

Variations in carbonaceous species at a high-altitude site in western India: Role of synoptic scale transport

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Abstract:

Atmospheric fine-mode particulate matter (PM_{2.5}), collected during January to December 2007 at a high-altitude site (Mt. Abu, 24.6 °N, 72.7 °E, 1680 m asl) in the western India, have been analyzed for carbonaceous and inorganic species to assess their temporal variability and the influence of emissions and transport processes, particularly from the Indo-Gangetic Plain (IGP). The mass concentrations ($\mu\text{g m}^{-3}$) of elemental carbon (EC), organic carbon (OC) and water-soluble OC (WSOC) are observed to be the highest during winter months, and found to vary between 0.2 – 2.8, 0.5-9.8 and 0.4-8.7, respectively. This variation in mass concentration is attributed to the synoptic scale long-range transport from the emission source regions in the Indo-Gangetic Plain (IGP). Relatively lower fractional contribution of carbonaceous species to PM_{2.5} mass is found during March – September. This is mainly attributed to the reduction in strength of biomass burning emissions near the study site, increase in boundary layer height and simultaneous increase in mineral dust concentration via transport from the Thar Desert and Arabian Peninsula. However, the OC/EC ratio is nearly uniform throughout the year (5.5 ± 1.6 , $n=71$) and indicate towards the dominance of biomass burning emissions at Mt Abu. This is further supported by a significant correlation between nss-K^+ and OC ($R^2=0.71$) with $\text{nss-K}^+/\text{OC}$ ratio averaged at 0.10 ± 0.04 . The higher WSOC/OC ratio (av: 0.65 ± 0.16 ; 1σ) compared to those in IGP, suggested formation of secondary organic aerosols during the transport, which is further attested by the observed strong correlation between secondary OC (SOC) and WSOC concentrations. A back-trajectory-assisted analysis has been performed to estimate the levels of OC, EC, WSOC, OC/EC and WSOC/OC in two distinct air-masses classified as the marine air mass and the IGP influenced air mass. This analysis shows significantly higher concentration of OC, EC and WSOC in the IGP influenced air masses by 64.9%, 121.4% and 113.2% respectively, as compared to the marine air masses. This important observation of carbonaceous aerosols at Mt Abu highlights the role of synoptic scale transport particularly from the biomass burning sources in the IGP.

Keywords: Carbonaceous aerosols, Elemental Carbon, Organic Carbon, Water –Soluble Organic Carbon, Indo-Gangetic Plain, High-altitude site.

1. INTRODUCTION:

Carbonaceous aerosols are recognized as one of the key components of atmospheric aerosol and influence the earth's radiation budget (Ramanathan et al, 2001). These aerosols, consisting of elemental carbon (EC or black carbon) and organic carbon (OC), contribute significantly to the ambient particulate matter (30-70 % of fine mass in the urban atmosphere; Cao et al., 2003; Fuzzi et al., 2006; Rengarajan et al., 2007) and exhibit large spatial and temporal variability (Jacobson et al, 2000; Turpin and Lim, 2001). EC (also referred as soot; Andreae and Crutzen, 1997), derived as primary particle from incomplete combustion processes (e.g. fossil fuel or biomass burning), is an efficient absorber of solar radiation (Horvath, 1993; Jacobson, 2001; Ramanathan and Carmichael, 2008). The absorbing nature of EC causes heating of aerosol layers and, subsequently suppresses the generation of convective clouds leading to inhibition of rainfall (Koren et al, 2004; Rosenfeld et al, 2008). In contrast, OC is composed of condensed organic matter and mainly scatters the solar radiation. However, some recent studies (Kirchstetter et al, 2004; Andreae and Gelencser, 2006) have reported the absorption of radiation by OC in freshly emitted biomass burning aerosols. The relative abundances of EC and OC (i.e. OC/EC ratios) are, thus, critical in assessing impact of carbonaceous species on the climate forcing (Novakov et al, 2005). However, these ratios used in the climate models are mostly derived based on emission inventories and therefore have large uncertainties, mainly due to the paucity of long-term observations missing in the literature. Furthermore, particulate organic carbon consists of a significant amount of water-soluble organic carbon (WSOC) (Sullivan et al, 2004, Jaffrezo et al, 2005; Miyazaki et al, 2006, Rengarajan et al, 2007, Ram et al, 2010) which is linked to the hygroscopic property of aerosols and thus influences the CCN activity of aerosols (Novakov and Penner, 1993; Saxena et al, 1995; Mircea et al, 2005). Several studies (Zappoli et al, 1999; Ho et al, 2006), have indicated enrichment of WSOC fraction at remote (e.g. rural or background) locations compared to that from the source region (polluted urban atmosphere), thus suggesting, the formation of more soluble organic compounds during the long-range transport.

Recent studies have indicated that developing nations in the tropics and south-east Asia are one of the major source regions for emission of carbonaceous species (Novakov et al, 2003; Bond et al, 2007; Streets et al, 2003). China and India are one of the significant contributor of EC and OC with India being largest OC emitter per unit surface area (Ramanathan et al, 2007). The distribution of carbonaceous aerosol loadings exhibit strong spatial heterogeneity with maximum loading over the densely populated and polluted Indo-Gangetic Plain established from the space-based observations (e. g. Fishman et al., 2003; Jethva et al., 2004) as well as chemistry transport simulations (Ojha et al., 2012; Kumar et al., 2012). Considering these aspects, time to time field experiments were conducted over Indian subcontinents such as Indo-Gangetic Plains (Tare et al, 2006; Rengarajan et al, 2007; Ram et al, 2010) and adjoining marine regions

(Sudheer and Sarin, 2008; Kumar et al, 2008; Kumar et al, 2010; Kumar et al, 2012). These studies have provided information about the emission sources and seasonal variability in aerosol chemical composition over northern India. However, influence of the IGP emissions coupled with the synoptic scale dynamics of Indian region on the carbonaceous species over the western Indian region are limited. The high-altitude observation site Mt. Abu is advantageous to be a better regional representative of the western Indian region due to its remoteness from direct anthropogenic emissions (Rastogi and Sarin, 2006; Kumar and Sarin, 2010a). In this context, a maiden year long (Jan-Dec 2007) observational dataset of EC, OC and WSOC in fine aerosols ($PM_{2.5}$; particulate matter with aerodynamic diameter $\leq 2.5 \mu m$) from Mt Abu is being presented. The aerosol chemical measurements (carbonaceous aerosol in particular) have been non-existing from high-altitude site in western India, which further inhibit use and validation of regional transport models. Therefore our study is aimed to fill this gap of observational data and at the same time to provide first information about seasonal variations and sources of carbonaceous aerosol over western India. The observations have been analyzed to investigate the seasonal variation of carbonaceous aerosols over the western India as well as to assess the influence of distinct air masses transported from cleaner marine and polluted Indo-Gangetic Plain (IGP) regions.

2. Sampling site and methodology:

The sampling site (Fig. 1) for the collection of fine ($PM_{2.5}$) aerosols, is located at Gurushikhar (more commonly known as Mt Abu, 24.6 °N, 72.7 °E, 1680m asl) - the highest peak in the Aravali range of mountain in western India. The annual rainfall at Mt Abu averages around 600-700 mm and most of it occur during the south-west (SW)-monsoon (Naja et al., 2003; Kumar and Sarin, 2009). The study location is considered as a remote site with almost negligible movement of vehicular traffic within the immediate vicinity. Considering the uniqueness of this site, several atmospheric measurements, e.g. trace gases and volatile organic compounds (Sahu and Lal, 2006), have been undertaken at this location to understand atmospheric chemistry at regional scale. The measurement of atmospheric compositions (trace gases and aerosols) over high altitude site provide a representative regional picture of the dynamic atmospheric processes. The sampling site represents free-tropospheric characteristics during winter months (Oct-Feb) and lies within the boundary layer during rest of the year (Kumar and Sarin, 2009). Based on the prevailing meteorology over this semi-arid region, the annual seasonal cycle has been defined as summer (Mar-June), monsoon (Jul-Sep) and winter (Oct-Dec; Jan and Feb). The winds, during onset of Indian summer monsoon, bring substantial amount of moisture to the sampling location. In contrast, winds during north-east monsoon (wintertime) shown in Fig 1b, favour long-range transport of continental air-mass enriched in chemical species derived from large scale anthropogenic activities. 10-days back-trajectories have been simulated 500 m above Mt Abu at 00, 06, 12 and 18 GMT for typical months (e.g. December, April and August) in three different seasons of the year 2007 (Fig. 2) using the Hybrid Single Particle

Lagrangian Integrated Trajectory (HYSPLIT) Model (refer to figure captions for detail). These back-trajectories clearly demonstrate transport of air-masses from distinct regions, e.g. Thar Desert, Arabian Sea and Indo-Gangetic Plain during summer, monsoon and winter seasons, respectively. The near surface wind speeds at the sampling location were significantly high during monsoon season (maximum speed recorded was 13.5 m s^{-1}). However, winds were usually weak during winter months, except for a few days in the month of Jan and Feb. We furthermore classified the observations according to the residence time of air masses, as shown by Fig. S1 (supplementary material), in which the individual trajectories for all the months considered in the study are presented. This technique of concentration-residence time tagging has been successfully used over north India (Kumar et al., 2010; Sarangi et al., 2014), western India (Srivastava et al., 2012); Japan (Naja and Akimoto, 2004) and Europe (Naja et al., 2003). Further relevant details of the sampling site and meteorological conditions have been described in our earlier publications (Kumar and Sarin, 2009; Kumar and Sarin, 2010a)

The fine ($\text{PM}_{2.5}$) aerosols were collected by operating a high-volume sampler (Thermo-Andersen); with sampling inlet having 50% cutoff size at $2.5 \mu\text{m}$ aerodynamic diameters. The high-volume sampler was equipped with volume flow controller to maintain constant flow rate. Furthermore, periodic calibration of the sampler was performed (once in every 2-3 weeks) to check on variation, if any, in the flow rate and typically the flow rate varied from $1.07\text{-}1.18 \text{ m}^3 \text{ min}^{-1}$ ($\text{av} = 1.1 \pm 0.1 \text{ m}^3 \text{ min}^{-1}$) with an uncertainty of 5%. Aerosol samples were collected on pre-combusted PALLFLEX™ tissuquartz filters ($20 \times 25 \text{ cm}^2$) over a time-period ranging from 12-15 hours. A total of 71 samples were collected in 2007 during the three different seasons viz. summer ($n = 28$), monsoon ($n = 9$) and winter ($n = 34$).

