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Water-Soluble Brown Carbon in Atmospheric Aerosols from Godavari (Nepal), a Regional Representative of South Asia

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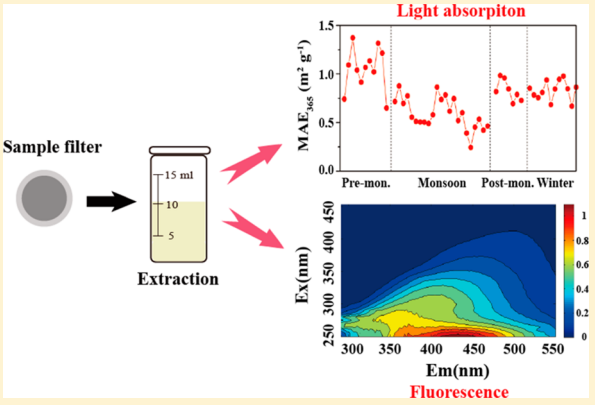
Supporting Information

ABSTRACT: Brown carbon (BrC) has recently emerged as an important light-absorbing aerosol. This study provides interannual and seasonal variations in light absorption properties, chemical composition, and sources of water-soluble BrC (WS-BrC) based on PM_{10} samples collected in Godavari, Nepal, from April 2012 to May 2014. The mass absorption efficiency of WS-BrC at 365 nm (MAE_{365}) shows a clear seasonal variability, with the highest MAE_{365} of 1.05 ± 0.21 m^2 g^{-1} in premonsoon season and the lowest in monsoon season (0.59 ± 0.16 m^2 g^{-1}). The higher MAE_{365} values in nonmonsoon seasons are associated with fresh biomass burning emissions. This is further substantiated by a strong correlation (r = 0.79, P < 0.01) between Abs_{365} (light absorption coefficient at 365 nm) and levoglucosan. We found, using fluorescence techniques, that humic-like and protein-like substances are the main chromophores in WS-BrC and responsible for 80.2 ± 4.1% and 19.8 ± 4.1% of the total fluorescence intensity, respectively. BrC contributes to 8.78 ± 3.74% of total light absorption over the 300−700 nm wavelength range. Considering the dominant contribution of biomass burning to BrC over Godavari, this study suggests that reduction in biomass burning emission may be a practical method for climate change mitigation in South Asia.



INTRODUCTION

South Asia is considered to be one of the most polluted regions in the world, with high loadings of aerosols and gaseous pollutants.[1,2] Anthropogenic emissions from biomass burning and fossil fuels,[3,4] along with loosely regulated emission norms,[5] have led to an increase in the air pollution over South Asia. The consequence of these emissions have led to the formation of the "atmospheric brown cloud" (ABC), which can cover the entire subcontinent and last as long as six months from November to May.[6] This brownish haze is mainly composed of organic matter, black carbon (BC), sulfate, and nitrate. It can deteriorate air

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Table 1. Concentration of Major Ions ($\mu g\ m^{-3}$), Carbonaceous Components ($\mu gC\ m^{-3}$), and Levoglucosan ($ng\ m^{-3}$) as Well as the Light Absorption and Fluorescence Properties of BrC in the PM_{10} Aerosols from Godavari

