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#### **Key Points:**

- Light absorption coefficient of BrC in the high Himalayas has a strong seasonal variability
- BrC absorbs on average 4 +/- 1% (WS-BrC) and 9 +/- 2% (MeS-BrC) of solar radiation compared to BC
- BrC light absorption properties in the high Himalayas are similar to those at low altitudes

Supporting Information: • Supporting Information S1

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# Light absorption properties of brown carbon in the high Himalayas

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Abstract The light-absorbing properties of water-soluble brown carbon (WS-BrC) and methanol-soluble brown carbon (MeS-BrC) were studied in PM<sub>10</sub> aerosols collected at the "Nepal Climate Observatory-Pyramid" (NCO-P) station (5079 m above sea level) during the period 2013-2014. The light absorption coefficients of WS-BrC and MeS-BrC were the highest during the premonsoon season and the lowest during monsoon. MeS-BrC absorbs about 2 times higher at 365 nm and about 3 times more at 550 nm compared to WS-BrC. The mass absorption cross section (MAC) of WS-BrC measured at 365 nm is similar to that observed previously at South Asian low-altitude sites. Fractional solar radiation absorption by BrC compared to BC considering the full solar spectrum showed that WS-BrC absorbs  $4 \pm 1\%$  and MeS-BrC absorbs  $9 \pm 2\%$  compared to BC at NCO-P. Such ratios become  $8 \pm 1\%$  (for WS-BrC respect to BC) and  $17 \pm 5\%$  (for MeS-BrC respect to BC) when accounting for correction factors proposed by previous studies to convert absorption coefficients in bulk solutions into light absorption by accumulation mode aerosol particles. These results confirm the importance of BrC in contributing to light-absorbing aerosols in this region of the world. However, the BrC absorption at 550 nm appears small compared to that of BC (1-5%, or 3-9% with conversion factors), and it is lower compared to global model estimates constrained by Aerosol Robotic Network observations. Finally, our study provides no clear evidence of a change in the fractional contribution of BrC with respect to BC to light absorption in the middle troposphere respect to the Indo-Gangetic plain boundary layer.

#### 1. Introduction

Atmospheric aerosols have significant influence on the radiative balance of the atmosphere, especially in the regions with high anthropogenic emissions like South Asia. In this region, particulate and gaseous pollutants in high concentrations form the so-called atmospheric brown clouds (ABC), 3 to 5 km thick haze layers that extend to the large area over India and the Indian Ocean [e.g., *Ramanathan et al.*, 2007a, 2007b; *Ramanathan and Carmichael*, 2008, and references therein]. These layers are characterized by anthropogenic aerosol optical depth (AOD) higher than 0.3, absorbing AOD higher than 0.03, and vertical extinction profiles with higher aerosol extinction below the planetary boundary layer (PBL, 2000–3000 m), which decreases with height [*Ramanathan et al.*, 2007b; *Ramanathan and Carmichael*, 2008; *Feng et al.*, 2016]. Recent studies report the transport of polluted air to the high Himalayas by upslope breezes [*Bonasoni et al.*, 2010; *Bonasoni et al.*, 2012; *Decesari et al.*, 2010; *Marinoni et al.*, 2010; *Reddy et al.*, 2015], where light-absorbing aerosols can contribute to the glaciers' retreat processes [*Ramanathan and Carmichael*, 2008]. The Himalayan glaciers represent a large area of seasonal and permanent snow cover, which determines the albedo of the mountains and provide the water supply that feeds large Asian river systems [e.g., *Yao et al.*, 2012]. Since the 1960s, a large amount of the glaciers has been retreating [e.g., *Kulkarni et al.*, 2011] and this process can lead to a water stress in densely populated northern India.

The dominant light-absorbing component of the aerosols is combustion-derived black carbon (BC), which absorbs solar light over a broad spectral range [e.g., *Bond et al.*, 2013]. Some components of organic carbon (OC) also absorb light but typically with more pronounced wavelength dependence—"brown carbon" (BrC) [*Bahadur et al.*, 2012; *Bond et al.*, 2013; *Chung et al.*, 2012b; *Laskin et al.*, 2015; *Sun et al.*, 2007]. It was estimated that BrC may account for 15–50% of light absorption in the atmosphere and in snow and ice [*Andreae and Ramanathan*, 2013]. The global top of the atmosphere climate forcing of BrC is positive (+0.04–0.11 W m<sup>-2</sup>), and it is even more substantial (above +0.25 W m<sup>-2</sup>) in South Asian region [*Feng et al.*, 2013]. Light-absorbing aerosols have the opposing effects of adding energy to the atmosphere and reducing it at the surface due to the dimming effect. Therefore, the atmospheric heating due to BC and BrC absorption

©2016. American Geophysical Union. All Rights Reserved. can be an important factor for the retreat of the Himalayan glaciers through melting. At the same time, the dimming decreases the land-sea contrast in surface temperature, which is the major monsoon driving force and thus weakens the monsoonal precipitation that feeds the Himalayan glaciers during summer [*Ramanathan and Carmichael*, 2008]. Compared to BC, a large fraction of BrC is soluble in water [e.g., *Hoffer et al.*, 2006]. Hence, it can be dissolved within cloud droplets forming homogeneous absorptive droplets that affect cloud albedo and cause heating and evaporation of clouds [*Andreae and Gelencser*, 2006; *Jacobson*, 2012]. Therefore, multiple climate effects of the light-absorbing aerosols need to be considered for the development of the climate models and estimation of the negative impact on the Himalayan environment.

The potential climate effects of BrC has recently been pointed out by a number of studies [e.g., Feng et al., 2013; Jo et al., 2015; Lin et al., 2014; Liu et al., 2015; Shamjad et al., 2015], but disentangling the BrC contribution to the direct radiative forcing from that of BC and dust particles is challenging. Besides the difference in the optical properties between BC and BrC, there is a fundamental distinction between the life cycle of the two classes of light-absorbing aerosols: BC is a purely primary component that is formed by combustion sources and is removed by wet and dry deposition. By contrast, BrC can share primary sources with BC and can also be formed by chemical reactions in the atmosphere [Hecobian et al., 2010; Laskin et al., 2015]. Therefore, contrary to BC, BrC can accumulate over time and increase its importance in respect to BC when traveling from near-source sites to remote locations [Alexander et al., 2008]. Analogously, the ratio between BrC and BC is expected to increase with altitude and above the PBL [Liu et al., 2014; Liu et al., 2015]. As the total aerosol light extinction depends on the vertical distribution of aerosol concentration and composition in the air column, the fact that most in situ observations are carried out at ground level at low altitudes may introduce a negative bias in the quantification of BrC radiative effects. In particular, such measurement bias is of major concern for the aerosol impact studies on high-altitude climates and ecosystems, because these locations are only marginally or intermittently affected by the transport of air masses rich of fresh pollutants, while being directly exposed to photochemically aged air rich of secondary components. This is the case of the Hindu Kush-Himalayan region, largely located above 4000–5000 m above sea level (asl) in the free troposphere, where atmospheric composition is greatly modified with respect to the low altitudes over the Indo-Gangetic Plain and the other anthropogenically affected regions of India and neighboring countries.

The very few investigations available in literature focused on the light-absorbing properties of water-soluble BrC (WS-BrC) aerosols over the Indo-Gangetic Plain (New Delhi, Kharagpur, Patiala), the Bay of Bengal, and the Indian Ocean show that near-surface WS-BrC accounts for 1–55% of the total direct solar absorbance relative to elemental carbon (EC), used as an operational mass-based definition of BC [*Bosch et al.*, 2014; *Kirillova et al.*, 2014a; *Srinivas and Sarin*, 2014; *Srinivas et al.*, 2016].

The light absorption of the aerosol in the Himalayas was previously assumed to derive purely from BC and dust particles and the presence of light-absorbing organic species has not been investigated yet. The objective of this study is the first year-round characterization of the light absorptive properties of waterand methanol-soluble BrC in the high Himalayas at the international research station "Nepal Climate Observatory-Pyramid" (NCO-P) at 5079 m asl, at the foothills of Mount Everest.

#### 2. Materials and Methods

#### 2.1. Sampling

Aerosol sampling was conducted at the Global Atmosphere Watch-World Meteorological Organization Global station Nepal Climate Observatory-Pyramid (NCO-P, Nepal, 27.95°N, 86.82°E) located in the high Khumbu Valley at 5079 m asl, at the foothills of Mount Everest (Figure 1). A full description of the station is provided by *Bonasoni et al.* [2008]. PM<sub>10</sub> aerosols were collected on precombusted at 800°C for 1 h 150 mm Ø quartz-fiber filters (Pallflex, Pall) using a custom-built high-volume sampler behind a DIGITEL PM<sub>10</sub> preseparator DPM10/30/00. The sample collection period was from July 2013 to November 2014. The aerosol sampling strategy was designed to discriminate between the afternoon valley breeze bringing polluted air masses to the observatory and the free tropospheric air during nighttime [*Bonasoni et al.*, 2010]. The sampling intervals were fixed from 14:00 to 18:00 (local time) for two consecutive days for daytime air masses impacted by upslope breezes and from 22:00 to 06:00 for two consecutive days for background/free troposphere air masses with a minimized impact of the upslope valley breeze [*Decesari* 



**Figure 1.** The Moderate Resolution Imaging Spectroradiometer (on NASA's Terra satellite) image acquired on 20 November 2015, with the location of NCO-P measurement site (27.95°N, 86.82°E). A clear accumulation of haze is visible along the Himalayan foothills.

et al., 2010]. Overall, 19 afternoon and 19 night samples were collected. Field blanks were collected before each afternoon sampling.