The $\text{PM}_{2.5}$ mass concentrations were ascertained gravimetrically (with a precision of 0.1 mg) by weighing full filter on a large pan (pan size 8.2" x 10.4") filter balance (Sartorius, model LA130S-F) before and after sampling. Prior to weighing, all filters were conditioned at a relative humidity of $40 \pm 5 \%$ and temperature of $22 \pm 1 \text{ }^\circ\text{C}$ for 5-6 hrs. The repeat measurement of the filter weights provide an uncertainty of $\pm 1 \text{ mg}$ which corresponds to an overall error of $\sim 15\%$ in the mass concentrations.

The concentration of elemental carbon (EC) and organic carbon (OC) were measured on a Thermal/Optical analyzer (Sunset Laboratory, USA) using NIOSH (National Institute of Occupational Safety and Health)-5040 protocol based on thermal-optical transmittance (TOT) protocol (Birch and Cary, 1996). Details of the analytical protocol on EC-OC measurements used in our laboratory have been described in our earlier publications (Ram et al., 2008; Ram and Sarin 2010; Rengarajan et al. 2007) and briefly discussed in the supplementary material. The replicate analyses of aerosol sample ($n=7$) provided a good analytical reproducibility (better than 5%) for OC and EC. Blank filters were also analyzed, similar to the procedure used for samples, in order to assess the analytical detection limits for OC and EC and blank corrections. The detection limits for OC was found to be $0.1 \mu\text{g m}^{-3}$ (using 3σ value of blank concentration of the filter and volume of

air sampled) whereas that for EC was estimated $0.05 \mu\text{g m}^{-3}$ (using $0.20 \mu\text{g cm}^{-2}$ as instrumental signal), as concentration for EC was zero in the blank filter.

Analytical protocol used for the analyses of water-soluble organic carbon (WSOC) and inorganic constituents (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-}) are detailed in supplementary material. The water-soluble organic carbon was obtained indirectly from the difference between the total carbon (TC) and the inorganic carbon (IC). The replicate analyses of the water-extracts provide relative standard deviation of 3% and 5% for TC and IC, respectively (for $n=8$). The water-extracts of blank filter were simultaneously analyzed for TC and IC, and the average WSOC from blank filter was less than 5% of WSOC measured in the samples. The anions (Cl^- , NO_3^- and SO_4^{2-}) and cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) were analyzed on DIONEX[®] Ion-Chromatograph equipped with suppressed conductivity detector (ED-50) (Kumar and Sarin, 2010a).

3. Results and Discussion

3.1 Temporal variability of $\text{PM}_{2.5}$, EC, OC and WSOC:

The temporal distribution of fine ($\text{PM}_{2.5}$) mass along with EC, OC and WSOC for each sample have been illustrated in Fig. 3. The $\text{PM}_{2.5}$ mass varies from 6.7 to $34.5 \mu\text{g m}^{-3}$ (av. = $16.2 \pm 7.1 \mu\text{g m}^{-3}$) and 1.6 to $46.1 \mu\text{g m}^{-3}$ (av. = $16.9 \pm 9.1 \mu\text{g m}^{-3}$) during summer and winter season, respectively. The box-whisker plot for the carbonaceous species as well as inorganic ions (nss- SO_4^{2-} , NH_4^+ and nss- K^+) for winter and summer season are shown in Fig. 4 and the mean, standard deviation, median as well as minimum and maximum values are summarized in Table-1. Although, average $\text{PM}_{2.5}$ mass is nearly same during two seasons; there is a large difference in concentration and fractional contribution of carbonaceous and inorganic species at Mt Abu. The higher concentration of EC, OC, and WSOC (a factor of two) are observed during winter season over this high-altitude site. These higher concentrations are mainly due to impact of anthropogenic sources which is evident from presence of higher level of trace metals (mainly derived from anthropogenic activities e.g. Pb and Cd) during the sampling period (Kumar and Sarin, 2010b).

Overall, there is a large annual variability in mass concentration of all measured chemical species and this is mostly driven by wind pattern prevailing over the sampling location. The wind pattern observed at Mt Abu (Kumar and Sarin, 2009), clearly indicate long-range advective transport of air parcels from polluted Indo-Gangetic Plains (IGP) during winter months. The northern part of India (Indo-Gangetic Plain), located upwind of the sampling site (Fig. 1a), is one of the densely populated areas in India. The emissions from biomass burning (agricultural crop waste) and combustion of bio-fuel are important source of carbonaceous species in the IGP during wintertime (Ram et al, 2010; Rengarajan et al, 2007). In addition, industrial (textiles, sports, and leather goods), transportation and power plant emissions also contribute to carbonaceous aerosol over IGP. The concentration of EC varied from 0.2 to 2.8 (0.8 ± 0.6) $\mu\text{g m}^{-3}$ and below detection limit to 0.6 (0.3 ± 0.1) $\mu\text{g m}^{-3}$ (Table-1) during winter and summer

respectively. A three-fold increase in EC concentration has been observed during wintertime which can be attributed to the long-range transport from northern part of India (IGP; Fig 1a). The boundary-layer dynamics, during winter months, may also play an important role in efficient trapping of the pollutants and their advection from the source region. On the contrary, lower values of EC observed during summer season suggest reduction in emission sources of carbonaceous aerosol; possibly due to switch off residential biomass burning emissions. Kumar and Sarin, (2009), have documented transport of dust (a major component during summer) from nearby Thar Desert and as far as from Arabian/Oman Desert (not a major source of carbonaceous species) during summer season. The concentration during monsoon period were found below detection limit for most of samples owing to washout of particles during precipitation prior to sample collection. On average, EC contributes $\sim 4\%$ of fine ($PM_{2.5}$) mass during winter month; however, its contribution is less than 2% during rest of the year at this high-altitude site.

The OC concentrations show similar kind of seasonal pattern over annual time scale as shown in Fig. 3 and 4. On average, OC contributes $\sim 22\%$ of the $PM_{2.5}$ mass during period when sampling site is mostly affected by long-range transport from IGP (i.e. winter season). However, during summer and monsoon, OC contribution is reduced to only $\sim 10\%$ (of $PM_{2.5}$ mass) when winds are either derived from marine or desert (arid/semi-arid) area (Fig. 3 and 4). The concentration of EC, OC and WSOC at different locations in India and adjoining marine region as well as at different locations on the globe are summarized in Table S1 (supplementary material). The urban locations in the IGP, dominated by anthropogenic activities, exhibit very high value of EC, OC and WSOC (Table S1). The average values of EC and OC over the IGP region are usually found to be more than $4\ \mu\text{g m}^{-3}$ and $30\ \mu\text{g m}^{-3}$ respectively (Table S1), an order of magnitude higher than that observed over the study site. This points to transport from north and north-eastern part of India under favourable meteorological condition are responsible for higher values of EC and OC at Mt. Abu during winter. Likewise, the concentrations of EC and OC over remote marine location were found somewhat comparable with those at Mt. Abu (Table S1). For example, the EC and OC values were found to be $0.4\text{-}2.0$ and $2.6\text{-}5.9\ \mu\text{g m}^{-3}$ respectively, over Bay of Bengal (Kumar et al. 2010; Srinivas and Sarin, 2014). One of the high altitude sites (Manora Peak, Nainital, 2100 m a.s.l) located in the IGP region exhibit higher value of EC and OC during Dec, 2007 – Feb, 2008, compared to Mt. Abu (Ram et al, 2010). The higher value of OC and EC at this location have been attributed to the proximity of its location from source region and transport from IGP. The concentration of OC and EC over the rural site (Jaduguda) in IGP are 35.3 ± 7.1 and $11.6\pm 2.0\ \mu\text{g m}^{-3}$ respectively, relatively higher than other rural locations (e.g Po Valley in Europe and Yorkville in USA) in different parts of world which is mainly attributed to the emissions from coal-based industry located nearby the sampling site (Ram and Sarin, 2010).

The concentration of WSOC followed a similar trend as shown by EC and OC (Fig. 3 and 4) during annual seasonal cycle in 2007. As summarized in Table -1, the concentration of WSOC ranged from 0.4 to 8.7 (average: 2.6 ± 1.9) $\mu\text{g m}^{-3}$ and 0.4 to 1.6 (average: 0.8 ± 0.3) $\mu\text{g m}^{-3}$ in winter and summer, respectively. Their average contribution of WSOC to total $\text{PM}_{2.5}$ mass is found to be 15.4 and 6.1 % in winter and summer respectively. The WSOC concentration is low at this high-altitude site compared to several urban locations over Indian region, except a comparable value observed over Manora Peak (another high-altitude site) during December, 2004 (Table-S1). However, at various locations in Europe, US, as well as over Asia, somewhat comparable values of WSOC have been observed (Table-S1).

In order to understand the impact of synoptic scale meteorology (e.g. wind pattern), 10-days back-trajectories simulation have been performed (Fig. 2 and S1). The analysis of the back-trajectories led to estimation of the residence time of air parcels (Sarangi et al., 2014) over two distinct domains. These two domains are Indo-Gangetic Plains (IGP) and marine region shown in Fig. S2 (refer to figure caption for detail). The air parcels derived from IGP and marine region are representative of air masses affected by a severely polluted and relatively clean regions, respectively. We defined cluster of air masses having a residence of 2 to 6 or more days over the IGP region and less than 1 day over the marine regions as the IGPAP (Fig. 2). While, the air masses having a residence of 2-6 days or more over the marine regions and less than 1 day over the IGP are classified as the MAP. This classification is done to assess the impact of air masses derived from on concentration of carbonaceous species at Mt Abu.

Based on this classification, data were segregated and average EC, OC and WSOC concentration as well as diagnostic ratios (e.g. OC/EC and WSOC/OC) were calculated for different air-masses (Fig. 5 and Table S2). The EC, OC and WSOC concentrations calculated during IGPAP regime are higher as compared to MAP period, which is consistent with observed temporal variability of carbonaceous aerosols discussed previously in this section. The impact of synoptic meteorology (e.g. wind pattern) on carbonaceous species is discernable based on back-trajectory assisted analyses wherein more than 100 % increment is seen in concentration of EC and WSOC, however, ~65% increase is observed for OC (Fig 5 and Table S2) during IGPAP.

