Enhanced Light-Absorption of Black Carbon in Rainwater Compared With Aerosols Over the Northern Indian Ocean

Krishnakant Budhavant1,2,3, August Andersson1, Henry Holmstrand1, Poonam Bikkina1,4, Srinivas Bikkina1, S. K. Satheesh3, and Örjan Gustafsson1

1Department of Environment Science and Analytical Chemistry (ACES), and the Bolin Centre for Climate Research, Stockholm University, Stockholm, Sweden, 2Maldives Climate Observatory at Hanimaadhoo, Hanimaadhoo, Maldives, 3Centre for Atmospheric and Oceanic Sciences and Divecha Centre for Climate Change, Indian Institute of Sciences (IISc), Bangalore, India, 4CSIR-National Institute of Oceanography, Visakhapatnam, India

Abstract Black carbon (BC) aerosols affect climate, especially in high aerosol loading regions such as South Asia. A key uncertainty for the climate effects of BC is the evolution of light-absorbing properties in the atmosphere. Here, we present a year-round comparison of the mass absorption cross section (MAC; 678 nm) of BC in air (PM10) and rain, for samples collected at the Maldives Climate Observatory at Hanimaadhoo. We develop a filter-loading correction scheme for estimating BC absorption on filters used in high-volume samplers. The year-round average MAC678 of BC in the rain is almost twice (13.3 ± 4.2 m2/g) compared to the PM10 aerosol (7.2 ± 2.6 m2/g). A possible explanation is the elevated ratio of organic carbon (OC) to BC observed in rain particulate matter (9.4 ± 6.3) compared to in the aerosols (OC/BC 2.6 ± 1.4 and water-insoluble organic carbon/BC 1.2 ± 0.8), indicating a coating-enhancement effect. In addition to BC, we also investigated the MAC365 of water-soluble brown carbon in PM10 (0.4 ± 0.4 m2/g, at 365 nm). In contrast to BC, MAC365brown carbon relates to air mass history, showing higher values for samples from air originating over the South Asian landmass. Furthermore, calculated washout ratios are much lower for BC compared to OC and inorganic ions such as sulfate, implying a longer atmospheric lifetime for BC. The wet deposition flux for BC during the high loading winter was 3 times higher than during the wet summer, despite much less precipitation in the winter.

1. Introduction

Sunlight-absorbing black carbon (BC) and brown carbon (BrC) aerosols may significantly contribute to the warming of the atmosphere. BC stays in the atmosphere for a shorter time (~1–2 weeks) in comparison with the major anthropogenic greenhouse gases (e.g., CO2, CH4, and N2O). Hence, the impact of BC is closer to the emission regions and thus especially strong in emission hotspots such as South Asia. Besides contributing to a positive radiative forcing (global average estimates ~ 0.2 to 1.2 W/m2, with higher values over regions such as South Asia), these aerosols also have other environmental effects, for example, surface dimming (affecting agriculture fields), glacier melt (affecting fresh water supply), and shifts of the storm frequency and monsoon system (Menon et al., 2010; Ramanathan et al., 2008; Xu et al., 2018). Furthermore, BC is one of the more health-detrimental components of aerosol pollution that kills more than 1 million people in South Asia per year (World Health Organization, 2016). Taken together, BC aerosols thus cause severe perturbations of the regional environmental system.

BC is released in the atmosphere from incomplete combustion practices, for example, traffic, industry, crop residue burning, and domestic activities. BrC is also emitted from incomplete combustion but is also—in contrast to BC—formed through secondary reactions in the atmosphere. Multiple uncertainties challenge assessment of the climate and environmental impacts of these components: atmospheric lifetime, distribution in the atmosphere, emissions and secondary formation, and light-absorbing properties (e.g., Bond et al., 2013; Gustafsson & Ramanathan, 2016).

The atmospheric lifetime of BC is governed by both wet and dry depositions. However, since BC-containing aerosols are typically fine mode, wet deposition is the driving sink. The propensity for a BC-containing aerosol to act as a cloud condensation nucleus depends on the mixing state, along with meteorological parameters, such as humidity and temperature (Dalirian et al., 2018; Vu et al., 2019). Taken together, the lifetime is expected to vary significantly between different regions and conditions. Given this complexity, including...
 difficulties of estimating lifetimes from observations and models, the lifetime is overall poorly constrained (Cape et al., 2012; Samset et al., 2014).

In this work, we address the ambient light-absorbing properties—the mass-absorption cross section (MAC)—of BC and BrC, at Maldives Climate Observatory at Hanimaadhoo (MCOH), a remote South Asian receptor site over northern Indian Ocean. BC-MAC is often used as a model input and has a significant effect on model approximations of the radiative forcing of BC. We compare the BC-MAC in the aerosol phase with the BC-MAC in the rainfall particulate matter (PM). We also develop a filter loading correction scheme for estimating BC absorption in heavily loaded quartz filters, typically used with high-volume samplers (these filters are thicker than on, e.g., Aethalometers), thus requiring a different correction scheme (e.g., Arnott et al., 2005; Schmid et al., 2006). Finally, we calculate the washout ratios (WRs) and wet deposition fluxes for BC, water-insoluble organic carbon (WIOC), and inorganic ions as a rough measure of the efficiency of the rain scavenging process.

2. Material and Methods

2.1. Sampling Site

The MCOH (6.77° N, 73.18° E) is located on the northern tip of the Island Hanimaadhoo, on the Haa Dhalu atoll in the Maldives (Figure 1). Inaugurated in 2004, MCOH is well documented to serve its purpose as South Asian regional receptor site, with little local influence (e.g., Budhavant et al., 2018; Dasari et al., 2019; Gustafsson et al., 2009; Ramanathan et al., 2007). Aerosol filter (PM10) and rainwater samples were collected at the top of the observatory tower (height of 15 m). Instrumentation and methods used to study the properties of aerosols and rain at the MCOH and in the laboratory are listed in Table 1.

