



Chemical Characteristics of Fine and Coarse Particles during Wintertime over Two Urban Cities in North India

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ABSTRACT

Water-soluble inorganic ions (WSII), organic carbon (OC) and elemental carbon (EC), and metals in the residue of the water-soluble fraction were studied in fine (PM_{2.5}) and coarse (PM_{2.5-10}) particles during winter over two urban cities, Amritsar (AMS) and New Delhi (DEL), in northern India. The PM_{2.5}/PM_{2.5-10} mass ratios at DEL and AMS were 3.6 and 2.79, respectively. \sum WSIIs was nearly 25% of the total mass in two size fractions and was higher in PM_{2.5} than PM_{2.5-10} at both sites. The secondary ions SO₄²⁻ and NH₄⁺ were dominant at both sites. The adsorption of fine particles onto larger ones may be a possible source of soluble ions in PM_{2.5-10}. SO₄²⁻ and NO₃⁻ were neutralized by NH₄⁺, and the formation of (NH₄)₂SO₄ dominated over NH₄NO₃ in PM_{2.5}, and by Ca²⁺ in PM_{2.5-10} over DEL. Coal burning, and agricultural and livestock emissions were potential sources of precursor gases of SO₄²⁻ and NH₄⁺. Plastic burning and the brick kiln industry contributed Cl⁻ in the PM_{2.5}. OC dominated over EC above both sites, and the total carbon (OC + EC) was higher over AMS than DEL. Emissions from low-temperature rather than high temperature combustion processes were dominant, as indicated by the higher quantity of char-EC than soot-EC. OC, EC, and K⁺ resulted from biomass burning over AMS, whereas they originated in multiple sources over DEL. The Al normalized ratios of elements in the samples compared to the crust were higher in PM_{2.5} than PM_{2.5-10}. Fe, Ti, and Mn ratios of < 1 were attributed to the silica dilution effect. The Pb, Cu, and Zn ratios in PM_{2.5} were 63, 18, and 13 over DEL and 2, 11, and 31 over AMS, respectively. Ba and Zn were contributed by vehicular emissions. A coefficient of divergence of > 0.5 indicated the spatial heterogeneity in the particle chemistry between the two sites. To improve the air quality and safeguard human health, biomass burning and the re-suspension of dust must be restricted.

Keywords: Aerosols; Sources; Processes; Transport; Biomass burning.

INTRODUCTION

The PM_{2.5} aerosols in ambient atmosphere are catching scientific attention due to their role in climate change, human health and atmospheric chemistry studies (Singh and Kaskaoutis, 2014; Pant *et al.*, 2015; Ram and Sarin, 2015). In rapidly growing mega cities like New Delhi in India, air quality often exceeds the National Ambient Air Quality Standards (NAAQS) and causes severe adverse health effects (Guttikunda and Goel, 2013; Guttikunda *et al.*, 2014; Yadav *et al.*, 2016). Poor air quality and health problems in this region are largely on account of PM_{2.5} in the ambient atmosphere. The PM_{2.5} concentrations are influenced by their source, source strength and meteorology factors such

as wind velocity, mixing height (Deshmukh *et al.*, 2012; Guttikunda *et al.*, 2014; Yadav *et al.*, 2016, Kumar *et al.*, 2017). Chemically, these particles are composed of water-soluble inorganic ions (WSII) of both primary and secondary origins, organic carbon (OC), elemental carbon (EC) and mineral matter of crustal origin. Multiplicity of their primary sources, particle formation by secondary processes and transport at regional, continental and trans-boundary levels result in their complex chemical characteristics. The WSII constitute nearly 30–50% of total mass in fine particles and are studied to understand the pollution sources and chemical transformation processes (Yttri *et al.*, 2007; Pavuluri *et al.*, 2011; Shen *et al.*, 2011; Kumar and Yadav, 2016; Kumar *et al.*, 2017). The OC and EC in particles have cooling and warming effects, respectively, and are used to understand net radiative effect of particles. The OC has two components, primary organic carbon (POC) which is directly emitted from source(s) and secondary organic carbon (SOC) which is formed from POC via photochemical reactions (Sudheer *et al.*, 2015; Villalobos *et al.*, 2015). In addition, presence of soluble ions such as sulfate in aerosols

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also introduces cooling effect. Ramana *et al.* (2010) have reported a good correlation between BC to sulfate ratio and the net warming over three cities in China. They further suggested that the warming effect of BC is more when it is internally mixed with sulfate aerosols and the climate change mitigation policies should focus on reducing BC/sulfate ratio. The elements in atmospheric particles such as Al, Ca, Fe, Mg, Mn, Na, K and P are considered as markers of crustally derived mineral mass in aerosols (Yadav and Rajamani, 2004) whereas the trace elements such as Ba, Zn, Pb, Sr, Cr, Ni are contributed by anthropogenic sources such as vehicular emissions, coal based power plants, industrial emissions (Yadav and Rajamani, 2006). Metals in fine particles are associated with pulmonary and cardiovascular diseases and cause oxidative stress (Dockery *et al.*, 1993). Therefore, the studies on WSII, carbon content and metal distribution in fine and coarse particles become important in understanding the sources of pollution, chemical transformations, radiative forcing and health effects.

In northern India, air pollution and air quality index remain very poor during winter season (November–January), largely on account of high PM_{2.5} levels. In addition to the regular emissions from vehicles, coal based thermal power plants, brick kiln industry, large scale open biomass and fossil fuel (mainly coal) burning by general public to get rid of near zero temperature conditions are winter season specific sources of air pollution. Low wind speed and lower mixing height due to temperature inversion conditions in this region restrict the dispersion of pollutants in ambient atmosphere (Ram and Sarin, 2010; Trivedi *et al.*, 2014; Kumar and Yadav, 2016). New Delhi has multiple sources of particles which show seasonal changes on year round basis (Yadav *et al.*, 2016; Kumar *et al.*, 2017). New Delhi, having a population of 20 million, is one of the most polluted city in the world. Air quality is also afflicted by pollutant transport from upwind regions in northwestern direction (Singh and Kaskaotis, 2014). The AMS, located in food basket of India in the state of Punjab, has nearly 20 times less population and is located in upwind regions and shares its boundary with Pakistan. Dominant air pollution sources over AMS includes vehicular emissions, biomass burning, agriculture and live stock, and trans-boundary transport from upwind regions in Pakistan. The present study was planned to collect PM_{2.5} and PM_{2.5-10} during wintertime from AMS and DEL and characterize them for WSII, OC, EC and metals in the residue sample after extracting water-soluble fraction. The data is used to understand air quality, pollution sources and chemical processes in two urban settings having similar meteorological conditions and to observe any wind assisted transport over New Delhi from upwind region. The study can eventually help in developing mitigation strategies for air pollution abatement in this region.

METHODOLOGY

PM_{2.5} and PM_{2.5-10} particles were collected using mass flow controlled high volume air sampler fitted with Cascade Impactor (Model TE-236; Tisch Environmental USA)

installed at the roof top of School of Environmental Science, Jawaharlal Nehru University (JNU), New Delhi (DEL) and at the rooftop of Science Building, Guru Nanak Dev University, Amritsar (AMS) (Fig. 1). PM_{2.5} particles were collected on pre-combusted and pre-weighed 20.3 × 25.4 cm quartz fiber filters whereas PM_{2.5-10} particles were collected on perforated quartz fiber filters. Each sample was collected for 24-hour duration. Twenty samples of PM_{2.5} and PM_{2.5-10} were collected from each sampling site during winter season from December 2011 to February 2012 with a frequency of two–three samples a week. Samples were not taken during rainy days and heavy foggy days. Average wind speed and relative humidity during the sampling period over AMS were 3.5 km hr⁻¹ and 78.14%, respectively, while over DEL, these parameters were 6.31 km hr⁻¹ and 78.14%, respectively. Meteorological parameters during the sampling period are provided in supplementary Table S1 (source: <http://www.Wunderground.com>).

An aliquot of the sample filter was extracted in Milli Q water using ultrasonicator and cations (Ca²⁺, Mg²⁺, Na⁺, K⁺, and NH₄⁺) and anions (F⁻, Cl⁻, NO₃⁻, NO₂⁻, and SO₄²⁻) were analyzed using ion chromatograph (IC; model 882 Compact IC Pro 1, Metrohm) as described in our previous publications (Kumar and Yadav, 2016; Kumar *et al.*, 2017). The residue filter after extracting water-soluble fraction was subjected to open acid digestion using a combination of mineral acids HF, HNO₃ and HClO₄ and the digested mass was picked in 2N HCl (for method details refer to Yadav and Rajamani, 2004; Pruseth *et al.*, 2005). Elemental analysis in the digested samples was done using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). All measurements, sample filtration, storage and ionic analysis were carried out inside a positive pressure clean lab having Class 1000 airflow.

Twenty percent of sample filters were subjected to re-extraction of water-soluble ions and the extraction efficiency (in % units) was calculated as [(C1/C1 + C2)] × 100 where C1 and C2 are concentrations of WSII during 1st and 2nd extractions, respectively. Average recoveries of soluble ions from QFFs were found in the range of 93–101% (for more details see Kumar and Yadav 2016; Kumar *et al.*, 2017). Average recoveries of soluble ions from the spiked quartz filter papers with known concentrations of ions (n = 6) were in the range of 90–100%. Multi-ion and multi-elemental standards procured from E-Merck Germany were used for the calibration of IC and ICP-OES, respectively. Standards in the desired range were prepared daily from stock solution following serial dilution method. Instrument performance was checked against the working standards after every five samples. Accuracy and precision of the IC data was within 5% error limits. The water-soluble extracts of field and laboratory blanks were also prepared and analyzed simultaneously with samples (for more details see Kumar and Yadav, 2016; Kumar *et al.*, 2017). The accuracy and precision data on the working standard and the repeat analysis of samples on ICP-OES are provided in the supplementary Table S2. The total cations (TC) to total anions (TA) ratios were 0.94 and 0.91 in PM_{2.5} over AMS and DEL, respectively (supplementary material Fig. S1).

