Bull Environ Contam Toxicol (2015) 95:661–669
DOI 10.1007/s00128-015-1660-z

Variation of Stable Carbon and Nitrogen Isotopic Composition of PM_{10} at Urban Sites of Indo Gangetic Plain (IGP) of India

S. K. Sharma[1] · T. K. Mandal[1] · D. M. Shenoy[2] · Pratirupa Bardhan[2] · Manoj K. Srivastava[3] · A. Chatterjee[4] · Mohit Saxena[1] · Saraswati[1] · B. P. Singh[3] · S. K. Ghosh[4]

Received: 13 February 2015 / Accepted: 15 September 2015 / Published online: 5 October 2015

Abstract This paper presents the variation of elemental concentrations of total carbon (TC), total nitrogen (TN) and isotopic ratios of $\delta^{13}C$ and $\delta^{15}N$ along with $\delta^{13}OC$ and OC of PM_{10} mass over Delhi, Varanasi and Kolkata of the Indo Gangetic Plain (IGP), India. For Delhi, the average concentrations of TC and TN of PM_{10} were 53.0 ± 33.6 and 14.9 ± 10.8 μg m^{-3}, whereas $\delta^{13}C$ and $\delta^{15}N$ of PM_{10} were −25.5 ± 0.5 and 9.6 ± 2.8 ‰, respectively. For Varanasi, the average values of $\delta^{13}C$ and $\delta^{15}N$ of PM_{10} were −25.4 ± 0.8 and 6.8 ± 2.4 ‰, respectively. For Kolkata, TC and TN values for PM_{10} ranged from 9.1–98.2 to 1.4–25.9 μg m^{-3}, respectively with average values of 32.6 ± 24.9 and 9.3 ± 8.2 μg m^{-3}, respectively. The average concentrations of $\delta^{13}C$ and $\delta^{15}N$ were −26.0 ± 0.4 and 7.4 ± 2.7 ‰, respectively over Kolkata with ranges of −26.6 to −24.9 ‰ and 2.8 ± 11.5 ‰, respectively. The isotopic analysis revealed that biomass burning, vehicular emission and secondary inorganic aerosols were likely sources of PM_{10} mass over IGP, India.

Keywords PM_{10} · Organic carbon · Elemental carbon · Carbon isotopes · Nitrogen isotopes

✉ S. K. Sharma
sudhircsir@gmail.com

[1] CSIR-National Physical Laboratory, Dr. K S Krishnan Road, New Delhi 110 012, India

[2] CSIR-National Institute of Oceanography, Dona Paula, Panaji, Goa 403 004, India

[3] Department of Geophysics, Banaras Hindu University, Varanasi 221 005, India

[4] Centre for Astroparticle Physics and Space Sciences, Bose Institute, Kolkata 700091, India

Aerosols containing carbonaceous particles lead to poor air quality and effects on climate as well as earth atmospheric system (Liousse et al. 1996; Jacobson 2001) and socio-economic issues in Asia. The organics comprise a major components of atmospheric aerosols, accounting for up to 70 % of fine aerosol mass (Jacobson 2001). The major sources of carbonaceous aerosols (CA) include biomass burning, combustion of biomass and fossil fuels etc. (Venkataraman et al. 2005; Wang and Kawamura 2006; Sharma et al. 2015). Several researchers have reported carbonaceous aerosols and chemical composition of total suspended particulates in the Indian region (Kulshrestha et al.1998; Venkataraman and Rao 2001; Tare et al. 2006; Parashar et al. 2005; Tiwari et al. 2009). The studies suggested that carbonaceous aerosols contribute ∼30 %–35 % of the total suspended particulate mass over IGP during winter (Rengarajan et al. 2007; Ram and Sarin 2010) whereas contribution of water soluble ionic component (WSIC) are of the order of 15 %–20 % (Tare et al. 2006; Rengarajan et al. 2007; Sharma et al. 2015). Ambient aerosols consist of mineral dust, metals, sea salts and secondary aerosol; and contain both inorganic and organic pollutants, with the relative abundance of these components being highly variable both spatially and seasonally (Rengarajan et al. 2007; Sharma et al. 2015). Carbonaceous aerosols (CA) are composed of organic carbon (OC) and black or elemental carbon (BC or EC) have important effect on climate. In contrast, OC is a mixture of primary and secondary organic aerosols since this fraction undergoes physical and chemical formation and transformations in the atmosphere. Knowledge about CA sources, which may be of both anthropogenic and biogenic origins, is a prerequisite for both improved system understanding and for guiding effective policy measures aimed at mitigating anthropogenic aerosol emissions.

Radiocarbon analysis has been reported to be a powerful technique for source apportionment for both BC aerosols (brown carbon and black carbon) (Chen et al. 2013; Gustafsson et al. 2009).

The analysis of stable isotopes of C and N ($\delta^{13}C$ and $\delta^{15}N$) are well recognized for decoding and tracking biogeochemical processes in oceanography and limnology. Court et al. (1981) was probably the first to suggest the utility of C isotopes in identifying urban air particulates. Widory et al. (2004) used C isotopes to identify and semi-quantify aerosol sources such as road traffic versus industrial emissions in a typical urban environment. $\delta^{13}C$ together with $\delta^{15}N$ of particulates were used in discerning C-3 and C-4 vegetation types (Martinelli et al. 2002; Kelly et al. 2005). Moore (1977) used $\delta^{15}N$ of NH_4^+ and NO_3^- in particulates to investigate atmospheric N cycling. Thereafter, $\delta^{15}N$ isotope has been widely used for several studies (Kawamura et al. 2004; Russell et al. 1998; Turekian et al. 1998; Widory 2007; Yeatman et al. 2001). However, exploitation of C and N isotopes for characterization of possible potential sources of particulates/aerosols over southeast Asia is limited. This kind of study is also limited over the IGP region of India. In the present study, the stable isotopes of C and N ($\delta^{13}C$ and $\delta^{15}N$) have been used to identify the possible sources of aerosol over IGP, India. This study presents the variations in TC, TN and isotopes ($\delta^{13}C$, $\delta^{15}N$ & $\delta^{13}OC$) of PM_{10} over the course of a year at three major cities in India.