The filter samples were stored in aluminum foil envelopes in double Ziploc bags under refrigeration at the International Pyramid Laboratory. From NCO-P to Kathmandu and CNR laboratories the filters were shipped sealed with ice packs (5–10 days of travel). The blanks were shipped, stored, and processed in an identical manner as the samples.

#### 2.2. Analysis of the Aerosol Carbonaceous Fractions

Total carbon (TC) was analyzed using a Multi N/C 2100 elemental analyzer (Analytik Jena, Germany), equipped with a solid furnace module. The  $1.13 \text{ cm}^2$  filter subsamples were combusted at 950°C in 100% oxygen, and TC was determined as total evolved CO<sub>2</sub> by a nondispersive infrared detector. The instrumental detection limit was 0.2 µg of carbon (µgC) and the accuracy of the TC measurement was better than 5% for 1 µgC. The limit of detection (LOD) of TC analysis estimated as 2 times standard deviation of blanks was 0.27 µgC m<sup>3</sup> (afternoon) and 0.13 µgC m<sup>3</sup> (night), uncertainty estimated using Monte Carlo simulation (see section 2.5) ranged from 12% at 6.9 µgC m<sup>3</sup> to 76% at 0.14 µgC m<sup>3</sup>.

Water-soluble organic carbon (WSOC) and water-soluble inorganic carbon (WSIC) were extracted from filter subsamples in ultrapure Milli-Q water through 30 min sonication. The extracts were filtered using 0.45  $\mu$ m cutoff PTFE syringe filters (Minisart-SRP 10, Sartorius Stedim Biotech, Germany). The concentration of WSOC and WSIC was quantified in the filtered solutions using a high-temperature catalytic oxidation instrument TOC-5000A (Shimadzu, Japan). The samples were neither acidified nor purged, to avoid the loss of volatile organic compounds. The accuracy of the measurement ranged from 7% for 1 ppm of carbon solution to 3% for concentrations higher than 2 ppm of carbon. LOD was 0.14  $\mu$ gC m<sup>3</sup> (afternoon) and 0.07  $\mu$ gC m<sup>3</sup> (night), uncertainty estimated using Monte Carlo simulation ranged from 4% at 4.0  $\mu$ gC m<sup>3</sup> to 52% at 0.07  $\mu$ gC m<sup>3</sup>.

The aerosol light absorption and the equivalent BC (using the mass absorption efficiency of  $6.5 \text{ m}^2 \text{ g}^{-1}$ ) are measured through a Multi-Angle Absorption Photometer (MAAP 5012, Thermo Electron Corporation) in total suspended particles (TSPs). The detection limit of the instrument was 11 ngC m<sup>-3</sup> with an integration time of 30 min basis. For more details, see *Marinoni et al.* [2010]. The MAAP BC concentrations were then averaged over the PM<sub>10</sub> filter sampling times. For selected samples (nine polluted and four background) the concentrations of OC and elemental carbon (EC) were measured at the Department of Environmental Science and Analytical Chemistry of Stockholm University with a thermo-optical transmission analyzer (Sunset Laboratory, Tigard, OR) using the standard NIOSH5040 method [*Birch and Cary*, 1996]. LOD was

 $0.58 \ \mu\text{gCm}^3$  (afternoon) and  $0.30 \ \mu\text{gCm}^3$  (night) for OC and  $0.009 \ \mu\text{gCm}^3$  (afternoon) and  $0.005 \ \mu\text{gCm}^3$  (night) for EC; uncertainty estimated using Monte Carlo simulation was 12% for OC and 7% for EC. The average EC/BC ratios were  $0.49 \pm 0.07$  and  $0.55 \pm 0.17$  for polluted and background samples, correspondingly. These ratios were applied to estimate EC concentrations of the rest of the samples from equivalent BC values measured by MAAP. Finally, OC concentrations, if not measured, were obtained by subtracting EC from TC measured by a Multi N/C 2100 elemental analyzer. The estimated uncertainties for this method of EC estimation were 22% (afternoon) and 54% (night).

#### 2.3. Measurements of the Light-Absorbing Properties of Brown Carbon

Brown carbon (BrC) was extracted from the 1.13 cm<sup>2</sup> filter subsamples by 30 min sonication in 5 mL of methanol or by shaking for 1.5 h in 5 mL of ultrapure Milli-Q water. The extracts were filtered using 0.45  $\mu$ m cutoff PTFE syringe filters (Minisart-SRP 10, Sartorius Stedim Biotech, Germany).

For the measurements of light absorption, a TIDAS E UV/visible light spectrometer (VIS) spectrophotometer (J&M Analitik AG, Germany) was equipped with a 0.5 m path length liquid waveguide capillary cell (LWCC-3050, World Precision Instruments, Sarasota, FL) with an internal volume of 125  $\mu$ L via fiber optic cables (FO-600-SMA1M, World Precision Instruments, Sarasota, FL). The water extracts were injected into the LWCC using a LWCC Continuous Flow Injection System (World Precision Instruments, Sarasota, FL) operating at a constant flow of 1 mL min<sup>-1</sup>. The methanol extracts were injected manually using a Sample injector kit (World Precision Instruments, Sarasota, FL), which includes a Teflon perfluoroalkoxy tubing, shaped to facilitate its introduction and withdrawal from the sample vessels and an external syringe adapter attached to the liquid outflow connection. In this case, the methanol extract was introduced into the LWCC by a syringe using steady pressure to avoid generating air bubbles.

Before starting the operation, the system was cleaned with 0.5 *M* potassium hydroxide in 100% ethanol, 100% methanol, and ultrapure Milli-Q water subsequently. Further, the system was cleaned with 100% methanol and ultrapure Milli-Q water before and after the measurements until a stable signal was observed.

A TidasDAQ3 software was used for operating the spectrophotometer and acquiring the data of the measured spectra. It was found that the optimal integration time providing about 75% of the light intensity in the reference spectra is 700 ms for methanol and 550 ms for Milli-Q water. The measurements were performed in the 190–720 nm wavelength range. Time scan mode was used to obtain a set of spectra measured within a minute after the injection of the sample into the LWCC. At least three spectra were used for the calculation of the average absorption spectra for each extract. The absorption spectra were blank corrected.

The wavelength ( $\lambda$ ) dependence of the light absorption by water-soluble brown carbon (WS-BrC) and methanol-soluble brown carbon (MeS-BrC) was investigated using an absorption Ångström Exponent (AAE). AAE was determined as a slope of linear regression fit of log of  $A_{10}^{\text{solution}}$  ( $\lambda$ ), the base-10 absorbance measured by UV-VIS spectrophotometer, versus log of  $\lambda$ .

AAE within the ranges 330–500 nm and 470–660 nm to avoid interference from light-absorbing inorganic compounds at shorter wavelengths and to compare with satellite measurements at the longer wavelengths.

The mass absorption cross section (MAC) for water and methanol extracts was computed at 365 nm using the following equation:

$$MAC_{365} = \frac{\left(A_{10}^{\text{solution}}(365) - A_{10}^{\text{solution}}(700)\right) \cdot \ln(10)}{C_{(WS)OC} \cdot L}$$
(1)

where  $A_{10}^{\text{solution}}$  (365) and  $A_{10}^{\text{solution}}$  (700) are the measured base-10 absorbance at 365 nm (averaged between 360 and 370 nm) and 700 nm (averaged between 695 and 705 nm),  $C_{(WS)OC}$  is the concentration of WSOC in water solution or estimated amount of OC in the methanol solution; *L* is the light path length (0.5 m, for the currently used LWCC). Absorbance at 700 nm is used to correct for the baseline drift during the analysis. To estimate the amount of OC in the methanol solution, we assumed that methanol extracts almost all OC from the filter [*Chen and Bond*, 2010]. Uncertainties in MAC<sub>365</sub> for WS-BrC estimated using Monte Carlo simulation ranged from 6% (WSOC concentrations 4.0–4.1 µgC m<sup>3</sup>) to 115% (WSOC concentrations 0.1 µgC m<sup>3</sup>). For MeS-BrC uncertainties ranged from 7% (OC concentrations 6.3–6.5 µgC m<sup>3</sup>) to 44% (OC concentrations 0.3 µgC m<sup>3</sup>). MAC<sub>365</sub> values with high uncertainties (>150%) were excluded.

