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RESEARCH ARTICLE

Characterization of $PM_{2.5}$ in Delhi: role and impact of secondary aerosol, burning of biomass, and municipal solid waste and crustal matter

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Abstract Delhi is one among the highly air polluted cities in the world. Absence of causal relationship between emitting sources of $PM_{2.5}$ and their impact has resulted in inadequate actions. This research combines a set of innovative and state-of-the-art analytical techniques to establish relative predominance of $PM_{2.5}$ sources. Air quality sampling at six sites in summer and winter for 40 days (at each site) showed alarmingly high $PM_{2.5}$ concentrations (340 ± 135 μg/m^3). The collected $PM_{2.5}$ was subjected to chemical speciation including ions, metals, organic and elemental carbons which followed application of chemical mass balance technique for source apportionment. The source apportionment results showed that secondary aerosols, biomass burning (BMB), vehicles, fugitive dust, coal and fly ash, and municipal solid waste burning were the important sources. It was observed that secondary aerosol and crustal matter accounted for over 50% of mass. The $PM_{2.5}$ levels were not solely result of emissions from Delhi; it is a larger regional problem caused by contiguous urban agglomerations. It was argued that emission reduction of precursors of secondary aerosol, SO_2, NO_x, and volatile organic compounds, which are unabated, is essential. A substantial reduction in BMB and suspension of crustal dust is equally important to ensure compliance with air quality standards.

Keywords $PM_{2.5}$ · Source apportionment · Biomass burning · MSW burning · Secondary aerosols

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Introduction

The first 2 weeks of November 2016 witnessed a high air pollution episode in the city of Delhi and surrounding areas causing widespread panic among general population, forcing closure of schools and limiting outdoor activities. The air quality index at five sites in Delhi was in worst pollution category (severe) for all these days (Fig. S1). The episodic conditions led to interventions from the courts and regulatory agencies. The important issue that came to the fore was to identify the sources and establish causal source-impact linkage and work out short and long-term action plans to prevent such episodes.

It is important not to see Delhi in isolation but as a large area of the Indo-Gangetic Plain (IGP; extending from 21°45′N, 74°15′E to 31°00′N, 91°30′E) (Nair et al. 2007). The IGP supports 40% of India's population (Nair et al. 2007) that includes the national capital region (NCR: 27°03′N, 76°07′E to 29°29′N, 78°29′E), of which, Delhi is a subset. About 46 million people (equivalent to about six

contiguous New York cities) reside in the NCR (population density of 11,297 persons per square kilometer). The NCR is the center of the nation having important commercial, economical, defense, industrial, and political establishments (Census-India 2012; NCRPB 2015). Unfortunately, the NCR which includes Delhi is one of the world's most air polluted regions (WHO 2014).

The large scale urbanization, industrialization, land-use changes, biomass, and fossil fuel burning, along with the unique topography of the basin (constrained dispersion due to the Himalayas in the north and north east) are responsible for the alarming levels of particulate pollution in the region (Nair et al. 2007; Prasad and Singh 2007; Ram et al. 2010; Pant et al. 2015). In addition, lack of year-round precipitation further leads to high aerosol loading over the entire IGP. Measurements of aerosol optical depth (AOD) have characterized IGP as a hotspot for anthropogenic aerosols in South-Asia (Ramanathan et al. 2007; Ram et al. 2012a). In IGP, the monthly mean of AOD levels suggest (Fig. S2) that the particulate levels are much higher in winter than in any other season. The region witnesses extreme variability in the climate throughout the year, which causes significant shifts in air quality from summer to winter (Mohan and Kandya 2007; Ram et al. 2010).

The IGP is characterized by severe haze during winter (November–January), which disrupts normal life and affects the public health. During 2001–2010, the annual mean concentration of PM_{10} (particulate matter of size 10 μm or less) in major cities in IGP (Delhi, Kanpur, Lucknow, Agra, Faridabad, Amritsar, Meerut, and Allahabad) exceeded the annual Indian National Ambient Air Quality Standard (NAAQS) of 60 $\mu g/m^3$ (three times of the WHO guideline of 20 $\mu g/m^3$) by a factor of 1.6–4.3 (CPCB 2012) and the mean concentrations in winter (October–March) were 338–548 $\mu g/m^3$ for PM_{10} and 236–389 $\mu g/m^3$ for $PM_{2.5}$ (Tiwari et al. 2012). The pollution levels are higher in winter than in other seasons due to increased emissions from biomass burning (BMB; which includes crop residue burning), heating, and unfavorable meteorological conditions for dispersion (Guttikunda and Gurjar 2012; Ram et al. 2012b).

Delhi being the capital city, its high pollution receives much attention from media, politicians, and even foreign embassies and High Commissions. The annual mean PM_{10} concentration is 261 $\mu g/m^3$ with a maximum daily mean of 748 $\mu g/m^3$ in 2010 (CPCB 2012), and the annual mean $PM_{2.5}$ concentration was153 $\mu g/m^3$ (WHO 2014; Myllyvirta and Dahiya 2015). The acute winter particulate pollution ($PM_{2.5}$ ~ 200 $\mu g/m^3$) was accompanied by extremely poor visibility and sharp increase in respiratory diseases (Liu et al. 2013; Huang et al. 2014; Saraswat et al. 2016).

