**Atmospheric
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Reducing uncertainties associated with filter-based optical measurements of soot aerosol particles with chemical information

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Abstract

Of the many identified and potential effects of atmospheric aerosol particles on climate, those of soot particles are the most uncertain, in that analytical techniques concerning soot are far from satisfactory. One concern when applying filter-based optical mea-
5 surements of soot is that they suffer from systematic errors due to the light scattering of non-absorbing particles co-deposited on the filter, such as inorganic salts and mineral dust. In addition to an optical correction of the non-absorbing material this study provides a protocol for correction of light scattering based on the chemical quantification of the material, which is a novelty. A newly designed Particle Soot Absorption
10 Photometer was constructed to measure light transmission on particle accumulating filters, which includes an additional sensor recording backscattered light. The choice of polycarbonate membrane filters avoided high chemical blank values and reduced errors associated with length of the light path through the filter.

Two protocols for corrections were applied to aerosol samples collected at the Mal-
15 dives Climate Observatory Hanimaadhoo during episodes with either continentally influenced air from the Indian/Arabian subcontinents (winter season) or pristine air from the Southern Indian Ocean (summer monsoon). The two ways of correction (optical and chemical) lowered the particle light absorption of soot by 63 to 61%, respectively, for data from the Arabian Sea sourced group, resulting in median soot absorption co-
20 efficients of 4.2 and 3.5 Mm^{-1}. Corresponding values for the South Indian Ocean data were 69 and 97% (0.38 and 0.02 Mm^{-1}).

A comparison with other studies in the area indicated an overestimation of their soot levels, by up to two orders of magnitude. This raises the necessity for chemical correction protocols on optical filter-based determinations of soot, before even the sign
25 on the radiative forcing based on their effects can be assessed.

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1 Introduction

Of the many identified and potential effects of atmospheric aerosol particles on climate (Forster et al., 2007), those of dark soot particles are the most uncertain for several reasons. Firstly, our understanding of the atmospheric life cycle of soot is incomplete

5 with possible changes of the surface character of soot from hydrophobic near combustion sources to wettable or even hydrophilic during its dispersion and ageing in the atmosphere, promoting its removal by wet-deposition. Secondly, sampling and analytical techniques concerning soot and its effects are far from satisfactory, in particular if its multi-component and multi-phase nature is considered. Thirdly, there are no generally

10 agreed physical-chemical definitions of soot and no established standards or reference materials.

Soot is referred to as black carbon (BC) when determined with techniques that are based on the optical property of soot being a strong absorber of light in the visible wavelength region (Bond et al., 1999; Petzold et al., 2005). Several extensive reviews

15 concerned with optical measurements of soot have been published in the literature (Clarke et al., 1987; Horvath, 1993; Sheridan et al., 2005; Bond and Bergstrom, 2006; Hitzenberger et al., 2006).

One worry when applying optical measurements of ambient soot concerns possible interferences with non-elemental carbon compounds. Carbon containing aerosol par-

20 ticles that absorb light can be regarded as a continuous spectrum of compounds, with soot as a strong absorber at 550 nm wavelength and organic carbon, OC, (originating from biological processes such as low temperature oxidation) absorbing towards shorter wavelengths in UV which gives the compounds a brown or yellow color. As OC does not absorb strongly where soot normally is measured its presence should

25 be of minor concern. However, it has also been shown that large amounts of OC are collected as liquid drops, rather than as solid particles, which can cause errors in the measured light absorption (Subramanian et al., 2007).

Light absorption can be estimated if the extinction (ext) and scattering (sca) by soot

is known (Eq. 1). The extinction can be measured as the ratio of incoming light (I_0) and transmitted light (I_1).

$$\text{ext} = \text{sca} + \text{abs} = \frac{I_0}{I_1}. \tag{1}$$

By monitoring the change in transmitted light through a filter, estimates of the absorption are possible. Commonly used filter types are made of glass or quartz fibers or consist of porous membranes.

The most reliable (according to Andreae and Gelencser, 2006) filter based optical method used is the Multiple Angle Absorption Photometer (MAAP) (Petzold et al., 2005) that measures both the transmission and scattering at several wavelengths. Another commonly used instrument is the Particle Soot Absorption Photometer (PSAP) (Bond et al., 1999) which does not record light scattering by the deposited particles.

The above well-established approaches for filter-based optical measurements of soot suffer however from systematic errors due to the optical effects of non-absorbing or low-absorbing particles, such as inorganic constituents (e.g., sulfate, nitrate, mineral dust, and sea salt), in the sample which relates to the dependence of aerosol light scattering on the chemical composition. To correct for these systematic errors the MAAP instrument has the advantage of continuously measuring light scattered back from the sample in two angles but without any direct information on chemical composition of the non-absorbing material. The PSAP instrument compensates for its lack of recording scattered light in a simplified way by applying a constant correction (Bond et al., 1999) and thus not accounting for changing aerosol composition.

In an attempt to further reduce errors dominated by the optical effects of non-absorbing particles this study will in addition to monitoring the scattered light provide a chemical quantification of the inorganic fraction of the non-absorbing material. The primary analytical instrument measured light transmission and scattering at 528 nm on particulate samples accumulated on polycarbonate membrane (PCMB) filters. The PCMB filters were selected to avoid high chemical blank values characteristic for the otherwise commonly used glass fiber filters (Bond et al., 1999).