In order to convert the absorption of BrC in solution to the absorption coefficient of ambient aerosol BrC ( $b_{abs}$ ) at 365 and 550 nm wavelength equation (4) suggested in *Hecobian et al.* [2010] was applied:

$$b_{\rm abs}(365/550) = \left(A_{10}^{\rm solution}(365/550) - A_{10}^{\rm solution}(700)\right) \frac{V_{W/Me}}{V_a \cdot L} \ln(10)$$
(2)

where  $V_{W/Me}$  is the volume of water or methanol into which the filter was extracted,  $V_a$  is the volume of air sampled through the extracted subsample, L is the light path length. Limit of detection for  $b_{abs365}$  of WS-BrC was 0.04 Mm<sup>-1</sup> (afternoon) and 0.02 Mm<sup>-1</sup> (night) and for MeS-BrC it was 0.12 Mm<sup>-1</sup> (afternoon) and 0.06 Mm<sup>-1</sup> (night). The estimated uncertainties at 365 nm in afternoon samples were on average 12% and 9% for WS-BrC and MeS-BrC, correspondingly. For low concentrated night samples the average uncertainties for b<sub>abs365</sub> were 65% and 17% for WS-BrC and MeS-BrC, correspondingly. At 550 nm the values of  $b_{\rm abs550}$  were close to LOD and the average uncertainties were higher (195% for WS-BrC and 55% for MeS-BrC in afternoon samples and 251% for WS-BrC and 99% for MeS-BrC in night samples). In equation (2) it is assumed that BrC aerosol in the extracts and in the air has the same absorbing properties, which is not necessarily true according to a recent study by Liu et al. [2013] reporting that the BrC light absorption in ambient aerosol is higher than the light absorption in the extracts a factor of 2 for water extracts and a factor of 1.8 for methanol extracts. It is not proven yet that the correction factors derived by Liu et al. [2013] are applicable to the Himalayan environment, although correction factors greater than 1, which are expected when light-absorbing compounds are enriched in the accumulation mode, seem reasonable for NCO-P. In this study the results are shown for both corrected and uncorrected for better comparison with other studies that have applied or not applied such correction.

#### 2.4. Comparison of the Direct Solar Absorbance of Brown Carbon and Black Carbon

The BC absorption coefficient values continuously measured by a MAAP system were averaged over the sampling period of each PM<sub>10</sub> filter sample. The fraction of solar energy (*f*) absorbed by WS-BrC and MeS-BrC relative to BC at ground level was estimated using the approach similar to that of *Kirchstetter and Thatcher* [2012] and *Kirillova et al.* [2014a, 2014b]. According to this approach, the wavelength-dependent attenuation of the solar light of BrC is normalized to that of BC as

$$f = \frac{\int i(\lambda) \cdot \left\{ \frac{Io - I}{Io}(\lambda, BrC) \right\} d\lambda}{\int i(\lambda) \cdot \left\{ \frac{Io - I}{Io}(\lambda, BC) \right\} d\lambda}$$
(3)

The solar flux  $i(\lambda)$  is obtained from the clear-sky Air Mass 1 Global Horizontal solar irradiance spectrum at the Earth's surface [Levinson et al., 2010].

The light attenuation by aerosol species *X*, where *X* is WS-BrC, MeS-BrC, or BC, is estimated by the Lambert-Beer law with the wavelength dependence of the absorption coefficient described in the following equation:

$$\frac{lo-l}{lo}(\lambda,X) = 1 - e^{-\left(b_{absX}\left(\frac{\lambda a}{\lambda}\right)^{AAE_X}\cdot h\right)}$$
(4)

where  $b_{absX}$  is the absorption coefficient at a given wavelength ( $\lambda_{0,WS-BrC} = 365 \text{ nm}$ ,  $\lambda_{0,MeS-BrC} = 365 \text{ nm$ 

For the computations, we used an air column height of 3921 m (from the 5079 m asl where the NCO-P station is located to 9000 m asl). The hypothesis made for the GAME code for aerosol radiative forcing calculations in the high Himalayas described in *Marcq et al.* [2010] was applied for our simplified model. According to this hypothesis, the atmosphere between 5000 m asl and 9000 m asl is divided into several layers and the aerosol intensive properties within each layer are originally derived from surface measurements with different degrees of mixing with typical free tropospheric air (Figure S1 in the supporting information). Layer 1 (5000 m asl and 5500 m asl) is the polluted layer for which the optical aerosol properties are provided by the direct measurements at NCO-P (afternoon samples). Layers 2–5 (5500 m asl and 7500 m asl) are resulting from the mixing between the polluted layer and the layers above (10% of the mass of the particles from Layer

1 and 90% of the mass of the particles from the Layers 6–8). Layers 6–8 (7500 m asl and 9000 m asl) are the free tropospheric layers that have uniform aerosol optical properties provided by the direct measurements at NCO-P (night samples).

Accounting for this layered structure of the atmosphere, equation (5) is modified as follows:

$$\frac{lo-l}{lo}(\lambda, X) = 1 - e^{-(\text{Layer}(1) + \text{Layer}(2-5) + \text{Layer}(6-8))}$$
(5)

where Layer(1), Layer(2–5), and Layer(6–8) are the absorption contributions of atmospheric layers described by equations 6–8.

$$Layer(1) = b_{absX,afternoon} \left(\frac{\lambda 0}{\lambda}\right)^{AAE_{X,afternoon}} \cdot 421$$
(6)

$$Layer(2-5) = \left(0.1 \cdot b_{absX,afternoon} \left(\frac{\lambda 0}{\lambda}\right)^{AAE_{X,afternoon}} + 0.9 \cdot b_{absX,night} \left(\frac{\lambda 0}{\lambda}\right)^{AAE_{X,night}}\right) \cdot 2000$$
(7)

$$Layer(6-8) = b_{absX,night} \left(\frac{\lambda 0}{\lambda}\right)^{AAE_{X,night}} \cdot 1500$$
(8)

The values of  $b_{abs}$  and AAE measured in consecutive afternoon and night samples were applied for each calculation.

#### 2.5. Uncertainty Estimation

To properly account for the uncertainties of WSOC and TC concentrations,  $b_{abs365}$  values and the fraction of solar energy (*f*) absorbed by WS-BrC and MeS-BrC relative to BC, we applied an error propagation scheme based on a Monte Carlo strategy as described previously [*Kirillova et al.*, 2013, 2014a, 2014b]. Different sources of uncertainties were considered, including the precision of the concentration measurements and the mass contributions from field blanks. In this procedure, the uncertainty for each parameter (e.g., field blank concentration) was represented by a normal distribution with zero mean value and a standard deviation equal to the measured uncertainty. Independent random samplings from the distributions representing the data were performed using a custom-made MATLAB script. For each point, 10,000 iterations of the random sampling scheme were conducted, allowing all major combinations to be sampled. The overall precision of a given parameter is estimated as the standard deviation for all 10,000 computed solutions.

#### 3. Results

#### 3.1. Seasonal and Diurnal Variations of TC and WSOC Concentrations

The meteorological conditions in the high Khumbu Valley are determined by the large-scale Asian monsoon system and the local mountain wind system with a strong diurnal up-valley wind and a weak upper mountain night breeze [*Bonasoni et al.*, 2010]. The time trends of the total carbon (TC) and water-soluble organic carbon (WSOC) concentrations measured at NCO-P in 2013–2014 are shown in Figures 2a and 2b.

Local circulation is determined by thermal upslope winds that bring the polluted air of the lower troposphere during the afternoon and downslope winds that transport free tropospheric air to NCO-P. The concentrations of TC and WSOC fractions exhibit a distinct diurnal variability with higher values for the afternoon samples impacted by the upslope breeze  $(1.9 \pm 2.0 \,\mu\text{gC}\,\text{m}^{-3} \text{ and } 1.0 \pm 1.1 \,\mu\text{gC}\,\text{m}^{-3}$ , correspondingly) compared to the night samples  $(0.5 \pm 0.6 \,\mu\text{gC}\,\text{m}^{-3} \text{ and } 0.2 \pm 0.3 \,\mu\text{gC}\,\text{m}^{-3}$ , correspondingly). The high concentrations of TC and WSOC observed during nighttime between 25 and 27 April show that the valley breeze can transport the pollutants upward to the middle troposphere and impact the background concentrations [*Decesari et al.*, 2010; *Marinoni et al.*, 2010]. The contribution of WSOC to TC on average is almost identical in the polluted afternoon samples  $(0.59 \pm 0.16)$  and the background night samples  $(0.59 \pm 0.17)$ .

The atmospheric aerosol concentrations and composition at NCO-P differ during dry winter, premonsoon, wet monsoon, and postmonsoon seasons [*Bonasoni et al.*, 2010; *Decesari et al.*, 2010; *Marinoni et al.*, 2010]. In this study, the highest concentrations of TC and WSOC were observed during the premonsoon season and the lowest during the monsoon season (Table 1), in agreement with the total aerosol load typical behavior. The premonsoon season is the most frequently influenced by a strong atmospheric brown cloud (ABC) transport to



Jun-2013 Aug-2013 Oct-2013 Dec-2013 Feb-2014 Apr-2014 Jun-2014 Aug-2014 Oct-2014 Dec-2014

**Figure 2.** Temporal variability of total carbon (TC) and water-soluble organic carbon (WSOC) in  $PM_{10}$  aerosols compared with the BrC light absorption coefficient at 365 nm ( $b_{abs365}$ ) measured in water (WS-BrC) and methanol (MeS-BrC) aerosol extracts (a) in polluted afternoon air masses and (b) in the nighttime background air; (c) light absorption coefficients of WS-BrC and MeS-BrC at 550 nm ( $b_{abs550}$ ) in afternoon and night aerosol samples. No correction factor was applied.