October–November months see a dramatic increase in the fine mode particulate levels (Badarinath et al. 2009; Awasthi et al. 2011; Ram et al. 2012b; Kaskaoutis et al. 2014). The meteorology, over Indian sub-continent, mostly favors the transport of emissions eastward along the Himalayas (Kaskaoutis et al. 2014). The increased PM concentration in October–November is possibly due to the effect of post-monsoon BMB which takes place in the states of Punjab and Haryana in North-West of Delhi. About 70–80 million tons of rice crop residue is disposed of through open field burning (Badarinath et al. 2006; Gadde et al. 2009). As soon as the BMB is reduced after the second week of November, the air quality begins to improve (Fig. S1).

Behera and Sharma (Behera and Sharma 2010) have reported that secondary aerosols contribute about 50% mass in $PM_{2.5}$; 34% of secondary inorganic aerosol (SIA) and 17% of secondary organic aerosol (SOA) in an urban area of IGP. Various studies have suggested that a significant mass of atmospheric PM in the IGP comprised carbonaceous aerosol (~ 30–35% of the PM) and water-soluble inorganic aerosol (~ 10–20% of the PM) (Tare et al. 2006; Rengarajan et al. 2007; Ram et al. 2010, 2012a; Deshmukh et al. 2011; Kothai et al. 2011).

In India, the causal relationship between emitting source and its impact in terms of $PM_{2.5}$ concentrations is not understood. This has resulted in inadequate actions and insignificant improvements in air quality. This research combines innovative and state-of-the-art analytical techniques to explain the chemical characteristics and relative predominance of the sources of particulate pollution during two seasons (winter: November 2013–February 2014 and summer: April–June 2014) in Delhi and in NCR (outside Delhi; winter: January 2015). Our analyses of results have set in a process of practical measures for $PM_{2.5}$ emission reductions and assist in preparation of action plan.

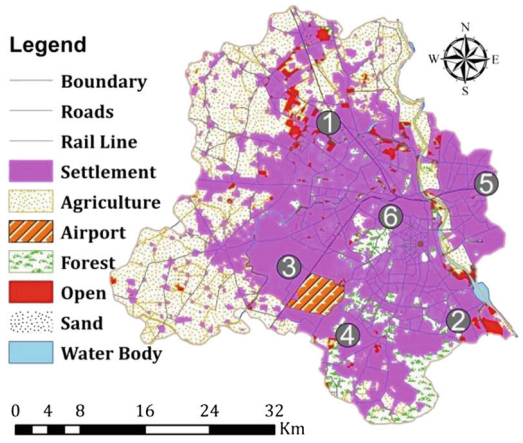
In summary, this research presents a comprehensive study that provides a framework for conducting a systematic and organized study for addressing most issues of air quality in urban areas which are relevant to developing countries. Specifically, the framework includes air quality monitoring, detailed particulate characterization, identification of sources, and their contributions to ambient air pollution.

Fig. 1 Chemical composition and source apportionment of $PM_{2.5}$ in **a** Delhi during winter and summer (November 2013–June 2014) at the six sites and **b** National Capital Region at three sites during winter (January 2015)

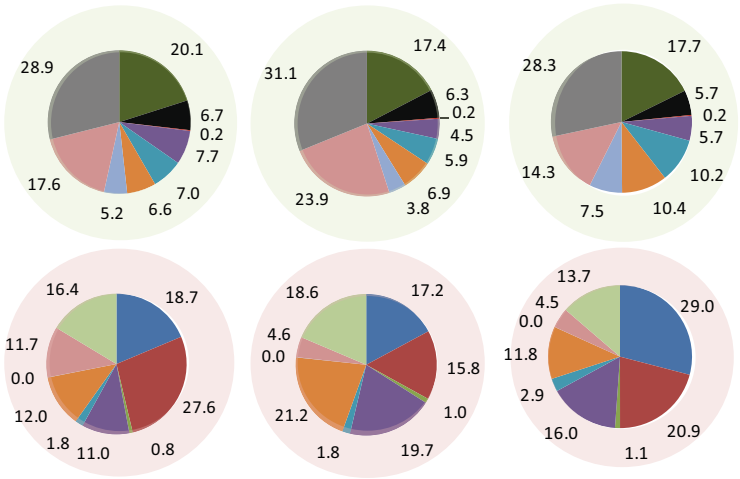
Materials and methods

Six air quality monitoring sites in the city of Delhi, which represented typical land-use patterns, were selected for air quality sampling (Fig. 1). The overall sampling plan, description of sites, and data captured are presented in Table 1.

