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Chemical characteristics and source apportionment of PM$_{2.5}$ using PCA/APCS, UNMIX, and PMF at an urban site of Delhi, India

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Abstract The present study investigated the comprehensive chemical composition [organic carbon (OC), elemental carbon (EC), water-soluble inorganic ionic components (WSICs), and major & trace elements] of particulate matter (PM$_{2.5}$) and scrutinized their emission sources for urban region of Delhi. The 135 PM$_{2.5}$ samples were collected from January 2013 to December 2014 and analyzed for chemical constituents for source apportionment study. The average concentration of PM$_{2.5}$ was recorded as 121.9 ± 93.2 µg m^{-3} (range 25.1–429.8 µg m^{-3}), whereas the total concentration of trace elements (Na, Ca, Mg, Al, S, Cl, K, Cr, Si, Ti, As, Br, Pb, Fe, Zn, and Mn) was accounted for ~17% of PM$_{2.5}$. Strong seasonal variation was observed in PM$_{2.5}$ mass concentration and its chemical composition with maxima during winter and minima during monsoon seasons. The chemical composition of the PM$_{2.5}$ was reconstructed using IMPROVE equation, which was observed to be in good agreement with the gravimetric mass. Source apportionment of PM$_{2.5}$ was carried out using the following three different receptor models: principal component analysis with absolute principal component scores (PCA/APCS), which identified five major sources; UNMIX which identified four major sources; and positive matrix factorization (PMF), which explored seven major sources. The applied models were able to identify the major sources contributing to the PM$_{2.5}$ and reconfirmed that secondary aerosols (SAs), soil/road dust (SD), vehicular emissions (VEs), biomass burning (BB), fossil fuel combustion (FFC), and industrial emission (IE) were dominant contributors to PM$_{2.5}$ in Delhi. The influences of local and regional sources were also explored using 5-day backward air mass trajectory analysis, cluster analysis, and potential source contribution function (PSCF). Cluster and PSCF results indicated that local as well as long-transported PM$_{2.5}$ from the north-west India and Pakistan were mostly pertinent.

Keywords Receptor model · PCA/APCS · UNMIX · PMF · PSCF · Source apportionment

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Introduction

Delhi, the capital of India, has ranked as one of the megacities with the worst air quality in the world (WHO 2016). Grave air pollution and its allied health impacts have grown to be one of the major and foremost perturb in India. According to World Health Organization report (2015), India's air quality is among the worst in the world, almost equivalent to China in respect of the population's share susceptible to average air pollution levels exceeding World Health Organization thresholds. Particulate matter (PM) is crucial urban ambient air pollutant, especially fine mode particles (PM$_{2.5}$), which are mainly produced by combustion processes, transformation of gaseous

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species, and forest fires (Sharma et al. 2007; Kong et al. 2011; Zheng et al. 2013; Sharma et al. 2016a, b). Fine mode particles have been reported to cause extensive detrimental effects on human health, environment, and climate (Schwartz and Dockery 1992; Buseck and Posfai 1999; Davidson et al. 2005; Ito et al. 2006; WHO 2009; Seinfeld and Pandis 2016). Several epidemiological studies conducted in recent years have revealed fine particulates to be causative of broad range of health effects, ranging from allergies, respiratory, cardiopulmonary, and cardiovascular diseases to premature mortality in severe cases (Ozkaynak and Thurston 1987; Pope and Dockery 2006; Mauderly and Chow 2008; Russell and Brunekreef 2009; Tie et al. 2009; Yan et al. 2009; Habre et al. 2011; Vernile et al. 2013), since fine particles have the ability to penetrate much deeper into the lungs and enter into bloodstream through human respiratory tract (Pope et al. 2002; Pope and Dockery 2006; Brauer et al. 2015; Van Donkelaar et al. 2015).

Particulate matter also plays an important role in climate change (IPCC 2013), and it tends to influence global climate change by absorption and scattering of solar radiation (Buseck and Posfai 1999; Seinfled and Pandis 2016). Furthermore, PM has other several pernicious influences on our environment like formation of smog/haze, material corrosion and damage, and ecosystem damage and visibility impairment (Reddy and Venkatraman 2000; Zhang et al. 2002). The small particle size of $PM_{2.5}$ leads to a greater atmospheric residence time and a propensity to spread over a much larger geographic region (Wolff et al. 1985; Eldred and Cahill 1994; Wilson and Suh 1995). Since, the physical and chemical properties of these fine particles vary significantly with time, region, meteorology, and source category (Chow et al. 1994; Malm et al. 1994; Chow et al. 1996; Watson and Chow 2002; Chu 2004). Thus, the exigency to comprehend the potential source categories and their contributions (source apportionment) has become imperative to reduce the PM pollution (Zheng et al. 2005; Sharma et al. 2014b, c; Sharma et al. 2016a; Panda et al. 2016). Source apportionment results can furnish the scientific auxiliary for air quality management resolutions.

To deal with this matter, many tools have been employed for identification and quantification of PM sources (Paatero and Tapper 1994; Paatero 1997; Ulbrich et al. 2009) including receptor modeling that proffers a manner to complete the process by evaluating the pollutant concentrations at a sampling site. Receptor models have been globally accepted to quantitatively apportion and identify the sources of PM in the atmosphere (Watson and Chow 2005; Hopke et al. 2006; Mazzei and Prati 2009; Kong et al. 2010; Pant and Harrison 2012; Belis et al. 2013; Bove et al. 2014; Banerjee et al. 2015). Two major classes of models that have been used worldwide are (i) chemical mass balance (CMB) model and (ii) multivariate factor analysis models (including principal component analysis with absolute principal component scores (PCA/APCS),

UNMIX, and positive matrix factorization (PMF)) (Hopke et al. 2003; Pandolfi et al. 2008; Alleman et al. 2010; Amodio et al. 2013). Both receptor and source profile data are required to be put in former class, whereas source profiles and their contributions can be extracted using latter set of models (Hopke 2003). The detailed principles and applications for PCA/APCS, UNMIX, and PMF models have been documented in literature (Thurston and Spengler 1985; Paatero 1997, 1999; Garcia et al. 2006; Song et al. 2006a; Chen et al. 2007; Gildemeister et al. 2007; Zheng et al. 2007; Olson and Norris 2008; Begum et al. 2010; Harrison et al. 2011; Gugamesetty et al. 2012; Wang et al. 2012; Lelpo et al. 2014; Shi et al. 2014) and our previous publications (Sharma et al. 2014b, c; Sharma et al. 2015; Sharma et al. 2016a, b). The detailed analysis of source apportionment of $PM_{2.5}$ using PMF model is also available in our previous paper and reference therein (Sharma et al. 2016b).

The strengths and weaknesses for these models have been recapitulated in literature (Callen et al. 2009; Pant and Harrison 2012; Banerjee et al. 2015). Briefly, PCA/APCS is an exploratory tool for investigating structure in multivariate data sets by combining factor analysis with multilinear regression which aids in quantifying particulate source contribution (Viana et al. 2008). It identifies individual components' group (PCs) using orthogonal decomposition, and loading factors connect these PCs with variables. PCs further connect with Varimax rotation to connect individual variables to different components (Chanand Mozurkewich 2007; Belis et al. 2013), whereas the UNMIX estimates the source number by minimizing the dimensionality of data by using singular value decomposition (SVD) method. High correlation exists within each component, while least or no correlation exists between individual components. PCA/APCS is considerably the most common model for source apportionment studies possibly because of its simplistic analytic procedure and have been frequently employed in the past for various source apportioning studies, but recently, a shift from PCA and classic factor analysis to PMF was observed mainly due to the ability of the model to provide better and more accurate results than PCA as PMF takes into account the uncertainty in the experimental data. PMF uses least squares approach and integrate non-negativity constraints in the optimization process in attempt to unravel the problem arising in factor analysis and utilize estimates of error for each data value as a point-by-point weight (Begum et al. 2004; Belis et al. 2013).

The present work aims to perform the comprehensive characterization of $PM_{2.5}$ for an urban site of Delhi, India, during the period of January 2013 to December 2014. The intercomparison of $PM_{2.5}$ source apportionment results achieved using three receptor models (PCA/APCS, UNMIX, and PMF) to study their performances in source identification and in the quantification of source contributions are performed.

Furthermore, the trajectory analysis and potential source contribution function (PSCF) are incorporated with secondary aerosol (SA) results to qualify the contribution of each identified local and long-range transport sources in a more accurate way (Kim et al. 2003; Kang et al. 2006; Lee and Hopke 2006; Heo et al. 2009).

Material and methods

Site description

Delhi, the capital of India, is surrounded by four different climatic zones (Himalayas in the north, central hot plains in the south, the Thar desert in the west, and the Indo-Gangetic Plain in the east), which influence its semi-arid climate and considered as one of the most polluted megacities in the world. $PM_{2.5}$ samples were collected at CSIR-National Physical Laboratory, New Delhi (28° 38′ N, 77° 10′ E; 216 m amsl) (Fig. 1), India. The sampling site represents a typical urban environment surrounded by a heavy roadside traffic and agricultural fields in the southwest direction. The area is under the influence of air mass flow from north-east to north-west in winter, south-east to south-west in summer, and south-east to south-west in monsoon (Goyal and Sidhartha 2002). Although the traffic could be one of the major sources of PM in Delhi, significant contributions from other sources, i.e., roadside dust, secondary aerosol, biomass burning, and industrial emissions, have also been observed (Sharma et al. 2014b, c). It also observes the alarming vehicular growth rate with around 8.29 million of registered vehicles in 2013–2014 (Statistical Abstract of Delhi 2014). The ambient temperature of sampling site varies from minimum (~3 °C) in winter (November to February) to maximum (~47 °C) in summer (March to June). The average rainfall in Delhi during monsoon (July to September) was of the order of ~900 mm. The detailed descriptions of sampling site including meteorology are available in Sharma et al. (2016a).

Sampling method

$PM_{2.5}$ samples were collected (n = 135) periodically on precombusted (~550 °C for at least 5 h to eradicate organic impurities) quartz micro-fiber filters (QM-A) during January 2013 to December 2014, using fine particle sampler (model APM 550, M/s. Envirotech, India), which was operated at an average flow rate of 1 m^3 h^{-1} (accuracy ±2%) at a height of 10 m (above ground level) for 24 h. The flowmeter of the sampler was calibrated (with the accuracy of ±2% of full scale) with Air Flow Calibrator traceable to National Standard. The pre-combusted filters were desiccated for 24 h before measuring the initial and final weight by a microbalance (M/s. Sartorius, resolution ±10 μg). After collecting

samples, filters were stored under dry conditions in the deep freezer at −20 °C prior to analysis.