2.2. Collection of Rainwater and Aerosol Samples

Twenty-six rain samples (in duplicates) were collected with two wet-only collectors at MCOH. The first of the rainwater collectors had a borosilicate glass funnel with an open area of 314 cm² and a 2-L borosilicate glass storage bottle, a movable lid, and sensor to control and stop each sampling collection, which is used for the analysis of carbonaceous matter. The second rain water collector, with similar dimensions, was made of polyethylene material and was used for measuring inorganic ions (Budhavant et al., 2016; Granat et al., 2010). Fifty aerosol filters samples were collected using a high-volume sampler operating at a flow rate of 500 L/min (Model DH77, DIGITEL Elektronik AG). Approximately 1-week-long aerosol sample
collections were performed from May 2014 to April 2015. The sample handling and analysis of the carbonaceous aerosols followed the analytical protocols described in Budhavant et al. (2018).

2.3. Rain Filtration

After each sample collection, a portion of the rain water samples was immediately transferred into 100-ml bottles for chemical analysis; these bottles were prepared to contain 40-mg thymol, which helps to prevent biological degradation in the samples (Gillett & Ayers, 1991). The rainwater samples collected with a glass collector were transferred into a stainless-steel cylinder for pressure (4 bar) filtration. The filtration was performed within a few hours after samples collections to prevent biological growth in the samples. To remove large objects in the rain samples (e.g., insects, plant debris, and large-size particles), 8.0-μm pore size prefilter was placed above the quartz fiber filter (Millipore, 37-mm diameter, 0.3-μm pore size, effective collection area 0.52 cm²) in the filter holder. After filtration, the filter was transferred to a Petri-slide with the lid one-fourth open until the filter was dry. After that, the Petri-slide was closed and stored frozen until further analysis.

2.4. Chemical Analyses

The mass concentrations of BC (here quantified as elemental carbon [EC]) and organic carbon (OC) were determined with a carbon analyzer from Sunset Laboratory (Tigard, OR, USA) using the National Institute for Occupational Safety and Health 5040 method (Birch & Cary, 1996). A Shimadzu TOC VCPH analyzer was used to measured water-soluble OC (WSOC) (Kirillova et al., 2010, 2013). OC on the rainwater filters was measured directly as WIOC, as the WSOC portion is washed out during filtration (e.g., Granat et al., 2010). WIOC for the ambient PM10 was estimated by difference (WIOC = OC − WSOC), where OC was estimated by the Sunset instrument and the WSOC concentration was estimated directly through our, by now, well-established protocol (Kirillova et al., 2010).

Filtration and transferring of a rain sample of the bottle and Petri-slide has been done in a well-established laboratory setup at MCOH—methods blanks have been assessed and found not to influence the results (Granat et al., 2010). All reported OC (2.5 ± 1.2 μg/cm²), WSOC (0.16 ± 0.03 μg/cm²), and WIOC (2.32 ± 0.49 μg/cm²) values were average field blank (n = 8) subtracted. EC was not detected in the field blanks. Before the analysis of each sample batch, the instruments were calibrated in the range 5–50 μg with sucrose solutions for assessing the accuracy of total carbon and were found to be within 5%. The detection limits in rainwater for BC and WIOC were below 1 μg/L.

A portion of each aerosol filter was extracted with Mill-Q water and analyzed for water-soluble inorganic ionic species (Na⁺, K⁺, Ca²⁺, Mg²⁺, NH₄⁺, Cl⁻, SO₄²⁻, and NO₃⁻) using an Ion Chromatograph (Thermo Scientific, Dionex Aquion). The instrument was calibrated using commercially available standards (Merck, ~1,000 ppm). The quality assurance of the analytical data (within 5% for anions and 10% for cations) was ascertained by preparing standard stock solutions from analytical grade reagents and salts. Sea salt ratios were calculated using Na⁺ as the reference element (Keene et al., 1986), to investigate the effects of marine influence on the rain and aerosol composition.

| Table 1 | Instrumentation and Methods Used to Study the Properties of Aerosols and Rain at The Maldives Climate Observatory at Hanimaadhoo and the Laboratory Equipment at Stockholm University |
|---|---|---|
| Instrument | Manufacture and model | Parameter measured |
| High-volume sampler | DIGITEL Elektronik AG, DH-77 | Particulate matter (PM₁₀) |
| Wet-only rain samplers | Stockholm University, Sweden | Rain water |
| Weather station | Vaisala WXT | Temperature, RH, pressure, wind speed and direction, rain |
| Aethalometer | Magee Scientific, AE-31 | Absorption coefficient, 660 nm and 880 nm |
| Thermal-optical transmission analyzer* | Sunset Laboratory, USA | Elemental carbon, organic carbon, 678 nm |
| Total organic carbon analyzer* | Shimadzu, Japan | Water-soluble organic carbon, 365 nm |
| Ion chromatograph* | Thermo Scientific, Dionex Aquion | Na⁺, K⁺, Ca²⁺, Mg²⁺, NH₄⁺, Cl⁻, SO₄²⁻, and NO₃⁻ |
| UV absorption spectrophotometer* | Hitachi U2010 | light extinction of water extracts (190 to 1,100 nm) |

*At Stockholm University.
2.5. Determination of Mass Absorption Cross Section of BC