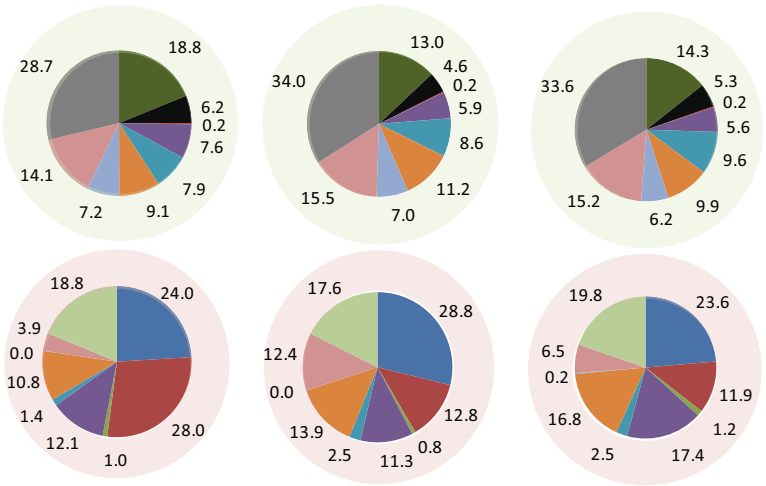
(a) Delhi



1. RHN (380 µg/m³) 2. OKH (422 µg/m³) 3. DWK (297 µg/m³)



4. VKJ (274 µg/m³) 5. DSG (355 µg/m³) 6. PUS (273 µg/m³)



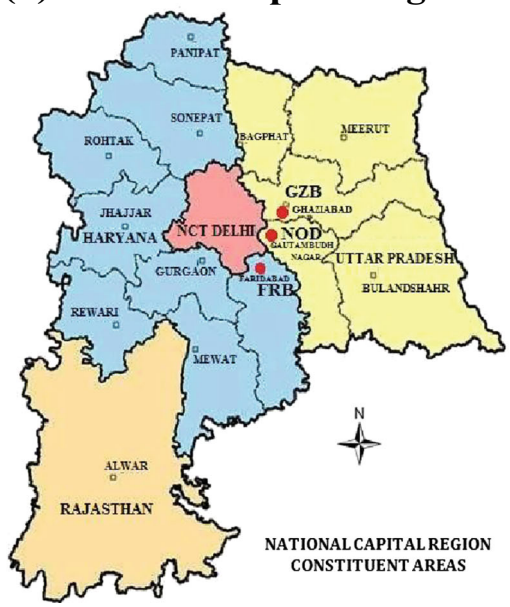
Composition (%)

- OM
- EC
- Flouride
- Chloride
- Nitrate
- Sulfate
- Ammonium
- Trace metals
- Unidentified

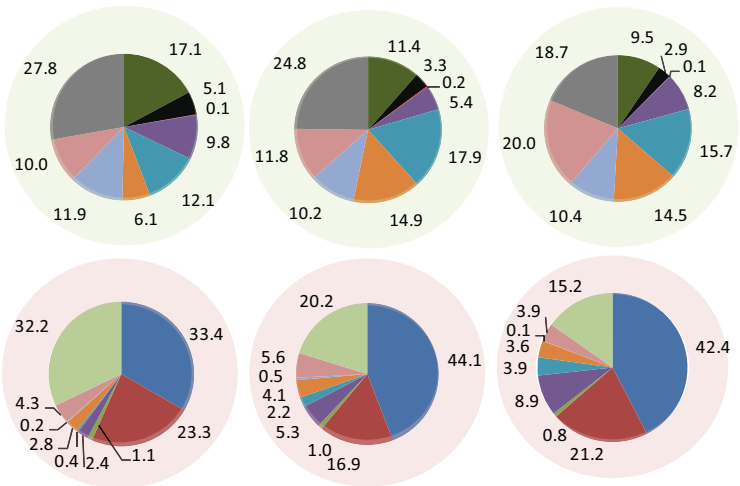
Source Contribution (%)

- SIA
- BMB
- Industrial
- Coal and Flyash
- Building Materials
- Fugitive Dust
- Boiler
- MSW Burning
- Vehicles

(b) National Capital Region



NOD (861 µg/m³) GZB (686 µg/m³) FRB (541 µg/m³)



* Legends are identical for pie charts in (a) and (b)

Further, a limited sampling was undertaken at three sites in the NCR region of outside Delhi to have the comprehensive air quality coverage of NCR (Table 1).

Sampling and chemical characterization of $PM_{2.5}$

The quality assurance and quality control (QA/QC) plan was designed and implemented for sampling, analytical procedures, and data processing. Standard operating procedures (SOPs) were developed for each activity in field and laboratory. Specifically, hands-on training was imparted to team before beginning of sampling and analysis. Separate codes for seasons, site locations, parameters, and time slots were adopted. The calibration of all samplers and instruments was carried out at regular intervals at the time of sampling and analyses. The calibration of analyzers was established by cross-checking it with known concentrations of the pollutants.

The USEPA-approved Partisol® Model 2300 4-CSS speciation samplers (Thermo Fisher Scientific Inc., USA) were deployed for monitoring of particulate matter at selected sites. A flow rate of 16.7 LPM was set for sampling $PM_{2.5}$. Two channels of the sampler were utilized. In the first channel, sample was collected on Teflon filters (Whatman grade PTFE filters of 47 mm diameter) for analysis of ions and metals, and in the second channel, samples were collected on quartz fiber filter (Whatman grade QMA quartz filters of 47 mm diameter) for analysis of organic carbon (OC) and elemental carbon (EC) in collected $PM_{2.5}$. $PM_{2.5}$ concentrations were determined gravimetrically by weighing the PTFE filters before and after the sampling using a digital microbalance (Metler-Toledo MX-5, USA) having a least count of one μg. Prior to weighing, Teflon filter papers were conditioned in desiccators for 24 h before and after sampling in humidity (40 ± 5%) and temperature (20 ± 2 °C) controlled room as per USEPA guideline (USEPA 1999a). The quartz filter papers were baked at 550 °C for 12 h to drive out any residual organics.

Water-soluble ions (anions: K^+, Na^+, Mg^{2+}, Ca^{2+}, and NH_4^+ and anions: SO_4^{2-}, NO_3^-, Cl^-, F^-) were extracted from the Teflon filters in ultra-pure (Milli-Q) water following the USEPA reference method IO-4.2 (USEPA 1999b). Ion analysis of extracted samples was carried out using Ion Chromatograph (Metrohm 882 compact IC, Switzerland). Ion recovery efficiencies were determined by spiking known quantity of ion mass, and reproducibility tests were performed by replicate analysis. Ion recovery was found between 90 and 106%, which was within ± 10% for all species which were analyzed.