	annual (n = 53)	premonsoon (n = 11)	monsoon (n = 23)	postmonsoon (n = 7)	winter (n = 12)
Ionic Species					
Na^+	0.81 ± 0.77	0.77 ± 0.36	1.11 ± 0.91	0.80 ± 0.89	0.29 ± 0.17
NH_4^+	0.27 ± 0.34	0.36 ± 0.17	0.05 ± 0.05	0.21 ± 0.20	0.64 ± 0.46
K^+	0.10 ± 0.07	0.14 ± 0.07	0.05 ± 0.04	0.12 ± 0.08	0.12 ± 0.04
Mg^{2+}	0.04 ± 0.03	0.04 ± 0.02	0.04 ± 0.04	0.03 ± 0.01	0.03 ± 0.02
Ca^{2+}	0.33 ± 0.47	0.39 ± 0.22	0.24 ± 0.27	0.72 ± 1.07	0.22 ± 0.12
Cl^-	0.05 ± 0.05	0.06 ± 0.05	0.05 ± 0.07	0.03 ± 0.01	0.03 ± 0.03
NO_3^-	0.42 ± 0.38	0.54 ± 0.24	0.27 ± 0.44	0.36 ± 0.24	0.60 ± 0.31
SO_4^{2-}	1.91 ± 1.33	2.46 ± 0.77	1.37 ± 1.33	1.72 ± 0.82	2.56 ± 1.50
Carbonaceous Components and Levoglucosan					
OC	2.93 ± 1.63	3.91 ± 2.31	2.04 ± 0.74	3.84 ± 1.90	3.19 ± 0.87
EC	0.77 ± 0.48	0.84 ± 0.41	0.44 ± 0.17	1.12 ± 0.57	1.14 ± 0.41
WSOC	1.66 ± 1.09	1.93 ± 0.95	0.97 ± 0.45	2.74 ± 1.81	2.09 ± 0.50
WSOC/OC	0.55 ± 0.17	0.53 ± 0.13	0.50 ± 0.19	0.55 ± 0.09	0.68 ± 0.14
OC/EC	4.12 ± 1.06	4.54 ± 0.82	4.65 ± 0.89	3.89 ± 0.84	2.88 ± 0.40
levoglucosan	55.8 ± 66.2	89.2 ± 92.4	12.1 ± 12.2	89.3 ± 69.3	89.4 ± 44.1
Light Absorption Properties					
MAE_{365} ($m^2\ g^{-1}$)[a]	0.77 ± 0.23	1.05 ± 0.21	0.59 ± 0.16	0.83 ± 0.10	0.83 ± 0.09
$AAE_{(300-400)}$	5.23 ± 0.52	5.18 ± 0.33	5.16 ± 0.68	5.31 ± 0.18	5.35 ± 0.40
f_{BrC} (%)	8.78 ± 3.74	12.1 ± 3.13	7.06 ± 3.49	10.1 ± 3.82	8.25 ± 2.04
Fluorescence Index					
F_f C1 (RU $m^2\ g^{-1}$)	2.34 ± 0.95	2.84 ± 0.59	1.78 ± 1.08	2.42 ± 0.51	2.91 ± 0.31
F_f C2 (RU $m^2\ g^{-1}$)	1.35 ± 0.43	1.83 ± 0.27	0.95 ± 0.24	1.44 ± 0.21	1.61 ± 0.14
F_f C3 (RU $m^2\ g^{-1}$)	0.87 ± 0.26	1.11 ± 0.30	0.68 ± 0.12	0.91 ± 0.15	0.98 ± 0.22

quality and visibility and affect ecosystems, agricultural productivity, and human health[7,8] as well as the Earth's radiative balance and hydrological cycle.[2,9]

The Kathmandu Valley in Nepal is located among the southern foothills of the Himalayas and frequently experiences accumulation of air pollutants due to high emissions and blocking by high mountains.[10,11] According to a recent study by Shakya et al.,[12] the 24 h average $PM_{2.5}$ concentration in winter ($76 \pm 18\ \mu g\ m^{-3}$) is approximately 3 times greater than the World Health Organization guideline.[7] Specifically, carbonaceous aerosols are the main components of $PM_{2.5}$ and contribute ~64% in mass.[13] Moreover, the organic carbon (OC) concentration is much higher than that of BC, with the OC/BC ratio ranging from 2 to 10 in Nepal,[13,14] highlighting the dominance of OC in aerosol composition.

Recently, a certain type of organics, termed brown carbon (BrC), has emerged as an important class of light-absorbing compounds, which exerts an increased light absorption capability from visible to ultraviolet wavelengths.[15−17] Modeling results show that the Kathmandu Valley is one of the most polluted regions in the world with respect to BrC[18] due to strong anthropogenic emissions.[19,20] However, most of the previous studies in Nepal have mainly focused on the abundance and climate effect of BC aerosol; there are relatively fewer reports on chemical characterization and optical properties of BrC. Moreover, most of these studies are limited to only specific seasons,[16,21] and long-term measurements of BrC are still sparse over the entire region of South Asia. Given the diverse emission sources and variable optical properties of BrC in the atmosphere,[15,16] more field observations are needed to assess its environmental effect over South Asia.

This study presents a 2 year measurement of water-soluble BrC (WS-BrC) and its optical properties in ambient aerosols (PM_{10}) collected from Godavari, located at the southeastern side of the Kathmandu Valley. We also used a fluorescence spectroscopy technique, a powerful and widely used tool to investigate the chemical properties and sources of organic matter,[22−24] to further reveal the possible chromophores in BrC. This study thus provides a comprehensive data set on seasonal variability in light absorption properties, chemical components, and sources of BrC, which may benefit the improvement of modeling and field observations in the future.

MATERIALS AND METHODS

Research Site and Aerosol Sampling. The PM_{10} samples were collected at the premises of the Training and Demonstration Site of Godavari of the International Centre for Integrated Mountain Development (ICIMOD) (27.59° N, 85.31° E, 1600 m asl; Figure S1). The site is located in the foothills of the Himalayas, about 15 km from the center of Kathmandu city, the capital of Nepal. Godavari has mixed aerosol composition from both local and regional emission sources; thus, it is a hot spot for air pollution observation in South Asia.[2] It serves as a natural laboratory to study aerosol chemistry and optical characteristics of local emissions as well as transport of aerosols.[14] A total of 53 PM_{10} samples were collected on prebaked quartz filter by a medium volume particulate sampler (URG-3000 ABC)[14] from April 12, 2012 to May 20, 2014. The classification of seasons and corresponding meteorological parameters (Table S1) as well as the detailed sampling protocol are provided in the Supporting Information.