The laser beam of the Sunset Laboratory aerosol carbon analyzer at wavelength 678 nm was used to measure the light attenuation (ATN = −ln(I/I0)) of the aerosols on the filter, a method that has been shown to be in good agreement with aethalometer and particle soot absorption photometers (Sciare et al., 2003; Ram & Sarin, 2009). To compute the light absorption, we use a filter-loading correction function. Due to the high filter loadings and the thickness of high-volume quartz filters relative to filters used in, for example, particle soot absorption photometer and aethalometer instruments, we developed a filter correction for heavy loading cases using the assumption that the scattering in the filter may be described as a diffusive light process (supporting information Figures S1 and S2). The MAC (MACBC) of BC was thereby calculated as

\[
\text{MAC}_{\text{BC}} = \frac{\text{ATN}^2}{\text{BCloading} \times MS}.
\]

Here MS is a heuristic multiple scattering correction factor implemented in most filter loading correction schemes, ranging between ~2 and 6, depending on mixing/coating of the BC and filter type (e.g., Arnott et al., 2005; Schmid et al., 2006; Weingartner et al., 2003). In the present work, a factor of 3.8 was chosen to estimate the multiple scattering effects (Weingartner et al., 2003). The BCloading is the loading of BC on the filter in unit mass per surface area. We compared the absorption coefficient derived from the Sunset Carbon Analyzer (678 nm) with Aethalometer (AE-31, 660 and 880 nm) (Figure S3), showing fair agreements between the two instruments.

2.6. Absorption Measurements of WS-BrC

The light absorption of the water extracts was measured using a Hitachi U2010 UV-VIS spectrophotometer. The MAC for water-soluble BrC (WS-BrC) was calculated as

\[
\text{MAC}_{\text{WS-BrC}} = \frac{\text{b}_{\text{abs,365}}}{[\text{WSOC}]},
\]

where WSOC is the water-soluble OC concentration, b_{abs,365} is the absorption coefficient at 365 nm. The absorption Ångström exponent (AAE) was estimated as the slope in a linear regression of the logarithm of the b_{abs} versus the logarithm of the wavelength (\lambda):

\[
\ln[b_{\text{abs}}(\lambda)] = - \text{AAE} \cdot \ln[\lambda] + \text{intercept}.
\]

The AAE was fitted within the range 330–400 nm to avoid interference from other light-absorbing solutes, for example, nitrite ions (Bosch et al., 2014; Cheng et al., 2011; Jacobson, 1999).

2.7. WRs

The WR is a measure of the wet scavenging for, for example, carbon and inorganic aerosols. The WR of a target component is the ratio between its concentration in rainwater and its concentration in the surface air (Barrie, 1985; Seinfeld & Pandis, 1998).

\[
\text{WR} = \frac{C_{\text{rain}} \cdot \rho_{\text{air}}}{C_{\text{aerosol}} \cdot \rho_{\text{water}}}.
\]

Here, C_{\text{rain}} is the concentration in rainwater, \rho_{\text{air}} the density of air (~1.16 kg/m³ at 30 °C, 1 atm) and \rho_{\text{water}} the density of water (~1.0 kg/m³ at 30 °C, 1 atm), and C_{\text{aerosol}} the concentration in aerosols.

2.8. Air Mass Trajectory Analysis

Ten-day air mass back trajectories at an arrival height of 100 m were computed for every 6 hr and were examined using the NOAA Hybrid Single-Particle Lagrangian Trajectory model (Stein et al., 2015). These individual trajectories were then clustered into NE monsoon (red, mostly air masses come from South Asia) and SW monsoon (green, mostly Indian Ocean origin) periods using Hybrid Single-Particle Lagrangian Trajectory, to evaluate the seasonal trends in source regions for the sampling site in the North Indian Ocean (Figure 1). The trajectory analysis results are given in Figures S6–S8.
3. Results and Discussion

3.1. Meteorology

The climate of South Asia is governed by the monsoon system, the wet southwest monsoon (June to September) and the dry northeast monsoon (November to April), with premonsoon (May) and postmonsoon (October) transition periods. The southwest monsoon is characterized by heavy rainfalls, southerly winds, and with an elevated atmospheric boundary layer, whereas the winds shifts to more northerly during the northeast monsoon period (Budhavant et al., 2015; Corrigan et al., 2006; Krishnamurti et al., 1998). Air mass back-trajectory analysis shows two main air mass transport pathways during the dry monsoon: from either east or west of India (Figure 1). During the wet period, the air masses mainly come from the southern Indian Ocean.

3.2. Carbonaceous Aerosol Concentrations

The carbonaceous aerosol loadings were divided into three specific fractions: BC, WIOC, and WSOC (OC = WIOC + WSOC). At MCOH, the WSOC pool is characterized by extensive photochemical aging during long-range transport (Dasari et al., 2019; Kirillova et al., 2013). In contrast, carbon isotope characterization ($\delta^{13}C$ and $\Delta^{14}C$) suggests that WIOC at MCOH is less affected by atmospheric oxidation, with source signatures that are more similar to BC than WSOC (Bosch et al., 2014; Budhavant et al., 2015; Sheesley et al., 2012). Thus, the WIOC/BC ratio is a more conservative marker during long-range transport compared with the OC/BC ratio.

The average BC and WIOC concentrations in rainwater were nearly 1 order of magnitude higher during the NE monsoon compared with the SW monsoon (Table 2), which reflects the strong seasonality of the long-range transport of air pollutants from the major emission regions of the South Asian subcontinent to the northern Indian Ocean (Figure 2a). The annual correlations between BC and WIOC were $R^2 = 0.76$ ($p < 0.01$) in rainwater and $R^2 = 0.79$ ($p < 0.01$) for PM$_{10}$ samples, indicating similar emissions sources.