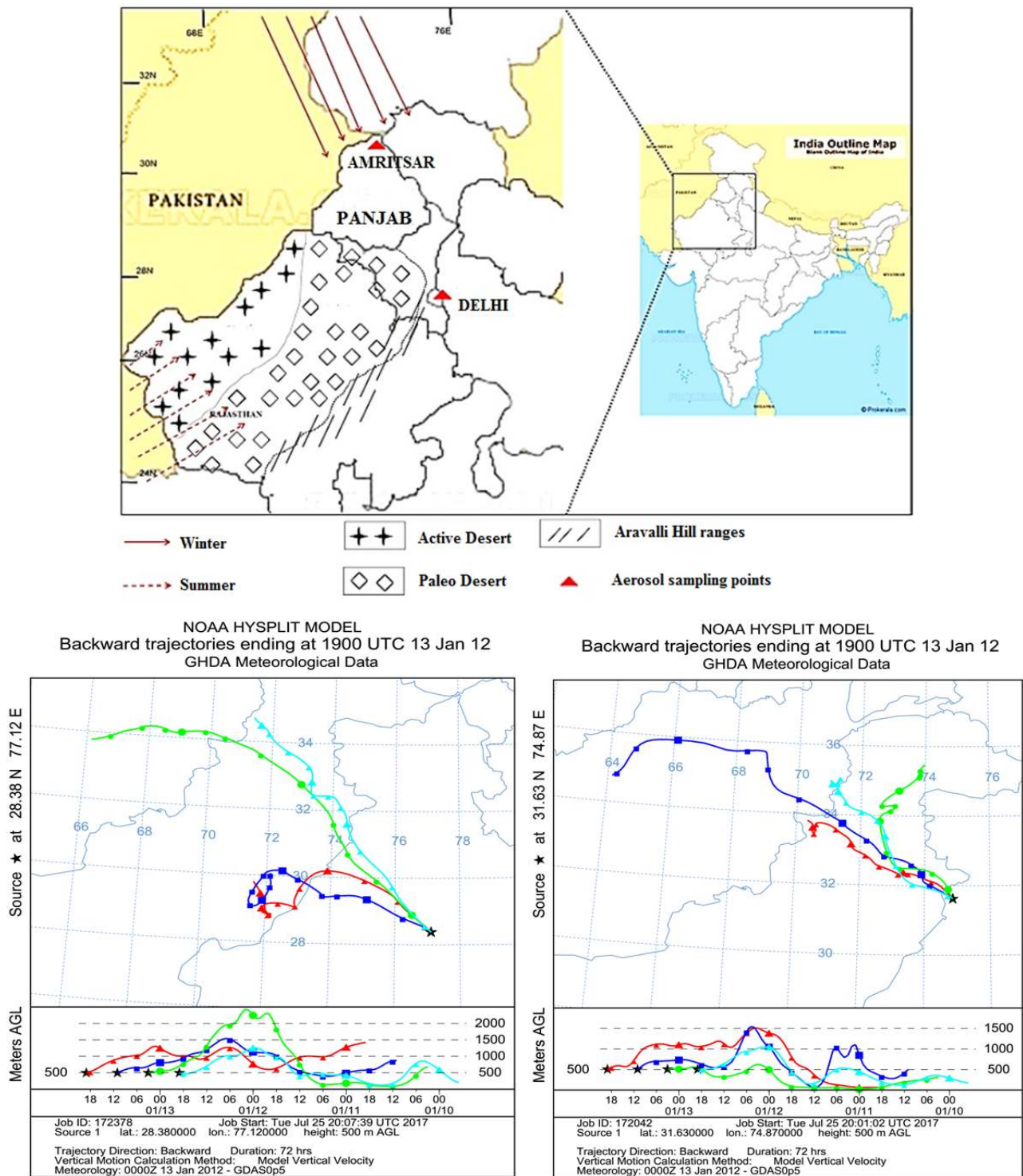


Fig. 1. Study area with wind direction and representative air back trajectories over Amritsar and New Delhi taken from National Oceanic Atmospheric Administration (NOAA; source: Draxler and Rolph, 2013; <http://www.arl.noaa.gov/HYSPLIT.php>).

The deficit could be on account of bicarbonate ions and organic acids not analyzed herein which are otherwise observed in PM_{2.5}. The scatter plots between TC and TA in both size fractions over AMS and DEL are also provided in supplementary Fig. S1.

The OC and EC concentrations were obtained following IMPROVE_A (Interagency Monitoring of Protected Visual

Environment) Thermal/Optical Reflectance (TOR) protocol (Chow *et al.*, 1993) on Desert Research Institute model 2001 Thermal/Optical analyser. A 0.526 cm² punch from the sample filter was heated stepwise in non-oxidising helium (He) atmosphere to obtain OC1, OC2, OC3 and OC4 at temperatures of 140°C, 280°C, 480°C and 580°C, respectively, and in an oxidizing atmosphere of 2% O₂/98%

He to obtain EC1, EC2 and EC3 at 550°C, 700°C, and 800°C along with pyrolyzed organic carbon (PyOC). In IMPROVE_TOR method, OC is operationally defined as OC1 + OC2 + OC3 + OC4 + OP and EC is defined as EC1 + EC2 + EC3 – OP (Chow *et al.*, 2007; Han *et al.*, 2010). EC is further divided into char-EC (EC1 – OP) and soot-EC (EC2 + EC3). All thermograms for OC/EC analysis were split time adjusted. The instrument performance was checked against the internal standards after analyzing every 6 samples. All reported concentrations were corrected for laboratory and field blanks. The analyzer was calibrated with known quantity of methane prior and after the measurements.

RESULTS AND DISCUSSION

PM_{2.5} and PM_{2.5-10} Concentrations

The average mass concentrations of PM_{2.5} and PM_{2.5-10} with minimum, maximum and standard deviation over Amritsar (AMS) and New Delhi (DEL) during winter season 2011–2012 are summarized in Table 1 and plotted in Fig. 2. In general, concentrations of both sized particles were more over DEL compared to AMS site (Table 1). The average PM_{2.5} mass over AMS and DEL was 147.6 µg m⁻³ (range: 51.4–309.8 µg m⁻³) and 357.3 µg m⁻³ (140.8–671 µg m⁻³), respectively. The average PM_{2.5-10} mass over AMS and DEL were 53.15 µg m⁻³ (range: 19.2–109.3 µg m⁻³) and 98.9 µg m⁻³ (range: 16.8–291.9 µg m⁻³), respectively. Average PM_{2.5} mass at both sites exceeded the National Ambient Air

Quality Standards (NAAQS) value of 60 µg m⁻³ for PM_{2.5} and even exceeded the limit of 100 µg m⁻³ for PM₁₀. The highest PM_{2.5} mass over DEL exceeded NAAQS by 11 times while it was 5 times higher over AMS indicating poor air quality for PM_{2.5} at both places. The intermittent lowering of planetary boundary layer and low wind speed could be responsible for such high mass concentrations (Kumar and Yadav, 2016). In addition, intermittent foggy conditions lead to more variations in concentrations during the sampling period. The PM_{2.5} concentration and their percentage contribution to PM₁₀ (sum of both fractions represented as ΣPM₁₀) were higher compared to that of PM_{2.5-10} at both sites. The percentage contributions of PM_{2.5} and PM_{2.5-10} to ΣPM₁₀ over AMS ranged from 56.6% to 84.8% (Avg.: 72.7%) and 15.2% to 43.4% (Avg.: 27.3%), respectively. Similarly, percentage contribution of PM_{2.5} and PM_{2.5-10} to ΣPM₁₀ over DEL ranged from 71.5% to 89.4% (Avg.: 78.5%) and from 10.7% to 28.5% (Avg.: 21.5%). The PM_{2.5}/PM_{2.5-10} mass ratios over DEL and AMS were 3.6 and 2.79, respectively. Such high PM_{2.5} levels could largely be responsible for increasing pulmonary and cardiovascular diseases during winter in this region (Lim *et al.*, 2012).

Water-Soluble Inorganic Ions

The data revealed that PM_{2.5} over AMS was composed (by weight) of WSII (27.35%), OC (20.9%), EC (10.7%) and residual insoluble mass (41.05%). The PM_{2.5} over DEL was composed of WSII (23.68%), OC (12.96%), EC (6.48%)

Table 1. Concentrations of water soluble inorganic ions (in µg m⁻³ units) in winter time PM_{2.5} and PM_{2.5-10} particles collected over New Delhi and Amritsar in north India and their percentage contribution to their total mass concentrations (Load).

	PM _{2.5}					PM _{2.5-10}				
	Min	Max	Average	Std. Dev.	% in load	Min	Max	Average	Std. Dev.	% in load
Amritsar										
F ⁻	0.01	0.09	0.01	0.03	0.006	0.03	0.4	0.14	0.09	0.28
Cl ⁻	0.1	4.14	1.08	1.11	0.69	0.3	9.1	2.3	2.5	4.32
NO ₃ ⁻	0.58	16.98	5.99	4.62	3.87	0.88	6.72	2.01	1.8	3.78
SO ₄ ²⁺	4.49	61.66	23.25	16.09	15.02	0.46	6.14	2.16	1.61	4.06
Na ⁺	0.33	0.99	0.6	0.17	0.38	0.02	0.59	0.19	0.17	0.35
NH ₄ ⁺	0.54	25.61	7.54	6.87	4.87	0.07	5.8	1.31	0.4	2.46
K ⁺	0.98	6.15	2.85	1.44	1.84	0.08	0.74	0.26	0.17	0.49
Ca ²⁺	0.16	4.04	0.91	0.92	0.58	0.52	1.94	1.12	0.42	2.11
Mg ²⁺	0.03	0.41	0.09	0.09	0.05	0.03	0.64	0.12	0.14	0.23
ΣWSII*	9.71	115.11	42.33	28.86	27.35	3.03	27.03	9.84	7.12	18.51
Load	51.42	309.83	154.76	78.78		19.22	109.34	53.15	26.63	
New Delhi										
F ⁻	0.01	0.37	0.1	0.1	0.02	0.04	0.68	0.24	0.16	0.24
Cl ⁻	0.33	19.94	5.27	7.03	1.47	0.49	15.83	4.99	3.91	5.04
NO ₃ ⁻	0.72	7.08	2.49	1.98	0.69	1.34	5.95	3.31	1.41	3.35
SO ₄ ²⁻	10.43	287.74	53.19	67.23	14.88	1.45	16.8	6.49	5.03	6.56
Na ⁺	0.38	5.69	1.38	1.31	0.38	0	0.41	0.28	0.20	0.28
NH ₄ ⁺	0.82	64.03	10.9	7.7	3.05	0.58	4.39	2.36	1.32	2.38
K ⁺	1.13	28.15	7.7	1.7	2.15	0.2	1.06	0.53	0.22	0.53
Ca ²⁺	0.2	10.58	3.06	2.58	0.85	0.4	5.00	2.54	1.22	2.56
Mg ²⁺	0.02	3.8	0.2	0.1	0.05	0.02	1.25	0.25	0.28	0.25
ΣWSII*	21.04	402.19	84.62	78.3	23.68	8.4	39.4	21.01	8.53	21.23
Load	140.76	670.94	357.3	175		16.77	291.91	98.93	59.34	

*ΣWSII represent total sum of all soluble ions.

