Investigating daytime and night-time differences with the seasonal trend and sources of inorganic fine aerosols in Indo-Gangetic plain

S CHANDRA^{1,3}, M J KULSHRESTHA^{1,*}, B KUMAR² and R K KOTNALA¹

¹CSIR–National Physical Laboratory, New Delhi 110 012, India.

²Jawaharlal Nehru University, New Delhi 110 067, India.

³Present address: Vivekananda College, University of Delhi, Delhi 110 095, India.

*Corresponding author. e-mail: monikajk@yahoo.com

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This study investigates the seasonal distribution of inorganic aerosols in Central New Delhi and identifies their potential source regions using concentration weighted trajectories (CWTs). Secondary inorganic aerosols (NO_3^- , SO_4^{2-} , NH_4^+) are the largest contributors to fine particulate matter in New Delhi, India. The concentrations of secondary inorganic aerosols showed very distinct seasonal patterns with higher concentrations in winter and post-monsoon seasons. Inorganic ions Ca^{2+} , Mg^{2+} and K^+ were also examined to understand their temporal trends. The primary aerosols were found to have smaller diurnal differences than secondary aerosols. The higher coefficient of divergence for secondary aerosols indicated a significant difference in their chemistry and/or meteorology during daytime and night-time, respectively. The backward trajectory analysis revealed the advection of ionic species from distant sources responsible for their significant seasonality. The highest concentrations of K^+ during the post-monsoon season were mainly influenced by air masses arriving from Punjab and Haryana regions resulting from the prominent agricultural crop residue burning in these areas. CWT also identified the Thar Desert and Punjab as potential regions for enhanced levels of Ca^{2+} and K^+ , respectively. Also, the brick kilns located in western UP were observed as the major potential sources for NO_3^- and SO_4^{2-} .

Keywords. $\text{PM}_{2.5}$; water-soluble inorganic species; secondary aerosols; coefficient of divergence; concentration weighted trajectory.

1. Introduction

The global mean aerosol burden of the atmosphere has significantly increased due to continuously increasing emissions from various anthropogenic activities such as industries, automobile vehicles and infrastructure buildings (Echalar *et al.*

1998; Kim *et al.* 2003; Ragosta *et al.* 2008; Righi *et al.* 2013). This has significantly affected the air quality, visibility, atmospheric composition, ecosystem and earth's radiation budget (Pope 2000; Hong *et al.* 2002; IPCC 2007). The combustion processes including automobile exhaust are well known to contribute to fine aerosols directly or through

the gas-to-particle conversion process (Jonathan *et al.* 1997). Fine mode aerosols further interact with atmospheric gaseous and secondary species resulting in the change in their chemical composition (Kumar and Sarin 2009). For example, NO_x oxidation leads to the formation of NO_3^- (Wang *et al.* 2006) which later on reacts with NH_3 present in the atmosphere forming NH_4NO_3 aerosols (Utsunomiya and Shinji 1996). Further, NO_3^- formation during day hours facilitates the production of secondary organic aerosols enhancing their hygroscopic nature thereby affecting the scattering properties of the atmosphere, thus reducing the visibility (Malm *et al.* 1996; Brown *et al.* 2006). Oxidation of SO_2 results in the formation of H_2SO_4 , which further reacts with atmospheric NH_3 forming particles like $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)\text{HSO}_4$ (Finlayson-Pitts and Pitts 2000). Hence, NO_3^- , SO_4^{2-} and NH_4^+ are considered as the secondary aerosols mainly contributed by pollution sources (Malm *et al.* 1996; Cheung *et al.* 2005). These ionic species constitute a significant fraction of fine aerosols (Karageorgos and Rapsomanikis 2007). The formation of secondary aerosols from pre-existed particles of primary origin has also been acknowledged as the main cause of the air pollution over mega-cities (Lee and Sequeira 2002; Dall'Osto *et al.* 2009; Guo *et al.* 2010; Zhang *et al.* 2010; Cheng *et al.* 2015).

New Delhi is rapidly becoming one of the most polluted cities in the world (WHO 2014) and the impact of particulate matter (PM) pollution is currently a major concern for the public health of the community in New Delhi (Kesavachandran *et al.* 2015). Secondary inorganics along with carbonaceous matter are the major components that need to be controlled to reduce particulate pollution in New Delhi (Bisht *et al.* 2015). There are a number of recent studies focusing on the sources and trends of carbonaceous aerosols in New Delhi (Miyazaki *et al.* 2009; Srivastava *et al.* 2014; Kumar *et al.* 2015) while less efforts have been made on the sources of fine inorganic aerosols (Bisht *et al.* 2015). Most of the earlier studies have reported water-soluble ions in TSPM, SPM or PM_{10} aerosols for selected cities such as Agra (Kulshrestha *et al.* 1998, 2009a), Kanpur (Ram and Sarin 2011) and Raipur (Deshmukh *et al.* 2010). The city such as Delhi, where population density is one of the highest compared to all other Indian States or Union Territories (11,297/km² according to 2011 Census), needs to be addressed for fine aerosols. In this paper, we report the daytime and

night-time seasonal variability of secondary and primary inorganic ionic species in $\text{PM}_{2.5}$. Also, we explore the potential source regions these components using concentration weighted trajectory (CWT).