3.2 Relationship between EC, OC, and WSOC

The linear regression analysis between EC and OC, for different season (summer and winter) is shown in Fig. 6a. A significant correlation ($R^2 = 0.80$) between EC and OC during winter, compared to that observed in summer season ($R^2 = 0.29$), suggests a common emission sources during winter time. The OC/EC ratio has been typically used for emission source identification of carbonaceous species (Chow et al, 1993; Novakov et al, 2005 and references therein). However, at a remote location, it is difficult to assess the source(s) of carbonaceous species based on OC/EC ratio as it is strongly influenced by complex physical and chemical processes during long-range transport. Nonetheless, OC/EC ratio, along with certain tracers (K^+ and K^+/OC ratio), can still be used for source

identification. Relatively higher K^+ concentration, K^+/OC and OC/EC ratios have been observed for biomass burning (Andreae and Merlet, 2001; Ram and Sarin, 2010, 2011; Ram et al., 2010; Sandradewi et al., 2008). The temporal variability of OC/EC ratio at this high-altitude site, during 2007, has been shown in Fig. 2. Exceptionally, higher values of OC/EC (>10) were observed for a few days in May, during summer season. Such higher values are mostly due to lower concentration of EC ($< 0.15 \mu\text{g m}^{-3}$) during this period. The lower EC values are also attributed to the prevailing winds from desert and marine region which lack carbonaceous aerosol sources, during summer season. In addition, the uncertainty in measurement of EC is relatively high at such lower concentrations which further aid to the uncertainty in OC/EC values. Therefore, data points with $EC \leq 0.15 \mu\text{g m}^{-3}$ were excluded while calculating average OC/EC ratios for summer months. The box-whisker plot for OC/EC ratio in winter and summer season are shown in Fig. 7. The average OC/EC ratio for summer (5.6 ± 1.7) and winter (5.3 ± 1.4) season was found to be similar within uncertainty limits. It has been suggested that low OC/EC ratios (typically $<2-3$) are primarily associated with fossil-fuel and vehicular emissions which produce elevated EC and lower OC concentrations during their emissions. However, higher OC/EC values, observed in this study, represent the dominant contribution of biomass-burning emission products to carbonaceous species. Several studies over Indian subcontinent have indicated the dominance of biomass (agricultural waste, crop residues, wood burning, and cow dung-cakes) burning emissions with significantly high OC/EC ratio (Rengarajan et al, 2007; Ram and Sarin, 2010, Ram et al, 2010; Rastogi et al, 2015) as well as using $\Delta^{14}\text{C}$ measurements (Gustafsson et al, 2009). Most of these studies have been undertaken at source region of the Indo-Gangetic Plain and western India, respectively. The OC/EC ratio at different location in IGP as well as in locations around the world ranging from urban, rural and remote locations (e.g. marine and high-altitude sites) have been summarized in Table S1. The densely populated urban site, Kanpur (26.5°N , 80.3°E), located in IGP, shows relatively higher value of OC/EC ratio (> 6 ; Table-S1) throughout the year, except during month of March (Ram et al, 2010). Few more locations in IGP, e.g. Kharagpur (22.02°N , 87.11°E) and Patiala (30.2°N , 76.3°E), which are urban location, also display higher OC/EC (~ 7 and 8.2 during winter; Table S1) ratio (Srinivas and Sarin, 2014; Rastogi et al., 2015). These higher ratio points to dominance of biomass burning emission contribution to total carbonaceous aerosols at the study site.

The spatial distributions of the fires (fire counts obtained from Moderate Resolution Imaging Spectroradiometer (MODIS) onboard Terra satellites; <http://modis-land.gsfc.nasa.gov/fire.html>) over India during three seasons namely winter (ONDJF), summer (MAMJ), and monsoon (JAS) for the year 2007 is shown in Fig. S3. These fire counts further corroborate to dominant contribution of carbonaceous species from biomass burning. A daily fire count time series (for the year 2007) over the defined IGP region is shown in Fig. 8. It is clearly seen from plot that, fire activity are prominent during March to June with small contribution during October-November. These fire counts are mainly observed because of agricultural waste burning over cropland areas

during the mentioned period, which is a seasonal activity in this region (Kumar et al, 2011). The wind patterns are mostly westerly/north-westerly and south-westerly during these periods. Due to this, impact of large scale biomass burning are not observed significantly at the study site. This is also confirmed from relatively lower concentration of carbonaceous species in summer and monsoon. However, during winter, the winds are mostly coming from north and north-east. These wind carries emission from IGP and indicate signature of IGP at the study site.

The scatter plot between WSOC and OC for winter and summer has been shown in Fig. 6b. A very excellent correlation between WSOC and OC is observed for winter samples ($R^2 = 0.96$) compared to summer samples ($R^2 = 0.43$). Such differences in correlation can be attributed to changes in the characteristics of emission sources as well as the influence of long-range transported aerosols. The temporal variability in WSOC/OC ratio and Box-whisker plot (for summer and winter) are shown in Fig. 2f and 7, respectively. Significantly higher WSOC/OC value (0.69 ± 0.13 ; Table-1) is observed during winter season as compared to a lower average in summer (0.51 ± 0.15 ; Table-1). This conspicuously high WSOC/OC ratio during winter is contrasting to the observation from other locations (Table-S1) including sites (e.g. Kanpur and Kharagpur) located in the Indo-Gangetic Plain (Ram and Sarin, 2010; Srinivas and Sarin, 2014). Relatively higher WSOC/OC ratio during winter season could be due to addition of Secondary Organic Aerosols (SOA) formed during transport from the IGP during wintertime. In contrast, SOA formation may be limited due to less availability of volatile organic compound (VOC) concentration during summer when wind pattern is south-westerly (absence of emission source) though; photochemical activity is higher in summer. However, it is difficult to conclude this hypothesis in absence of VOC data. The seasonal variability of WSOC fraction in the French Alps (Jaffrezo et al, 2005), have shown higher WSOC contribution in summer season at two different urban locations (Table-S1). However, Ho et al, (2006), have reported higher WSOC/OC ratio at two different locations (Polytechnic University and Kwun Tong) in winter compared to summer (Table-S1) similar to observations at Mt. Abu. Such contrast may be explained by lack of VOC concentration and hence, the SOA formation, which essentially contributes to WSOC, during long-range transport in summer months. The pre-requisite for SOA formation are volatile organic compounds (VOCs) and oxidizing species, which mediates oxidation process leading to higher abundances of SOA. Based on summer wind patterns (Fig. 2), it is evident that air-parcels are mainly originating from Thar Desert as well as from Arabia and Oman desert which are abundant in mineral dust. These Desert regions are deficient in VOCs, compared to the IGP, and thus limit SOA formation during summer. It is also evident based on several studies that WSOC fraction increases from source (typically urban and industrial region) to background and remote regions (Salma et al, 2001; Pio et al, 2007; Park and Cho, 2010).

Trajectory assisted analyses (discussed in previous section) have clearly shown an increase in concentration of carbonaceous aerosols in IGPAP compared to MAP.

However, contrastingly, OC/EC ratio is found lower, in the IGPAP and comparable to ratios observed in IGP, suggesting significant impact of emissions from the IGP. During MAP regime, EC sources are insignificant, however, oceanic processes (or emissions) may contribute significantly to OC in form of primary organic matter (POM), which has been highlighted by many recent studies (e.g. Spracklen et al., 2008; Fu et al., 2013). These contribution from oceanic emissions are comparable in magnitude to the OC derived from fossil fuel combustion (Spracklen et al., 2008). Thus, during MAP regime, POM from oceanic sources must be contributing to the OC which is a missing component in IGPAP owing to meteorological constraints. Also, the EC sources are insignificant during MAP period and hence there is an increased OC/EC ratio observed compared to IGPAP. An increase in the concentrations of WSOC and WSOC/OC ratio during IGPAP, suggest an increased contribution from SOA during transport.

3.3 Relationship among carbonaceous species and inorganic ions

Various studies have indicated that emission of biomass-burning led to injection of organic species in the atmosphere (Schauer et al, 2001; Mayol-Bracero et al, 2002; Simoneit et al, 2004). One of the diagnostic tracers which can be used as an indicator for biomass burning aerosols is nss-K⁺ (non-sea-salt K⁺; Andreae, 1983; Cachier et al, 1991; Andreae and Merlet, 2001). The nss-K⁺ shows a significant correlation with OC (R² = 0.71) during winter month supporting dominance of biomass burning emissions towards carbonaceous species. Further, OC/EC, nss-K⁺/OC and nss-K⁺/EC ratios can be used to infer biomass and/or fossil-fuel emission sources (Ram and Sarin, 2011; Srinivas and Sarin, 2014). The nss-K⁺/OC and nss-K⁺/EC ratios at the sampling site for summer and winter season have been summarized in Table-2 and compared with ratio observed at different locations (Table-3). The nss-K⁺/OC ratio varied from 0.06 – 0.18 (mean = 0.10±0.04; Table-2) and 0.03 – 0.16 (mean = 0.08±0.03; Table-2) in winter and summer, respectively. It is interesting to note that transport pattern of aerosols being quite different during summer and winter (from south-west India and IGP, respectively), the diagnostic ratios point to dominance of biomass burning emission for carbonaceous aerosols. The nss-K⁺/OC ratios during summer and winter are comparable with the values (Table-3) reported by Ram and Sarin (2011) at Kanpur as well as various locations in the Indo-Gangetic Plain (Ram and Sarin, 2010; Rengarajan et al, 2007; Srinivas and Sarin, 2014). Gustaffson et al., (2009) have concluded that biomass combustion contributes to two-thirds of total OC over south-India, based on a robust radiocarbon (¹⁴C) analysis in ambient aerosols. Khalil and Rasmussen, (2003), have observed K⁺/OC value in the range of 0.011-0.014 at Olympia, USA, when the sampling site was strongly impacted by residential wood burning. Similarly, the ratios have been found to be 0.005 and 0.011 for burning of pine and oak respectively (Schauer et al, 2001). The values observed in present study are relatively higher than that reported by Schauer et al, (2001), however, ratios reported by Andreae and Merlet, (2001), for agricultural waste burning (range: 0.04 – 0.13) is similar to that observed at this site (Mt. Abu) throughout the year. Furthermore, nss-K⁺/EC ratio varies from 0.26-1.01

(0.53 ± 0.18 ; Table-2) and 0.23-0.89 (0.53 ± 0.14 ; Table-2) during summer and winter respectively. These values are again comparable with the range found for typical biomass burning emissions (~ 0.1 to ~ 0.6 , Andreae and Merlet, 2001) as well as ratios observed over Indo-Gangetic Plain (Table-3; Ram and Sarin, 2010; 2011; Rengarajan et al, 2007; Srinivas and Sarin, 2014). Thus, based on OC/EC, nss-K⁺/OC and nss-K⁺/EC diagnostic ratios, we conclude dominance of biomass-burning derived carbonaceous aerosols over Mt Abu.