Analysis of Carbonaceous Species, Major Ions, and Levoglucosan. Abundances of OC and elemental carbon (EC) were analyzed using a carbon analyzer (DRI model 2001), based on the IMPROVE-A thermal/optical reflectance protocol.[25] The detailed description of the analysis can be found elsewhere.[26] The water-soluble organic carbon (WSOC) was measured using a total carbon analyzer (TOC-L, Shimadzu,

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Environ. Sci. Technol. 2019, 53, 3471−3479

Japan). Major ions and levoglucosan were determined by a Dionex ICS 5000+ system (Thermo Fisher Scientific, U.S.).[27] The relevant details of the measurement, including detection limitations and reproducibility, of WSOC, major ions, and levoglucosan are presented in the Supporting Information.

Measurement of Light Absorption and Fluorescence Properties of BrC. Ultrapure water (18.2 MΩ·cm) was used to extract WS-BrC under sonication for 30 min for each sample. Then the light absorption of WS-BrC was measured by an ultraviolet−visible Spectrophotometer (UV-3600, Shimadzu, Japan) following the protocol described in Wu et al.[28] and the Supporting Information. Light absorption of WS-BrC was converted to light absorption coefficient (Abs) using optical length (l, 1 cm), volume of extraction (ml), and sampled air through the filter during the sampling (m^3). Because of weak absorption at wavelength 365 nm from other nonorganic compounds in water extraction,[29] the mass absorption efficiency (MAE_{365}) and light absorption coefficient (Abs_{365}) of WS-BrC at 365 nm were taken as the surrogate for BrC in this study. The MAE_{365} was derived by dividing the Abs_{365} values by corresponding WSOC concentrations. The specific equations used for calculation of Abs and MAE are described in detail in the Supporting Information.

The fluorescence properties of WS-BrC were characterized using a Horiba Fluoromax-4 fluorometer at room temperature.[22] The data were collected in S/R (signal/reference) mode and further calibrated by inner filter correction, Raman normalization, and blank subtraction. Moreover, the fluorescent intensities (F_o) were normalized against corresponding WSOC abundances in solution (C_s, $\mu g\ mL^{-1}$) and optical length (l, 1 cm) for each sample:

$$F_f = \frac{F_o}{l \cdot C_s} \quad (1)$$

Therefore, the final fluorescent intensity (F_f) was reported in units of $RU \cdot m^2\ g^{-1}$ (RU: Raman unit). The PARAFAC (parallel factor) model was used to explore the fluorescent components in WS-BrC based on the protocol established by Murphy et al.[30] The analytical uncertainty for fluorescence spectra was less than 2%.[22]

RESULTS AND DISCUSSION

Abundance and Seasonal Variation of Ions, OC, and EC. The annual mean concentrations of ion species show the following order: $SO_4^{2-} > Na^+ > NO_3^- > Ca^{2+} > NH_4^+ > K^+ > Cl^- > Mg^{2+}$ (Table 1). SO_4^{2-} is the dominant anion with annual concentration of $1.91 \pm 1.33\ \mu g\ m^{-3}$ followed by NO_3^-. SO_4^{2-} and NO_3^- show relatively higher concentrations during premonsoon and winter seasons, with values almost a factor of 2 higher than that in the monsoon season. In addition, SO_4^{2-} exhibits a strong correlation with NO_3^- ($r = 0.86$, $P < 0.01$, $n = 53$), indicating they may share similar emission sources. A consistent seasonal variation is also found in the case of NH_4^+, which has a strong linear relationship with SO_4^{2-} ($r = 0.83$, $P < 0.01$, $n = 53$). SO_4^{2-}, NO_3^-, and NH_4^+ are generally considered to be products of anthropogenic activities, such as fossil fuel (e.g., coal, gasoline, or diesel) combustion.[13,31] The high concentrations of anthropogenic ions during premonsoon and winter seasons are also coincident with the annual outbreak of widespread ABC over South Asia.[4,32]