For metal analysis, Teflon filters were digested in hydrochloric and nitric acid solution using the microwave digestion system (Anton-Paar, Austria) as per USEPA method IO-3.1 (USEPA 1999a). The digested samples were filtered and diluted to 25 mL with de-ionized (ultra-pure) water. The digested samples for metals were analyzed using inductively coupled plasma mass spectrometry (ICP-MS; Thermo fisher Scientific Inc., USA) (USEPA 1999c). The following 25 metals were analyzed: Be, B, Na, Mg, Al, Si, P, K, Ca, Cr, V, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Cd, Cs, Ba, and Pb.

In addition to conventional pollutants, EC and the fractions of OC (OC1, OC2, OC3, and OC4) representing organic carbon in the order of decreasing volatility was analyzed using thermal/optical transmittance Carbon Analyzer (Model 2001A, Desert Research Institute, Reno, NV) (Aatmeeyata and Sharma 2010). OC was translated into organic matter (OM) by multiplying by a factor of 1.6 to account for hydrogen, oxygen, and nitrogen present in OM (Ram et al. 2014; Srinivas and Sarin 2014).

Table 1 Sampling plan for study

S. no.	Sampling site	Site code	Description of site	Planned sampling period	Data capture (%)
1.	Rohini	RHN	Residential, industrial	03–23 Nov, 2013 04–23 Apr, 2014	100
2.	Okhla	OKH	Industrial	03–23 Nov, 2013 04–24 Apr, 2014	100
3.	Dwarka	DWK	Residential	02–22 Dec, 2013 01–21 May, 2014	100
4.	Vasantkunj	VKJ	Residential, commercial	15 Dec, 2013–04 Jan, 2014 29 Apr–19 May, 2014	98
5.	Dilshad Garden	DSG	Industrial	24 Jan–13 Feb, 2014 26 May–14 Jun, 2014	98
6.	Pusa Road	PUS	Residential, commercial	30 Jan–19 Feb, 2014 25 May–16 Jun, 2014	91
7.	Noida	NOD	Residential, commercial	15–18 Jan, 2015	100
8.	Ghaziabad	GZB	Residential, commercial	19–23 Jan, 2015	80
9.	Faridabad	FRB	Residential	27–29 Jan, 2015	100

Emission inventory (EI)

A detailed EI was prepared for the city of Delhi based on bottom-up approach for the year 2014. The land-use map was developed for the city using GIS (geographic information system) tool that included settlements, forests, agriculture, road network, water bodies, etc. The city was divided into 441 grids of 2 km × 2 km. The primary activity data from different emitting sources were obtained from on-field surveys and various agencies. The emission factors from CPCB (CPCB 2011) and AP-42 (USEPA 2000) along with activity data were used to estimate emission of $PM_{2.5}$ in each grid (Sharma and Dikshit 2016).

Receptor modeling for source apportionment

In a complex urban atmosphere, it is challenging to identify and quantify contribution of multiple emitting sources to air quality. The $PM_{2.5}$ monitoring data along with results of chemical speciation have been used in chemical mass balance CMB 8.2 model (USEPA 1981, 2004) for apportioning the contribution of various emitting sources to ambient air quality. The CMB model was run for each site for each day of sampling of two seasons (summer and winter). The model results were analyzed in terms of R-square (model fitting) and model-computed percent mass (compared to the measured mass). Since for $PM_{2.5}$, Indian or Delhi specific source profiles were not available except for vehicular sources (ARAI 2007), the source profiles (except for vehicles) were taken from "SPECIATE version 3.2" (Hsu et al. 2006). "SPECIATE" is a repository of total organic compound (TOC) and PM-speciated profiles for a variety of sources for use in source apportionment studies (Hsu et al. 2006).

Results and discussion

Monitoring of $PM_{2.5}$ and receptor modeling

The EI of $PM_{2.5}$ was developed for each source with spatial sensitivity. The total estimated emission was 58.7 t/day. The major sources include: road dust (38%), vehicles (20%), domestic fuel burning (12%), industrial point sources (11%), concrete batching plant (6%), hotels/restaurants (3%), and municipal solid waste (MSW) burning (3%) (Fig. S3). While the EI gives good idea of major sources, their contributions to air quality, may vary disproportionately.

Figure 1 shows the pie charts, $PM_{2.5}$ chemical composition, and mean CMB-computed source contributions (in winter and summer seasons) at each site. The daily mean $PM_{2.5}$ concentrations during monitoring period was highest at OKH (422 ± 133 μg/m^3) followed by RHN (380 ± 129 μg/m^3). The mean $PM_{2.5}$ concentrations at other sites were 297 ± 138 μg/m^3 (DWK), 274 ± 93 μg/m^3 (VKJ), 355 ± 186 μg/m^3 (DSG), and 273 ± 98 μg/m^3 (PUS). The measured $PM_{2.5}$ concentrations are approximately 4–7 times higher than the 24-h Indian NAAQS of 60 μg/m^3.

There were four sites (Anand Vihar, Mandir Marg, Panjabi Bagh, and R K Puram), other than those selected for this study, having continuous real-time air quality monitoring. The data from these four sites have been analyzed to obtain the annual (October 2013–September 2014) air quality pattern (Fig. S4). The $PM_{2.5}$ levels exceed the Indian NAAQS except for few days during monsoon months (July–September). The air quality pattern is characterized by a sudden rise in $PM_{2.5}$ concentration from the latter half of October and continues till the first half of January, thereafter, levels drop.

In terms of chemical composition, it was observed that SIA (16–28%; as sum of nitrate, sulfate, and ammonia), OM (13–20%), EC (4.6–6.3%), chloride (4.5–7.9%), and metals (14–24%) are the major constituents of $PM_{2.5}$. A significant mass (19–34%) was unaccounted. Part of unaccounted mass can be attributed to oxygen and other elements which are part of $PM_{2.5}$ and are not measured. Huang et al. (Huang et al. 2014) have reported unaccounted mass in the range of 10–35% for the cities in China; at a high concentration (over 345 μg/m^3), the unaccounted mass was over 35%.