The average ratio of BC to WIOC in the rainwater was 11 ± 7%. This was approximately 4 to 5 times lower than that in the aerosols (51 ± 11%), which suggests that wet deposition was more efficient at removing WIOC from the atmosphere. The low contribution of BC to water-insoluble total carbon (WITC) likely reflects lower incorporation (in rain) of BC than of WIOC as well as a higher relative input of WIOC. Hence, these results seem to support the idea that BC particles may have a lower ability to act as cloud condensation nuclei compared to WIOC (Cerqueira et al., 2010). In reported studies (Table 3), the relative contribution of BC to WITC range from 2% at the Azores (Portugal) to 31% at Mace Head (Ireland); such differences may be explained by the diversity of emission sources of the carbonaceous matter affecting these study areas. Our result is consistent with low contributions of BC to WITC at remote sites in the marine boundary layer or within the free troposphere (Cerqueira et al., 2010; Huo et al., 2016), suggesting a higher relative input of WIOC at these sites compared with urban/continental locations.

WSOC is potentially a substantial yet highly variable portion of total carbonaceous aerosols (e.g., Dasari et al., 2019; Kirillova et al., 2013). Here, the WSOc in the rainwater samples were not estimated due to interference with thymol (the preservative). The yearly average concentrations of WSOC were 0.49 ± 0.46 μg/m$^3$ in PM$_{10}$ with roughly 4 times higher values during NE monsoon compared to the SE monsoon (Figure 3b), likely due to wet scavenging of aerosols during long-range transport and the presence of cleaner marine air masses during the SW monsoon period (Figures 1 and 3). The WSOc correlated with nss-K ($R^2 = 0.72$, $p < 0.01$), OC ($R^2 = 0.70$, $p < 0.01$), and BC ($R^2 = 0.67$, $p < 0.01$) also indicating an important impact of biomass combustion during the study period.

3.3. Water-Soluble Inorganic Ions

Water-soluble inorganic ions provide insights into aerosol sources and transformations and play a vital role in the rain and aerosol chemistry. We found a clear difference in the chemical composition of rainwater and aerosols between the continentally affected and marine background air masses at MCOH (Table 2). In rainwater, the ratio of average concentration in NE monsoon to that in SW monsoon was largest for nss-K$^+$ (a factor of 8), NH$_4^+$ (4), nss-SO$_4^{2-}$ (1.3), and NO$_3^-$ (1.2). While in aerosols, the ratio was largest for NH$_4^+$ (8), nss-K$^+$ (5), nss-SO$_4^{2-}$ (3), and NO$_3^-$ (2). These components likely have substantial anthropogenic sources located on the Indian subcontinent. On the other hand, the concentration of nss-Ca$^{2+}$ (1.5)
Table 2

| Mass Absorption Cross Section (MAC) and Concentrations of Black Carbon (BC) and Brown Carbon (BrC) (m²/g) in Both Rainwater and Dry Aerosols (PM₁₀) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Component | BC | BrC | WIOC | NO₃⁻ | NH₄⁺ | SO₄²⁻ | Ca²⁺ | nss-K⁺ | Mg²⁺ | Na⁺ | Cl⁻ | R² | p-value |
| Rainwater | 9.1 ± 7.5 | 4.5 ± 4 | 4.5 ± 4 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 |
| Aerosol | 14.9 ± 3.3 | 8.1 ± 6.9 | 8.1 ± 6.9 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 |
| SW Monsoon | 9.1 ± 7.5 | 4.5 ± 4 | 4.5 ± 4 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 | 0.5 ± 0.5 |
| Post-transition | 14.9 ± 3.3 | 8.1 ± 6.9 | 8.1 ± 6.9 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 |
| NE Monsoon | 8.3 ± 2.1 | 5.4 ± 1.3 | 5.4 ± 1.3 | 0.4 ± 0.4 | 0.4 ± 0.4 | 0.4 ± 0.4 | 0.4 ± 0.4 | 0.4 ± 0.4 | 0.4 ± 0.4 | 0.4 ± 0.4 | 0.4 ± 0.4 | 0.4 ± 0.4 | 0.4 ± 0.4 | 0.4 ± 0.4 |
| Pre-transition | 14.5 ± 4.5 | 7.9 ± 3.1 | 7.9 ± 3.1 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 | 0.8 ± 0.8 |

Note: The concentration of BC, water-insoluble organic carbon (WIOC), and water-soluble inorganic carbon (WSOC), and various ionic concentrations in rainwater (μmol L⁻¹) and air (mmol m⁻³) were measured in samples collected at the Maldives Climate Observatory-Hanimaadhoo for different seasonal periods during May 2014 to April 2015.

Correlation analysis of aerosol species may provide insights into emission sources (Tables S1 and S2). Here, BC correlates with nss-K⁺ (R² = 0.88, p < 0.01), WIOC (R² = 0.79, p < 0.01), and WSOC (R² = 0.67, p < 0.01) in aerosols indicating important contributions from biomass burning. The nss-K⁺ is a diagnostic proxy for identifying regional impact of biomass burning emissions (Andreae, 1993; Budhavant et al., 2018; Paris et al., 2010). As expected, Na⁺, Cl⁻, and Mg²⁺ were correlated (R² > 0.69, p < 0.01) among in rainwater and aerosols, indicating that these ions mainly come from sea spray. The main source of sea salt aerosol over the open ocean is sea spray droplets (Blanchard & Woodcock, 1980; Martensson et al., 2003).

