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1 **Brown carbon in atmospheric outflow from the Indo-Gangetic Plain:**
2 **Mass absorption efficiency and temporal variability**

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36 **Abstract**

37 The simultaneous measurements of brown carbon (BrC) and elemental carbon (EC) are made
38 in ambient aerosols (PM_{2.5}), collected from a site in north-east India during November'09-
39 March'10, representing the atmospheric outflow from the Indo-Gangetic Plain (IGP) to the
40 Bay of Bengal (BoB). The absorption coefficient of BrC (b_{abs}), assessed from water-soluble
41 organic carbon (WSOC) at 365 nm, varies from 2 to 21 Mm⁻¹ and exhibits significant linear
42 relationship ($P < 0.05$) with WSOC concentration (3 – 29 $\mu\text{g m}^{-3}$). The angstrom exponent (α :
43 8.3 ± 2.6 , where $b_{abs} \approx \lambda^{-\alpha}$) is consistent with that reported for humic-like substances
44 (HULIS) from biomass burning emissions (BBE). The impact of BBE is also discernible
45 from mass ratios of nss-K⁺/EC (0.2 – 1.4) and OC/EC (3.4 – 11.5). The mass fraction of
46 WSOC (10 – 23 %) in PM_{2.5} and mass absorption efficiency of BrC ($\sigma_{abs-BrC}$: 0.5 – 1.2 m² g⁻¹)
47 bring to focus the significance of brown carbon in atmospheric radiative forcing due to
48 anthropogenic aerosols over the Indo-Gangetic Plain.

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50 **Words: 161**

51

52 1. Introduction

53 The light absorbing species of atmospheric particulate matter are gaining considerable
54 interest in recent years owing to their significant role in regional as well as global climate
55 change [Fuzzi *et al.*, 2006]. Although several studies have evaluated their impact on the
56 atmospheric environment, uncertainties associated with the regional scenario are still large
57 and demand further detailed assessment. One of the possible sources of uncertainty could be
58 attributed to poor characterization of organic aerosols in the atmospheric particulate matter
59 [Huebert and Charlson, 2000]. In this context, detailed information on sources, size-
60 distribution and compositional changes during transport of carbonaceous aerosols is essential
61 for assessing their atmospheric radiative forcing.

62 Among the carbonaceous species, two distinct forms of carbon [elemental or black
63 carbon (EC or BC) and brown carbon (BrC)] are of particular interest due to their light
64 absorbing properties. The EC absorbs solar radiation in the visible region [Bond, 2001; Bond
65 *et al.*, 2013], whereas BrC shows prominent absorption in the near UV-region [Alexander *et al.*,
66 2008; Andreae and Gelencsér, 2006; Hecobian *et al.*, 2010; Lack *et al.*, 2012; Liu *et al.*,
67 2014; Lukács *et al.*, 2007; Yang *et al.*, 2009]. However, real time data on absorption
68 properties of BrC are rather limited. The omnipresence of BrC in rural, urban and remote
69 environments has been emphasized by Graber and Rudich, [2006] suggesting the need for its
70 adequate representation in climate model simulations.

71 The presence of brown carbon is documented based on the absorption spectra of
72 aqueous extracts of ambient aerosols [Havers *et al.*, 1998; Kirchstetter *et al.*, 2004; Zhang *et al.*,
73 2013]. Furthermore, its abundance has been studied using aerosol light absorption
74 measurements near to the specific combustion sources [Bond, 2001]. A significant overlap in
75 the spectral properties of BrC (assessed from water-soluble organic carbon, WSOC) and
76 humic-like substances (HULIS), derived from the biomass burning emissions, has been
77 reported during the LBA-SMOCC (Large scale Biosphere atmosphere experiment in
78 Amazonia – SMOke aerosols, Clouds, rainfall and Climate) Experiment [Hoffer *et al.*, 2006].
79 The emission from biomass burning is recognized as a primary source of HULIS and of
80 brown carbon [Andreae and Gelencsér, 2006; Park *et al.*, 2010]. It has been also suggested
81 that tar balls from smoldering combustion of bio-fuels (or biomass) are a significant source of
82 atmospheric brown carbon [Chakrabarty *et al.*, 2010]. In addition to emissions from specific
83 sources, formation of brown carbon through heterogeneous reactions of secondary organic
84 aerosols (emitted from biogenic and anthropogenic precursors like terpenes) with ammonia is
85 also documented by Updyke *et al.*, [2012].

86 Uncertainties in atmospheric radiative forcing estimates continue to cause major
87 debate (IPCC-2007), largely arising from the poor representation of the organic carbon
88 fraction in atmospheric aerosols [Forster, 2007]. More recently, Feng et al., [2013] have
89 emphasized the importance of brown carbon absorption in aerosol radiative forcing (~ 0.25
90 W.m^{-2}) using a general circulation model coupled to a chemical transport model. Their
91 results suggest that atmospheric brown carbon could contribute nearly 19 % of the total
92 absorption by anthropogenic aerosols; whereas 71 % is attributable to that from BC (or EC)
93 and ~ 9 % is from sulphates and coatings of non absorbing organic compounds on soot
94 carbon [Feng et al., 2013]. Furthermore, their study also highlights an overall mismatch
95 between observations and model results for the simulated aerosol radiative forcing and
96 suggests the need to incorporate absorption due to brown carbon in the global models. In this
97 study, we have made simultaneous measurements of BrC and EC in ambient aerosols ($\text{PM}_{2.5}$)
98 collected from a downwind sampling site in the Indo-Gangetic Plain, representing the
99 atmospheric outflow. We have also assessed the mass absorption efficiency of BrC from
100 water-extracts of aerosols.

101 **2. Materials and Methods**

102 *2.1. Site description and meteorology*

103 The Indo-Gangetic Plain (IGP), situated in the northern part of the Indian peninsula,
104 generates a host of airborne pollutants. Fossil-fuel combustion, biomass burning (mainly
105 agricultural crop-residue) and bio-fuel (wood) are some of the characteristic sources of
106 pollutants. The impact of anthropogenic aerosols on oceanic regions located downwind of
107 pollution sources in the Indo-Gangetic Plain has been well documented through field
108 experiments such as INDOEX (Ramanathan et al., 2001; Lelieveld et al, 2001; Mayol-
109 Bracero et al., 2002) and ICARB (Sudheer and Sarin, 2008; Sarin et al., 2011; Kumar et al.,
110 2008; Srinivas and Sarin, 2012; Srinivas and Sarin, 2013). Under favourable meteorological
111 conditions (shallow boundary height and north-easterly/westerly winds), the downwind
112 transport of pollutants from the IGP to the Bay of Bengal is a conspicuous feature during the
113 wintertime (from December to March).

