Environ Sci Pollut Res (2014) 21:8678–8691
DOI 10.1007/s11356-014-2768-0

RESEARCH ARTICLE

Sources and characteristics of carbonaceous aerosols at Agra "World heritage site" and Delhi "capital city of India"

A. S. Pipal · S. Tiwari · P. G. Satsangi · Ajay Taneja · D.S. Bisht · A. K. Srivastava · M. K. Srivastava

Received: 9 December 2013 / Accepted: 10 March 2014 /

Abstract Agra, one of the oldest cities "World Heritage site", and Delhi, the capital city of India are both located in the border of Indo-Gangetic Plains (IGP) and heavily loaded with atmospheric aerosols due to tourist place, anthropogenic activities, and its topography, respectively. Therefore, there is need for monitoring of atmospheric aerosols to perceive the scenario and effects of particles over northern part of India. The present study was carried out at Agra (AGR) as well as Delhi (DEL) during winter period from November 2011 to February 2012 of fine particulate ($PM_{2.5}$: $d<2.5$ μm) as well as associated carbonaceous aerosols. $PM_{2.5}$ was collected at both places using medium volume air sampler (offline measurement) and analyzed for organic carbon (OC) and elemental carbon (EC). Also, simultaneously, black carbon (BC) was measured (online) at DEL. The average mass concentration of $PM_{2.5}$ was 165.42±119.46 μg m^{-3} at AGR while at DEL it was 211.67±41.94 μg m^{-3} which is ~27 % higher at DEL than AGR whereas the BC mass concentration was 10.60 μg m^{-3}. The $PM_{2.5}$ was substantially higher than the annual standard stipulated by central pollution control board and United States Environmental Protection Agency standards. The average concentrations of OC and EC were 69.96±34.42 and 9.53±7.27 μm m^{-3}, respectively. Total carbon (TC) was 79.01±38.98 μg m^{-3} at AGR, while it was 50.11±11.93 (OC), 10.67±3.56 μg m^{-3} (EC), and 60.78±14.56 μg m^{-3} (TC) at DEL. The OC/EC ratio was 13.75 at (AGR) and 5.45 at (DEL). The higher OC/EC ratio at Agra indicates that the formation of secondary organic aerosol which emitted from variable primary sources. Significant correlation between $PM_{2.5}$ and its carbonaceous species were observed indicating similarity in sources at both sites. The average concentrations of secondary organic carbon (SOC) and primary organic carbon (POC) at AGR were 48.16 and 26.52 μg m^{-3} while at DEL it was 38.78 and 27.55 μg m^{-3}, respectively. In the case of POC, similar concentrations were observed at both places but in the case of SOC higher over AGR by 24 in comparison to DEL, it is due to the high concentration of OC over AGR. Secondary organic aerosol (SOA) was 42 % higher at AGR than DEL which confirms the formation of secondary aerosol at AGR due to rural environment with higher concentrations of coarse mode particles. The SOA contribution in $PM_{2.5}$ was also estimated and was ~32 and 12 % at AGR and DEL respectively. Being high loading of fine particles along with carbonaceous aerosol, it is suggested to take necessary and immediate action in mitigation of the emission of carbonaceous aerosol in the northern part of India.

Keywords $PM_{2.5}$ · Carbonaceous aerosols · Black carbon · Secondary organic aerosol · India

---

Responsible editor: Gerhard Lammel

A. S. Pipal · P. G. Satsangi
Department of Chemistry, University of Pune, Pune, India 411007

A. S. Pipal
e-mail: aspippal@gmail.com

S. Tiwari · D. Bisht · A. K. Srivastava
Indian Institute of Tropical Meteorological, New Delhi Branch, India 110060

A. Taneja (✉)
Department of Chemistry, Dr. B. R. Ambedkar University, Agra, India 282002
e-mail: ataneja5@hotmail.com

M. K. Srivastava
Department of Geophysics, Banaras Hindu University, Varanasi, India 221005

Introduction

Atmospheric aerosols play an important role in climate change and atmospheric chemistry in the troposphere because of the direct effect on the radiative balance of the Earth's atmosphere by scattering or absorbing incoming shortwave radiation and through indirect effect by acting as Cloud Condensation Nuclei (CCN) (Andreae and Crutzen 1997; Rastogi and Sarin 2006). Carbonaceous aerosol, which is a large fraction of atmospheric aerosols, played a crucial role in air pollution, adverse health, visibility reduction and climate effects. They constitutes a significant fraction in fine particles ($PM_{2.5}$), and it could be accounted for up to 40 % of mass of $PM_{2.5}$ in urban atmosphere (Seinfeld and Pandis 1998), however, in rural atmosphere it accounted up to 77 % (Ancelet et al. 2013). The carbon fractions composing ambient particulate matter are commonly divided into two types, depending on their interaction with light and their volatility (Chow and Watson 1993; Birch and Cary 1996; Schauer et al. 2002). Light absorbing particles are referred to as elemental carbon (EC), and non-absorbing particles are referred to as organic carbon (OC) (Chow et al. 2001). A significant fraction of OC is water soluble, making it important into particle–cloud interactions (Decesari et al. 2000) and influence many heterogeneous reactions involving atmospheric particles and trace gases (Begum and Minar 2012). Although, the study of EC and OC are important in atmospheric chemistry and physics, information concerning their spatial and temporal variability is quite limited. Carbonaceous aerosol, which consists of OC and black carbon (BC) or EC, are of the major research interest due to their ubiquitous nature and abundance, particularly in fine-mode ($PM_{2.5}$) (Lonati et al. 2007; Dutkiewicz et al. 2009). On the other hand, OC is either emitted directly from sources (primary) or formed from the condensation of low volatility products of the oxidation of hydrocarbons (secondary). Carbonaceous particles (elemental and organic carbon) both terms represent rather complex species since even the elemental carbon contains a number of functional groups such as alcoholic, phenolic, carbonylic, carboxylic (Akhter et al. 1985). Moreover, the surface of elemental carbon particles contains numerous adsorption sites which are capable of enhancing catalytic processes. It is the second most important component of global warming, after CO_2 (Hansen et al. 2000; Jacobson 2001). Organic carbon represents a large variety of organic compounds such as aliphatic, aromatic compounds, acids, etc. On the other hand, OC is mainly a scattering medium and exerts a negative climate forcing influence (Houghton et al. 2001). Thus, carbonaceous studies demand more attention and research, thus measurement of OC and EC is important.

A growing body of evidence suggests that both primary and secondary organic aerosol (POA and SOA) undergo multistage heterogeneous oxidation and evaporation condensation processes as they age (Robinson et al. 2007; Donahue et al. 2009; Weitkamp et al. 2009). EC, POA, and VOCs are emitted in the course of the combustion process. A significant portion of POA is semi-volatile and evaporates on dilution as it moves away from the source and reacts with oxidants in the gas phase, forming less volatile material that condenses back to produce SOA (Robinson et al. 2007). POA containing carbonyl compounds also participates in heterogeneous oxidation reactions in the aerosol phase to produce more polar and water-soluble compounds (Weitkamp et al. 2007, 2009). Thus, a significant portion of POA is converted into SOA during its atmospheric life span (Donahue et al. 2009). SOA is oxygenated material containing a large fraction of water-soluble organic compounds (Blando and Turpin 2000; Matsui et al. 2009; Asa-Awuku et al. 2010) and is continuously oxidized in the atmosphere via heterogeneous reaction mechanisms as it ages (Robinson et al. 2007; Donahue et al. 2009).

Secondary particles are formed in the atmosphere through a combination of chemical and physical reactions among primary pollutants such as the direct emissions of gaseous pollutants such as oxides of sulfur, nitrogen, ammonia, etc. It is difficult to predict ambient concentrations of these secondary air pollutants because they are also affected by long-range transport, and their formation is dependent on unstable factors such as ambient temperature and humidity. Analysis of the carbonaceous component of particles has traditionally distinguished between EC and OC where the EC is loosely associated with the terms soot and OC is everything else. There is a separable issue of whether the material collected on filters is representative of carbonaceous material in the ambient atmosphere, as it is well-known that semi-volatile organic compounds, for example, can lead to significant variations in collected material depending on the collection conditions (e.g., Turpin et al. 1993; Eatough et al. 1993).

Agra and Delhi are located in Indo-Gangetic Plain (IGP) region, which is one of the most polluted regions in northern India and is influenced by various emission sources such as fossil fuel combustion from industries, vehicular, thermal power plant, post-harvesting of agricultural residue burning, and a lot of minor sources such as textile mills, brick kilns etc. In thermal power plants, they are using coal which is also affecting carbonaceous aerosols concentrations (Schwarz et al. 2008; Salma et al. 2004). Apart from this, due to its topography and being situated in the foot hills of Himalayas, long-range of transport of mineral dust imparts significant variability of aerosols over this region. Due to above said importance, the present study has been conducted in northern part of India at two different well-known places, i.e., Agra which one of the oldest city "world heritage city" in the presence of the Taj Mahal and Delhi, which is the capital city of India with huge population (~18 millions). Thus the objectives of this study are: to determine the mass concentration level of fine particulate matter ($PM_{2.5}$) at Agra as well as Delhi, to characterized fine particulate matter in terms of carbonaceous species (OC and EC), to determined the relationship between $PM_{2.5}$ and its associated carbonaceous species, and tried to find out their sources over study region of India. During the same period, soot particle called black carbon (BC) was also studied and data was compared with EC.