The average annual abundance of OC is $2.93 \pm 1.63\ \mu g\ m^{-3}$, with the concentration in the monsoon nearly half of these in premonsoon and postmonsoon and two-thirds of that in winter (Table 1). The lower OC values may be due to the washout by rainfall and/or less emissions in monsoon season. The annual concentration of EC is $0.77 \pm 0.48\ \mu g\ m^{-3}$ and exhibits a seasonal variation similar to OC. The abundances of OC and EC are comparable to those previously reported at the same site.[14] Interestingly, the concentration of OC at Godavari is relatively lower than those from Nam Co (OC, $4.52 \pm 2.07\ \mu g\ m^{-3}$; EC, $0.18 \pm 0.10\ \mu g\ m^{-3}$), central Tibetan Plateau (TP),[33] but the EC abundance is considerably higher. This may demonstrate Godavari suffers more air pollution from primary emissions, because EC mainly derives from incomplete combustion of biomass and fossil fuels.[34,35] However, OC and EC concentrations in this study are significantly lower than those from typical urban environments in South Asia, i.e., Delhi (OC, $26.7 \pm 9.2\ \mu g\ m^{-3}$; EC, $6.1 \pm 3.9\ \mu g\ m^{-3}$)[36] and Kanpur (OC, $25.8 \pm 16.1\ \mu g\ m^{-3}$; EC, $3.8 \pm 2.3\ \mu g\ m^{-3}$).[37] Nonetheless, OC and EC concentrations at Godavari are much higher than those observed at high-altitude sites, such as Nepal Climate Observatory-Pyramid (NCO-P, 5079 m a.s.l.; OC, 0.36−1.8 $\mu g\ m^{-3}$; EC, 0.02−0.36 $\mu g\ m^{-3}$), located in the southern Himalayan region.[38]

Optical Properties of BrC. The MAE_{365} shows a distinct seasonal trend with the lowest value ($0.59 \pm 0.16\ m^2\ g^{-1}$) in the monsoon season and the highest value in the premonsoon season ($1.05 \pm 0.21\ m^2\ g^{-1}$) (Table 1), demonstrating WS-BrC's light absorption capabilities can vary among seasons. In comparison to those over remote TP (Figure 1), the annual

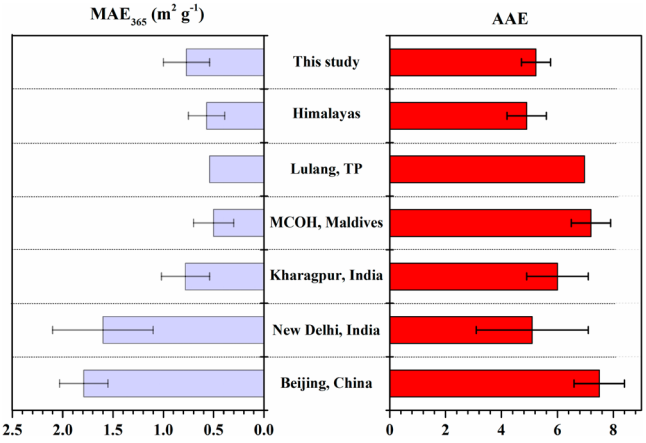

Figure 1. Comparisons of MAE (left column) and AAE (right column) values of WS-BrC at Godavari with those from Himalayas;[39] Lulang (southeast of TP);[40] MCOH (Maldives Climate Observatory at Hanimaadhoo);[41] Kharagpur (India);[44] New Delhi (India);[42] and Beijing, China.[43]

average MAE_{365} value at Godavari is almost 1.5 times those from the high Himalayas ($0.57\ m^2\ g^{-1}$)[39] and southeast of TP ($0.54\ m^2\ g^{-1}$).[40] It is also higher than that over a remote marine site (i.e., Maldives Climate Observatory at Hanimaadhoo, MCOH; $0.50\ m^2\ g^{-1}$) located at the outflow of Indian subcontinent.[41] However, the atmospheric WS-BrC at Godavari has weaker light absorption capability compared to those over megacities, e.g., New Delhi, India ($1.6\ m^2\ g^{-1}$)[42] and Beijing, China ($1.79\ m^2\ g^{-1}$).[43] Thus, atmospheric WS-BrC exhibits stronger light absorption capability in polluted environments than in remote and background regions with sparse population density and fewer anthropogenic emissions.

The absorption Ångström exponent (AAE) indicates the wavelength dependence of light absorption, which is a useful

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Environ. Sci. Technol. 2019, 53, 3471−3479

parameter to extrapolate the optical properties of BrC at unknown wavelength. In this study, the AAE values of BrC were calculated between wavelengths of 300 and 400 nm (for the specific calculation equation, see the Supporting Information) and are presented in Table 1. The AAE values range from 3.66 to 6.49 during the entire sampling period without obvious seasonal variations. In comparison to previous studies, AAE values at Godavari are comparable to those from sites in the IGP, namely New Delhi,[42] Kharagpur,[44] and Himalayas[39] (Figure 1). However, they are slightly lower than those from southeast of TP[40] and out-flow of Indian continent, i.e., MCOH.[41] The AAE value higher than one indicates the absorption increase as wavelength decrease. Therefore, the relatively lower AAE value at Godavari compared to those at remote sites (e.g., Lulang and MCOH) means that Godavari BrC has weak wavelength dependence. This may indicate the different formation or emission sources of BrC between polluted regions and remote sites. Furthermore, the AAE of BrC at Godavari is nearly 5 times higher than the typical values of freshly emitted BC (i.e., AAE = 1.0), which indicates that the atmospheric BrC has stronger absorption in the solar radiation over the ultraviolet wavelength.