A preliminary analysis of source apportionment was done using positive matrix factorization (PMF) (USEPA 2008). The PMF analysis identified five major factors (indicator of sources). In fact, more sources were identified from the on-field exercise undertaken for developing EI. To identify and quantify these sources, CMB modeling was undertaken.

The broad source apportionment results show SIA, BMB, vehicles, fugitive dust, coal and fly ash, and MSW burning are the important contributors (Fig. 1). It is noteworthy that PM_{10} source apportionment study in Delhi conducted in 2006–2007 (NEERI 2008) had also identified similar sources except for the fact that MSW burning and BMB were not identified as the major contributors. Our study, in addition to CMB analysis, has carried out ground truthing and has found MSW burning and BMB (especially in winters) are quite rampant and consistent. Nagpure et al. (Nagpure et al. 2015) have estimated that 2–3% of MSW (8390 t/day) is burnt in Delhi alone. Further during the ground truthing, it was observed that the three large sanitary landfills frequently catch fire and cause large emissions—no system was in place to extinguish or prevent the fires.

Figure 1b shows location of sampling sites in NCR (outside Delhi) along with pie charts of chemical composition and mean CMB-computed source contributions (estimated from limited sampling in January 2015) at each site. The $PM_{2.5}$ levels (541–861 μg/m^3) were 9–14 times higher than the NAAQS. It may be noted that limited sampling at NOD, FRB, GZB, outside Delhi in NCR region, showed very high $PM_{2.5}$ concentration but similar source contribution in the

order of SIA, BMB, vehicles, coal and fly ash, and MSW burning. The above analyses establish that entire NCR is enveloped by a layer of $PM_{2.5}$ all around with contribution from multiple sources within Delhi, local, regional, and from long range transport. It is clear that the NCR is a contiguous area with similarities in emitting sources, thus, it is essential that control actions are implemented in the entire NCR. In addition to the broad control actions for large contributing sources, some local efforts will be required to ensure that the city of Delhi and NCR attain air quality standards. The overall contributions of the sources in winter and summer are shown in Fig. 2.

As seen (Fig. 2), the sources contributing to winter and summer air pollution are different. Levels of $PM_{2.5}$ are statistically higher (at most locations) in winter than in summer months by about 20–30%. In general, air pollution levels are uniform across the city suggesting entire city is stressed under high pollution.

In summer, based on chemical composition, the crustal metals (Si + Al + Fe + Ca) account for about 20% of mass of $PM_{2.5}$ (Table 2). This suggests soil and road dust and airborne fly ash is a significant source of $PM_{2.5}$ pollution in summer. The second important constituent is SIA, which accounts 17% of total $PM_{2.5}$ and combustion related total carbonaceous matter (EC + OM) accounts for about 12% (Table 2). The Cl^- content in $PM_{2.5}$ in summer is also consistent at 6%, which is an indicator of burning of MSW.

The CMB-computed contributions of sources in summer include: coal and fly ash (26 ± 6.5%), fugitive dust (27 ± 4.9%), SIA (15 ± 1.3%), BMB (12 ± 9.2%), vehicles (9 ± 2.3%), and MSW burning (7 ± 3.1%) (Fig. 2). The summer conditions are characterized by high temperature (25–45 °C) and relatively high wind speed (> 5 km/h) (Tiwari et al. 2010; Mohan et al. 2014) which make the sources of fugitive dust including construction activities important resulting in summer peaks.

In winter, based on chemical composition, the important constituents are SIA, which accounts for about 28% of $PM_{2.5}$, and combustion-related total carbonaceous matter (EC+OM) accounts for about 31% (Table 2). The Cl^- content in $PM_{2.5}$ in winter is also consistent at 7% (Table 2), which is relatively higher in winter than in summer. It was observed that in winter, the atmosphere looks very hazy and characterized by smoky and unhealthy air. In winter, the CMB-computed source contributions include: SIA (30 ± 8.5%), vehicles (25 ± 3.8%), BMB (26 ± 8.2%), MSW burning (8 ± 4.8%), and to a lesser extent fugitive dust (4 ± 3.6%) (Fig. 2). The contribution of sources at six sampling sites in winter and summer is given in Fig. S5.

The two most consistent contributors to $PM_{2.5}$ in both the seasons are SIA and vehicles. The other sources on average may contribute more (or less) but their contributions are variable. Most variable source was BMB followed by MSW burning. A discussion on major sources/constituents of $PM_{2.5}$ is presented below.

Vehicles

There were 8.83 million registered vehicles in 2014–2015 in Delhi (Directorate of Economics & Statistics 2016). The control strategy will require an estimate of contribution from various vehicle types. The EI of vehicular sources (Sharma and Dikshit 2016) has estimated the total $PM_{2.5}$ emission as 11.62 t per day. The breakup of PM emission is: trucks 46%, two-wheelers (2-w) 33%, cars and light commercial vehicles (LCV) 14%, and compressed natural gas (CNG) based busses 5%. It is assumed that the contribution of vehicle type will be in proportion to their emission quantity and thus in the overall source contribution (based on 25% contribution from CMB analysis), it is expected that trucks could contribute about 12%, 2-w 8%, cars and LCV 4%, and CNG-based busses 1% in winter. In summer, vehicles contribute about 9% and the breakup as per the vehicle type can be estimated.