114 Ambient aerosols ($\text{PM}_{2.5} \approx$ particulate matter whose aerodynamic diameter is less than
115 $2.5 \mu\text{m}$) were collected during November'09 - March'10 from a downwind site (Kharagpur:
116 22.3°N , 87.3°E) in the Indo-Gangetic Plain (IGP). During the wintertime, the sampling site
117 is influenced by long-range transport of pollutants from upwind sources in the IGP. Surface
118 level meteorological parameters were obtained from NCEP (National Centre for

119 Environmental Predictions)-NCAR reanalysis data sets. The winds were predominantly
120 north-easterly (0.5 to 3.8 m s^{-1}), and relative humidity and surface temperature varied from 38
121 to 58 % and 21.5 to 30.4 $^{\circ}\text{C}$, respectively. The air mass back trajectories (7-day AMBTs),
122 computed from the NOAA website using hybrid single particle Lagrangian integrated
123 trajectory model (HYSPLIT, version 4.0; [Draxler, 2002]), suggest transport of pollutants
124 from the upwind source regions.

125 2.2. Methodology

126 Aerosol samples ($\text{PM}_{2.5}$, $N = 46$) were collected on pre-combusted tisuquartz filters
127 (PALLFLEX[®]TM) using a high-volume (~ 1.13 m^3 min^{-1}) air sampler (HVS- $\text{PM}_{2.5}$, Thermo-
128 Anderson Inc.). Most of the samples ($N = 42$) were collected over a period of ~ 22 hrs. After
129 collection, all samples were stored in a deep freezer at -19°C until the time of their chemical
130 analysis. For all chemical analyses, sample filters were handled under a clean laminar flow
131 bench (Class – 1000). The absorption spectra of aqueous extracts of aerosols were measured
132 on a UV-Vis Spectrophotometer (Model: USB-4000) coupled to a 2 m long waveguide
133 capillary column. Deuterium and tungsten halogen lamps (DT-Mini-2, Ocean Optics) are
134 used as a light source. Liquid samples were injected via capillary injector into Liquid-core
135 Waveguide Capillary Cell (LWCC from World Precision Instrument, Sarasota, FL), with an
136 internal volume of 250 μL . Absorption spectra were recorded over a wavelength range of 300
137 to 800 nm with an Ocean Optics Spectra-Suite data acquisition software system (Ocean
138 Optics, Dunedin, FL). Simultaneously, concentrations of organic and elemental carbon (OC
139 and EC) were also measured by thermo-optical transmittance method using Sunset-Lab EC-
140 OC Analyzer. Water-soluble organic carbon (WSOC) was measured on total organic carbon
141 analyzer (model: Shimadzu, TOC-5000a). Along with the samples, filter (and field) blanks
142 were also analyzed for OC and WSOC. The contribution from blank signals was found to
143 vary from 4 to 29 % and 0.1 to 14 % of the maximum and minimum signals measured for OC
144 and WSOC, respectively. Based on the repeat measurements, the overall analytical
145 reproducibility was better than 5 % for OC and WSOC, whereas it was less than 10 % for EC.
146 For further details regarding the experimental protocol and method detection limits for OC,
147 EC and WSOC, reference is made to our earlier publications [Ram *et al.*, 2010; Rengarajan *et*
148 *al.*, 2007].

149 2.3. Absorption coefficient

150 In this study, absorption spectra of water extracts of aerosols (representing bulk of the
151 water-soluble organic carbon) have been used to assess the absorption coefficient (b_{abs})
152 similar to that described by Hecobian et al., [2010] and is expressed as:

$$153 \quad b_{abs} = (A_{365} - A_{700}) \times (V_{ext} \times 8) \times \ln(10) / (V_{aero} \times L)$$

154 In this equation, A_{365} and A_{700} correspond to measured absorbance at 365 and 700 nm,
155 respectively. V_{ext} refers to volume of the aqueous extract (~ 50 ml) in which $1/8^{th}$ portion of
156 aerosol filter is extracted and factor '8' is used to estimate the absorption signal for the full
157 filter. V_{aero} corresponds to volume of air filtered ($\sim 1400 \text{ m}^3 = 1.4 \times 10^9$ ml) through quartz
158 substrates and L is the path length of the cell (i.e., ~ 2 m). We have used absorbance at 365 nm
159 to estimate the absorption coefficient (b_{abs}) of light absorbing water-soluble organic carbon
160 (also referred as BrC). It is relevant to state that light absorption by OC in solvent extracts is
161 underestimated by a factor of two than that of particulate OC [Liu et al., 2013]. Earlier
162 studies have investigated the association of brown carbon with humic like substances in
163 ambient aerosols [Lukács et al., 2007 and references therein]; however, separation of these
164 compounds from the aqueous filter extracts is rather complex and experimentally tedious.
165 Based on the replicate analyses of samples ($N = 15$), reproducibility of the absorbance signal
166 was ascertained to be within 5 %. The contribution from filter blank to sample signal varied
167 from 0.13 to 1.5 % of the maximum and minimum signal measured on LWCC. The error
168 propagation, involving sample collection, extraction and measurement of WSOC, yield an
169 analytical uncertainty of no more than 19 % in the mass absorption efficiency of light
170 absorbing WSOC.

171 **3. Results and Discussion**

172 *3.1. Angstrom exponent (α) and Mass Absorption efficiency (MAE or σ_{abs})*

173 The absorption coefficient of an aerosol in the ambient atmosphere is a function of
174 wavelength of incident light, and is described by a power law. The power exponent of
175 wavelength is referred as Angstrom exponent (α) of a particular species and its magnitude
176 depends on aerosol size and composition. Using a similar analogy, Hecobian et al., [2010]
177 have described absorption coefficient of a light absorbing species in the aqueous extracts
178 which is dependent on wavelength, and is given by the following relation.

$$179 \quad b_{abs} \sim \lambda^{-\alpha}$$

$$180 \quad b_{abs} \approx K \cdot \lambda^{-\alpha}; K = \text{constant}$$

181 Here b_{abs} is expressed in units of M m^{-1} (or 10^{-6} m^{-1}) and α denotes Angstrom Exponent of
182 light absorbing component of water-soluble organic matter, referred here as Brown Carbon

183 (BrC). A value of ~ 7 for α has been reported for humic like substances extracted from
184 aerosols, sampled from the Amazonian forest fires [Hoffer *et al.*, 2006]. Likewise, smoke
185 from smouldering of various bio-fuels has a typical value for α between 7 and 16 [Chen and
186 Bond, 2010]. Likewise, in an earlier study by Bones *et al.*, [2010], have estimated α as ~ 7
187 for freshly formed secondary organic aerosols (SOAs) compared to that observed for aged
188 SOAs (~ 4.7). More recently, Hecobian *et al.*, [2010] have reported that α ranges between \sim
189 6 and 8 for biomass burning aerosols. However, their study also indicates that significant
190 differences are observed between the biomass burning and non-burning periods.