2. Method and materials

2.1 Study site

$\text{PM}_{2.5}$ samples were collected at the National Physical Laboratory India (NPLI) located in central Delhi (28°38'N and 77°12'E, 283 m above sea level) (figure 1). The NPL campus is surrounded by the farms of Indian Agricultural Research Institute (~500 ha), Central Delhi ridge (~864 ha forest cover), commercial and residential areas. About 8000 factories are registered in the city, e.g., 1759 metal, 293 chemical products, 557 rubber/plastic and 279 leather factories (Economy Survey of Delhi, 2012–2013). Besides, 7.4 million motor vehicles are registered in the city. Major air pollution sources include automobile transport and industries.

2.2 Sample collection

The sample collection was carried out during the year 2011 at the terrace of the NPL building at a height of ~15 m above the ground level. $\text{PM}_{2.5}$ samples were collected on 47 mm quartz filters (Whatman) by using a low-volume sampler operated at an average flow rate of 1 m³/hr. The samples were collected at 12 h interval (daytime and night-time basis) for ~5 days (~10 samples and one field blank) every month during the year 2011. A total of 118 samples (winter, $n = 36$; summer, $n = 46$; monsoon, $n = 22$; post-monsoon, $n = 14$) were collected during the study period. The collected samples were stored in pre-cleaned polypropylene Petri-dishes and refrigerated at 0°C. The blanks were also processed in the same manner as the actual samples.

2.3 Sample analysis

A 0.5 cm² circular piece was cut from the collected filter of each sample and extracted into 10 ml ultrapure water (Millipore, specific resistance: 18.2 MΩ cm) for 75 min by using an ultrasonic bath (the water was replaced every 20 min to avoid extra heating of samples). The solution was filtered through a micro-porous membrane filter

Figure 1. Location of sampling site, prevailing wind pattern and trajectory map (not to scale).

(PALL, Ultipor N Nylon 6, 6-membrane, pore size 0.45 μm , diameter 25 mm). The extracted samples were stored in a refrigerator at 0°C until the further chemical analysis. Repeated extraction of the same filter provided extraction efficiency of $\sim 99.9\%$. The ion chromatograph (Metrohm 883) was used to measure water-soluble ionic species (NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , NO_3^- and SO_4^{2-}) in the aqueous extract of samples. The determination of these ions was done by using separation columns (Metrosep C2-100 and Metrosep A supp 5-100) for cations and anions, respectively. For cations, a mixture of 4.0 mM tartaric acid and 0.75 mM 2, 6-pyridine dicarboxylic acid at a flow rate of 1.0 ml/min was used as eluent. While for anions, a mixture of 3.2 mM Na_2CO_3 and 1.0 mM NaHCO_3 was used at a flow rate of 1.0 ml/min with Metrohm suppressor technique. The standards of known concentrations were used for making three-point calibration curves ($R^2 = 1$ for all ions with maximum RSD within 2.5%). The standards (Merck) used for cations (NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}) were 2, 5 and 10 ppm while 1, 2 and 5 ppm for anions. The per cent relative standard deviation for samples was within 7% as measured by analysing a set of five replicate samples for all major ions. The blank filters were also analysed and the concentrations of all the major ionic species were noted below the detection limit (the detection limits for SO_4^{2-} , NO_3^- , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+} for the instrument were 5, 5, 2, 5, 10 and 5 ppb, respectively).

2.4 Meteorology in Delhi

The Delhi region experiences four distinct seasons, viz., summer (March–June), monsoon (July–September), post-monsoon (October–November) and winter (December–February) in a year. Frequent dust storms are observed during the summer season. Monsoon season is known for maximum rainfall ($\sim 90\%$) followed by the post-monsoon season having moderate weather conditions. Winter season is observed with low temperature and calm wind conditions. The wind patterns showed more frequent calm conditions during night-time as compared to daytime (figure 1). The mixing height during daytime was observed to be higher as compared to night-time (figure 2). The annual mean of mixing heights for daytime and night-time was calculated as 984 and 147 m, respectively (using data from <http://ready.arl.noaa.gov/READYamet.php>).

3. Data analysis

3.1 Coefficient of divergence (COD)

The COD was used to provide information on the degree of uniformity between day and night at the sampling site:

$$\text{COD}_{fh} = \sqrt{\frac{1}{P} \sum_{l=1}^p \left(\frac{x_{if} - x_{ih}}{x_{if} + x_{ih}} \right)^2},$$

where x_{if} is the i th hourly averaged concentration at a given size interval measured at two different times, f and h are two different times, and p is the number of observations (Wilson *et al.* 2005).