Experimental methods

Site description

Agra (27°10′ N 78°02′ E), which is located in the northern part of India and is about 204 km of south of Delhi in the state of Uttar Pradesh. It is one of the most famous tourist spots in India because of the presence of Taj Mahal, situated on the west bank of river the Yamuna. The climate during winter is cooled with moisture; the temperature ranges from 3.5 to 30.5 °C and downwind West–North–West, i.e., WNW 9.4 % and North–North–West 11.8 %. The atmospheric pollution load was higher when wind blows from WNW because oil refinery at Mathura (50 km far from the centre of the city) which is located there and pollutants may be transported. Agra has about 1.3 million inhabitants and the population density is about 21,150 persons km^{-2} with 386,635 vehicles registered and 32,030 generator sets. In Agra, 60 % pollution is mainly due to vehicular emissions from three national highways (NH-2, NH-3, and NH-11) cross the city (Pipal et al. 2011). Delhi (28° 35′ N; 77° 12′ E; 217 masl), the capital city of India is situated between the rich rain-washed Gangetic plain in the east and semi-arid tracts of Rajasthan to the southwest which is about 1,100 km away from the nearer coast of Arabian Sea and considered as the fourth most polluted city in the world with respect to suspended particulate matter having ~18 million inhabitants (Goyal and Sidharta 2002, Tiwari et al. 2012). In addition to this, 4.8 million registered vehicles, three coal-based thermal power plants, and 125,000 small- and medium-scale industrial units are situated in Delhi (Srivastava et al. 2009). The major sources of pollution over Delhi are power plants, road transport, small–scale industries and domestic cooking. The cold and dry weather associated with the northwesterly coming from northwest Himalayas is characteristic of the winter season over central IGB (Mishra and Shibata 2012).

Sample collection and analysis

Aerosol samples were collected at two sites, the first site is a roadside (Agra) and another site is Indian Institute of Tropical Meteorology Pune, New Delhi, on the rooftop of the building (15 m above the ground level) during winter season (2011–2012) (Fig. 1).

Aerosol samples were collected for 24 h on quartz filter papers by a medium volume sampler (model: APM 550, Envirotech, New Delhi) at flow rate, 16.6 l min^{-1}). There is more chance in varying the $PM_{2.5}$ mass and its carbonaceous species in winter due to vehicular activities and local sources like wood, cow dung, and crop residue burning for space heating. The quality control in monitoring was made to check the daily flow rate calculation to make sure that the fluctuation in flow rate was within the range. The cascaded impactor was used to classify aerosols depending on their sizes of 10–2.5 μm ($PM_{10–2.5}$) and less than 2.5 μm ($PM_{2.5}$). The impactor filter was changed after 48 h of sampling or when the filter gets clogged. Periodic cleaning of the sampler was done to make the sampler dust free so that the dust on the sampler may not be counted with the mass concentration of the sample. These precautions were help in monitoring for OC concentration to overcome for positive (adsorption) or negative (volatilization) artifacts of the carbon concentration in carbonaceous aerosols at the time of sampling (Turpin et al. 2000; Mader and Pankow 2001). Backup filters have been used to evaluate and to correct for the positive sampling artifact. Artifacts were also prevented by deploying by sampling setups such as diffusion denuders / particle trap impactor to remove gaseous OC from the sample air-stream and the use of filters in series, impregnated or not by different adsorbents (Mader et al. 2003). It was suggested that the particle trap impactor which provides a sharp size cutoff with maximum collection efficiency, moreover, the efficiency was constant at high particle loadings. These properties of particles trap impactors make them suitable for sampling of carbonaceous aerosols.

Before exposure, the quartz fiber filter papers were pre-baked at 450 °C for 2 h to eliminate the organic species. The filter papers were conditioned in desiccators at 20–30 °C and relative humidity of 20–35 % in humidity controlled room for 24 h and weighed on electronic balance (A&D, model GR-202, Japan). After the samples collection, they were kept in desiccators for 24 h and weighed. The conditioned and weighed $PM_{2.5}$ filters were placed in cassettes and placed inside polyethylene zip-lock bags and taken to the field for sampling to avoid contamination of the filters on the way. Laboratory blank filters were also collected to reduce gravimetric bias due to filter handling during and after sampling. Filters were handled only with tweezers coated with Teflon tape to reduce the possibility of contamination. After weighing, the samples were wrapped in aluminum foil and sealed in polyethylene zip-lock bags and stored in desiccators until the time of analysis of OC-EC to prevent the degradation of organic compounds due to photo-oxidation. The exposure filters were analyzed within a month period of sampling. Blank sample was also taken on the sampler and all data were reported against the field blank value.

The particle concentrations were determined gravimetrically by the difference in their weights before and after the sampling. Then those exposed filter papers were analyzed for the

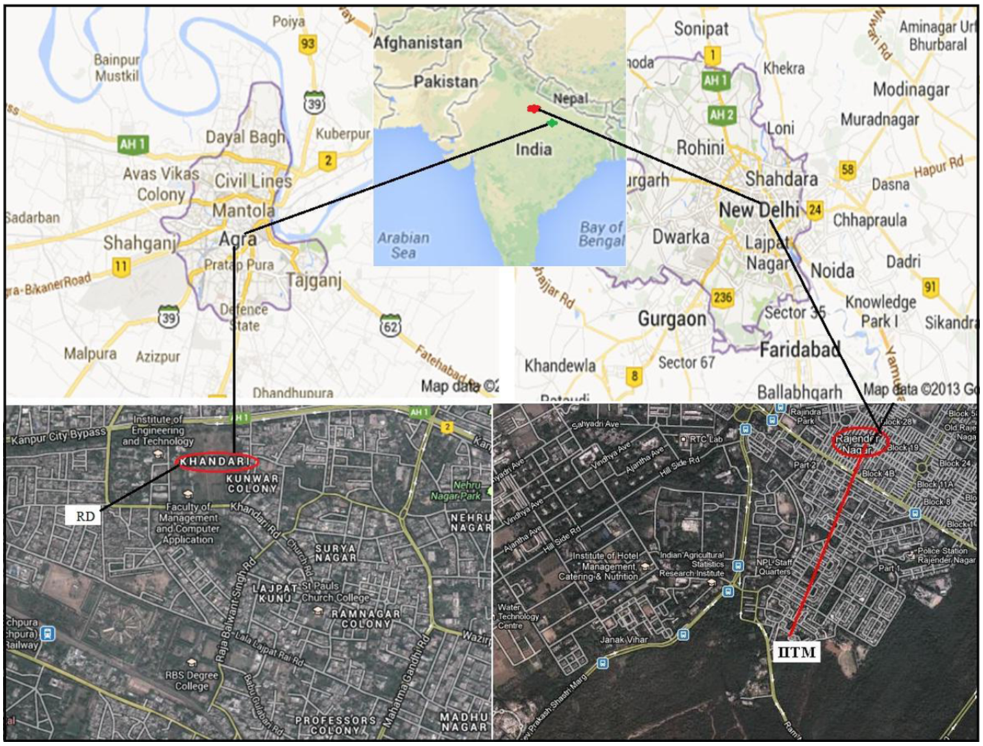


Fig. 1 Google map indicating sampling site over Agra (AGR) and Delhi (DEL)

concentrations of OC and EC by semi-continuous thermal/optical carbon analyzer (Sunset Laboratory Inc. Model 4L) using NIOSH 5040 (National Institute for Occupational Safety and Health) protocol (Birch and Cary 1996). An aliquot of sample filter (2.1 cm^2) is stepwise heated in a furnace up to 840 °C in a non-oxidizing atmosphere (100 % He); furnace is then cooled to 550 °C and filter is stepwise heated to 850 °C in an oxidizing atmosphere (90 % He, 10 % O_2), during each temperature step, evolved carbon is converted to methane and detected by a flame ionization detector. A calibration is performed at the end of each analysis by introducing a known amount of methane gas into the oven and measuring its constant response. The carbon evolved before the split line is considered as OC, which evolved after the split line is quantified as EC (Tiwari et al. 2013a). The measurements of BC mass concentrations were carried out by seven-wavelength Aethalometer (Model AE-31, Magee Scientific Company, Berkley, CA, USA) with temporal resolution of 5 min. The BC was estimated from the light attenuation at 880 nm using a specific mass absorption cross-section of 16.6 m^2g^{-1}(Hansen 2005; Tiwari et al. 2013a). The data of BC was retrieved on high-resolution data of 5-min interval and made hourly data for interpretation. The statistical analysis such as correlation and t-test of data were performed using Microsoft Excel and SPSS software.

Meteorological status over AGR and DEL locations

The meteorological parameters such as temperature (Tem.), wind direction (WD), wind speed (WS), and relative humidity (RH) were monitored at AGR and DEL stations by automatic weather monitor (Envirotech WM251). Average values of Tem., WS, WD, and RH were 16.7 °C, 2.5 m s^{-1}, 174°, and 62.1 % at AGR while at DEL it was 15.89 °C, 9.50 m s^{-1}, and 67.28 % for Tem., WS and RH respectively. Figures 2 and 3 show the day to day variability of meteorological parameters at AGR and DEL, respectively. The relative humidity was higher more than 46 % for most of the study period; it is due to temperature along with the climatic conditions mostly dry. These meteorological parameters may play crucial role in atmospheric organic and elemental carbon, chemistry, and photochemistry of mineral dust particles. Moreover, these meteorological parameters can change the atmospheric conditions, which resulted in variations of PM mass and its carbonaceous aerosol concentrations level in distinction season in northern part of India. The meteorological conditions may also act as an important factor in the distribution of carbonaceous aerosol from long range transportation (detail discussed in "OC/EC ratios and sources of carbonaceous aerosols" section.