191 In this study, absorption spectra of aqueous extracts were recorded between 300 nm
192 and 800 nm for each sample. The absorbance at 365 nm (in near UV region) relative to 700
193 nm was obtained for all samples in order to estimate b_{abs} . Earlier studies have documented
194 strong UV-absorption of water-soluble BrC at 350 to 370 nm [Hecobian *et al.*, 2010 and
195 references therein]. Therefore, we attribute the prominent absorption at this wavelength range
196 to the presence of brown carbon (BrC), in order to estimate the absorption coefficient of
197 water-soluble organic carbon ($b_{abs-365}$). It is noteworthy that a significant linear relationship
198 (slope = 0.70; $R^2 = 0.54$; P-value < 0.05) is observed between ($b_{abs-365}$) and WSOC (Fig.1);
199 validating dominant absorption due to BrC in the water-extracts. Furthermore, co-variability
200 in the temporal trend between concentration of WSOC and non-sea-salt-potassium ion (nss-
201 K^+), suggests their common source from biomass burning emissions (Fig.2a). A significant
202 correlation between WSOC and OC (P-value < 0.05) with an average WSOC/OC ratio of
203 0.52 ± 0.10 has been reported during the study period [Srinivas and Sarin, 2013b]. It is, thus,
204 inferred that BrC contribute significantly to the mass concentration of particulate organic
205 carbon in the atmospheric outflow from the IGP.

206 Further, we have calculated b_{abs} at varying wavelength (from 300 to 700 nm)
207 relative to 700 nm. The b_{abs} shows wavelength dependency as $\lambda^{-\alpha}$, where α refers to Angstrom
208 exponent (see supporting figure, Fig. S1). It is evident that the absorption signal of WSOC
209 shows a sharp increase with decrease in wavelength (i.e., $b_{abs} \sim \lambda^{-6}$; See Table S1 for
210 goodness of fit parameters for the power relation) and, thus, confirming the presence of
211 brown carbon in aqueous extracts. This is consistent with earlier observations demonstrating
212 the similar spectral absorption characteristics of the ambient particulate matter [Andreae and
213 Gelencsér, 2006; Cheng *et al.*, 2011; Hecobian *et al.*, 2010; Lukacs *et al.*, 2007]. The
214 angstrom exponent (α) of light absorbing WSOC in the IGP-outflow varied from 4.5 to 9.9
215 (Av: 6.0 ± 1.1). However, for most of the sampling days, α values are greater than 6 (Fig.2b).

216 The impact of biomass burning emissions is also evident through other diagnostic ratios (high
217 OC/EC: 7.0 ± 2.0 and nss-K⁺/EC: 0.49 ± 0.21) in the IGP-outflow [*Srinivas and Sarin,*
218 2013b]. As stated above, for HULIS type compounds from biomass burning emissions and
219 bio-fuel emissions, the angstrom exponent is reported to be greater than 6. Recently, Cheng
220 et al., [2011] have estimated \AA_p value of ~ 7 in the aqueous extracts of aerosols from the
221 Beijing outflow and attributed it to the presence of Brown Carbon. Therefore, the major
222 source of BrC over the Indo-Gangetic Plain is attributed to biomass and bio-fuel burning
223 during the study period. A more recent study by Zhang et al., [2013] had demonstrated the
224 significant differences in the angstrom exponent of light absorbing WSOC between the
225 offline filter-based aqueous ($\sim 7.6 \pm 0.5$) and methanol ($\sim 4.8 \pm 0.5$) extracts with those
226 obtained through online measurements using PILS ($\sim 3.2 \pm 1.2$). However, the angstrom
227 exponent of light absorbing WSOC measured at 365 nm (this study) is consistent with that
228 reported for biomass burning emissions (See Table 1).

229 We have also estimated the mass absorption efficiency of light absorbing water-
230 soluble organics as follows.

231
$$\text{MAE of BrC} = \sigma_{abs-BrC} (m^2 g^{-1}) = (b_{abs-365})/WSOC$$

232 In this study, the $\sigma_{abs-BrC}$ varied between 0.21 and 1.46 (Av: 0.78 ± 0.24) $m^2 g^{-1}$ in the
233 atmospheric outflow from Indo-Gangetic Plain (Fig.2b). The slope of regression line (0.70
234 $m^2 g^{-1}$) in Fig. 1 also provides a robust estimate of mass absorption efficiency of BrC (σ_{abs-}
235 BrC) in the atmospheric outflow from the Indo-Gangetic Plain. Lack et al., (2012) have
236 reported a $\sigma_{abs-BrC}$ of $0.83 \pm 0.42 m^2 g^{-1}$ (measured at 404 nm using multi-wavelength Photo
237 Acoustic measurements), in aerosols collected from the intense biomass burning emissions.
238 Likewise, Hecobian et al., (2010) had reported a $\sigma_{abs-BrC}$ of ~ 0.60 and $0.58 m^2 g^{-1}$ for urban
239 and rural sites, respectively (those characterized by high concentrations of levoglucosan). It
240 is noteworthy that the mass absorption efficiency of BrC ($\sigma_{abs-BrC}$) documented for the IGP-
241 outflow is consistent with that for biomass burning emissions reported in the literature
242 [*Hoffer et al., 2006; Lack et al., 2012; Yang et al., 2009*]; as summarized in Table 1.

243 3.2. Source apportionment

244 The light absorbing organics in the atmosphere can originate either from primary or
245 secondary processes. Incomplete combustion of biomass/bio-fuel burning and smoldering
246 combustion processes are suggested as significant primary sources of brown carbon
247 [*Chakrabarty et al., 2010; Chakrabarty et al., 2013; Cheng et al., 2011; Hecobian et al.,*
248 2010; *Hoffer et al., 2006; Kirchstetter and Thatcher, 2012; Lukacs et al., 2007*]. However,

249 recent studies have documented the possible formation of atmospheric brown carbon through
250 secondary processes such as heterogeneous reactions of isoprene in the presence of sulphuric
251 acid vapour [Limbeck *et al.*, 2003]. Also, through multiphase chemistry of lignin type of
252 compounds in the cloud water [Gelencser *et al.*, 2003; Gelencser and Varga, 2005; Nguyen *et al.*,
253 *et al.*, 2010; Nguyen *et al.*, 2012], low temperature combustion of lignin pyrolysis products
254 [Sareen *et al.*, 2010] and reaction of secondary organic aerosols with NH₃ [Nguyen *et al.*,
255 2013; Updyke *et al.*, 2012]. Therefore, in order to assess the sources of atmospheric brown
256 carbon, primary and secondary organic carbon fractions were estimated for the sampling days
257 using EC-tracer method [Ram and Sarin, 2010; 2011].

258 A notable feature of the data is seen as co-variability in the temporal trends of both
259 primary and secondary organic carbon fractions with WSOC (See Supporting Fig. S2). The
260 fractional contribution of OC_{sec} in total organic carbon (OC) varied from 11 to 70 % (Av: 50
261 ± 15 %). Although analytical uncertainty is large in the assessment of secondary organic
262 carbon (OC_{sec}) based on EC-tracer method, it can be inferred that OC_{sec} contributes
263 significantly to the total OC in the IGP-outflow during November'09-March'10. It is
264 noteworthy that the mass absorption coefficient of light absorbing WSOC ($b_{\text{abs-365}}$) shows a
265 positive correlation with estimated abundance of secondary organic carbon (OC_{sec}) and nss-
266 K⁺ (Fig.3). As stated earlier, OC_{sec} can be sourced from the atmospheric reactions of
267 precursor VOCs produced from either biomass burning emissions or from fossil-fuel
268 combustion sources. A recent study by Zhang *et al.*, [2011] had shown significant differences
269 in the light absorption properties of water-soluble organic carbon in aerosols derived from
270 fossil-fuel combustion (wherein absorption signal measured at 365 nm is relatively 4 to 6
271 times higher) and that from biomass burning emissions collected over Los Angeles and
272 Georgia, respectively. Furthermore, their study highlighted the enhancement in light
273 absorption by secondary aerosols of nitro aromatics from fossil-fuel combustion sources over
274 Los Angeles. In the IGP-outflow, temporal variability in the mass absorption efficiency of
275 light absorbing WSOC (measured at 365 nm) is not significant during the study period
276 (November'09- March'10) and is consistent with that reported for biomass burning emission
277 (Table 1). Based on these observations, a likely explanation could be that biogenic secondary
278 organic aerosols contribute significantly to light absorbing organics over the Indo-Gangetic
279 Plain.