NCO-P due to the highest seasonal mixing layer height over South Asia, the highest up-valley wind speed, and the increase of emission, especially due to biomass burning from agriculture practices along Himalayan foothills and the Indo-Gangetic Plain (IGP). In contrast, the monsoon season is characterized by a weakened wind regime when southerly upslope winds are observed at NCO-P [*Bonasoni et al.*, 2010]. A large amount of the air pollution in South Asia is efficiently removed by wet scavenging during the monsoon season [e.g., *Bisht et al.*, 2015; *Kirillova et al.*, 2013, *Yadav et al.*, 2015]. During the dry winter season the South Asian region experiences the ABC influence and the highest concentrations of carbonaceous aerosols are often observed in both the source regions [e.g., *Bam and Sarin*, 2015; *Tiwari et al.*, 2015; *Villalobos et al.*, 2014] and the regional background sites [e.g., *Budhavant et al.*, 2015; *Kirillova* et al., 2013; *Sheesley* et al., 2012]. During winter, the average concentrations of TC and WSOC at NCO-P are lower compared to the premonsoon season, which can be explained by very low mixing layer heights during winter [*Bonasoni et al.*, 2010; *Pan et al.*, 2015; *Tiwari et al.*, 2015] that reduce the possibility of pollution transport to the high Himalayas. **Table 1.** Seasonal Averages of the TC and WSOC Concentrations and the Brown Carbon Absorption Characteristics (Absorption Coefficient at 365 nm ( $b_{abs}$ ) Without Application of the Correction Factors, Mass Absorption Cross Section at 365 nm (MAC<sub>365</sub>), and Absorption Ångström Exponent (AAE) for 330–500 nm and 470–660 nm) for the Aerosols Collected at NCO-P Station During 2013–2014<sup>a</sup>

		Premonsoon $(n = 5)$	Monsoon $(n = 7)$	Postmonsoon $(n = 1)$	Dry Winter Season ( $n = 6$ )
TC ( $\mu$ g m <sup>-3</sup> ) (this study)	Afternoon	$4.2 \pm 2.7$	$0.7 \pm 0.5$	1.3	$1.1 \pm 0.4$
	Night	$0.8 \pm 0.9$	$0.2 \pm 0.1$	BDL <sup>b</sup>	$0.3 \pm 0.6$
TC ( $\mu$ g m <sup>-3</sup> ) [Decesari et al., 2010]	Afternoon	$2.2 \pm 1.4$	$0.48 \pm 0.41$	$1.0 \pm 0.36$	$1.1 \pm 0.64$
	Night	$1.4 \pm 1.4$	$0.74 \pm 1.1$	$0.44 \pm 0.31$	$0.46 \pm 0.32$
WSOC ( $\mu$ g m <sup>-3</sup> ) (this study)	Afternoon	$2.3 \pm 1.5$	$0.5 \pm 0.2$	0.8	$0.5 \pm 0.1$
	Night	$0.5 \pm 0.6$	$0.1 \pm 0.1$	0.2	$0.2 \pm 0.3$
WSOC ( $\mu$ g m <sup>-3</sup> ) [ <i>Decesari et al.</i> , 2010]	Afternoon	$1.2 \pm 0.83$	$0.48 \pm 0.56$	$0.73 \pm 0.21$	$0.57 \pm 0.42$
	Night	$0.81 \pm 0.80$	$0.55 \pm 0.77$	$0.32 \pm 0.21$	$0.23 \pm 0.24$
$b_{abs365}$ water (Mm <sup>-1</sup> )	Afternoon	1.83 ± 1.46	0.21 ± 0.22	0.30	$0.31 \pm 0.08$
	Night	$0.32 \pm 0.39$	$0.08 \pm 0.05^{t}$	0.04	$0.09 \pm 0.07^{h}$
$b_{abs365}$ methanol (Mm <sup>-1</sup> )	Afternoon	$2.86 \pm 2.49$	$0.32 \pm 0.29$	0.72	0.61 ± 0.20
	Night	$0.40 \pm 0.37$	$0.11 \pm 0.06^{t}$	0.05	$0.16 \pm 0.14^{h}$
$b_{abs550}$ water (Mm <sup>-1</sup> )	Afternoon	$0.15 \pm 0.11$	$0.03 \pm 0.03^{T}$	0.01	$0.02 \pm 0.01^{9}$
	Night	0.03 ± 0.03 <sup>g</sup>	$0.01 \pm 0.002^{e}$	BDL <sup>D</sup>	$0.01 \pm 0.01^{t}$
$b_{abs550}$ methanol (Mm <sup>-1</sup> )	Afternoon	$0.33 \pm 0.29$	0.14 <sup>a</sup>	0.10	$0.09 \pm 0.03^9$
	Night	0.06 ± 0.04 <sup>g</sup>	0.02 <sup>a</sup>	BDL <sup>D</sup>	$0.04 \pm 0.04^{e}$
$MAC_{365}$ water <sup>c</sup> (m <sup>2</sup> g <sup>-1</sup> )	Afternoon	$0.72 \pm 0.15$	$0.45 \pm 0.18^{1}$	0.36	$0.61 \pm 0.08$
- 2 1	Night	0.66 ± 0.07 <sup>9</sup>	$0.50 \pm 0.03^{e}$	0.29	$0.42 \pm 0.21$
$MAC_{365}$ methanol <sup>C</sup> (m <sup>2</sup> g <sup>-1</sup> )	Afternoon	$0.77 \pm 0.18$	$0.51 \pm 0.15^9$	0.65	$0.71 \pm 0.13$
	Night	0.64 ± 0.15 <sup>g</sup>	0.61 <sup>a</sup>	-	$0.61 \pm 0.21^{e}$
AAE 330–500 nm water	Afternoon	$5.1 \pm 0.3$	$4.2 \pm 0.6$	5.6	$5.4 \pm 0.6$
	Night	$4.9\pm0.8$	$4.9 \pm 0.9$	4.1	$3.9 \pm 0.9$
AAE 470–660 nm water	Afternoon	$3.9 \pm 0.6$	$2.2 \pm 0.8$	2.7	$3.5 \pm 1.0$
	Night	$2.8 \pm 1.1$	$3.0 \pm 2.2$	1.8	$1.9 \pm 1.7$
AAE 330–500 nm methanol	Afternoon	$3.9 \pm 0.5$	$4.4 \pm 1.4$	3.3	$3.8\pm0.8$
	Night	$3.6 \pm 0.3$	$3.4 \pm 0.8$	3.3	$4.2 \pm 0.3$
AAE 470–660 nm methanol	Afternoon	$3.2 \pm 0.5$	$3.2 \pm 0.7$	2.2	$3.4 \pm 2.2$
	Night	$2.6 \pm 0.3$	$2.5 \pm 0.7$	2.3	$2.3 \pm 0.5$

<sup>a</sup>Data are reported as average ± standard deviation.

<sup>b</sup>BDL—below detection limit.

<sup>C</sup>The values with high uncertainty (>150%) were excluded from the calculation of the seasonal averages of MAC<sub>365</sub>.

 $a_{n=1}^{a}$  $a_{n=2}^{e}$ 

 $f_{n=3.}^{n=2.}$ 

 $g_{n=4}$ 

n = 5.

n = 6.

The average seasonal values of TC and WSOC carbon fractions were compared with the previous measurements at NCO-P station in 2006–2008 [*Decesari et al.*, 2010]. The average TC and WSOC concentrations in the polluted afternoon air masses were about 2 times higher during the premonsoon season in 2013–2014  $(4.2 \pm 2.7 \,\mu\text{gC} \,\text{m}^{-3} \text{ and } 2.3 \pm 1.5 \,\mu\text{gC} \,\text{m}^{-3}$ , correspondingly) than in 2006–2008 ( $2.2 \pm 1.4 \,\mu\text{gC} \,\text{m}^{-3}$  and  $1.2 \pm$  $0.8 \,\mu\text{gC} \,\text{m}^{-3}$ , correspondingly). The average TC concentration in the afternoon samples during the monsoon season was also higher in 2013–2014 ( $0.7 \pm 0.5 \,\mu\text{gC} \,\text{m}^{-3}$ ) compared to 2006–2008 ( $0.48 \pm 0.41 \,\mu\text{gC} \,\text{m}^{-3}$ ). In contrast, the average values of TC and WSOC measured during nighttime in the premonsoon and monsoon seasons were lower in 2013–2014 than in the previous study (Table 1). During the dry winter season, the values for the TC and WSOC concentrations were similar for both study periods. The only afternoon and night samples collected during the postmonsoon season in 2014 exhibit levels of TC and WSOC within the range measured for the same season in 2006–2008 (Table 1).

TC and WSOC concentrations correlated well (Spearman's correlation coefficients are 0.91 and 0.92, correspondingly) with equivalent BC (eqBC) concentrations measured by MAAP in the polluted afternoon air masses (Table S1) pointing at the combustion origin of the carbonaceous aerosols coming at NCO-P from the valley below. In the night air the correlation of TC and WSOC with eqBC was lower (0.85 and 0.66, Table S1), pointing to modifications in the organic aerosol loadings due to chemical aging and/or to mixing of boundary layer air particles with background aerosols.



**Figure 3.** The light absorption coefficient ( $b_{abs}$  at 365 nm, no correction applied) as a function of WSOC concentration for WS-BrC and OC concentration for MeS-BrC. The slopes were calculated using Theil-Sen estimator, and the correlation is expressed as Spearman's rank correlation coefficient ( $\rho$ ).