Chemical analysis

The quantitative elemental analyses of $PM_{2.5}$ filters were carried out first by a non-destructive method using Rigaku ZSX Primus wavelength dispersive X-ray fluorescence spectrometer (WD-XRF). Then, ~6.92 cm^2 (size ½ of the filter) of QM-A filters was used for analysis of water-soluble inorganic ionic component (WSIC) using ion chromatograph, and rest of the filter was used for organic carbon (OC)/elemental carbon (EC) analysis using OC/EC carbon analyzer. Details of the $PM_{2.5}$ filters analysis are given below.

WD-XRF (Rigaku ZSX Primus) was used for quantitative analysis of major and trace elements in $PM_{2.5}$ (Al, Mg, S, Si, Cl, K, Ca, Ti, Cu, Mn, Fe, Zn, Br, Cr, As, and Pb). The spectrometer consists of scintillation counter (SC) and flow proportional counter (F-PC), detectors for heavy and light elements, respectively, sealed X-ray tube for excitation, end window, and an Rh target. The readings were taken in vacuum conditions at a temperature of 36 °C and a tube rating of 2.4 kW. The scan was made to identify all elements in the loaded filter except Si. The k–α X-spectral lines identify elements (Al, Mg, S, K, Cl, Ca, Ti, Si, Cr, Zn, Fe, and Mn) under particular conditions, i.e., F-PC detector for Mg, Al, P, S, Cl, K, and Ca; RX25 analyzer crystal for Mg; PET analyzer crystal for Al; Ge analyzer crystal for P, Cl, and S; LiF (200) analyzer crystal for Ca and K; and SC detector and LiF(200) analyzer crystal for Ti, Cr, Mn, Fe, and Zn. Measurements on blank filter were also taken, and correction in the intensities was done for loaded filters. Quantitative analysis was carried out using parameter method through ZSX software (Rigaku Corporation, Japan).

The EC and OC of $PM_{2.5}$ were analyzed using OC/EC carbon analyzer (model DRI 2001A; Atmoslytic Inc., Calabasas, CA, USA) following the USEPA "IMPROVE protocol" with negative pyrolysis areas zeroed (Chow et al. 2004). The OC/EC carbon analyzer (DRI 2001A) works on the principle of the preferential oxidation of OC and EC, in which the sample heated at four different temperatures (140, 280, 480, and 580 °C) in pure helium and at three different temperatures (580, 740, and 840 °C) in 98% helium and 2% oxygen, since OC can be volatilized from the sample in a non-oxidizing helium atmosphere and EC is volatilized through combustion by an oxidizer. Correction for pyrolysis and charring of OC compounds into EC are predominantly carried by the optical component (laser reflectance and transmittance) of the analyzer (Chow et al. 2004). Approximately 0.536-cm^2 area of QM-A filter was taken, cutting though the proper punch, and the values are given in μg cm^{-2} by the analysis software (CarbonNet). Each filter was analyzed triplicate with blank filters to get the concentrations of OC and EC in $PM_{2.5}$
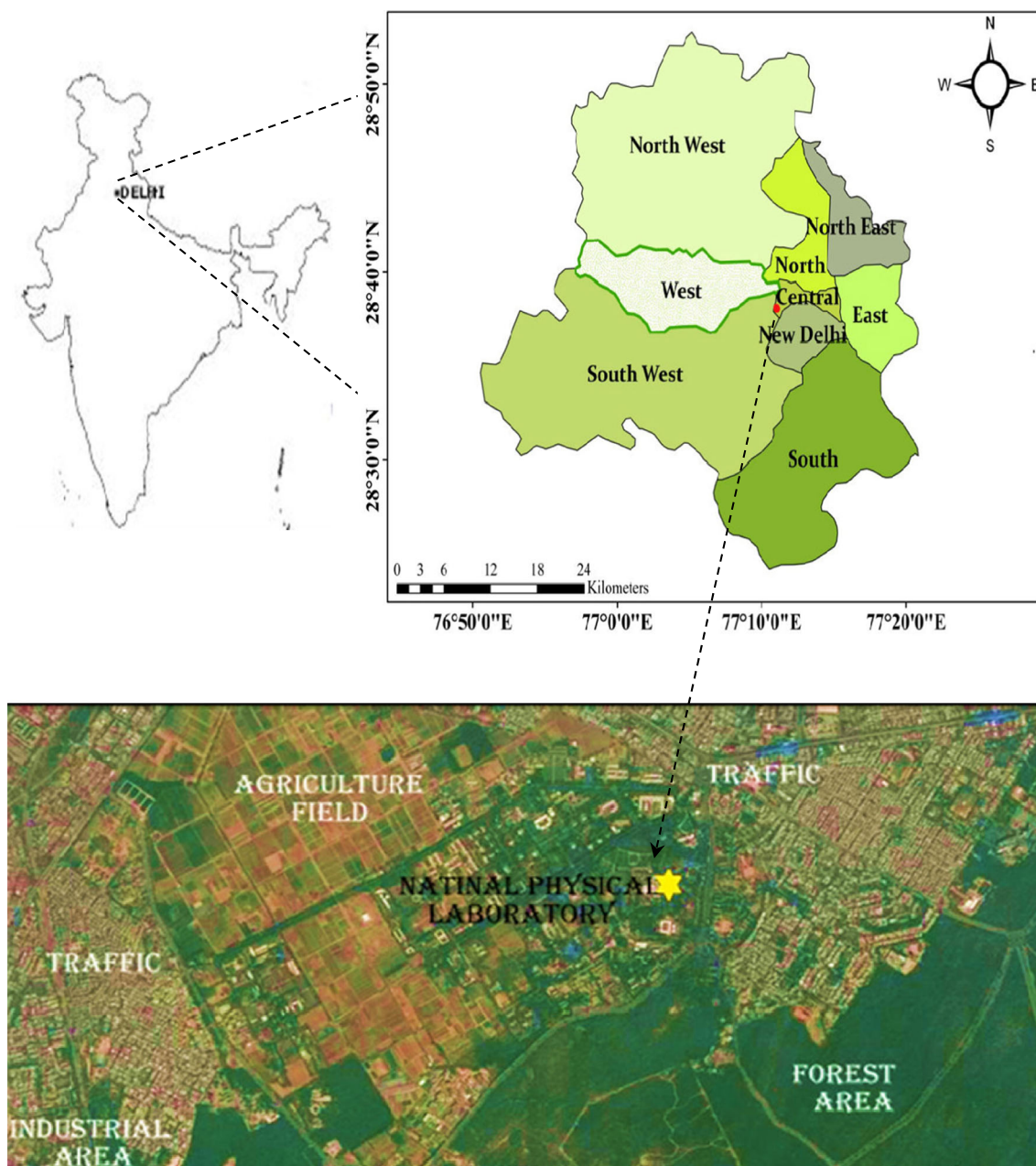
Fig. 1 Map of the study site (*Source*: Google maps)

mass. The OC/EC analyzer was calibrated every day before analysis of the samples using mixture of 5% CH_4 + balance helium standard gases (for OC/EC peak verification). The process was repeated after every five-sample analysis. A mixture of 4.8% CO_2 + balance helium standard gases were used periodically for calibration of OC/EC analyzer in addition to calibration with KHP and sucrose. Details of OC and EC analysis of PM have been given in Sharma et al. (2014b).

For estimation of WSIC (Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, F^-, Cl^-, NO^{3-}, and SO_4^{2-}) of $PM_{2.5}$, filters (~6.92 cm²) were extracted in de-ionized water (resistivity 18.2 MΩ cm) for 90 min in ultrasonic extractor. The extract was filtered through

0.22-µm nylon membrane filters and transferred to polypropylene sample bottles and analyzed by ion chromatograph (model DIONEX-ICS-3000, Sunnyvale, CA, USA). The concentrations of F^-, Cl^-, NO_3^-, and SO_4^{2-} were determined by using an Ion Pac-AS11-HC analytical column with a guard column, ASRS-300 4-mm anion micro-membrane suppressor, 20 mM sodium hydroxide (NaOH; 50% *w/w*) as eluent, and de-ionized water as regenerator. Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+} were evaluated by using a guard column with a separation column, suppressor CSRS-300, and 5 mM methane sulfonic acid (MSA) as eluent. Chromeleon® software was used to process the chromatograms, and data of

chromatography was collected at 5 Hz. Calibration standards have been prepared by National Institute of Standards and Technology (NIST, USA), traceable certified standards for calibration of ion chromatograph (Sharma et al. 2014a). The blank filters were also analyzed for cations (Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+}) and anions (F^-, Cl^-, NO^{3-}, and SO_4^{2-}). The analytical error (repeatability) was approximated to be 3–5% based on triplicate analysis of each filter. Detailed principle and analytical procedure of WSIC of PM are described in Sharma et al. (2012a, b).

Descriptions of PCA/APCS, UNMIX, and PMF

Principal component analysis (PCA) is a statistical tool that identifies patterns in data, revealing their differences and similarities. It was performed to identify the possible sources of $PM_{2.5}$ mass over the selected site. Orthogonal transformation method with Varimax rotation in PCA was employed in present study. The lowest eigenvalue for extracted factors was restricted to more than 1. Total 22 constituents/species of $PM_{2.5}$ were used as variable in the data set. In PCA, dimensionless standardized form has been transformed from the chemical data:

$$Z_{ij} = \frac{C_{ij} - \overline{C_j}}{\sigma_j} \qquad (1)$$

where $i = 1, \ldots, n$ samples; $j = 1, \ldots m$ elements; C_{ij} is the concentration of element j in sample i; and C_j and σ_j are the arithmetic mean concentration and the standard deviation for element j, respectively. The PCA model is expressed as

$$Z_{ij} = \sum_{k=1}^{p} g_{ik} h_{kj} \qquad (2)$$

where $k = 1, \ldots, p$ sources and g_{ik} and h_{kj} are the factor loadings and the factor scores, respectively. Eigenvector decomposition helps in solving this equation (Song et al. 2006).

Source profiles and source contributions are then estimated quantitatively based on factor loading scores of PCA by using APCS method (Thurston and Spengler 1985; Henry and Hidy 1979). Since the data for PCA results are normalized, thus for each factor score, the true zero is derived as

$$(Z_0)_j = \frac{0 - \overline{C_j}}{\sigma_j} = -\frac{\overline{C_j}}{\sigma_j} \qquad (3)$$

The re-scale scores are known as APCS and further source contribution is obtained by linear regression using the following equation:

$$M_i = \zeta_0 + \sum_{k=1}^{p} \zeta_k \text{APCS}_{ki} \qquad (4)$$

where M_i is the measured mass concentrations in sample i and ζ_0 is the mass contribution made by sources unaccounted for in the PCA. APCS_{ki} is the rotated absolute

component score for source k in sample i, and $\zeta_k \text{APCS}_{ki}$ is the mass contribution in the sample i made by the source k. It follows the regression of the sample concentrations on these APCS to get each identified source's estimated mass contribution, i.e., regression between C_{ij} and APCS_{ki} (Song et al. 2006).

