Investigating Day and Night Time Variability of Major Water-Soluble Inorganic Species and Role of Reactive Nitrogen Species In PM$_{2.5}$ and PM$_{10}$-A Two Year Study

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Abstract

The study reports day and nighttime temporal variation of prominent water-soluble inorganic species (WSIS) of fine and coarse mode particulate matter at a site in central Delhi for 2012 and 2013. The two years' concentrations of major ionic species (NH$_4^+$, K$^+$, Ca^{2+} and Mg^{2+} and NO$_3^-$, SO$_4^{2-}$) showed that mean levels of both ∑cations and ∑anions were higher in nighttime than daytime in both PM$_{2.5}$ and PM$_{10}$. Moreover, the difference of mean levels in daytime and nighttime was noticed higher in PM$_{2.5}$ compared to PM$_{10}$. Among anions, more variation was observed for NO$_3^-$, i.e., ~49% higher values in nighttime compared to daytime, while~9% higher values in the nighttime for SO$_4^{2-}$. The Higher variation of NO$_3^-$ level might be due to active participation of NOx in daytime photo-oxidation process. Among cations,Ca^{2+} and Mg^{2+} showed higher concentration in daytime compared to nighttime. Higher day and nighttime variation of Ca^{2+} and Mg^{2+} in coarse particulate matter suggested their dominance in PM$_{10}$ compared to PM$_{2.5}$. In PM$_{10}$, the highest Ca^{2+} concentration was observed in daytime summer and least in nighttime monsoon, indicating the role of loose soil and meteorological conditions. The higher daytime SO$_4^{2-}$ concentration in monsoon compared to summer showed its significant formation as secondary aerosols in fine mode. The reactive nitrogen species NO$_3^-$ and NH$_4^+$ were correlated during the day and nighttime in PM$_{2.5}$ and PM$_{10}$. Moreover, NH$_4^+$ was highly correlated to SO$_4^{2-}$ and NO$_3^-$, mainly in the form of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$.

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Introduction

The physicochemical properties of the atmosphere get affected by particulate matter by altering its composition and thus may alter ambient air quality, visibility, cloud formation, and consecutively energy entering, absorbed, reflected, and emitted by earth system.[1-3] Moreover, it can also affect human health adversely and may also alter the ecosystem.[4-6] Therefore, the chemical characterization of PM is necessary for the development of an air quality improvement programme to control the implications.[7-8] Delhi is considered a city where PM load is usually higher than the permissible limits, and hence its chemical description is needed at regular intervals of time. The primary sources of pollutants impacting the air of Delhi are the burning of fossil and biomass fuels, rapid urbanization, industrialization, and transportation.[9-11] Due to the potential effect of water-soluble components on rain chemistry, human health, and air quality, water-soluble inorganic components are studied extensively.[12-16] Several anthropogenic activities such as agricultural, vehicular, industrial, and burning of biomass consecutively transform secondary inorganic particles such as sulphate and nitrate.[9,17-19]

Delhi is a typical site for studying the chemistry of primary pollutants and the role of the transformation of secondary pollutants due to the high loading of particulate matter. In India, most studies on chemical characteristics are reported on a 24 hours basis sampling, whereas data on day and nighttime during different seasons for PM is limited. This study presents the temporal variability (day and nighttime) of the chemical composition of ambient aerosols for the years 2012 and 2013. The importance of day and nighttime variability, and the role of seasonal and transport patterns of long-range major water-soluble ionic species (WSIS), including reactive nitrogen species in $PM_{2.5}$ and PM_{10} aerosols at a site in central Delhi, have been discussed.
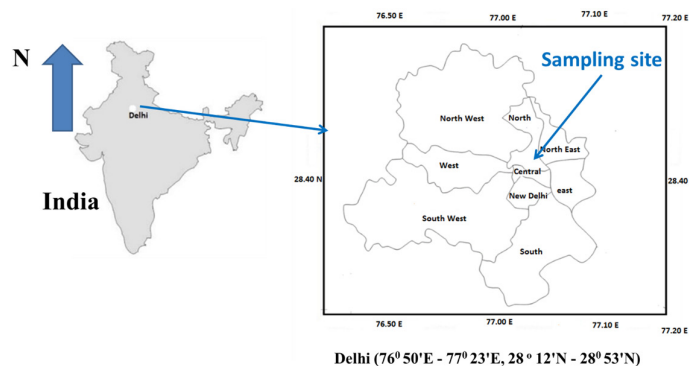