Materials and Methods

PM_{10} samples were collected periodically at the urban sites of Delhi, Varanasi and Kolkata (Fig. 1) of IGP, India during January–December 2011. The IGP is a great alluvial crescent stretching from the Indus River system in Pakistan to the Punjab Plain (in both Pakistan and India) and the Haryana Plains to the delta of the river Ganga in Bangladesh. IGP, India is comprised of the states of Punjab, Haryana, Delhi, Uttarakhand, Uttar Pradesh, Bihar and West Bengal. A detailed description of the IGP India is available in Saud et al. (2012). A description of the sampling sites is given below:

Delhi PM_{10} samples (n = 20) were collected at the CSIR-National Physical Laboratory (CSIR-NPL), New Delhi (28°38′N, 77°10′E; 218 m amsl). The sampling site represents a typical urban atmosphere, surrounded by heavy roadside traffic and agricultural fields in the southwest direction. The total number of registered vehicles in the city was of the order of ~7.74 million in 2011–2012 (Delhi Statistical Handbook 2012). This area is under the influence of air mass flow from northeast to northwest in winter and from southeast to southwest in the summer (Goyal and Sidhartha 2002). Roadside vehicles, industrial emissions and biomass burning are the major sources of carbonaceous aerosols and several other pollutants. The occasional occurrence of dust storms may contribute significantly to the presence of mineral dust as a part of the aerosol loading in the summer (Ram and Sarin 2010). The temperature of Delhi varies from minimum (1°C) in winter (November to February) to maximum (48°C) in summer (March to June) (Fig. 2). The average rainfall in Delhi during the monsoon season (July to October) is of the order of 780 mm.

Varanasi PM_{10} samples (n = 20) were collected at the Department of Geophysics (25°18′N, 83°03′E; 129 m amsl), Banaras Hindu University (BHU), Varanasi, Uttar Pradesh (India) during January–December 2011. Varanasi is located in the middle Ganges valley of North India, in the Eastern part of the state of Uttar Pradesh, along the left crescent-shaped bank of the Ganges, averaging between 15 and 21 m above the river. Varanasi experiences a humid subtropical climate with large variations between summer and winter temperatures. Summer are long, from early April to October with intervening monsoon seasons, and are also extremely hot, even by South Asian standards. The temperature ranges between 22 and 46°C in the summers (Fig. 2). Winters in Varanasi have large diurnal variations, with warm days and cold nights. Cold waves from the Himalayan region cause temperatures to dip across the city in the winter from December to February and temperatures below 5°C are not uncommon. The average annual rainfall is 1110 mm.

Kolkata The PM_{10} samples (n = 18) were collected at Bose Institute, Kankurgachi, Kolkata. Kolkata, formerly known as Calcutta (22°33′N, 88°20′E; 6 m amsl) is the second most populous city of India after Mumbai. The city is bounded to the west and north-west by the Houghly river spread along 80 km. The core area is flat with elevations near 6 m above the mean sea level (amsl). The Sundarban mangroves forest, the world's largest mangrove eco-region at the land–ocean boundary of the Ganges delta, is located about 100 km from Kolkata. The temperature, RH and wind speed varied from 18–33°C, 45 %–98 % and 0.8–3.3 ms^{-1}, respectively.

At all three locations, the PM_{10} samples were collected on pre-baked (at 550°C at least 5 h) and dessicator-stored quartz microfibre filters (Whatman QM-A) by using a particle sampler (Envirotech APM 460NL, Mumbai, IN). Ambient air was passed through a filter at a flow rate of 1.12 m^3 min^{-1} (accuracy ±2 %) for 8 h on day and night basis [during the daytime (1000–1800 h) and nighttime (1900–0300 h)]. The filters were weighed before and after the sampling during the experiment in order to determine the mass of the PM_{10} collected. After sampling, the filter was placed in a clean glass jar and stored at −20°C prior to analysis.