UNMIX is a multivariate model with non-negativity constraints. It evaluates the source number by means of reducing data space dimensionality m to p through the SVD method (Henry 2003). The UNMIX model can be represented as

$$C_{ij} = \sum_{l=1}^{p} \left(\sum_{k=1}^{p} U_{ik} D_{kl} \right) V_{lj} + \varepsilon_{ij} \qquad (5)$$

where V, U, and D are the $p \times$ m matrices and $n \times p$ and $p \times p$ diagonal, respectively. E_{ij} is the error term comprising C_{ij} variability, which is not accounted for by the first principal component (p). UNMIX uses self-modeling curve resolution to make sure that the results follow (within error) the non-negative constraints on source compositions and contributions. It ensures that all the species are on the same scale with a mean of 1 by normalizing the data set and then projected it perpendicular to the first axis of p-dimensional space. UNMIX finds edges in m-dimensional space using principal component analysis which are then used to compute vertices, where m is the number of ambient species. These vertices with the SVD decomposed matrices are used to find source profiles. The UNMIX version used for this study was the stand-alone EPA UNMIX 6.0.

PMF is a multivariate factor analysis receptor model that distributed the speciated sample data matrix into two matrices, which are factor contributions and factor profiles. The PMF in detail has been described in Paatero and Tapper (1994) and Paatero (1997). A speciated data set can be considered as a data matrix X of i by j dimensions, in which the number of samples (i) and chemical species (j) are measured. The purpose of PMF is to recognize the species profile (f) of each source, factors (p), and the amount of mass (g) contributed to each individual sample by each factor which is given as

$$X_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad (6)$$

where e_{ij} is the residual for each sample/species.

For samples to have no negative contribution, the results are constrained accordingly. PMF weighs each data point individually, which permits the adjustment of the influence of each data point. Perhaps, below detection limit data can be taken in the model for use, with the associated uncertainty adjusted so these data points have less influence on the solution than the above detection limit measurements. The object

function (Q) gets minimized by the PMF solution, based upon these uncertainties (u) as follows:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{X_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2 \tag{7}$$

where X_{ij} are the measured concentration (in µg m^{-3}), u_{ij} are the estimated uncertainty (in µg m^{-3}), n is the number of samples, m is the number of species, and p is the number of sources included in the analysis. The detail descriptions of EPA PMF v3.0 are described in Gugamsetty et al. (2012) and EPA PMF User Guide (2008).

In this study, information on chemical properties of 135 PM$_{2.5}$ samples has been used as input to the PMF model for the total of 22 parameters. The method detection limit (MDL) of each chemical species (OC, EC, WSIC, and major and trace elements) is calculated as 3 times of the average standard deviation of 10 replicates of filter blanks analysis. Overall, MDL were reported in Table 1. The signal-to-noise ratio (S/N ratio) is calculated by PMF model as per EPA PMF User Guide (2008), wherein species which have S/$N \geq 2$ were categorized as strong in data quality. Species with S/N between 0.2 and 2 indicate weak data quality and are improbable to provide enough variation in concentration and consequently contribute to the noise in the results (if the S/N ratio of species are below 0.2, then they are classified as bad values and are thus excluded from further analysis). In the present case, S/N ratios of the species are estimated as >0.6 (Pb and Cu were estimated as 0.62 and 0.78, respectively).

In the present study, the model performance in a base run showed determination coefficient (R^2) between the modeled and experimental concentrations of PM$_{2.5}$, OC, EC, NH$_4^+$, SO$_4^{2-}$, and NO$_3^-$ of 0.87, 0.86, 0.87, 0.97, 0.76, and 0.83, respectively (Table 1). Most of the other chemical species are also well reconstructed, except for some trace elements like Cr ($R^2 = 0.55$), Cu ($R^2 = 0.57$), and Al ($R^2 = 0.54$) (Table 1). These results are within the range of those presented in many PMF studies, with for example, values 0.71 reported for a study in Spain (Cusack et al. 2013) and of 0.96 for a study in Germany (Beuck et al. 2011) for PM$_{2.5}$ mass reconstruction. Scaled residuals between −3 and +3 are obtained for all of the major components, and the value of Q robust is strictly identical to the value of Q true, all of these showing that no specific event is affecting the results and that the base run can be regarded as stable.

Table 1 The average concentrations of constituents of PM$_{2.5}$ (µg m^{-3}) in Delhi and coefficient of correlation (R^2) between measured and modeled concentrations along with S/N ratio in the base run of PM$_{2.5}$ and MDL

Species	Average	R^2	S/N	MDL
PM$_{2.5}$	121.9 ± 93.2	0.874	1.17	–
OC	17.6 ± 14.1	0.861	1.57	0.94
EC	10.2 ± 7.54	0.869	2.95	0.35
F$^-$	0.89 ± 0.59	0.964	4.61	0.28
Cl$^-$	7.70 ± 5.71	0.851	3.07	0.25
SO$_4^{2-}$	12.75 ± 8.01	0.761	2.66	0.21
NO$_3^-$	9.70 ± 7.82	0.826	2.79	0.28
NH$_4^+$	9.35 ± 8.23	0.973	10.21	0.20
Na$^+$	5.01 ± 3.12	0.801	9.95	0.42
K$^+$	4.08 ± 2.71	0.873	5.77	0.46
Mg	0.94 ± 0.81	0.859	6.01	0.17
Ca	2.84 ± 2.23	0.834	4.54	0.29
Al	2.80 ± 0.92	0.539	1.66	0.16
Si	1.70 ± 0.62	0.858	7.15	0.12
Cr	0.04 ± 0.13	0.554	3.62	0.01
Ti	0.11 ± 0.21	0.935	5.15	0.03
Fe	0.26 ± 0.42	0.758	2.29	0.06
Zn	0.12 ± 0.21	0.948	5.00	0.07
Mn	0.02 ± 0.02	0.895	2.52	0.01
Cu	0.04 ± 0.06	0.571	0.78	0.01
As	0.06 ± 0.16	0.829	9.65	0.02
Br	0.04 ± 0.11	0.698	3.02	0.01
Pb	0.02 ± 0.03	0.598	0.62	0.01

± Standard deviation

Air mass back trajectory and cluster analysis

In order to identify and trace the trans-boundary movement of PM$_{2.5}$ from their potential source of origin to the receptor site, 24-h backward air mass trajectories for each experimental day (sampling was performed at 1030 h IST), starting at 0500 h Universal Coordinated Time (UTC) at height of 500 m above ground level (agl) at the sampling site, were plotted employing the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory's (ARL) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (http://ready.arl.noaa.gov/HYSPLIT.php) with the Global Data Assimilation System (GDAS) data as input (Draxler and Rolph 2003; Wang et al. 2015).

Cluster analysis aids in classifying trajectories with similar pathways, differentiating the mean transport pathway from the numerous existent trajectories to the receptor site, thereby demarcating trajectories into the clusters carrying maximum homogeneity within and maximum heterogeneity between themselves (Brankov et al. 1998; Wang et al. 2009). The groups of trajectories have been clustered together to represent the four major directions of trans-boundary migration of polluted air mass and to present an enhanced visualization for recognition of source regions. It must be taken into consideration that cluster analysis can only depict the general directions in which the potential sources may lie, but fall short in indicating the precise locations of the sources.

PSCF analysis

To identify the potential source regions contributing to $PM_{2.5}$ mass over the observational site, the PSCF was employed for the study period, using air mass trajectory statistics software, TrajStat (version 1.2.2.6). PSCF is a hybrid receptor model applied to estimate the air parcel carrying the certain level of pollutant concentration advancing through explicit upwind source area (Ashbaugh et al. 1985; Hwang and Hopke 2007). The probable source area is divided into a gridded i by j array. PSCF follows the following equation:

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \tag{8}$$

where $PSCF_{ij}$ is the probability that air mass originates in the ijth cell on days with high species concentrations, $m(ij)$ is the number of times that the concentration is higher than the predetermined criterion value (75th percentile of $PM_{2.5}$ is taken in the present study) at the receptor site, and $n(ij)$ is the number of times that the trajectories passed through the cell (i, j). A cell with PSCF value close to 1 indicates probable source location.

Results and discussions

Elemental concentration and reconstructed $PM_{2.5}$

The mass concentration of $PM_{2.5}$ has ranged from 25.1 to 429.8 µg m^{-3} with an average value of 121.9 ± 93.3 µg m^{-3} during January 2013 to December 2014. The seasonal variation and average concentrations of OC, EC, WSIC, and major and trace elements of $PM_{2.5}$ with maxima and minima are listed in Table 2. Mandal et al. (2014) also reported the similar average concentration of $PM_{2.5}$ (142.50 ± 23.57 µg m^{-3}) for an industrial area of Delhi, whereas Panda et al. () reported higher concentration of $PM_{2.5}$ (186.25 ± 47.46 µg m^{-3}) at Delhi. Other studies have also reported higher ambient $PM_{2.5}$ concentrations in New Delhi (Singh et al. 2011; Tiwari et al. 2014; Trivedi et al. 2014), and most of them exceed the National Ambient Air Quality Standards (60 µg m^{-3} for 24-h average and 40 µg m^{-3} for annual average).

The average concentrations of OC and EC of $PM_{2.5}$ were 17.6 ± 14.1 µg m^{-3} (~14.4% of $PM_{2.5}$ mass) and 10.2 ± 7.5 µg m^{-3} (~8.4% of $PM_{2.5}$ mass), respectively. Whereas the contribution of total carbon (TC = OC + EC) was ~22.8% of $PM_{2.5}$ mass during the study. Panda et al. (2016) have reported the lower values of percentage contribution of TC in $PM_{2.5}$ (~15.0% of $PM_{2.5}$ mass) at Delhi while higher values were obtained at Bhubaneswar (~30.4% of $PM_{2.5}$ mass), whereas Mandal et al. (2014) reported the

higher percentage of TC in $PM_{2.5}$ (37.3% of $PM_{2.5}$ mass) in an industrial area of Delhi. Ram and Sarin (2011) observed higher percent contribution of TC in $PM_{2.5}$ at Kanpur (~50% of $PM_{2.5}$ mass). The emissions from vehicles and biomass burning (agricultural waste burning and wood burning) significantly contribute to the atmospheric concentrations of OC and EC (Ram and Sarin 2011; Sharma et al. 2016a). The concentrations of OC and EC of $PM_{2.5}$ varied significantly during winter, summer, and monsoon seasons (Table 2). During winter, the concentrations of OC and EC of $PM_{2.5}$ were recorded more than twice of the concentrations of OC and EC during summer and monsoon seasons. The scatter plots between OC vs. EC, OC vs. $PM_{2.5}$, and EC vs. $PM_{2.5}$ for the winter, summer, and monsoon seasons are depicted in Fig. 2. A significant positive linear trend between OC and EC have been observed during winter ($R^2 = 0.81$; $p < 0.05$), summer ($R^2 = 0.75$; $p < 0.05$), and monsoon ($R^2 = 0.96$; $p < 0.05$) seasons, which is indicative of their common sources, i.e., vehicular emissions and biomass burning (Salma et al. 2004; Sharma et al. 2014c). While weakly correlated values of OC and EC signify the formation of secondary aerosols in the atmosphere through a photochemical reaction under conditions favorable for gas to particle conversion of VOCs (Begum et al. 2010).