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Additional errors are associated with the filter itself (referred to as filter effects in Sect. 2.3.1), which will affect the length of the light path through the filter. This can lead to multiple light paths resulting in an overestimation of the recorded light absorption. Both the MAAP and PSAP methods apply protocols to correct for errors associated with filter effects based on artificial and ambient sample characterizations of the absorption (Petzold et al., 2005 and Bond et al., 1999). A similar protocol but specifically characterized for the application of PCMB filters was used in this study. The choice of PCMB filters instead of glass fiber filter is also advantageous since the particles are deposited on the filter surface and not further embedded in the filter texture.

The methods of corrections derived in this study were applied to ambient aerosol samples collected at the Maldives Climate Observatory Hanimaadhoo (MCOH). The samples were collected during episodes with both continental influenced air from the Indian/Arabian subcontinents and pristine air from the Southern Indian Ocean.

2 Measuring site and methods

2.1 Maldives Climate Observatory Hanimaadhoo (MCOH)

MCOH is located on the northern point of Hanimaadhoo, an island in the northern part of the Maldives (longitude 73° E 10′59″, latitude 6° N 46′34″), and stretching 4 km north to south and 1 km east to west. The Maldives consist of an archipelago of nearly 2000 coral atolls covering 800 km north to south in the Indian Ocean at a distance of between 200 and 1200 km southwest of the south cape of the Indian subcontinent (Fig. 1). The topography of the islands is low and no natural point rises above 3 m. The islands therefore have a very small effect on the atmospheric circulation and serve as good locations for atmospheric in situ measurements of air originating from either the Asian continent or the Southern Hemisphere. Hanimaadhoo has a population of around 1200 and is free from influence by population centers and industries. The location of the observatory, at the northern cape of the island with ocean on three sides at most 100 m

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away, ensures that the prevailing wind comes from over the ocean. Thus the site has no significant local soot emissions upwind of the station, and the composition of the air and rain is dominated by the regional sources (Corrigan et al., 2006).

Air was sampled from a 15 m high tower where various sensors and the inlets for air sampling were mounted. A 15 m long stainless steel tube (diameter 20 cm) led the sampled air down to the instruments with a laminar flow of 300 dm^3 min^{-1}. The air inlet was equipped with a cyclone discarding supermicrometer particles, implying that only particles smaller than 10 μm in equivalent aerodynamic diameter (EAD) passed. The aerosol instruments were installed at surface level in the building within a temperature and humidity controlled environment to avoid condensation of water inside the instruments due to a lower temperature (Corrigan et al., 2006). Inside the building aluminum tubing (diameter 15 cm, concentric head) selected the air in the middle of the larger tube to avoid wall effects. Subsequently the airflow was distributed to the instruments. Depending on the expected ambient mass concentrations, Nuclepore® polycarbonate membrane (PCMB) filter (0.4 μm pore size, 37 mm diameter) samples were taken for 24 or 48 h, through isokinetic take off lines from the main inlet pipe. Sampling flow was 2.0 dm^3 min^{-1} and a cyclone with a size cut of Dp_{50}=2 μm was mounted upstream of the sampler. The exposed filter surface was masked to 8 mm sampling diameter (0.5 cm^2 area). The geometric configuration (Hansson et al., 1987) of the sample spot on the filter surface was used to optimize the analytical conditions (increase the signal to noise ratio) for the post-sampling analyses (soot and non-light absorbing particulate ionic mass) on the PCMB Nuclepore® filters. Prior to analyses the PCMB Nuclepore® filters were stored in filter cassettes, which were sealed with parafilm.

2.2 Determination of light absorption and backscattering

At stable condition back at the laboratory of the Department of Meteorology, Stockholm University (MISU), a soot photometer constructed in accord with the setup by Heintzenberg (1988), detected the attenuation of light transmitted through the particles that had accumulated on the PCMB Nuclepore® filter. The light source was a light emitting diod

(LED) operating at 528 nm. Light transmission through the sample spot and a reference spot (on which no particles accumulated) was sensed by photo diodes. Behind sample and reference spots there was a Teflon® plate acting as a Lambertian diffuser, causing the light reaching the detector to be diffuse. The soot photometer also measures the light backscattered from the filter surface at 40° which enabled correction for scattering (Fig. 2).

The filter transmittance is the inverse of the extinction and is calculated as:

$$\tau = \frac{1}{\text{ext}} = \frac{I_1}{I_0},$$

(2)

where I_0 is the intensity of the incoming light and I_1 of the transmitted light.

The difference in intensity of transmitted light between exposed and unexposed filter surface can be used for the calculation of the optical density (Od) for any filter-based method:

$$\text{Od} = ln\left[\frac{I_1}{I_2}\right].$$

(3)

Here I_1 is the average light intensity transmitted through the unexposed filter and I_2 through the exposed filter. A photodiode was used to measure I_1 and I_2 (Fig. 2). The light absorption coefficient due to particulate matter (σ'_{ap}) is defined as Od per meter air column and is calculated by multiplying the spot area and dividing by the volume of air sampled:

$$\sigma'_{ap} = \frac{A}{V} ln\left[\frac{I_1}{I_2}\right].$$

(4)

A is the soot-spot area on the PCMB filter (0.5 cm^2 or 8 mm in diameter) and V the volume of air passing through the filter during a given period of time. A second sensor measured the back-scattered light, $I_{40;1}$ and $I_{40;2}$ at 40° relative to the incoming light in

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front of the filter, which enabled a correction for light scattering (Fig. 2). A scattering density (Sd_{40}) for each interval was calculated according to:

$$Sd_{40} = ln\left[\frac{I_{40;1}}{I_{40;2}}\right].$$ (5)