Results and discussion

Mass concentration levels of fine aerosols particles ($PM_{2.5}$) over AGR and DEL

Figure 4 presents the mass concentration of $PM_{2.5}$ measured during sampling period in winter of 2011–2012 (November to February) from Agra and Delhi, respectively. The average

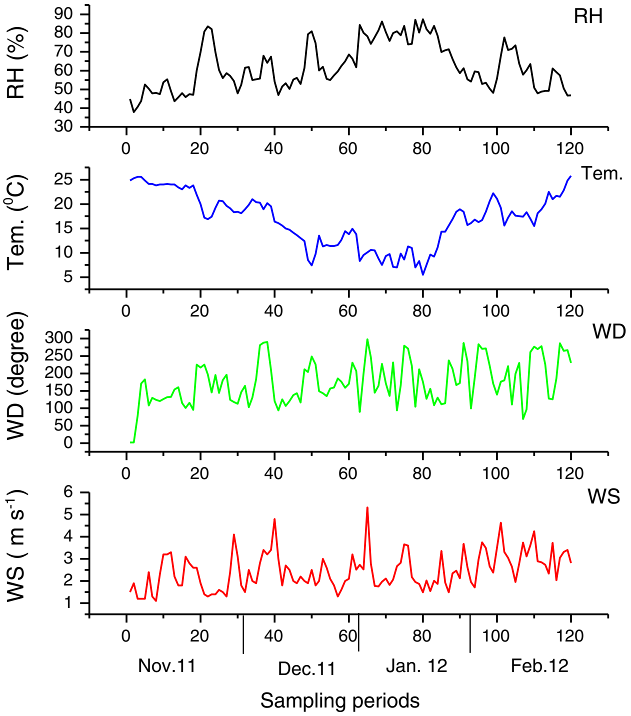


Fig. 2 Day to day variability of meteorological conditions (wind speed (*WS*), wind direction (*WD*), atmospheric temperature (*Tem.*), and relative humidity (*RH*) at AGR

$PM_{2.5}$ concentration was 165.42±119.46 μg m^{-3} at Agra while 211.67±41.94 μg m^{-3} at Delhi. It is substantially higher than the annual standard stipulated by central pollution control board called national ambient air quality standard (NAAQS) (http://www.cpcb.nic.in/National-Ambient-Air-Quality-Standards.php) for fine (40 μg m^{-3}) and by the United States Environmental Protection Agency (USEPA) ($PM_{2.5}$= 15 μg m^{-3}) standards (http://www.epa.gov/air/criteria.html). The average concentration of $PM_{2.5}$ was 27 % higher at DEL than AGR in entire period of study. The results are similar and sometimes much higher than the earlier reported values of fine particles over IGP region such as at Agra ($PM_{2.5}$=90.16±7.21 μg m^{-3}, Pipal et al. 2011), Delhi ($PM_{2.5}$=148.4±67 μg m^{-3}, Dey et al. 2012; $PM_{2.5}$=97±56 μg m^{-3} and 122.30±90.70 μg m^{-3}, Tiwari et al. 2010, 2013b; $PM_{2.5}$=123± 87 μg m^{-3}, Guttikunda and Calori 2013), Lucknow ($PM_{2.5}$=101.05±22.50 μg m^{-3}, Pandey et al. 2012), and Kanpur ($PM_{2.5}$=95 μg m^{-3}, Sharma and Maloo 2005). Apart from these recent studies, some studies also reported similar values obtained for $PM_{2.5}$ during the winter (190±109 μg m^{-3}) at Gual Pahari, a station close to Agra and different to New Delhi. However, the level of $PM_{2.5}$ in Agra and Delhi is higher than Beijing, China (115 μg m^{-3}), as reported by He et al. (2001). Study done by Watson et al. (2002) has reported the $PM_{2.5}$ concentration of 138 μg m^{-3} during wintertime at the California's San Joaquin Valley, USA, which is lower than that of Agra and Delhi. Simultaneously, black carbon (BC) was also measured at Delhi and was 10.6 μg m^{-3} which is approximately 6 % of fine particles and their day to day variability is depicted in Fig. 5. Similar contribution was reported by Hussain et al. (2007) ~5–15 % at urban air of Lahore; ~7 to 15 % at Kanpur by Tripathi et al. (2005), ~4 to 15 % at Delhi by Ganguly et al. (2006), 7 % at Hyderabad by Latha and Badrinath (2005),

Fig. 3 Day to day variability of meteorological conditions (wind speed (*WS*), atmospheric temperature (*AT*), and relative humidity (*RH*) at DEL

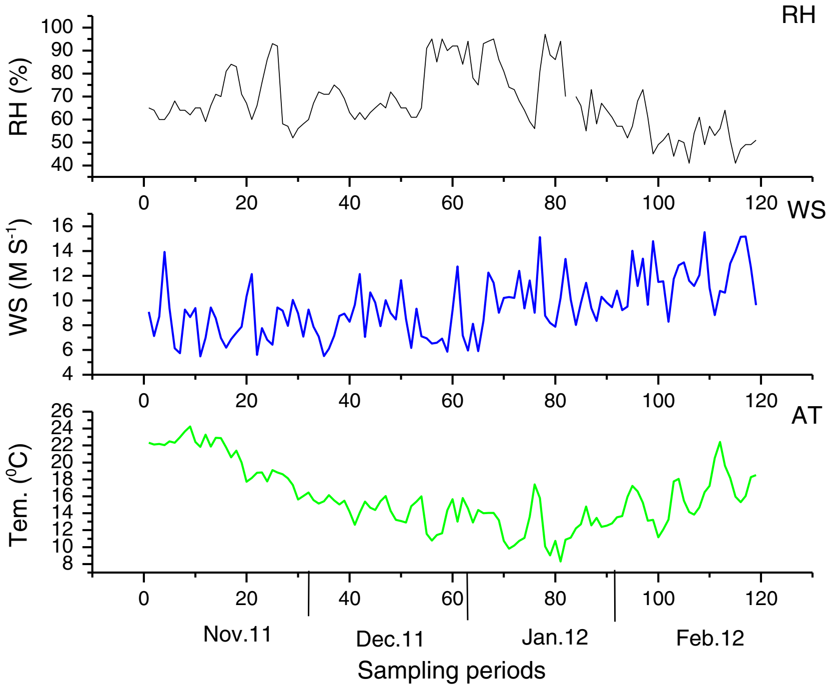
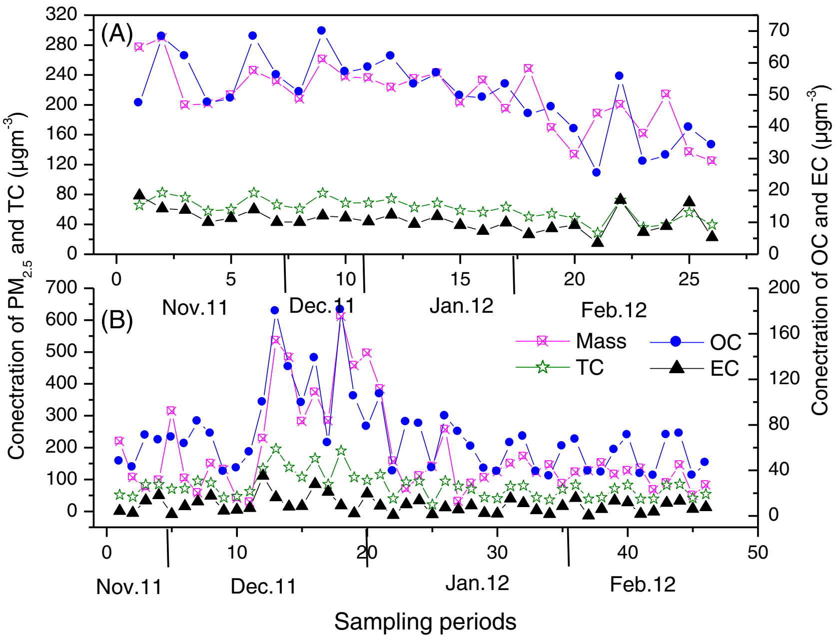


Fig. 4 Day to day variability of mass $PM_{2.5}$ and carbonaceous species at DEL (*A*) and AGR (*B*)



whereas lower in Pune ~2.3 % by Safai et al.(2007). Monthly BC was also separated and was in the order of December (17.6 μg m^{-3})>January (11.7 μg m^{-3})>November (8.3 μg m^{-3}) >February (5.1 μg m^{-3}). The concentration of BC in December is higher due to meteorological effect (Tiwari and Singh 2013.

Table 1 shows the monthly mean mass concentrations of $PM_{2.5}$ at both sites along with carbonaceous aerosols. Month wise, higher concentration was observed in December (285.87 μg m^{-3}) at Agra (AGR) and in November (241.92 μg m^{-3}) at Delhi (DEL) while lower concentration was in February (109.08 μg m^{-3}, AGR; 219.50 μg m^{-3}, DEL) at both sites. The monthly characteristics of $PM_{2.5}$ trend observed is as December>January>November>February at AGR whereas at DEL, the trend was as November>January> December>February. A large variation in mass concentrations $PM_{2.5}$ was observed due to different emissions sources at both places. Over all significantly higher at the DEL may be due to combined effect of climatic conditions and anthropogenic emissions such as vehicular exhaust, waste incineration, coal and biomass and bio-fuel combustion, and re-suspended soil dust. These highest concentrations of fine particles during winter period were due to low wind speed, low mixing height, as well as low temperature. During stable and cold conditions, the pollutant could not disperse and accumulation of pollutants. Whereas the concentrations of $PM_{2.5}$ was also significantly higher than NAAQS standard at AGR which is influenced by traffic emission thus may be due to vehicular activities, soil dust and fugitive and re-suspension of road dust. Apart from these sources the accumulation of particles especially in fine size due to thermal inversion is the major cause for these high concentrations of $PM_{2.5}$ over north central region during the winter period, and the source for these particles could mostly be from the local emission sources such as combustion of biomass, biofuel, and fossil fuel. Awasthi et al. (2011) reported that higher $PM_{2.5}$ over northern part of India was due to biomass burning which was transported from western part of India.