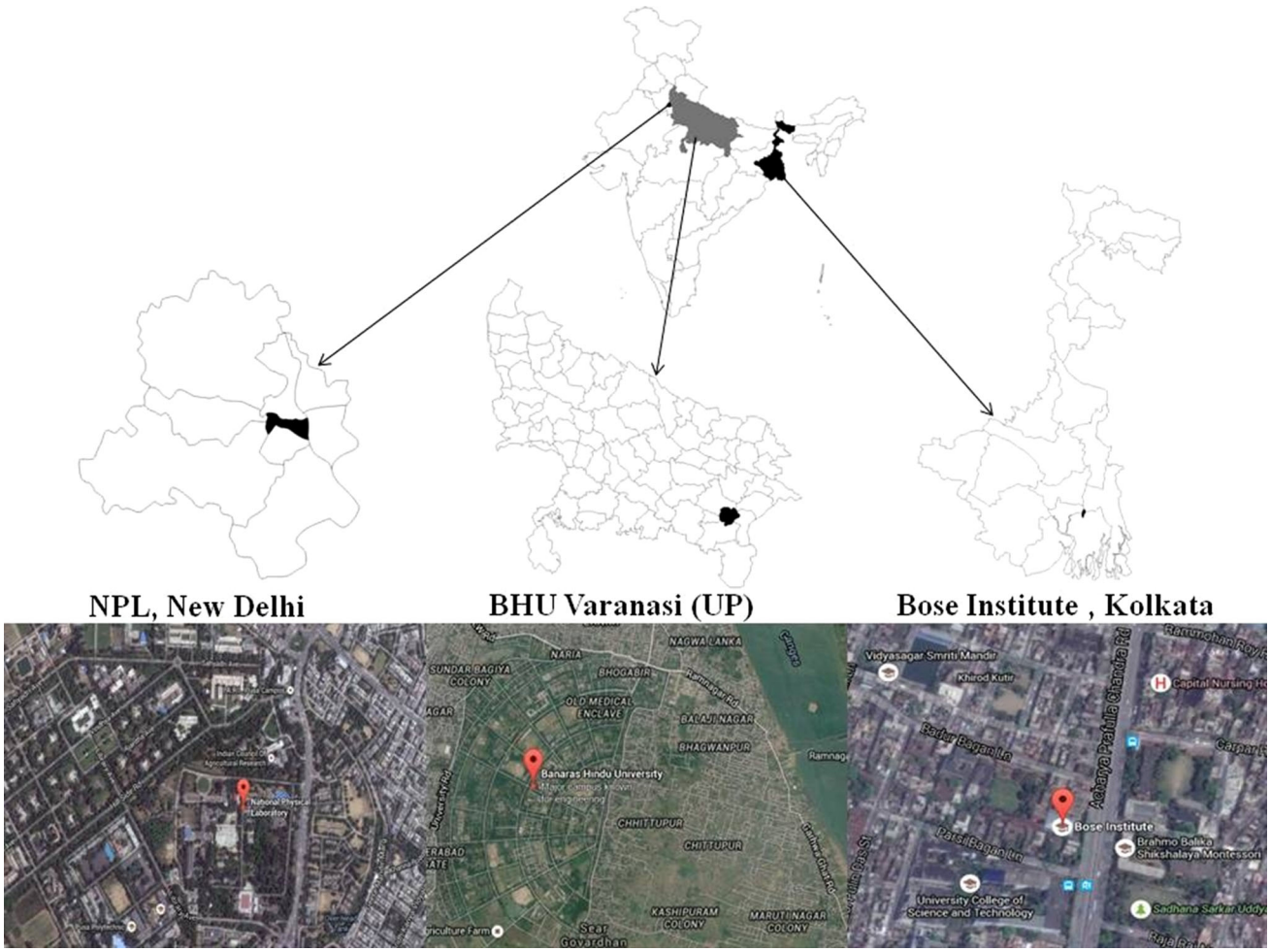

Fig. 1 Map of PM_{10} sample collection sites (Delhi, Varanasi and Kolkata) of the IGP India

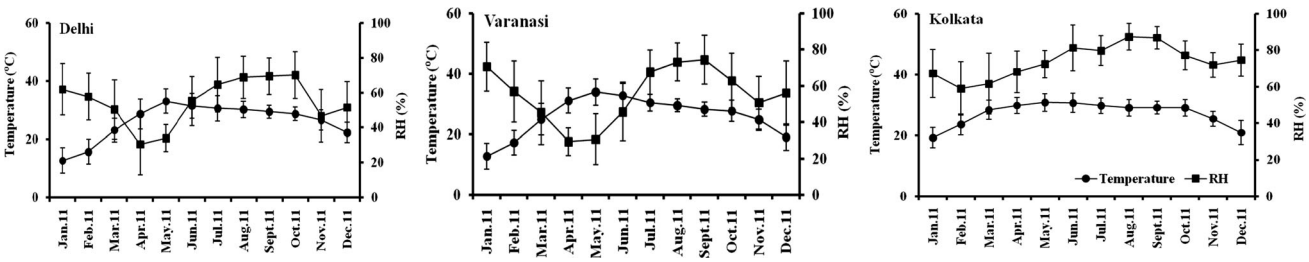

Fig. 2 Variation in monthly average temperature and relative humidity (RH) over Delhi, Varanasi and Kolkata

The $^{13}C/^{12}C$ and $^{15}N/^{14}N$ ratios together with TC and TN content were measured using an isotope-ratio mass spectrometer (IRMS; Delta V plus, Thermo®, Waltham, MA, USA) coupled with an elemental analyzer (EURO3000, EuroVector, Milan IT). The details of collection and isotopic analyses of PM10 samples are described in Agnihotri et al. (2011). Briefly, two aliquots, each of 11 mm were sub-sectioned from each quartz filter and packed in clean tin cups to form compact pellets. These pellets were then analysed in the EA-IRMS in a continuous-flow mode. The final results are expressed as $\delta^{13}C$ and $\delta^{15}N$ relative to V-PDB (Vienna-Peedee Belemnite) and atmospheric N2 standards respectively and defined as:

$$\delta^{13}C \text{ and } \delta^{15}N = \left(\left(R_{sample} - R_{standard}\right)/R_{standard}\right) \times 1000 \quad (1)$$

where, $R = {}^{13}C/{}^{12}C$ and $^{15}N/^{14}N$.

Carbon and nitrogen reference gases were calibrated using international standards with a wide range of isotopic values. Analytical precision was estimated by repeated measurements (after every 5 samples) of a laboratory standard ACA (ε-Amino-n-Caproic Acid; $\delta^{13}C = -25.3$ ‰ and $\delta^{15}N = +4.6$ ‰) and an in-house sedimentary standard COD ($\delta^{13}C = -21.08$ ‰ and $\delta^{15}N = +7.38$ ‰). Analytical precision (1 SD) was better than ±0.3 ‰ for $\delta^{13}C$ and $\delta^{15}N$. TC and TN contents in the samples were calculated from a calibration curve made of four ACA standards ranging from 1 to 4 μmol for N and 6–24 μmol for C.

Analysis of OC and EC on ambient PM_{10} samples was performed using an OC/EC carbon analyzer (Model DRI 2001A, Atmoslytic Inc., Calabasas, CA, USA) following the method in Chow et al. (2004) with negative pyrolysis areas zeroed. The principal function of the optical component (laser reflectance and transmittance) of the analyzer is to correct for pyrolysis, charring of OC compounds into EC. The thermal optical reflectance (TOR) charring corrections are not necessarily the same, owing to charring of organic vapors within the QM-A filter (Chow et al. 2004). Approximately 0.536 cm^2 area of QM-A filter was cut using the proper punch and the values were reported as μg cm^{-2} as given by the instrumental analysis software. Details of OC and EC analysis of PM_{10} are given in Sharma et al. (2014a, b). The concentrations of water soluble inorganic ionic (Cl^-, NO_3^-, SO_4^{2-} Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+} etc.,) components (WSIC) of PM_{10} were determined by ion chromatography (Dionex ICS-3000, Sunnyvale, CA, USA). Details of WSIC analysis of PM_{10} are discussed in our earlier paper Sharma et al. (2012). Each filter was analyzed in triplicate with several blank filter runs to obtain the representative estimates of the concentrations of OC, EC and WSIC in the PM_{10} mass. The instruments which were used for analysis of PM_{10} mass were calibrated before analysis of the samples with traceable standards as per recommended standard procedures of the respective instruments.