Light Absorption of BrC Relative to Total Aerosol Absorption. BrC and BC are the two dominant light-absorbing carbonaceous species in atmospheric aerosols.[17,18,45] However, the relative contribution of BrC to total light absorption of aerosol (f_{BrC}) is still poorly quantified mainly because of diversity in emission sources and optical properties. In this study, we calculated the f_{BrC} due to WS-BrC over the wavelength ranging from 300 to 700 nm (refer to specific equation in the Supporting Information). We found that atmospheric BrC could annually contribute to 8.78 ± 3.74% of total absorption based on the measured MAE and $AAE_{(300-400)}$ values of BrC in this study as well as assuming an AAE_{BC} value of 1.0 for BC[45] and MAE_{BC} = 6.1 $m^2\ g^{-1}$.[46] The f_{BrC} exhibits obvious seasonal variation with the highest value in premonsoon season (12.1 ± 3.1%), which is nearly twice that in the monsoon season (7.06 ± 3.49%) (Table 1). Meanwhile, because of the strong wavelength dependence (as depicted by AAE values) in light absorption properties of BrC, the f_{BrC} value increases dramatically from 1.03 ± 0.60% at 700 nm to 25.3 ± 9.0% at 300 nm (Figure 2). The strong light absorption of BrC in the ultraviolet wavelengths could bring considerable influence on atmospheric chemical reactions by impacting the formation of ozone and other radicals (e.g., OH and HO_2).[17,47] It should also be noted that the measured absorption of BrC in extract may be underestimated by a factor of 2 than that in ambient conditions,[48] because the effect of size-distribution of BrC in absorption was not considered for the extraction protocol. Moreover, large amounts of BrC are insoluble in water but soluble in organic solvents (e.g., methanol) and have light absorption capability 3−4 times that of the water-soluble portion.[39,48] Therefore, the actual absorption capability of BrC in ambient conditions may be higher than the estimation of this study. Because of the limitation of measurement method, optical properties of water-insoluble brown carbon were not analyzed in this study.

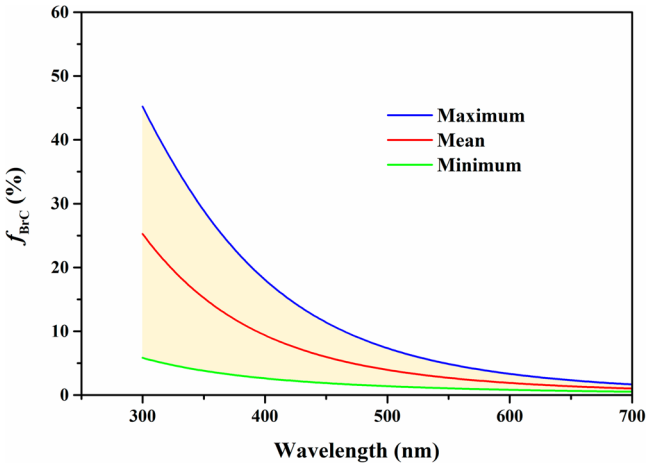

Figure 2. Light absorption of WS-BrC relative to total aerosol (f_{BrC}) at Godavari.

In addition, the MAE value of BC used in the calculation of f_{BrC} is 6.1 $m^2\ g^{-1}$, which is derived from previous research at a rural site (Jaduguda) in South Asia.[46] However, this value may not be a true representative of MAE of BC at Godavari because of its large variability. Therefore, we summarized MAE_{BC} values (Table S2) reported in South Asia and Tibetan Plateau. Based on the summary, the minimum (3.6 $m^2\ g^{-1}$, 365 nm)[49] and maximum (14.5 $m^2\ g^{-1}$, 678 nm)[46] of MAE_{BC} were employed to estimate the uncertainty in f_{BrC} calculation. The corresponding f_{BrC} values are 22.4% and 3.72%, respectively, with a decrease of ∼1.48% per unit increase in MAE_{BC} at 678 nm.