#### 3.2. Light Absorption by Brown Carbon (BrC) in Water and Methanol Extracts at NCO-P

#### 3.2.1. Brown Carbon Light Absorption Coefficient

The light absorption coefficient at 365 nm ( $b_{abs365}$ ) of WS-BrC correlates with the concentrations of WSOC, and  $b_{abs365}$  of MeS-BrC aerosol shows a good correlation with OC concentrations calculated as described in section 2.2 (Figures 2a, 2b, and 3). Nonparametric statistical methods (Theil-Sen estimator and Spearman's rank correlation coefficient) for determination of the relationships between the light absorption coefficients and the concentrations of the organic aerosol concentrations were applied, to account for the presence of several samples with the organic aerosol loadings considerably higher than that of the other samples. Assuming that

OC is almost fully extracted by methanol (92% of primary OC based on *Chen and Bond* [2010]), the similar slopes (Figure 3) obtained for water and methanol extracts indicates that the higher  $b_{abs}$  recorded at short wavelengths for the methanol extracts with respect to water are mainly due to the fact that more organic matter is extracted in methanol than in water.

Our results for water extracts (Theil-Sen estimator-based slope = 0.86 in polluted afternoon samples and slope = 0.78 in night samples, Figure 3) are comparable with the linear relationship between the  $b_{abs365}$  of WS-BrC and WSOC concentrations reported in previous studies at low altitudes: in Khagapur, a site influenced by long-range transport of pollution from the IGP sources (slope = 0.7,  $R^2 = 0.57$  [*Srinivas and Sarin*, 2014]) and in Patiala, a biomass burning source region in the IGP (slope = 0.75,  $R^2 = 0.34$  (day), slope = 1.13,  $R^2 = 0.77$  (night) [*Srinivas et al.*, 2016]).

Analogously to TC and WSOC,  $b_{abs}$  of WS-BrC and MeS-BrC were very well correlated with eqBC concentrations in the afternoon samples (Spearman's correlation coefficient 0.93, Table S1) and somewhat less correlated with eqBC in the free tropospheric air masses (0.86 and 0.89, correspondingly). The correlation coefficients between BrC and eqBC remain, however, always higher than that between WSOC and eqBC at night (0.66): we can speculate that the concentrations of light-absorbing organic components are less influenced by aging or mixing in the free troposphere than the concentrations of total organic particles and that the sources of BrC observed at nighttime at NCO-P are mainly from recirculated boundary layer air masses.

Figures 2a and 2b show the time trend of the brown carbon absorption coefficients at NCO-P between 2013 and 2014. The average  $b_{abs365}$  is significantly higher for the afternoon samples  $(1.1 \pm 1.6 \text{ Mm}^{-1} \text{ MeS-BrC} \text{ and } 0.7 \pm 1.0 \text{ Mm}^{-1} \text{ WS-BrC})$  compared to the night samples  $(0.2 \pm 0.3 \text{ Mm}^{-1} \text{ in both MeS-BrC} \text{ and WS-BrC})$ . The same trend was observed for the light absorption coefficient at 550 nm ( $b_{abs550}$ ) with the afternoon values  $(0.20 \pm 0.22 \text{ Mm}^{-1} \text{ MeS-BrC} \text{ and } 0.07 \pm 0.09 \text{ Mm}^{-1} \text{ WS-BrC})$  higher than night values  $(0.05 \pm 0.03 \text{ Mm}^{-1} \text{ MeS-BrC} \text{ and } 0.02 \pm 0.02 \text{ Mm}^{-1} \text{ WS-BrC})$  (Figure 2c and Table 2); however, the uncertainties in the measurements at 550 nm were much higher compared to those at 365 nm. The highest values of the BrC light absorption coefficient were observed during the premonsoon season (Figures 2a and 2b and Table 1) following the seasonal trend of WSOC and OC concentrations.

MeS-BrC demonstrated higher  $b_{abs365}$  and  $b_{abs550}$  values compared to WS-BrC (Figure 2 and Table 1). Light absorption by MeS-BrC was on average 2 times higher at 365 nm and 3 times higher at 550 nm than that by WS-BrC. The observed trend is in agreement with other studies [*Chen and Bond*, 2010; *Liu et al.*, 2013; *Zhang et al.*, 2013], since methanol extracts a greater range of compounds than water. In particular, the much greater

Site	Collection Period	Size	$b_{abs} (Mm^{-1})^a$	MAC $(m^2 g^{-1})^a$	AAE <sup>g</sup> BrC	Relative Light Absorption <sup>q</sup>	Method	Reference
NCO-P, Nepal	Jun 2013 to Nov 2014	PM <sub>10</sub>	0.67 ± 1.0 <sup>b</sup>	South. 0.57 ± 0.18 <sup>b</sup>	Asia 4.9 ± 0.7 <sup>h</sup>	4 ± 1% <sup>u</sup>	Spectrophotometry	This study
(polluted)		2	$0.07 \pm 0.09^{c}$		3.1 ± 1.1 <sup>i</sup>	$8 \pm 1\%^{V}$	in water extracts	
NCO-P, Nepal	Jun 2013 to Nov 2014	$PM_{10}$	$1.10 \pm 1.62^{b}$	0.69 ± 0.17 <sup>b</sup>	$4.0 \pm 1.0^{h}$	$10 \pm 3\%^{\rm u}$	Spectrophotometry	This study
(polluted)			$0.20 \pm 0.22^{\circ}$	oro orop	3.2 ± 1.3'	$18\pm6\%$	in methanol extracts	This structure
(froc tronscribero)	Jun 2013 to Nov 2014	PIM10	0.16±0.25	81.U ± 26.U	4.6 ± 0.8 2 ∈ ± 1 ∈ <sup>i</sup>	•	spectrophotometry	Inis study
NCO-P, Nepal	Jun 2013 to Nov 2014	PM <sub>10</sub>	$0.22 \pm 0.25^{b}$	0.63 ± 0.14 <sup>b</sup>	$2.0 \pm 1.3$ $3.7 \pm 1.3^{h}$		Spectrophotometry	This study
(free troposphere)			0.05 ± 0.03 <sup>c</sup>	q-	$2.5 \pm 0.5^{1}$		in methanol extracts	
New Delhi (IGP), India	Oct 2010 to Mar 2011	PM <sub>2.5</sub>	ŀ	$1.6 \pm 0.5$	5.1 ± 2.0'	3-11% (Brc/EC)	Spectrophotometry in water extracts	Kirillova et al. [2014a]
Kharagpur (IGP), India	Nov 2009 to Mar 2010	PM <sub>2.5</sub>	11±5 <sup>b</sup>	0.78±0.24 <sup>b</sup>	6.0 ± 1.1 <sup>k</sup>	2-34% (BrC/EC)	ı	Srinivas and Sarin [2014]
Kanpur (IGP), India	Feb to Mar 2013	I	ŗ	I	6.6 ± 0.3 <sup>1</sup>	10–15% (BrC/total aerosol)	Photo Acoustic Soot Spectrometer + Mie	Shamjad et al. [2015]
Patiala (IGP), India	Oct to Dec 2011	PM <sub>2.5</sub>	40 ± 18 <sup>b</sup>	1.3 ± 0.7 <sup>b</sup>	$5.1 \pm 1.9^{k}$	51-61% <sup>r</sup> , 35-47%	Spectrophotometry	Srinivas et al. [2016]
(day) Patiala (IGP), India	Oct to Dec 2011	PM <sub>2.5</sub>	52 ± 27 <sup>b</sup>	$1.3 \pm 0.5^{\rm b}$	$5.3 \pm 2.0^{k}$	(BrC/EC) 46–96% <sup>r</sup> , 40–55%	in water extracts Spectrophotometry	Srinivas et al. [2016]
(night) Bay of Bengal/N Indian	Nov 2008	TSP	3.6 ± 2.0 <sup>b</sup>	$0.6 \pm 0.2^{\rm b}$	$5.8 \pm 1.5^{k}$	(BrC/EC) -	in water extracts Spectrophotometry	Srinivas and Sarin [2013]
Ocean (IGP outflow)	Jan 2009	PM <sub>10</sub>	2.2 ± 1.3 <sup>b</sup>	0.4±0.1 <sup>b</sup>	$9.1 \pm 2.5^{k}$		in water extracts Spectrophotometry	Srinivas and Sarin [2013]
Bay of Bengal (South-	Jan 2009	PM <sub>10</sub>	1.4 ± 1.1 <sup>b</sup>	$0.5 \pm 0.2^{\rm b}$	6.9 ± 1.9 <sup>k</sup>		in water extracts Spectrophotometry	Srinivas and Sarin [2013]
East Asia outflow) Indian Ocean, MCOH, Maldives	Feb to Mar 2012	PM <sub>2.5</sub>	0.1–0.5 <sup>b</sup>	$0.46 \pm 0.18^{\rm b}$	$7.2 \pm 0.7^{j}$	0.7±0.2% (RrC/FC)	in water extracts Spectrophotometry in water extracts	Bosch et al. [2014]
		DAN		East A	lsia 7 E ± 0.0 <sup>m</sup>			
beijirig, Ciliria (winter)		FIN12.5	I	1.79 ± 0.24	v.∪ ± c. /		pectropriotorneury in water extracts	LITERIY EL UL. [2011]
Beijing, China	Summer 2009	$PM_{2.5}$		0.71 ± 0.20 <sup>b</sup>	$7.0 \pm 0.8^{m}$		Spectrophotometry	Cheng et al. [2011]
(summer) Beijing, China	Oct 2010 to Nov 2011	$PM_{2.5}$	10.1 ± 8.6 <sup>b</sup>	1.26 <sup>b</sup>	7.5 <sup>n</sup>		In water extracts Spectrophotometry	<i>Du et al.</i> [2014]
(winter) Beijing, China	Oct 2010 to Nov 2011	$PM_{2.5}$	4.6±4.2 <sup>b</sup>		7.5 <sup>n</sup>		in water extracts Spectrophotometry	Du et al. [2014]
(spring) Beijing, China	Oct 2010 to Nov 2011	PM <sub>2.5</sub>	3.7 ± 3.8 <sup>b</sup>	0.51 <sup>b</sup>	7.5 <sup>n</sup>		in water extracts Spectrophotometry	Du et al. [2014]
(summer) Beijing, China	Oct 2010 to Nov 2011	PM <sub>2.5</sub>	10.2 ± 8.5 <sup>b</sup>		7.5 <sup>n</sup>		in water extracts Spectrophotometry	Du et al. [2014]
(fall)			$(2010), 8.0 \pm 6.8^{\circ}$ (2011)				in water extracts	
Beijing, China	Apr to May and Oct to Nov 2012	TSP		0.92 <sup>d</sup>	6.2 <sup>0</sup>		Sun-sky radiometer + Mie theory	Wang et al. [2013]
Beijing, China	Jan 2013	PM <sub>2.5</sub>	I	1.54 ± 0.16 <sup>b</sup>	$5.30 \pm 0.44^{j}$	10.7 ± 3.0%	Spectrophotometry	<i>Yan et al.</i> [2015]
(winter) Beijing, China (summer)	Jun 2013	PM <sub>2.5</sub>		0.73±0.15 <sup>b</sup>	$5.83 \pm 0.51^{j}$	(biC/LC) 5.7±2.5% (BrC/EC)	Spectrophotometry in water extracts	Yan et al. [2015]
Xianghe, China Gosan, Korea (Eact Asian outflow)	Mar 2005 Mar 2011	PM <sub>10</sub> PM <sub>2.5</sub>	1 1	2.2 <sup>e</sup> , 0.5 <sup>c</sup> 0.65 ± 0.23 <sup>b</sup>	3.5 <sup>i</sup> 6.35 ± 0.63 <sup>j</sup>	30% <sup>s</sup> (BrC/total aerosol) 6.1 ± 2.2% (BrC/EC)	Aethalometer Spectrophotometry in water extracts	Yang et al. [2009] Kirillova et al. [2014b]