Composition of ambient aerosol is influenced by its source region and transport pathway. In order to identify the possible transport pathways of PM_{10} from their potential sources of origin to Delhi, Varanasi and Kolkata, 5 days backward trajectories were calculated using the hybrid single particle Lagrangian integrated trajectory (HYSPLIT) model (Draxler and Rolph 2003). Air mass back-trajectories for each experimental day for 500 m above the ground level (AGL) during January-December 2011 were calculated using GDAS (Global Data Assimilation System) meteorological data. HYSPLIT was run every day starting at 0500 h, UTC at a starting height of 500 m AGL on an hourly basis. This height was chosen to diminish the effects of surface friction and to represent winds in the low boundary layer. The PM_{10} has the ability to travel long distance, therefore, 5 days were selected to calculate backward trajectories using HYSPLIT.

Results and Discussion

Monthly variations in concentrations of PM_{10} mass along with TC and OC over Delhi, Varanasi and Kolkata are shown in Fig. 3. The average mass concentration of PM_{10} over Delhi (range 51.1–376.3 μg m^{-3}), Varanasi (range 48.3–387.3 μg m^{-3}) and Kolkata (range 92.9–312.4 μg m^{-3}) were recorded as 213.8 ± 46.0, 185.5 ± 67.3 and 157.1 ± 60.7 μg m^{-3} (average ± SD), respectively during January–December 2011. Highest monthly concentrations of PM_{10} were 333.6 and 366.6 μg m^{-3} over Delhi and Varanasi, respectively, in December 2011; whereas the highest monthly PM_{10} mass concentration was 244.3 μg m^{-3} over Kolkata during February 2011.

The average elemental concentrations of total carbon, total nitrogen (TC and TN) and isotopic ratios of $\delta^{13}C$ & $\delta^{15}N$ along with $\delta^{13}OC$ & OC of PM_{10} mass over Delhi, Varanasi and Kolkata are summarized in Table 1. The average concentrations of TC and TN of PM_{10} were 52.9 ± 33.6 and 14.9 ± 10.8 μg m^{-3} over Delhi, whereas $\delta^{13}C$ and $\delta^{15}N$ of PM_{10} varied in a narrow range of −25.5 ± 0.5–9.6 ± 2.8 ‰, respectively. The TC/TN ratio of PM_{10} over Delhi ranged from 4.8 to 20.2 with an average value of 9.8 ± 3.7 (Table 1). The average elemental concentrations of $\delta^{13}OC$ and OC of PM_{10} over Delhi were −25.5 ± 0.4 ‰ and 25.3 ± 19.3 μg m^{-3}, respectively (Table 1). The average value of $\delta^{13}C$ and $\delta^{15}N$ of PM_{10} were −25.4 ± 0.8 and 6.8 ± 2.4 ‰, respectively, over Varanasi with a range of −26.4 to −23.3 and 2.8 to 11.0 ‰, respectively. The average concentrations of $\delta^{13}OC$ and OC of PM_{10} were −25.3 ± 0.7 ‰ and 11.6 ± 7.6 μg m^{-3}, respectively over Varanasi (Table 1). The average concentration of $\delta^{13}C$ and $\delta^{15}N$ were −26.0 ± 0.4 and 7.4 ± 2.7 ‰, respectively over Kolkata. The concentrations of $\delta^{13}OC$ and OC of PM_{10} were −26.1 ± 0.7 ‰ and 23.4 ± 19.7 μg m^{-3}, respectively over Kolkata. The average TC/TN ratio of PM_{10} was 11.1 ± 5.7 with a range of 4.4–25.9 over Kolkata. Bosch et al. (2014) studied the dual C isotope signatures and optical properties of CA simultaneously for the South Asian outflow during an intensive campaign at the Maldives Climate Observatory on Hanimaadhoo (MCOH). The radiocarbon ($\Delta^{14}C$) data showed that water soluble organic carbon (WSOC) had a significantly higher biomass/biogenic contribution (86 ± 5 %) compared to EC (59 ± 4 %). The more ^{13}C-enriched signature of MCOH-WSOC (−20.8 ± 0.7 ‰) compared to MCOH-EC (−25.8 ± 0.3 ‰) and megacity Delhi WSOC