Delhi (76^0 50'E - 77^0 23'E, 28 º 12'N - 28^0 53'N)

Fig.1: Location of sampling site

Methodology
Site Description

The samples (PM_{10} and $PM_{2.5}$) were collected at the terrace of CSIR-National Physical Laboratory (28°38′N, 77°10′E; 218 m amsl) (Fig.1), New Delhi. The site is located in central Delhi, surrounded by IARI farmland, commercial and residential areas. The site also experiences local, regional, and long-range transport of pollutants depending on meteorological conditions. Therefore, the study site is under the influence of both local as well as transported particulate matter.

Among the local sources,~7.4 million automotive and registered factories (~8000), including rubber/ plastic, chemical, metal, and, leather affect the level of pollutants in the city. The study area also experiences the seasonality in the transport of pollutants from regional to distant sources. During summer, the site is under the influence of local to regional transport from North-west while in winter regional to long-range transport. In addition, calm wind conditions, lower mixing height with haze and, foggy conditions prevail in winter, whereas in summer, frequent dust storms and higher mixing height have been observed at the study site.

Sampling of PM_{10} and $PM_{2.5}$

High and low volume samplers were used for collecting PM_{10}(n= 160), and $PM_{2.5}$ (n = 188)

samples respectively. The pre-combusted (at 550ºC for 5h) Whatman Quartz Microfibre filters (QM-A) were used to collect samples. The samples were stored in desiccators for 24 h before and after sample collection. Respirable particle sampler (PM_{10}, Envirotech, APM 460 BL) and fine particulate sampler ($PM_{2.5}$, Envirotech, APM 550) were run for 12 hrs daytime (07:00–19:00h) and 12 hrs nighttime (19:00–07:00h next day). After collecting samples, filters were stored at low temperature in a refrigerator till further analysis. PM_{10} sampler was operated in the flow range of 0.9-1.4 m^3/min while $PM_{2.5}$ sampler at a 1 m^3/hr flow rate.

Analysis

For the analysis of WSIS, filter cuts (0.536 cm^2 area) of collected samples were extracted in de-ionized water (Millipore, specific resistance: 18.2 MΩ-cm) using a sonicator for 90 minutes. A microporous membrane filter (PALL, Ultipor N Nylon 6, 6-Membrane, pore size 0.45-μm diameter 25 mm) was used to filter the extracted solution. After the extraction, water-soluble cations (Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+}) and anions (Cl^-, SO_4^{2-} and NO_3^-) in $PM_{2.5}$ and PM_{10} aerosols were determined using Ion Chromatograph (Metrohm 883). Similarly, the concentrations of these water-soluble ionic species were also estimated in blank filters. Every time,

before the analysis, a three-point calibration curve was also achieved for each species (R^2=1).

Meteorological Parameters and Trajectory Analysis

For the years 2012 and 2013, meteorological parameters such as temperature (T), relative humidity (RH), and mixing height (MH)were downloaded from http://ready.arl.noaa.gov/READYamet.php link. A clear seasonality was observed for T, which was lowest in winter and highest in summer months. The highest monthly mean value of T was observed in May, while minima were recorded in January. The monthly mean of T varied from approximately 10ºC to 40ºC. A higher difference between day and nighttime mean temperature was observed during winter and summer compared to the monsoon season. The monthly mean of RH varied from approx. 15 to 75%. The diurnal variation of RH revealed higher nighttime levels than daytime. The mixing height (MH) at the site represented the potential of convective current in the lower atmosphere. MH for winter months was observed a few hundred meters, while for summer months, it went up to few thousand meters. Day and nighttime mean mixing height explain much higher daytime value compared to nighttime during summer season, while this difference gradually decreases during monsoon and winter seasons (Fig.2).
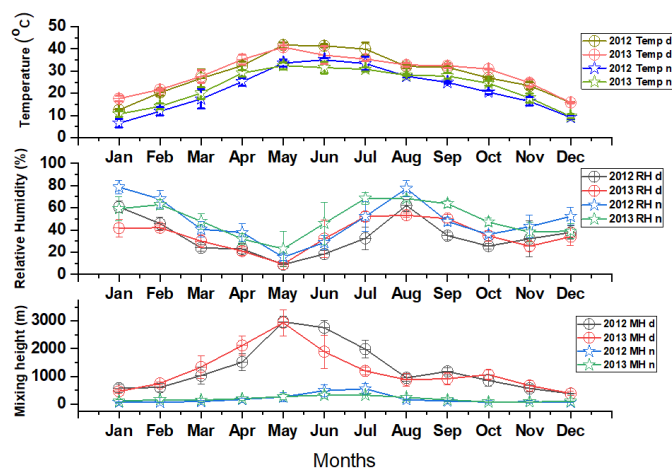