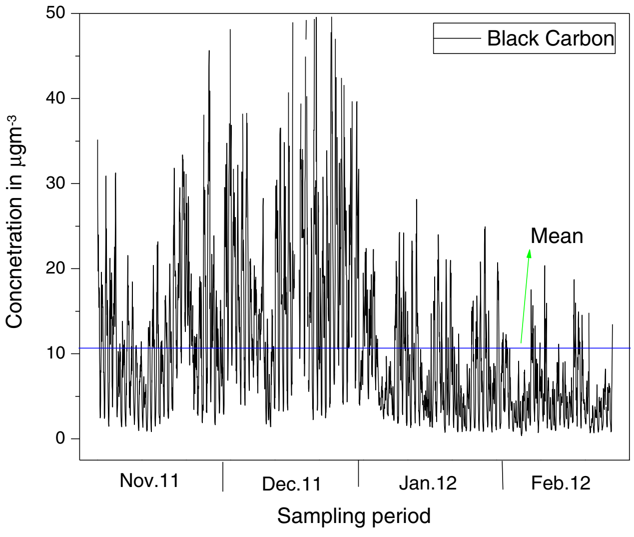


Fig. 5 Day to day variability of black carbon over DEL during study period

Carbonaceous aerosols

Figure 4 also shows the day to day variability of OC, EC, and TC along with mass of $PM_{2.5}$, during study period over AGR and DEL. Average concentration of OC, EC, and TC were 69.96±34.42, 9.53±7.27, and 79.01±38.98 μg m^{-3} at AGR,

Table 1 Monthly mean mass concentrations of PM$_{2.5}$, carbonaceous species (OC and EC), OA, and TCA at AGR and DEL

AGR							
Months	Mass	OC	OA[a]	EC	TCA	OC/EC	TCA/PM2.5
Nov 11	124.32	56.80	90.87	9.65	100.52	9.08	80.86
Dec 11	285.87	93.68	149.90	12.84	162.74	13.10	56.93
Jan 12	141.48	61.79	98.87	7.44	106.31	13.94	75.14
Feb 12	109.08	50.33	80.53	7.56	88.10	18.87	80.76
Avg	165.19	65.65	105.04	9.37	114.41	13.75	73.42
Max	285.87	93.68	149.90	12.84	162.73	18.87	80.76
Min	109.08	50.33	80.53	7.44	88.10	9.08	56.93
SD	81.54	19.27	30.83	2.52	33.10	4.02	11.32
DEL							
Months	Mass	OC	OA	EC	TCA	OC/EC	TCA/PM2.5
Nov 11	241.92	56.29	90.07	14.18	104.25	4.33	43.09
Dec 11	224.38	56.00	89.59	11.38	100.98	5.12	45.00
Jan 12	238.96	59.58	95.33	11.28	106.60	5.95	44.61
Feb 12	219.50	48.98	78.36	8.15	86.51	6.34	39.41
Avg	231.19	55.21	88.34	11.25	99.58	5.43	43.03
Max	241.92	59.58	95.33	14.18	106.60	6.34	45.00
Min	219.50	48.98	78.36	8.15	86.51	4.33	39.41
SD	10.93	4.46	7.14	2.47	9.02	0.90	2.55

SD standard deviation, *Avg* average, *Max* maximum, *Min* minimum, *OC* organic carbon, *EC* elemental carbon, *TCA* total carbon aerosol

[a] An OC to OA conversion factor of 1.6 was used to evaluate the organic aerosol (OA) concentration

while 50.11±11.93, 10.67±3.56, and 60.78±14.56 μg m^{-3} at DEL, respectively. Higher OC was observed in AGR and DEL it is due to more biomass burning during winter. Monthly OC was higher in December at AGR and DEL and the lower was in February at both sites. In the case of EC, it follows the similar trend as OC at both sites. The EC was observed higher than BC over DEL during study period. Generally, the EC may be lower as compared to BC (Hussain et al. 2007), but at present study, it was taken by offline techniques with limited time period so we got lower value of BC over. The higher concentrations of OC and EC in November are due to the long-range transport of primary pollutants as well as local emissions such as festival effect called Deewali and burning of fossil fuel along with meteorological impact during December and January (Tiwari et al. 2013b). OC concentrations ranked in the order of December>January>November>February whereas EC concentrations were in order December>November>February>January at AGR while at DEL, it followed January>November>December>February for OC and the increasing order for EC, i.e., November>December>January>February. High contributions of OC and EC in the month of November and December are attributed to more incidences of domestic biomass burning and impact of late afternoon traffic loads. In addition to this, during festival period, people play with fire crackers and produce huge amount of smoke over Delhi (Attri et al. 2001) during winter this leads to formation of secondary aerosols by condensation processes fostered by the low temperature and the low boundary layer height. In fact, condensation of semi-volatile gaseous precursors is enhanced by low temperatures, whereas temperature inversions limit their dilution and allow for supersaturating conditions with the exceedance of the equilibrium vapor pressure. Other processes that can contribute to cold-season OC levels are the adsorption of semi-volatile OCs onto existing solid particles and the dissolution of soluble gases that can undergo reactions in particles (Pandis et al. 1992).

The total carbon aerosol (TCA) was determined as the sum of organic aerosol (OA) and EC. OA is calculated as OC multiply by factor 1.6 (Feng et al. 2009; Satsangi et al. 2012; Turpin and Lim 2001). The earlier studies done on carbonaceous aerosols reported that the conversion factor 1.6 for urban aerosols and 2.1 for non-urban aerosols (Chen and Yu 2007; Satsangi et al. 2012). The thousands of individual organic compounds constitute the OC fraction, the composition of which varies widely in both space and time. This prevents a bottom up approach to derive at OA, i.e., obtaining OA by summing up individual organic groups or functional groups (Welthagen et al. 2003).

TCA was higher at AGR (114.41 μg m^{-3}) than DEL (99.58 μg m^{-3}). The percentage contribution of TCA in PM was at AGR (58.67 %) than DEL (41.67 %). The monthly characteristic of TCA is as follows: December>January>November>February at Agra, while January>November>December>February at Delhi (Fig. 6). In a recent study at Kanpur, Ram and Sarin (2010) have reported about one-third contributions of carbonaceous aerosols to the PM_{10} mass during the winter period. They further reported a three- to fourfold increase in the concentration of OC and suggested biomass burning (wood fuel and agricultural waste) emission as a dominant source over the station. It is also due to long-range transportation of aerosol during winter, the enhancement of aerosol concentrations due to massive biomass burning over western part of India especially Haryana and Punjab states (Kaupp and McLachlan 1999; Awasthi et al. 2011). Apart from these, the IGP and semi-arid tract region also contribute to air pollutants over the northern part of India. It is important to measure carbonaceous species in particles in such areas in this region to understand transport and transformation characteristics of anthropogenic air pollutants and their effects on various aspects of regional and global environment changes. Carbonaceous species in particles may play an important role in global climate change by affecting radiative forcing (Crutzen and Andreae 1990; IPCC 1996).

OC/EC ratios and sources of carbonaceous aerosols

Table 2 shows the OC/EC during the present study over AGR and DEL along with other studies carried out in India and other parts of the world. The ratios of OC to EC concentrations (OC/EC) is used to assess emission and transportation characteristics of carbonaceous aerosols (OC and EC), secondary organic aerosol formation and different removal rates by deposition of OC and EC (Cachier et al. 1996). Ambient OC to EC ratios greater than those characteristic of the primary emissions for a given area are used as an indicator for the SOA formation. The OC to EC ratio is also influenced by the measurement methods because OC and EC values greatly depend on the sampling and analytical methods (Turpin et al. 2000; Jacobson et al. 2000). If the OC/EC ratio value is found to be greater than 2, it suggests the formation of secondary organic aerosols apart from primary emission sources. Therefore, the OC/EC has been used to indicate the presence of primary and secondary organic aerosols (Gray et al. 1986). Some studies have reported that the OC/EC ratios values from different sources such as diesel- and gasoline-powered vehicles if the OC/EC=1–4.2 (Schauer et al. 2001), residential coal smoke has OC/EC=2.5–10.5 (Chen et al. 2006), and biomass burning with OC/EC=7.7 (Zhang et al. 2007). The OC/EC ratios are 13.75 and 5.43 at AGR and DEL, respectively, this can be said on the basis of reported ratios that sources may like is from vehicular exhaust, residential coal smoke, and biomass and diesel burning. The ratio was similar in all months over DEL however large variations were seen at AGR (Fig. 6) with higher during February 2012 and lower in November 2011. The relatively higher ratio values during winter may be due to the change in the relative strength of their sources. As mentioned in "Carbonaceous aerosols" section, the higher OC at AGR may be more biomass burning as compared to DEL because it is surrounded by rural environment. The OC and EC values reported at Agra of this study are higher than those of all other studies (Satsangi et al. 2012,

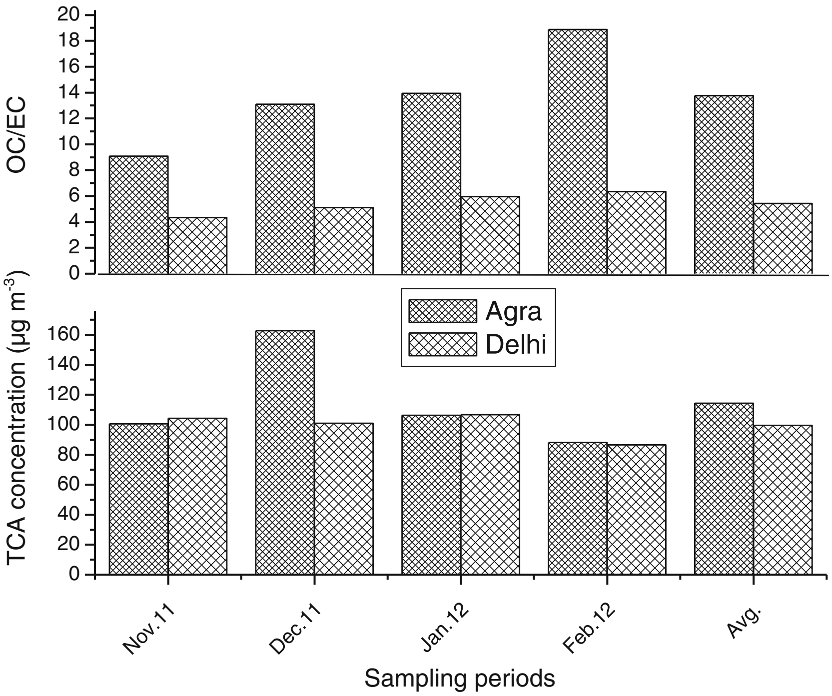


Fig. 6 Comparison of TCA and OC/EC ratios between AGR and DEL

Table 2 The OC, EC, and OC/EC of the present study along with other studies done in the World