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Table 2. (continued)									
Site	<b>Collection Period</b>	Size	$b_{ m abs}~({ m Mm}^{-1})^{ m a}$	MAC $(m^2 g^{-1})^a$	AAE <sup>g</sup> BrC	Relative Light Absorption <sup>q</sup>	Method	Reference	
Gosan, Korea (East Asian outflow)	Mar 2011	TSP		0.75±0.22 <sup>b</sup>	6.37 ± 0.49 <sup>j</sup>	4.8 ± 1.6% (BrC/EC)	Spectrophotometry in water extracts	Kirillova et al. [2014b]	
Gosan, Korea (East Asian outflow)	Oct 2009 to Jun 2010	TSP	ı	1.4 (0.8-2.0) <sup>f</sup>	1.7 (1.6–1.8) <sup>p</sup>	45% <sup>t</sup> (BrC/BC)	Aethalometer	Chung et al. [2012a]	
<sup>a</sup> b <sub>abs</sub> and MAC values a b365 nm,	are calculated at the follo	owing wav	elengths. No corre	ction factor is appl	ied to the $b_{ m abs}$ v	/alues.			
<sup>c</sup> 550 nm, d40 nm									
<sup>e</sup> 370 nm,									
<sup>1</sup> 520 nm.									
<sup>9</sup> AAE values are calculat	ited within the following	ranges.							
'330–500 nm,									
4/0-660 nm,									
/300–700 nm. k_330–480 nm									
1330–480 nm.									
<sup>m</sup> 300–500 nm.									
<sup>n</sup> 440, 670, 870, and 102 <sup>o</sup> 370–950 nm. Relative li	20 nm, light absorption by BrC i	s calculate	d for the whole so	lar spectrum, excer	ot for the follow	ina.			
<sup>P</sup> At 365 nm. <sup>q</sup> At 370 nm.	-			- -		5			
<sup>r</sup> At 520 nm. No correctic	on factor is applied to th	ie b <sub>abs</sub> vali	ues. Relative light a	absorption is calcul	ated using AAE <sub>t</sub>	$_{3C} = 1$ and reported based on	the following.		
the value corrected value value	ues. Irina a factor of 2 for MG	י הייך יייק י	المحلمة مولوا والمحلمة	And But following I					
<sup>u</sup> Relative light absorptic <sup>v</sup> Polotion light absorptic	on is calculated using A/		d reported based o	in non corrected b	abs values.	مرحم د المد المراحم مع د محمد مع د المحمد مع م	بند بو 1 ہو جب 2000 این وہ		
	on is carculated using Ar	VEBC-1 dil	n nasen nasen n		erteu usiliy a la	ננטו טו ב וטו אש-פור מווע מ ומר		ינכוסבן מו גע אוואסוו	



**Figure 4.** Wavelength dependence of BrC light absorption expressed as Ångström Exponent (AAE) calculated within the wavelength ranges 330–500 nm and 470–660 nm for water and methanol extracts of the afternoon and night PM<sub>10</sub> samples.

capacity of MeS-BrC to absorb light at longer wavelength (550 nm) indicates that the organic compounds bearing chromophores capable to absorb light at long wavelengths can be extracted in methanol but only very poorly in water. By contrast, at short wavelengths (365 nm), both WSOC and water-insoluble OC contributes approximately equally to light absorption, and the ratio between the *b*<sub>abs365</sub> coefficients of WS-BrC and of MeS-BrC reflects broadly the WSOC/OC ratio.

Finally, it should be noted that the reported above  $b_{abs365}$  and  $b_{abs550}$  values are based on the absorption measurements in the solutions and that deriving the corresponding absorption coefficient for an aerosol population can require correction factors [Sun et al., 2007]. Such factors can be greater

than 1 when the light-absorbing compounds are enriched accumulation mode aerosols. For instance, *Liu et al.* [2013] reported a study in urban and rural sites in Georgia showing that the BrC light absorption in ambient aerosol is higher than the light absorption in the bulk liquid extracts of a factor of 2 for water extracts and a factor of 1.8 for methanol extracts. In the following discussion, we report both uncorrected and corrected absorption coefficients assuming the conversion factors reported by *Liu et al.* [2013].

#### 3.2.2. Mass Absorption Cross Section of BrC

The mass absorption cross section values measured at 365 nm (MAC<sub>365</sub>) in the water extracts were 0.29–0.87 m<sup>2</sup> g<sup>-1</sup> (0.57 ± 0.18 m<sup>2</sup> g<sup>-1</sup>) for the afternoon samples and 0.28–0.70 m<sup>2</sup> g<sup>-1</sup> (0.52 ± 0.18 m<sup>2</sup> g<sup>-1</sup>) for the night samples (Table 2). In methanol extracts MAC<sub>365</sub> was 0.34–0.98 m<sup>2</sup> g<sup>-1</sup> (0.68 ± 0.16 m<sup>2</sup> g<sup>-1</sup>) for the afternoon samples and 0.25–0.80 m<sup>2</sup> g<sup>-1</sup> (0.59 ± 0.18 m<sup>2</sup> g<sup>-1</sup>) for the night samples (Table 2). Results indicate that organic aerosol transported from the valley to the high Himalayas absorbs UV-visible light only slightly more efficiently than organic aerosol from the free troposphere. The fact that we do not observe the significant difference between MAC<sub>365</sub> in water and methanol-extracted solutions shows that water-insoluble carbon extracted by methanol does not have higher light-absorbing properties per mass compared to WSOC at short wavelength (see previous section).

The averaged MAC<sub>365</sub> values in the polluted afternoon air during premonsoon and winter seasons were higher compared to the monsoon and postmonsoon values (Table 1). During monsoon season night MAC<sub>365</sub> values are similar or higher than MAC<sub>365</sub> in the afternoon air masses, which can be explained by the presence of the upslope winds bringing pollution from the valley also during nighttime [Bonasoni et al., 2010]. During the dry winter season we observed the largest difference between the afternoon (0.61  $\pm$  0.08 m<sup>2</sup> g<sup>-1</sup> for WS-BrC and 0.71  $\pm$  0.13 m<sup>2</sup> g<sup>-1</sup> for MeS-BrC) and the night (0.42  $\pm$  0.27 m<sup>2</sup> g<sup>-1</sup> for WS-BrC and  $0.49 \pm 0.01 \text{ m}^2 \text{ g}^{-1}$  for MeS-BrC) MAC<sub>365</sub> values at NCO-P. The high afternoon values overlap with the high WS-BrC MAC<sub>365</sub> data found during winter in the pollution outflow from the IGP plain measured at a receptor site directly on the IGP ( $0.78 \pm 0.24 \text{ m}^2 \text{ g}^{-1}$  in PM<sub>2.5</sub> [Srinivas and Sarin, 2014]) and over the Bay of Bengal ( $0.6 \pm 0.2 \text{ m}^2 \text{g}^{-1}$  in TSP in November 2008 [Srinivas and Sarin, 2013]). By contrast, the lower nighttime values (more characteristic of background air) are in line with the low MAC<sub>365</sub> data for low-altitude stations in remote areas of the Bay of Bengal and the Indian Ocean  $(0.4 \pm 0.1 \text{ m}^2 \text{ g}^{-1} \text{ in PM}_{10}$ in January 2009 [Srinivas and Sarin, 2013];  $0.46 \pm 0.18 \text{ m}^2 \text{ g}^{-1}$  in PM<sub>2.5</sub> [Bosch et al., 2014]). The winter WS-BrC MAC365 values at NCO-P are lower than those in the pollution source regions on the IGP: the megacity New Delhi  $(1.6 \pm 0.5 \text{ m}^2 \text{ g}^{-1} \text{ in } \text{PM}_{2.5} \text{ [Kirillova et al., 2014a]})$  and Patiala  $(1.3 \pm 0.7 \text{ m}^2 \text{ g}^{-1} \text{ in } \text{PM}_{2.5} \text{ m}^2 \text{ g}^{-1})$ PM<sub>2.5</sub> [Srinivas et al., 2016]) (Tables 1 and 2). These data show that water-soluble organic aerosol tends to have higher MAC<sub>365</sub> values in polluted conditions compared to background air and aged long-range transported pollution.