Fig.2: Meteorological conditions during sampling period

Results and Discussion
Annual Mean Day and Nighttime WSIS in $PM_{2.5}$ and PM_{10}

Fig.3 shows two years'average of mass concentrations of major ionic species in fine and

coarse particles. Almost similar levels of Ca^{2+} and Mg^{2+} were observed during the day and nighttime in fine mode, while in coarse mode, significant variation with higher daytime values were observed.

Daytime and nighttime levels of Ca^{2+} in PM_{10} were observed as 7.32 and 4.25 $\mu g/m^3$, respectively. The higher daytime levels might be due to more resuspension of crustal Ca^{2+} due to agricultural and commercial activities, as the soil is the prime source of Ca^{2+}. On the contrary, higher levels of NH_4^+ and K^+ were observed in nighttime compared to daytime in both $PM_{2.5}$ and PM_{10} among cations. NH_4^+ was observed as 1.49 $\mu g/m^3$ during the day and 2.50 $\mu g/m^3$ during the nighttime in fine mode while 2.39 and 5.54 $\mu g/m^3$, respectively in the coarse mode. A similar trend was also reported from other study,[20] which reported higher nighttime levels of NH_4^+ owing to the variation in emission sources and temperature difference during nighttime. Day and nighttime levels of K^+ were observed as 1.11 and 1.65 $\mu g/m^3$ in fine and 2.69 and 3.74 $\mu g/m^3$ in coarse particles, respectively. Both the anionic species showed the same trend with higher levels in nighttime than daytime. During the day and nighttime, NO_3^- was observed as 3.18 and 4.75 $\mu g/m^3$ in $PM_{2.5}$ while 7.37 and 9.47 $\mu g\ m^{-3}$ in PM_{10}, respectively. The high concentrations of NO_3^- during nighttime might be due to the formation of NO_3^- through hydrolysis of N_2O_5 under high humidity conditions and stability of NH_4NO_3 at a lower temperature during nighttime.[21-22] Similarly, low concentrations of NO_3^- during daytime might be due to evaporative loss of NH_4NO_3 at higher temperature.[23-24] A similar trend was also reported in an earlier study at Kanpur,[25] with a higher NO_3^- in nighttime (12.9 $\mu g/m^3$) than daytime (5.4 $\mu g/m^3$) in PM_{10}. Day and nighttime levels of SO_4^{2-} were observed as 8.66 and 9.25 $\mu g/m^3$ in $PM_{2.5}$ while 12.80 and 12.95 $\mu g/m^3$ in PM_{10}, respectively.

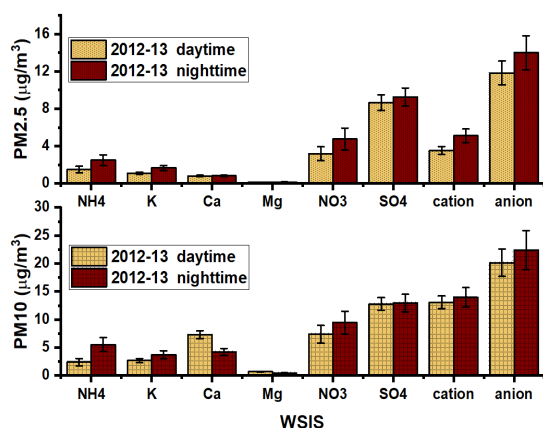**Fig. 3: Annual mean day and night time concentrations of WSIS in $PM_{2.5}$ and PM_{10}**