Location	Period	OC	EC	OC/EC	References
AGR	Nov 2011 to Feb 2012	69.96	9.53	13.75	Present study
DEL	Nov 2011 to Feb 2012	50.11	10.67	5.43	Present study
Agra	Jan to Dec 2012			8.7±6.5	Satsangi et al. (2012)
Agra	May 2010 to April 2011			6.6	Pachauri et al. (2013)
Delhi	Nov 2011 to Feb 2012			5.0±2.0	Tiwari and Singh (2013)
Kanpur	Jan to March 2007			6.2±3.7	Ram and Sarin (2010)
Hisar	4 Dec	33	3.8	8.5±2.2	Rengarajan et al. (2007)
Allahabad	4 Dec			8.1±1.7	Ram and Sarin (2010)
Mt. Abu	2005 to 2006			6.1±2.0	Ram et al. (2008)
Ahmadabad		13	2.1	11.7	Rastogi and Sarin (2009)
Mumbai		25	13	8.3	Venkataraman et al. (2002)
Hong Kong		12	3.4	3.5	Duan et al. (2007)
Dhaka		46	22	2.1	Salam et al. (2003)
Taiwan		15	6.1	2.4	Lin and Tai (2001)
Lahore	Sep 1992 to Oct 1993			4.4	Smith et al. (1996)
Beijing	July to Nov			3.8	Feng et al. (2006)
Budapest	April to May 2002			2.1	Salma et al. (2004)
Europe				3.5	Viana et al. (2007)
Shanghai	2003 to 2006	14.7–17.4	2.8–3	5–5.6	Feng et al. (2009)
Canada	July			10.5	Far et al. (2003)
USA	April to May 1991			6.1	Lewtas et al. (2011)
Italy	2002 to 2003			6.9	Lonati et al. (2007)

Agra; Pachauri et al. 2013, Agra; Tiwari et al. 2013b, Delhi; Ram and Sarin 2010, Kanpur; Rengarajan et al. 2007, Hisar; Ram et al. 2010b, Allahabad; Ram et al. 2008, Mt. Abu; Rastogi and Sarin 2009, Ahmadabad; Venkataraman et al. 2002, Mumbai; Salam et al. 2003, Dhaka; Duan et al. 2007, Hongkong; Lin and Tai 2001, Taiwan; Smith et al. 1996, Lahore; Feng et al. 2006, Beijing; Salma et al. 2004, Budapest; Viana et al. 2007, Europe; Feng et al. 2009, Shanghai; Fan et al. 2003, Canada; Lewtas et al. 2001, USA; and Lonati et al. 2007, Italy. At DEL, the ratios were similar at other locations mentioned earlier references. In comparison with DEL and AGR, very low ratio were observed in Dhaka (Salam et al. 2003), Hongkong (Duan et al. 2007), Taiwan (Lin and Tai 2001), Beijing (Feng et al. 2006), Budapest (Salma et al. 2004), and Europe (Viana et al. 2007). In order to know, the transport pathways of the carbonaceous species in the atmospheric aerosols over the northern part of India, monthly 7-days air mass backward trajectory analysis was carried out at height of 500 m based on National Oceanic and Atmospheric Administration (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectories (HYSPLIT) model (Draxler and Rolph 2003). The back trajectory analysis provides a three-dimensional (latitude, longitude, and altitude) description of the pathways followed by air mass as a function of time by using National Centre for Environmental prediction (NCEP) reanalysis wind as input to the model. The back trajectories are very important to identify the origin of source regions and the transport pathways of aerosols to reach the measurement site and also to investigate the aerosol properties and types (Bian et al. 2011).

Figures 7 and 8 show that monthly 7-day air mass backward trajectory clusters analysis at Agra and Delhi during study period which supports the transport of aerosols from the long range transportation from Thar Desert and other part of the world over northern Indian region. During the months of December, January, and February air masses appear to be transported from the Neighboring countries such as Pakistan, Afghanistan, Iran, and Turkmenistan, and South Indian part and India ocean at low altitudes passes over Thar Desert before entering into Agra and IGB (Tiwari et al. 2012). While in the month of November, it was seen from north Indian region and local sources. Marine environment (Arabian Sea as well as Bay-of- Bengal) and carry mostly sea salt aerosols while traversing through the continental mainland before they reach the measurement site (Reddy et al. 2011). Whereas at Delhi, it was seen from Middle Eastern and Arabian Sea covering south Indian part and Thar Desert for the months of January and February, while during the month of November and December, the air masses over DEL passes mostly in Indian sub-continental region as well as ocean. Ramachandran and Rajesh (2007) reported the impact of long-range transport and meteorological conditions

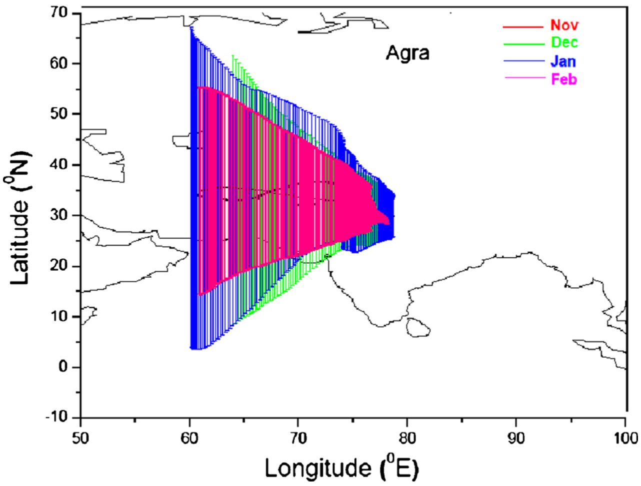


Fig. 7 Monthly 7-day air mass backward trajectory clusters analysis at Agra during Nov 2011, Dec 2011, Jan 2012, and Feb 2012 (*vertical lines* show standard deviation, representing latitudinal air mass spreading)

in higher carbonaceous aerosol. The air masses from different source regions lead to the formation of different aerosol types (Reddy et al. 2011).

Assessment of SOC, POC, and SOA in AGR and DEL

The secondary organic carbon (SOC) fraction in aerosol is either estimated using the EC tracer method (Cabada et al. 2004) or by adding up all the oxidation products found in aerosols (Schauer et al. 1996). The EC-tracer method has been widely used in many studies (Docherty et al. 2008; Lin et al. 2009) which are very suitable for the regions where the source apportionment studies are still lacking such as India, since it only requires ambient OC and EC concentrations. In the EC-tracer method, ambient OC to EC ratios greater than those characteristic of the primary emissions for a given area are used as an indicator for the SOA formation. The estimation of secondary organic aerosol (SOA) is also important because it plays an important role in the formation of haze, visibility degradation, climate, and health. It is very difficult to directly separate the secondary organic carbon (SOC) and primary organic carbon (POC) from total OC and estimation of SOA. Turpin and Huntzicker (1995) have suggested a mathematical equation for quantification of SOC using EC as the tracer for POC. The mathematical equation for the measurement of SOC is given below:

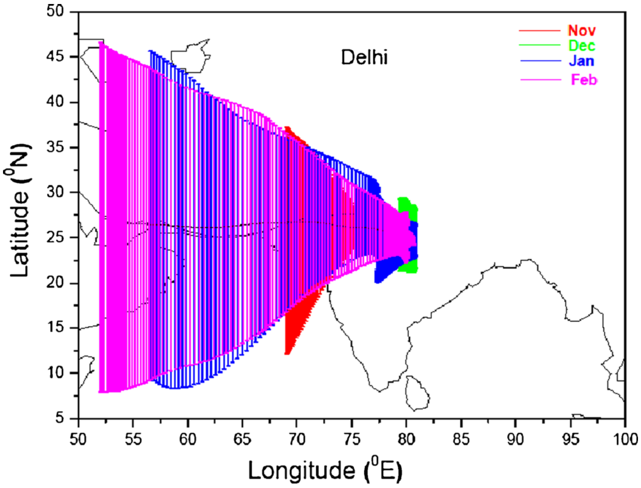


Fig. 8 Monthly seven day air mass backward trajectory clusters analysis at Agra during Nov 2011, Dec 2011, Jan 2012, and Feb 2012 (*vertical lines* show standard deviation, representing latitudinal air mass spreading)

$$\mathrm{SOC} = \mathrm{TOC}-\mathrm{EC} \times (\mathrm{OC}/\mathrm{EC})_{\mathrm{primary}}$$