3.2 Concentration weighted trajectory

The CWT analysis was done using TrajStat: GIS-based software (http://www.meteothinker.com/Documents/Wang_Trajstat_Manuscript.pdf) to estimate the local *vs.* regional contribution to inorganic ions in $\text{PM}_{2.5}$ at the receptor site. CWT is a type of hybrid receptor model used in the study of pollutants transport by using isentropic backward air trajectory and their estimated concentrations (Beegum *et al.* 2012; Cheng *et al.* 2013). This approach facilitates to identify the potential source regions or determine the relative significance of source regions contributing to pollutants at the receptor site (Seibert *et al.* 1994; Stohl 1996; Hsu *et al.* 2003). It has been used to provide the spatial pattern of potential sources of Hg (Cheng *et al.* 2013), Pb (Chandra *et al.* 2014), aerosol optical depth (AOD) (Beegum *et al.* 2012), organic carbon/elemental carbon (OC/EC) (Singh *et al.* 2016) and trace metals (Chandra *et al.* 2017) at the receptor sites.

In this technique, each grid cell gets a weighted value obtained by averaging the concentration measured at the receptor site as the associated trajectory crosses the grid cell as follows:

$$C_{ij} = \frac{1}{\sum_{l=1}^M \tau_{ijl}} \sum_{l=1}^M C_l \tau_{ijl},$$

where C_{ij} is the average weighted concentration of species in the grid cell (i, j), l is the index of the trajectory, M is the total number of trajectories, C_l is the concentration observed at the receptor site on the arrival of trajectory l and τ_{ijl} is the residence time of trajectory l in the grid cell (i, j).

Figure 2. Variation of $\sum$ major ions *vs.* mixing height during daytime and night-time.

4. Results and discussion

4.1 Variation of major ionic species during daytime and night-time

The annual mean concentrations of major ionic species followed the order $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Ca}^{2+} > \text{K}^+ > \text{NH}_4^+ > \text{Mg}^{2+}$ during daytime, while $\text{SO}_4^{2-} > \text{NO}_3^- > \text{K}^+ > \text{NH}_4^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$ in night-time (figure 3a). Among all the analysed ionic species, the annual mean concentration of SO_4^{2-} had the highest fraction contributing $\sim 46\%$ to the total major ions ($25.8 \mu\text{g}/\text{m}^3$) while NO_3^- and NH_4^+ contributed 33% and 7%, respectively (Supplementary table S1). On an average, SO_4^{2-} , NH_4^+ and NO_3^- together contributed $\sim 85\%$

to total major ions indicating the dominance of secondary aerosols. Xiao *et al.* (2014) also reported the secondary sulphate as the main source of $\text{PM}_{2.5}$ (23%), followed by secondary nitrate (16%) in Baoji, China. The high fractional contribution of SO_4^{2-} and NO_3^- to total major ions suggested that the large amount of SO_2 and NO_2 is oxidised forming SO_4^{2-} and NO_3^- aerosols, respectively, which further react with NH_3 possibly forming $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 and NH_4HSO_4 (Finlayson-Pitts and Pitts 2000). The loss of ammonium happens due to many factors affecting the equilibrium gas-particle partitioning in the atmosphere e.g., the extent of changes in diurnal temperature and relative humidity can strongly influence the equilibrium. In addition, the changes in the

Figure 3. (a) Daytime and night-time concentrations of major ionic species for annual mean and (b) during different seasons (W: winter; S: summer; M: monsoon; PM: post-monsoon).

composition of air mass during sample collection also affect the level of resulting sampling artefacts. Further, the possibility of ammonia loss from the sampling filter is also influenced by the composition of collected aerosol particles (Bassett and Seinfeld 1983; Yuc *et al.* 2006).

The SO_2 and NO_2 are primarily contributed by automobiles and industries. However, a significant amount of SO_2 and NO_2 is also contributed by brick kilns located in the nearby western part of Uttar Pradesh. Song *et al.* (2014) reported

the role of SO_2 emitted from coal burning in SO_4^{2-} production after the reaction of pre-existing carbonate particles. The sources of NH_3 include agriculture, human and animal waste, etc. Small fractions of SO_4^{2-} , NO_3^- and NH_4^+ are also contributed by agriculture and crop residue burning in Punjab and Haryana. The fine mode dominance of these ions has been reported by other researchers at various sites as shown in table 1. In these studies also, the ionic species were observed with a significant seasonality, e.g., winter period

Table 1. Major water-soluble ionic species in different size range PM.