We have also investigated some of the diagnostic ratios (summarized in Table-3) to characterize aerosols over the study site as well as to study importance of scattering and absorbing aerosols at Mt. Abu. The nss-SO₄²⁻/EC and nss-SO₄²⁻/OC are also used as an important proxy for distinguishing relative dominance of fossil-fuel combustion vis-à-vis biomass burning emissions. The nss-SO₄²⁻/EC and nss-SO₄²⁻/OC mass ratios were varied from 2.3 to 20.5 ($A_v = 8.6 \pm 4.0$) and 0.6 to 4.75 ($A_v = 1.7 \pm 0.9$) during winter months. Interestingly, observed ratios are higher compared to those measured during wintertime at an urban location (Kanpur) in the Indo-Gangetic Plain (2.9 ± 1.5 and 0.44 ± 0.30 respectively; Ram et al, 2010). Also, ratios at a high-altitude site (Manora Peak), located in central Himalaya, are 2.9 ± 1.0 and 0.51 ± 0.20 (Rengarajan et al, 2007), during winter period. An increase in these ratios have been observed in the Bay of Bengal during the period of continental outflow in March 2006, wherein reported ratios were observed around 15 and 3 respectively (Sudheer and Sarin, 2008). On the contrary, a very conservative nss-SO₄²⁻/EC (~ 6) ratio was found in Bay of Bengal during a cruise conducted in January, 2009 (Kumar et al., 2010; Srinivas and Sarin, 2014). The aerosols collected at remote locations had undergone long-range transport tend to show an increased ratio, possibly, because of preferential removal of carbonaceous species compared to sulphates. Furthermore, during long-range transport, the mineral dust/sea-salt present in air-parcel may undergo chemical processing and formation of calcium sulphate/sodium sulphate may enhance nss-SO₄²⁻, eventually leading to high nss-SO₄²⁻/EC (or OC) ratios. The enhanced SO₄²⁻/EC ratios at remote locations suggest relative dominance of scattering SO₄²⁻ aerosols; which can have implications to estimation of single scattering albedo and radiative forcing.

3.4 Estimation of secondary organic carbon

SOAs are produced by photochemical oxidation of gaseous organic precursors and subsequent condensation onto particulate phase, constitute a significant fraction of total organic mass (Seinfeld and Pandis, 1998). In order to estimate secondary organic carbon (SOC), primary OC is calculated using a primary OC/EC ratio which is derived considering EC as a tracer for primary emissions of carbonaceous aerosols (the EC-tracer method; Turpin and Huntzicker, 1995). Primary organic carbon ([OC]_p) is calculated using the following equation:

$$[\text{OC}]_p = [\text{OC}/\text{EC}]_p * [\text{EC}] \dots\dots\dots (1)$$

where $[OC/EC]_p$ is the estimated primary OC/EC ratio and $[EC]$ is the measured elemental carbon concentration. In present study, minimum OC/EC value for each season (summer and winter; Table-4) has been used as $[OC/EC]_p$ to estimate primary OC. Subsequently, secondary organic carbon (SOC) is calculated from difference between $[OC]$ i.e. total organic carbon and $[OC]_p$ using the following equation:

$$SOC = [OC] - [OC]_p \quad \dots\dots\dots (2).$$

It is implicit in estimation of SOC using the EC-tracer method that compositions of primary OC as well as their sources are spatially invariant (Castro et al, 1999). The minimum, maximum and average values for estimated SOC and SOC/OC for winter and summer have been summarized in Table-4. Using the EC-tracer method, average SOC concentration has been found to vary from 0.14 to 4.45 $\mu\text{g m}^{-3}$ (av. = $1.51 \pm 1.00 \mu\text{g m}^{-3}$; Table-4) and 0.02 – 2.63 $\mu\text{g m}^{-3}$ (av. = $0.80 \pm 0.60 \mu\text{g m}^{-3}$; Table-4) in winter and summer season respectively. However, fractional contribution of SOC to total organic carbon was found to be similar in both seasons (Table-4). On average, estimated SOC accounted for ~50% of OC throughout the year at this high-altitude site. It is important to reiterate here that the sampling site witnesses long-range transported air-mass from Indo-Gangetic Plain during winter months.

We further examined relationship between measured WSOC and estimated SOC. Scatter plot between WSOC and SOC for winter data has been shown in Fig. 9. A significant correlation ($r^2 = 0.72$) is observed between two parameters for winter samples, however, large scatter is found during summer month. Such significant correlation suggests similar chemical behaviour of SOC and WSOC during wintertime. Furthermore, it is interesting to highlight that WSOC/SOC ratio is found to be higher than unity (av. WSOC/SOC = 1.66 ± 0.83) for winter data. This higher ratio suggests that all WSOC at the sampling site is not only due to secondary processes but there is contribution of WSOC from primary emission at the source region (IGP). Study by Zappoli et al, (1999); conducted at background site (K-pusztá and San Pietro Capofiume) in Europe have revealed the presence of water-soluble macromolecular compounds (20-50 % of water-soluble organic fraction) analogous to naturally occurring compounds like Fulvic and Humic acid. Emissions of these compounds have been attributed to biomass burning (Zappoli et al, 1999; Mukai and Ambe, 1986). It is also argued that under-estimation of SOC by the EC-tracer method (Ram et al, 2008) may also be attributing to higher WSOC/SOC ratio observed at Mt Abu. Similar kind of correlation has been observed at an urban site in Tokyo (Miyazaki et al, 2006) during three different seasons (viz. summer, winter and fall). However, WSOC/SOC ratio was found lower than unity and suggested that all the SOC are not water soluble.

4. Summary and Conclusions

This study represents a comprehensive one-year data set on seasonal characteristics of atmospheric carbonaceous aerosols at a high-altitude site (Mt Abu) in western India. The study brings out dominance of anthropogenic aerosols (produced from biomass

burning emission and secondary formation) transported from the IGP during wintertime. The important conclusions are:

- 1) A strong seasonal variability is observed in mass concentration of carbonaceous components (viz. EC, OC and WSOC) and inorganic species (nss-SO_4^{2-} , NH_4^+ and nss-K^+) with minimum concentrations observed during summer and monsoon and maximum in winter.
- 2) The average OC/EC reflects dominance of biomass burning emission in the IGP and subsequent transport at Mt Abu. The $\text{nss-K}^+/\text{EC}$ and $\text{nss-K}^+/\text{OC}$ ratio observed at the study site further corroborate to the influence of biomass burning emissions.
- 3) The relatively high WSOC/OC ratio is conspicuous during winter season and suggests the processing (or aging) of aerosols during long-range down-wind transport from the IGP. The higher WSOC/OC ratios and presence of acidic species (SO_4^{2-} and NO_3^-) can lead to changes in morphological features, mixing state and optical properties of aerosols during transport.
- 4) Back-trajectory analysis clearly indicates role of synoptic-scale long range transport in seasonal variability of carbonaceous aerosols over western India, in particular from the polluted Indo-Gangetic Plain region

Acknowledgement:

We would like to thank Prof. Manmohan Sarin for support and encouragement during this study. We thank ISRO-Geosphere-Biosphere Program (Department of Space, India) for providing partial financial support during the course of this study. A. Kumar and K. Ram thanks Department of Science and Technology, Govt. of India for providing financial support under the INSPIRE Faculty scheme (IFA13-EAS-13 and IFA-EAS-02). The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model (<http://www.ready.noaa.gov>) used in this publication. We thank the three anonymous reviewer for constructive suggestions and comments.

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Figure captions:

- Fig. 1:** (a) Map of India showing the sampling site Mt. Abu located in a semi-arid region of western India (Image taken from Google earth). (b) The rose diagram showing the wind speed (m s^{-1}) and wind direction measured at the sampling site, Mt Abu, during 2007.
- Fig. 2:** 10 days air-mass back trajectories of a typical month in 2007 (December, April and August) for three seasons. Green lines represent all trajectories for the month. Mean flow for the month is shown as blue colour (with filtered trajectories outside 1 sigma). Red cluster is mean transport pattern of the trajectories which spent 6 or more days over IGP (during December) to show spatial extent. Altitude variations of the trajectories are depicted using pressure along trajectory (hPa) in the bottom panel.
- Fig. 3:** Temporal variability of (a) $\text{PM}_{2.5}$ Mass, (b) OC, (c) EC, (d) WSOC, (e) OC/EC and (f) WSOC/OC during 2007 at the study site.
- Fig. 4:** Box-whisker plots representing the mean (dotted line), median (solid line), and different percentile levels (95^{th} , 75^{th} , 25^{th} and 5^{th}) of various inorganic and carbonaceous components (in $\mu\text{g m}^{-3}$) of $\text{PM}_{2.5}$ during winter and summer season. Points lying outside the whisker are shown as open circle denotes outliers.
- Fig. 5:** A vertical bar chart showing the comparison of OC, EC, WSOC (in $\mu\text{g m}^{-3}$), OC/EC, WSOC/OC levels with 1-sigma in the marine air mass (MAP) and IGP influenced air mass (IGPAP), using trajectory assisted analyses (discussed in section 3.1) over Mt. Abu during 2007.
- Fig. 6:** Relationship between (a) EC and OC and (b) WSOC and OC for $\text{PM}_{2.5}$ during two different seasons.
- Fig. 7:** Box-whisker plots representing the mean (dotted line), median (solid line), and different percentile levels (95^{th} , 75^{th} , 25^{th} and 5^{th}) of OC/EC and WSOC/OC ratio in $\text{PM}_{2.5}$ from high-altitude site in western India.
- Fig. 8:** Time series of daily total fire counts during January-December 2007 over Indo-Gangetic Plains obtained from the MODIS aboard Terra satellite with detection confidence higher than 80%.
- Fig. 9:** Scatter plot showing a significant correlation between WSOC and SOC suggesting similar chemical behaviour of both species during winter time at this high-altitude site.