3.4. WRs

The WRs were calculated (equation (4)) based on the rainwater and aerosol samples collected during the full year to assess differences in scavenging (atmospheric longevity) of different components (Figure 4). The WR reveals that wet scavenging is less efficient in removing BC from the atmosphere compared with WIOC, nss-SO₄²⁻, and nss-K⁺ throughout the year. These results are in line with the relative affinity of substances for the water phase. Fresh BC is generally hydrophilic and only becomes partly hydrophobic during transport (aging) by being coated with hygroscopic non-BC compounds (Croft et al., 2005; Li et al., 2018). Although WIOC is water insoluble, it is in general less hydrophobic than BC, while the potassium and sulfate ions are water soluble. A similar trend of higher scavenging of OC than of BC was also observed in other studies (Dasch & Cadle, 1989; Sonwani & Kulshrestha, 2019). Moteki et al. (2012) suggested that BC particles, which also had coating material, were more efficiently removed by this process which indicates they have been scavenged by nucleation. In our recent paper from this North Indian Ocean site, Budhavant et al. (2018) reported the comparison between the coarse (PM₁₀) and fine (PM₂.₅) aerosols (November 2014 to April 2015) from the filter samples at MCOH shows that Na⁺, Cl⁻, NO₃⁻, nss-Ca²⁺, and nss-Mg²⁺ are mainly found in coarse size aerosols and nss-SO₄²⁻, nss-K⁺, and EC in fine size aerosols. Coarse size particles have systematically higher WRs than those occurring in fine size aerosols (Figure 4). This is consistent with other reported studies from the station/region (Budhavant et al., 2010; Granat et al., 2010).

3.5. Wet Deposition Fluxes

Wet removal is the dominant sink mechanism for aerosols and an important component in model schemes seeking to simulate BC loading and BC lifetime in the atmosphere. The wet deposition fluxes of BC and WIOC were estimated by multiplying individual event concentrations by the event rain amount. Average deposition fluxes for BC of 135 and WIOC of 1,100 μg/m²/day were thus obtained at MCOH from May 2014 to April 2015. The range of BC deposition fluxes was from 25 to 360 μg/m²/day (Figure 5). These wet depositions were 3 times higher during the NE monsoon than during SW monsoon. The seasonality in this BC wet deposition flux probably largely reflects the much stronger anthropogenic emissions during the winter, outweighing the lower overall precipitation. The observed relative trends in BC and OC deposition fluxes are consistent with previous measurements (Custodio et al., 2014), who reported similar kind of results from the Central North Atlantic Ocean where BC fluxes (BC = 47 ± 108 μg/m²/day) were 8 times lower than WIOC fluxes. A modeling study (Jurado et al., 2008) provided estimates for BC (180 μg/m²/day) and for OC (700 μg/m²/day) fluxes based on satellite and ground-based measurements, estimated for a latitude band extending from 0° N to 30° N. The magnitude of these values is comparable to that of the measurements performed at MCOH for northern Indian Ocean, despite the uncertainty associated with model predictions of wet deposition fluxes.

3.6. MAC

Estimations of the MAC of BC and differences between BC in cloud droplets (and rain) and ambient aerosols impact climate modeling. This study documents large differences in BC-
MAC between aerosols and rainwater, with some seasonal variations for both phases (Figure 2b and Table 2). The average BC MAC$_{678}$ was $14.5 \pm 4.5$ m$^2$/g in rainwater and $8.3 \pm 2.1$ m$^2$/g in aerosols during NE monsoon. The average BC MAC$_{678}$ was $12.5 \pm 4.6$ m$^2$/g in rainwater and $6.5 \pm 2.5$ m$^2$/g in aerosols during SW monsoon. The seasonal variations may due to varying contributions of non-BC particles to light absorption and/or due to different air mass origins. The OC aerosol have been recognized to contribute some to the light absorption coefficient (Andreae & Gelencsér, 2006).

The year-round average BC MAC$_{678}$ in rainwater ($13.3 \pm 4.2$ m$^2$/g) was almost double that simultaneously measured in aerosols ($7.2 \pm 2.6$ m$^2$/g). Using an unpaired double-sided heteroscedastic $T$ test, we find that the difference is significant, with $p < 0.01$. The higher WIOC/BC ratios in rainwater compared with aerosols may be a key factor controlling the differences in MAC$_{678}$ of BC (Figure 2c). In particular, during the 15 February 2015 to 15 April 2015 period, the MACs are largely overlapping. As mentioned, this overlap is not consistent with the explanation that the WIOC/BC is the overall cause for the elevated MAC in rain.

| Sampling site       | Site type  | BC ($\mu$g L$^{-1}$) | WIOC ($\mu$g L$^{-1}$) | WIOC/BC | References                  |
|---------------------|------------|----------------------|------------------------|---------|-----------------------------|
| MCOH, Maldives      | Marine     | 9                    | 87                     | 9.7     | Present study               |
| Mace Head, Ireland  | Marine     | 31                   | 69                     | 2.2     | Ducret and Cachier (1992)   |
| Azores, Portugal    | Marine     | 2.8                  | 113                    | 40      | Cerqueira et al. (2010)     |
| Niigata, Japan      | Rural      | 25                   | 274                    | 11      | Huo et al. (2016)           |
| Tokyo, Japan        | Urban      | 79                   | 657                    | 8.3     | Huo et al. (2016)           |
| Sado, Japan         | Remote     | 26                   | 274                    | 11      | Huo et al. (2016)           |
| Paris, France       | Urban      | 330                  | 871                    | 2.6     | Ducret and Cachier (1992)   |
| Sonnblick, Austria  | Mountain   | 5.2                  | 145                    | 28      | Cerqueira et al. (2010)     |

Figure 2. Comparison of concentrations and optical properties of dry aerosols (PM$_{10}$) and rainwater with a focus on black carbon (BC) for Maldives Climate Observatory-Hanimaadhoo from April 2014 to April 2015. (a) Black carbon (BC) concentrations in the suspended aerosol (PM, particulate matter) and in the rain (RP, rain particle), (b) BC mass absorption cross section (MAC) in the aerosol and in rainwater, and (c) water-insoluble organic carbon (WIOC)/BC ratios in aerosols and rainwater. The vertically shaded bars indicate rough transition periods between the two seasons, and the horizontal bars represent aerosol sampling duration.
In contrast, for the period 15 May 2014 to 1 July 2014, the WIOC/BC ratios for rain and PM$_{10}$ are roughly equal, while the MACs are different. Clearly, although the WIOC/BC-ratio appears to be linked to the observed differences in MAC between rain and PM$_{10}$, it is not the only determinant for the differences in MAC between rain and PM$_{10}$. We can only speculate on other factors, such as that the WIOC and BC have different optical properties during the different seasons, such as originating from different sources and atmospheric processing.