The average concentration of major and trace elements in $PM_{2.5}$ was recorded as 20.2 ± 2.4 µg m^{-3} which accounts for ~17% of $PM_{2.5}$, whereas the WSIC accounts for ~38% of $PM_{2.5}$ mass concentration. The average concentrations of NH_4^+, SO_4^{2-}, and NO_3^- of $PM_{2.5}$ were recorded as 9.4 ± 8.2, 12.8 ± 8.0, and 9.7 ± 7.8 µg m^{-3}, respectively (Table 2). Figure 3 shows the charge balance between NH_4^+ and SO_4^{2-}, NO_3^-, and Cl^- of $PM_{2.5}$ during winter ($R^2 = 0.68$), summer ($R^2 = 0.12$), and monsoon ($R^2 = 0.07$) seasons. During winter, the molar mass of SO_4^{2-}, NO_3^-, and Cl^- are significantly correlated with molar mass of NH_4^+, which indicates the possible formation of secondary aerosols [$(NH_4)_2SO_4$, NH_4NO_3, and NH_4Cl] (Sharma et al. 2012b; Sharma et al. 2015), whereas during summer and monsoon seasons, molar mass of SO_4^{2-}, NO_3^-, and Cl^- are nonsignificantly correlated with molar mass of NH_4^+ ions. In $(NH_4)_2SO_4$, the molar ratio of NH_4^+ to SO_4^{2-} is 2:1. The molar ratio of greater than 2 signifies the abundance of NH_4^+, which has potential to combine with NO_3^- or other ions (Sharma et al. 2012b; Sharma et al. 2014a, c). In the present study, the equivalent molar ratio of NH_4^+/SO_4^{2-} is >2, which shows the complete neutralization of atmospheric acid gas H_2SO_4 and predominant to aerosol formation during winter season. Meteorological conditions (temperature and RH) play an important role in the formation of secondary aerosols (NH_4NO_3, NH_4HSO_4, and $(NH_4)_2SO_4$). The reaction of H_2SO_4 with NH_3 is favored leading to the formation of $(NH_4)_2SO_4$ and NH_4HSO_4, left over NH_3, then react with HNO_3 to form NH_4NO_3 (Meng et al. 2011; Li et al. 2013;

Table 2 The average concentrations of particulate matter (PM$_{2.5}$), OC, EC, WSIC, and trace elements of PM$_{2.5}$ (μg m^{-3}) in Delhi

Species	Average ($n = 135$)	Range	Seasons		
			Winter ($n = 47$)	Summer ($n = 44$)	Monsoon ($n = 44$)
PM$_{2.5}$	121.9 ± 93.2	25.1–429.8	215.7[a] ± 93.2	81.5[a] ± 25.2	68.6[a] ± 57.1
OC	17.6 ± 14.1	3.25–69.1	30.9[a] ± 15.1	11.5[a] ± 3.76	10.2[a] ± 9.27
EC	10.2 ± 7.54	0.85–35.3	17.9[a] ± 7.78	7.09[a] ± 3.06	5.65[a] ± 5.54
F$^-$	0.89 ± 0.59	0.25–3.72	1.06[b] ± 0.80	0.87[b] ± 0.50	0.73[b] ± 0.71
Cl$^-$	7.70 ± 5.71	0.89–31.3	10.9[a] ± 6.67	5.66[a] ± 3.04	6.53[a] ± 5.26
SO$_4^{2-}$	12.75 ± 8.01	1.97–56.2	16.8[b] ± 11.3	10.0[b] ± 3.53	11.4[b] ± 5.21
NO$_3^-$	9.70 ± 7.82	0.21–52.2	19.0[a] ± 11.3	5.82[a] ± 2.05	4.31[a] ± 3.19
NH$_4^+$	9.35 ± 8.23	0.17–45.3	16.1[a] ± 10.4	8.43[a] ± 2.95	3.44[a] ± 3.82
Na$^+$	5.01 ± 3.12	0.94–18.7	5.11[b] ± 2.83	3.80[b] ± 1.74	6.13[b] ± 3.88
K$^+$	4.08 ± 2.71	0.41–16.8	5.21[b] ± 2.51	4.02[b] ± 2.46	3.02[b] ± 2.63
Mg	0.94 ± 0.81	0.11–4.28	1.33[b] ± 1.61	0.44[b] ± 0.25	1.05[b] ± 0.63
Ca	2.84 ± 2.23	0.35–13.7	3.41[b] ± 2.76	3.04[b] ± 1.72	2.08[b] ± 1.73
Al	2.80 ± 0.92	0.27–5.29	3.51[b] ± 0.80	2.39[b] ± 0.81	2.40[b] ± 1.04
S	2.83 ± 1.65	0.13–5.62	3.39[a] ± 1.56	1.27[a] ± 0.97	1.48[a] ± 0.89
Si	1.70 ± 0.62	0.42–4.64	2.18[a] ± 0.53	1.52[a] ± 0.59	1.40[a] ± 0.50
Cr	0.04 ± 0.13	0.03–0.93	0.12[b] ± 0.22	0.02[b] ± 0.01	0.01[b] ± 0.01
Ti	0.11 ± 0.21	0.01–0.98	0.23[b] ± 0.30	0.05[b] ± 0.04	0.05[b] ± 0.10
Fe	0.26 ± 0.42	0.08–2.02	0.60[b] ± 0.57	0.11[b] ± 0.17	0.07[b] ± 0.15
Zn	0.12 ± 0.21	0.02–1.36	0.30[b] ± 0.28	0.03[b] ± 0.02	0.04[b] ± 0.07
Mn	0.02 ± 0.02	0.002–0.12	0.02[b] ± 0.02	0.02[b] ± 0.02	0.01[b] ± 0.02
Cu	0.04 ± 0.06	0.002–0.13	0.10[b] ± 0.22	0.02[b] ± 0.02	0.01[b] ± 0.02
As	0.06 ± 0.16	0.002–0.68	0.17[b] ± 0.25	0.01[b] ± 0.02	0.01[b] ± 0.02
Br	0.04 ± 0.11	0.003–0.42	0.08[b] ± 0.17	0.01[b] ± 0.01	0.03[b] ± 0.05
Pb	0.02 ± 0.03	0.001–0.15	0.05[b] ± 0.03	0.01[b] ± 0.01	0.01[b] ± 0.02

± Standard deviation

[a] Significantly different ($p < 0.05$)

[b] Not significantly different ($p > 0.05$)

Sharma et al. 2014b). In summer and monsoon, NH$_4^+$ was not significantly correlated with anions; this particular observation alludes towards the active role of NH$_4^+$ in particulate formation during winter seasons (Saxena et al. 2017).

Reconstructed mass of PM$_{2.5}$

Chemical constituents/species of PM$_{2.5}$ mass were reconstructed (RCPM$_{2.5}$) to determine the relative contribution of measured chemical species to the measured PM$_{2.5}$ mass and their respective relationships using IMPROVE equation (Chan et al. 1997; Malm et al. 2007). In the present study, RCPM$_{2.5}$ was calculated using Eq. 9.

$$\text{RCPM}_{2.5} = [\text{AS}] + [\text{AN}] + [\text{POM}] + [\text{LAC}] + [\text{SS}] + [\text{soil}] \quad (9)$$

where AS is the ammonium sulfate, AN is the ammonium nitrate, POM is the particulate organic matter, LAC is the light-absorbing carbon, and SS is the sea salt. The concentrations of the respective factors in Eq. 9 are calculated by