Sd_{40} is a measure of the change in intensity of the scattered light due to particles accumulated on the filter surface. By also taking the sampled air volume (V) and the soot spot area (A) into account, a scattering coefficient ($\sigma_{sp;40}$) for the back scattered light at 40° was calculated,

$$\sigma_{sp;40} = \frac{A}{V}ln\left[\frac{I_{40;1}}{I_{40;2}}\right].$$ (6)

With measurements from the two sensors a Single Scattering Albedo (SSA) was estimated. This was obtained through:

$$SSA_x = \frac{\sigma_{sp;x}}{\sigma_{ap} + \sigma_{spx}},$$ (7)

where x denotes the method used to estimate σ_{sp}. An absolute value of SSA is however not possible to calculate because the sensor measuring the back scattering only registers a defined angle of the backscattered light. Nevertheless the information is useful in undertaking scattering corrections of the optical effects of non-absorbing particles on the measured light absorption (see next section).

To establish the mass concentration of soot from the estimated light absorption, a mass absorption cross-section (MAC) was used. Notably, this factor is unique for each composition of aerosol particles and wavelength, thus adding further uncertainties to the estimate of atmospheric soot abundances. Bond and Bergstrom (2006) recommend a MAC value of $7.5\pm1.2\,m^2\,g^{-1}$ for airborne uncoated soot particles, but due to the ageing processes of soot during its atmospheric lifetime, this value can only be

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expected to be relevant for measurements close to the source. Therefore a value of $MAC=10\,m^2 g^{-1}$ was applied to estimate the concentration of ambient aerosol particles aged in the atmosphere (Heintzenberg, 1982).

Through laboratory tests with filtered air (free from particles) the standard deviation (1σ) of the soot photometer instrument were established to be 0.0006 in units of Od and in units of σ_{ap} 0.002 Mm^{-1} (in relative measures better than 8, 0.04 and 0.01% for σ_{ap} >0.02, 5 and 15 Mm^{-1}, respectively) and the detection limit (3σ) 0.006 Mm^{-1}. By using a MAC value of 10 $m^2 g^{-1}$ the obtained soot mass concentrations were 0.2 $ngCm^{-3}$ (in relative measures better than 8, 0.04 and 0.01 % for concentrations >2, 500 and 1500 $ng\,C\,m^{-3}$, respectively) and the resulting detection limit (3σ) 0.6 $ngCm^{-3}$. The overall coefficient of variation was estimated to be 6%.

2.3 Correction of light absorption measurements

2.3.1 Optical correction

The measured light absorption from the soot photometer instrument had to be corrected for light scattering by the non-absorbing matter and for filter effects that both would influence the signal measured by the detector of the transmitted light through the PCMB filter. As mentioned in the introduction the filter effect depends on whether or not the particles are collected on the filter surface or embedded in the filter texture or both. This affects the length of the light path through the filter, which can lead to multiple absorption or scattering. The length of the light path is also affected by which angle the light is scattered (phase function). In conditions with high ambient particle concentrations in combination with a too long sampling period the determined soot levels constitute likely an underestimate, due to overloading of the filter samples. This is referred to as the filter shadowing effect in that aerosol particles are shadowed by other aerosol particles in the sample, and then not detected by the instrument. The shadowing effect can be reduced by adjusting the length of the sampling periods.

For the soot photometer using PCMB filters the optical filter correction due to filter

effects and scattering is given by:

$$\sigma_{ap;\text{optic-corr}} = \sigma'_{ap} \cdot (\tau \cdot k_1 + k_2) + \sigma_{sp;40} \cdot k_3. \tag{8}$$

Here $\sigma_{ap;\text{optic-corr}}$ is the corrected light absorption coefficient and σ'_{ap} the uncorrected absorption coefficient from the soot photometer. τ is the transmittance of the filter sample and together with k_1 (0.0628) and k_2 (0.326) forms the optical correction for filter effects. $\sigma_{sp;40}$ is the measured backscattered light at 40° and multiplied with k_3 (0.00822) constitutes the optical correction for scattering, that is a calculated measure of the dependence of aerosol light scattering on the non-absorbing chemical composition. k_1, k_2 and k_3 are empirical constants combining the former effect with errors related to filter effects. These constants were acquired by comparing the MISU soot photometer and a MAAP (Petzold et al., 2005). The inlets of the two instruments were connected to a mixing chamber where synthetic soot and ammonium sulfate particles were continuously mixed. The single scattering albedo of the mixed particles during the comparison varied between 0.98 and 0.75. After sampling the best combination of k_1, k_2 and k_3 were seeked, to acquire a σ_{ap} from the soot photometer using Eq. (8) as close as possible to the σ_{ap} from the MAAP instrument. This was performed using the solver function of Microsoft Excel®.

2.3.2 Chemical correction

By subsequent chemical quantification of each PCMB filter sample a direct estimate of the scattering effect of non-absorbing inorganic particles was provided. This was carried out for samples collected during two periods characterized with either continental (Arabian Sea) or remote marine (South Indian Ocean) influenced air (defined in Sect. 3.1).