Reference	PM type	Study site	Study period	Comparative study					
				NH ₄ ⁺ (μg/m ³)	K ⁺ (μg/m ³)	Mg ²⁺ (μg/m ³)	Ca ²⁺ (μg/m ³)	NO ₃ ⁻ (μg/m ³)	SO ₄ ²⁻ (μg/m ³)
Present study	PM _{2.5}	Central Delhi, India	Jan–Dec 2011	1.10 ^d	1.35 ^d	0.04 ^d	1.66 ^d	8.11 ^d	11.34 ^d
Deshmukh <i>et al.</i> (2011)	PM _{2.5}	Durg city, Chhattisgarh, India	Jul 2009–Jun 2010	2.53 ⁿ	3.05 ⁿ	0.15 ⁿ	1.35 ⁿ	8.75 ⁿ	12.13 ⁿ
Ghosh <i>et al.</i> (2014)	PM _{2.5}	Kanpur, India	Apr–Jul 2011	2.13	0.87	0.18	0.70	3.16	6.75
Tiwari <i>et al.</i> (2009)	PM _{2.5}	Delhi, India	Jan–Jun, Oct–Dec 2007	2.54	1.20	0.55	1.14	3.10	5.38
Kumar and Sarin (2010)	PM _{2.5}	Gurushikhar, India	Jan–Dec 2007	NR	4.8	0.9	2.7	6.4	19.8
				0.77 ^s	0.14 ^s	0.06 ^s	0.41 ^s	0.26 ^s	3.13 ^s
				0.92 ^m	0.10 ^m	0.06 ^m	0.19 ^m	–	3.56 ^m
				1.83 ^w	0.36 ^w	0.03 ^w	0.18 ^w	0.34 ^w	4.98 ^w
Ram and Sarin (2011)	PM _{2.5}	Kanpur, India	19–30 Oct 2008	5.2 ^d	2.2 ^d	0.05 ^d	0.3 ^d	2.1 ^d	13.6 ^d
				5.3 ⁿ	2.6 ⁿ	0.04 ⁿ	0.3 ⁿ	9.4 ⁿ	13.5 ⁿ
Other countries									
Tsai <i>et al.</i> (2012)	PM _{1.8}	Dalio, Taiwan	Jan, Mar, Aug, Dec 2006 and Jul 2007	2.16	0.26	0.10	0.28	1.48	4.46
Tsai <i>et al.</i> (2011)	PM _{2.5}	Taiwan	Aug, Nov 2006 and Jan, Mar, May 2007	2.12–4.21	0.57–0.62	0.13–0.49	0.54–0.66	1.39–3.13	5.02–13.21
Huang <i>et al.</i> (2013)	PM _{2.5}	Qingcheng, Qingyun, China	Aug 5–16 2009 and Jan 24–Feb 4, 2010	2.70 ^s	0.44 ^s	0.05 ^s	0.51 ^s	2.52 ^s	10.5 ^s
				8.01 ^w	1.11 ^w	0.05 ^w	0.44 ^w	11.3 ^w	13.8 ^w
Shen <i>et al.</i> (2011)	PM _{2.5}	Tongyu, China	14 Apr–21 Jun, 2006	1.2 ^{ds}	1.7 ^{ds}	1.0 ^{ds}	12.5 ^{ds}	4.6 ^{ds}	11.8 ^{ds}
				0.6 ^{nds}	0.8 ^{nds}	0.3 ^{nds}	4.5 ^{nds}	3.0 ^{nds}	5.7 ^{nds}

PM = particulate matter; NR = not reported; s = summer; m = monsoon; w = winter; d = daytime; n = nighttime; ds = dust storm days; nds = non-dust storm days.

showed higher concentrations of NO_3^- and SO_4^{2-} as compared to summer. The Ca^{2+} was observed with slightly higher values during summer than winter (Huang *et al.* 2013). In addition, the Ca^{2+} concentration was observed 3 times higher in the dusty period as compared to normal days (Shen *et al.* 2011). These ionic species also showed a variation along the altitude, IGP regions showed ~ 2 – 5 times higher SO_4^{2-} and 10 – 20 times higher NO_3^- as compared to mountainous region (Tiwari *et al.* 2009; Kumar and Sarin 2010; Ram and Sarin 2011; Ghosh *et al.* 2014). The study on daytime and night-time variability of secondary ions showed a higher concentration of NO_3^- in night-time as compared to daytime while in case of SO_4^{2-} and NH_4^+ ions, daytime and night-time concentrations were almost comparable (Ram and Sarin 2011). Another study at Durg city showed the mass concentration of NO_3^- , SO_4^{2-} and NH_4^+ as 3.16 , 6.75 and $2.13 \mu\text{g}/\text{m}^3$, respectively, in fine particles (Deshmukh *et al.* 2011). Similarly, among secondary ions, the highest concentration was observed for SO_4^{2-} followed by NO_3^- and NH_4^+ at a location in the IGP region (Ghosh *et al.* 2014).

Figure 3(b) shows the seasonal mean concentrations of major ionic species during daytime and night-time. The variation in mean concentrations of major ionic species between different seasons was observed to be significantly high. A sharp rise in both daytime and night-time concentrations of most of the major ions was observed during post-monsoon. The winter was observed with slightly higher concentrations during daytime and night-time for Ca^{2+} , NH_4^+ , Mg^{2+} and SO_4^{2-} except K^+ . The NH_4^+ showed higher levels during daytime of winter and post-monsoon. The NH_4^+ concentration was found to be 1.7 times higher in daytime than night-time during the post-monsoon. While NH_4^+ had 11.5 and 3.7 times higher concentrations during post-monsoon as compared to monsoon for daytime and night-time, respectively. K^+ showed significantly high concentrations (~ 4.4 times) in the night-time as compared to daytime during the post-monsoon.