multiplying their individual concentration with their conversion factors as described in Table S-1 (in supplementary information). The mass difference (dM = PM$_{2.5}$ − RCPM$_{2.5}$) of PM$_{2.5}$ was calculated by subtracting RCPM$_{2.5}$ from measured PM$_{2.5}$ (Chan et al. 1997; Malm et al. 2007; Sharma et al. 2014c). The average mass difference between PM$_{2.5}$ and RCPM$_{2.5}$ was recorded as 18.0 μg m^{-3} (~15% of PM$_{2.5}$ mass) during the study period which may be attributable to unidentified mass (UM) of PM$_{2.5}$. The mass difference (UM) could be due to carbonate-rich minerals, calcium sulfate, and alumino-silicates (Zhang et al. 2010; Ram et al. 2012). The observed average re-constructed concentration of all factors and their percent contributions to PM$_{2.5}$ are given in Table S-1 and Fig. 4, respectively. The result showed that the contributions of AN and AS to PM$_{2.5}$ were ~10 and ~15%, respectively. Majorly, AS is produced in the atmosphere through the chemical reactions of SO$_2$, which emits from combustion of fossil fuels (coal and diesel) and AN is produced through reversible reactions of gas-phase NH$_3$ and HNO$_3$, aided by the formation of oxidized nitrogen through
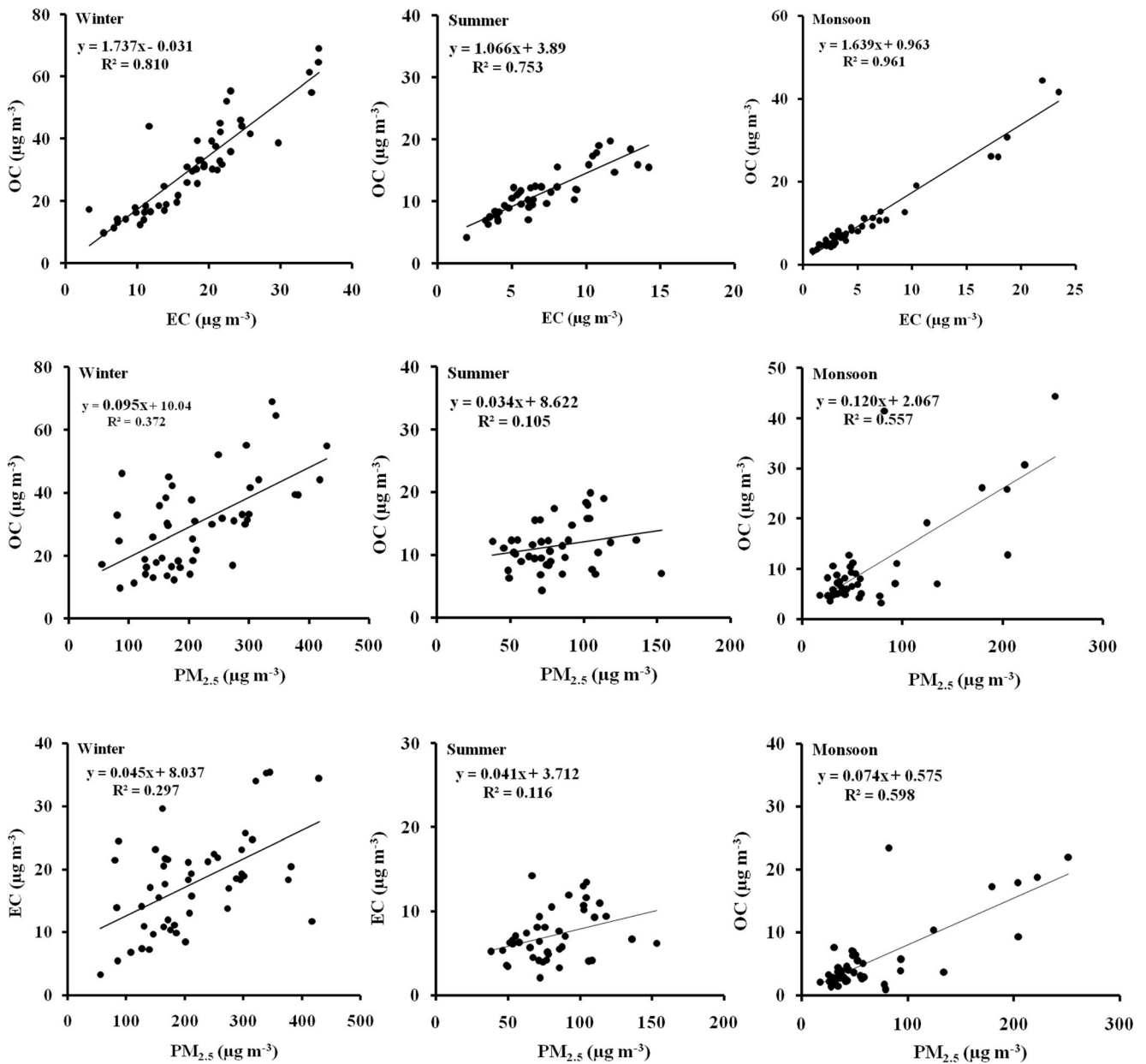
Fig. 2 Scatter plots between OC and EC, OC and PM$_{2.5}$, and EC and PM$_{2.5}$ during winter, summer, and monsoon seasons at Delhi
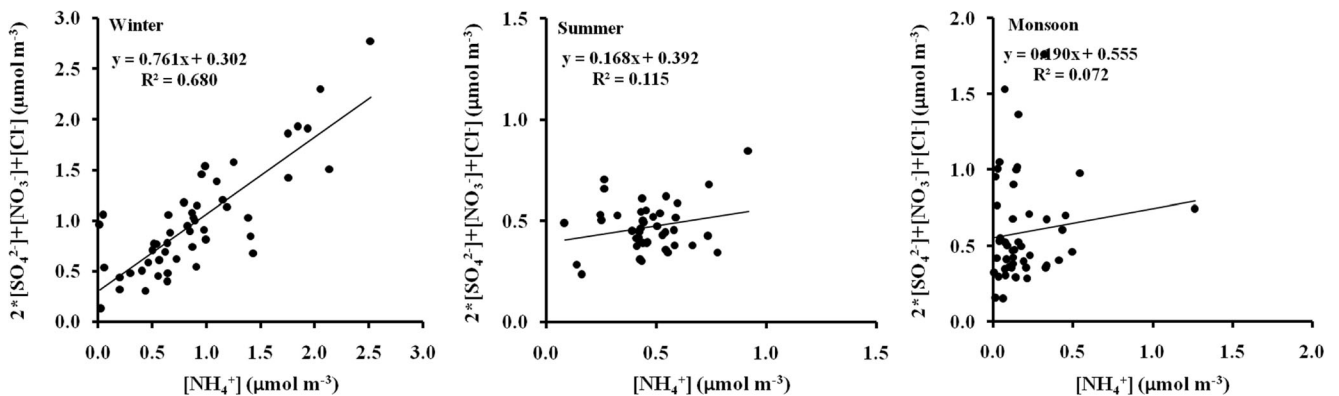

Fig. 3 Charge balance between NH$_4^+$, NO$_3^-$, Cl$^-$, and NH$_4^+$ of PM$_{2.5}$ during winter, summer, and monsoon seasons
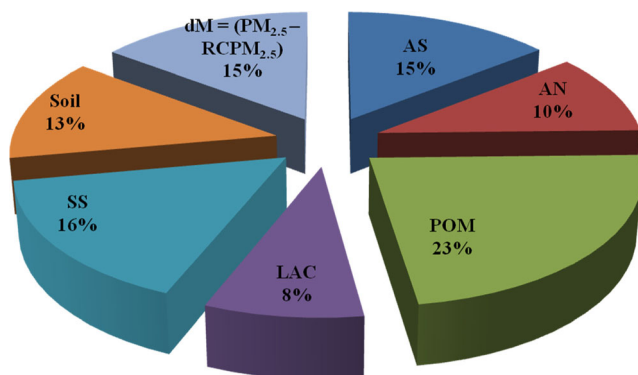
Fig. 4 Reconstructed PM$_{2.5}$ mass (*AS* ammonium sulfate, *AN* ammonium nitrate, *POM* particulate organic matter, *LAC* light absorbing carbon, *SS* sea salts, soil, and dM) by using IMPROVE equation

combustion of fossil fuels and vehicular emissions (Ram et al. 2012; Sharma et al. 2015, 2016a). The POM (1.6 [OC]) contributed 23% of RCPM$_{2.5}$. The sources of POM in the atmosphere are both primary (combustion of fossil fuel or biomass) and secondary (secondary organic aerosols formed through oxidation of gas phase precursors) formation. POM was found to be the most abundant species in PM$_{2.5}$, which is similar with other urban or roadside measurements (Phuleria et al. 2007; Chen et al. 2010; Gugamsetty et al. 2012; Sharma et al. 2014c). The annual average LAC was estimated as 10.2 μg m^{-3} (~8% of RCPM$_{2.5}$). LAC (black carbon, elemental carbon, or graphite carbon) is largely emitted through incomplete combustion of fossil fuels and biomass burning. The observed contribution of soil dust was 13%, which is expected to be higher at sampling location due to impact of local as well as trans-boundary transport from the Thar desert and other Asian regions. The sequence of percentage contribution of these components to PM$_{2.5}$ mass is POM > SS > AS > soil > AN > LAC (Fig. 3).

Source apportionment

In the present study, PCA, UNMIX, and PMF analyses have been done to estimate source profiles and contributions to PM$_{2.5}$ and results have been inter-compared. PCA/APCS, UNMIX, and PMF extracted sources and their source contributions are summarized in Tables 3 and 4, respectively. Summary of the average percent contribution of major source types of PM$_{2.5}$ mass at Delhi, India, and other countries are summarized in Table 5.

PCA/APCS

In total, 22 variables (constituents of PM$_{2.5}$) with 135 PM$_{2.5}$ samples have been analyzed through PCA coupled with APCS using software package SPSS version 11.5 and Varimax rotation has been employed. All variables were

typified and transformed into a dimensionless standardized form prior to statistical analysis, and the lowest eigenvalue for extracted factors was restricted to more than 1 that explained the 72.4% of the variance of the data. PCA/APCS analysis identified five different sources of PM$_{2.5}$ based on the loading of the variables in the factor (Table 3).

The first factor was dominated by high nitrate, sulfate, and ammonium, which marks the presence of secondary sulfate and secondary nitrate mixture. These secondary products are formed in the atmosphere, being emitted either by natural or anthropogenic sources. This source has explained about 23.4% variance and contributed to about 27.2% for PM$_{2.5}$ mass concentration. Also, the abundances of elements like As, Zn, Fe, Cu, Cr, Pb, and S indicate the emissions arriving from the industrial source, thus making this factor to be a mixed type source (SA + industrial emission (IE)). The secondary nitrate is formed by the oxidation of NO$_x$ and is favored by low temperature (Li et al. 2004), while high temperature and strong solar radiations favor the formation of secondary sulfates through photochemical reactions (Seinfield and Pandis 2016). The presence of secondary aerosols over Delhi is in agreement with the studies done on trace gases, i.e., NH$_3$, SO$_2$, and NO$_x$ by Sharma et al. (2012b) and Sharma et al. (2014b). NH$_4^+$ and SO$_4^{2-}$ have also been used as a marker for biomass burning and coal combustion, respectively (Pant and Harrison 2012). Kumar et al. (2001) used Cu, Mn, and Ni as tracers for industrial emissions in Mumbai; Sharma et al. (2014b) used Cu, Cr, Mn, Ni, Co, and Zn as industrial emission tracers for metal manufacturing plants in Delhi; Kulshrestha et al. (2009) used a combination of Ni, Cu, Fe, and Cr as a marker for construction activities in Agra; and Kar et al. (2010) used Zn, Cu, and Ni as tracers of galvanizing, metallurgy, and electroplating industries while Cr from tannery industry in Kolkata.

The second factor was associated to vehicular emission and it explained 22.4% of the variance. The high loading of OC, EC, Zn, Fe, Mn, and Pb attributed to vehicular emissions contributes ~23.5% to PM$_{2.5}$ mass. EC is used extensively as marker for diesel exhaust (Song et al. 2006; Yin et al. 2010) and it is predominantly emitted from combustion sources and shows limited chemical transformations, while OC can be contributed directly by primary emission sources (vaporization and combustion of solvents and fuel) and through chemical reactions among primary gaseous OC in the atmosphere (Turpin et al. 1991; Ho et al. 2003; Behera and Sharma 2010). The source represents the abundances of Pb, Zn, Fe, Mn, Cu, and Al, which are also related to the traffic source profiles. Zn comes from two stroke engines as it is used as a fuel additive and tire wear (Kothai et al. 2008), Fe from wear and tear of break and wear of metal in the exhaust system (Gupta et al. 2007; Karar and Gupta 2007), and Pb from gasoline additives, brake pads, and road dust re-suspensions (Pant and Harrison 2012). Mn is used as an additive in unleaded