The two years mean (daytime + nighttime) concentration difference in $PM_{2.5}$ and PM_{10} was observed the highest for Ca^{2+} while lowest for Mg^{2+}. Around 5 times higher concentration of Ca^{2+} was observed in PM_{10} (5.8 $\mu g/m^3$) compared to $PM_{2.5}$ (0.8 $\mu g/m^3$). These observations are consistent with the other study, which reported higher Ca^{2+} in coarse than fine particulate matter.[20] The mean concentration of Mg^{2+} was 0.1 and 0.6 $\mu g/m^3$ in $PM_{2.5}$ and PM_{10}, respectively. Similarly, NO_3^- and SO_4^{2-} were observed with ~4.5 and 3.9 times higher concentrations in PM_{10} than $PM_{2.5}$, respectively. The levels of NO_3^- were observed as 4.0 and 8.4 $\mu g/m^3$ in $PM_{2.5}$ and PM_{10}. SO_4^{2-} was observed as 9.0 and 12.9 $\mu g/m^3$ in $PM_{2.5}$ and PM_{10}, respectively. K^+ showed ~ 1.8 times mean concentration in PM_{10} (3.2 $\mu g/m^3$) compared to $PM_{2.5}$ (1.4 $\mu g/m^3$).

Variation of WSIS in $PM_{2.5}$ and PM_{10}
Several studies on water-soluble ionic species in particulate matter over Delhi and other cities of India have been carried out earlier.[9,25-26] For example, Chandra *et al.*[9] reported that the secondary inorganic aerosols (NO_3^-, SO_4^{2-} and NH_4^+) contributed up to 85% of the annual average concentration.

In this study, the highest difference was observed for Ca^{2+}, which showed ~9 times higher mean concentration in PM_{10} than $PM_{2.5}$ in the daytime (Fig.4). The levels for NH_4^+, K^+, and Mg^{2+} were observed as 1.6, 2.4, and 5.4 times higher in PM_{10} than $PM_{2.5}$. For NO_3^- and SO_4^{2-}, ~2.3 and 1.5 times higher mean concentrations were observed in PM_{10} than $PM_{2.5}$. This suggested the dominance of Ca^{2+} and Mg^{2+} among all species in coarse mode, while the dominance of NO_3^- and SO_4^{2-} in fine mode. In daytime, the trend of WSIS in $PM_{2.5}$ and PM_{10} was observed as $SO_4^{2-}>NO_3^->NH_4^+>K^+>Ca^{2+}>Mg^{2+}$ and $SO_4^{2-}>NO_3^->Ca^{2+}>K^+>NH_4^+>Mg^{2+}$ respectively. Previous studies[27-28] also showed the dominance of SO_4^{2-}, NO_3^- and NH_4^+ in $PM_{2.5}$ and PM_{10}.

During nighttime, the trends of WSIS in $PM_{2.5}$ and PM_{10} were observed as $SO_4^{2-}>NO_3^->NH_4^+>K^+>Ca^{2+}>Mg^{2+}$ and $SO_4^{2-}>NO_3^->NH_4^+>Ca^{2+}>K^+>Mg^{2+}$ respectively. Among cations,~ 5.3 times higher Ca^{2+} was observed in PM_{10} compared to $PM_{2.5}$. Similarly, 2.2, 2.3 and, 3.2 times higher levels for NH_4^+, K^+, and Mg^{2+} were observed in PM_{10} than $PM_{2.5}$. NO_3^- and SO_4^{2-} also showed ~2 and 1.4 times higher levels in PM_{10} than $PM_{2.5}$, respectively.
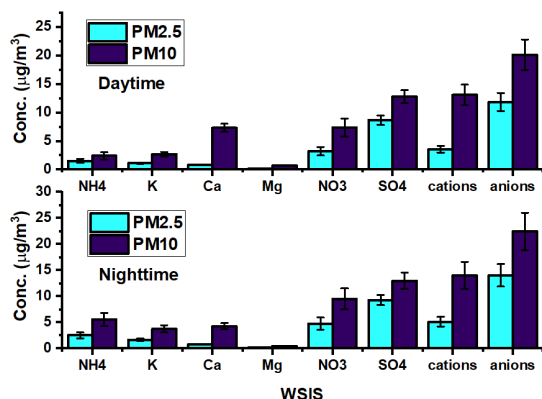
Fig. 4: Mean concentrations of WSIS during day and night time in $PM_{2.5}$ and PM_{10}

Comparison of WSIS for the Year 2012 vs. 2013
A comparative study of WSIS in $PM_{2.5}$ and PM_{10} was done for 2012 vs. 2013 (Fig. 5). In $PM_{2.5}$, daytime concentration difference between 2012 and 2013 was observed as the highest for NO_3^- (5.01 and 1.36 $\mu g/m^3$) and the lowest for Mg^{2+} (0.16 and 0.07$\mu g/m^3$).