Table captions:

- Table-1 Statistics of carbonaceous and inorganic components during two different seasons at the high-altitude site in western India. All concentrations are in $\mu\text{g m}^{-3}$.
- Table-2: Statistics of various diagnostic ratios observed in the ambient $\text{PM}_{2.5}$ at high-altitude site, Mt. Abu during two different seasons.
- Table-3: The average $\text{nss-K}^+/\text{EC}$ and $\text{nss-K}^+/\text{OC}$ ratio observed at different locations in the Indo-Gangetic Plain as well as in different continents. The ratios observed for pure wood burning (of different species) have been included in the table.
- Table-4: Statistics of secondary organic carbon (SOC; in $\mu\text{g m}^{-3}$) and fraction of SOC (in total OC) in $\text{PM}_{2.5}$ at Mt. Abu for summer and winter. All concentrations are in $\mu\text{g m}^{-3}$.



Fig. 1a

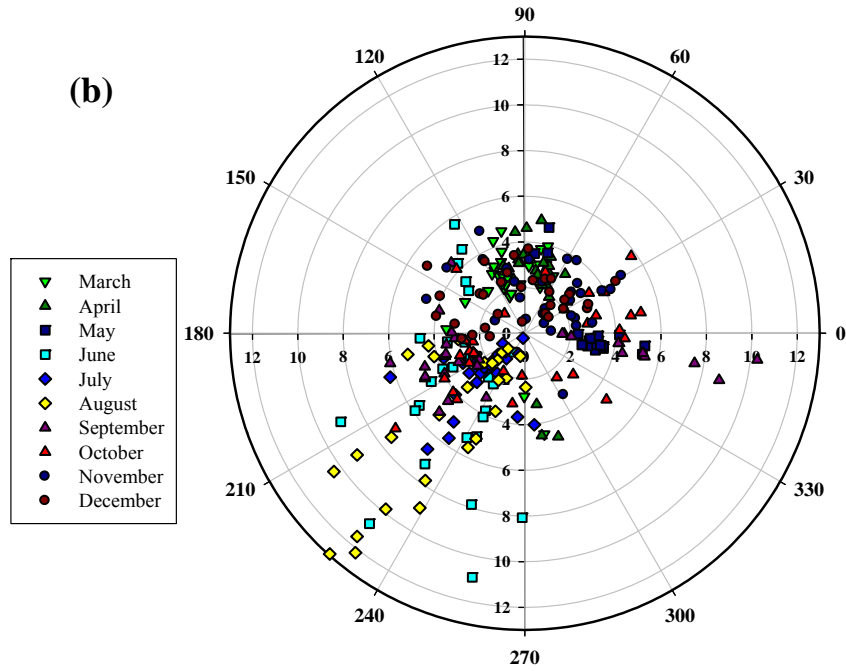


Fig. 1b

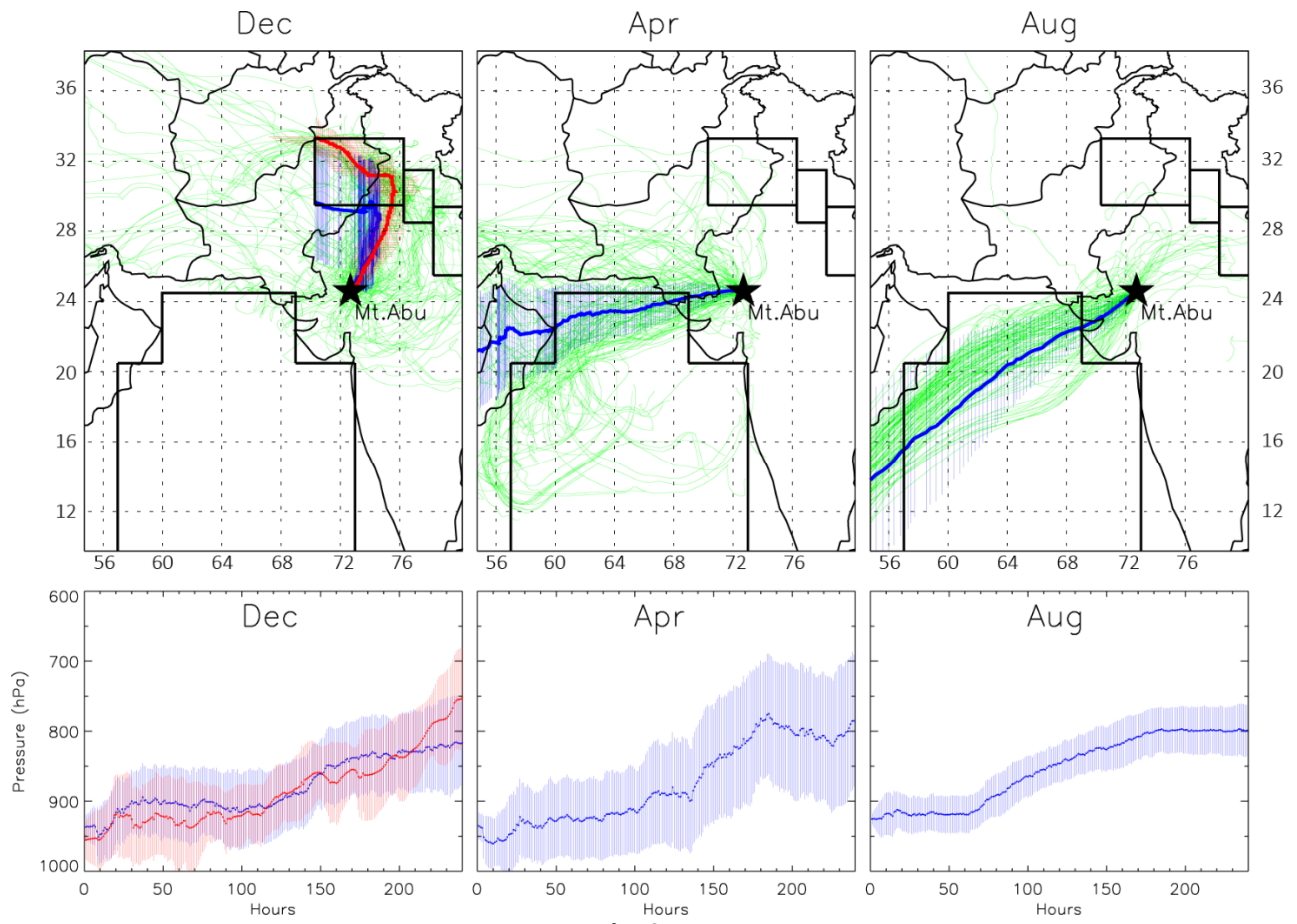


Fig. 2

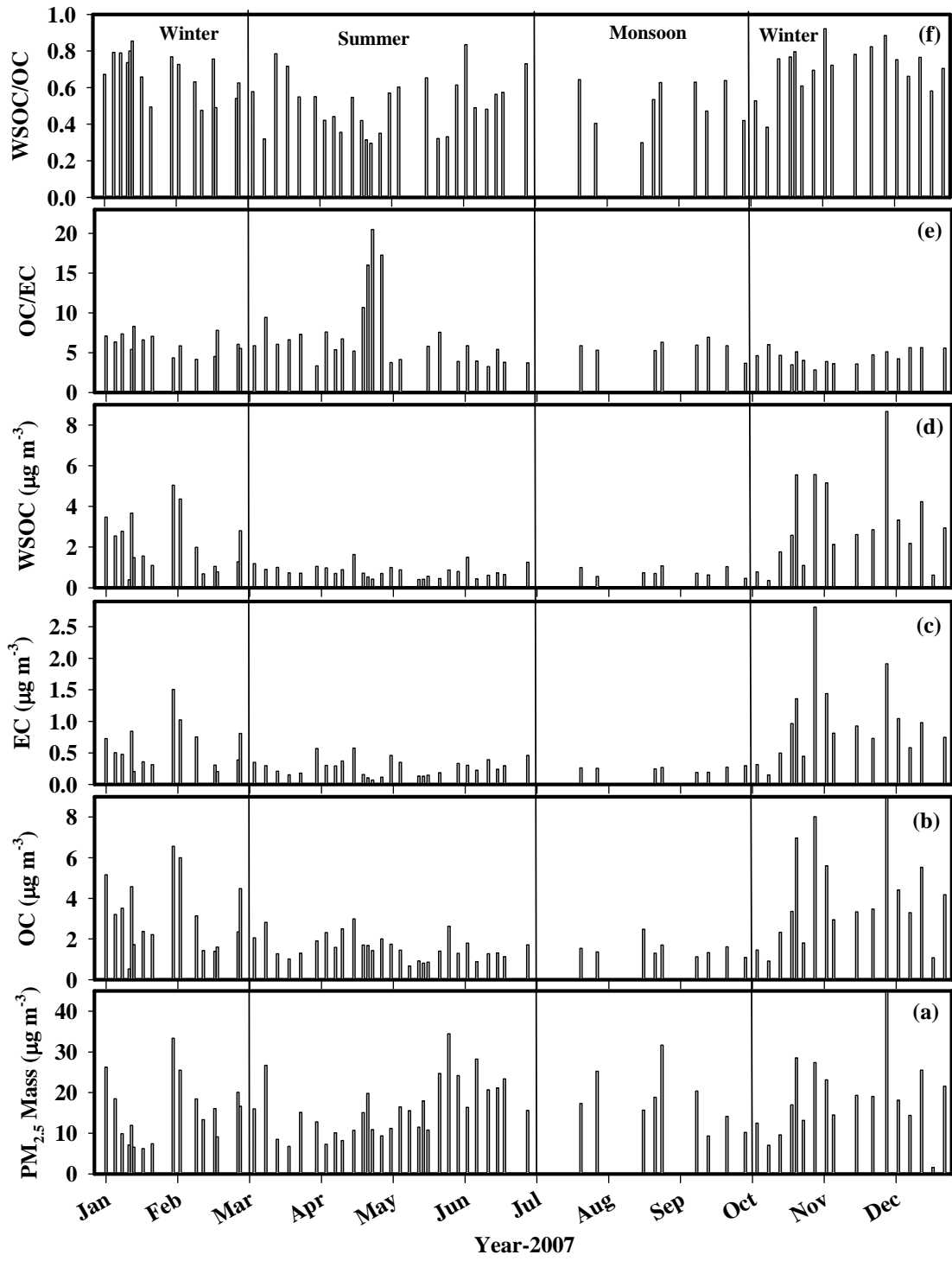


Fig. 3

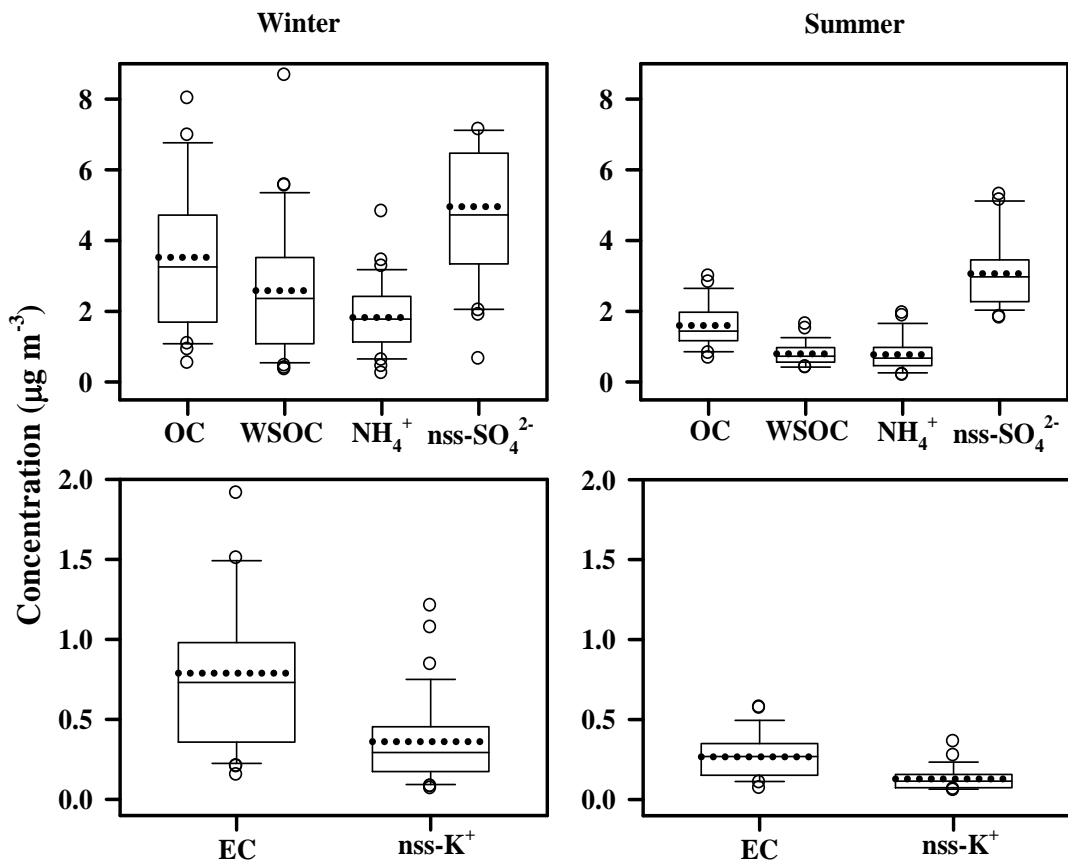


Fig. 4

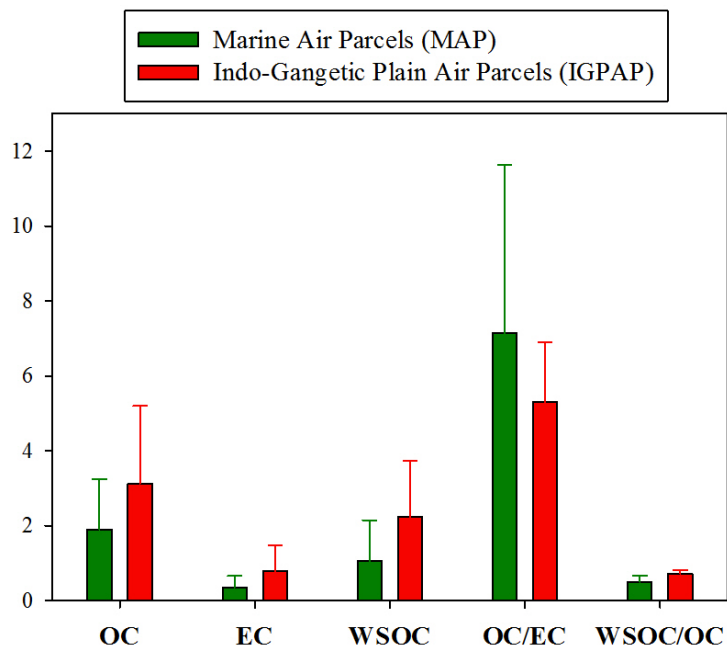


Fig. 5

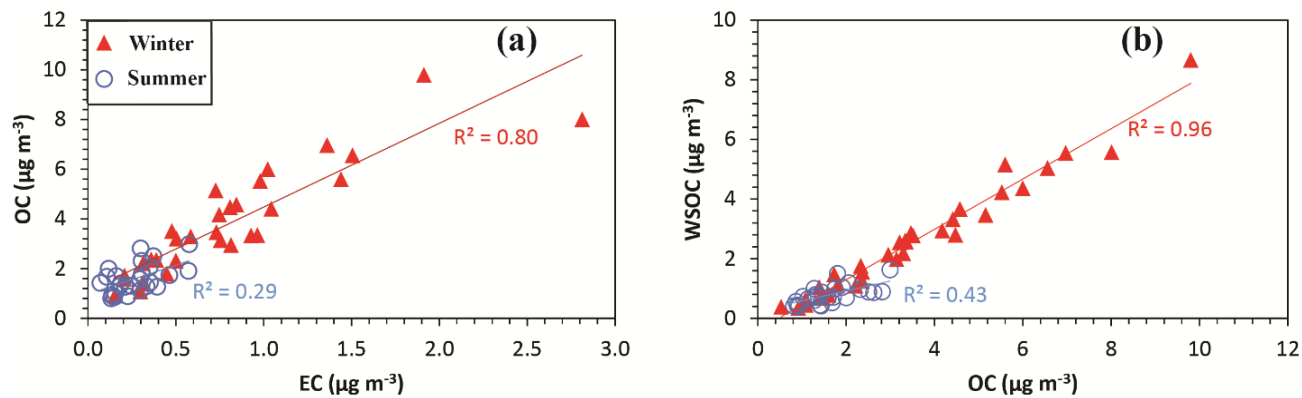


Fig. 6

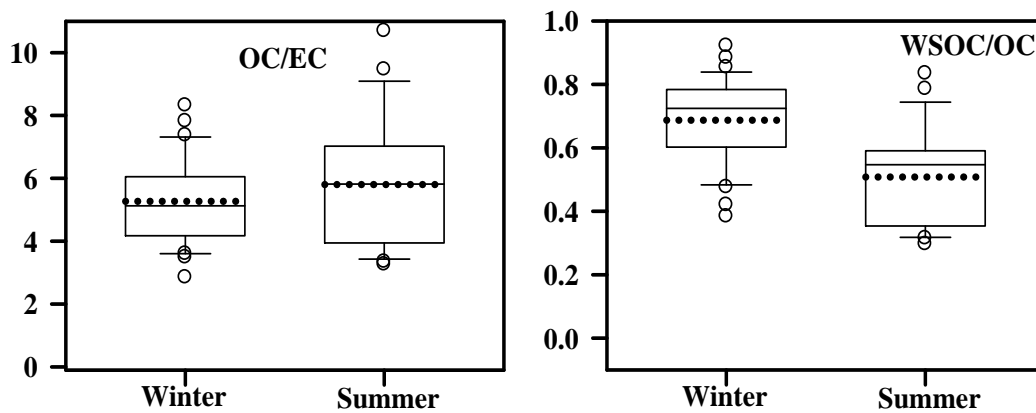


Fig. 7

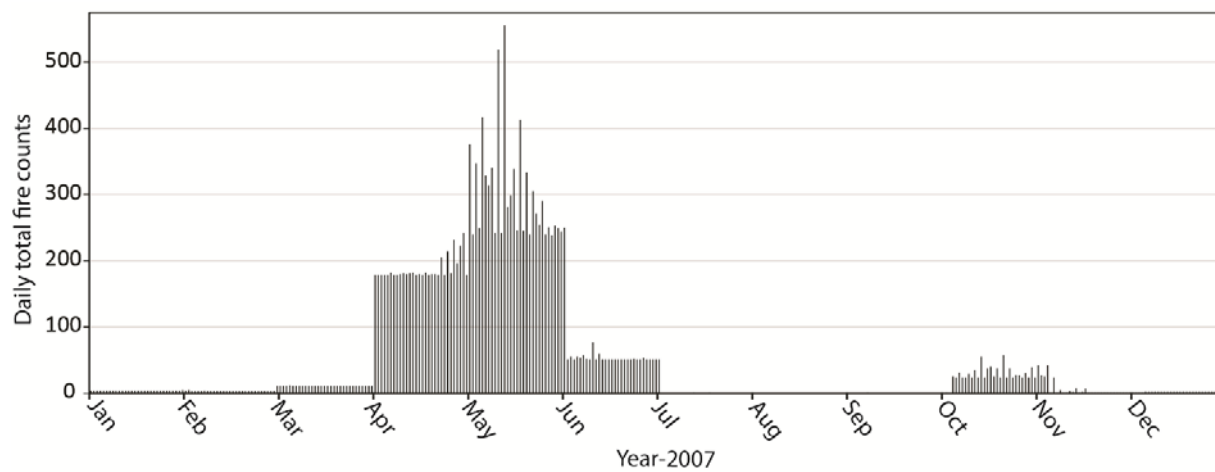


Fig. 8

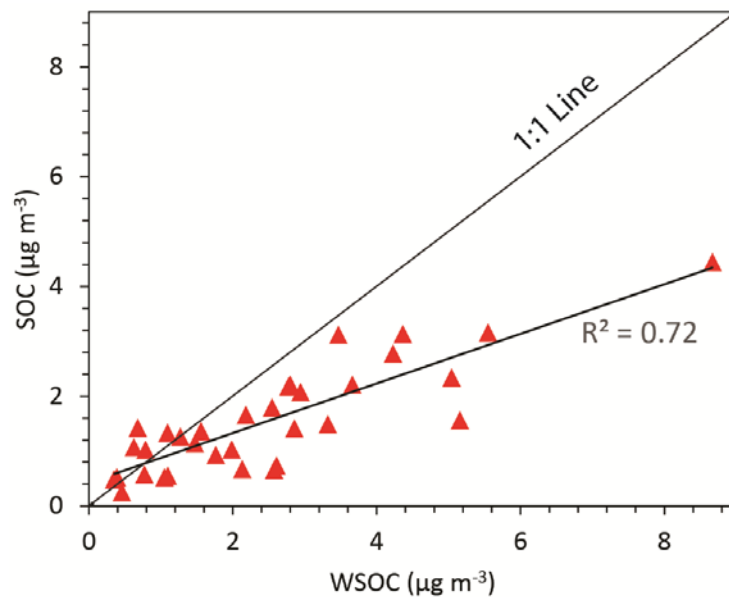


Fig. 9

Table-1

	Winter (n = 34)					Summer (n = 28)				
	Mean	S.D	Median	Minimum	Maximum	Mean	S.D	Median	Minimum	Maximum
OC	3.5	2.2	3.3	0.5	9.8	1.6	0.6	1.4	0.7	3.0
EC	0.8	0.6	0.7	0.2	2.8	0.3	0.1	0.3	bdl	0.6
WSOC	2.6	1.9	2.4	0.4	8.7	0.8	0.3	0.7	0.4	1.6
NH_4^+	1.8	1.0	1.8	0.2	4.8	0.8	0.5	0.7	0.2	2.0
nss-SO_4^{2-}	5.0	2.3	4.7	0.7	11.8	3.1	1.0	3.0	1.8	5.3
nss-K^+	0.4	0.3	0.3	0.1	1.2	0.1	0.1	0.1	0.1	0.4
OC/EC	5.3	1.4	5.1	2.9	8.3	5.6	1.7	5.6	3.3	10.7
WSOC/OC	0.69	0.13	0.72	0.38	0.92	0.51	0.15	0.55	0.30	0.83

Table-2

	Winter					Summer				
	Mean	S.D	Median	Minimum	Maximum	Mean	S.D	Median	Minimum	Maximum
nss-K ⁺ /EC	0.53	0.14	0.55	0.23	0.89	0.53	0.18	0.52	0.26	1.01
nss-K ⁺ /OC	0.10	0.04	0.10	0.06	0.18	0.08	0.03	0.08	0.03	0.16
nss-SO ₄ ²⁻ /EC	8.56	4.00	7.30	2.33	20.5	14.00	6.80	11.50	6.71	30.1
nss-SO ₄ ²⁻ /OC	1.70	0.90	1.43	0.60	4.75	2.17	1.00	1.92	0.91	4.88

Table-3

Site	Location Type	Sampling period	nss-K+/OC	nss-K+/EC	References
Mt.Abu	High-altitude, Remote	Mar-Jun, 2007	0.08±0.03	0.53±0.18	This Study