The daytime and night-time concentrations of NO_3^- were recorded as higher in winter (20.5 and $18.0 \mu\text{g}/\text{m}^3$) than post-monsoon (11.0 and $14.8 \mu\text{g}/\text{m}^3$). The rise in NO_3^- concentration during the post-monsoon might be attributed to lower ambient temperature which reduces the volatilisation of NO_3^- (Seinfeld and Pandis 1998; Kulshrestha *et al.* 2009b). The NO_3^- showed 22.6 and 23.2 times higher concentrations during the

post-monsoon than monsoon for daytime and night-time, respectively. The NO_3^- and SO_4^{2-} were also found to be with 1.3 and 1.5 times higher concentrations, respectively, in night-time during the post-monsoon. The concentrations of SO_4^{2-} were observed as 5.5 and 9.8 times higher for daytime and night-time during the same period. The SO_4^{2-} was also observed with slightly higher concentration during winter (19.9 and $19.7 \mu\text{g}/\text{m}^3$ for daytime and night-time, respectively) than post-monsoon (15.1 and $22.1 \mu\text{g}/\text{m}^3$ for daytime and night-time, respectively).

The monthly average concentration of SO_4^{2-} was observed to be the highest during December ($32.9 \pm 2.9 \mu\text{g}/\text{m}^3$) and the lowest during July ($2.3 \pm 0.6 \mu\text{g}/\text{m}^3$). The concentration of NO_3^- was recorded to be the highest in December ($31.4 \pm 2.5 \mu\text{g}/\text{m}^3$) and the lowest in May ($0.2 \pm 0.2 \mu\text{g}/\text{m}^3$). Ram and Sarin (2011) also found very high (up to 90% of total WSIS) contribution of these three ions (SO_4^{2-} , NO_3^- and NH_4^+) in $\text{PM}_{2.5}$ at Kanpur. Rengarajan *et al.* (2011) reported SO_4^{2-} as the most abundant among water-soluble inorganic species in $\text{PM}_{2.5}$ at Ahmedabad, western India. The high concentrations of SO_4^{2-} and NO_3^- among all water-soluble inorganic ions were also reported in Japan and Spain (Khana *et al.* 2010; Mirante *et al.* 2014). A comparative study on different size range aerosols suggested that SO_4^{2-} , NO_3^- and NH_4^+ had a higher contribution in fine mode (Kulshrestha *et al.* 1998). Kulshrestha *et al.* (2009b) reported 87% contribution of these ionic species in PM_{10} aerosols at Allahabad. The annual mean concentrations of K^+ , Ca^{2+} and Mg^{2+} were found to be 2.2 , 1.5 and $0.1 \mu\text{g}/\text{m}^3$, respectively, constituting $\sim 15\%$ of inorganic species in $\text{PM}_{2.5}$. The cations such as Ca^{2+} and Mg^{2+} are of crustal origin while K^+ is mainly contributed by biomass burning in $\text{PM}_{2.5}$.

4.2 Ratios of major ionic species during daytime and night-time

The mass ratios (day/night) of major ions were calculated for different seasons as shown in figure 4(a). The mass ratios varied from 0.12 to 2.27 for all major ions, being maximum for the winter and minimum for the summer. The day/night-time mass ratios for Ca^{2+} were found to be >1 during winter, summer and monsoon seasons suggesting that Ca^{2+} had higher concentration mostly during daytime as compared to night-time. This might be attributed to the crustal sources due to the

Figure 4. (a) Mass ratio of day *vs.* night-time concentrations of ionic species for different seasons (W: winter; S: summer; M: monsoon and PM: post-monsoon), (b) equivalent ratio of Σanions *vs.* $\Sigma\text{cations}$ and (c) mass ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ during daytime and night-time of different seasons.

higher suspension of dust from roads, vehicular and construction activities during daytime. Besides this, comparatively high temperature and less relative humidity also add to high loading of crustal aerosols (supplementary figure S1 for temperature and relative humidity).

Furthermore, the equivalent ratios of total anions *vs.* cations during different seasons were calculated for daytime and night-time. The equivalent ratios were observed as 0.9 and 0.7 in winter during daytime and night-time, respectively. The summer season was observed with equivalent ratios as 1.2 and 0.5 for daytime and night-time, respectively (figure 4b).