Table 3　PCA factor loading, UNMIX source composition (mass fraction), and PMF percent contribution for PM$_{2.5}$

| | PCA factor loading | | | | | UNMIX source composition | | | | PMF percent contribution | | | | | | |
	F1	F2	F3	F4	F5	S1	S2	S3	S4	P1	P2	P3	P4	P5	P6	P7
OC	0.277	0.822	0.119	0.241	0.147	0.154	0.155	0.151	0.103	6.61	34.05	4.24	1.58	49.74	4.99	2.58
EC	0.311	0.809	0.115	0.196	0.145	0.079	0.093	0.088	0.052	1.58	51.36	3.64	1.5	40.32	2.08	1.42
SO$_4^{2-}$	0.700	0.268	0.217	0.373	0.000	0.068	0.105	0.120	0.047	1.33	2.36	5.11	41.76	35.31	1.34	26.47
NO$_3^-$	0.653	0.542	0.136	0.270	0.000	0.078	0.087	0.144	0.041	1.45	17.34	13.47	49.5	10.09	2.35	9.54
NH$_4^+$	0.702	0.431	0.262	0.125	0.387	0.066	0.093	0.117	0.021	5.1	5.14	15.13	54.5	3.62	5.49	11.79
Al	0.205	0.275	0.249	0.533	0.176	0.026	0.013	0.013	0.006	29.83	15.82	1.55	5.09	6.1	3.46	41.32
Ti	0.269	0.398	0.000	0.535	0.088	0.003	0.000	0.002	0.002	45.03	14.78	1.33	17.87	0.46	16.6	4.26
Si	0.144	0.069	0.258	0.690	0.182	–	–	–	–	45.85	18.94	1.54	11.02	15.23	0.79	5.84
Fe	0.467	0.558	0.027	0.510	0.049	0.006	0.004	0.001	0.004	32.61	11.79	0.37	1.28	1.18	38.9	23.45
Cu	0.729	0.148	0.040	0.399	0.116	0.000	0.000	0.000	0.003	19.36	32.71	1.82	2.88	7.8	45.82	5.88
Zn	0.605	0.549	0.052	0.397	0.142	0.001	0.004	0.000	0.002	0.51	42.61	0.53	1.42	0.62	39.93	23.94
As	0.750	0.373	0.134	0.344	0.066	0.000	0.000	0.001	0.003	11.51	13.16	11.15	0.98	16.3	13.58	21.5
Br	0.682	0.188	0.054	0.597	0.128	0.000	0.000	0.000	0.001	9.17	39.85	1.32	21.45	0.7	16.96	9.78
Pb	0.286	0.657	0.099	0.413	0.000	0.000	0.000	0.000	0.000	10.63	43.52	0.42	23.48	3.71	13.06	4.97
Cr	0.829	0.215	0.142	0.094	0.038	0.000	0.000	0.000	0.004	21.62	29.42	0.74	2.5	2.37	32.09	25.56
F$^-$	0.090	0.111	0.000	0.065	0.681	0.005	0.009	0.004	0.001	7.54	5.49	4.92	9.4	5.58	13.23	10.91
Cl$^-$	0.185	0.122	0.636	0.175	0.516	0.059	0.086	0.059	0.011	2.04	5.91	47.69	13.84	2.96	2.51	32.86
Na$^+$	0.000	0.203	0.610	0.321	0.178	0.014	0.045	0.006	0.019	5.83	1.4	52.27	23.46	13.79	2.7	1.98
K$^+$	0.079	0.252	0.412	0.068	0.707	0.022	0.046	0.019	0.005	6.45	12.16	22.06	2.02	57.91	1.47	8.08
Mg	0.124	0.176	0.771	0.089	0.000	0.004	0.013	0.003	0.000	2.83	39.83	27.23	15.27	3.58	3.94	10.12
Ca	0.000	0.000	0.605	0.427	0.217	0.011	0.037	0.007	0.005	47	1.74	11.63	4.53	10.37	3.22	24.29
Mn	0.619	0.354	0.000	0.000	0.163	0.000	0.000	0.000	0.000	31.34	26.92	4.3	7.2	2.62	33.75	1.47
	SA	VE	SS	SD	BB	SD	VE + BB + SS	SA	IE	SD	VE	SS	SA	BB	IE	FFC

gasoline (Kulshrestha et al. 2009), and combinations of Cu and Al signify emissions from brake lining wearing (Srimuruganandam and Nagendra 2012a, 2012b).

Third factor is rich in Na$^+$, Cl$^-$, Mg^{2+}, and K$^+$, representing the sea salt source, and it explained 12.2% of variance. None of the less, the use of some markers is rather perplexing and

Table 4　Sources and source contributions (%) calculated by the three receptor models

Identified sources	PCA/APCS	UNMIX	PMF
Soil dust	21.5	24.3	20.5
Vehicular emissions	22.4	–	19.7
Industrial emissions		13.4	6.2
Secondary aerosols	–	30.0	20.5
Biomass burning	12.3	–	14.3
Sea salt	12.2	–	4.3
Fossil fuel combustion	–	–	13.7
Secondary aerosols + industrial emissions	27.2	–	–
Vehicular emissions + biomass burning + sea salt	–	32.2	–

may be influenced by different sources like K$^+$ from biomass and wood burning, Cl$^-$ from coal burning, and Mg from crustal emissions. The presence of NO$_3^-$ in this source concurs with the possibility of its marine origin through condensation of HNO$_3$ (Srimuruganandam and Nagendra 2012a, 2012b). PCA analysis reveals that sea salt has contributed 15.4% to PM$_{2.5}$ concentration.

Fourth factor represents the soil-related sources with crustal elements, i.e., Al, Si, Ca, Mn, Mg, and Fe. It explained 8.4% variance and 21.5% contribution to PM$_{2.5}$ concentration. Wide range of elements (Al, Ca, Si, Ti, Mg, Pb, Cu, Cr, Ni, Co, Na, K, and Zn) have been used as tracer species for crustal elements in India (Balachandran et al. 2000; Khillare et al. 2004; Chelani et al. 2008; Chakrobarty and Gupta 2010; Shridhar et al. 2010). The presence of Cl$^-$ and SO$_4^{2-}$ with OC and TC signifies the soil dust emissions, while occurrence of Fe with OC and TC marked for road dust (Gupta et al. 2007; Banerjee et al. 2015). Hence, the presence of both combinations in the present study manifests the mixed emissions from road and soil dust.

Fifth factor is dominated by K$^+$ and NH$_4^+$, signifying the source of biomass burning emissions, and it explained 7.4% variance. In India, biomass burning commonly alludes to

Table 5 Summary of average contribution (%) of major source types of PM$_{2.5}$ mass at megacities of India and other countries

Location	PM (µg m^{-3})	No. of factors	Sea salt (%)	Crustal/soil dust (%)	Vehicle emission (%)	Secondary aerosol (%)	Other combustion/industrial emission (%)	Reference
Delhi, India	121.9	7	4.3	20.5	19.7	20.5	34.2 (FFC, BB, IE)	Present study
Delhi, India	–	6	–	6.0	22.0	21.0	45.5 (other)	CPCB Report (2010)
Beijing, China	57.4	5	–	15.4	26.3	–	58.4 (other)	Jin et al. (2016)
Beijing, China	135	6	–	15	4	26	55 (FFC, BB, IE)	Zhang et al. (2013)
Ile-Ife, Nigeria	216.3	4	–	12	22	–	66 (other)	Ogundele et al. (2016)
Salamanca, Mexico	45.0	6	–	19.9	12.8	14.2	1.82	Murillo et al. (2012)
Ordos, China	51.8	4	–	35.81	22.67	32.35	4.57	Wang et al. (2012)
Athens, Greece	41.0	5	24.0	30.0	50.0	–	–	Karanasiou et al. (2009)
Shinjung, Taiwan	21.8	5	1.12	20.14	33.03	22.27	23.42 (IE)	Gugamsetty et al. (2012)
Seattle, Washington	8.86	9	3	14	22	18	43 (BB, FFC, IE, other)	Maykut et al. (2003)

combination of cow dung and fuel wood burning, agricultural burning, and wildfire. K$^+$ is used in many source apportionment studies conducted in Asia and Europe as a marker of biomass burning (Rodriguez et al. 2004; Andersen et al. 2007; Pant and Harrison 2012). Also, NH$_4^+$ with K$^+$ has been used as a marker combination to identify the burning emissions (Khare and Baruah 2010; Sharma et al. 2014c), which justifies the presence of NH$_4^+$ with K$^+$ in the present study and thus representing this source to be of biomass burning emission. Biomass burning contributes 12.3% to PM$_{2.5}$ mass concentration in the present study.

UNMIX

The 22 species were taken into account and PM$_{2.5}$ was considered as the total mass in UNMIX model, which identified four sources. Silicon (Si) was discarded by the model according to suggested exclusion. Numerical values for the solution's diagnostic indicators ($R^2 = 0.76$ and S/N ratio = 2.07) were consistent with recommendations. UNMIX re-samples the data 100 times and uses the bootstrap method to calculate uncertainties.

Source 1: This source was inferred as soil/road dust (SD) due to high composition of crustal elements (Al, Ti, Fe, Ca, and Mg) in the UNMIX results, and the results are comparable with PCA and PMF output. UNMIX analysis showed that soil dust has contributed 24.3% to PM$_{2.5}$ mass. Crustal elements are major constituents of airborne soil and road dust and generally contribute to coarse aerosols, including Al, Si, Ca, Ti, Mg, Fe, and Na that are used as tracers for soil dust and/or crustal re-suspension (Lough et al. 2005; Begum et al. 2011; Yin et al. 2010; Pant et al. 2012).

Source 2: Higher concentrations of OC, EC, Zn, Fe, K$^+$, Na$^+$, Cl$^-$, Ca, Mg, and SO$_4^{2-}$ indicate that this source may have been a mixture of vehicular emissions, biomass burning, coal combustion, and aged sea salt and contributed to about

32.2% for PM$_{2.5}$ mass concentration. Higher concentrations of OC, EC, Zn, and Fe indicate the possible contribution of vehicular emission (Yin et al. 2010; Sharma et al. 2016b). Biomass burning and coal combustion are characterized by the high concentrations of K$^+$, Cl$^-$, and SO$_4^{2-}$ (Pant and Harrison 2012; Banerjee et al. 2015), since the results of UNMIX showed the high concentrations of Na$^+$ and Mg^{2+} along with K$^+$ and Cl$^-$. Hence, it is considered as a mixed source, whereas PCA and PMF results well differentiated the two sources (biomass burning and sea salt).

Source 3: This source corresponds to secondary aerosols due to the presence of high concentrations of nitrate, sulfate, and ammonium. Thus, this source was identified as a mixture of secondary nitrate and secondary sulfate in UNMIX analysis. UNMIX analysis shows 30% contribution of secondary aerosols to PM$_{2.5}$ in the present study.

Source 4: It is observed as IE source as UNMIX analysis results show high-factor loading by the heavy metal elements like Cr, Zn, As, Fe, and Cu, which were also dominant in the PMF industry source. Some industrial sources such as metal manufacturing plants and storage are located near the sampling site, and these could probably affect it. Largely, Zn, Cu, As, Fe, Cr, Cd, Mo, Ni, and S have been used as marker species for industrial emanations (Sharma et al., 2016a, b). Present UNMIX analysis recognizes that IE have contributed to about 13.4% for PM$_{2.5}$ mass concentration.

