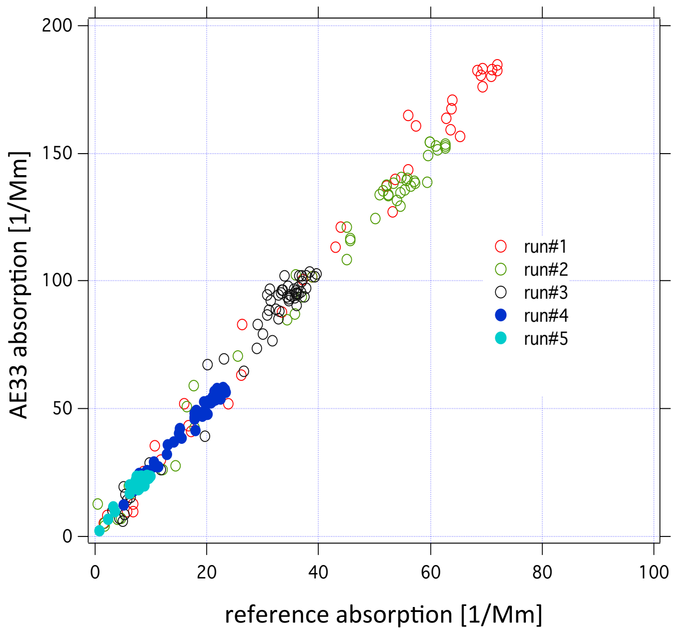

Figure 8: Attenuation coefficient from AE33 versus reference particle light absorption coefficient.

The ratio of the PSAP and reference particle light absorption coefficient absorption is called enhancement factor. The enhancement factor is plotted versus the volume mean diameter. Figure 9 summarizes results from the workshops EUSAAR2009 and ACTRIS2013. For EUSAAR2009 the reference absorption was the average absorption measured by two photo-acoustic photometers, whereas the photo-acoustic instruments differed by up to 20%. In addition, a parameterization derived in Nakayama et al. (2010) is shown. Unfortunately, the reference absorption in Nakayama was not measured but calculated by Mie scattering calculation using measured particle number size distributions and an estimated refractive index for soot.

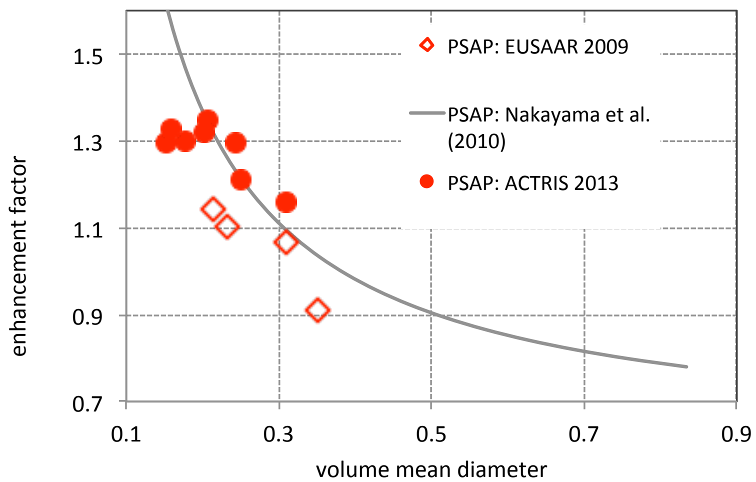

Figure 9: Size dependent enhancement factors for PSAP from two workshops and literature.

For the Aethalometers AE31 and AE33, the ratios of the attenuation coefficient and reference particle light absorption coefficient are the so-called "C_0" value. Figure 10 shows C_0 values from the EUSAAR 2009 and ACTRIS 2013 workshops. The C_0 values for AE31 are about a factor of 2 higher than values for AE33. This difference reflects the different conversion factors for calculating BC concentrations. One important finding is the smaller size dependence of AE33 compared to AE31.

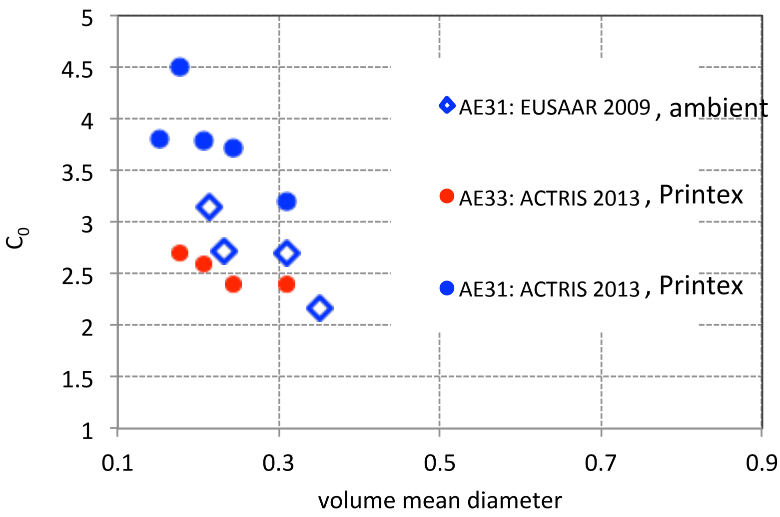

Figure 10: Size dependent C_0 values for AE31 and AE33.

4 Summary and next steps

A first characterization of the extinction cell (CAPS) showed that the instrument parameters agree well to the manufacturer specifications. Comparison of integrating nephelometers and CAPS showed that both instruments types agree well for white aerosols. Correction of truncation errors of integrating nephelometers and a matching of integrating nephelometers to CAPS is necessary. First calibration experiments for filter-based absorption photometers were successfully conducted.

The next steps are:

I. Extending the setup with two more CAPS instruments with wavelengths of 450 and 660 nm.

II. Theoretical and experimental investigation of the truncation error of integrating nephelometer with the goal of a reduction of systematic errors.

III. Development of a detailed protocol for calibrating instruments and quality assurance for reference absorption.

IV. Performing a series of calibration experiments, which correspond to different atmospheric aerosols.

A protocol for providing a high quality and reproducible absorption reference should be as follows:

a) Calibration of integrating nephelometer with $C0_2$
b) Noise characterization of CAPS and integrating nephelometer
c) Matching integrating nephelometer and CAPS with a defined and reproducible white aerosol.
d) Testing the reproducibility of the setup using a well defined black/grey reference aerosol, e.g. colored PSL particle of defined size.

For each step a strictly defined procedure will be defined. To test the repeatability steps a) to d) will be repeated over a period a several months.

5 References

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