The scattering of light by the analyzed inorganic mass fraction deposit on each filter sample ($\sigma_{sp;\text{ionmass}}$) was estimated through multiplying the total detected ionic mass (C_{ionmass}) by the mass scattering efficiency specific to the source area of the selected

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periods (MSE) (Eq. 9).

$$\sigma_{sp;\text{ionmass}} = C_{\text{ionmass}} \cdot \text{MSE}. \tag{9}$$

A value of $3.8\,\text{m}^2\,\text{g}^{-1}$ was used for MSE as reported by Clarke et al. (2002). A linear regression analysis was then performed on the measured σ'_{ap} and the calculated $\sigma_{sp;\text{ionmass}}$. From the obtained relationship in Eq. (10)

$$\sigma'_{ap} = k \cdot \sigma_{sp;\text{ionmass}} + c, \tag{10}$$

the slope k multiplied with $\sigma_{sp;\text{ionmass}}$ is an estimate of the fraction of the measured light absorption σ'_{ap} resulting from the scattering by non-absorbing inorganic matter. The value determined for the linear regression correction parameter k was 0.247 for the Arabian Sea group and 0.081 for the South Indian Ocean group.

The intercept c in Eq. (10) represents the "true" absorption together with added errors associated with the PCBM filter itself ("filter effects"). A constant $c=0.268$ was used in the corrections for all samples. It was estimated from the samples collected in air with a minimum influence of continental combustion sources and was chosen to represent the least absorption from aerosol particles that could have interfered with the estimation of the filter effect itself.

The corrected light absorption coefficient $\sigma_{ap;\text{chem-corr}}$ was obtained applying Eq. (11) to each individual sample:

$$\sigma_{ap;\text{chem-corr}} = \sigma'_{ap} - k \cdot \sigma_{sp;\text{ionmass}} - 0.268. \tag{11}$$

2.4 Chemical analyses of the Nuclepore® filters using IC

To allow for subsequent chemical determinations all PCMB filters, ambient samples and blanks were carefully handled in a glove box (free from particles, sulfur dioxide and ammonia) both prior to and after sampling. At the time of the chemical analyses, still in the glove-box, the filters were extracted (in centrifuge tubes) with $5\,\text{cm}^3$

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deionized water (18 MΩcm). For sufficient extraction the filter extracts were finally placed in an ultra sonic bath for 60 min. The extracts were then analyzed for major cations, anions and weak anions by chemically suppressed ion chromatography (IC, Dionex ICS-2000). The anions were analyzed with Dionex AG11/AS11 columns and the cations with CG16/CS16. The injection volume was 50 μdm^3. Quality checks of the analyses were performed with both internal and external reference samples (BMC). The analytical detection limits obtained for the various ions, defined as twice the level of peak-to-peak instrument noise, were 0.20, 0.05, 0.10, 0.01, 0.01 and 0.25, 0.02, 0.01, and 0.001 μeq dm^{-3}, for sodium (Na$^+$), ammonium (NH$_4^+$), potassium (K$^+$), magnesium (Mg^{2+}), calcium (Ca^{2+}), and chloride (Cl$^-$), nitrate (NO$_3^-$), sulfate (SO$_4^{2-}$), and methane sulfonate (MSA), respectively. The overall analytical accuracy was better than 5% and 7% for the anions and cations. The average particulate Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, NO$_3^-$ and SO$_4^{2-}$ blank concentrations were <5%, <3%, <1%, <0.2%, <0.3%, <6%, <32% and <0.2% of the sample, respectively. Non-sea-salt (nss)-SO$_4^{2-}$-concentrations were calculated by using sodium concentrations and seawater composition taken from Stumm and Morgan (1981). The sea-salt contribution was on average less than 0.5% ("Arabian Sea"); 4% ("South Indian Ocean") of the total submicrometer SO$_4^{2-}$-concentrations.

2.5 Trajectory analysis

To evaluate possible source regions for air sampled at surface level at MCOH, modeled trajectories were used. These were calculated backwards for 10 days with the Hysplit model (version 4.8) developed at NOAA (Draxler and Rolph, 2003). The choice of 10 days was made according to the expected lifetime of the sampled aerosol particles. The arrival height for the trajectories was set to 50 m. When using trajectory data, one must take in to account the numbre of uncertainties in the trajectory models, as discussed by (Stohl, 1998) among others.

3 Results and discussion

3.1 Data selection

During the winter season (November–April), the mean wind direction at MCOH is north-easterly associated with air influenced by anthropogenic activities from the Indian sub-
5   continent, such as combustion. During the summer monsoon (June–September), the mean wind direction at MCOH is southwesterly associated with marine air from the Southern Hemisphere Indian Ocean. The air masses accumulate moisture over the Indian Ocean and deposit large amounts of precipitation over India and the surround-ing regions. Between the two seasons a transition occurs with variable wind directions
10   lasting for about 4 to 5 weeks (Corrigan et al., 2006).

The Indian subcontinent is a major source region of anthropogenic emissions from biomass burning and fossil fuel combustion (Reddy et al., 2004 and Nair et al., 2005), with the former dominating the soot composition according to C-14 analysis performed at samples from MCOH (Gustafsson et al., 2009). Mineral dust from the Middle East/
15   Arabian peninsula is transported southwards over the Arabian Sea mixed with anthro-pogenic influenced aerosol particles from the Indian subcontinent and sea salt before reaching the MCOH (Nair et al., 2005). The South Indian Ocean region is mainly a contributor of biogenic derived sulfur containing particles and sea salts (Norman et al., 2003).

20   Considering both the source regions and the meteorological situation leads to the election of two time periods being representative for continental influenced air with relatively high light absorption of soot ($4\,\mathrm{Mm}^{-1}$) and for air with a minimal influence from combustion sources ($0.4\,\mathrm{Mm}^{-1}$). Section 3.2 and Table 1 give further details of the estimates. The first period (17 March to 3 May 2007) occurred within the winter season
25   and was characterized by trajectories starting in the northern part of the Arabian Sea, then moving south along the west coast of the Indian subcontinent to finally end at MCOH (Figs. 3 and 4). During the second period within the summer monsoon (1 June 2007 to 24 September 2007) the 10-day trajectories originated from the southeast with

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the remote marine Southern Indian Ocean as source region.