4.3 NO_3^- *vs.* SO_4^{2-} mass ratios during daytime and night-time

The mass ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ can be used as a marker for the relative contribution of mobile *vs.* stationary sources of nitrogen and sulphur species in the atmosphere (Arimoto *et al.* 1996; Yao *et al.* 2002; Xiao and Liu 2004; Khoder and Hassan 2008). The mass ratios of $\text{NO}_3^-/\text{SO}_4^{2-}$ with values >1 indicate the predominance of mobile sources whereas the mass ratios of $\text{NO}_3^-/\text{SO}_4^{2-} < 1$ suggest the dominance of stationary sources (Arimoto *et al.* 1996). In this study, the annual average mass ratios of $\text{NO}_3^-/\text{SO}_4^{2-}$ in $\text{PM}_{2.5}$ were found to be 0.7 during both daytime and night-time. The mass ratios of $\text{NO}_3^-/\text{SO}_4^{2-}$ were also calculated to observe the dominance of mobile *vs.* stationary sources during different seasons for daytime and night-time (figure 4c). The $\text{NO}_3^-/\text{SO}_4^{2-}$ mass ratios showed a significant variation with the highest values for winter and the least for summer and monsoon seasons. The lower $\text{NO}_3^-/\text{SO}_4^{2-}$ mass ratios during summer and monsoon seasons may be attributed to semi-volatile nature of NO_3^- due to high temperature. During summer, the $\text{NO}_3^-/\text{SO}_4^{2-}$ mass ratios were observed as 0.16 and 0.45 for daytime and night-time, respectively; while during winter, the $\text{NO}_3^-/\text{SO}_4^{2-}$ mass ratios were observed as 1.02 and 0.91 for daytime and night-time, respectively. Khoder and Hassan (2008) reported $\text{NO}_3^-/\text{SO}_4^{2-}$ mass ratios as 0.41 and 0.34 for weekdays and weekends, respectively. The ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ with values < 1 were also reported during weekdays at various sites (Fang *et al.* 2002; Hu *et al.* 2002; Yao *et al.* 2002; Xiao and Liu 2004).

4.4 Temporal variability of major water-soluble ionic species

The temporal variability of different ionic species was assessed by calculating the COD between daytime and night-time. The COD is used to reduce the possibility of incorrect assumptions about the heterogeneity of data (Wilson *et al.* 2005). It provides an accurate assessment of intra-temporal variability using correlation coefficients in conjunction with COD and absolute difference between daytime and night-time concentrations (Wilson *et al.* 2005).

A total of 118 samples (59 each for daytime and night-time) were taken into consideration for the calculation of COD. The lower COD values

Figure 5. COD analysis for daytime and night-time concentrations of ionic species.

imply similarities between daytime and night-time concentrations while COD values approaching unity indicate vast differences (Krudysz1 *et al.* 2009). The COD values showed a large variability ranging from 0.56 to 0.16 in this study (figure 5). The highest COD_{dn} was noticed for NH₄⁺ (0.56) whereas the lowest for Ca²⁺ (0.16). According to the reports, COD values less than 0.27 shows uniformity between two different factors whereas COD values higher than 0.27 is considered as a high degree of variation (Wilson *et al.* 2005; Krudysz1 *et al.* 2009). It is to be noted that the secondary aerosols such as NH₄⁺, NO₃⁻ and SO₄²⁻ showed higher COD values indicating a significant difference in the sources, chemistry and meteorology during daytime and night-time, respectively.

4.5 Seasonal variation of major ionic species

A significant seasonal variation was observed for major ionic species (Supplementary tables S2–S5). Both NO₃⁻ and SO₄²⁻ concentrations showed a similar seasonal variation in the order winter > post-monsoon > summer > monsoon. The NH₄⁺ and Ca²⁺ were also observed with a seasonal variation which followed the order summer > winter > post-monsoon > monsoon. The K⁺ exhibited about 65 times increase in its concentration during the post-monsoon than monsoon. NO₃⁻ was also observed with a significant increase (23 times) during the same period. The significant seasonal increase of K⁺ reveals the contribution of large-scale biomass crop residue burning in the NW direction, which is also supported by backward trajectory analysis. The SO₄²⁻ had the highest concentration among all the major ions during

all seasons. The major contribution of SO₄²⁻ in fine mode was also reported by Kumar and Sarin (2010). The SO₄²⁻ concentrations during the winter and summer seasons were found as 19.8 and 7.8 µg/m³, respectively. Similar observations with higher SO₄²⁻ concentrations (13.8 µg/m³) during winter than summer (10.5 µg/m³) were reported at an industrial site in China (Huang *et al.* 2013). However, a study on PM_{2.5} reported by Tsai *et al.* (2011) showed a comparable range for SO₄²⁻ (5.0–13.2 µg/m³) and NH₄⁺ (2.1–4.2 µg/m³) while lesser for NO₃⁻ (1.4–3.1 µg/m³) than our study. The concentrations SO₄²⁻ and NO₃⁻ were recorded as 2.6 and 8 times higher, respectively, during winter than summer. The higher concentrations during winter might be attributed to calm wind conditions and lower mixing height (235 m). Karar and Gupta (2006) also suggested an increase in pollution levels due to prevailing low wind conditions. The lower mixing height during winter (approximately 1/4 of the summer season) suppresses the convective mixing thereby enhancing the ambient levels of NO₃⁻ and SO₄²⁻. For these two ionic species, the least concentrations were observed during summer which might be attributed to more dilution facilitated by convection due to higher mixing height. These two species have vehicular and industrial as their major sources showing uniform source strength throughout different seasons of the year. Hence, the concentration variation of these two ions is highly influenced with mixing height than the rest of the ions during different seasons of the year. The remaining ionic species (NH₄⁺, K⁺ and Ca²⁺) are influenced by seasonal activities, e.g., agriculture, biomass burning and crustal re-suspension, respectively. The Ca²⁺ was found to be the highest during summer due to more active crustal sources, while K⁺ was the highest during post-monsoon due to more biomass burning in Northern India (Kaskaoutis *et al.* 2013). Also, emissions of brick kilns located in neighbourhood state Uttar Pradesh might have contributed a significant fraction of these components depending on meteorological conditions (wind speed and wind direction) favouring such transport.