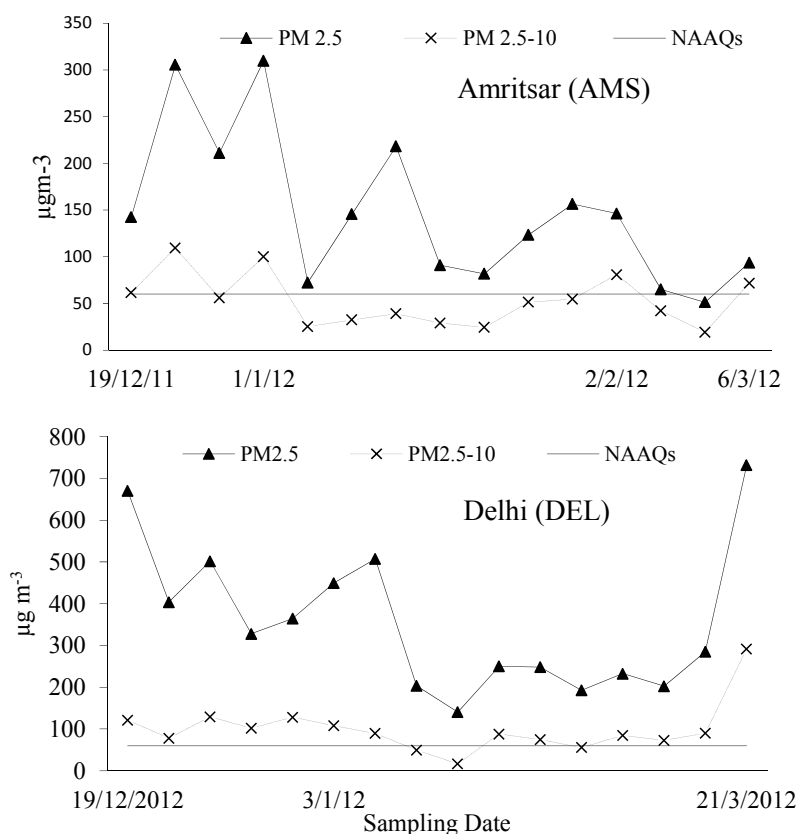


Fig. 2. Mass concentration of $PM_{2.5}$ and $PM_{2.5-10}$ over AMS and DEL on different sampling dates. Horizontal line represents National Ambient Air Quality Standard (NAAQS; $60 \mu\text{g m}^{-3}$ for 24-hr average).

and residual insoluble mass (56.08%). Similar observations are reported over Indian cities such as Ahmadabad (Rengarajan *et al.*, 2011), Kanpur (Behera and Sharma, 2010) and Allahabad (Ram *et al.*, 2012). The mass concentrations of both sized particles were higher over DEL in comparisons to AMS but the percentage contributions of OC and EC were higher over AMS. This indicated the higher contributions of combustion sources to $PM_{2.5}$ over AMS compared to that over DEL. The residual insoluble mass could be representative of crustally derived water insoluble mineral matter. The higher unanalyzed insoluble mass over DEL could be related to contributions by local re-suspension of surface dust of crustal origin (Yadav and Rajamani, 2004; Tandon *et al.*, 2008). Such insoluble material in atmospheric particles could provide the surface for the heterogeneous reactions for formation of secondary ions (Tobo *et al.*, 2010).

Average mass concentrations of WSII with range (minimum and maximum) and standard deviation are summarized in Table 1 and plotted in box and whisker graph in Fig. 3. The soluble ions were more in $PM_{2.5}$ compared to $PM_{2.5-10}$ over both sites (Fig. 3). The average mass concentrations of all soluble ions (\sum WSII) in $PM_{2.5}$ were $42.3 \mu\text{g m}^{-3}$ (27.4% of load) and $84.6 \mu\text{g m}^{-3}$ (23.7% of load) over AMS and DEL, respectively. However, \sum WSII in $PM_{2.5-10}$ was $9.8 \mu\text{g m}^{-3}$ (18.5% of load) and $21.0 \mu\text{g m}^{-3}$ (21.23% of load) over AMS and DEL, respectively. In $PM_{2.5}$, ion concentrations decreased in the order: $\text{SO}_4^{2-} > \text{NH}_4^+ > \text{NO}_3^- > \text{K}^+ > \text{Cl}^- > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{F}^-$ over AMS

and $\text{SO}_4^{2-} > \text{NH}_4^+ > \text{Cl}^- > \text{K}^+ > \text{Ca}^{2+} > \text{NO}_3^- > \text{Na}^+ > \text{Mg}^{2+} > \text{F}^-$ over DEL. For $PM_{2.5-10}$, the order was $\text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Mg}^{2+} > \text{F}^-$ over AMS and $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{NH}_4^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Na}^+ > \text{Mg}^{2+} > \text{F}^-$ over DEL. Kumar *et al.* (2016) reported similar trends of WSII over DEL. The $PM_{2.5}$ compositions over both sites were dominated by SO_4^{2-} followed by NH_4^+ , K^+ and Cl^- . Ca^{2+} and Mg^{2+} remained in low amounts at both sites. Similar trends of sulfate dominance followed by ammonium ions in tropical aerosols over Indian region have been reported by Pavuluri *et al.* (2011). Compared to this, $PM_{2.5-10}$, Cl^- becomes second dominant ion after sulfate and nitrate, calcium showed up along with ammonium ions (Fig. 3). Such compositional changes among two sized particles suggest that they have different sources. It can be observed that $PM_{2.5}$ composition is largely influenced by secondary soluble ions (SSI), i.e., SO_4^{2-} , NH_4^+ followed by K^+ and Cl^- . SO_4^{2-} , NH_4^+ could have formed in ambient atmosphere from their precursor gases SO_2 and NH_3 released from coal combustion, and agricultural fields, livestock/animal breeding and biomass burnings, respectively (Aneja *et al.*, 2012). In northern India, wheat is a major crop and fertilizers such as diammonium phosphate are applied intensively during winter period which coincided with the sampling time of this study. Air back trajectories, passing over agricultural fields before reaching DEL, could also contribute ammonia (Fig. 1). In DEL region, release of NH_3 from vehicular emission during the reduction of NO_x to molecular nitrogen