The total analyzed inorganic mass composition showed that the air arriving from the Arabian Sea (9.1 µgm^{-3}, median value) had a 5-fold higher mass, compared to South Indian Ocean (1.7 µgm^{-3}, median value). SO_4^{2-}, followed by NH_4^+, Na^+ and soot dominated the samples with source regions over the Arabian Sea and the Indian subcontinent (Table 2, Fig. 5). The strong contribution from nss-SO_4^{2-}, K^+ and NH_4^+, being indicators of combustion and agriculture, is in alignment with the closeness to the Indian subcontinent. An additional feature was the elevated concentration of Ca^{2+} measured, which indicated transport of crustal material from the large desert areas in the Middle East. Both recent satellite retrievals (Kaufman et al., 2001) and data from the AERONET network of ground-based radiometers (Dubovik et al., 2002) from the Middle East/Arabian peninsula show low light absorption by dust in the visible to near-infrared wavelengths. Therefore it is assumed that in this case the main influence of crustal material on optical measurements of soot is through light scattering.

When the air originated from the South Indian Ocean SO_4^{2-} still dominated the inorganic mass composition, with the two sea salt components Na^+ and Cl^- being the second most common. The strong contribution from nss-SO_4^{2-} was in agreement with previous findings where virtually all nss-SO_4^{2-} was likely to have been derived from the marine biogenic source of dimethyl sulfide (Norman et al., 2003). The strong contribution from NaCl, as expected in marine influenced air, was also in agreement with Norman et al., 2003.

3.2 Implementation of the correction methods on PCMB filter-based optical measurements of soot

To reduce systematic errors dominated by the optical effects of non-absorbing particles when using filter-based determinations of soot, the two independent methods of corrections described in Sect. 2.3 (the optical MAAP and the chemical based on the linear regression of the uncorrected σ'_{ap} and $\sigma_{sp;\text{ionmass}}$) were each applied to the un-

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corrected light absorption coefficient , σ'_{ap} , measured in the samples collected at the MCOH. Based on a trajectory analyses and verified by the chemical quantifications (Fig. 5, Tables 1 and 2) the samples were representative for episodes with either continental influenced air from the Indian/Arabian subcontinents or pristine air from the
5 Southern Indian Ocean.

Through the optical correction, the empirically derived values of k_1, k_2 and k_3 in Eq. (8), were applied to both data selections. The benefits in using the chemical quantification of the non-absorbing matter collected on the PCMB filters was that a C_{ionmass} could be quantified for each of the two groups separately (Sect. 2.3.2).

10 The optical correction resulted in a median σ_{ap} for the "Arabian Sea" of 4.2±0.04 (90% confidence interval) Mm^{-1} (Table 1). The "Arabian Sea" median σ_{ap} from the chemical correction (3.5±0.04 Mm^{-1}) was less than 20% lower compared to the optical correction. For the "South Indian Ocean" group corresponding values, 0.38±0.02 and 0.02±0.02 Mm^{-1}, were significantly different at a 90% confidence interval, with the
15 chemical corrections not statistically separated from zero. The optical correction lowered the σ_{ap} with 61% for the samples collected within the "Arabian Sea" group and with 63% for the "South Indian Ocean" group. The chemical correction lowered the σ_{ap} with 69% and as much as 97% for the "Arabian Sea" and "South Indian Ocean" data selections, respectively (Table 3 and Fig. 6). The resulting relative strong chemical
20 correction for the "South Indian Ocean" data suggests the optical correction to be less sensitive to the amount of non-absorbing particle matter deposit on the filter.

Table 4 gives a comparison of the soot mass concentrations derived in this study with two other studies performed within the Indian Ocean region. Reported values for the winter season varied between 1 to 5 Mm^{-1} (Quinn et al., 2002) and 7.1 to 19 Mm^{-1}
25 (Corrigan et al., 2006). The former levels were in the same range as the values reported in this study with the latter range being 2 to 5 times higher. During the summer monsoon the reported conditions in this study were dissimilar in comparison with the Corrigan et al. elevated data in being up to two orders of magnitude in difference.

Quinn et al., 2002 measured the light absorption coefficient with a PSAP instrument

using the correction protocol of Bond et al., 1999. It takes into account the effect of scattering in general, but uses pre set values for the correction parameters and by that does not account for variations in the scattering by the non-absorbing aerosol material. This was motivated by the (2%) increase in light absorption due to scattering.

Corrigan et al., 2006 used an aethalometer to measure the light absorption coefficient and implemented a correction protocol developed by Arnott et al., 2005. The protocol was optimized for continental conditions and applied an empirically derived routine based on laboratory and field absorption measurements performed together with a photoacoustic photometer to acquire corrected light absorption coefficients. The parameters in this method were fixed to certain pre set values and not adjusted continuously to take into account variations in the optical properties of the aerosol particles collected. The correction method developed by Arnott et al., 2005 were not valid for clean air conditions at the MCOH as negative σ_{ap} were retrieved. To solve this problem the scattering correction in Arnott et al. was tuned to only generate positive σ_{ap} values. After this adjustment the results of Corrigan et al., 2006 showed a contribution of scattering to the absorption measurements similar to the low 2% reported by Bond et al., 1999.