The per cent contribution of major ionic species to the total major ions has been shown in figure 6. The winter season was observed with the highest concentration (44.7 µg/m³) of total ions in PM_{2.5}. Similarly, the post-monsoon season was also observed with relatively high concentrations (44.3 µg/m³) of total major ionic species due to

Figure 6. Fractional contribution (%) of major ionic species (i.e., NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , NO_3^- and SO_4^{2-}) to the total studied WSIC during the different seasons.

a significant rise in K^+ levels (~ 5 times of winter season). The total major water-soluble ions during the summer and monsoon were recorded as 15.8 and 3.9 $\mu\text{g}/\text{m}^3$, respectively. The highest mean K^+ levels during the post-monsoon, whereas the highest concentrations of NO_3^- and SO_4^{2-} during the winter season were observed (Wang *et al.* 2006; Kumar *et al.* 2007). The increased anthropogenic activities (biomass burning) and temperature inversion frequency may contribute to enhanced levels of K^+ (Rajput *et al.* 2014). Besides, the backward trajectory analysis reveals that more than 90% wind advected to the receptor site influenced with Punjab region experiencing large-scale biomass burning during this season enhancing K^+ levels (Kaskaoutis *et al.* 2013). The lowest concentrations of NO_3^- and SO_4^{2-} during the monsoon period may be due to frequent washout processes and comparatively higher mixing height (about 2.3 times higher than winter). The NO_3^- levels during summer reduced up to one-eighth of the winter

time, whereas SO_4^{2-} reduced up to one-third of the winter time. The increased temperature and low relative humidity during summer might favour volatilisation of NH_4NO_3 and reduces the NO_3^- levels (Seinfeld and Pandis 1998; Kulshrestha *et al.* 2009b). The NH_4^+ levels were also found to be the lowest during the monsoon season whereas its highest concentration was observed during the summer season. However, the high concentration of NH_4^+ during summer was observed mainly during night-time. This may be due to the fact that fields are kept ready during the summer season for sowing of rice during monsoon in Northern India. During this process, a lot of fertilisers and manure are used in the fields contributing to the high concentration of NH_4^+ during night-time.

The Ca^{2+} , a tracer of crustal dust, was found to be the highest during the summer season due to the prevailing high mean temperature, high wind speed resulting in more re-suspension of soil dust and road dust. Han *et al.* (2015) also

suggested increased levels of crustal elements during spring (similar to the summer season in India) due to high wind speed. The lowest levels of Ca^{2+} were observed during the monsoon season when high humidity and rain events minimised the re-suspension of crustal dust. Although very less number of rain events was observed during monsoon, the lowest Ca^{2+} concentration during monsoon might be attributed to the washout effect which suppresses the re-suspension of crustal components (Kulshrestha *et al.* 2009c).

Owing to the per cent contribution to total ions, SO_4^{2-} had the highest per cent contribution among all the ions ranging from 41.9% to 63.7% for post-monsoon and monsoon seasons, respectively. This is probably due to humidity during

the rainy season which facilitates the conversion of SO_2 to SO_4^{2-} (Kulshrestha *et al.* 2009b). Mg^{2+} contributed the least fraction among all the ions ranging from 0.06% to 1.26% for winter and post-monsoon seasons, respectively. The Ca^{2+} was noticed with the highest percentage during summer, which might be attributed to suitable meteorological conditions for more soil re-suspension and frequent dust storms. The NO_3^- contributed the highest fraction (43.1%) to total ions during winter whereas the least (14.3%) during monsoon. The sharp decrease in NO_3^- in summer might be due to volatilisation of NO_3^- particulates (Seinfeld and Pandis 1998; Kulshrestha *et al.* 2009b).

An attempt to observe the correlation between SO_4^{2-} , NO_3^- , Ca^{2+} and NH_4^+ has been made, as

Figure 7. Correlation between NO_3^- and SO_4^{2-} during different seasons and correlation of NH_4^+ and Ca^{2+} with NO_3^- and SO_4^{2-} .