		Jan-Feb, Oct-Dec, 2007	0.10±0.04	0.53±0.14	This Study
Kanpur	Urban	Oct, 2008	0.06±0.02	0.28±0.10	Ram and Sarin, 2010b
		Jan-Feb, 2007	0.04±0.01	0.42±0.18	Ram and Sarin, 2010a
Allahabad	Urban	Dec, 2004	0.05±0.01	0.44±0.11	Ram and Sarin, 2010a
Hisar	Urban	Dec, 2004	0.08±0.02	0.64±0.19	Rengarajan et al, 2007
Kharagpur	Urban	Nov,2009-Mar,2010	0.07±0.04	0.49±0.22	Srinivas and Sarin, 2014
Olympia, USA	Residential Wood burning		0.011-0.014		Khalil and Rasmussen, 2003
Oak			0.005	0.20	Schauer et al, 2001
Pine	Residential fireplace combustion		0.011	0.20	
Eucalyptus			0.018	0.31	

Table-4

	(OC/EC) _p	SOC			SOC/OC		
		Median (Mean±Std Dev)	Minimum	Maximum	Median (Mean±Std Dev)	Minimum	Maximum
Summer	3.26	0.67 (0.82±0.60)	0.02	2.63	0.47 (0.49±0.26)	0.03	1.00
Winter	2.80	1.35 (1.51±1.00)	0.14	4.45	0.49 (0.48±0.22)	0.02	1.00

Highlights

1. Temporal variability of carbonaceous species at high-altitude site in western India.
2. Sources of carbonaceous aerosol are dominated by biomass burning emissions.
3. Role of synoptic scale transport on variation of EC, OC and WSOC is highlighted.

Supplementary material: Manuscript number- ATMENV-D-15-00481R1

1. Details of analytical procedure

EC and OC measurement

The thermal, chemical and optical properties of OC and EC were used for their measurements. The OC and EC fractions were measured by stepwise heating them in an inert (100% He) and oxidizing medium (10% O₂+90% He, vol/vol), respectively to convert them into CO₂. The evolved CO₂ during these heating steps is subsequently reduced to methane using heated Ni/Pt catalyst and qualitatively measured on a flame ionization detector (FID). The initial transmittance through the sample filter, measured using a 678 nm laser source, was used to define the split-point between OC and EC and to correct for the pyrolyzed carbon produced by charring of organic compounds in an inert atmosphere. At the end of every analytical run, a fixed volume of methane (5% CH₄+95% He, vol/vol) is injected as an internal standard to assess the performance of FID; whereas Potassium Hydrogen Phthalate (KHP) is used as an external standard.

WSOC and inorganic constituents