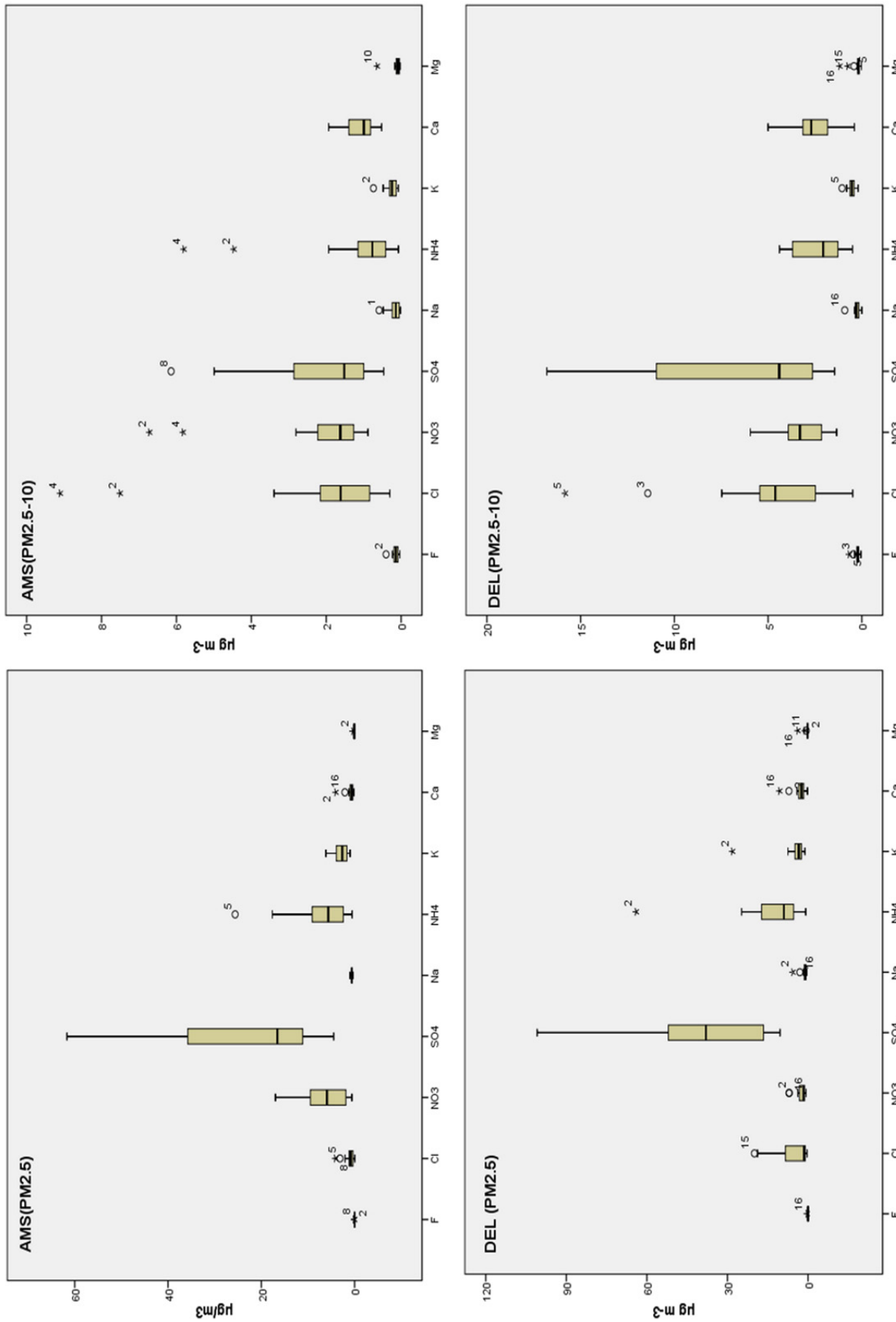


Fig. 3. Mass concentration ($\mu g m^{-3}$) of water soluble inorganic ions (WSII) in $PM_{2.5}$ and $PM_{2.5-10}$ aerosols collected over Amritsar and Delhi [lower line of box indicate 1st quartile i.e., 25% of the data is less than this value; middle line in box represent median or second quartile i.e., 50% data is higher than this value; upper line of box indicate 3rd or 75% quartile i.e., 25% of data is greater than this value; upper and lower whiskers indicate maximum and minimum values excluding outliers; outliers indicate more than 3/2 times higher and lower value than the upper and lower quartile respectively].

in catalytic convertor-fitted vehicles has been reported as potential source of high NH_4^+ in rain water (Yadav and Kumar, 2014). The presence of K^+ in $\text{PM}_{2.5}$ (AMS = $2.8 \mu\text{g m}^{-3}$; DEL = $5.1 \mu\text{g m}^{-3}$) and in $\text{PM}_{2.5-10}$ (AMS = $0.3 \mu\text{g m}^{-3}$; DEL = $0.5 \mu\text{g m}^{-3}$) indicated that biomass and crop residue burning, and direct emissions from vegetation remain possible sources of K^+ (Srinivas and Sarin, 2014). The positive correlation of K^+ with OC (discussed later) further supports these possible sources for K^+ . The high contribution of Cl^- in $\text{PM}_{2.5}$ (AMS = $1.08 \mu\text{g m}^{-3}$; DEL = $5.27 \mu\text{g m}^{-3}$) as well as in $\text{PM}_{2.5-10}$ (AMS = $2.3 \mu\text{g m}^{-3}$; DEL = $4.9 \mu\text{g m}^{-3}$) could be linked to brick kiln industry, and coal and plastic burnings (Kumar *et al.*, 2015; Kumar and Yadav, 2016; Rastogi *et al.*, 2016). In addition, Cl^- is also naturally contributed by sea salt. Chlorine reacts with gases like SO_2 and NO_x and release the HCl which further combines with NH_3 to form NH_4Cl in the ambient atmosphere (Radhi *et al.*, 2010; Tobo *et al.*, 2010).

The $\text{PM}_{2.5-10}$ particles have lower WSII compared to $\text{PM}_{2.5}$ at both sites (Fig. 3). Sulfate is dominant ion followed by Cl^- , NO_3^- and Ca^{2+} and NH_4^+ . This requires explanation as particles in this size range in this region are largely of crustal origin (Yadav and Rajamani, 2004, 2006). It is suggested that the presence of sulfate ions in $\text{PM}_{2.5-10}$ could be via adsorption of finer particles onto larger particles as the secondary ions formed via gas-to-particle conversion are not in this size range. The area around AMS site remain lush green on account of wheat crop and therefore, the concentrations of soluble ions remained low and so was the total $\text{PM}_{2.5-10}$ load over AMS compared to that over DEL. In all cases, the ion concentrations were more in $\text{PM}_{2.5}$ compared to $\text{PM}_{2.5-10}$ and the samples over DEL has higher concentrations compared to those collected over AMS (Fig. 3). This is because of large number of sources of particles at DEL compared to AMS. In addition, DEL is a downwind site which also receives pollutants from upwind region along the wind path.

In order to understand possible sources and chemical transformation, the inter-ionic associations are shown in Fig. 4. Poor correlation among sulfate and nitrates indicated that they are emitted by different source though they carry some linkage over DEL and this remained true for both sized particles (Fig. 4, panels A, C, E and G). A good correlation between ammonium ions and the sum of sulfate and nitrate suggested that formation of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 could represent effective neutralization reactions (Fig. 4, panels B and F). NH_3 plays a significant role in the formation of secondary soluble ions containing ammonium ion in presence of SO_2 , NO_x and constitute major fraction of $\text{PM}_{2.5}$. Stockwell *et al.* (2000) suggested that formations of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 are favored by high humidity and low temperature conditions similar to that observed in our study region during winter season. However, poor correlation among NH_4^+ and NO_3^- suggested that formation of $(\text{NH}_4)_2\text{SO}_4$ is more favored over NH_4NO_3 in the atmosphere (graph not shown). Poor correlation between the sum of Ca^{2+} and Mg^{2+} and SO_4^{2-} suggested that formations of calcium or magnesium sulfate are not preferred neutralization reactions during winters. Overall, this can

be suggested that the soluble ion concentrations are specific to size fractions, the secondary soluble ions dominate in $\text{PM}_{2.5}$ compared to $\text{PM}_{2.5-10}$ and the DEL site is more polluted due to its own emissions and transported materials from upwind areas.

Estimations of OC and EC

Total carbon (TC = OC + EC) was dominated by OC over EC in $\text{PM}_{2.5}$ at both sites (Fig. 5). The OC ranged between $10.4 \mu\text{g m}^{-3}$ to $62.1 \mu\text{g m}^{-3}$ (Avg.: $31.5 \pm 17.2 \mu\text{g m}^{-3}$) while EC ranged between $5.6 \mu\text{g m}^{-3}$ to $27.8 \mu\text{g m}^{-3}$ (Avg.: $15.6 \pm 7 \mu\text{g m}^{-3}$) $\mu\text{g m}^{-3}$ over AMS (Table 2). Compared to AMS data, OC and EC concentrations were higher in $\text{PM}_{2.5}$ over New Delhi and ranged between $16.9 \mu\text{g m}^{-3}$ to $94.7 \mu\text{g m}^{-3}$ (Avg.: 44 ± 19.7) $\mu\text{g m}^{-3}$ and between $3.2 \mu\text{g m}^{-3}$ to $32.7 \mu\text{g m}^{-3}$ (Avg.: $19.3 \pm 7.7 \mu\text{g m}^{-3}$), respectively (Table 2; Fig. 5). In spite of the fact that OC and EC concentrations were higher in $\text{PM}_{2.5}$ over DEL compared to AMS, the percentage contribution of OC and EC to total load was higher at AMS site compared to DEL site. Contribution of OC and EC to the total mass of $\text{PM}_{2.5}$ was 20% and 11.0% over AMS and 13% and 6.5% over DEL (Table 2). This was so because the total mass of $\text{PM}_{2.5}$ was higher over DEL compared to AMS site (Table 1) and hence, similar concentrations of OC and EC would account for less percentage contribution over DEL. The OC and EC could have been contributed by crop residue burning, biomass and coal burning for heating purpose in AMS region (Panicker *et al.*, 2015). The additional sources of OC and EC over DEL include vehicular emissions and coal based thermal power plants. Good linear relationship between OC and $\text{PM}_{2.5}$ mass over AMS ($R^2 = 0.93$; p value < 0.001) indicates the dominant contribution of OC to $\text{PM}_{2.5}$. While moderate relationship between OC and $\text{PM}_{2.5}$ mass ($R^2 = 0.51$; p value < 0.001) over DEL indicated that there could be other sources of $\text{PM}_{2.5}$ over New Delhi. The average EC concentration of $15.6 \mu\text{g m}^{-3}$ and $19.3 \mu\text{g m}^{-3}$ at AMS and DEL, respectively, were higher as compared to other Indian as well as Asian cities (Table 3). However, average OC concentration ($31.5 \mu\text{g m}^{-3}$ at AMS) was comparable to those in Kharagpur and Hisar while average OC concentration ($44 \mu\text{g m}^{-3}$ at DEL) were comparable to those in Kanpur and Allahabad (Table 3). The observed OC concentrations were slightly lower compared to other neighboring Asian cities like Beijing, Dhaka, Lahore and Indian cities like Jaduguda and Kanpur but EC was higher in comparison to those reported from other Indian cities like Mumbai, Ahmedabad, Agra and neighboring Asian cities such as Shanghai, Hangzhou and Tianjin in China and Kaohsiung in Taiwan (Table 3). The difference can be attributed to sampling time and location and to the fact DEL has more vehicular emissions as compared to other Asian cities.

The OC includes both primary organic carbon (POC) and secondary organic carbon (SOC) but direct estimation of SOC is not possible in the EC–OC analyzer. Therefore, POC was calculated following the “EC tracer method” based on the assumption that EC being exclusively primary in origin and that EC and POC have common emission sources (Lim and Turpin, 2002).