PMF

The PMF model identified 7 sources (secondary aerosol, soil dust, vehicular emission, biomass burning, fossil fuel combustion, industrial emissions, and sea salt) using 22 chemical species of 135 PM$_{2.5}$ samples collected during the study period (Fig. 5 and Table 4). In order to diminish the influence of extreme values in the PMF solution, model was made to run in the default robust mode and different numbers of sources were
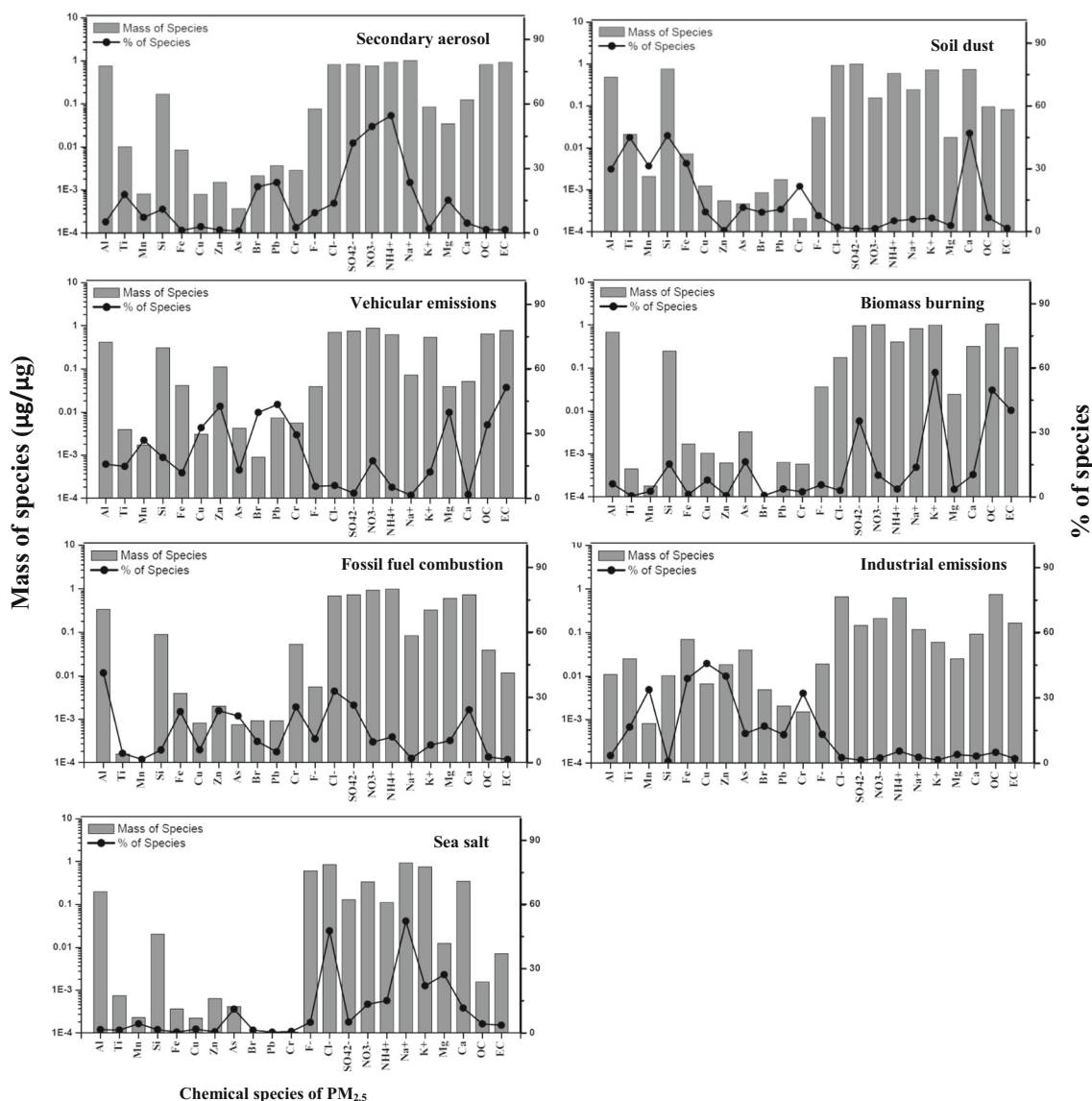
Fig. 5 PMF source profile of secondary aerosol, soil dust, vehicular emissions, biomass burning, fossil fuel combustion, industrial emissions, and sea salt in Delhi for PM$_{2.5}$ mass

identified using a trial-and-error method to find the optimal number of sources. Further, the data sets using factors were entered into the PMF model for final analysis and the resultant change in the Q values was examined. In this study, the theoretical Q value was estimated to be approximately 2970 (i.e., 135×22). Robust Q value was the value for which the impact of outlier was minimized, while true Q value was the value for which the influence of extreme values was not controlled. The robust Q values were close to the true Q values in this study, which entails the reasonable fitness of the model with the outlier. Also, it is imperative that the range of Q values should be adequately small from the random runs (100 runs in the present study) to corroborate the attainment of a similar global minimum and thus confirms the fitness of outliers equally well for each random run. At the 7% of the error constant, over

95% of Q values were nearly to 2970 for seven-factor solution, indicating the global minimum of the Q value. Based on the estimation of the model results, the Q value variations in the model, the seven-factor solution delivered the most viable results. The descriptions of the PMF model and source apportionment of PM$_{2.5}$ have been discussed in detail in our previous paper Sharma et al. (2016b) and reference therein.

Source 1: PMF analysis shows that secondary aerosols have contributed to about 21.3% for PM$_{2.5}$ mass concentrations with the dominated key markers of NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$ (Fig. 5). The secondary aerosols are mainly composed of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ deriving from the gaseous precursors NH$_3$, SO$_2$, and NO$_x$. The study evidenced the abundances of ambient NH$_3$, NO$_x$, and SO$_2$ over Delhi (Sharma et al. 2014a).

Source 2: Soil dust includes most of the crustal elements and has high concentrations of Fe, Si, Ca, Na, Cu, Mg, and Al. PMF analysis showed that soil dust has contributed 20.5% to $PM_{2.5}$ mass. Many other researchers cite these elements (Fe, Si, Ca, Na, Mg, Cu, Ni, and Al) as a soil dust source (Moreno et al. 2013; Mustaffa et al. 2014; Shen et al. 2010; Waked et al. 2014). A whole array of marker elements that have been used in India for identification of soil dust include Al, Si, Ca, Ti, Fe, Pb, Cu, Cr, Ni, Co, and Mn (Killare et al. 2004; Chelani et al. 2008; Gupta et al. 2012; Sharma et al. 2016a). Cu, Zn, and Ba are associated with road dust due to the release of these marker elements from cars and from non-exhaust sources.

Source 3: In this source, Cu, Zn, Mn, Pb, and EC contributed significantly, which have been considered as an indicator of vehicle emission. PMF analysis indicates that vehicle emissions have contributed 19.7% in $PM_{2.5}$ at sampling site of Delhi. Vehicular emissions are a major source of the PM, and research indicates that they contribute 10 to 80% to PM in cities across India (Sharma et al. 2014c; Banerjee et al. 2015; Sharma et al. 2016b). But various studies have computed different vehicular sources (exhausts, re-suspension, abrasion, etc.) which make their comparison more complicated. A study by Begum et al. (2010) conducted in Dhaka and by Santoso et al. (2013) at roadside in Jakarta defined Pb in $PM_{2.5}$ releasing from the pre-existing road dust by PMF. Choi et al. (2013) also introduced Pb in $PM_{2.5}$ as a tracer for motor vehicle source. Further, Zn in $PM_{2.5}$ appeared to have a motor vehicle as resolved by PMF (Brown et al. 2007).

Source 4: Emission from biomass burning, wood burning, and vegetative burning have been characterized as presence of high concentration of K^+ (Ram et al. 2010; Pant and Harison. 2012). The K^+ ion has been widely cited in the literature as an excellent tracer representing a wood or biomass burning source (Mustaffa et al. 2014). In India, K^+ has also been used as a key marker of biomass burning for PM (Ram et al. 2010), whereas levoglucosan is the key organic marker (Chowdhury et al. 2007). PMF analysis reveals that biomass burning has contributed 14.3% for $PM_{2.5}$ mass in the present study. Depending on the season and location, biomass burning has been assessed to contribute in the range of 7–20% (Chowdhury et al. 2007), which has been reported to be one of the major sources in Delhi, predominantly in winter due to combustion of wood (Sharma et al. 2003; Srivastava and Jain 2007).

Source 5: Abundance of marker elements Al, Cl, Fe, Zn, Cr, and SO_4^{2-} at the sampling site indicate the source of fossil fuel combustion to $PM_{2.5}$ mass. Zn and Se are marker species for coal combustion and oil-fired power plants, respectively (Lee et al. 2002), whereas Ni and V are tracer species for the combustion of heating oils (Vallius et al. 2005). PMF analysis shows that fossil fuel combustion has contributed 13.7% for $PM_{2.5}$ mass in the present study. Gupta et al. (2007) used As, Se, Te, and SO_4^{2-} as markers for coal combustion and reported the contribution of 6–30% to PM mass.

Source 6: The industrial emissions are characterized by high concentrations of Cr, Mn, Zn, and S, possibly emanates from metal manufacturing plants and storage which are located near the sampling location. An array of tracer species (Ni, Cr, Co, Cd, Zn, As, Fe, Cu, Mn, S, and Mo) have been used in India to identify specific industrial emissions (Banerjee et al. 2015; Sharma et al. 2014c). In this study, PMF resolved 6.2% contribution to industrial emissions for $PM_{2.5}$ mass.

Source 7: The higher concentrations of Na^+, K^+, and Cl^- in $PM_{2.5}$ mass indicate the contribution of sea salt. The present study shows that sea salt contributed to about 4.3% for $PM_{2.5}$. The presence of K^+ along with Na^+ and Cl^- in $PM_{2.5}$ offers possible confusion with wood/biomass/coal burning, but a combination of four elements (Na, K, Cl, and Mg) should provide a reliable signature (Sharma et al. 2016a). Begum et al. (2010) identified sea salt in $PM_{2.5}$ by PMF in Dhaka based on the presence of Na^+ and Cl^-. Choi et al. (2013) defined sea salt source in Seoul, Korea, due to the high contribution of Na^+ and Cl^- in $PM_{2.5}$ concentration. Several other studies in East, Southeast, and South Asia assigned a sea salt source in $PM_{2.5}$ considering Na^+ and Cl^- from the model output of PMF (Lee et al., 1999; Santoso et al. 2013; Senevirante et al. 2011).