Composition of BrC Revealed by Fluorescence Technique. The light absorption properties of BrC are closely related with different chromophores within it, which are still poorly understood.[16,50,51] In this study, a fluorescence spectroscopy technique was used to investigate the chromophores in WS-BrC through the whole sampling period (for specific reasons, see the Supporting Information). Three different chromophores (i.e., C1, C2, and C3, Figure 3) are identified by PARAFAC model with the explained variance and core consistency values of 99.7% and 88.2%, respectively. The fluorescence intensities of these chromophores, calculated by eq 1, are listed in Table 1. Both of the chromophores, C1 (ex/em = 305 nm/410 nm, 250 nm/410 nm) and C2 (ex/em = 355 nm/480 nm, 250 nm/480 nm), have two distinct fluorescent peaks and belong to the HULIS (Humic-like substance) category.[52] C1 is the dominant chromophore with the contribution of 50.5 ± 5.2% to the total fluorescence intensity (Figure S2), followed by C2 (29.7 ± 3.4%). In addition, we also used an excitation−emission matrix (EEM) to understand the molecular structure and degree of unsaturation in these chromophores. Compared with the EEM spectrum of component C2, an obvious shift of excitation and emission maxima to the lower wavelengths can be found in C1, which indicates the presence of fewer aromatic and unsaturated bonds in C1.[53] According to previous studies, C1 is more likely to be produced by breakdown of macromolecules via photodegradation,[50] while the component C2 is related to condensation reactions that could result in more unsaturated chemical structures.[53]

Another important fluorescence component, identified as C3 (Figure 3), has ex/em peaks at 275/320 nm and is defined as a protein-like substance (PRLIS).[22,52] However, C3 has less contribution to the total fluorescence intensity (19.8 ± 4.1%). In addition, C3 exhibits only one excitation/emission maxima peak, which is different from those of C1 and C2. Recently, Mladenov et al.[54] and Matos et al.[53] have revealed that C3 could be derived from vehicle emissions, especially in aerosols impacted by anthropogenic activities. In our study, OC and EC are strongly correlated ($r > 0.86$) during the entire sampling period, indicating OC is mainly derived from primary combustion (further discussed in the next section). Meanwhile,

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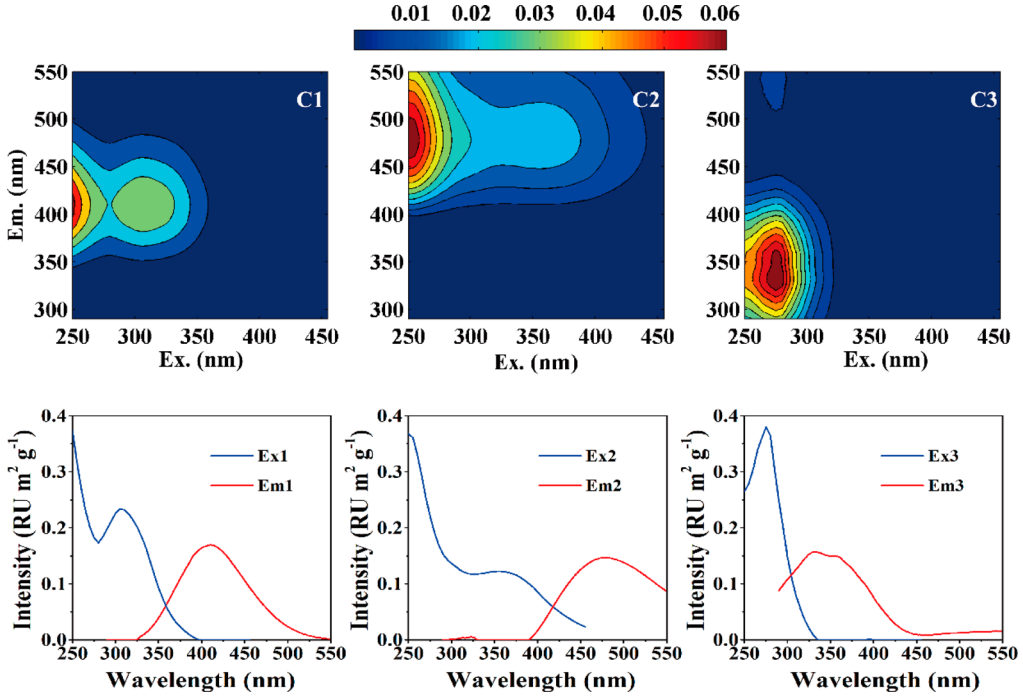

Figure 3. Three components (C1, C2, and C3) of WS-BrC identified by PARAFAC model in Godavari. The upper row is the three-dimensional EEM (excitation−emission matrix) of each component. The bottom row presents the fluorescent intensities of excitation (blue) and emission (red) of each component at peak emission and excitation wavelengths, respectively.

the EEM of C3 is highly overlapped with that of standard naphthalene (GBW(E)082494a, TMRM Standard Material Center, China, Figure S3), a typical compound released from fossil fuel combustion. Although biogenic emissions could also contribute to the chromophores in aerosols,[55] the excitation and emission maxima of bioaerosols tend to peak at longer emission wavelength (>340 nm)[56,57] compared to C3 and naphthalene. Therefore, we conclude, based on the above facts, that C3 at Godavari is more likely related with fossil fuel combustion.