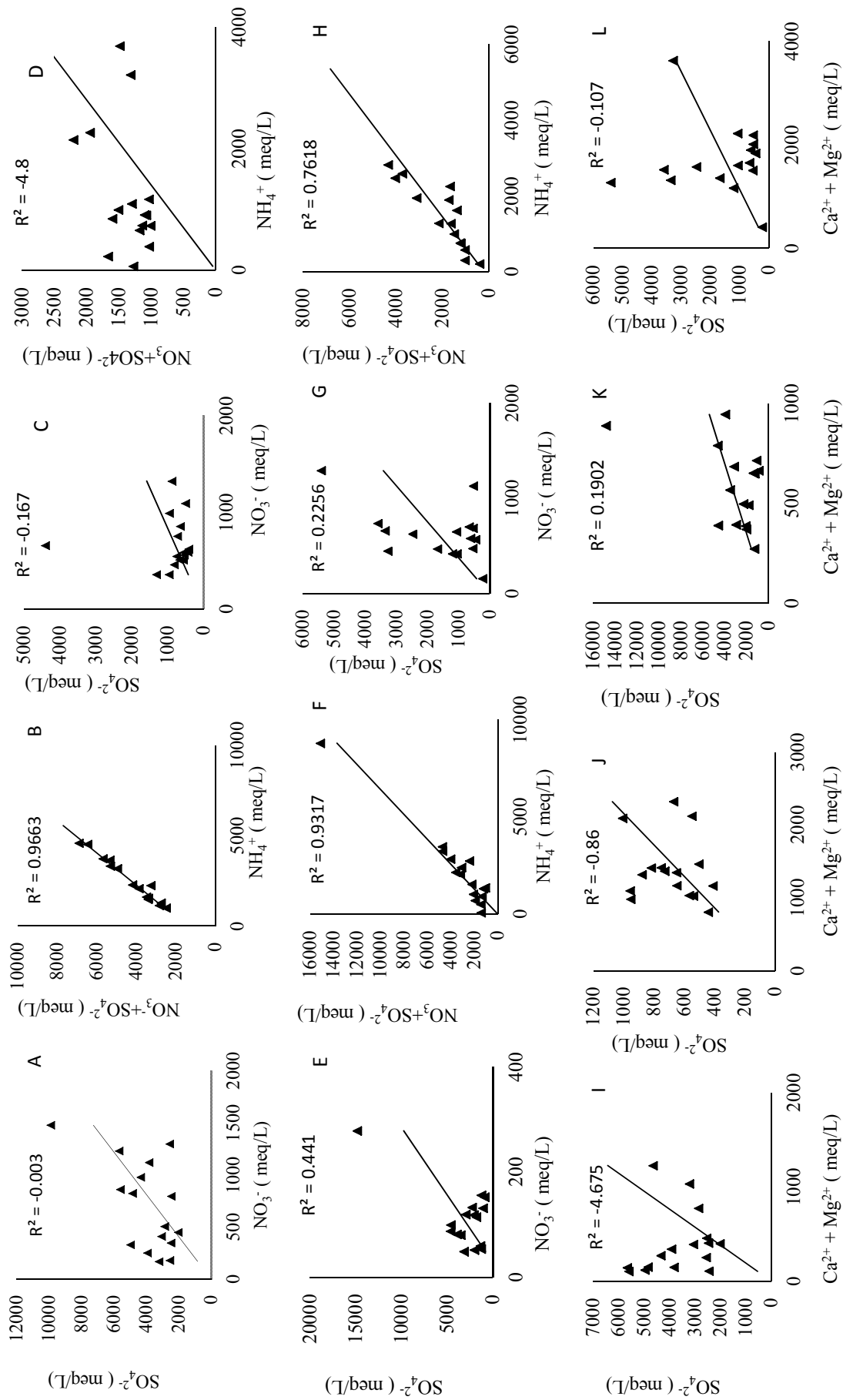


Fig. 4. Correlation between different soluble ions over (A, B, I = $\text{PM}_{2.5}$; C, D, J = $\text{PM}_{2.5}$; E, F, K = $\text{PM}_{2.5}$; G, H, L = $\text{PM}_{2.5-10}$) Delhi.

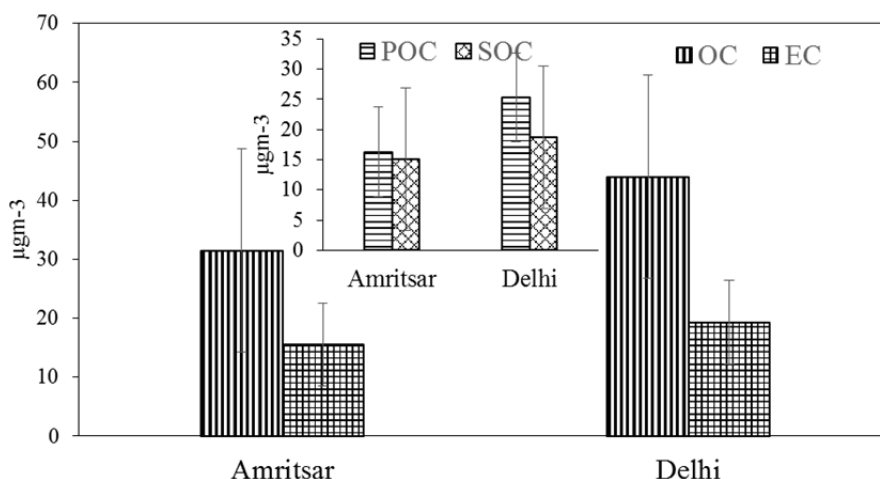


Fig. 5. Average mass concentrations (μgm^{-3}) of OC, EC, POC and SOC in $\text{PM}_{2.5}$ aerosols over Amritsar and New Delhi.

$$\text{SOC} = (\text{OC})_{\text{tot}} - \text{POC} \quad (1) \quad \text{PM}_{2.5} \text{ over AMS compared to that over DEL.}$$

$$\text{POC} = [(\text{OC}/\text{EC})_{\text{min}} \times \text{EC}] \quad (2)$$

Castro *et al.* (1999) suggested the use of minimum value of OC/EC ratio in SOC calculations which was 1.01 at AMS and 1.27 at DEL. SOC was estimated by subtracting POC from OC as measured in the EC–OC analyzer (Table 5). The concentrations and percentage contributions of POC and SOC in OC are summarized in Table 2 and shown in Fig. 5. Like OC, POC was more at DEL compared to AMS. Though POC was higher than SOC but SOC did show good proportion in OC at both sites (Fig. 5, Table 2). Kumar and Yadav (2016) have also reported SOC contribution to OC in PM_{10} during winter compared to summer over DEL. The SOC is formed via photochemical reactions in ambient atmosphere and presence of particles does help in this transformation. But photochemical reactions may not be possible pathways for SOC formation due to poor sunlight during winters in this region. Thus, SOC could be formed via condensation/cooling of hot vapors of organic volatile organic compounds released during biomass and coal and plastic combustion by general public to get rid of near zero cold conditions. Direct emission from sources such as fossil fuel combustion, vehicle and biomass burning could be possible sources of POC (Singh *et al.*, 2016; Kumar and Yadav, 2016; Kumar *et al.*, 2016; Kumar *et al.*, 2017).

Total carbonaceous matter (TCM) was calculated as

$$\text{TCM} = \text{Organic matter (OM)} + \text{Elemental matter (EM)} \quad (3)$$

where $\text{OM} = \text{OC} \times 1.6$ and $\text{EM} = \text{EC} \times 1.1$.

These factors of 1.6 and 1.1 for the calculation of OM and EM, respectively, has been widely used and accepted for urban aerosols (Turpin and Lim, 2001; Cao *et al.*, 2003; Gu *et al.*, 2010). The average TCM contributed 44.1% and 27.4% of the total $\text{PM}_{2.5}$ over AMS and DEL, respectively (Table 2). The contribution of OM in TCM is double compared to EM due to higher concentration of OC and the conversion factor. Again the higher contribution of TCM to total $\text{PM}_{2.5}$ is linked to lower total concentrations of

Diagnostic Ratios and Source Apportionment

The average OC/EC ratios were 2.0 at AMS and 2.8 at DEL (Table 2), similar to those reported from other cities such as Mumbai, Dhaka and Shanghai (Table 4). Low values of OC/EC suggested that anthropogenic emission were dominated mainly by fossil fuel combustion while this ratio for biomass burning ratio is expected to be higher (~8) (Rengarajan *et al.*, 2011). Data summarized in Table 4 give overview of comparison of various diagnostic ratios calculated in this study with other Indian cities. Several studies have used $\text{nss-K}^+/\text{OC}$ as diagnostic proxy for emission from biomass burning. It varied from 0.07 to 0.14 in our study over AMS (Avg.: 0.09 ± 0.02) and from 0.05 to 0.45 over DEL (Avg.: 0.11 ± 0.09) and were similar to those reported in literature with range from 0.02 to 0.15 (Table 4). The $\text{nss-K}^+/\text{EC}$ ratio in the range of 0.21–0.46 have been reported for biomass burning and lower values (0.025–0.09) for fossil fuel combustion (Andreae and Gelenser, 2006). The higher $\text{nss-K}^+/\text{EC}$ values over DEL compared to AMS could be due to higher K^+ concentrations. The $\text{nss-K}^+/\text{EC}$ ratio was lower in present study in comparison to other studies conducted over different Indian cities like Patiala, Kharagpur, Agra, Ahmedabad, Kanpur, Allahabad except Hisar (Table 4). This could be linked to higher EC emission over DEL compared to other studies reported in Table 4. The $\text{nss-SO}_4^{2-}/\text{EC}$ ratios were relatively lower than those reported elsewhere (Table 4). This could be due to higher EC observed in $\text{PM}_{2.5}$ over two sites compared to other cities (Table 3). Ramana *et al.* (2010) used ration of BC to sulfate to understand the net warming effect of aerosols and recorded this ratio in the range of 0.02–0.06 for three Chinese cities. They further suggested that the warming effect of BC is more when it is internally mixed with sulfate aerosols which appear to be a case in this study as well. The BC to sulfate ratio was 0.67 and 0.34 over AMS and DEL in this study which suggest that the aerosols are expected to result net warming in the region.

Further, the good correlation between OC and EC indicates their similar/common sources while poor correlation

Table 2. Concentrations organic carbon (OC) and elemental carbon (EC) in $\mu\text{g m}^{-3}$ units of in winter time $\text{PM}_{2.5}$ particles collected over Amritsar and New Delhi in north India.