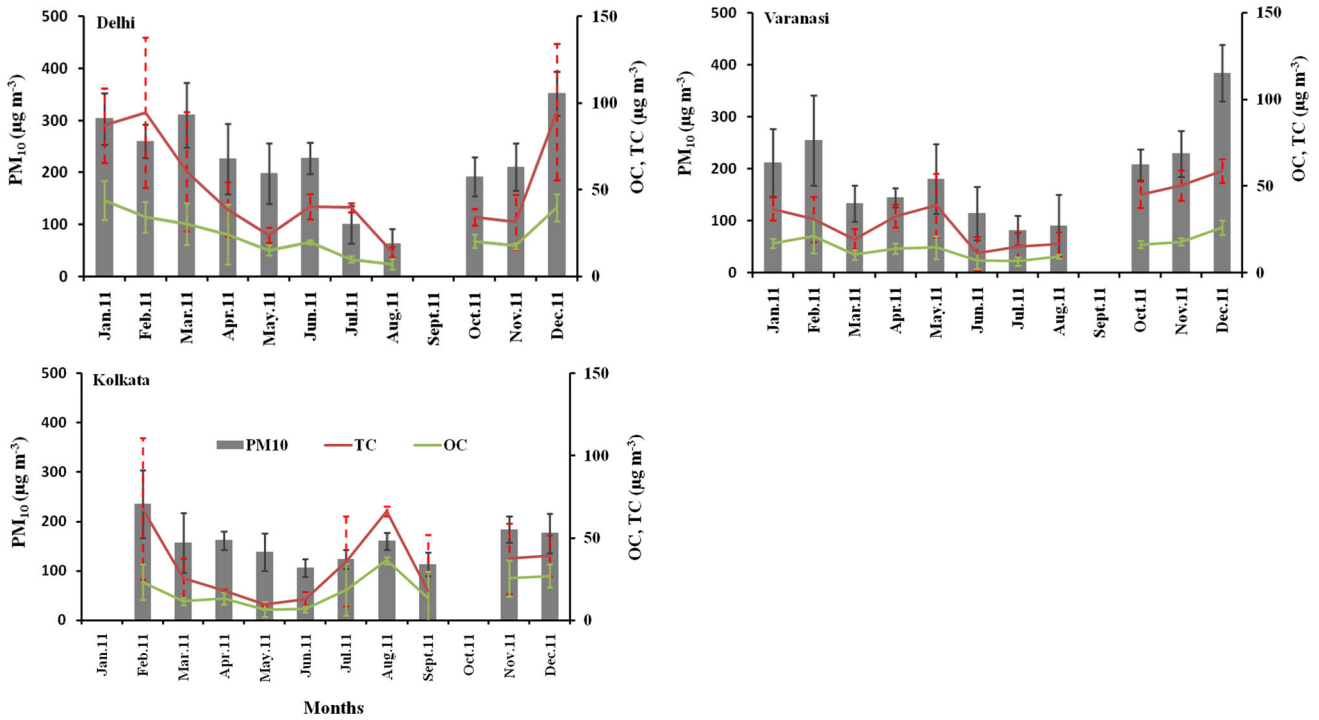

Fig. 3 Monthly variations in concentrations of PM_{10}, OC and TC over Delhi, Varanasi and Kolkata, India

Table 1 Annual average elemental concentrations of total C & N, and their isotopes $\delta^{13}C$, $\delta^{15}N$ with TC/TN ratios of PM_{10} collected over IGP India

Parameters	Delhi (n = 20)		Varanasi (n = 20)		Kolkata (n = 18)	
	Range	Average	Range	Average	Range	Average
$\delta^{13}C$	−26.4 to −24.8	−25.5 ± 0.5	−26.4 to −23.3	−25.4 ± 0.8	−26.6 to −24.9	−26.0 ± 0.4
$\delta^{15}N$	3.3 to 14.3	9.6 ± 2.8	2.8 to 11.0	6.8 ± 2.4	2.8 to 11.5	7.4 ± 2.7
μg C m^{-3} (TC)	13.1 to 125.9	53.0 ± 33.6	9.3 to 51.9	27.1 ± 13.2	9.1 to 98.2	32.6 ± 24.9
μg N m^{-3} (TN)	1.5 to 42.6	14.9 ± 10.8	2.3 to 36.6	9.8 ± 9.7	1.4 to 25.9	9.3 ± 8.2
TC/TN	4.8 to 20.2	9.8 ± 3.7	2.1 to 16.3	9.2 ± 4.0	4.4 to 25.9	11.1 ± 5.7
δ^{13} OC	−26.6 to −24.9	−25.5 ± 0.4	−26.3 to −24.6	−25.3 ± 0.7	−27.3 to −25.0	−26.1 ± 0.7
μg OC m^{-3}	3.3 to 61.1	25.3 ± 19.3	4.3 to 39.9	11.5 ± 7.6	6.1 to 66.9	23.4 ± 19.7

± Standard deviation

(−24.1 ± 0.9 ‰) suggests that WSOC is significantly more affected by aging during long-range transport than EC. The average day and night ratio of PM_{10} and other chemical species of PM_{10} mass over Delhi, Varanasi and Kolkata were recorded <1 during the study period. Ram and Sarin (2011) reported similar day and night variations in PM concentration at Kanpur, India (another urban location in the IGP). They attributed this to the increase PM mass during night time might be due to increase in the source strenght of cabonaceous species and trapping of aerosols due to lowering of boundary layer height (Sharma et al. 2014c).

The average value of $\delta^{13}C$ of PM_{10} over all locations was −25.6 ± 0.6 ‰. This represents an intermediate value of aerosols emitted from predominantly C-3 type vegetation burning (∼ −27 ‰) and coal combustion (average ∼ −23 ‰). Emissions from increased road traffic, and industry also could be significant sources of PM_{10} especially in urban/sub-urban areas. Sampling locations in Delhi and Kolkata represent the influence of heavy road side traffic, and $\delta^{13}C$ of PM_{10} was recorded as ∼ −25.5 and ∼ −25.9 ‰ at these locations, respectively (Table 1). In contrast, corresponding TC concentrations were almost a factor of 2 greater at Delhi than at Varanasi and Kolkata. This may be due to highest diesel-based road traffic, which is a potential source of higher TC in the PM_{10} aerosol fraction than gasoline-based traffic (Sharma et al. 2014c). Widory et al. (2004) reported the value of $\delta^{13}C$

−26.5 ± 0.5 ‰ indicates the other sources (fossil fuel, coal etc.,) of C in ambient urban area. Agnihotri et al. (2015) discussed in detail about the end member isotopic values ($\delta^{13}C$ and $\delta^{15}N$) of major typical sources.

The analysis of OC and EC concentrations over Delhi, Varanasi and Kolkata are attributed to the combined effects of traffic emission and biomass burning (including wood burning and crop residue burning). Figure 4 shows the scatter plot between OC and EC during the study period for Delhi ($r^2 = 0.78$), Varanasi ($r^2 = 0.88$) and Kolkata ($r^2 = 0.81$). Ram and Sarin (2011) reported a significant linear relation between OC and EC ($r^2 = 0.66$) and OC and K^+ ($r^2 = 0.59$) of PM_{10} at Kanpur, IGP of India, and considered biomass burning emissions as one of the sources of PM. A significant correlation between OC and EC is usually indicative of their common sources like vehicular traffic, biomass burning etc., (Salma et al. 2004; Sharma et al. 2014a, b; Sharma et al. 2015). In contrast, a poor correlation between OC and EC indicates the formation of secondary aerosols under favorable conditions for the gas to particle conversion of volatile organic compounds through a photochemical reaction in the atmosphere (Salma et al. 2004). Overall, significant positive linear trends are observed between OC and EC for urban sites of Delhi, Varanasi and Kolkata, also indicating the influence of vehicular emissions as well as biomass burning emissions at the sample collection sites (Fig. 4). In the present case, a weak positive correlation between $\delta^{13}C$ values and TC values were recorded over Delhi ($r^2 = 0.268$), Varanasi ($r^2 = 0.168$) and Kolkata ($r^2 = 0.453$) (Table 2) indicating the presence of inorganic C in ambient air.