Where $(\mathrm{OC}/\mathrm{EC})_{\mathrm{primary}}$ is the ratio for primary sources. The EC tracer was also applied in many studies, they were estimated $(\mathrm{OC}/\mathrm{EC})_{\mathrm{primary}}$ from atmospheric concentrations assuming that either the lowest observed OC/EC ratio represents the pure primary aerosol (Castro et al. 1999), or the data for the days when SOA formation could obviously be excluded were averaged (Strader et al. 1999).Chow et al. (1996) proposed a ratio value (2.0) between OC and EC to estimate SOC, however, the primary ratio of OC/EC is usually not available because it is affected by many factors such as the type of emission sources as well as its temporal and spatial variation, atmospheric temperature, etc. Castro et al. (1999) discussed in details about (OC/EC) primary which represented by the observed minimum ratio [(OC/EC) min]. In addition, in the EC tracer method, it is supposed that the primary OC and EC have the same source, and representing as OC/EC ratio for the primary aerosol ($(\mathrm{OC}/\mathrm{EC})_{\mathrm{primary}}$), EC is primary in origin. The obligations can be met in the $\mathrm{PM}_{2.5}$ size fraction, since OC in the coarse fraction originates from other sources such as pollen, spores, plant debris, tyre rubber, and paved road dust than EC. OC can sometimes be solely primary in origin under favorable meteorological conditions and close to the main primary source of OC. Kleeman et al. (2000) was measured a ratio 1.1 for pure primary aerosol from diesel engines. It has to be emphasized that the calculation approaches yield semi-quantitative information only because of the large uncertainties associated with them. Apart from this, the good correlation between OC and EC indicates similar sources, it may be transported or localized. Due to these reasons, it is assumed that the primary OC and EC have the same source and considered as OC/EC ratio for the primary aerosol ($(\mathrm{OC}/\mathrm{EC})_{\mathrm{primary}}$). If the OC/EC is not significant, since EC are mostly emitted from anthropogenic activities, in that case, OC and EC are both emitted from different sources and or not transported. In this, $(\mathrm{OC}/\mathrm{EC})_{\mathrm{primary}}$ emission rates vary by sources, and, therefore, the ratio is influenced by meteorology, time fluctuations in emissions, and local

Table 3 Level of SOC, POC, and SOA in AGR and DEL during study period

AGR								
Months	OC	EC	OC/EC	SOC	POC	SOC/OC	SOA	SOA/PM2.5 (%)
Nov 2011	56.80	9.65	9.08	39.14	27.30	71.79	29.49	26.94
Dec 2011	93.68	12.84	13.10	50.18	36.32	72.88	57.36	31.85
Jan 2012	61.79	7.44	13.94	46.81	21.05	76.13	40.75	39.73
Feb 2012	50.33	7.56	18.87	36.49	21.41	74.34	28.93	28.38
Avg	65.65	9.37	13.75	48.16	26.52	73.79	39.13	31.72
Max	93.68	12.84	18.87	50.18	36.32	76.13	57.36	39.73
Min	50.33	7.44	9.08	36.49	21.05	71.79	28.93	26.94
SD	19.27	2.52	4.02	15.32	7.14	1.88	13.32	5.72
DEL								
Months	OC	EC	OC/EC	SOC	POC	SOC/OC	SOA	SOA/PM2.5 (%)
Nov 2011	56.29	14.18	4.33	35.73	34.74	62.48	21.55	9.40
Dec 2011	56.00	11.38	5.12	39.49	27.89	70.42	28.11	12.46
Jan 2012	59.58	11.28	5.95	43.23	27.63	72.50	31.95	13.35
Feb 2012	48.40	8.14	6.43	36.60	19.94	75.73	28.46	13.76
Avg	55.07	11.24	5.46	38.76	27.55	70.28	27.52	12.24
Max	59.58	14.18	6.43	43.23	34.74	75.73	31.95	13.76
Min	48.40	8.14	4.33	35.73	19.94	62.48	21.55	9.40
SD	4.73	2.47	0.93	3.38	6.05	5.64	4.34	1.97

SD standard deviation, *Avg* average, *Max* maximum, *Min* minimum, *SOC* secondary organic carbon, *POC* primary organic carbon

sources such as vehicles, fireplaces, cooking operations (Seinfeld and Pandis 1998).

The monthly SOC and POC were estimated on the basis of above equation and depicted in Table 3 for AGR and DEL. The average concentration of SOC and POC at AGR were 48.16 and 26.52 μg m^{-3} while at DEL it was 38.78 and 27.55 μg m^{-3}, respectively. In the case of POC, similar concentrations were observed at both places but in the case of SOC, it was 24 % higher over AGR as compared to DEL it is due to the high concentration of OC over AGR. Secondary organic aerosol (SOA) was also determined and was 42 % higher at AGR than DEL which indicates that the secondary aerosol formation at AGR are more, it is due to rural environment and higher concentrations of coarse mode particles. The SOA contribution in $PM_{2.5}$ was also estimated and was ~32 and 12 % at AGR and DEL, respectively. The correlation coefficient analysis was performed to measure the degree of linear relationship between two variables. For source identification, the relationship and *t* test between $PM_{2.5}$ and OC/EC species were studied (Table 4). The correlation coefficient between OC and $PM_{2.5}$ is positively significant at AGR (0.78) and DEL (0.60) while in the case of EC to $PM_{2.5}$, it is less significant at both places which indicate the major contribution of OC in PM mass as compared to EC. The correlation between OC and EC at both places were significantly correlated (0.47, AGR and 0.53, DEL) it is due to the common sources emission for OC and EC over study region. The *t* test carried out indicates that the there is significant differences in $PM_{2.5}$, OC, and EC concentrations between both sites.

Table 4 Correlation coefficient between $PM_{2.5}$ and carbonaceous species at AGR and DEL

Correlation				
Site		Mass	OC	EC
AGR	Mass			
	OC	0.78[a]		
	EC	0.23	0.47[a]	
DEL	Mass			
	OC	0.60[a]		
	EC	0.26	0.53[a]	
T test				
Site		Mean	SD	
AGR	Mass	165.42	119.46	
	OC	69.91	34.42	
	EC	9.48	7.27	
DEL	Mass	215.10	38.77	
	OC	50.69	11.71	
	EC	10.84	3.45	

SD standard deviation

Conclusions

Carbonaceous species in particles may play an important role in global climate change by affecting radiative forcing.

Therefore, it is important to easure carbonaceous species in particles at such areas in the region to understand transport and transformation characteristics of anthropogenic air pollutants and their effects on various aspects of regional and global environment changes. Due to lack of in situ measurements of atmospheric carbonaceous aerosols over northern part of India, continuous monitoring of fine particles and its carbonaceous constituents were monitored at two places (AGR and DEL) in northern part of India during winter season of 2011–12. The atmospheric aerosol ($PM_{2.5}$) were collected at AGR and DEL using medium volume air sampler (offline measurement) and characterized for its carbonaceous aerosols [organic carbon (OC) and elemental carbon (EC)] along with BC (online) and their results were presented. The average $PM_{2.5}$ concentration was 165.42±119.46 $\mu g\ m^{-3}$ at Agra while at Delhi it was 211.67±41.94 $\mu g\ m^{-3}$. It is substantially higher than NAAQS and USEPAS. Simultaneously, Black Carbon (BC) was 10.6 $\mu g\ m^{-3}$ which is approximately 6 % of fine particles. Monthly BC was also separated, it was in the order of December (17.6 $\mu g\ m^{-3}$)>January (11.7 $\mu g\ m^{-3}$)> November (8.3 $\mu g\ m^{-3}$)>February (5.1 $\mu g\ m^{-3}$). The average concentration of PM was 27 % higher at DEL than AGR of the total PM concentrations. The average concentration of OC and EC were 69.96±34.42 and 9.53±7.27 $\mu g\ m^{-3}$, respectively. Total carbon (TC) was 79.01±38.98 $\mu g\ m^{-3}$ at Agra, while it was 50.11±11.93 (OC), 10.67±3.56 $\mu g\ m^{-3}$ (EC), and 60.78±14.56 $\mu g\ m^{-3}$ (TC) at Delhi. The OC/EC ratios were 13.75 and 5.45 at Agra and Delhi, respectively. The higher OC/EC ratio at AGR indicates that the formation of secondary organic aerosol and from variable primary sources. Significant correlation between $PM_{2.5}$ and its carbonaceous species were observed indicating similarity in sources at both sides. The average concentration of SOC and POC at AGR were 48.16 and 26.52 $\mu g\ m^{-3}$ while at DEL, it was 38.78 and 27.55 $\mu g\ m^{-3}$, respectively. In the case of POC, similar concentrations were observed at both places but in the case of SOC, it was about 24 % higher over AGR as compared to DEL due to the high concentration of OC over AGR. Secondary organic aerosol (SOA) was 42 % higher at AGR than DEL which indicates that the secondary aerosol formation at AGR is more; it may be due to the rural environment. The SOA contribution in $PM_{2.5}$ was also estimated and was ~32 and 12 % at AGR and DEL, respectively. Back trajectories was calculated and indicates that the long-range pathways of aerosols over north part of India from the Pakistan, Afghanistan, Iran, Turkmenistan, Middle Eastern, Indian Ocean, and Arabian Sea covering south Indian part and passes over Thar desert before entering into northern Indian and IGB. Being highly loaded of fine particles along with carbonaceous aerosol, it is suggested to take necessary and immediate action in mitigation of the emission of carbonaceous aerosol in the northern part of India.

Acknowledgements Authors are thankful to University Grant Commission (RGNF-2011-12) New Delhi for financial support and Department of Chemistry, University of Pune and Dr B R Ambedkar University Agra for providing necessary facilities to complete this work. We are also thankful to Indian Institute Tropical Meteorology (IITM) laboratory New Delhi for analyzing the carbonaceous aerosols.