Figure 3. Comparison of concentrations and optical properties in dry aerosols (PM$_{10}$) and in rainwater with a focus on organic (carbon) aerosols for Maldives Climate Observatory-Hanimaadhoo from April 2014 to April 2015. (a) Water insoluble organic carbon (WIOC) concentration in PM$_{10}$ aerosol (PM, particulate mass) and in rain (RP, rain particle), (b) water-soluble organic carbon (WSOC) concentration and absorption coefficient at 365 nm ($b'_{abs,365}$) in PM aerosol, and (c) mass-absorption cross section of WS-BrC at 365 nm (MAC$_{WSBrC,365}$) and Absorption Ångström Exponent (AAE) for 330–400 nm in PM. The vertically shaded bars indicate rough transition periods between the two seasons, and the horizontal bars represent aerosol sampling duration.

In contrast, for the period 15 May 2014 to 1 July 2014, the WIOC/BC ratios for rain and PM$_{10}$ are roughly equal, while the MACs are different. Clearly, although the WIOC/BC-ratio appears to be linked to the observed differences in MAC between rain and PM$_{10}$, it is not the only determinant for the differences in MAC between rain and PM$_{10}$. We can only speculate on other factors, such as that the WIOC and BC have different optical properties during the different seasons, such as originating from different sources and atmospheric processing.

Figure 4. Washout ratios measured for various ionic components, black carbon (BC) and water-insoluble organic carbon (WIOC) in different periods at Maldives Climate Observatory at Hanimaadhoo from May 2014 to April 2015. Vertical lines (black color) represent the standard deviation. Note the different scale for the carbonaceous components.
The significant differences in MAC-BC in rain versus aerosols may be related to morphological factors. For example, if the BC were in highly fractal shapes, then it is expected that there would be no or only small shifts in BC MAC between rain and dry aerosols (Gao et al., 2008). This extreme is however unlikely, as BC tends to collapse from a fractal to a denser morphology with increasing age and processing (Bai et al., 2018; Fuller et al., 1999; Gustafsson & Ramanathan, 2016; Peng et al., 2016; Slowik et al., 2007). BC in the atmosphere may become further coated with various nonabsorbing compounds (e.g., sulfate, organic molecules, and water). Such coatings may lead to enhanced absorption up to a factor 2 compared to freshly emitted particles (Bai et al., 2018; Bond et al., 2006; Cheng et al., 2011; Cui et al., 2016; Gustafsson & Ramanathan, 2016; Knox et al., 2009; Peng et al., 2016). The MAC reported here for PM$_{10}$ is similar to the values observed for freshly emitted BC, suggesting little enhancement from coatings. The OC/BC ratios at MCOH are generally lower (~2) than what often is observed closer to sources in South Asia (~5–10) (Budhavant et al., 2018; Sheesley et al., 2012). There is thus a loss of OC during long-range transport. One reason for this may be the higher WR for OC in general. Another reason is that the OC tends to become oxidized during transport (Dasari et al., 2019). The fresh BC-like MAC observed in ambient aerosols may therefore reflect the loss of coatings during long-range transport.

The light absorption of aerosols is also influenced by other absorbing components like BrC and mineral dust (Andreae & Gelencsér, 2006; Bahadur et al., 2012; Bond et al., 2006; Samset et al., 2018). In this work, the MAC$_{365}$ of WS-BrC in aerosols was $0.4 \pm 0.4$ m$^2$/g (Figure 3c), with higher values in NW monsoon (0.6 to 0.5) and lower during SE monsoon (0.2 to 0.1 m$^2$/g). Similar MAC$_{365}$ values ($0.5 \pm 0.2$ m$^2$/g) was reported from MCOH during the Cloud-Aerosol Radiative Forcing Dynamic Experiment (2012) (Bosch et al., 2014) and the South Asian Pollution Experiment (2016) (Dasari et al., 2019). The AAE calculated by equation (3) showed seasonal variation with higher values in SW monsoon ($8.8 \pm 5.7$) and lower during NE monsoon ($6.8 \pm 1.1$) (Figure 3c). Similar AAE values for WS-BrC have been reported from the region, Delhi 5.1 ± 2.0 (Kirillova et al., 2014), IGP 6.0 ± 1.1 (Bikkina & Sarin, 2014), and for the NE monsoon at MCOH (Bosch et al., 2014).
4. Conclusions

In this study, year-round BC MAC$_{678}$ in both rainwater and aerosols were studied simultaneously in South Asia. The year-round average MAC$_{678}$ of BC in rainwater was almost twice that simultaneously measured for aerosols. This might be due to a higher WIOC to BC ratio in the filtered rain particles than in the aerosol particles (PM$_{10}$). The MAC$_{678}$ for BC particles in the dry aerosol phase is nearly constant (and close to the value of fresh BC MAC) throughout the year and regardless of air mass origin. MAC$_{678}$ for BC during the SW Monsoon fluctuates more relative to NE monsoon, but this is likely due to low BC concentrations (and therefore higher noise in retrieving MAC BC). This appears to indicate that BC particles in the aerosol are not coated to the extent that the MAC is enhanced. For the MAC$_{365}$ of BrC, we observed a clear trend with air mass history, with higher values for samples with air originating over the South Asian landmass. The study shows that BC may be more efficient in absorbing light when in cloud droplets. Furthermore, the atmospheric longevity of BC in the South Asian outflow may be much longer than for other components such as for BrC and sulfate. Taken together, the different light absorption properties of BC is quite different in dry aerosol versus in rain (and presumably therefore also in clouds)—this may have repercussion on the accuracy of current estimates of aerosol radiative forcing for South Asia and the northern Indian Ocean.