Nitrogen in ambient particulate matter (PM) is present mainly in the forms of nitrate (NO_3^-) and ammonium (NH_4^+) (Seinfeld and Pandis 1998; Sharma et al. 2014c; Sharma et al. 2015). Roadside vehicles and industrial activities in urban areas also contribute N in particulates through oxidation of gaseous NO_x (NO and NO_2). The major N compound in particulates/aerosol i.e., NH_4NO_3 and $(NH_4)_2SO_4$ may be produced mainly through gas to particle conversion or a neutralization process of NH_3 gas with atmospheric acid gases, i.e., HNO_3 and H_2SO_4 (Seinfeld and Pandis 1998). Hence, the addition of N to atmospheric particulates may involve complex chemical reactions, resulting in a very broad range of $\delta^{15}N$ from −15 to +30 ‰. The results have shown weak positive correlation between $\delta^{15}N$ and TN concentrations of PM_{10} over Delhi ($r^2 = 0.340$) and Varanasi ($r^2 = 0.098$), whereas a significant positive correlation was obtained over Kolkata ($r^2 = 0.627$; Table 2). This indicates the presence of NH_4NO_3 and $(NH_4)_2SO_4$ in the PM_{10} mass over Kolkata. Significant positive correlations between TN & NO_3^- and TN & SO_4^{2-} were recorded at all collection sites, also indicating the presence of N concentrations in PM_{10} in the form of a secondary inorganic aerosol. Pavuluri et al. (2010) has reported the concentration of $\delta^{15}N$ (15.7 to 32.2 ‰; with an average value of 23.9 ± 3.3 ‰) in aerosol samples over Chennai, India, and expressed the source to be local animal excreta and biofuel/biomass burning from south a source.

In the present case, we observed average concentrtaion of $\delta^{15}N$ in PM_{10} mass over Delhi, Varanasi and Kolkata as 9.6 ± 2.8, 6.8 ± 2.4 and 7.4 ± 2.7 ‰, respectively. Widory (2007) reported that nitrogen in the atmospheric particles in an urban area results from complex primary and secondary processes, which render the identification of its origin somewhat complicated. They also concluded that $\delta^{15}N$ appears to be a reliable tool for discriminating the different PM_{10} pollution sources in Paris (heating, waste incineration and road traffic). The combustion conditions (temperature, supply of O_2, etc.,) seem to influence the $\delta^{15}N$, as various emission sources may present a slight to substantial enrichment of ^{15}N (waste incineration, road traffic and natural gas), while others have a negative nitrogen isotope composition (fuel oil and coal) (Widory 2007).

The HYSPLIT model has provided the trajectories for air mass parcels from long range transport at the receptor sites (Fig. 5). During the study, the approaching air mass at the

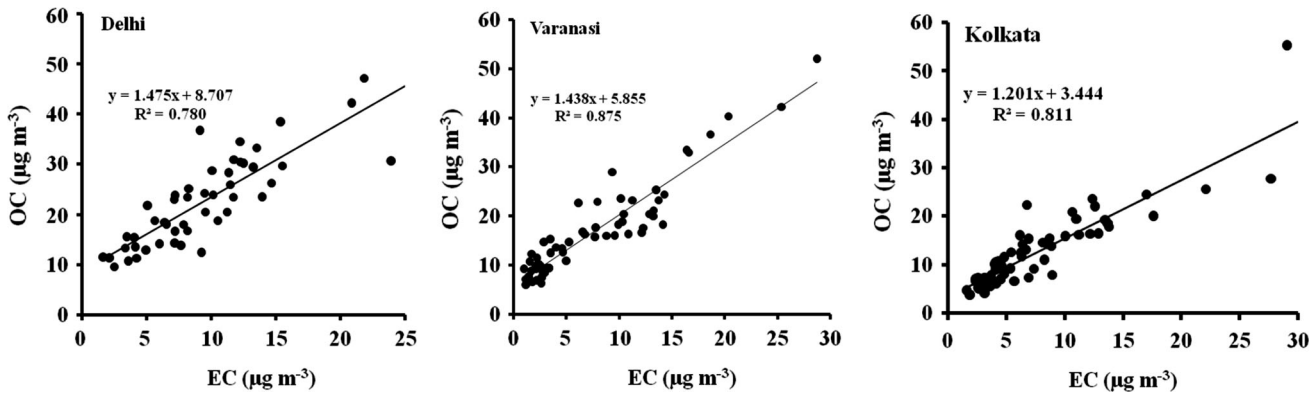

Fig. 4 Scatter plot of OC and EC of PM_{10} over Delhi, Varanasi and Kolkata of IGP India

Table 2 Correlation matrix for total C & N, and their isotopes $\delta^{13}C$, $\delta^{15}N$ over IGP India

Parameters	Delhi (n = 20)	Varanasi (n = 20)	Kolkata (n = 18)
$\delta^{13}C$ versus $\delta^{15}N$	0.147	0.305	0.417
$\delta^{13}C$ versus TC	−0.268	0.168	0.453
$\delta^{15}N$ versus TN	0.340	0.091	0.627[a]
δ^{13} OC versus OC	0.032	0.197	0.470[a]
TC versus OC	0.855[a]	0.461[a]	0.742[a]
$\delta^{15}N$ versus NH_4^+	0.266	−0.125	−0.051
$\delta^{15}N$ versus NO_3^-	0.098	−0.038	0.244
TN versus NH_4^+	0.544[a]	0.840[a]	0.350
TN versus NO_3^-	0.639[a]	0.905[a]	0.730[a]

[a] Significant at $p < 0.05$

receptor site Delhi was mainly a continental type that was transported from the IGP, Pakistan, Afghanistan and its surrounding areas. Sharma et al. (2014c) also observed similar trajectories at Delhi during winter, 2012. The approaching air mass at the receptor site Varanasi was mainly from the IGP and surrounding area, whereas at Kolkata it approached from IGP, Bay of Bengal, Arabian sea, and coastal sites of West Bengal, Orissa and Andhara Pradesh. Venkataraman et al. (2005) reported high emissions of BC aerosols from the IGP and the central, east coast and south Indian regions due to extensive use of biomass fuels, particularly wood.