	Amritsar						Delhi					
	Min	Max	Average	Std. Dev.	% in load	Min	Max	Average	Std. Dev.	% in load		
OC	10.44	62.14	31.48	17.21	20.19	16.93	94.69	44	19.65	12.96		
EC	5.55	27.83	15.56	7.03	10.74	3.2	32.74	19.33	8	6.48		
TC	16.7	84	47.04	23.4	30.9	25.9	122.6	63.3	25.1	19		
POC ^a	5.8(33.3)*	29.2(78.2)*	16.3(57.3)*	7.4(18.2)*	11.3(11.2)*	4.2(9.9)*	42.8(71.5)*	25.3(61.2)*	10.5(21.6)*	8(7.9)*		
SOC ^b	3.9(21.7)*	39.1(66.6)*	15.1(42.7)*	11.8(18.2)*	8.9(8.9)*	0.12(28.5)*	58.1(90.1)*	18.7(38.6)*	16.3(21.6)*	5(4.9)*		
OM ^c	16.71	99.42	50.37	27.53	32.31	27.09	151.5	70.4	31.4	20.7		
EM ^d	6.1	30.6	17.1	7.7	11.8	3.4	36	21.3	8.8	7		
TCM ^e	23.6	123.5	67.5	34.2	44.1	37	182	91.7	37.1	27.4		
OC/EC	1	3.2	2	0.59		1.3	13.2	2.9	2.8			
TC/EC	2.1	4.1	3	0.6		2.3	14.2	3.8	2.8			
Char-EC	5.4	27.9	15.30	6.9		1.5	32.4	18.9	8.1			
Soot-EC	0.81	0.08	0.26	0.19		0.1	1.8	0.4	0.3			

^a $(\text{OC}/\text{EC})_{\text{pri}} = (\text{OC}/\text{EC})_{\text{min}} \times (\text{EC})$; ^b $(\text{OC})_{\text{sec}} = (\text{OC})_{\text{tot}} - (\text{OC})_{\text{pri}}$; ^c Organic matter (OM) = $1.6 \times \text{OC}$; ^d Elemental matter (EM) = $1.1 \times \text{EC}$; ^e Total Carbonaceous materials (TCM) = OM + EM; * indicates the % Contributions of POC and SOC to organic carbon (OC) in brackets. char-EC = EC1, soot-EC = EC2 + EC3.

Table 3. Comparison of OC and EC data of present study with previous studies reported from India and other Asian countries.

City	Period	OC	EC	OC/EC	Sample Type	Measure Method	Reference
Amritsar, India	Winter 2011–12	31.48	15.56	2.00	$\text{PM}_{2.5}$	IMPROVE TOR	This study
Delhi, India	Winter 2011–12	44.00	19.65	2.86	$\text{PM}_{2.5}$	IMPROVE TOR	This study
Mumbai, India		25.3	12.6	2			Venkataraman et al. (2002)
Kharagpur, India	Winter 2009–2010	30.7	4.5	7		TOT	Srinivas and Sarin (2014)
Ahmedabad, India	2002	12.8	2.1	8.3		TOT	Rastogi and Sarin (2009)
Hisar, India	Dec, 2004	30.9	3.8	8.5	TSP	TOT	Rengarajan et al. (2007)
Agra, India	May 2010–April 2011	22.8	3.4	6.6	$\text{PM}_{2.5}$	TOT	Pachauri et al. (2013)
Jaduguda, India	Dec, 2004	35.3	11.6	3.1	TSP	TOT	Ram and Sarin (2010)
Allahabad, India	Dec, 2004	49	6.2	8.1	TSP	TOT	Ram and Sarin (2010)
Kanpur, India	Jan–March 2007	25	4.8	6.2	TSP	TOT	Ram and Sarin (2010)
Dhaka, Bangladesh		46	22	2.1			Salam et al. (2003)
Lahore, Pakistan		110	18	5.6			Hussain et al. (2007)
Kaohsiung, Taiwan	Nov 1998–April 1999	14.5	6.1	2.4	PM_{10}	Elemental Analyser	Lin and Tai (2001)
Beijing, China	Winter 2002	36.7	15.2	3.5	$\text{PM}_{2.5}$	Elemental Analyser	Dan et al. (2004)
Tianjin, China	Winter, 2008	22.9	5.6	3.8	$\text{PM}_{2.5}$	IMPROVE TOR	Gu et al. (2010)
Xi'an, China	Winter, 2003	61.9	12.3	5.1	$\text{PM}_{2.5,6}$	IMPROVE TOR	Cao et al. (2005)

Table 4. Comparison of diagnostic ratios calculated in the present study with previous studies from different cities in India.

Sites	Time period	OC/EC	TC/EC	nss-K ⁺ /OC	nss-K ⁺ /EC	nss-SO ₄ ²⁻ /EC	References
Amritsar	Winter 2011–12	2.00 ± 0.59	2.91 ± 0.58	0.09 ± 0.02	0.17 ± 0.03	1.83 ± 1.11	This study
Delhi	Winter 2011–12	2.86 ± 2.8	3.81 ± 2.79	0.11 ± 0.09	0.29 ± 0.36	2.92 ± 3.6	This study
Patiala	Oct–Nov	11.0 ± 2.0	N.A.	0.06 ± 0.00	N.A.	N.A.	Rajput et al. (2014)
Patiala	April–May	3.0 ± 0.4	N.A.	0.14 ± 0.01	N.A.	N.A.	Rajput et al. (2014)
Kharagpur	Nov-09–Mar-10	7.0 ± 2.2	8.0 ± 2.2	0.07 ± 0.04	0.49 ± 0.22	3.9 ± 2.1	Srinivas and Sarin (2014)
Agra	10-Dec	6.6 ± 2.8(PM _{2.5})	N.A.	0.15 ± 0.11	0.52 ± 0.27	N.A.	Pachauri et al. (2013)
Agra	May–June 10	6.9 ± 3.6 (TSP)	N.A.	0.02 ± 0.01	0.37 ± 0.27	N.A.	Pachauri et al. (2013)
Ahmedabad	7-Dec	6.2 ± 0.8	N.A.	~0.05	~0.30	~3.20	Rengarajan et al. (2011)
Kanpur	8-Oct	N.A.	N.A.	0.06 ± 0.02	0.28 ± 0.10	N.A.	Ram and Sarin (2010)
Allahabad	4-Dec	8.1	N.A.	0.05 ± 0.01	0.44 ± 0.11	N.A.	Ram and Sarin (2010)
Hisar	4-Dec	8.5 ± 2.2	0.07 ± 0.02	0.63 ± 0.19	3.9 ± 2.1	N.A.	Rengarajan et al. (2007)

suggests different sources (Ram and Sarin, 2010). A good correlation between OC and EC over AMS suggested that they have common sources where multiplicity of their sources resulted in very poor correlation over DEL (Fig. 6). The nss-K⁺ is used as indicator of biomass burning and its significant correlation with OC ($R^2 = 0.85$) over AMS suggested contribution of biomass burning while relatively lower R^2 value of 0.74 over DEL suggested that other sources such as vehicular emission, road dust, industrial emission of OC (Fig. 6) (Ram and Sarin, 2011). Good correlation among K⁺ and EC and OC over AMS could suggest that biomass burning contribute both OC and EC where as a poor correlation between K⁺ and EC over DEL suggested that they have different sources. The other studies have used EC/TC ratio to differentiate between contributions from biomass burning and fossil fuel (Lim et al., 2012; Kumar et al., 2017). This ratio was consistently higher than 0.2 at both sites suggesting the dominance of fossil fuel contributions. However, these observations should be read with caution as OC included in TC had 42.7% and 38.6% contribution from SOC over AMS and DEL, respectively.

Analysis of Carbon Fractions

Percentage contributions of eight carbon fractions (OC1, OC2, OC3, OC4, EC1, EC2, EC3 and OP) to TC in PM_{2.5} over AMS and DEL are plotted in Fig. 7. Each of these operationally defined carbon fractions have different sources and therefore, can be used as an indicator of source(s) (Chow et al., 2004; Han et al., 2010). OC1 indicates the presence of volatile organic carbon and biomass burning. OC2 is contributed by coal combustion while OC3 and OC4 are indicative of road dust (Cao et al., 2005). EC1, also termed as char-EC, indicates emissions from biomass burning and other low temperature burnings (Cao et al., 2005) while EC2 and EC3, jointly termed as soot-EC, are contributed by high temperature combustion processes (coal combustion and vehicular emissions) and can also come via gas-to-particle conversion (Han et al., 2010). OP fraction is related to presence of polar organic compounds. At both sites OC2 and OC3 contributed nearly 17–18% in comparison to 4% or less contribution each by OC1 and OC4 (Fig. 7). Among the EC fractions, char-EC (EC1) was significantly higher (30–33%) than soot-EC (EC2 and EC3) at both sites (Fig. 7). Higher OC2 and OC3 indicated the contributions from coal combustion and road dust. Speciation of carbon fractions indicated that diffused sources contribute more to OC and low temperature combustion processes were dominant contributor to EC compared to high temperature combustion.