Acknowledgments

The authors are thankful to the Maldives Meteorological services (MMS) and the Government of the Republic of the Maldives for their support of MCOH. The MCOH technicians Miss Mariyam and Mr. Sharafulla Thoha assisted in this work. We acknowledge the financial support for this work from the Swedish Energy Agency (STEM, 2015-002538), the Swedish funding agency FORMAS (Grant 942-2015-1061), and the Swedish Research Council (VR Grants 2015-03279 and 2017-01601). The author (K. B.) is grateful for additional funding support from the Vinnova Programme (VINNMER Marie Curie, 2016-04078). The presented data are available at the Stockholm University Bolin Centre database (https://doi.org/10.17043/budhavant-2019).

References

Andreae, M. O. (1983). Soot carbon and excess fine potassium: Longrange transport of combustion-derived aerosols. Science, 220(4602), 1148–1151. https://doi.org/10.1126/science.220.4602.1148

Andreae, M. O., & Gelencser, A. (2006). Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols. Atmospheric Chemistry and Physics, 6(10), 3131–3148. https://doi.org/10.5194/acp-6-3131-2006

Arnott, W. P., Hamasha, K., Moosmüller, H., Sheridan, P. J., & Ogren, J. A. (2005). Towards aerosol light-absorption measurements with a 7-wavelength aethalometer: Evaluation with a photoacoustic instrument and 3-wavelength nephelometer. Aerosol Science and Technology, 39(1), 17–29. https://doi.org/10.1080/027868295091972

Bahadur, R., Praveen, P. S., Xu, Y., & Ramanathan, V. (2012). Solar absorption by elemental and brown carbon determined from spectral observations. Proceedings of the National Academy of Sciences U.S.A., 109, 17,366–17,371. https://doi.org/10.1073/pnas.1205910109

Bai, Z., Cui, X., Wang, X., Xie, H., & Chen, B. (2018). Science of the total environment light absorption of black carbon is doubled at Mt. Tai and typical urban area in North China. Science of the Total Environment, 635, 1144–1151. https://doi.org/10.1016/j.scitotenv.2018.04.244

Barrie, L. A. (1985). Features of the atmospheric cycle of aerosol trace elements and sulfur dioxide revealed by baseline observations in Canada. Journal of Atmospheric Chemistry, 1(1), 139–152. https://doi.org/10.1007/bf00049373

Bikkina, S., & Sarin, M. M. (2014). PM$_{2.5}$, EC and OC in atmospheric outflow from the Indo-Gangetic Plain: Temporal variability and aerosol organic carbon-to-organic mass conversion factor. Science of the Total Environment, 487(1), 196–205. https://doi.org/10.1016/j.scitotenv.2014.09.002

Birch, M. E., & Cary, R. A. (1996). Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. Aerosol Science and Technology, 25(3), 221–241. https://doi.org/10.1080/02786869608965393

Blanchard, D. C., & Woodcock, A. H. (1980). The production, concentration, and vertical distribution of the sea-salt aerosol. Annals of the New York Academy of Sciences, 338(1), 330–347. https://doi.org/10.1111/j.1749-6630.1980.tb17130.x

Bond, T. C., Doherty, S. J., Fahey, D. W., Forster, P. M., Berntsen, T., DeAngelo, B. J., et al. (2013). Bounding the role of black carbon in the climate system: A scientific assessment. Journal of Geophysical Research: Atmospheres, 118, 5380–5552. https://doi.org/10.1002/jgrd.50171

Bond, T. C., Habib, G., & Bergstrom, R. W. (2006). Limitations in the enhancement of visible light absorption due to mixing state. Journal of Geophysical Research, 111(D20), 1–13. https://doi.org/10.1029/2006JD007315

Bosch, C., Andersson, A., Kirilova, E. N., Budhavant, K., Tiwari, S., Praveen, P. S., et al. (2014). Source-diagnostic dual-isotope composition and optical properties of water-soluble organic carbon and elemental carbon in the South Asian outflow intercepted over the Indian Ocean (pp. 743–759). Journal of Geophysical Research: Atmospheres. https://doi.org/10.1002/2014JD022127

Budhavant, K., Andersson, A., Bosch, C., Krusé, M., Kirilova, E. N., Sheesley, R. J., et al. (2015). Radiocarbon-based source apportionment of elemental carbon aerosols at two South Asian receptor observatories over a full annual cycle. Environmental Research Letters, 10(6), 064004. https://doi.org/10.1088/1748-9216/10/06/064004

Budhavant, K., Bikkina, S., Andersson, A., Asemi, E., Kesti, J., Zahid, H., et al. (2018). Anthropogenic fine aerosol dominates the wintertime regime over the northern Indian Ocean. Tellus Series B: Chemical and Physical Meteorology, 70(1), 1–15. https://doi.org/10.1080/16000889.2018.1464871

Budhavant, K. B., Rao, P. S. P., Safai, P. D., Gawhane, R. D., & Raju, M. P. (2010). Chemistry of rainwater and aerosols over Bay of Bengal during CTACZ program. Journal of Atmospheric Chemistry, 65, 171–183. https://doi.org/10.1007/s10874-011-9187-0