From the seasonal patterns of ratios of fluorescence intensity between the three identified atmospheric chromophores, the ratio of chromophore C1 to C2 is relatively stable throughout the sampling period (Figure S4), which suggests that they might share same sources and/or have consistent relative emission factors. In contrast, the ratios of C3 to C1 and C2 are relatively higher during monsoon season compared to that in non-monsoon. This is reasonable because biomass burning activities (represented by C1 and C2)[47] mainly take place during nonmonsoon seasons and to a lesser extent in the monsoon season. However, vehicle emissions are relatively constant through the year, which makes them an important source of organic aerosols during the monsoon season.[58] Thus, atmospheric WS-BrC at Godavari are complex organic mixtures composed of HULIS and PRLIS.

Origins of BrC. EC is mainly derived from incomplete combustion of biomass and fossil fuels.[14,35] The refractory nature of EC makes it an important and specific tracer for combustion emissions.[34] In this study, OC and EC are significantly correlated during the entire sampling period ($r \geq 0.86$, Figure 4a), highlighting the contribution of primary emissions to OC and EC. The Abs_{365} is usually taken as proxy of BrC in extraction.[42,43,59] Therefore, a good linear correlation between Abs_{365} and EC ($r = 0.69$, $P < 0.01$, Figure 4b) indicates that combustion emissions are important sources of BrC in both nonmonsoon and monsoon seasons.

Levoglucosan is a unique tracer of fresh biomass burning emissions, because it is monosaccharide derivative which is produced only from the breakdown of cellulose during biomass burning.[60] Therefore, relationships between Abs_{365} and levoglucosan are further analyzed during nonmonsoon seasons. A linear relationship between them ($r = 0.71$, $P < 0.01$, Figure 4c) suggests that WS-BrC could be derived from fresh biomass burning emissions. The strong relationship between Abs_{365} and another biomass burning tracer (i.e., K^+) ($r = 0.79$, $P < 0.01$, Figure 4d) during nonmonsoon seasons further supports this observation. This finding is also supported by the densely distributed active fire spots obtained from MODIS and seven-day air mass backward trajectories during nonmonsoon seasons (Figure S5). In addition, biomass burning has been recently reported to be important source of ambient BrC in Nepal, with an emission factor of 8.59 ± 5.62 g kg^{-1} for household hardwood burning and 10.9 ± 6.5 g kg^{-1} for crop residue burning, which are almost 40 and 10 times higher than that of BC,[20] respectively.

In monsoon season, levoglucosan concentration is nearly a factor of 9 lower than those in nonmonsoon seasons (Table 1). In addition, the absence of linear relationship with Abs_{365} during monsoon season (Figure 4c) indicates no influences from biomass burning emissions. This is reasonable because, in South Asia, biomass burning mainly occurs during premonsoon from wheat residue burning and forest fires, postmonsoon from paddy residue burning, and winter from heating by wood but less in monsoon season.[58] Therefore, in monsoon season, the most likely primary emission sources of BrC may be fossil fuel combustion (FFC), e.g., vehicle emissions and coal usage. NO_3^- and SO_4^{2-} are the typical oxidation productions from precursors NOx and SO_2, respectively, which are generally related with the emissions from FFC.[31,61] In Godavari aerosols, the NO_3^- ($r = 0.66$, $P < 0.01$, Figure 4e) and SO_4^{2-} ($r = 0.75$, $P < 0.01$, Figure 4f) are moderate or well-correlated with Abs_{365} during monsoon