From the EI, the fuel specific breakup of $PM_{2.5}$ emission from vehicles is estimated as: 67% diesel, 29% gasoline, and 4% CNG. Based on this breakup, the overall fuel specific vehicular contribution to air quality was worked out as: (i) winter: diesel: 17%; gasoline: 7%, and CNG: 1% and (ii) summer: diesel: 6%; gasoline: 2.6% and CNG: 0.4%.

The above analysis suggests reducing emissions from trucks, 2-w, cars and LCV can significantly improve the air quality. It may be noted that the gaseous emissions from vehicles will also contribute to both SIA and SOA, which have been discussed later.

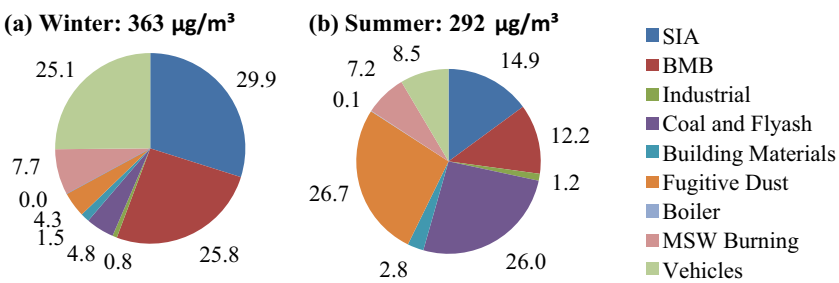


Fig. 2 Source apportionment of $PM_{2.5}$ in Delhi during **a** winter and **b** summer

Table 2 Percent composition of major components of $PM_{2.5}$

Season	Site	$PM_{2.5}$ (μg/m^3)	% crustal metals	% SIA	% SOA	% (EC+OM)	% OM	% K^+	% Cl^-
Winter	RHN	438	4.24	18.56	17.01	38.18	29.06	3.01	6.25
	OKH	433	7.12	18.71	15.28	36.63	27.28	3.38	3.75
	DWK	362	2.59	35.00	14.56	31.08	23.68	1.65	4.04
	VKJ	315	1.46	29.31	16.89	35.08	26.53	1.26	7.21
	DSG	435	3.03	33.06	9.57	19.62	14.88	1.36	7.31
	PUS	278	2.76	31.54	12.89	27.16	20.46	1.35	6.86
	Mean	377	3.53	27.70	14.36	31.29	23.65	2.00	5.90
	SD	69	1.97	7.26	2.56	6.98	5.25	0.94	1.60
Summer	RHN	323	14.39	19.12	5.30	11.41	7.97	1.49	9.57
	OKH	412	27.56	14.39	4.39	10.15	7.01	1.32	5.20
	DWK	233	19.05	17.44	5.68	11.45	8.46	1.95	8.21
	VKJ	252	20.37	16.25	6.05	12.67	9.23	1.93	6.38
	DSG	276	20.00	16.92	6.41	14.40	9.99	1.21	3.80
	PUS	269	16.72	19.57	5.33	11.92	8.00	1.54	4.29
	Mean	294	19.68	17.28	5.53	12.00	8.44	1.57	6.24
	SD	65	4.47	1.91	0.64	1.44	1.05	0.31	2.27
Overall	RHN	380	8.55	18.80	11.02	26.81	20.10	2.37	7.66
	OKH	422	17.08	16.60	9.15	23.73	17.40	2.38	4.46
	DWK	297	9.04	28.12	12.12	23.40	17.73	1.77	5.67
	VKJ	283	9.87	23.50	8.28	25.11	18.84	1.56	6.84
	DSG	355	9.62	26.79	9.66	17.59	12.98	1.30	5.95
	PUS	273	9.62	25.66	10.58	19.67	14.34	1.44	5.59
	Mean	335	10.63	23.25	10.1	22.72	16.90	1.80	6.03
	SD	60	3.20	4.61	1.26	3.45	2.72	0.47	1.11

BMB

CMB-computed $PM_{2.5}$ contribution of BMB in winter is quite high at 26% and it has a large variation. After harvesting, about 70–80 million tonnes of rice crop residue is disposed of through open field burning (Badarinath et al. 2006; Gadde et al. 2009) in the states of Punjab and Haryana (situated in NW of Delhi) in the month of November; Fig. 3a shows the number of fires. The back trajectory analyses using HYSPLIT model (NOAA 2013) (Fig. S6) suggest that the crop residue burning (CRB) and other biomass emissions are transported to Delhi from the sources upwind of Delhi (in NW direction) (Sharma and Dikshit 2016). Potassium, an indicator of BMB registered the highest concentration of 20 μg/m^3 in the beginning of November due to CRB and it stabilizes around 5 μg/m^3 (which is also high) in the rest of the winter months (Fig. 3)b. The contribution of BMB in the month of November is about two times higher than in other winter months. The contribution of BMB in the first 3 weeks of November could be as high as 120 μg/m^3 (Fig. 3b). As the CRB ceases in the third week of November, the contribution of BMB dramatically reduces (Fig. 3); however, contribution of BMB to a smaller extent continues in the month of December from the local sources present in Delhi and nearby areas.