Budhavant, K. B., Rao, P. S. P., Safai, P. D., Leck, C., & Rodhe, H. (2016). Black carbon in cloud-water and rainwater during monsoon season at a high altitude station in India. Atmospheric Environment, 129, 256–264. https://doi.org/10.1016/j.atmosenv.2016.03.028

Cape, J. N., Coyle, M., & Dumitrean, P. (2012). The atmospheric lifetime of black carbon. Atmospheric Environment, 59, 256–263. https://doi.org/10.1016/j.atmosenv.2012.05.030

Cerqueira, M., Pio, C., Legrand, M., Puxbaum, H., Kasper-Giebl, A., Afonso, J., et al. (2010). Particulate carbon in precipitation at European background sites. Journal of Aerosol Science, 41(1), 51–61. https://doi.org/10.1016/j.jaerosci.2009.08.002

Cheng, Y., He, K.-B., Zheng, M., Duan, F.-K., Du, Z.-Y., Ma, Y.-L., et al. (2011). Mass absorption efficiency of elemental carbon and water-soluble organic carbon in Beijing, China. Atmospheric Chemistry and Physics, 11, 4971–510. https://doi.org/10.5194/acp-11-4971-2011
Ramanathan, V., Li, F., Ramana, M. V., Praveen, P. S., Kim, D., Corrigan, C. E., et al. (2007). Atmospheric brown clouds: Hemispherical and regional variations in long-range transport, absorption, and radiative forcing. *Journal of Geophysical Research, 112*(22), 1–26. https://doi.org/10.1029/2006JD007124

Samset, B. H., Myhre, G., Herber, A., Kondo, Y., Li, S., Moteki, N., et al. (2014). Modelled black carbon radiative forcing and atmospheric lifetime in AeroCom Phase II constrained by aircraft observations. *Atmospheric Chemistry and Physics, 14*(May), 12465–12477. https://doi.org/10.5194/acp-14-12465-2014

Samset, B. H., Stjern, C. W., Andrews, E., Kahn, R. A., Myhre, G., Schulz, M., & Schuster, G. L. (2018). Aerosol absorption: Progress towards global and regional constraints. *Current Climate Change Reports, 4*(2), 65–83. https://doi.org/10.1007/s40641-018-0091-4

Schmid, O., Artaxo, P., Arnott, W. P., Chand, D., Gatti, L. V., Frank, G. P., et al. (2006). Spectral light absorption by ambient aerosols influenced by biomass burning in the Amazon Basin. I: Comparison and field calibration of absorption measurement techniques. *Atmospheric Chemistry and Physics, 6*(11), 3443–3462. https://doi.org/10.5194/acp-6-3443-2006

Sciare, J., Cachier, H., Oikonomou, K., Ausset, P., Sarda-Estève, R., & Mihalopoulos, N. (2003). Characterization of carbonaceous aerosols during the MINOS campaign in Crete, July–August 2001: a multi-analytical approach. *Atmospheric Chemistry and Physics, 3*, 1743–1757. https://doi.org/10.5194/acp-3-1743-2003

Seinfeld, J. H., & Pandis, S. N. (1998). *Atmospheric chemistry and physics: From air pollution to climate change.* New York, USA: John Wiley & Sons, Inc.

Sheesley, R. J., Kirillova, E., Andersson, A., Krusa, M., Praveen, P. S., Budhavant, K., et al. (2012). Year-round radiocarbon-based source apportionment of carbonaceous aerosols at two background sites in South Asia. *Journal of Geophysical Research, 117*(10), 1–16. https://doi.org/10.1029/2011JD017161

Slowik, J. G., Cross, E. S., Han, J.-H., Davidovits, P., Onasch, T. B., Jayne, J. T., et al. (2007). An inter-comparison of instruments measuring black carbon content of soot particles. *Aerosol Science and Technology, 41*(3), 295–314. https://doi.org/10.1080/02786820701197078

Sonwani, S., & Kulshrestha, U. C. (2019). PM10 carbonaceous aerosols and their real-time wet scavenging during monsoon and non-monsoon seasons at Delhi, India. *Journal of Atmospheric Chemistry, 76*, 171–200. https://doi.org/10.1016/S0021-8502(03)00359-z

Stein, A. F., Draxler, R. R., Rolph, G. D., Stunder, B. J. B., & Cohen, M. D. (2015). NOAA's HYSPLIT Atmospheric Transport and Dispersion Modeling System. *Bulletin of the American Meteorological Society, 96*, 2059–2078. https://doi.org/10.1175/BAMS-D-14-00110.1

Vu, D., Gao, S., Berte, T., Kacarab, M., Yao, Q., Vafai, K., & Asa-Awukwa, A. (2019). External and internal cloud condensation nuclei (CCN) mixtures: Controlled laboratory studies of varying mixing states. *Atmospheric Measurement Techniques, 12*, 4277–4289. https://doi.org/10.5194/amt-12-4277-2019

Weingartner, E., Saathoff, H., Schnaiter, M., Streit, N., Bitnar, B., & Baltensperger, U. (2003). Absorption of light by soot particles: Determination of the absorption coefficient by means of aethalometers. *Journal of Aerosol Science, 34*(10), 1445–1463. https://doi.org/10.1016/S0021-8502(03)00359-8

World Health Organization (2016). Ambient air pollution: A global assessment of exposure and burden of disease, Tech. rep., WHO. https://www.who.int/phe/publications/air-pollution-global-assessment/en/

Xu, R., Tie, X., Li, G., Zhao, S., Cao, J., Feng, T., & Long, X. (2018). Effect of biomass burning on black carbon (BC) in South Asia and Tibetan Plateau: The analysis of WRF-Chem modeling. *Science of the Total Environment, 645*, 901–912. https://doi.org/10.1016/J.SCITOTENV.2018.07.165