In order to measure the water-soluble organic carbon (WSOC) and inorganic constituents (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, and SO₄²⁻), quarter of filter was cut and transferred to Teflon vial under a clean laminar flow bench. The filters were soaked in 50 ml of Milli-Q water (resistivity = 18.2 MΩ cm) for 3-4 hrs following the initial ultrasonic treatment for 15 min. Subsequently, water extract was centrifuged and supernatant fraction was transferred to pre-cleaned polypropylene bottles (keeping them soaked in Milli-Q water for ~72 hrs) and stored for the analysis of inorganic species. One portion of supernatant fraction was transferred to glass vials to measure the WSOC concentrations using a total organic carbon (TOC) analyzer (Shimadzu, model 5000A; Rengarajan et al, 2007; Ram and Sarin, 2010; 2011). 25 μL of water-extract is injected into the furnace packed with Pt catalyst at a temperature of 680 °C and evolved CO₂ is measured using a non-dispersive infrared (NDIR) detector to assess total carbon (TC) content. Another aliquot of the solution (100 μL) is acidified with 25% phosphoric acid (25% H₃PO₄, vol/vol) and the evolved CO₂ is considered as inorganic carbon (IC).

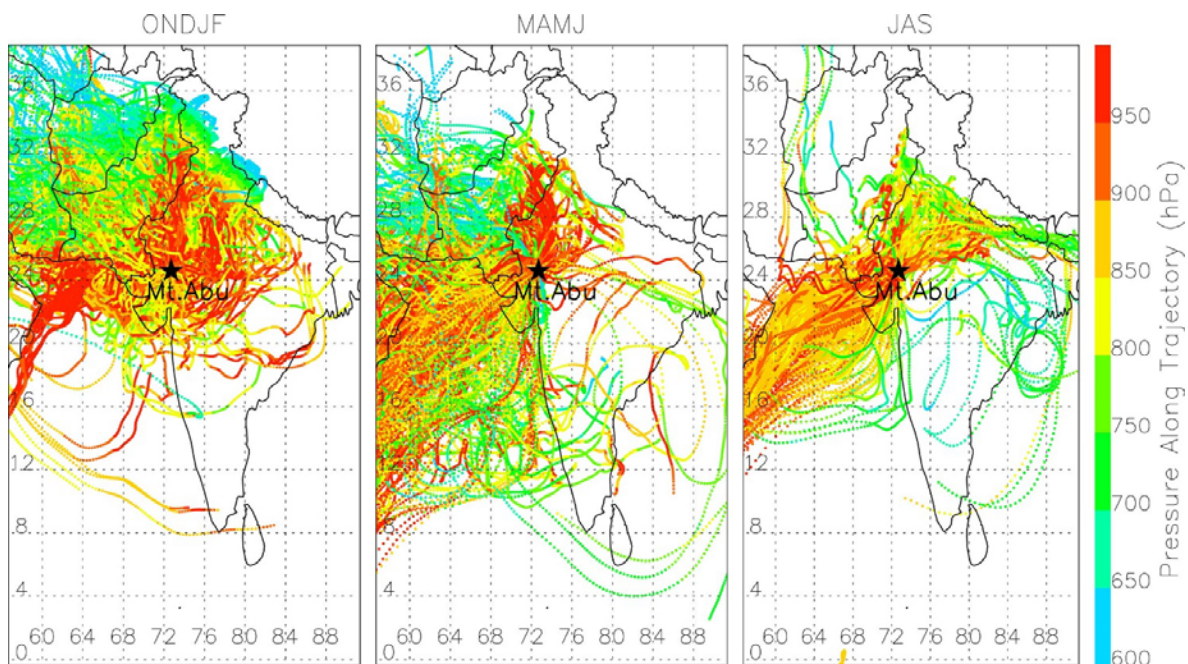


Fig. S1: 10-days back air trajectories at Mt. Abu simulated using HYSPLIT (<http://www.arl.noaa.gov/HYSPLIT.php>) for winter (ONDJF), summer (MAMJ) and monsoon (SON) for the year 2007. Altitude variations of the trajectories are depicted using pressure along trajectory (hPa). Air trajectories have been colour coded according to the air pressure (hPa) along the trajectory to show the altitude variations of the air masses before arriving to the observation site. The model has been driven by the NCEP/NCAR meteorological fields at $2.5^\circ \times 2.5^\circ$ available every 6 hours. More details of the HYSPLIT model, input meteorological datasets can be seen on the model website <https://ready.arl.noaa.gov/HYSPLIT.php> or in the Draxler and Rolph, (2013).

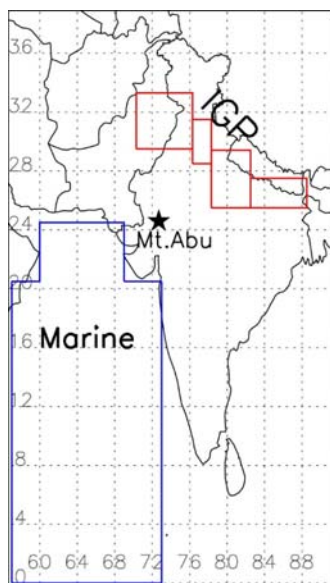


Fig. S2: The four boxes in red colour represent IGP region and that in blue colour indicate marine region. Air masses having a residence of 2 to 6 or more days over the IGP region and less than 1 day over the marine regions are termed as IGPAP. While, the air masses having a residence of 2-6 days or more over the marine regions and less than 1 day over the IGP are classified as the MAP.