Elemental Distribution

The statistical data on elemental concentrations in $\mu\text{g m}^{-3}$ units in the residue of water-soluble fraction of PM_{2.5} and PM_{2.5-10} over AMS and DEL are provided in Table 5. Among major elements Al was most abundant followed by Ca, Ti and Mn in both sized particles and at both sites. This trend is conformity with previous finding on PM₁₀ in this region (Yadav and Rajamani, 2004, 2006). These elements are largely of crustal origin and are contributed to very limited

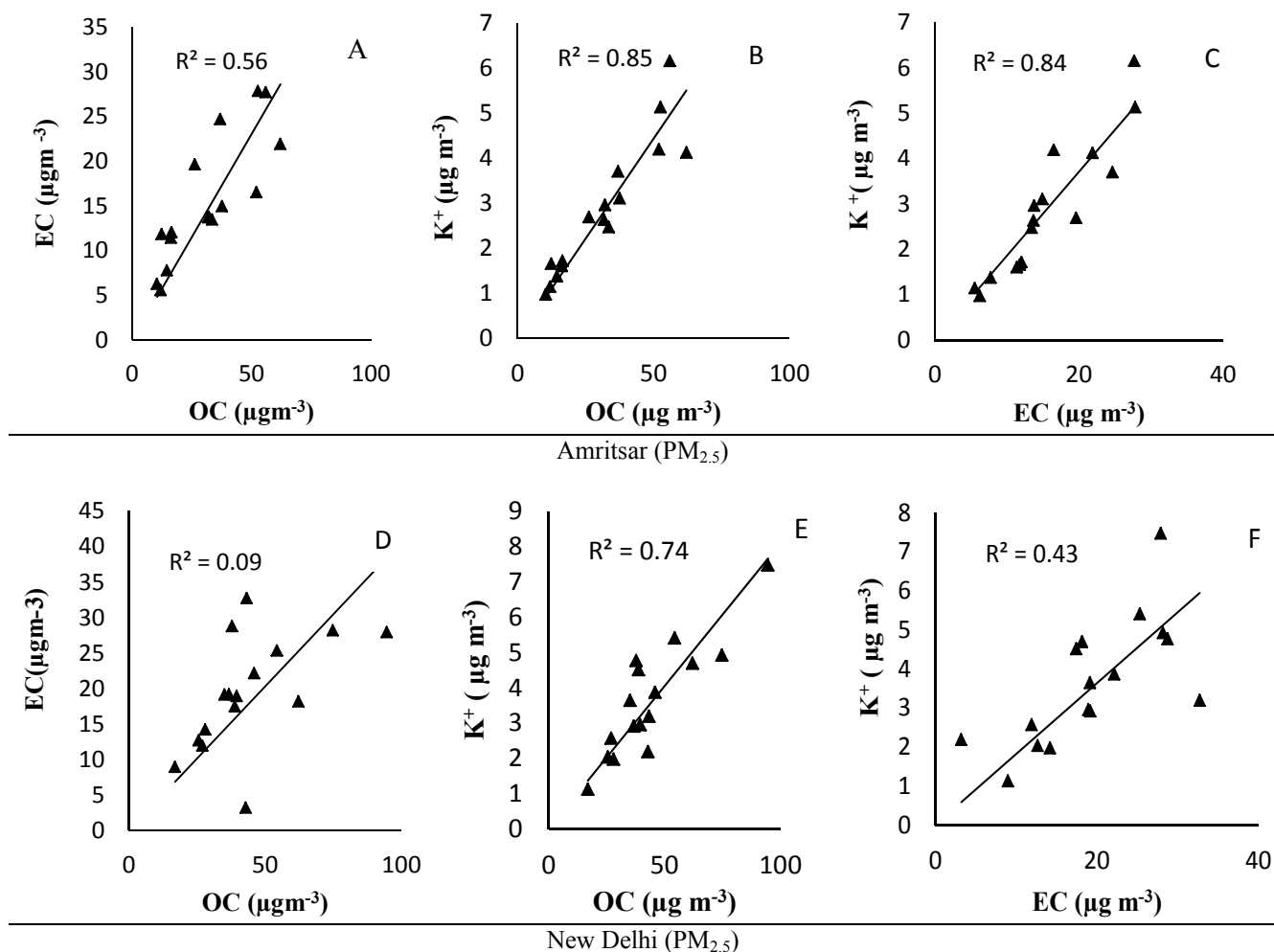


Fig. 6. Correlation between OC, EC and K⁺ over (A, B and C) Amritsar and (D, E and F) New Delhi.

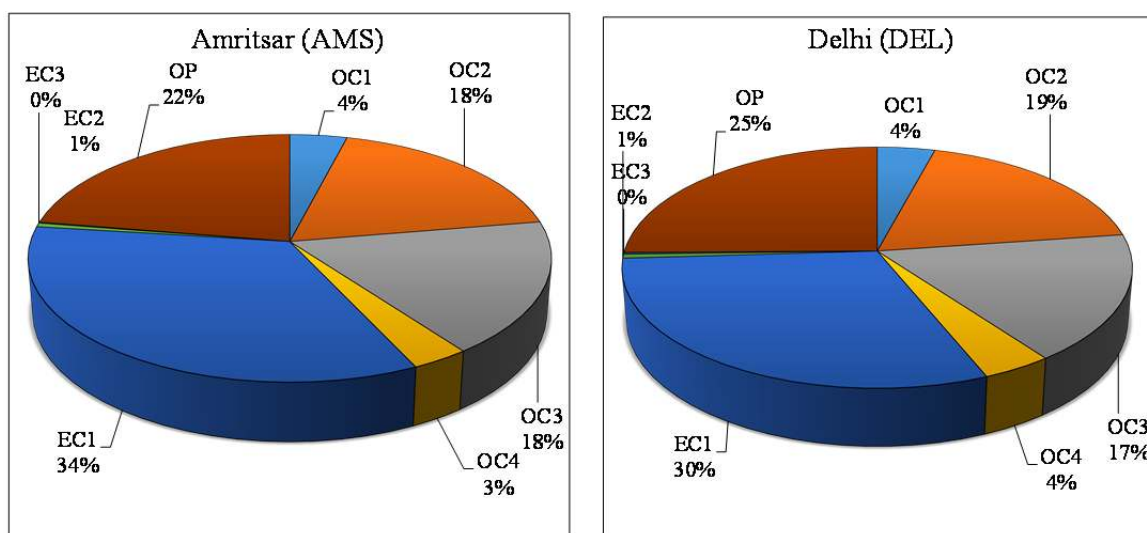


Fig. 7. Percentage contributions of eight carbon fractions to the total carbon content in PM_{2.5} collected over Amritsar and New Delhi.

extent by anthropogenic sources. Their concentrations are lower in PM_{2.5} compared to that in PM_{2.5-10}, an observation true for both sites. This suggested that PM_{2.5} have lower

contribution from crustal sources compared to other fraction. The DEL samples have higher elemental concentrations compared to that over AMS suggesting that the crustal

contribution are more over DEL. Re-suspension on account of large number of vehicular movement and availability of loose material along road sites could be a possible explanation. The re-suspension activity is limited over AMS due to limited number of vehicles and scarcity of loose material due more vegetation and greenery around the AMS site. The concentrations of trace elements were high in PM_{2.5} compared to PM_{2.5-10} and the variability among two sized particles and two sites was more (Table 5). Lead and zinc were most abundant compared to other trace elements. We tried to look into the crustal component comparing the sample Ca/Al ratio with that in Upper Continental Crust (UCC ratio = 0.38; McLennan, 2001). This ratio in PM_{2.5} over AMS and DEL was 0.87 and 0.53, respectively. The Ca/Al ratio in PM_{2.5-10} confirms with the UCC ratio over AMS and was lower (0.29) over DEL. This suggested that PM_{2.5} have more contributions of calcium carbonates compared to PM_{2.5-10} which is expected to have more contributions of aluminosilicate minerals. In northern India Ca/Al ratio has been reported in the range of 0.73–1.74 (Kumar and Sarin, 2009; Sudheer and Rangarajan 2012). The straight comparison with previous work is difficult to make due to the sample digestion protocols. Here the concentrations are on complete digestion basis compared to leaching procedures used in previous studies.

Further, the enrichment ratio (ER) of elements in two sized particles over two sites were calculated to differentiate between natural (crustal) and cultural (anthropogenic) sources. Aluminum is a common indicator of crustal sources and has limited mobility in geochemical systems (Yadav and Rajamani, 2004). ER of an element is the ratio of concentration of the element X in the samples to that in UCC, both normalized with their respective Al concentration. The ERs were calculated as:

$$ER = (C_{Xs}/Al_s)/(C_{XC}/Al_C) \quad (4)$$

where C_{Xs} and C_{XC} are the concentrations of element X in

the sample and UCC, respectively. Similarly, Al_s and Al_C represent the concentrations of Al in the sample and UCC, respectively. The ERs of all elements are provided in Table 6 and those having high ER have been plotted in Fig. 8. Among major elements only Ca shows enrichment except PM_{2.5-10} over DEL. The ER value of less than 1 for Al, Fe, Mn, Ti and in some cases Ca is due to the dilution effect of silica. Compared to UCC, the sediments in northern India have high silica and result in dilution in the concentrations of other major elements (Tripathi and Rajamani, 1999; Yadav and Rajamani, 2004). All trace elements, except Cd, Co and Ba showed significantly high ER in both sized particles and both sites (Table 6; Fig. 8). High ER of trace elements over DEL site compared to AMS indicated high degree of pollution over DEL. Pb showed highest ER of 63 and 45 followed by Cu (18 and 6) and Zn (13 and 6) in PM_{2.5} and PM_{2.5-10}, respectively, over DEL. Though usage of Pb in petrol has been phased out in India but the lead present in the surface dust could be possible source in aerosols (Pathak *et al.*, 2013). Zn finds its source through abrasion of vehicular parts such as tyres and brake pads (Yadav and Rajamani, 2006). High ER of Zn over AMS in both sized particles could be due to transported particles from upwind site in Pakistan region. The enrichment of Ba in particles suggested the anthropogenic contributions via vehicular emissions as the surface material in this region are of Himalayan origin and are inherently depleted in Ba (Tripathi and Rajamani, 1999). Ba and Zn shows good correlation with R² value of 0.9 and 0.7 in PM_{2.5} and PM_{2.5-10} over DEL suggesting their sources as vehicular emissions as has also been suggested by Morawska and Zhang (2002) and Yadav and Rajamani (2006). Cu showed ER of more than 10 and 5 in PM_{2.5} and PM_{2.5-10}, respectively, over both sites. PM₁₀ in DEL has been reported to have significantly high (26,000 PPM) Cu on account of electrical wire burnings and transport processes (Yadav and Rajamani, 2003). The ERs of Cr were less than 5 over both sites. The ER reported here in two sized particles over two cities are lower than those

Table 5. Elemental concentrations (in ng m⁻³ units) in winter time PM_{2.5} and PM_{2.5-10} particles collected over Amritsar and New Delhi in north India.