280 In a laboratory study, Nguyen *et al.*, [2013] have documented the formation of light
281 absorbing organic species based on reaction of ketolimononaldehyde (C₉H₁₄O₃), a SOA
282 formed by the ozonolysis of limonene (C₁₀H₆), with amino acids (e.g. glycine) and NH₄⁺. A

283 similar study by Saleh et al., [2013] had provided the first direct evidence for the formation of
284 light absorbing organics through secondary processes in the aged biomass/bio-fuel burning
285 aerosols. In this study, we have not investigated the atmospheric reactions of SOAs at the
286 molecular level. Nevertheless, in view of significant linear relationship among OC_{sec} , mass
287 absorption efficiency of WSOC ($\sigma_{abs-WSOC}$ at 365 nm) and $nss-K^+$ (a proxy for biomass
288 burning emissions), it can be inferred that secondary aerosol formation contribute
289 significantly to atmospheric brown carbon.

290 Long ago, it was suggested by Andr ea [1983] that the association of potassium with
291 soot carbon (or EC) in ambient aerosols signifies the importance of biomass/bio-fuel burning
292 emissions. Since then, the mass ratio of $nss-K^+/EC$ in fine mode aerosols has been used as a
293 proxy for assessing the qualitative contribution of biomass burning emissions [*Andreae et al.*,
294 1984; *Andreae and Merlet*, 2001; *Flament et al.*, 2011; *Guazzotti et al.*, 2003; *Ram and Sarin*,
295 2010; *Srinivas et al.*, 2011; *Wang et al.*, 2005]. It is noteworthy that the $nss-K^+/EC$ ratio in
296 the IGP-outflow during November'09-March'10 (Figure 4) is consistent with that reported
297 for biomass/bio-fuel burning emissions. Based on radiocarbon data, Gustaffson et al., [2009]
298 highlighted the significance of residential bio-fuel and agricultural crop-residue burning
299 emissions from the IGP as a major source of carbonaceous aerosols over the south Asia
300 (particular in the Northern India). In addition, it has also been suggested that biomass burning
301 emissions contribute significantly to atmospheric water-soluble (primary and secondary)
302 organics [*Kawamura et al.*, 2013; *Sciare et al.*, 2008; *Timonen et al.*, 2012]. However, the
303 volatile organic compounds (VOCs) emitted from the biomass/bio-fuel burning also
304 contribute to atmospheric water-soluble organics through photochemical aging during the
305 long-range atmospheric transport. In this regard, several studies have documented the high
306 WSOC/OC and OC_{sec}/OC ratios from the biomass burning emissions [*Agarwal et al.*, 2010;
307 *Favez et al.*, 2009; *Sciare et al.*, 2008].

308 As stated earlier, the study site is influenced by long-range transport of bio-mass/bio-
309 fuel burning emissions from the upwind source regions in the IGP. We have investigated the
310 temporal variability of WSOC/OC, $nss-K^+/EC$, $\sigma_{abs-BrC}$ and OC_{sec}/OC (Fig.4). No significant
311 ($P > 0.05$) differences are observed for the diagnostic mass ratio of $nss-K^+/EC$ during the
312 sampling period (See Table S2). A large spread in the $nss-K^+/EC$ ratio for biomass burning
313 emissions has been reported [*Mayol-Bracero et al.*, 2002; *Novakov et al.*, 2000] compared to
314 that for fossil-fuel combustion. The near constancy of monthly-mean $nss-K^+/EC$ ratio
315 overlaps with the reported range for BBEs. It is also noteworthy that near constancy of mass

316 absorption efficiency of light absorbing WSOC ($\sigma_{\text{abs-WSOC}}$) is comparable with that
317 documented for biomass burning emissions [Cheng *et al.*, 2011; Hecobian *et al.*, 2010;
318 Kirillova *et al.*, 2014].

319 A near constancy of nss-K⁺/EC and mass absorption efficiency of light absorbing
320 water-soluble carbon ($\sigma_{\text{abs-WSOC}}$) in the IGP-outflow to the Bay of Bengal (Supporting
321 information, one-way ANOVA results given in Table S2) indicate biomass burning emissions
322 as a significant source of brown carbon over the study site. Several studies have suggested
323 that biomass burning emissions contribute significantly to atmospheric water-soluble
324 organics [Falkovich *et al.*, 2005; Graham *et al.*, 2002; Mayol-Bracero *et al.*, 2002; Saarikoski
325 *et al.*, 2007; Sciare *et al.*, 2008; Timonen *et al.*, 2012]. Although WSOC/OC ratio exhibits
326 small variability during the winter months (December-February; $\text{Av} \pm \text{Sd}$: 0.50 ± 0.13 ; $P >$
327 0.05); lower (0.41 ± 0.04) and higher (0.70 ± 0.18) contribution of WSOC to total OC is
328 noteworthy in early and late sampling days in November and March. The relatively high
329 mass ratio of WSOC/OC in the early spring-intermonsoon (in March) can be explained by the
330 relative increase in solar radiation enhancing the photochemical aging of secondary organic
331 aerosols over the IGP. Similar to WSOC/OC, the fractional contribution of secondary organic
332 carbon in total OC during winter months show small variability compared to that in preceding
333 sampling days (in March, Figure 4). The relative decrease in percentage contribution of OC_{sec}
334 to total OC mass in late winter is due to decrease in source strength of biomass burning
335 emissions relative to that from the fossil- fuel combustion in the upwind source regions of
336 IGP and its subsequent long-range atmospheric to the sampling site.

337 3.3. Comparison of mass absorption efficiencies of WSOC and EC

338 The absorption of solar radiation by the EC or light absorbing WSOC can be
339 represented by the following equation.