Comparing with East Asia (Table 2), MAC<sub>365</sub> values in the polluted air masses at NCO-P are similar to WS-BrC MAC<sub>365</sub> values measured in the East Asian outflow at Gosan site on Jeju Island (0.65–0.75 m<sup>2</sup> g<sup>-1</sup> in PM<sub>2.5</sub> and TSP) and in Beijing during summer (0.51–0.73 m<sup>2</sup> g<sup>-1</sup> in PM<sub>2.5</sub>), but lower than in Beijing during winter time (1.26–1.79 m<sup>2</sup> g<sup>-1</sup> in PM<sub>2.5</sub>) [*Cheng et al.*, 2011; *Du et al.*, 2014; *Kirillova et al.*, 2014b; *Yan et al.*, 2015].

In conclusion, the MAC<sub>365</sub> determined at NCO-P fall in the range of values observed at several low-altitude stations in South and East Asia. Such range is broad and must be affected by the sources of variability such as the different inlets used (TSP,  $PM_{10}$ , and  $PM_{2.5}$ ). The effects of such variable cannot be easily disentangled from the genuine changes in the MAC<sub>365</sub> between aerosols in the different environments based on this simple compilation.

#### 3.2.3. Wavelength Dependence of BrC Light Absorption

The summary of the calculated absorption Angström Exponent (AAE) representing the wavelength dependence of the light absorption of BrC in the high Himalayas is shown in Figure 4, the time trends of AAE in water and methanol extracts are presented in Figure S1, and the seasonal AAE averages are shown in Table 1. The wavelength dependence of the light absorption in the UV/visible range by water-soluble brown carbon (WS-BrC) and methanol-soluble brown carbon (MeS-BrC) did not exhibit a clear seasonal variability (Figure 4, Table 1, and Figure S1). A diurnal variability was observed only for WS-BrC during the winter season when AAE values both in 330–500 nm and 470–660 nm ranges were on average higher in the polluter air masses compared to those in free tropospheric night air (Table 1). The annual average values of WS-BrC AAE within 330-500 nm range ( $4.9 \pm 0.7$  afternoon,  $4.6 \pm 0.8$  night) and the winter season average values (5.4±0.6 afternoon, 3.9±0.9 night) are comparable to AAE values measured previously (Table 2) in New Delhi in winter 2010–2011 (5.1±2.0, 330–400 nm in PM<sub>2.5</sub> [Kirillova et al., 2014a]), over IGP in winter 2009–2010 ( $6.0 \pm 1.1$ , 300–700 nm in PM<sub>2.5</sub> [Srinivas and Sarin, 2014]), in winter in PM<sub>2.5</sub> 2011 ( $5.1 \pm 1.9$  day, 5.3 ± 2.0 night, 300-700 nm [Srinivas et al., 2016]), in winter-spring 2013 (6.6 ± 0.3, 405 and 781 nm [Shamjad et al., 2015]), and in the IGP outflow to the North Indian Ocean in November 2008 ( $5.8 \pm 1.5$ , 300-700 nm in TSP [Srinivas and Sarin, 2013]). However, they are lower than AAE of the IGP outflow measured over the Bay of Bengal during winter months in 2008–2009 (9.1  $\pm$  2.5, 300–700 nm in PM<sub>10</sub> [Srinivas and Sarin, 2013]) and at the Indian Ocean site on Hanimaadhoo Island, the Maldives, during February–March 2012 (7.2  $\pm$ 0.7, 330-400 nm in PM<sub>2.5</sub> [Bosch et al., 2014]). Here we observe the difference in the properties of winter time WS-BrC between the aerosols collected at the low-altitude remote sites in the Bay of Bengal and the Indian Ocean and at the high-altitude NCO-P site: MAC<sub>365</sub> is similar, but AAE is different (lower at NCO-P). It shows that the absorption by WSOC at longer wavelengths (>365 nm) is higher at NCO-P site than at the lowaltitude remote marine sites influenced by South Asian pollution outflow.

The average values of MeS-BrC AAE within 330–500 nm ( $4.0 \pm 1.0$  afternoon,  $3.7 \pm 1.3$  night) are comparable to AAE values in methanol extracts of PM<sub>2.5</sub> particles from Los Angeles Basin ( $4.82 \pm 0.49$ , 300–600 nm [*Zhang et al.*, 2013]) and of <3.1 µm particles collected in an urban site of Atlanta, GA (4.98, 300–500 nm [*Liu et al.*, 2013]). However, the comparison of AAE values from different studies is challenging as they are fitted within different wavelength ranges. AAE of MeS-BrC was on average slightly lower than that of WS-BrC within 330–500 nm wavelength range (Figures 4 and S1). The same trend was observed previously in the aerosol samples from the U.S. [*Liu et al.*, 2013; *Liu et al.*, 2015; *Zhang et al.*, 2013] and in the samples of wood smoke [*Chen and Bond*, 2010]. The slower decrease of absorption at shorter wavelengths can be determined by the absorption above 400 nm of higher molecular weight chromophores that are extracted only in methanol [*Liu et al.*, 2013; *Zhang et al.*, 2013], as confirmed by the higher absorption coefficient of methanol extracts at 500 nm. However, there was no difference observed in AAE of WS-BrC and MeS-BrC for longer wavelengths (470–660 nm, Figure 4).

#### 3.2.4. Comparison of the Light Absorption by BrC and BC

In order to compare black carbon (BC) light absorption coefficient at 635 nm ( $b_{abs635}$ ) measured (see section 2.2) with the light absorption by BrC, the light absorption coefficients of BC at 365 and 550 nm were calculated using the power law wavelength ( $\lambda$ ) dependence of  $b_{abs}$ :

$$b_{\text{abs-BC-}\lambda} = b_{\text{abs-BC-}635} \cdot (635/\lambda)^{\text{AAE}}$$
(9)



**Figure 5.** Relative absorbance by WS-BrC and MeS-BrC compared to BC at 360 and 550 nm ( $AAE_{BC} = 1$ ). Error bars indicate the range between the values calculated using  $AAE_{BC} = 1.4$  and  $AAE_{BC} = 0.8$ . Samples marked by a star represent the samples with  $b_{abs}$  values of BrC or BC below detection limit. No correction factor was applied to  $b_{abs-BrC}$  values.

where the absorption Ångström exponent (AAE) for BC, which is uncertain, is here assumed to be in the range between 0.8 and 1.4 [e.g., *Lack and Langridge*, 2013; *Yuan et al.*, 2015] and the  $b_{abs\lambda}$  were calculated using  $AAE_{BC} = 0.8$ , 1, and 1.4 (Table S2).

In order to compare with the BC light absorption from MAAP, the absorption coefficients of BrC, which are measured in bulk solutions, must be converted into absorption coefficients for an aerosol population (see section 3.2.1). In the following discussion, we report both uncorrected (conversion factor = 1) and corrected (correction factors from *Liu et al.* [2013]) values for  $b_{abs}$ -BrC (Tables S3 and S4).

In the polluted afternoon samples, at the short wavelength (365 nm) BrC absorbs on average  $17 \pm 8\%$  (34 ± 16% corrected) for WS-BrC and 29 ± 14% (53 ± 26% corrected) for MeS-BrC relative to BC when AAE<sub>BC</sub> = 1 was applied (Figure 5 and Tables S3 and S4). At longer wavelengths (550 nm) BrC absorption decreased to 2±0.5% (3 ± 1% corrected) for WS-BrC and 5 ± 2% (9 ± 3% corrected) for MeS-BrC compared to BC absorption (AAE<sub>BC</sub> = 1). The relative light absorbance of BrC compared to BC on average did not differ between the polluted afternoon samples and the background air samples when AAE<sub>BC</sub> = 1 was used (Tables S1 and S1).