References

Akhter MS, Chughtal AR, Smith DM (1985) The structure of hexane soot. I. Spectroscopic studies. Appl Spect 39:143–153

Ancelet T, Davy PK, Trompetter WJ, Markwitz A, Weatherburn DC (2013) Carbonaceous aerosols in a wood burning community in rural New Zealand. Atmos Poll Res 4:245–249

Andreae MO, Crutzen PJ (1997) Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry. Science 276:1052–1058

Asa-Awuku A, Nenes A, Gao S, Flagan RC, Seinfeld JH (2010) Water-soluble SOA from alkene ozonolysis: composition and droplet activation kinetics inferences from analysis of CCN activity. Atmos Chem Phys Discus 10:1585–1597

Attri AK, Kumar U, Jain VK (2001) Formation of ozone by fireworks. Nature 411:1015

Awasthi AR, Agarwal SK, Mittal N, Singh K, Gupta PK (2011) Study of size and mass distribution of particulate matter due to crop residue burning with seasonal variation in rural area of Punjab, India. J Environ Monit 13:1073–1081

Begum M, Minar MH (2012) Comparative study about body composition of different sis, shell fish and ilish; commonly available in Bangladesh. Trends Fish Res 1(1):38–42

Bian H, Tie X, Cao J, Ying Z, Han S, Xue Y (2011) Analysis of a severe dust storm event over China: application of the WRF-dust model. Aerosol Air Qual Res 11:419–428

Birch ME, Cary RA (1996) Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. Aerosol Sci Technol 25:221–241

Blando JD, Turpin BJ (2000) Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of plausibility. Atmos Environ 34:1623–1632

Cabada JC, Pandis SN, Subramanian R, Robinson AL, Polidori A, Turpin B (2004) Estimating the secondary organic aerosol contribution to $PM_{2.5}$ using the EC tracer method. Aerosol Sci Technol 38:140–155

Cachier H, Liousse C, Pertuisol MH, Gaudichet A, Echalar F, Lacaux JP (1996) African fine particulate emissions and atmospheric influence. In: Levine EJS (ed) Biomass burning and global change. MIT Press, London, pp 428–440

Castro LM, Pio CA, Harrison RM, Smith DJT (1999) Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations. Atmos Environ 33:2771–2781

Chen X, Yu JZ (2007) Measurement of organic mass to organic carbon ratio in ambient aerosol samples using a gravimetric technique in combination with chemical analysis. Atmos Environ 41:8857–8864

Chen Y, Zhi G, Feng Y, Fu J, Feng J, Sheng G, Simoneit BRT (2006) Measurements of emission factors for primary carbonaceous particles from residential raw-coal combustion in China. Geophys Res Lett 33. http://dx.doi.org/10.1029/2006GL026966.

Chow JC, Watson JG (1993) The DRI thermal/optical reflectance carbon analysis system: description, evaluation, and applications in U.S. air quality studies. Atmos Environ 27A:1185–1201

Chow JC, Watson JG, Crow D, Lowenthal DH, Merrifield T (2001) Comparison of IMPROVE and NIOSH carbon measurements. Aerosol Sci Technol 34: 23–34

Chow JC, Watson JG, Lu Z, Lowenthal DH, Frazier CA, Solomon PA, Thuillier RH, Magliano K (1996) Descriptive analysis of PM2.5 and

PM10 at regionally representative locations during SJVAQS/AUSPEX. Atmos Environ 30:2079–2112

Crutzen PJ and Andreae MO (1990) Biomass burning in the tropics: impact on atmospheric chemistry and biogeochemical cycles. Science 250:1669–1678

Decesari S, Facchini MC, Fuzzi S, Tagliavini E (2000) Characterization of water-soluble organic compounds in atmospheric aerosol: a new approach. J Geophys Res 105:1481–1489

Dey S, Girolamo LD, Donkelaar AV, Tripathi SN, Gupta T, Mohan M (2012) Variability of outdoor fine particulate (PM2.5) concentration in the Indian Subcontinent: a remote sensing approach. Remote Sanhsing Environ 127:153–161

Docherty KS, Stone EA, Ulbrich IM, DeCarlo PF, Snyder DC, Schauer JJ, Peltier RE, Weber RJ, Murphy SM, Seinfeld JH, Grover BD, Eatough DJ, Jimenez JL (2008) Apportionment of primary and secondary organic aerosols in southern California during the 2005 Study of Organic Aerosols in Riverside (SOAR-1). Environ Sci Technol 42:7655–7662

Donahue NM, Robinson AL, Pandis SN (2009) Atmospheric organic particulate matter: from smoke to secondary organic aerosol. Atmos Environ 43:94–106

Draxler RR, Rolph GD (2003) HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) Model, report, Air Resource Laboratory, NOAA, Silver, Spring, Md. http://www.arl.noaa.gov/ready/hyspli t4.html

Duan JC, Tan JH, Cheng DX, Bi XH, Deng WJ, Sheng GY, Fu JM, Wong MH (2007) Sources and characteristics of carbonaceous aerosol in two largest cities in Pearl River Delta Region, China. Atmos Environ 41:2895–2903

Dutkiewicz VA, Alvi S, Ghauri BM, Choudhary MI, Husain L (2009) Black carbon aerosols in urban air in South Asia. Atmos Environ 43: 1737–1744

Eatough DJ, Wadsworth A, Eatough DA, Crawford JW, Hansen LD, Lewis EA (1993) A multiple-system, multi-channel diffusion denuder sampler for the determination of fine-particulate organic material in the atmosphere. Atmos Environ 27:1213–1219

Fan X, Brook JR, Mabury SA (2003) Sampling atmospheric carbonaceous aerosols using an integrated organic gas and particle sampler. Environ Sci Tech 37:3145–3151

Feng J, Chan CK, Fang M, Hu M, He L, Tang X (2006) Characteristics of organic matter in PM2.5 in Shanghai. Chemosphere 64:1393–1400

Feng Y, Chen Y, Guo H, Zhi G, Xiong S, Li J, Sheng G, Fu J (2009) Characteristics of organic carbon in $PM_{2.5}$ samples in Shanghai, China. Atmos Res 92:434–442

Ganguly D, Jayaraman A, Rajesh TA, Gadhavi H (2006) Wintertime aerosol properties during foggy and non-foggy days over urban center Delhi and their implications for shortwave radiative forcing. J Geophys Res 111, D15217. doi:10.1029/2005JD007029

Goyal P, Sidharta (2002) Effect of wind on SO2 & SPM concentration in Delhi. Atmos Environ 36: 2925–2930

Gray HA, Cass GR, Huntzicker JJ, Heyerdahl EK, Rau JA (1986) Characteristics of atmospheric organic and elemental carbon particle concentrations in Los Angeles. Environ Sci Tech 20:580–589

Guttikunda SK, Calori G (2013) A GIS based emissions inventory at 1 km×1 km spatial resolution for air pollution analysis in Delhi, India. Atmos Environ 67:101–111

Hansen ADA (2005) The Aethalometer, manual. Magee Scientific, Berkeley, California, USA

Hansen J, Sato M, Ruedy R, Lacis A, Oinas V (2000) Global warming in the twenty-first century: an alternative scenario. Proc Natl Acad Sci 97:9875–9880

He K, Yang F, Ma Y, Zhang Q, Yao X, Chan CK (2001) The characteristics of PM2.5 in Beijing, China. Atmos Environ 35:4959–4970

Houghton JT, Ding Y, Griggs DJ, Noguer M, Van der Linden PJ, Dai X, Maskell K, Johnson CA (2001) Climate change 2001: the scientific basis: contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, New York

Hussain L, Dutkiewicz VA, Khan AJ, Ghauri BM (2007) Characterization of carbonaceous aerosols in urban air. Atmos Environ 41:6872–6883

IPCC (1996) Intergovernmental Panel on Climate Change, Climate change 1995. Cambridge University Press, UK. pp. 17–26

Jacobson MZ (2001) Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. Nature 409:695–697

Jacobson MC, Hansson HC, Noone KJ, Charlson RJ (2000) Organic atmospheric aerosols: review and state of the science. Rev Geophys 38: 267–294

Kaupp H, McLachlan MS (1999) Atmospheric particle size distributions of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polycyclic aromatic hydrocarbons (PAHs) and their implications for wet and dry deposition. Atmos Environ 33(1):85–95

Kleeman MJ, Schauer JJ, Cass GR (2000) Size and composition distribution of fine particulate matter emitted from motor vehicles. Environ Sci Technol 34:1132–1142

Latha KM, Badrinath KVS (2005) Seasonal variations of black carbon aerosols and total aerosols mass concentrations over urban environment in India. Atmos Environ 39:4129–4141

Lewtas J, Pang YB, Booth D, Reimer S, Eatough DJ, Gundel LA (2001) Comparison of sampling methods for semi-volatile organic carbon associated with $PM_{2.5}$. Aerosol Sci Tech 34(1):9–22

Lin JJ, Tai HS (2001) Concentrations and distributions of carbonaceous species in ambient particles in Kaohsiung City, Taiwan. Atmos Environ 35:2627–2636

Lin P, Hu M, Deng Z, Slanina J, Han S, Kondo Y, Takegawa N, Miyazaki Y, Zhao Y, Sugimoto N (2009) Seasonal and diurnal variations of organic carbon in PM2.5 in Beijing and the estimation of secondary organic carbon. J Geophys Res 114: (D00G11). doi:10.1029/2008JD010902.