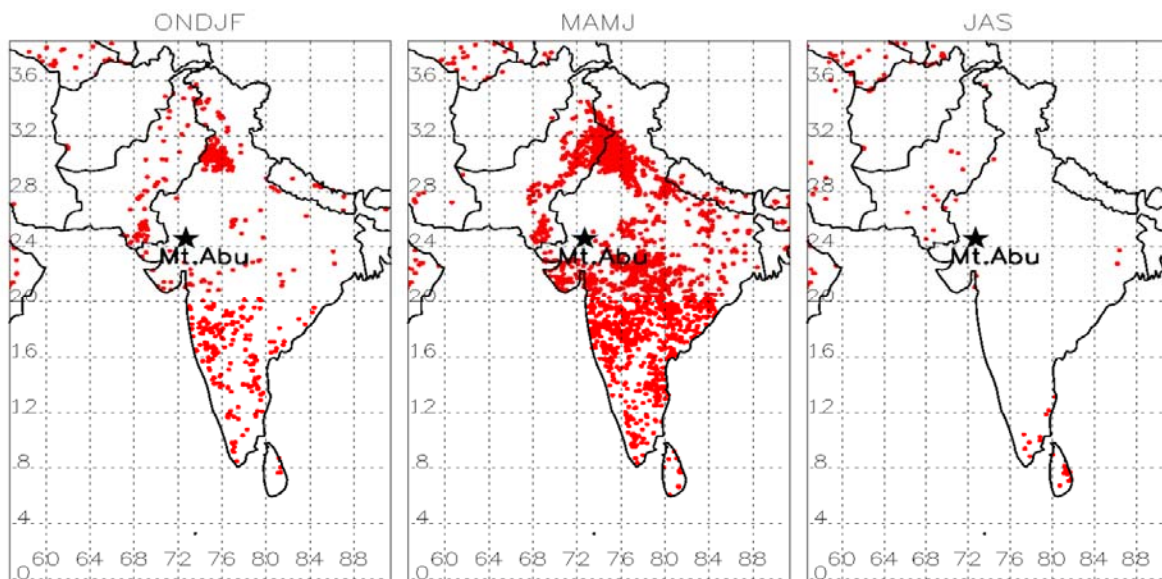


Fig. S3: Spatial distribution of fire counts for three seasons winter (ONDJF), summer (MAMJ) and monsoon (SON) for the year 2007. Fire count data (red circles) are derived from MODIS aboard Terra satellite with detection confidence higher than 80% is shown.

Table-S1: Mass concentrations ($\mu\text{g m}^{-3}$) EC, OC, WSOC and OC/EC and WSOC/OC ratios at different location across the globe. References: 1. Ram et al, (2010), 2. Ram and Sarin, (2010), 3. Rengarajan et al, (2007), 4. Kumar et al, (2008), 5. Decesari et al, (2001), 6. Krivacsy et al, (2001), 7. Aymoz et al, (2007), 8. Jafrezzo et al, (2005), 9. Viana et al, (2007), 10. Sullivan et al, (2004), 11. Weber et al, (2007), 12. Ho et al, (2006), 13. Miyazaki et al, (2006), 14. Sahu et al, (2009) (Urban-1: Korean air-mass and Urban-2 : Chinese air-mass), 15. Park and Cho, 2010, 16. Srinivas and Sarin, (2014), 17. Kumar et al., (2010) (IGP : Indo-Gangetic outflow ; SEA : South-east Asian out flow), 18. Sahu et al., (2011).

Site	Location Type	Sampling period	OC	EC	WSOC	OC/EC	WSOC/OC	References
Kanpur	Urban	Apr-Jun, 2007	12.9±5.9	2.0±1.3	6.1±3.6	7.3±5.	0.50±0.2	1
		Dec, 2007-Feb, 2008	46.7±25.	5.3±1.9	17.4±11	9.3±6.	0.37±0.1	
		Oct, 2008	45.8±22.	8.2±3.7	25.7±18	6.1±2.	0.57±0.1	2
Allahabad	Urban	Dec, 2004	49.0±14.	6.2±2.0	17.7±5.	8.1±1.	0.37±0.0	1
			1		9	7	8	
Jaduguda	Rural	Dec, 2004	35.3±7.1	11.6±2.	16.2±3.	3.1±0.	0.47±0.1	3
				0	5	6	1	
Hisar	Urban	Dec, 2004	30.9±17.	3.8±1.4	10.7±4.	8.5±2.	0.32±0.1	3
			9		5	2	4	
Manora Peak	High-altitude	Dec, 2004	4.8±1.1	0.9±0.3	2.0±0.7	6.0±1.	0.42±0.1	4
					9	4		
Bay of Bengal Arabian	Marine	Dec, 2007-Feb, 2008	13.0±6.1	2.0±0.9	6.7±3.2	6.5±1.	0.52±0.1	4
					6	2		
		Mar-Apr, 2006	1.9±1.6	0.4±0.2		4.3±2.		4
					4			
		Apr-May,	0.3±0.2	0.1±0.0		2.8±1.		

Sea PoValley		2006		3		1			
		Jan-Feb, 1998	16.0±8.8	1.0±0.6	7.1±3.1	16	0.47±0.08	5	
		May-Sep, 1998	2.9±0.9	0.3±0.3	1.4±0.5	9.7	0.50±0.06		
		Dec-Feb, 98-99	14.5±4.8	0.4±0.1	2.4±2.8	36.25	0.38±0.10		
Jungfraujo ch	High-altitude	Jul-Aug, 1998	1.05	0.29	0.63	3.6	0.6	6	
K-Puszt	Rural	Jul-Aug, 1998	7.60	0.75	0.75	10.1	0.1		
Mace Head, Chamonix	Marine	Jul-Aug, 1998	0.61	0.03	0.03	20.3	0.05		
	Krebside	Feb, 2001-Jul, 2003	8.97±5.22	1.89±1.43	7.20±3.25	4.8	0.8	7,8	
St.Jean	Urban	Feb, 2001-Jun, 2003	6.32±3.08	0.95±0.66	4.75±3.15	6.7	0.75		
Barcelona	Krebside	Jul-Sep, 2004	3.7	0.8	1.6	4.6	0.43	9	
		Nov-Dec, 2004	6.7	1.2	2.1	5.6	0.31		
Ghent	Urban	Jun-Jul, 2004	2.3	0.7	1.0	3.3	0.43		
		Jan-Feb, 2005	5.4	1.0	2.3	5.4	0.43		
St. Louis	Urban	Jun, 2003	4.76±2.53	0.80±0.57	2.87±1.41	5.9	0.64±0.13	10	
		Aug, 2003	4.04±1.75	0.62±0.51	2.40±0.78	6.5	0.61±0.16		
		Oct, 2003	4.55±3.62	1.11±1.01	1.33±0.75	4.1	0.31±0.11		
Georgia	Urban	Jul, 2005	10.50±1.75	0.90±0.24	6.72±1.41	11.7	0.64±0.05	11	
Yorkville	Rural	Jul, 2005	8.51±1.72	0.15±0.01	6.26±1.29	5.7	0.74±0.04		
Hongkong	Roadside	Nov 2000-Feb 2001	11.2±1.8	6.4±1.2	3.5±0.5	1.8	0.32±0.05	12	
		Jun-Aug, 2001	10.2±2.4	5.9±0.3	2.1±0.3	1.7	0.22±0.06		
Kwun Tong, Hongkong	Urban	Nov 2000-Feb 2001	8.8±1.8	4.8±0.6	3.4±1.0	1.8	0.38±0.07		
		Jun-Aug, 2001	5.9±2.5	4.5±0.6	2.1±0.9	1.6	0.34±0.11		
Hok Tsui	Urban	Nov 2000-Feb 2001	5.5±1.1	1.4±0.4	2.8±0.6	4.1	0.51±0.07		
Tokyo	Urban	Jan-Feb 2004	5.00±2.78	2.46±1.33	1.05±0.91	2	0.19±0.08	13	
		Aug, 2004	3.98±2.68	1.69±1.17	1.28±1.18	2.4	0.35±0.15		
		Nov, 2004	5.95±2.37	3.52±2.32	2.38±1.84	1.7	0.37±0.14		
Gosan	Marine	Mar-Apr, 2005	3.1±0.6	0.35±0.16	0.30±0.21	8.8	0.1±0.06	14	
	Urban-1		4.6±1.3	1.5±0.31	1.8±0.32	3.1	0.40±0.01		

	Urban-2		5.5±1.3	1.9±0.9 2	2.0±1.1	2.9	0.35±0.1 5	
Gwangju	Urban	Jun-Aug, 2008	5.0	1.6	2.8	3.1	0.55	15
		Dec, 2008- Feb, 2009	8.4	3.1	3.7	3.0	0.44	
Kharagpur	Urban	Nov, 2009- Mar, 2010	30.7±12. 1	4.5 ±1.6	14.8±5. 2	7.0±2. 2	0.52±0.1 6	16
Bay of Bengal	Marine			2.0±1.3				17
		Jan 2009 (IGP outflow)	5.9±3.7 2.6±1.9	1.2±0.4	4.3±2.3 2.3±1.4	2.9±0. 8	0.77±0.1 0	
	Urban	(SEA outflow)		3.8±0.9		2.0±1.	0.91±0.1	18
Bangkok		Apr, 2007- Mar, 2008	8.4±4.6		2.5±0.7	3	2	

Table S2: Estimated levels of carbonaceous species in the marine air parcel (MAP) and IGP influenced air parcel (IGPAP). The percentage change from MAP to IGPAP air mass is also given in percentage. +ve sign indicates higher levels in the IGP air mass while -ve sign indicates lower levels in IGP air mass as compared to marine air mass.

	MAP	IGPAP	Change (%)
OC	1.90 ± 1.34	3.13 ± 2.07	+ 64.9
EC	0.35 ± 0.31	0.78 ± 0.70	+ 121.4
WSOC	1.05 ± 1.10	2.24 ± 1.49	+ 113.2
OC/EC	7.14 ± 4.49	5.30 ± 1.60	- 25.8
WSOC/OC	0.51 ± 0.16	0.71 ± 0.09	+ 40.8

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