It was shown above that the applied methods of correcting for optical effects of non-absorbing particles gave a different weighting to the errors involved in optical filter-based determinations of soot. The largest errors were attributed to the most simplified protocol applied, in which not only the correction of the light scattering was assumed independent on changes in aerosol composition and amount but also tuned to generate positive soot levels.

4 Conclusions

By monitoring the change in transmitted light, at a wavelength of about 550 nm, through a filter loaded with aerosol particles, estimates of the light absorption of soot are possible. In spite of several well-established approaches on filter-based optical measure-

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ments of soot the reported data suffer however from systematic errors that could lead to an overestimation of the recorded light absorption of soot. The errors are dominated by the dependence of aerosol light scattering on the chemical composition of non-absorbing particles, such as inorganic salts and mineral dust, in the sample.

5   This study establishes protocols for correction of light scattering provided by the chemical quantification of the non-absorbing material collected on the filter and measured back-scattered light. A newly designed soot photometer instrument was constructed to measure light transmission, at 528 nm, and features an additional sensor recording the backscattered light at 40° relative to the incoming light in front of the fil-

10 ter. The choice of PCMB filters instead of the otherwise so commonly used glass fiber filters was not only advantageous in avoiding high chemical blank values but also to reduce errors associated with length of the light path through the filter since the particles are deposit on the filter surface and not embedded in the filter texture.

The two protocols of corrections were applied to ambient aerosol samples collected

15 at the Maldives Climate Observatory Hanimaadhoo during episodes with either continental influenced air from the Indian/Arabian subcontinents representative for the winter season or pristine air from the Southern Indian Ocean during the summer monsoon.

The optical correction lowered the determined light absorption of soot with 61% for the samples collected within the "Arabian Sea" group and with 63% for the "South

20 Indian Ocean" group. Corresponding values for the chemical correction were 69% and 97%. This result indicates that the optical correction is less sensitive to the amount of non-absorbing particle matter deposit on the filter. In a comparison with other studies in the area resulting in an overestimation of the σ_{ap}, by up to two orders of magnitude, when data were corrected with the most simplified protocol applied, in which the light

25 scattering was assumed independent of changes in aerosol composition and amount. Therefore, this study emphasis the need to reduce errors dominated by optical effects of non-absorbing particles in filter-based measurements of soot by applying protocols on the dependence of aerosol chemical composition.

Despite the soot-related uncertainties referred to in this study trends in atmospheric

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Interactive Discussion

soot burdens due to the increased use of soot-producing combustion sources have led to a rapidly increasing number of model simulations, which ascribe strong climate forcing to the black material in soot (Jacobson, 2000). In some of these studies the modeled positive forcing becomes comparable to those of carbon dioxide (Jacobson, 2005), from which the authors concluded that a reduction of soot emissions might be immediately more efficient and cost-effective than concentrating abatement strategies on greenhouse gases. Thus the necessity for chemical correction protocols raised here, before even the sign on the radiative forcing by dark soot particles can be assessed, will certainly be controversial. What is required is not automatic rejection but careful future consideration.

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Fig. 1. The location of the ABC station MCOH in the Maldives (longitude 73° E 10′59″, latitude 6° N 46′34″.

Light source

Detector

I_1

I_2

$I_{40;1}$
$I_{40;2}$

Soot

Filter

Diffusor

Detector
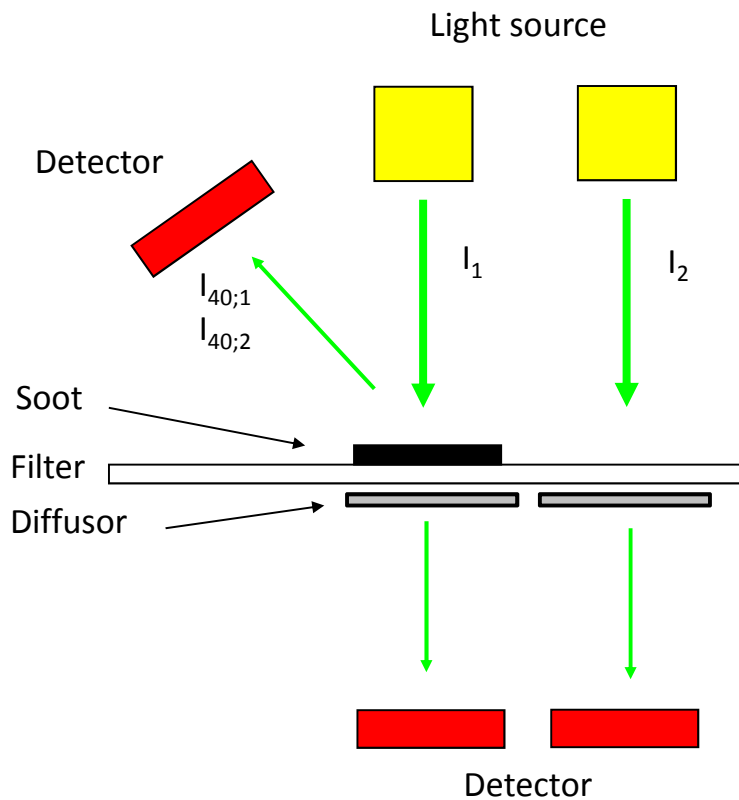
Fig. 2. The principle of the soot photometer instrument.