Lonati G, Ozgen S, Giugliano M (2007) Primary and secondary carbonaceous species in $PM_{2.5}$ samples in Milan (Italy). Atmos Environ 41(22):4599–4610

Mader BT, Pankow JF (2001) Gas/solid partitioning of semivolatile organic compounds (SOCs) to air filters. 3. An analysis of gas adsorption artifacts in measurements of atmospheric SOCs and organic carbon (OC) when using Teflon membrane filters and quartz fiber filters. Environ Sci Technol 35:3422–3432

Mader BT, Schauer JJ, Seinfeld JH, Flagan RC, Yu JZ, Yang H, Lim HJ, Turpin BJ, Deminter JT, Heidemann G, Bae MS, Quinn P, Bates T, Eatough DJ, Huebert BJ, Bertram T, Howell S (2003) Sampling methods used for the collection of particle-phase organic and elemental carbon during ACE-Asia. Atmos Environ 37:1435–1449

Matsui H, Koike M, Takegawa N, Kondo Y, Griffin RJ, Miyazaki Y, Yokouchi Y, Ohara T (2009) Secondary organic aerosol formation in urban air: temporal variations and possible contributions from unidentified hydrocarbons. J Geophys Res Atmos 114: D04201. doi:10.1029/2008JD010164

Mishra AK, Shibata T (2012) Climatologically aspects of seasonal variation of aerosol vertical distribution over central Indo-Gangetic belt (IGB) inferred by the space-borne lidar CALIOP. Atmos Environ 46:365–375

Pachauri T, Singla V, Satsangi A, Lakhani A, Kumari KM (2013) Characterization of carbonaceous aerosols with special reference to episodic events at Agra, India. Atmos Res 128:98–110

Pandey P, Khan AH, Verma AK, Singh KA, Mathur N, Kisku GC, Barman SC (2012) Seasonal trends of $PM_{2.5}$ and PM_{10} in ambient air and their correlation in ambient air of Lucknow City, India. Bull Environ Contam Toxicol 88(2):265–270

Pandis SN, Harley RA, Cass GR, Seinfeld JH (1992) Secondary organic aerosol formation and transport. Atmos Environ 26A:2269–2282

Pipal AS, Kulshrestha A, Taneja A (2011) Characterization and morphological analysis of airborne $PM_{2.5}$ and PM_{10} in Agra located in North Central part of India. Atmos Environ 45:3621–3630

Ram K, Sarin MM (2010) Spatio-temporal variability in atmospheric abundances of EC, OC and WSOC over Northern India. J Aerosol Sci 41:88–98

Ram K, Sarin MM, Hegde P (2008) atmospheric abundances of primary and secondary carbonaceous species at two high-altitude sites in India: sources and temporal variability. Atmos Environ 42:6785–6796

Ram K, Sarin MM, Tripathi SN (2010) A 1 year record of carbonaceous aerosols from an urban site in the Indo-Gangetic Plain: characterization, sources and temporal variability. J Geophys Res 115, D24313. doi:10.1029/2010JD014188

Ramachandran S, Rajesh TA (2007) Black carbon aerosol mass concentrations over Ahmedabad, an urban location in western India: comparison with urban sites in Asia, Europe, Canada, and the United States. J Geophys Res 112:D06211

Rastogi N, Sarin MM (2006) Chemistry of aerosols over a semi-arid region: evidence for acid neutralization by mineral dust. Geophys Res Lett 33:L23815. doi:10.1029/2006GL027708

Rastogi N, Sarin MM (2009) Quantitative chemical composition and characteristics of aerosols over western India: one-year record of temporal variability. Atmos Environ 43(22–23):3481–3488

Reddy BSK, Kumar KR, Balakrishnaiah G, Gopal KR, Reddy RR, Reddy LSS, Narasimhulu K, Vijaya Bhaskara Rao S, Kiran Kumar T, Balanarayana C, Krishna Moorthy K, Suresh Babu S (2011) Aerosol climatology over an urban site, Tirupati (India) derived from columnar and surface measurements: first time results obtained from a 30-day campaign. J Atmos Sol Terr Phys 73:1727–1738

Rengarajan R, Sarin MM, Sudheer AK (2007) Carbonaceous and inorganic species in atmospheric aerosols during wintertime over urban and high-altitude sites in North India. J Geophys Res 112, D21307. doi:10.1029/2006JD008150

Robinson AL, Donahue NM, Shrivastava MK, Weitkamp EA, Sage AM, Grieshop AP, Lane TE, Pierce JR, Pandis SN (2007) Rethinking organic aerosols: semivolatile emissions and photochemical aging. Science 315:1259–1262

Safai PD, Kewat S, Praveen PS, Rao PSP, Momin GA, Ali K, Devara PCS (2007) Seasonal variation of black carbon aerosols over a tropical urban city of Pune, India. Atmos Environ 41:2699–2709

Salam A, Bauer H, Kassin K, Ullah SM, Puxbaum H (2003) Aerosol chemical characteristics of a mega-city in Southeast Asia (Dhaka-Bangladesh). Atmos Environ 37(18):2517–2528

Salma I, Chi X, Maenhaut W (2004) Elemental and organic carbon in urban canyon and background environments in Budapest, Hungary. Atmos Environ 38:27–36

Satsangi A, Pachauri T, Singla V, Lakhani A, Kumari MK (2012) Organic and elemental carbon aerosols at a suburban site. Atmos Res 113:13–21

Schauer JJ, Rogge WF, Hildemann LM, Mazurek MA, Cass GR, Simoneit BRT (1996) Source apportionment of airborne particulate matter using organic compounds as tracers. Atmos Environ 30:3837–3855

Schauer JJ, Kleeman MJ, Cass GR, Simoneit BRT (2001) Measurement of emissions from air pollution sources. 3. C1–C29 organic compounds from fireplace combustion of wood. Environ Sci Tech 35:1716–1728

Schauer JJ, Kleeman MJ, Cass GR, Simoneit BRT (2002) Measurement of emissions from air pollution sources. 5. C1–C32 organic compounds from gasoline-powered motor vehicles. Environ Sci Tech 36:1169–1180

Schwarz J, Chi X, Maenhaut W, Civiš M, Hovorka J, Smolík J (2008) Elemental and organic carbon in atmospheric aerosols at downtown and suburban sites in Prague. Atmos Res 90:287–302

Seinfeld JH, Pandis SN (1998) Atmospheric chemistry and physics: from air pollution to climate change. Wiley, New York

Sharma M, Maloo S (2005) Assessment of ambient air PM10 and PM2.5 and characterization of PM10 in the city of Kanpur, India. Atmos Environ 39:6015–6026

Smith DJT, Harrison RM, Luhana L, Pio CA, Castro LM, Tariq MN, Harat S, Quraishi T (1996) Concentrations of particulate airborne polycyclic aromatic hydrocarbons and metals collected in Lahore, Pakistan. Atmos Environ 30:4031–4040

Srivastava A, Jain VK, Srivastava A (2009) SEM-EDX analysis of various sizes aerosols in Delhi India. Environ Monit Assess 150: 405–416

Strader R, Lurman F, Pandis SN (1999) Evaluation of secondary organic aerosol formation in winter. Atmos Environ 33:4849–4863

Tiwari S, Singh AK (2013) Variability of aerosol parameters derived from ground and satellite measurements over varanasi located in the Indo-Gangetic Basin. Aerosol Air Qual Res 13:627–638

Tiwari S, Srivastava AK, Bisht DS, Bano T, Singh S, Behura S, Srivastava MK, Chate DM, Padmanabhamurty B (2010) Black carbon and chemical characteristics of PM10 and PM2.5 at an urban site of North India. Int J Atmospheric Chem 62(3):193–209

Tiwari S, Srivastava AK, Bisht DS, Safai PD, Parmita P (2012) Assessment of carbonaceous aerosol over Delhi in the Indo-Gangetic Basin: characterization, sources and temporal variability. Nat Hazard doi: 10.1007/s11069-012-0449-1.

Tiwari S, Srivastava AK, Bisht DS, Parmita P, Srivastava MK, Attri SD (2013a) Diurnal and seasonal variations of black carbon and PM2.5 over New Delhi, India: influence of meteorology. Atmos Res 125–126:50–62

Tiwari S, Srivastava AK, Bisht DS, Safai PD, Parmita P (2013b) Assessment of carbonaceous aerosol over Delhi in the Indo-Gangetic Basin: characterization, sources and temporal variability. Nat Hazard 65:1745–1764

Tripathi SN, Dey S, Tare V, Satheesh SK (2005) Aerosol black carbon radiative forcing at an industrial city in northern India. Geophys Res Lett 32:L08802. doi:10.1029/2005GL022515

Turpin BJ, Huntzicker JJ (1995) Identification of secondary organic aerosol episodes and quantification of primary and secondary organic aerosol concentrations during SCAQS. Atmos Environ 29:3527–3544

Turpin BJ, Lim HJ (2001) Species contributions to PM2.5 mass concentrations: revisiting common assumptions for estimating organic mass. Aerosol Sci Technol 35:602–610

Turpin BJ, Liu SP, Podolske KS, Gomes MSP, Elsenrelch SJ, McMurry PH (1993) Design and evaluation of a novel diffusion separator for measuring gas/ particle distributions of semivolatile organic compounds. Environ Sci Tech 27:2441–2449

Turpin BJ, Saxena P, Andrews E (2000) Measuring and simulating particulate organics in the atmosphere: problems and prospects. Atmos Environ 34:2983–3013

Venkataraman C, Reddy CK, Josson S, Reddy MS (2002) Aerosol size and chemical characteristics at Mumbai, India, during the INDOEX-IFP (1999). Atmos Environ 36:1979–1991

Viana M, Maenhaut W, Ten Brink HM, Chi X, Weijers E, Querol X, Alastuey A, Mikulski P, Vecera Z (2007) Comparative analysis of organic and elemental carbon concentrations in carbonaceous aerosols in three European cities. Atmos Environ 41:5972–5983

Watson JG, Judith C, Chow A (2002) Wintertime PM2.5 episode at the Fresno, CA, supersite. Atmos Environ 36:465–475

Weitkamp EA, Sage AM, Pierce JR, Donahue NM, Robinson AL (2007) Organic aerosol formation from photochemical oxidation of diesel exhaust in a smog chamber. Environ Sci Tech 41:6969–6975

Weitkamp EA, Lambe AT, Donahue NM, Robinson AL (2009) Laboratory measurements of the heterogeneous oxidation of condensed-phase organic molecular markers for motor vehicle exhaust. Environ Sci Tech 43: doi:10.1021/es800745x

Welthagen W, Schnelle-Kreis J, Zimmermann R (2003) Search criteria and rules for comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometry analysis of airborne particulate matter. J Chromat 1019:233–249

Zhang Y, Shao M, Zhang Y, Zeng L, He L, Zhu B, Wei Y, Zhu X (2007) Source profiles of particulate organic matters emitted from cereal straw burnings. J Environ Sci 19:167–175