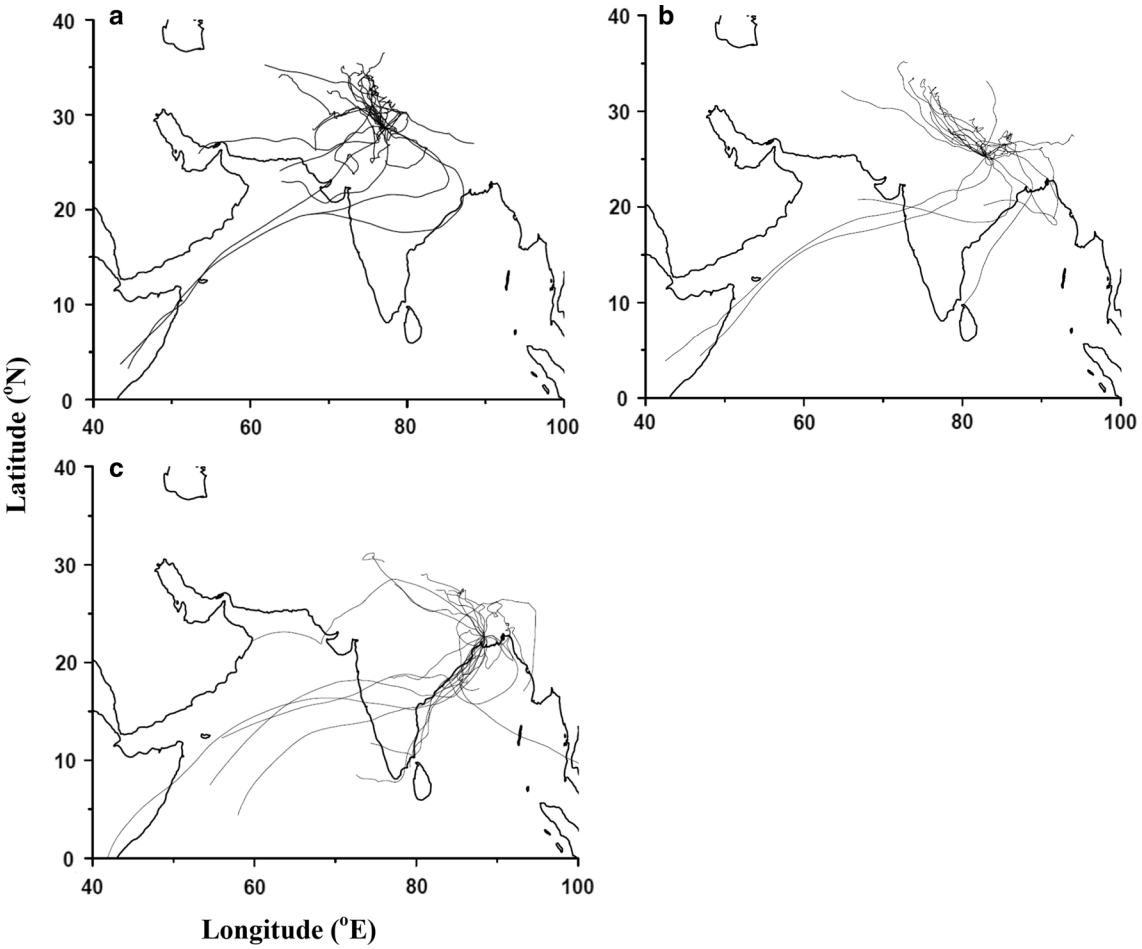

Fig. 5 Air parcel back trajectories over **a** Delhi, **b** Varanasi and **c** Kolkata during 2011

Acknowledgments The authors are thankful to the Director, CSIR-NPL, New Delhi and Head, Radio and Atmospheric Sciences Division, NPL, New Delhi for their encouragement and support for this study. The authors also acknowledge the Council of Scientific and Industrial Research (CSIR), New Delhi for providing financial support for this study (CSIR-EMPOWER Project: OLP-102132). Authors are thankful to the anonymous reviewers for their constructive suggestions to improve the manuscript.

References

Agnihotri R, Mandal TK, Karapurkar SG, Naja M et al (2011) Stable carbon and nitrogen isotopic composition of bulk aerosols over India and northern Indian Ocean. Atmos Environ 45:2828–2835

Agnihotri R, Karapurkar SG, Sarma VVSS, Yadav K, Kumar MD, Sharma C, Prasad MVSN (2015) Stable isotopic chemical characteristics of bulk aerosol during winter and summer season at a station in western coast of India (Goa). Aerosol Air Qual Res. doi:10.4209/aaqr.2014.07.0127

Bosch C, Andersson A, Kirrillova EN, Budhavant K, Tiwari S, Praveen PS, Russell LM, Beres ND, Ramanathan V, Gustafsson O (2014) Source-diagnostic dual isotope composition and optical properties of water soluble organic carbon and elemental carbon in the South Asian outflow intercepted over Indian ocean. J Geophys Res Atmos 119:11743–11759

Chen B, Andersson A, Lee M, Kirillova EN, Xiao Q, Kruså M, Shi M, Hu K, Lu Z, Streets DG, Du K, Gustafsson Ö (2013) Source forensics of black carbon aerosols from China. Environ Sci Technol 47:9102–9108

Chow JC, Watson JG, Chen LWA, Arnott WP, Moosmuller H (2004) Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols. Environ Sci Technol 38:4414–4422

Court JD, Goldsack JR, Ferrari LM, Polach HA (1981) The use of carbon isotopes in identifying urban air particulate sources. Clean Air 15:6–11

Delhi Statistical Handbook (2012) Registered vehicles in Delhi. Directorate of Economics and Statistics, Govt of National Capital Delhi. http://www.des.delhigovt.nic.in

Draxler RR, Rolph GD (2003) HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, MD

Goyal P, Sidhartha (2002) Effect of winds on SO_2 and SPM concentration in Delhi. Atmos Environ 36:2925–2930

Gustafsson O, Kruså M, Zencak Z, Sheesley RJ, Granat L, Engström E, Praveen PS, Rao PS, Leck C, Rodhe H (2009) Brown clouds over South Asia: biomass or fossil fuel combustion. Science 323:495–498