Model comparison

The present study depicts the analysis by three different receptor models of same $PM_{2.5}$ data set which provides an opportunity to shape the decision about evaluation of the degree to which these models concur, differ, or complement one another. The PMF analysis identified seven sources (SD, vehicular emission (VE), SA, biomass burning (BB), SS, IE, fossil fuel combustion (FFC)), whereas UNMIX and PCA showed four sources [SD, mixed type (VE + BB + SS), SA, and IE] and five sources (SD, mixed type (SA + IE), VE, SS, BB), respectively. The UNMIX analysis resulted in one mixed type source, combining traffic, biomass burning, and sea salt precursors together and PCA resulted in mixed secondary aerosol and industrial emission markers, whereas in PMF results, these sources were well differentiated by their corresponding tracers. Each receptor model identifies sources differently, majorly based on the considerations of the models to choose the species selected as variables. PCA and PMF extracted similar sources; however, the former was unable to differentiate the fossil fuel factor from the vehicular factor. Comparable study was also done by Callen et al. (2009) and similar results were observed (Cesari et al. 2016). It is noteworthy that the primary disparity between PCA and PMF lies in the non-negativity of loadings and score factors (built in PMF) and inclusion of individual data uncertainties. In many ways, PMF resembles PCA except in exclusion of all the negative entries (Paatero and Tappert 1994). Additionally, it has an edge over PCA in handling missing or below detection level

data. UNMIX can be easily used in data sets which do not have comprehensive source profile information. It is helpful in distinguishing the most influential sources, whereas it underperforms to make agreement between expected and estimated contributions for weaker sources (Henry 2003). UNMIX differs from PCA; in that, it uses a new conversion method to derive significant factors based on the self-modeling curve resolution technique. The UNMIX solution is greatly reliant on the selected species, and on the other hand, this model showed problem in identifying the sources with low percentage to the total mass corroborating the weakness of UNMIX related to identify infrequent and relatively small sources. Moreover, it does not account uncertainties in ambient measurements and is unable to process samples with missing data (Banerjee et al. 2015), whereas PMF analyzes individual data points separately, normalizing the influences of each data points on the basis of measurement confidence (USEPA 2008).

Since, PMF employs a point-by-point least squares minimization scheme and not the correlation matrix information. Thus, the resulting profiles can be compared directly to the input matrix without transformation. However, PMF requires a large data set, preferably much more than the numbers of concerned factors, and allocation of weighing factor associated with each measurement is to be done. Contrastingly in PCA, the load matrix is non-dimensional and has to be combined with multilinear regression analysis to procure the source profiles. PCA tends to generalize the information that the data set originally have, as it depends on statistical association of data and not on chemical nature of particulates. PCA does not account a non-negativity constraint which makes it different from UNMIX and PMF. Another drawback of PCA is the use of single marker for multiple sources or availability of specific tracers (Belis et al. 2013). Furthermore, the model assumes the normal distribution of data set which may not be effective for all the cases, but error on the reconstructed concentration matrix is less when the APCS is used (Cesari et al. 2016). UNMIX provides a relatively coarse means of down-weighting outliers and PMF employs point-by-point error estimation in the data, allowing down-weighting of missing observations and outliers. This limitation is related to the models (PCA and UNMIX) because they do not take into account the uncertainty in the experimental data. That could be one of the reasons why PMF model provided better results than PCA and UNMIX model (Banerjee et al. 2015; Sharma et al. 2015).

Backward air mass trajectory and cluster analysis

It has become evident from Fig. 6 that majority of the air mass parcel during the study period is approaching to receptor site from arid landscapes of Rajasthan (Thar desert), Pakistan, Afghanistan, Indo-Gangetic Plain (IGP) region, and its surrounding areas during winter and summer seasons, whereas during monsoon season, the approaching air mass is

transported from IGP region, Bay of Bengal, and Arabian Sea through Thar desert. The trajectories have been plotted to trace the origin and transport pathways of air masses as they are ascribed to letting influx of pollutants and their precursors in the city. These groups of trajectories have been clustered together (Fig. 6) to evince the major transport pathways of the polluted air mass flow, so as to provide an envisage of dominant source regions precisely. It can be discerned that the source regions are both trans-boundary and locally originated from continental landmass, which is also supported by the chemical composition of the pollutants found at the observational site. Sharma et al. (2014a) had also observed the similar trajectories at Delhi.

PSCF

To delineate the probable source regions which could be causative of augmenting $PM_{2.5}$ concentration at the receptor site, a PSCF analysis was done (Fig. 6) for the study period. In the present study, the pollution criterion value was considered to be 75th percentile of $PM_{2.5}$ concentration. The grids with a probability of <0.1 are transparent, and different colors (as shown in the PSCF map) denote the lowest to highest probability grids. Delhi was observed to have a significant amount of potential source areas within highly polluted and populated regions of north-western India such as Punjab, Haryana, Rajasthan, Uttar Pradesh, and parts of Pakistan and Afghanistan which contain key oil fields, refineries, and major thermal power plants (Naja et al. 2014) during winter and summer seasons and IGP region including coastal areas of Bay of Bengal and Arabian Sea during monsoon season. Therefore, the air mass parcels traveling from these regions are inevitably carry pollutant-laden air masses to the receptor site.

Conclusion

This study attempts to investigate the comprehensive characterization, and source apportionment of $PM_{2.5}$ at an urban site of Delhi, India, from January 2013 to December 2014 provides the following points:

- During the study, the average concentration of $PM_{2.5}$ was 121.9 ± 93.2 μg m^{-3} with a range of 25.1–429.8 μg m^{-3}. The average concentrations of OC and EC of $PM_{2.5}$ were recorded as 17.6 ± 14.1 and 10.2 ± 7.5 μg m^{-3}, respectively. Strong seasonal variation was recorded in $PM_{2.5}$ concentration and its chemical composition with maxima during winter and minima during monsoon season.
- The chemical composition of the $PM_{2.5}$ was reconstructed using IMPROVE equation from the analyzed chemical composition. The highest contribution comes from
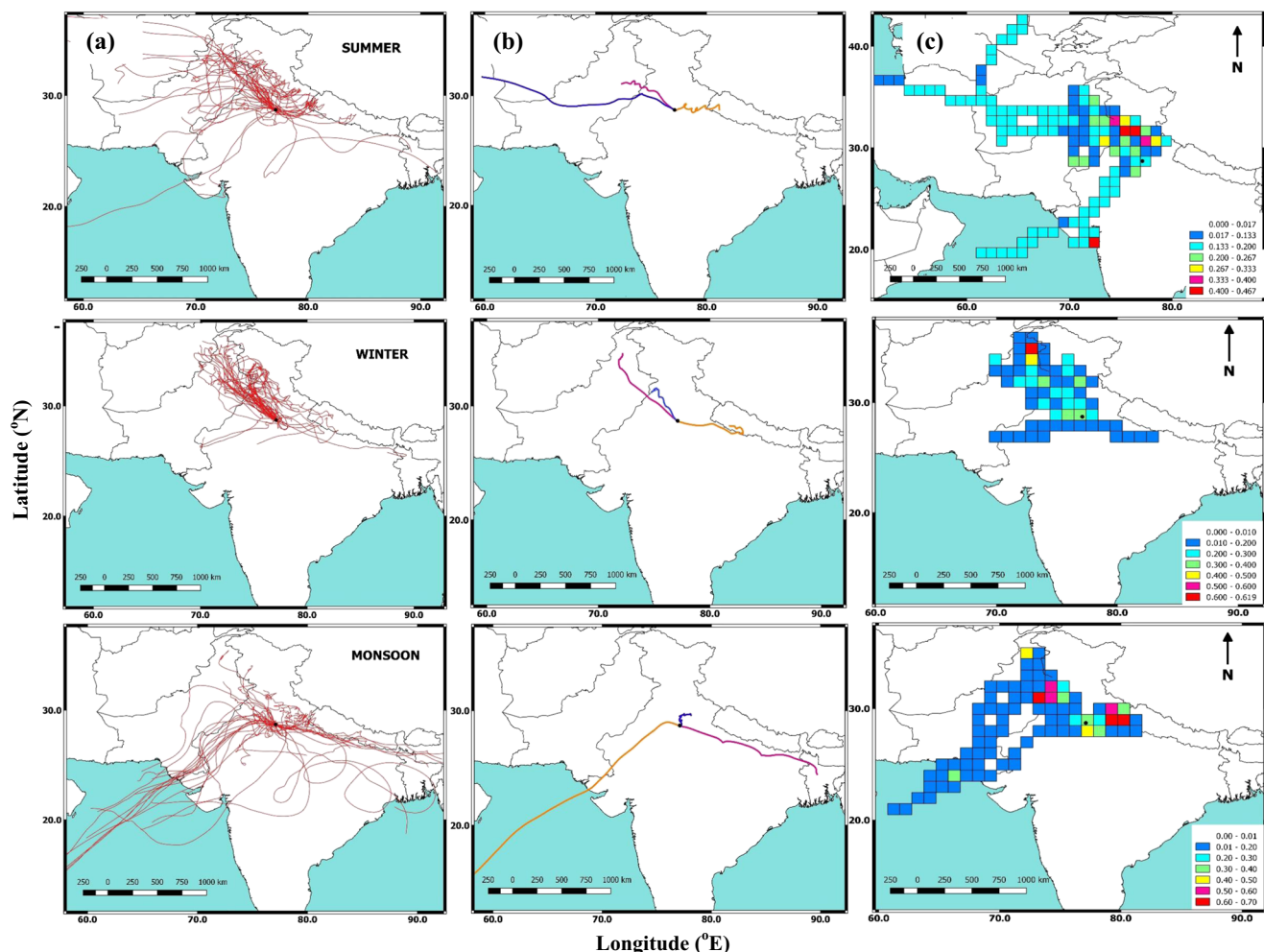
Fig. 6 The 120-h air mass HYSPLIT back trajectories (**a**), trajectory cluster (**b**), and PSCF (**c**) plots for winter, summer, and monsoon seasons at the sampling site

particulate organic matter (23%), followed by sea salt (16%), ammonium sulfate (15%), soil/crustal matter (13%), ammonium nitrate (10%), and light-absorbing carbon (8%).

- All the three models (PCA/APCS, UNMIX, and PMF) agreed on the sources of $PM_{2.5}$ and majority to be soil dust, secondary aerosols, vehicle emissions, industrial emissions, and biomass burning. PCA/APCS extracted five sources of $PM_{2.5}$ (soil dust, vehicle exhaust, secondary aerosols + industrial emissions, biomass burning, and sea salt), whereas PMF model identified seven sources of $PM_{2.5}$ (secondary aerosol, soil dust, vehicular emission, fossil fuel combustion, biomass burning, industrial emission, and sea salt). UNMIX model revealed four sources of $PM_{2.5}$ (soil dust, secondary aerosols, vehicle exhaust + biomass burning + sea salt, and industrial emission).

- The 24-h backward trajectories were traced and cluster analysis was performed on a seasonal basis to trace the air mass flow pathways, and PSCF was also done to identify the potential source regions. North-west India, regions

of Pakistan, and Afghanistan were found to be more dominant during summer and winter seasons, and IGP region, coastal areas of Bay of Bengal, and Arabian Sea were more prevailing during monsoon season.

- This study can help the stakeholders and policymakers to know more about the attributes of $PM_{2.5}$, the influence of regional and local sources, and their effect on air quality of the region. A definitive objective is to upgrade emanation control strategies, enhance general well-being, and to improve the overall quality of ambient air.

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