340 Absorption $\propto \lambda^{-\alpha}$; where alpha refers to angstrom exponent.

341 Since the mass absorption efficiency of an absorbing component is proportional to the
342 absorption; the above equation can be rewritten as follows:

343 Mass absorption efficiency (MAE or σ) $\propto \lambda^{-\alpha}$

344 Here the mass absorption efficiency is expressed in terms of $\text{m}^2 \text{g}^{-1}$. It has been suggested that
345 EC shows little dependency on wavelength with an angstrom exponent of around 1
346 (Kirchstetter *et al.*, 2004). However, significantly higher alpha (α) values were documented
347 in the literature for particulate organic matter from biomass/bio-fuel burning emissions
348 (Hoffer *et al.*, 2006; Kirchstetter *et al.*, 2004; Lukacs *et al.*, 2007; Hecobian *et al.*, 2010;

349 Cheng et al., 2011; Kirchstetter and Thatcher., 2012; Chakraborty et al., 2013; Feng et al.,
350 2013).

351 For comparison, we have also estimated the MAE of EC (similar to the approach
352 suggested by Ram and Sarin, [2009]) using Sun-set EC-OC analyzer where the attenuation of
353 light by EC is measured at 678 nm. Since the MAE of EC is inversely proportional to
354 wavelength (the suggested angstrom exponent value is one for EC by Kirchstetter et al.,
355 2004), we can estimate the mass absorption efficiency of EC at other wavelengths (i.e., < 678
356 nm).

$$357 \quad (\sigma_{\text{EC}})_{\lambda_1} \approx \lambda_1^{-1} \text{ and } (\sigma_{\text{EC}})_{\lambda_2} \approx \lambda_2^{-1}$$

358 In this equation, the monthly averaged MAE of EC at 678 nm has been used to estimate the
359 σ_{EC} at other wavelengths as follows.

$$360 \quad (\sigma_{\text{EC}})_{\lambda_2} = (\sigma_{\text{EC}})_{\lambda_1} * [\lambda_2/\lambda_1]^{-1}$$

361 Likewise, we have used the MAE of light absorbing WSOC measured at 365 nm to obtain
362 MAE at other wavelengths

$$363 \quad (\sigma_{\text{wsoc}})_{\lambda_2} = (\sigma_{\text{wsoc}})_{\lambda_1} * [\lambda_2/\lambda_1]^{-\alpha}$$

364 Fig.5 depicts the relative contribution of MAE of WSOC to that of EC, assessed based on
365 monthly averaged σ_{EC} and σ_{wsoc} during the atmospheric outflow to the Bay of Bengal during
366 November'09-March'10. From this figure, it can be inferred that the relative contribution of
367 MAE of WSOC is maximum during the wintertime (January), compared to remaining
368 sampling days (Fig 5), when the ratio of mass absorption efficiency of light absorbing WSOC
369 relative to EC is ~ 0.72 . It is important to note that relatively higher contribution in early
370 winter samples could be due to dominant contribution from agricultural crop-residue burning
371 emissions which occur in the upwind source regions of the IGP during October-November
372 [Rajput et al., 2014]. However, the impact of bio-fuel emissions in the IGP is more
373 pronounced during the continental outflow to the Bay of Bengal [Kumar et al., 2010; Ram
374 and Sarin, 2011; Ram et al., 2012; Srinivas et al., 2011; Srinivas and Sarin, 2013c]. The
375 results reported in this study are somewhat consistent with that documented for residential
376 bio-fuels by Kirchstetter and Thatcher, [2012]. Their study documented that the fraction of
377 solar radiation absorbed by particulate organics generated from the bio-fuel emissions show a
378 peak at 0.7 at 300 nm and decreased to 0.26 at 550 nm.

379 3.4. Implications

380 The measurements of optical and chemical properties of atmospheric constituents have
381 shown the dominant nature of the anthropogenic aerosols over the Bay of Bengal compared
382 to that over the Arabian Sea [Kedia *et al.*, 2010; Kumar *et al.*, 2008; Srinivas *et al.*, 2011;
383 Srinivas and Sarin, 2013a; Sudheer and Sarin, 2008; Vinoj *et al.*, 2004]. In this context,
384 atmospheric outflow from the Indo-Gangetic Plain is responsible for wide spread dispersal of
385 pollutants over the Bay of Bengal. The atmospheric radiative forcing estimates have
386 suggested a relative decrease in solar insolation at the surface Bay of Bengal compared to the
387 Arabian Sea [Kedia *et al.*, 2010; Vinoj *et al.*, 2004]. Furthermore, it is suggested that aerosols
388 over BoB are of “more absorbing” type compared to that over the ARS [Kedia *et al.*, 2010;
389 Nair *et al.*, 2008]. Therefore, aerosol direct radiative forcing estimate increases with the
390 absorbing BC concentration over this oceanic region. Our study demonstrates ubiquitous
391 presence of BrC in the atmospheric outflow from the Indo-Gangetic Plain. Due to the
392 dominance of particulate organic matter in the IGP-outflow (OC: ~ 34 % of PM_{2.5} mass;
393 WSOC/OC: 0.52 ± 0.10) compared to EC (Av: ~ 5 %), it is, thus, important to include the
394 absorption from brown carbon in radiative forcing estimates over the oceanic regions (BoB)
395 located downwind of the pollution sources. Thus, presence of BrC over Bay of Bengal in
396 addition to EC [Srinivas and Sarin, 2013a], would lead to further decrease in incoming short
397 wave (solar) radiation and, therefore, would reduce surface radiative forcing estimates. Any
398 changes that decrease the solar insolation can influence circulation pattern in the ocean
399 surface. To sum-up, we suggest that the combined effect of BrC and BC needs reassessment
400 in model estimates of aerosol radiative forcing over the Northern Indian Ocean.

401 The absorption of solar radiation by atmospheric water-soluble organic carbon
402 (WSOC), relative to that by elemental carbon (EC), in the atmospheric outflow from the IGP
403 is estimated by following the approach similar to that suggested by Kirillova *et al.* [2014].
404 Briefly, the absorption by WSOC is estimated as a product of the solar emission flux and the
405 attenuation of light by WSOC (integrated over a broad wavelength range between 300 to
406 2500 nm) and normalized to that of EC. The wavelength dependent solar emission flux ($I_0(\lambda)$)
407 is obtained through the clear sky Air Mass 1 Global Horizontal (AM1GH) solar irradiance
408 model by Levinson *et al.*, [2010]. The light attenuation in the atmosphere by an absorbing
409 species (in this case, WSOC and EC) can be estimated from the Beer-Lambert’s law (for
410 more details, see [Kirillova *et al.*, 2014 and references therein]) as follows:

$$\frac{I_0 - I}{I_0}(\lambda, X) = 1 - e^{-\left(\sigma_X \left[\frac{\lambda_0}{\lambda}\right]^\alpha C_X h_{ABL}\right)}$$

411

412 Here σ_x and α refers to mass absorption cross section or efficiency (expressed in $\text{m}^2 \text{g}^{-1}$) and
 413 angstrom exponent, respectively, for the absorbing species X (i.e., WSOC or EC); λ_0 is 365
 414 nm for WSOC and 678 nm for EC (as explained above) whereas λ refer to any wavelength
 415 between 300 to 2500 nm. Likewise, C_x and h_{ABL} correspond to mass concentration of
 416 absorbing species (g m^{-3}) and atmospheric boundary layer height (1000 m), respectively.