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Fig. 3. Trajectory cluster for the data selection "Arabian Sea".
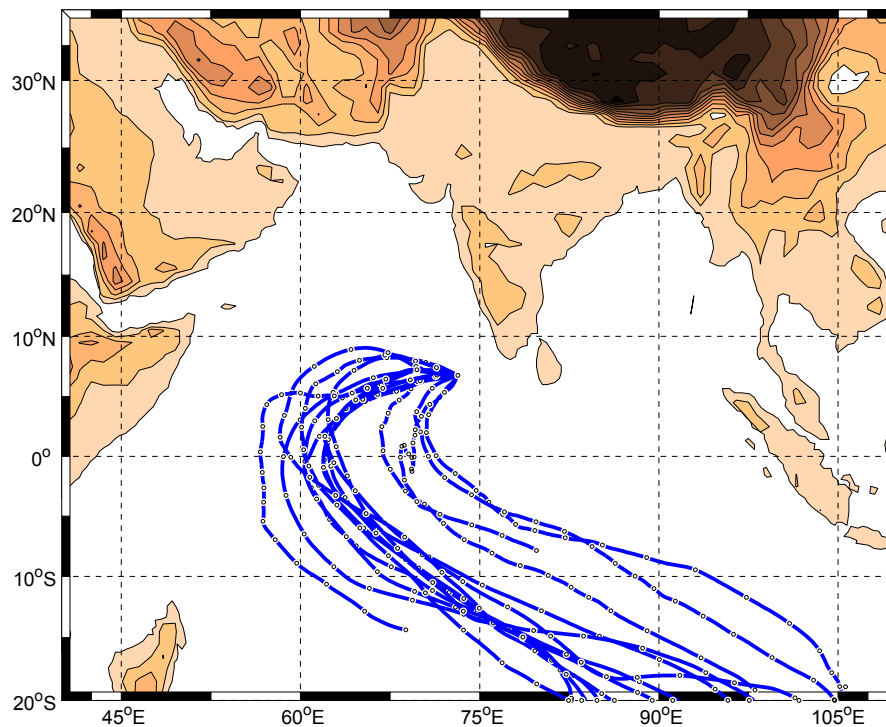
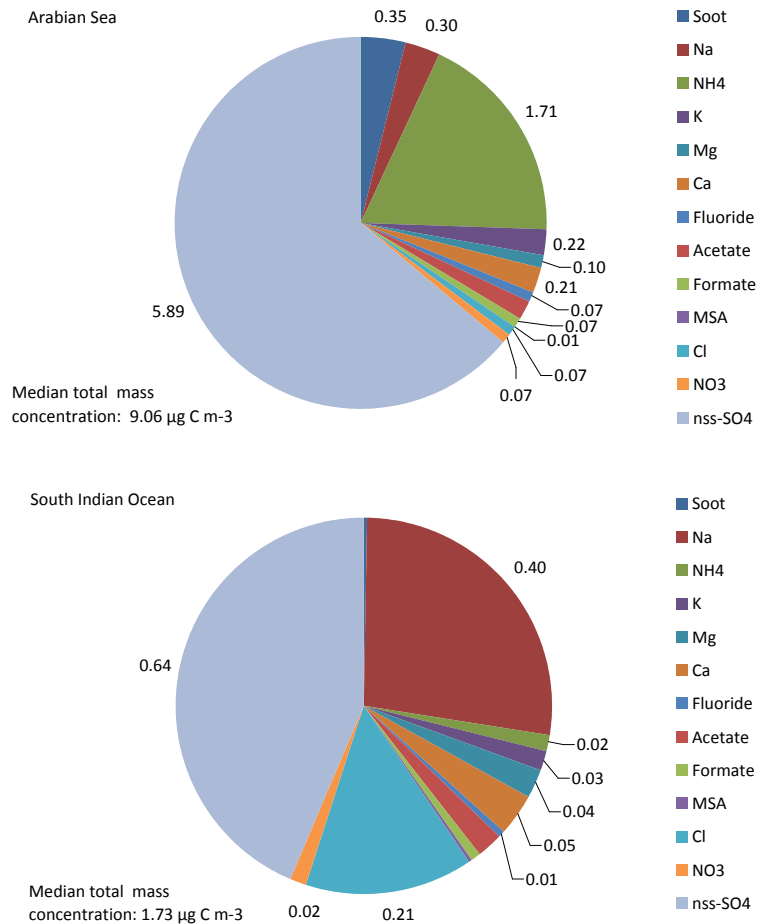**Fig. 4.** Trajectory cluster for the data selection "South Indian Ocean".

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Fig. 5. Median aerosol composition and the sum of median total ion mass and median soot mass (derived using the chemical correction) for the two data selections. Units are given in $\mu g\,C\,m^{-3}$.
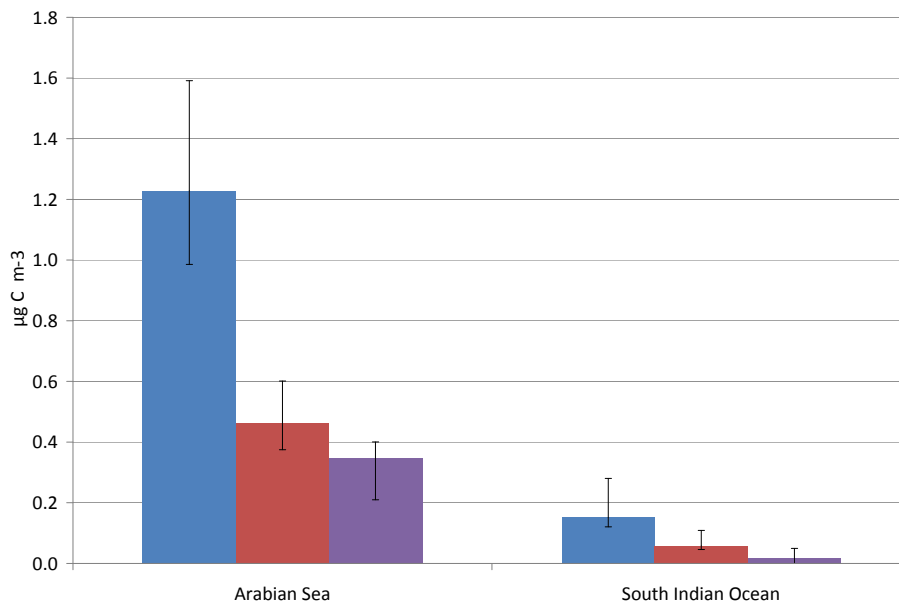
Fig. 6. Uncorrected absorption coefficient values (blue), compared with two different methods of correction (optical correction=red and chemical correction=purple) implemented on the uncorrected values for the two data selections. Bars indicate 75 and 25 percentiles.