	Amritsar				New Delhi			
	PM _{2.5}		PM _{2.5-10}		PM _{2.5}		PM _{2.5-10}	
	Aver	Std	Aver	Std	Aver	Std	Aver	Std
Al *	7.0	3.7	4.6	2.4	36.6	28.2	14.5	9.1
Ca*	6.1	2.1	1.8	1.2	19.5	14.2	4.3	3.4
Fe *	0.7	0.3	1.4	0.7	6.2	8.0	3.8	2.2
Ti *	0.1	0.2	0.1	0.1	0.7	0.8	0.4	0.2
Mn*	0.02	0.01	0.02	0.01	0.1	0.1	0.08	0.08
Ba	52.4	38.8	14.0	11.3	200.9	151.0	70.6	54.4
Cd	1.3	0.9	0.9	1.6	8.4	9.8	2.7	5.4
Co	0.5	0.6	0.6	0.4	85.5	129.5	449.2	627.1
Cr	9.3	6.7	5.2	4.8	53.9	46.0	25.9	26.2
Cu	18.5	11.6	6.1	3.8	133.0	118.2	37.2	30.9
Pb	342.9	303.0	40.6	37.7	536.5	382.3	201.3	272.9
Sr	38.2	28.1	4.6	3.0	129.9	100.7	17.6	15.4
Zn	159.8	117.2	54.6	37.2	291.9	307.2	156.7	101.4

* = μg m⁻³.

Table 6. Enrichment ratio (ER) of elements in PM_{2.5} and PM_{2.5-10} collected over Amritsar and New Delhi in north India.

	Amritsar				New Delhi			
	PM _{2.5}		PM _{2.5-10}		PM _{2.5}		PM _{2.5-10}	
	Aver	std	Aver	std	Aver	std	Aver	std
Ca	2.5	0.6	1.1	0.5	1.7	0.8	0.7	0.3
Fe	0.3	0.1	0.7	0.3	0.3	0.2	0.6	0.2
Ti	0.6	0.8	0.8	0.2	0.5	0.2	0.8	0.2
Mn	0.4	0.2	0.5	0.3	0.5	0.3	0.7	0.3
Ba	1.4	0.5	0.4	0.2	1.1	0.5	0.3	0.3
Cd	0.2	0.1	0.1	0.2	0.3	0.4	0.6	0.6
Co	0.7	0.3	1.1	0.6	0.6	0.4	0.5	0.5
Cr	3.9	0.8	2.5	1.7	4.4	2.2	2.0	2.0
Cu	11.1	6.7	4.7	3.2	18.5	16.3	5.7	5.7
Pb	2.0	1.2	1.1	0.6	63.2	40.4	45.7	45.7
Sr	2.0	1.2	1.1	0.6	1.2	0.6	0.1	0.1
Zn	31.2	15.7	14.2	9.1	13.0	9.0	6.2	6.2

ER = $(C_{Xs}/Al_s)/(C_{XC}/Al_C)$, where C_{Xs} and C_{XC} are the concentration of element X in the sample and upper continental crust (UCC), respectively. Similarly Al_s and Al_C represent the concentration of Al in the sample and UCC, respectively (UCC values are taken from McLennan, 2001).

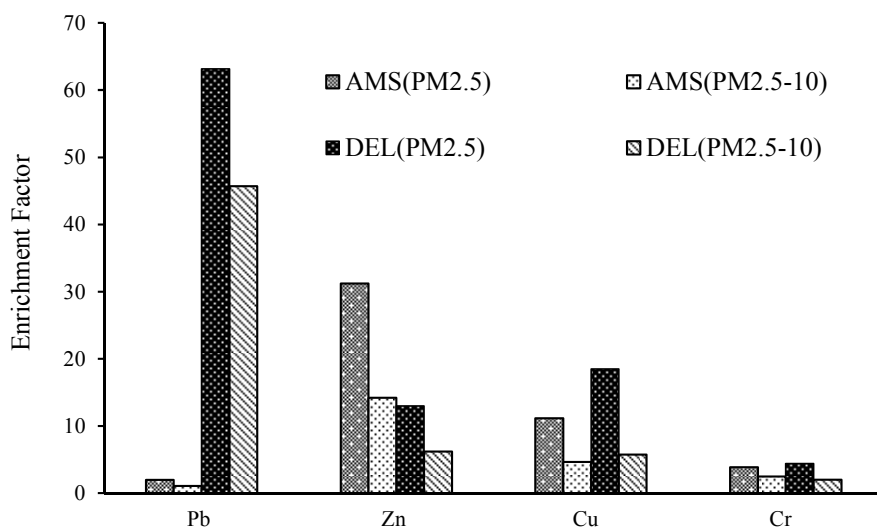


Fig. 8. Enrichment ratio (ER) of elements PM_{2.5} and PM_{2.5-10} over AMS and DEL. ER = $(C_{Xs}/Al_s)/(C_{XC}/Al_C)$, where C_{Xs} and C_{XC} are the concentration of element X in the sample and upper continental crust (UCC), respectively. Similarly Al_s and Al_C represent the concentration of Al in the sample and UCC, respectively (UCC values are taken from McLennan, 2001).

reported by Lee and Hieu (2011) in Korea, Vasconcellos *et al.* (2007) in Brazil and Sudheer and Rangarajan (2012) over Ahmedabad in India. These observations suggested that anthropogenic contributions were more over DEL compared to AMS.

Overall, the fine and coarse particles chemistry differs between the two sampling sites having similar meteorological conditions. To compare the two sites, coefficient of divergence (CD) was calculated following the equation:

$$CD_{mn} = \sqrt{\frac{1}{p} \sum_{i=1}^p \left(\frac{X_{im} - X_{in}}{X_{im} + X_{in}} \right)^2} \quad (5)$$

where m and n represent two sampling sites, X_{im} and X_{in} represent the average concentration of chemical constituent

i at site m and n, respectively. P is the total number of chemical constituents considered while calculating the CD. CD is self normalized dimensionless qualitative measure of homogeneity/heterogeneity in particle chemistry between the two sampling sites and can be used for short-term or long-term measurements over spatial distributed sampling sites (Shen *et al.*, 2011, and more references therein). The near to zero value of CD indicate homogeneity in the chemical constituents of particles over two sites, i.e., two sites are similar for the studied chemical species, and the values of CD approaching unity would indicate heterogeneity, i.e., the particle composition are very different at two sampling sites. Here, a total of 25 chemical constituents (OC, EC, TC, Al, Fe, Ca, Mn, Ti, Ba, Co, Cd, Cu, Cr, Sr, Pb, Zn, SO_4^{2-} , NH_4^+ , NO_3^- , K^+ , Cl^- , Ca^{2+} , Mg^{2+} , Na^+ , F^-) were considered for calculating CD between AMS and DEL

sites. The CD value of 0.57 and 0.52 for fine and coarse particles, respectively, indicated that the particle composition is different at two locations. The differences could be attributed to the geographical settings of two sites. The site specificity of sources of PM_{2.5} and PM_{2.5-10} introduces this heterogeneity in particle chemistry. Re-suspension of crustally derived surface dust and vehicular emissions dominates over DEL whereas low combustion processes dominate over AMS.

CONCLUSIONS

Air quality was very poor throughout the winter season at both locations. The highest PM_{2.5} load over DEL and AMS exceeded NAAQS by 11 times (a 24-hr average value of 60 µg m⁻³) and 5 times, respectively. The PM_{2.5} was composed of WSII (25.8%), OC (32.3%), EC (10.7%), and unanalyzed insoluble mass (39.4%) over AMS and of WSII (24.2%), OC (20.7%), EC (6.5%), and unanalyzed insoluble mass (58.8%) over DEL. The PM_{2.5} composition over both sites was dominated by the secondary soluble ions SO₄²⁻ and NH₄⁺. Ca²⁺ and Mg²⁺ remained low because of limited dust contributions due to low wind speed. SO₄²⁻ and NH₄⁺ may have formed in the ambient atmosphere from their precursor gases, SO₂ and NH₃, being released from coal combustion, and agricultural fields, livestock/animal breeding, and biomass burnings, respectively. Biomass burning, and low temperature coal and plastic burning contributed K⁺ and Cl⁻, respectively. The SSI in PM_{2.5-10} could be due to the adsorption of finer particles onto larger ones, as the secondary ions formed via gas-to-particle conversion do not belong in this size range.

Crop residue burning, and biomass and coal burning for heating purposes were the dominant sources of OC and EC in PM_{2.5}. Additional sources of OC and EC over DEL included vehicular emissions and coal based thermal power plants. The average TCM contributed 44.12% and 27.42% of the total PM_{2.5} over AMS and DEL, respectively. Although biomass burning is a significant source of carbon emissions, the speciation of carbon fractions indicated that diffused coal combustion contributed more to the OC and low temperature combustion processes dominated over high temperature ones.

The Al normalized ratios of elements in the samples compared to the crust were higher in PM_{2.5} than PM_{2.5-10}. Fe, Ti, and Mn ratios of < 1 were attributed to the silica dilution effect. The Pb, Cu, and Zn ratios in PM_{2.5} were 63, 18, and 13 over DEL and 2, 11, and 31 over AMS, respectively. Ba and Zn were contributed by vehicular emissions. CD values of 0.57 and 0.52 for fine and coarse particles, respectively, indicated that the particle composition differs at the two locations. Although the sources of particles are largely the same, their respective contributions in a size fraction vary due to the location and the level of urbanization. Compared to AMS, DEL receives additional pollution from upwind regions. The re-suspension of crustally derived surface dust, and vehicular emissions dominate the atmosphere above DEL, whereas emissions from low combustion processes dominate the atmosphere over AMS. Such levels of PM_{2.5}

could be largely responsible for the increased rate of pulmonary and cardiovascular disease during winter in this region.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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