417 Using this equation, we have estimated attenuation of solar radiation by WSOC and
 418 EC in the atmospheric outflow from the IGP. Furthermore, the fractional contribution of solar
 419 absorption by WSOC relative to EC is estimated as follows (adopted from Kirillova et al.,
 420 [2014]).

$$f = \frac{\int_{300}^{2500} I_0(\lambda) \left[\frac{I_0 - I}{I_0}(\lambda, WSOC) \right] d\lambda}{\int_{300}^{2500} I_0(\lambda) \left[\frac{I_0 - I}{I_0}(\lambda, EC) \right] d\lambda}$$

421

422 We have estimated the fractional contribution of solar absorption by light absorbing WSOC
 423 relative to that of EC in the atmospheric outflow from the Indo-Gangetic Plain to the Bay of
 424 Bengal. Fig. 6 depicts the fractional solar absorption of WSOC relative to that of EC in the
 425 IGP-outflow during the study period. From this figure, it is implicit to infer that the amount
 426 of solar radiation absorbed by WSOC relative to that by EC varied from 2 – 34 %.

427 Although absorption of solar radiation by WSOC (relative to EC) is estimated using
 428 a simple approach (this study), caution needs to be exercised while interpreting these results
 429 Fig. 6). It has been suggested that light absorption of OC in the solvent extracts could be
 430 underestimated by a factor of two [Liu et al., 2013]. Therefore, the estimated relative
 431 radiative forcing of light absorbing WSOC relative to EC has inherent uncertainty. However,
 432 the recent study by Kirillova et al., [2014] suggested that the warming effect caused by
 433 atmospheric brown carbon (through direct and indirect effects) could offset the net cooling
 434 effect estimated for projected WSOC concentrations. Based on radiative transfer modelling, it
 435 is suggested that brown carbon could reduce radiative forcing by ~ 20 %, at top of the
 436 atmosphere, on a global scale; thus, emphasizing this component as crucial for assessing the
 437 aerosol direct effect [Liu et al., 2014]. The significant contribution of light absorbing WSOC

438 in the atmospheric outflow from IGP, therefore, suggests a need for reassessment of the
439 climate impact of this species on a global scale.

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445

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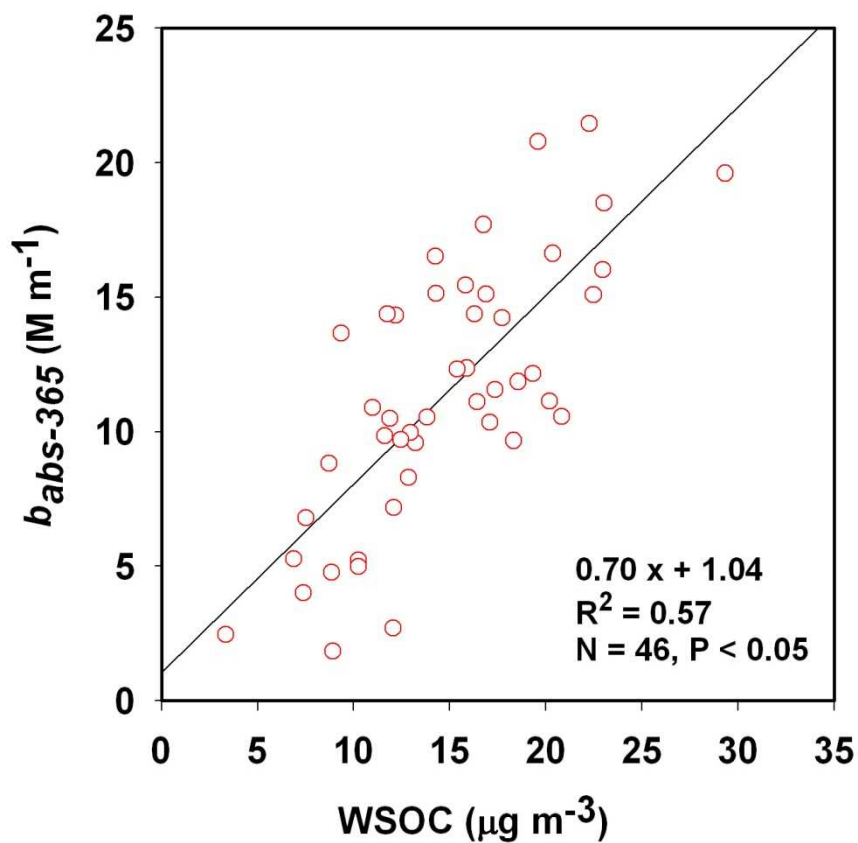
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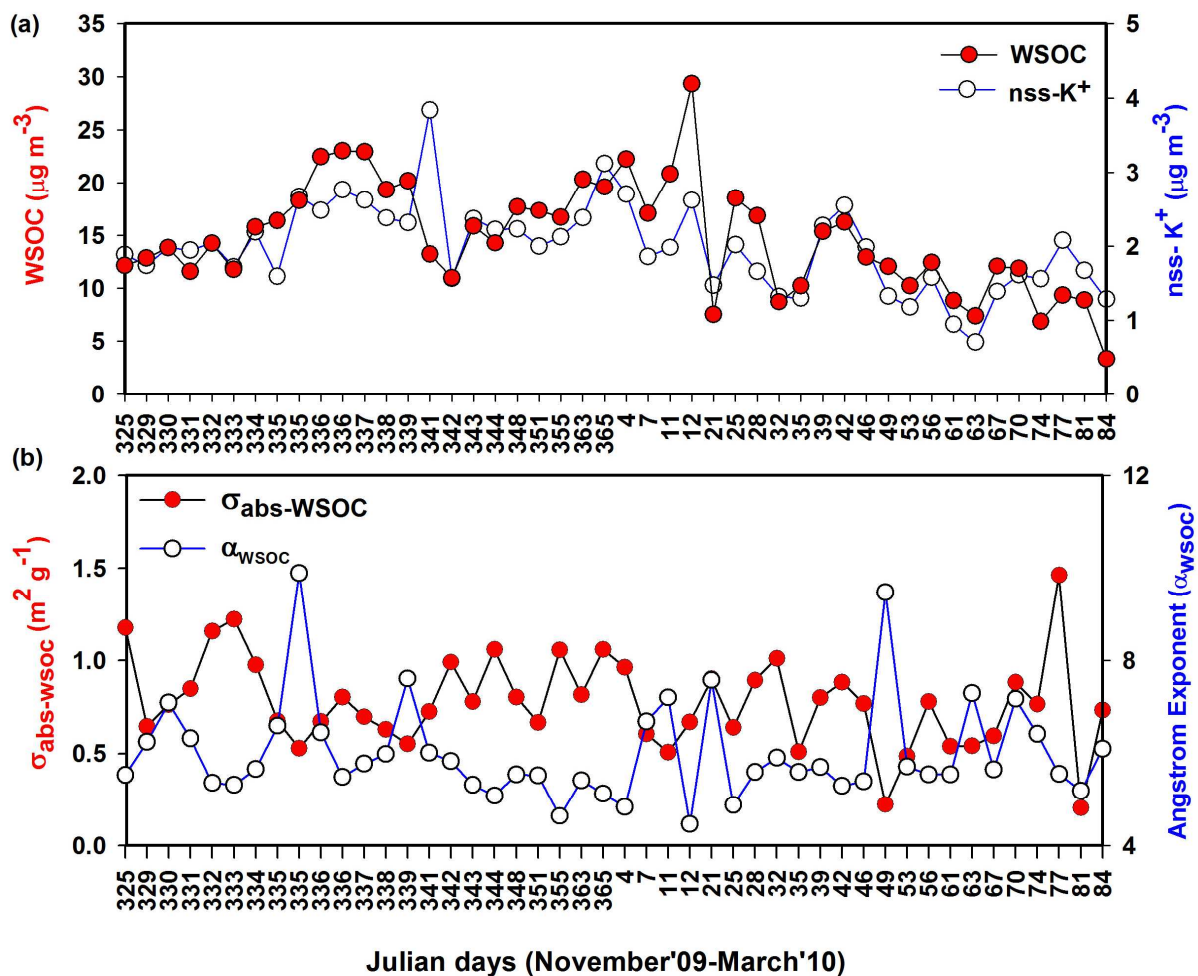


665 *Fig.1.* Scatter plot for mass concentration of water-soluble organic carbon (WSOC) and
666 absorption coefficient (b_{abs}) at 365 nm (where $M = x 10^{-6}$).