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Table 1. Samples collected at MCOH during the two data selections. Data shown are uncorrected absorption coefficient (σ_{ap}) values and soot mass concentrations, data corrected with the optical protocol and data corrected with the chemical protocol. Also shown are scattering coefficient (σ_{sp}) values calculated using measured ion mass and a mass scattering efficiency of $3.8\,\mathrm{m^2\,g^{-1}}$. Units for ($\sigma_{ap}$) and ($\sigma_{sp}$) are in $\mathrm{Mm^{-1}}$ and for soot mass concentration in $\mathrm{\mu g\,m^{-3}}$.

	Soot uncorrected σ_{ap}	Soot optical corrected σ_{ap}	Soot chemical corrected σ_{ap}	σ_{sp} from total ion mass	Soot uncorrected	Soot optical corrected	Soot chemical corrected
Arabian Sea			18 Mars 2007 to 3 May 2007				
No. of samples: 40							
Average	12	4.6	3.5	36	1.2	0.46	0.35
50th percentile (median)	11	4.2	3.5	33	1.1	0.42	0.35
75th percentile	15	5.6	4.0	47	1.5	0.56	0.40
25th percentile	8.8	3.3	2.1	28	0.88	0.33	0.21
South Indian Ocean			1 June 2007 to 23 September 2007				
No. of samples: 15							
Average	1.5	0.58	0.17	6.8	0.15	0.058	0.017
50th percentile (median)	1.0	0.38	0.026	6.8	0.10	0.038	0.0026
75th percentile	2.3	0.88	0.36	7.8	0.23	0.088	0.036
25th percentile	0.67	0.26	−0.20	4.4	0.067	0.026	−0.020

Table 2. Samples collected at MCOH during the two data selections. Data shown are ion mass concentrations and the sum of ion mass and soot mass derived using the chemical correction protocol. Units are $\mu g m^{-3}$.

	SO_4^{2-}	nss-SO_4^{2-}	NH_4^+	Na^+	K^+	Ca^{2+}	Total ion and soot mass
Arabian Sea	18 Mars 2007 to 3 May 2007						
No. of samples: 40							
Average	6.5	6.5	1.7	0.42	0.26	0.23	15
50th percentile (median)	5.9	5.9	1.7	0.30	0.22	0.21	9.1
75th percentile	8.5	8.4	2.1	0.49	0.38	0.30	13
25th percentile	4.8	4.8	1.2	0.23	0.16	0.11	7.2
South Indian Ocean	1 June 2007 to 23 September 2007						
No. of samples: 15							
Average	0.84	0.81	0.061	0.43	0.040	0.055	2.1
50th percentile (median)	0.67	0.64	0.018	0.40	0.028	0.051	1.7
75th percentile	0.98	0.96	0.063	0.49	0.041	0.056	2.0
25th percentile	0.56	0.54	0.016	0.27	0.020	0.043	1.2

Table 3. Samples collected at MCOH during the two data selections. SSA is the single scattering albedo calculated from the estimated backscattering of light, due to the analyzed inorganic mass, relative to the measured light absorption. The average of median values is calculated using the median values from the optical and chemical corrected soot concentrations. Soot average values are in µgCm^{-3}, all other values are dimensionless ratios.

	SSA	Soot/Total mass	Soot Average of median mass	Optical correction effect	Chemical correction effect
Arabian Sea			18 Mars 2007 to 3 May 2007		
No. of samples: 15					
Average	0.73	0.026	0.40	0.62	0.72
50th percentile (median)	0.73	0.041	0.38	0.63	0.69
75th percentile	0.77				
25th percentile	0.71				
South Indian Ocean			1 June 2007 to 23 September 2007		
No. of samples: 15					
Average	0.86	0.017	0.037	0.62	0.89
50th percentile (median)	0.87	0.012	0.0020	0.61	0.97
75th percentile	0.91				
25th percentile	0.83				
Average of median values	0.79	0.021	0.22	0.62	0.80

Table 4. Absorption coefficient values in air measured with optical techniques in the Indian Ocean region. Soot mass concentrations were derived using a mass absorption cross section of $10\,m^2\,g^{-1}$.

Study	Summer monsoon Mm^{-1}	Winter season Mm^{-1}	Summer monsoon $\mu g\,m^{-3}$	Winter season $\mu g\,m^{-3}$
Engström and Leck (2009)	0.02–0.38	3.5–4.2	0.002–0.038	0.35–0.42
Corrigan et al. (2006)	0.87±0.56	11.7±4.6	0.087±0.056	1.17±0.46
Quinn et al. (2002)	<LOD(0.34)	1.0–5.0	<LOD(0.034)	0.1–0.5