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

Kawamura K, Kobayashi M, Tsubonuma N, Mochida M, Watanabe T, Lee M (2004) Organic and inorganic compositions of marine aerosols from East Asia: seasonal variations of water-soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition. In: Hill RJ et al. (eds) Geochemical investigations in earth and space science: a tribute to Isaac R. Kaplan. Geochemical Society publication no. 9, pp 243–265

Kelly SD, Stein C, Jickells TD (2005) Carbon and nitrogen isotopic analysis of atmospheric organic matter. Atmos Environ 39:6007–6011

Kulshrestha UC, Saxena A, Kumar N, Kumari KM, Srivastava SS (1998) Chemical composition and size differentiated aerosols at a suburban site in a semi-arid tract of India. J Atmos Chem 29:109–118

Liousse C, Penner JE, Chuang C, Walton JJ, Eddleman H, Cachier H (1996) A global three-dimensional model study of carbonaceous aerosol. J Geophy Res 101:19411–19432

Martinelli LA, Camargo PB, Lara LBLS, Victoria RL, Artaxo P (2002) Stable carbon and nitrogen isotope composition of bulk aerosol particles in a C4 plant landscape of southeast Brazil. Atmos Environ 36:2427–2432

Moore H (1977) The isotopic composition of ammonia, nitrogen dioxide and nitrate in the atmosphere. Atmos Environ 11:1239–1243

Parashar DC, Gadi R, Mandal TK, Mitra AP (2005) Carbonaceous aerosol emissions from India. Atmos Environ 39:7861–7871

Pavuluri CM, Kawamura K, Tachibana E, Swaminathan T (2010) Elevated nitrogen isotope ratios of tropical Indian aerosols from Chennai: implication for the origins of aerosol nitrogen in South and Southeast Asia. Atmos Environ 44:3597–3604

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 (2011) Day–night variability of EC, OC, WSOC and inorganic ions in urban environment of Indo-Gangetic Plain: implications to secondary aerosol formation. Atmos Environ 45:460–468

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

Russell KM, Galloway JN, Macko SA, Moody JL, Scudlark JR (1998) Sources of nitrogen in wet deposition to the Chesapeake Bay region. Atmos Environ 32:2453–2465

Salma I, Chi XG, Maenhaut W (2004) Elemental and organic carbon in urban canyon and background environments in Budapest, Hungary. Atmos Environ 38:2517–2528

Saud T, Gautam R, Mandal TK, Gadi R, Singh DP, Sharma SK, Dahiya M, Saxena M (2012) Emission estimates of organic and elemental carbon from household biomass fuel used over the Indo Gangetic Plain (IGP), India. Atmos Environ 61:212–220

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

Sharma SK, Singh AK, Saud T, Mandal TK, Saxena M, Singh S, Ghosh S, Raha S (2012) Study on water soluble ionic composition of PM_{10} and trace gases over Bay of Bengal during W_ICARB campaign. Meteol Atmos Physics 118:37–51

Sharma SK, Kumar M, Rohtash, Gupta NC, Saraswati S, Saxena M, Mandal TK (2014a) Characteristics of ambient ammonia over Delhi, India. Meteol Atmos Physics 124:67–82

Sharma SK, Mandal TK, Saxena M, Rashmi, Rohtash, Sharma A, Saud A (2014b) Variation of OC, EC, WSIC and trace metals of PM_{10} in Delhi. J Atmos Solar Terrest Phys 113:10–22

Sharma SK, Mandal TK, Saxena M, Rashmi, Rohtash, Sharma A, Gautam R (2014c) Source apportionment of PM_{10} by using positive matrix factorization at an urban site of Delhi, India. Urban Climate 10:656–670

Sharma SK, Sharma A, Saxena M, Choudhary N, Masiwal R, Mandal TK, Sharma C (2015) Chemical characterization and source apportionment of aerosol at an urban area of central Delhi, India. Atmos Pollut Res. doi:10.1016/j.apr.2015.08.002

Tare V, Tripathi SN, Chinnam N, Srivastava AK, Dey S, Manar M, Kanawade VP, Aggarwal A, Kishore L, Lal RB, Sharma M (2006) Measurement of atmospheric parameters during Indian space research organization geosphere biosphere program land campaign II at a typical location in the Ganga Basin: 2. Chemical

properties. J Geophys Res 111:D23210. doi:10.1029/2006/JD007279

Tiwari S, Srivastava AK, Bisht DS, Bano T, Singh S, Behura S, Srivastava MK, Chate DM, Padmanabhamurthy B (2009) Black carbon and chemical characteristics of PM_{10} and $PM_{2.5}$ at an urban site of North India. J Atmos Chem 62:193–209

Turekian VC, Macko S, Ballentine DS, Robert J, Garstang M (1998) Causes of bulk carbon and nitrogen isotopic fractionations in the products of vegetation burns: laboratory studies. Chem Geol 152:181–192

Venkataraman C, Rao GUM (2001) Emission factors of carbon monoxide and size-resolved aerosols from biofuel combustion. Environ Sci Technol 35:2100–2107

Venkataraman C, Habib G, Eiguren-Fernandez A, Miguel AH, Friedlander SK (2005) Residential biofuels in south Asia: carbonaceous aerosol emissions and climate impacts. Science 307:1454–1456

Wang HB, Kawamura K (2006) Stable carbon isotopic composition of low-molecular-weight dicarboxylic acids and ketoacids in remote marine aerosols. J Geophys Res 111:D07304. doi:10.1029/2005JD006466

Widory D (2007) Nitrogen isotopes: tracers of origin and processes affecting PM_{10} in the atmosphere of Paris. Atmos Environ 41:2382–2390

Widory D, Roy S, Moullec Y, Le Goupil G, Cocherie A, Guerrot C (2004) The origin of atmospheric particles in Paris: a view through carbon and lead isotopes. Atmos Environ 38:953–961

Yeatman SG, Spokes LJ, Dennis PF, Jickells TD (2001) Comparisons of aerosol nitrogen isotopic composition at two polluted coastal sites. Atmos Environ 35:1307–1320