Secondary aerosol and crustal matter

It is easy to quantify SIA by directly measuring sulfate, nitrate, and ammonium in PM but not the SOA. Several compounds of SOA can be formed through condensation of low-volatility oxidation products of hydrocarbons in the atmosphere (Watson et al. 2005). Behera and Sharma (Behera and Sharma 2010) have estimated that SOA contributes about 18% mass in winter and 12% mass in summer to $PM_{2.5}$ in Kanpur city in IGP. Higher molecular organic compounds having low volatility represented by OC3 and OC4 fractions are expected to be of secondary origin. A simple estimate of SOA can be assumed as sum of OC3 and OC4 multiplied by a factor of 1.6 to account for molecules other than carbon (Ram et al. 2014; Srinivas and Sarin 2014). Based on the above premise, the SOA is contributing 53 ± 23 μg/m^3(14.5 ± 4.4% of $PM_{2.5}$ mass) in winter and 16 ± 6 μg/m^3 (5.8 ± 2.6% of $PM_{2.5}$ mass) in summer. The SOA fraction in summer is lower due to presence of larger fraction of dust and

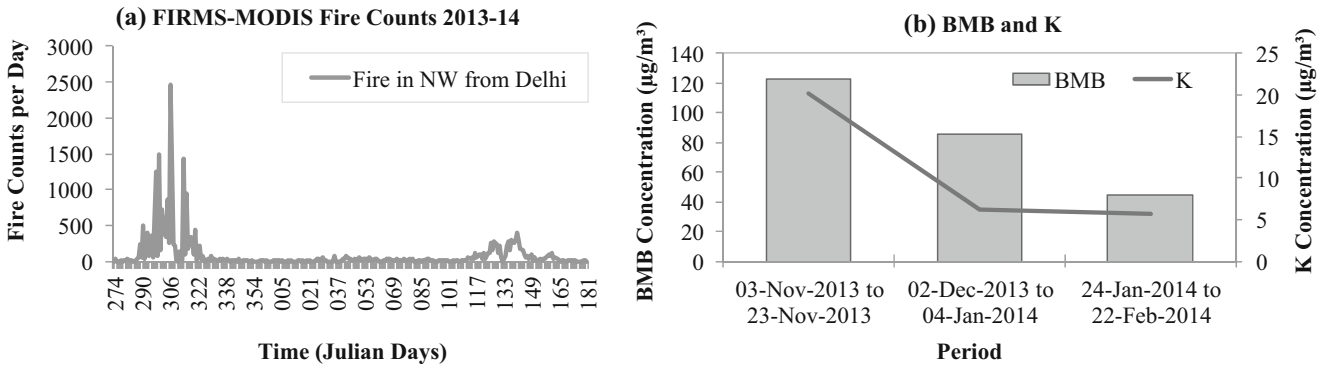


Fig. 3 (**a**) Fire counts from October 01, 2013 (Julian day 274) to June 30, 2014 (Julian day 181) and (**b**) biomass burning and potassium during winter season

crustal matter. A significantly large SOA formation under winter conditions has been reported by Huang et al. (Huang et al. 2014) in their low-temperature smog chamber studies due to aging of emissions from BMB.

SIA contributes about 102 ± 57 μg/m^3 (28 ± 10.4% of $PM_{2.5}$ mass) and 51 ± 19 μg/m^3 (17 ± 5.4% of $PM_{2.5}$ mass) in winter and summer, respectively. It is estimated that the total secondary aerosols (SA) contribute a major portion of $PM_{2.5}$ at about 42 ± 10% in winter and 23 ± 6% in summer.

The crustal matter is the portion of $PM_{2.5}$ that is estimated based on the concentration of oxides of Al, Si, Ca, Fe, and K and can be estimated using Eq. (1) (Eldred et al. 1987; Marcazzan et al. 2001; Behera and Sharma 2010).

$$CrustalMatter = 1.15 \times (1.89Al + 2.14Si + 1.4Ca + 1.36Fe + 1.2K) \quad (1)$$

Where Fe and K show the part of iron and potassium concentration considered of natural origin. The factor 1.15 was used for compensating Na and Mg oxides (Eldred et al. 1987).

The mass of crustal matter is estimated 42 ± 15.1% (133 ± 88 μg/m^3) in summer and 9 ± 6.7% (35 ± 28 μg/m^3) in winter.

It is seen that SA and crustal matter (largely as fugitive emission) account for 52% in winter and 65% in summer. Therefore, any strategy to improve $PM_{2.5}$ air quality must include control of secondary and crustal component.

In Fig. 4, we have examined the contribution of SA and crustal matter as a function of $PM_{2.5}$ concentration. The linear relationship shows that contributions of SA and crustal matter are significant at all levels of $PM_{2.5}$. Specifically, Table 3 presents the slope of regression line indicating rate of change of SIA, SOA, SA, and crustal matter with $PM_{2.5}$ concentration. In winter, SA alone may contribute about 37% and crustal matter may contribute about 63% in summer. In general, except for SOA in summer, all components contribute significantly in a statistical sense. It suggests that the control strategy should address all the sources regardless of seasonal importance. It is concluded that SIA is a major contributor to $PM_{2.5}$ irrespective of season. It requires control at the sources (e.g., power plants, vehicles, BMB, etc.) which are emitting the primary precursor gases that are responsible for the formation of SIA.