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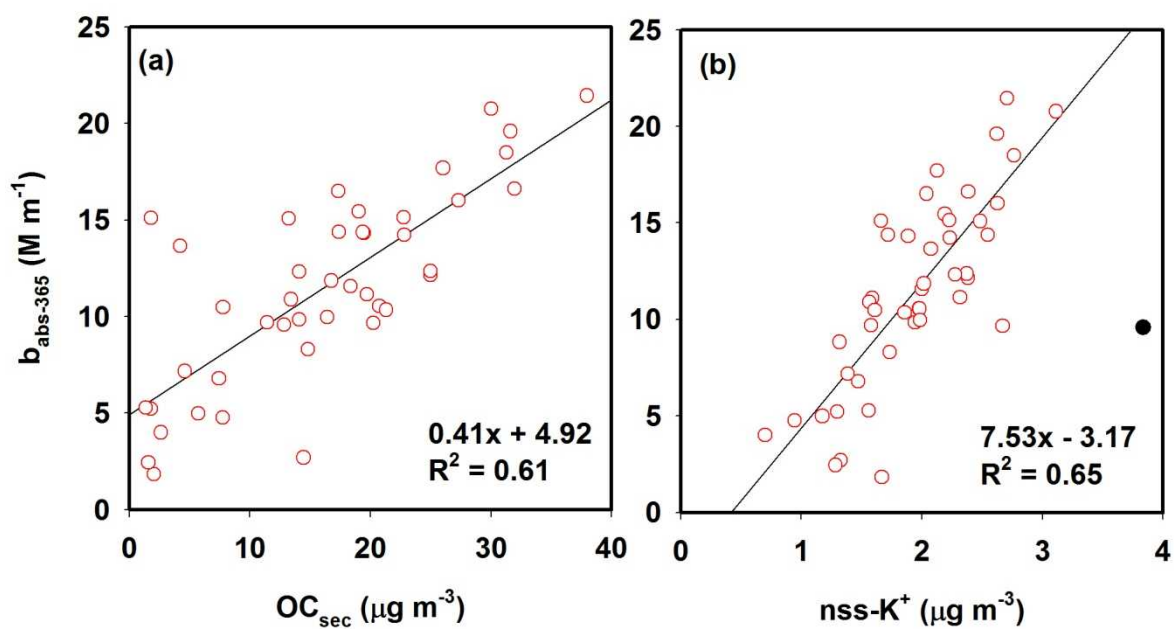
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Fig.2. (a) Temporal variability of WSOC and nss- K^+ concentrations suggest their common source from biomass burning emissions, (b) temporal variability of mass absorption efficiency of light absorbing water-soluble organic carbon ($\sigma_{\text{abs-WSOC}}$) and the Angstrom exponent (α_{WSOC}).

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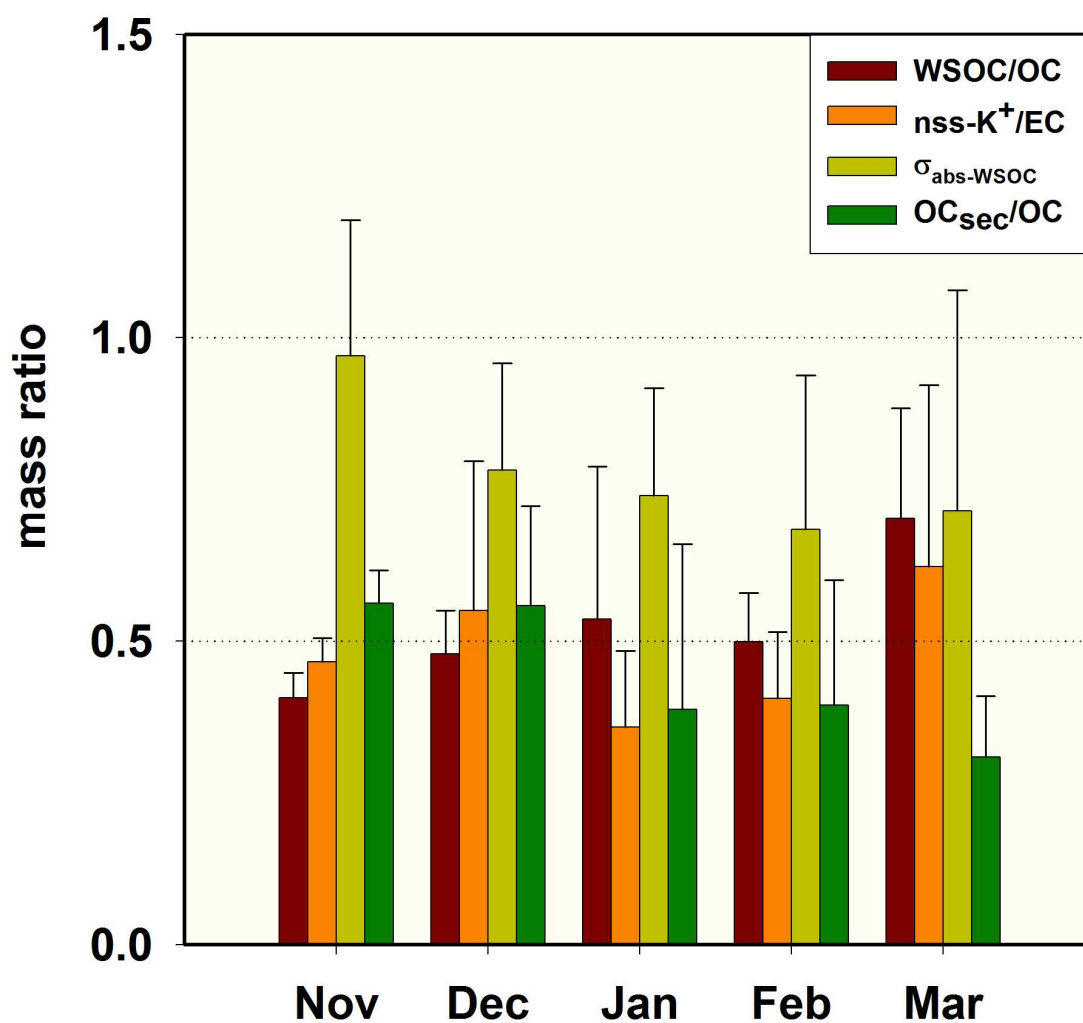


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Fig. 3. A strong positive relationship of mass absorption coefficient of water-soluble organic (brown) carbon with the abundance of secondary organic carbon (OC_{sec}) and nss-K^+ , suggests the formation of atmospheric brown carbon from biogenic secondary organic aerosols over the IGP.