Figure 8. CWT analysis of SO_4^{2-} , NO_3^- , K^+ , Ca^{2+} , Mg^{2+} and NH_4^+ (maps not to scale).

shown in figure 7. The NO_3^- and SO_4^{2-} showed a good correlation during winter ($r = 0.87$), post-monsoon ($r = 0.95$) and monsoon ($r = 0.73$), whereas a relatively weak correlation during summer ($r = 0.58$). The correlation during winter, post-monsoon and monsoon suggested their

emission from common origin influenced by anthropogenic activities. The lowest observed correlation during summer may be due to volatilisation of NO_3^- . This study found good correlation between NO_3^- and NH_4^+ ($r = 0.67$ and $n = 53$) which explains that NO_3^- is mainly neutralised by

NH_4^+ while SO_4^{2-} showed a moderate correlation with NH_4^+ ($r = 0.53$ and $n = 53$), and significant positive correlation with Ca^{2+} ($r = 0.69$ and $n = 53$) (Supplementary table S6). The good correlation between SO_4^{2-} and Ca^{2+} in this study suggested a preferable neutralisation of SO_4^{2-} by mineral dust (Kulshrestha *et al.* 1998; Ghosh *et al.* 2014). The neutralisation of acidic constituents by mineral dust has been discussed in detail in an earlier study done by Rastogi and Sarin (2006).

4.6 CWT analysis

For CWT analysis, 12 hourly mean concentrations were estimated for each species. Each concentration value was incorporated with one back trajectory corresponding to the same time interval (Wang *et al.* 2009). The CWT plots for six major water-soluble ions of $\text{PM}_{2.5}$ have been shown in figure 8. This analysis revealed potential source regions for each species contributing to the receptor site. The major regions were identified as Northern Gangetic plain (western Uttar Pradesh), Thar Desert, eastern states and central Asian countries.

For NO_3^- , a few trajectories passing over western Uttar Pradesh, Punjab and Central Pakistan were identified as major contributors to the site, while a majority of trajectories were identified with weak or moderate contributions from Northern and South Western Indian states. CWT analysis of SO_4^{2-} revealed that it was contributed from wider regions than NO_3^- . The potential regions contributing to SO_4^{2-} were the western states including Punjab and Central Pakistan. Few trajectories were found to be originated from the Arabian Sea, central Asia and northern African regions showing weak source strength. On the contrary, Zhang *et al.* (2014) suggested long-range transport of SO_4^{2-} ion from Eastern China to Northeastern Tibetan Plateau.

The western Uttar Pradesh and Punjab regions were identified as potential contributors of K^+ at the receptor site (figure 8). As K^+ has been reported as a tracer of biomass burning (Nair *et al.* 2006; Kundu *et al.* 2010) and hence, it may be attributed to biomass and crop residue burning activities in identified regions.

The CWT analysis for Ca^{2+} showed that most of the trajectories had a weak potential to the receptor site. A very confined potential region located in the SW direction (the Thar Desert of Rajasthan and Southern Pakistan region) was

identified for the transport of Ca^{2+} to the sampling site. Although Mg^{2+} levels were found to be insignificant during the study, the CWT analysis for Mg^{2+} identified Punjab, Central Pakistan and the Thar Desert as major contributors to the receptor site. For NH_4^+ , western UP, Punjab and Central Pakistan were identified as the potential contributors to the receptor site. These regions experience extensive agriculture activities contributing the emissions of NH_4^+ into the atmosphere. However, the long-range transport for NH_4^+ was identified with weak potential which implies that the CWT analysis for NH_4^+ showed higher grid values for local and regional areas only. A few long-range trajectories with lower grid value were observed. A comprehensive long-term study is needed for further verification of different source regions.

5. Conclusions

A comprehensive chemical analysis of primary and secondary inorganic species in $\text{PM}_{2.5}$ was examined in this study to observe their daytime and nighttime variation in Delhi. The chemical components of $\text{PM}_{2.5}$ showed significant seasonal variation due to advection from distant sources. The rise in the ambient level of SO_4^{2-} in winter might be due to less dispersion, prevalent calm wind conditions and shallow boundary layer. Also, emissions from brick kilns in the nearby western part of Uttar Pradesh state also contributed to SO_4^{2-} and NO_3^- significantly in $\text{PM}_{2.5}$. The maximum concentrations during the post-monsoon for K^+ might be due to air masses coming from Punjab and Haryana regions having frequent crop residue burning activity during this period. The significant seasonal variation of K^+ reveals the contribution of large-scale biomass or crop residue burning in the NW direction. The CWT analysis for Ca^{2+} showed a very confined potential region located in the SW direction (the Thar Desert of Rajasthan and southern Pakistan regions). The CWT analysis for Mg^{2+} identified Punjab, central Pakistan and the Thar Desert as major contributors to the receptor site. For NH_4^+ , western Uttar Pradesh, Punjab and central Pakistan were identified as the potential contributors to the receptor site. The CWT of NO_3^- revealed regions of western Uttar Pradesh, Punjab and central Pakistan as major contributors to the site. The potential regions contributing to SO_4^{2-} were the western states including Punjab and Central Pakistan. This study

suggests that the proper understanding of potential source regions to control the emissions of precursors of secondary inorganic species is important for New Delhi. This will help to improve the air quality in this heavily polluted city of India.

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