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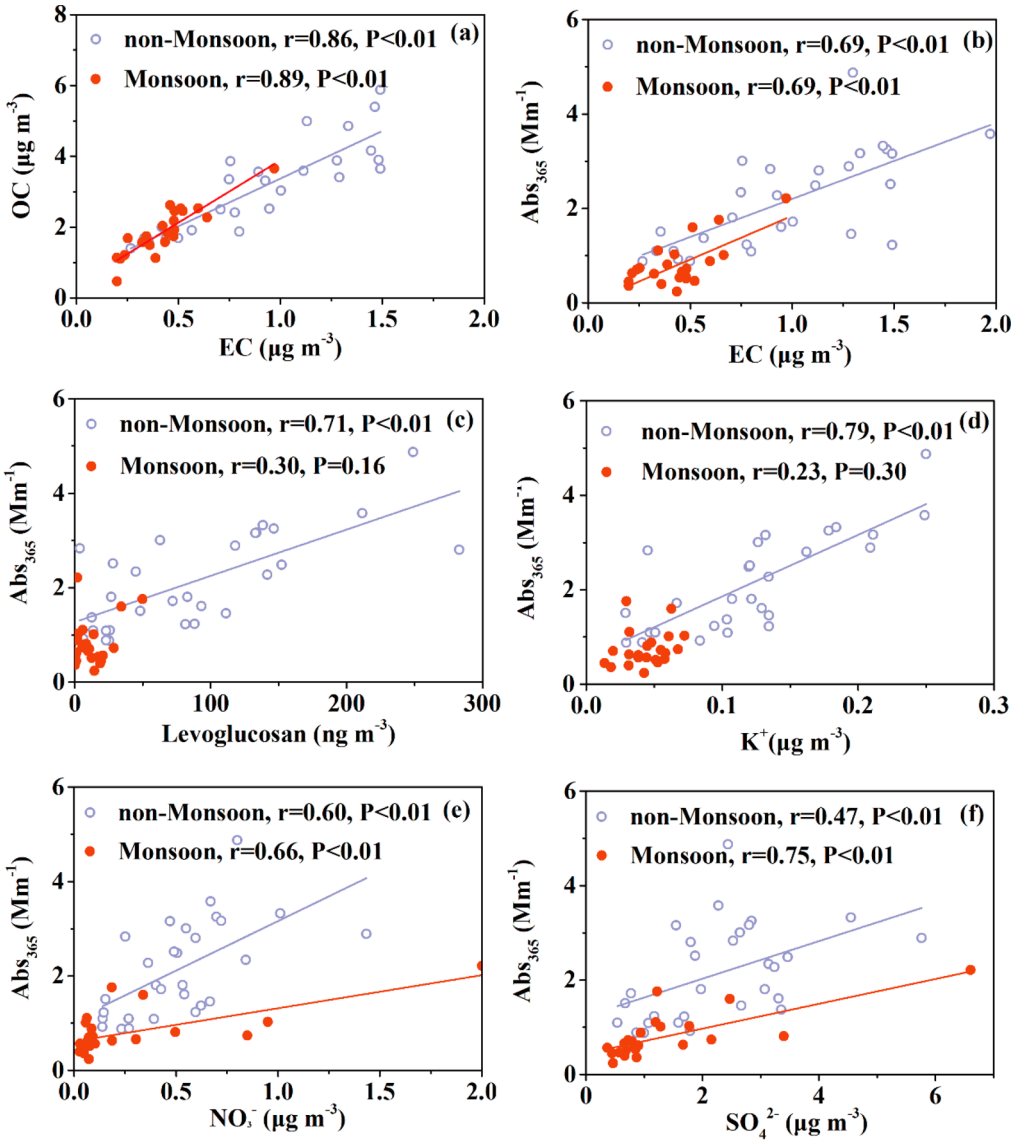

Figure 4. Linear correlations of OC with EC (a) as well as Abs_{365} with EC (b), levoglucosan (c), K^+ (d), NO_3^- (e), and SO_4^{2-} (f) in PM_{10} samples from Godavari.

season, which indicates the possible emissions of WS-BrC from FFC. The primary emissions of BrC from FFC have also been reported in Central Indo-Gangetic Plain during the late evening to early morning when emissions from FFC are prevalent.[59] Godavari is only 15 km from the center of Kathmandu, the capital city of Nepal, which makes it vulnerable to emissions from FFC. Furthermore, vehicle emission is recognized as the second largest source for organic aerosol after biomass burning emission in South Asia and contributes to 37 ± 20% of $PM_{2.5}$ mass loading.[31,58] As discussed above, the fossil fuel combustion-related PRLIS in WS-BrC also shows relatively higher ratio to the other two chromophores in monsoon season (Figure S4), which further supports that BrC may be impacted by FFC.

IMPLICATIONS AND RECOMMENDATIONS

This study reported interannual and seasonal variations in light absorption properties and sources of water-soluble BrC (WS-BrC) in PM_{10} samples from Godavari, Nepal from April 2012 to May 2014. The results highlight that the MAE values of WS-BrC at Godavari lie between those of remote and urban/polluted sites, and thus, it is necessary to characterize BrC's sources and optical properties on temporal and spatial scales. Furthermore, this study provides new insights into chemical composition of WS-BrC using fluorescence spectroscopy techniques. The results indicate that WS-BrC consists of both HULIS and PRLIS, which may benefit the understanding of the relationship between BrC's molecular and optical properties. It should be noted that uncertainties still exist in using fluorescence spectroscopy techniques to characterize sources of BrC because of a lack of a standard EEM profile for each component in BrC, and more studies are needed in the future, especially regarding source-specific research (e.g., biomass burning, bioaerosols, and fossil-fuel emissions). Our study also confirms that biomass burning emissions are the dominant source of carbonaceous aerosols and BrC at Godavari, Nepal throughout the year, except monsoon season. Therefore, mitigation of biomass burning emissions in Nepal and neighboring areas is an urgent need for these regions.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b00596.

Detailed methods; meteorological data; MAE_{BC} in previous studies; map of sampling site; contribution of chromophores to total fluorescence; intensity ratios between chromophores; EEM of naphthene; air-mass trajectories and distribution of fire spots (PDF)

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The authors declare no competing financial interest.

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