The ratios  $b_{abs}$ -BrC/ $b_{abs}$ -BC increased by 10% (365 nm) and 5% (550 nm) when applying AAE<sub>BC</sub> = 0.8 and decreased by 20% (365 nm) and 9% (550 nm) when applying AAE<sub>BC</sub> = 1.4 compared to the ratios calculated using  $AAE_{BC} = 1$  (Figure 5 and Tables S3 and S4). Taking into account this variability, light absorption by BrC compared to that by BC at 365 nm ranged between 12 and 71% (21-128% corrected) for MeS-BrC and 8-43% (16-85% corrected) for WS-BrC in the polluted afternoon samples and between 6 and 33% (11-59% corrected) for MeS-BrC and 4-19% (9-38% corrected) for WS-BrC in the night samples. For the longer wavelengths (550 nm)  $b_{abs}$ -BrC/ $b_{abs}$ -BC was within 2–9% (5–16% corrected) for MeS-BrC and 1–3% (2-5% corrected) for WS-BrC in the polluted air masses and between 2 and 7% (3-12% corrected) for MeS-BrC and 1–2% (1–5% corrected) for WS-BrC in the free tropospheric air (Tables S3 and S4). Considering the seasonal difference, the  $b_{abs}$ -BrC/ $b_{abs}$ -BC ratios in the afternoon polluted were slightly higher during monsoon season compared to other seasons due to low level of BC (Figure 5 and Tables S3 and S4). Clearly, the assessment of the relative absorption of BrC with respect to BC is largely affected by the uncertainties in the actual AAE<sub>BC</sub> and in the measurement correction factors for BrC  $b_{abs}$  (from solutions to particles). Even accounting for these uncertainties, our findings indicate that MeS-BrC absorption in the near-UV (365 nm) can be one third or of the same order of magnitude of BC absorption. By contrast, at 550 nm BC absorption is 10 or even more than 20 times greater than that of BrC. Finally, the BrC fractional absorption is higher in the afternoon (polluted) air masses than at nighttime (free tropospheric conditions).

In this last part of the discussion section, we provide an estimate of the total (wavelength-integrated) columnar light absorption of BrC respect to BC in the high Himalayas. Several previous studies indicated the importance of BrC as an absorbing component of atmospheric aerosols (Table 2). Source studies show that the wood smoke OC absorbs about 14% of total absorbed solar radiation (by OC and BC) and 49% at the wavelengths below 400 nm [*Kirchstetter and Thatcher*, 2012] and in HULIS BrC contribution is 6–9% of the total light absorption [*Hoffer et al.*, 2006]. Aerosol Robotic Network (AERONET)-based study reported the contribution of BrC to aerosol forcing of 20–50% over the regions dominated by biomass burning and biofuel combustion [*Feng et al.*, 2013]. Photo acoustic soot spectrometer measurements with Mie theory calculations show that in the city of Kanpur located in the IGP, BrC accounts for 10–15% of the total aerosol absorption in the atmosphere within all the solar spectrum in winter-spring season [*Shamjad et al.*, 2015].

The comparison of in situ BrC  $b_{abs}$  observations at ground level with (columnar) BrC absorption optical thickness data are complicated by the fact that the altitudinal changes in the BrC distribution are generally unknown. Only at a few sites, a complete vertical profile of BrC and BC  $b_{abs}$  could be determined, as from the aircraft observations in North America described by *Liu et al.* [2014, 2015].

For sake of simplicity, in this study the fractional solar radiation absorption by BrC compared to BC was applied following the approaches described in *Kirchstetter and Thatcher* [2012] and *Kirillova et al.* [2014a, 2014b] and a scheme of atmospheric layering above NCO-P was derived by the work of *Marcq et al.* [2010] (see section 2.4). At 3 m above the ground level at NCO-P, which is 5079 m asl, the amount of solar radiation absorbed by WS-BrC compared to BC was  $4 \pm 1\%$  ( $8 \pm 1\%$  applying the *Liu et al.* [2013] corrections) and for MeS-BrC was average  $9 \pm 2\%$  ( $17 \pm 5\%$  corrected) Figure 6. The same method has been applied to estimate the absorption of BrC relative to BC at low altitudes in South and East Asia [*Bosch et al.*, 2014; *Kirillova* 



**Figure 6.** Fractional solar radiation absorption by MeS-BrC and WS-BrC (no correction factor applied) relative to BC at NCO-P station showing the range of the values calculated using  $AAE_{BC} = 0.8$ , 1, and 1.4.

*et al.*, 2014a, 2014b; *Srinivas and Sarin*, 2014; *Srinivas et al.*, 2016; *Yan et al.*, 2015]. Our results are similar to the relative fractional solar absorption by WS-BrC of 3–11% (in PM<sub>2.5</sub>, no corrections applied) in New Delhi during winter [*Kirillova et al.*, 2014a], 5.7  $\pm$  2.5% (summer) and 10.7  $\pm$  3.0% (winter) in Beijing [*Yan et al.*, 2015], and 2–10% (in PM<sub>2.5</sub> and TSP, no corrections applied) in the East Asian outflow in March [*Kirillova et al.*, 2014b]. It also fits within the range measured in the IGP outflow during winter season 2–34% (in PM<sub>2.5</sub>, no corrections applied) at a regional receptor site Kharagpur [*Srinivas and Sarin*, 2014]. Much stronger BrC light absorption was registered at a biomass burning source region of Patiala where in winter the fractional solar radiation absorption (within the whole solar spectrum) by WS-BrC compared to EC was 40–55% (in PM<sub>2.5</sub>, no corrections applied) [*Srinivas et al.*, 2016]. However, our results are higher than the fractional solar radiation absorption measured in the South Asian outflow at the Maldives climate observatory in the Indian Ocean (0.7 ± 0.2%; in PM<sub>2.5</sub>, no corrections applied) [*Bosch et al.*, 2014]).

Therefore, the importance of BrC as a light absorber measured in the high Himalayas is similar to this measured at the low-altitude continental pollution receptor sites and urban source regions in South and East Asia but lower than that at a biomass burning pollution site in the IGP. Thus, our results do not show any clear increase of the BrC absorption relative to BC with increasing altitude as it would be expected under the hypothesis that BrC is not only advected from the boundary layer to the free troposphere but also produced there by secondary reactions.

#### 4. Conclusions

This study reports the main light-absorbing properties of the water and methanol-extracted brown carbon in the atmospheric aerosols collected during a year-round (2013–2014) sampling campaign at Nepal Climate Observatory-Pyramid (NCO-P, 5079 m asl) at the foot of Mount Everest in the high Himalayas. The light absorption coefficients of WS-BrC and MeS-BrC follow the diurnal and seasonal trends of the organic aerosol components (WSOC and OC). The light absorption coefficient values are higher in the afternoon polluted samples impacted by upslope valley breeze, compared to the night samples representing free tropospheric air. During the premonsoon season when the high boundary layer allows the high level of pollution to reach the high Himalayas, the absorption coefficients of WS-BrC and MeS-BrC and MeS-BrC are the highest both in afternoon and night samples at a shorter (365 nm) and longer (550 nm) wavelengths. MeS-BrC absorbs about 2 times higher at 365 nm and about 3 times higher at 550 nm compared to WS-BrC. Since WSOC accounts for approximately half of OC, the spectrophotometric analyses indicate that WSOC and water-insoluble OC contribute to the same extent to BrC absorption in the near UV, while the absorption in the mid-VIS is dominated by water-insoluble organic compounds.

At NCO-P the wavelength dependence of light absorption by BrC (AAE) did not exhibit any seasonal trend. During dry winter season the higher AAE values for WS-BrC was observed in the polluted afternoon air

masses compared to the free tropospheric air. These values in the high Himalayas were lower compared to AAE measured previously at the low-altitude South Asian remote background sites in the Bay of Bengal and the Indian Ocean, but the mass absorption cross section of WS-BrC at 365 nm was similar, indicating a higher absorption in the visible light by WSOC in the high Himalayas compared to the low-altitude marine sites influenced by South Asian pollution outflow.

The comparison of the light absorption coefficient of BrC and BC showed that at 365 nm the absorption was on average 15% (30% when using the correction factors of Liu et al. [2013]) by WS-BrC and about 25% (46% correction factor 1.8) by MeS-BrC compared to the absorption by BC, when  $AAE_{BC} = 1$  was applied. At 550 nm the absorption by WS-BrC was only 1–2% (3% applying correction factors) and by MeS-BrC was 4–5% (8% applying correction factors) compared to BC absorption ( $AAE_{BC} = 1$ ), and there were relatively large uncertainties in the measurements of light absorption by BrC. Therefore, the contribution of BrC to light absorption was significant compared to that BC in the near UV and much smaller in the middle-visible spectrum. Solar light absorption by BrC and BC considering all the solar spectrum showed that at the ground level at NCO-P WS-BrC absorbs  $4 \pm 1\%$  (8  $\pm 1$  applying correction factors) and MeS-BrC absorbs  $9 \pm 2\%$  (17  $\pm 5\%$ applying correction factors) compared to BC. These values are higher than those in the South Asian pollution outflow measured at a remote site in the Indian Ocean but the same or lower than the BrC absorption in respect of BC observed in the low-altitude source regions in the IGP. Hence, there is no evidence of any enhancements of BrC absorption with respect to BC in the middle troposphere when comparing our results with the results obtained at low altitudes in South Asia [Kirillova et al., 2014a; Srinivas and Sarin, 2014; Srinivas et al., 2016]. When considering the in situ BrC measurements at low altitude and at NCO-P all together, we conclude that the BrC contribution to solar absorption is significant over the Indian subcontinent. However, such contribution in the long wavelength is smaller than the estimates (20% with respect to BC at 550 nm) derived by semiempirical approaches based on AERONET (columnar) observations [Chung et al., 2012b]. Overall, the atmospheric heating by BC seems to be the larger climate forcer in the Himalayan region. BrC absorption is still an important additional factor, although our observations support the inclusion of BrC as "moderately absorbing" species rather than "strongly absorbing" [Feng et al., 2013] in atmospheric models aiming to predict the radiative forcing of carbonaceous aerosols in this region of the world.

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