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691 *Fig.4.* Temporal variability of diagnostic mass ratios (WSOC/OC, nss-K⁺/EC, OC_{sec}/OC) and
692 mass absorption efficiency of light absorbing brown carbon ($\sigma_{\text{abs-WSOC}}$).

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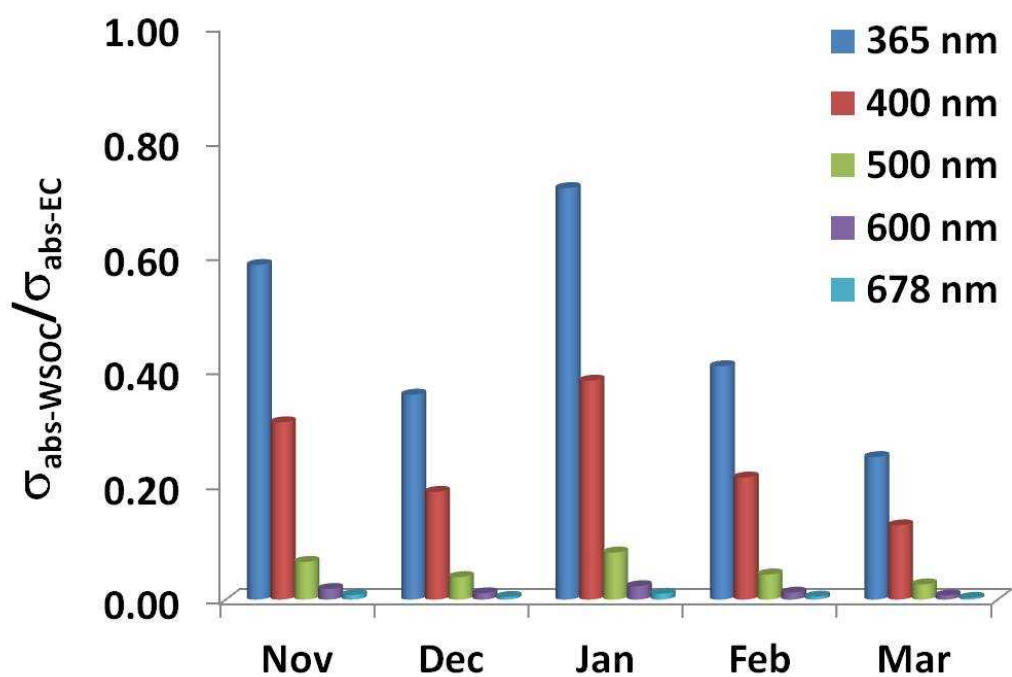


Fig.5. Fractional contribution of mass absorption efficiency of light absorbing water-soluble organic carbon (WSOC) to that of elemental carbon (EC) in the atmospheric outflow to the Bay of Bengal during November'09 – March'10.

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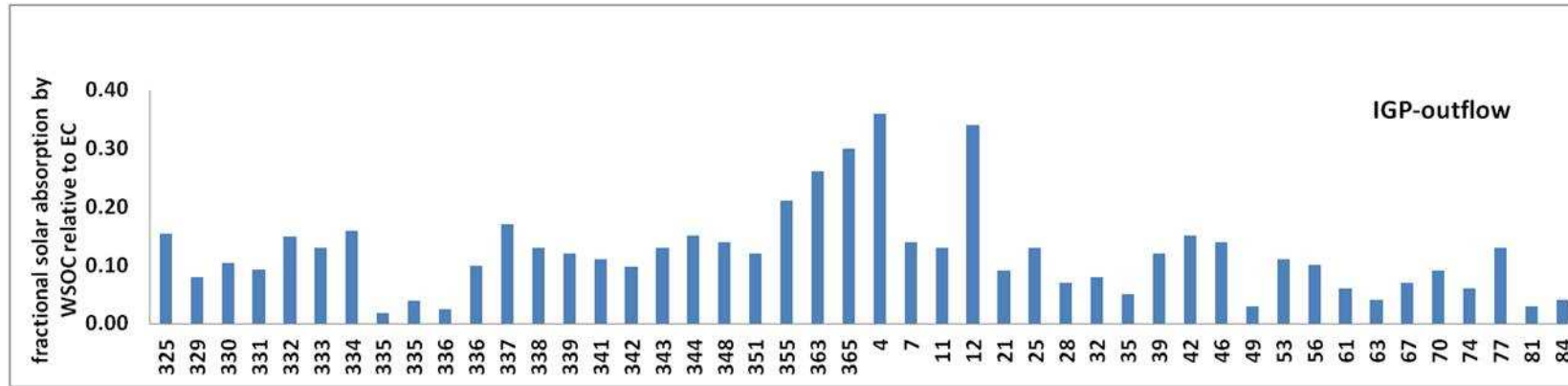
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729 *Fig.6.* Solar absorption by WSOC relative to EC in the atmospheric outflow from the Indo-Gangetic Plain to the Bay of Bengal during
730 November'09 – March'10.

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734 **Table 1.** Comparison of mass absorption efficiency (σ_{abs}) and angstrom exponent (\AA_p) of
 735 brown carbon (BrC) in the atmospheric outflow from the Indo-Gangetic Plain with other
 736 literature studies.

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Region	Source	$\lambda(\text{nm})$	$\sigma_{\text{abs-BrC}} (\text{m}^2 \text{g}^{-1})$	α_{wsoc}	Reference
Indo-Gangetic Plain	BB/BF-E	365	0.78 ± 0.24	6.0 ± 1.1	This study
Bay of Bengal (IGP-outflow)	BB/BF-E	365	0.4 ± 0.1	9.1 ± 2.5	Srinivas and Sarin, 2013a
Bay of Bengal (SEA-outflow)	BB/BF-E	365	0.5 ± 0.2	6.9 ± 1.9	Srinivas and Sarin, 2013a
Los-Angeles, USA	BBE	365	0.71	7.6 ± 0.5	Zhang et al., 2013
North America	BBE	404	0.82 ± 0.43	-	Lack et al., 2012
Beijing, China	BBE	550	0.5	-	Yang et al., 2009
Beijing, China	BBE	365	1.8 ± 0.2 (summer)	7.5 ± 0.9	Cheng et al., 2011
Beijing, China	BBE	365	0.7 ± 0.2 (Winter)	7.0 ± 0.8	Cheng et al., 2011
South-eastern US & Atlanta, Georgia	BBE	365	0.64 (urban) & 0.58 (rural)	7 ± 1	Hecobian et al., 2010
Amazon basin	BBE	350 - 400	$\sim 0.5 - 1.5$	$\sim 6 - 7$	Hoffer et al., 2006

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