The important point that has come to the fore is that $PM_{2.5}$ levels in Delhi are not solely result of emissions from Delhi; it is a much larger regional problem caused by large contiguous urban agglomeration which extends to hundreds of kilometers from Delhi in all directions, typically referred to as NCR in this study. The important grace is that sources are similar (vehicles, other combustion activities, fugitive dust) in the

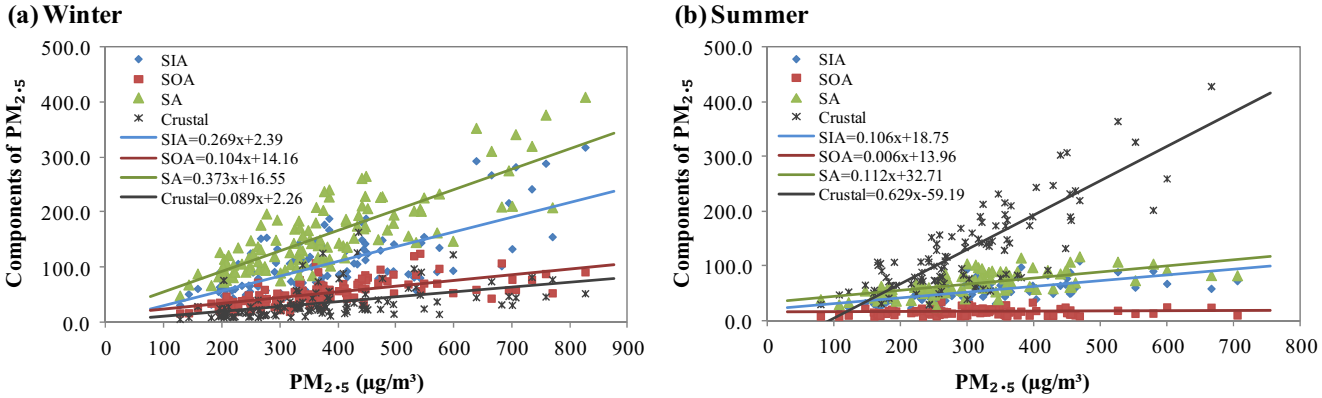


Fig. 4 Trend of secondary aerosol and crustal matter in **a** winter and **b** summer

Table 3 Statistical summary of regression analysis (ANOVA)

Parameter	Slope of regression ± 95% CI (μg/m^3 per μg/m^3) in Fig. 4		Statistical significance
	Winter	Summer	
SOA	0.104 ± 0.021	0.006 ± 0.010	Winter
SIA	0.269 ± 0.051	0.106 ± 0.026	Summer and winter
SA	0.373 ± 0.049	0.112 ± 0.027	Summer and winter
Crustal Matter	0.089 ± 0.031	0.629 ± 0.088	Summer and winter

region and a common strategy might just work to clean the Delhi and the entire NCR.

The high $PM_{2.5}$ levels require a control strategy that explores the emission reduction at all sources in a large region. Our analysis suggests that $PM_{2.5}$ emission control approach, in addition to control of primary particulate emissions, should include the emission reduction of precursors of secondary aerosol, SO_2, NH_3, NO_x, and volatile organic compounds (VOCs). There are some regulatory efforts to reduce SO_2 and NO_x emissions to 100 mg/Nm^3 for power plants in India (MoEFCC 2015) which appears inadequate as the new regulation is applicable for plants coming into operation from January 2017. There are 13 coal-based thermal power plants with a total capacity of over 11,000 MW within the radius of 300 km from Delhi, which are expected to contribute to SA. Further, the major source of NO_x is vehicles which are soaring and do not have effective NO_x control. In 2010, the annual non-methane volatile organic compound (NMVOC) emission in India was estimated at 9.81 Tg (Sharma et al. 2015). The highest emission intensities are observed in IGP because of high population density, use of biomass for cooking and heating, and contributions from vehicular sources. The major source of NMOVC emission in Delhi is due to the presence of large numbers of gasoline vehicles and use of solvents (Sharma et al. 2015). The importance of VOCs in controlling PM has not been acknowledged in India, even the basic vapor recovery system at gas stations has not been installed. Control of BMB activities could be an effective approach in all regions, especially in suburban and rural areas where emissions are significant. Alternatives to BMB include removal of the straw from the field and its use for other economic activities: energy production, biogas generation, commercial feedstock for cattle, composting, conversion in biochar, raw material for industry (John 2013).

The sources for control of primary emissions are enumerated here from the survey and inventory of the area. These include BMB, vehicles, hotels/restaurant, domestic sector, MSW burning, construction and demolition, ready mix concrete batching, road dust, industries, diesel generator sets, and fly ash (Sharma and Dikshit 2016).

Our analyses clearly establish that reduction in SIA and SOA precursors (NO_x, SO_2, NH_3, and particularly, the VOCs) along with primary particulate emissions can help in attaining $PM_{2.5}$ air quality standards. The suggested measures should be considered by policy makers as the high pollution episodes now occur consistently in winter in Delhi and surrounding areas. The current research along with other studies (Jain and Palwa 2015; Chowdhury and Dey 2016; International Energy Agency 2016) on air pollution, energy, and health makes a sound basis for air pollution control in NCR including Delhi.

Conclusion

The comprehensive study presented here has provided insight into $PM_{2.5}$ measurements, its chemical composition and source-receptor impact analyses in the city of Delhi. The problem of high $PM_{2.5}$ levels in Delhi is a regional problem caused by emissions from Delhi and surrounding contiguous urban agglomerations. In addition to expected primary sources (vehicles, fugitive dust, coal and fly ash), the new identified sources include MSW burning (about 7–8%) and BMB (about 30%) in the month of November when CRB is at its peak. It was estimated that the total secondary aerosols (SA) contribute a major portion of $PM_{2.5}$ at about 42 ± 10% in winter and 23 ± 6% in summer. The mass of crustal matter is estimated 42 ± 15.1% (133 ± 88 μg/m^3) in summer and 9 ± 6.7% (35 ± 28 μg/m^3) in winter. It is seen that SA and crustal matter (largely as fugitive emission) account for 52% in winter and 65% in summer. The reduction in emission from sources identified can bring economical and health benefits. The current research makes a sound argument and basis for investing in air pollution control in NCR including Delhi.

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