On the other hand, in PM_{10}, the daytime difference between 2012 and 2013 was the highest for Ca^{2+} (10.12 and 4.51 $\mu g/m^3$) and the lowest for Mg^{2+} (0.93 and 0.47 $\mu g/m^3$).

In the day time, all WSIS in $PM_{2.5}$ and PM_{10} were found higher in 2012 compared to 2013 except K^+. K^+ in PM_{10} showed comparable levels in both 2012 (2.64 $\mu g/m^3$) and 2013 (2.73 $\mu g/m^3$). In 2012, NH_4^+, and Ca^{2+} in PM_{10} were 3.53 and 10.12 $\mu g/m^3$ respectively. Significantly high daytime Ca^{2+} in PM_{10} suggested their dominance in coarse mode and favourable meteorological conditions due to solar, wind, and anthropogenic activities that induce mineral resuspension from the earth's crust. The daytime NO_3^- and SO_4^{2-} in PM_{10} were observed as 8.97 and 13.41 $\mu g/m^3$ for 2012 and 5.78 and 12.18 $\mu g/m^3$ for 2013, respectively. Moreover, daytime NO_3^- and SO_4^{2-} in $PM_{2.5}$ were observed as 5.01 and 10.31 $\mu g/m^3$ for 2012 and 1.36 and 7.01 $\mu g/m^3$ for 2013, respectively.
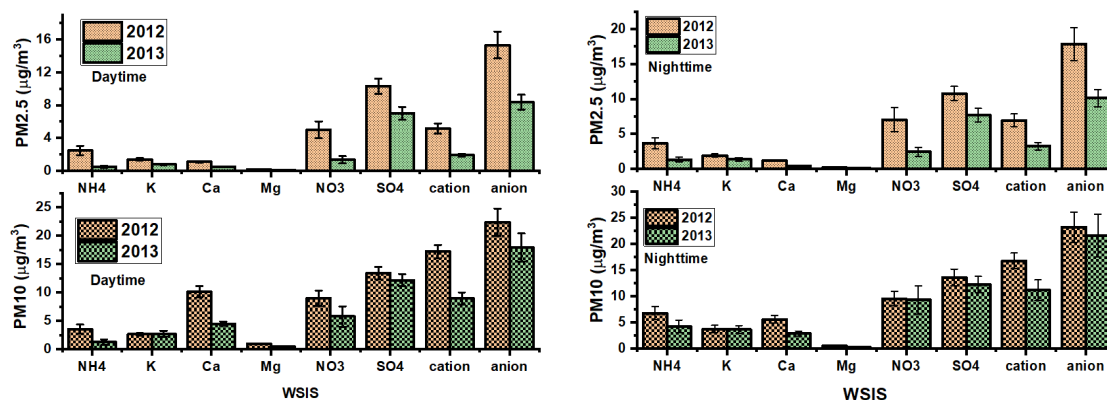

Fig. 5: Mean concentration of WSIS during day and night time in $PM_{2.5}$ and PM_{10}

In the nighttime, levels of all WSIS were observed higher in 2012 compared to 2013 in $PM_{2.5}$ and PM_{10}. In $PM_{2.5}$, NH_4^+, K^+, and Ca^{2+} were found 3.67, 1.94 and 1.17 $\mu g/m^3$ in 2012, and 1.33, 1.37 and 0.45 $\mu g/m^3$ respectively in 2013. Moreover, in PM_{10}, levels of NH_4^+, K^+, and Ca^{2+} were found as 6.80, 3.80, and 5.60 $\mu g/m^3$ in 2012, and 4.29, 3.67, and 2.89 $\mu g/m^3$ respectively in 2013. The nighttime levels of NO_3^- and SO_4^{2-} in $PM_{2.5}$ were observed as 7.06 and 10.80 $\mu g/m^3$ for 2012 and 2.45 and 7.70 $\mu g/m^3$ respectively in 2013. Moreover, nighttime levels of NO_3^- and SO_4^{2-} in PM_{10} were observed as 9.57 and 13.63 $\mu g/m^3$ for 2012 and 9.36, and 12.27 $\mu g/m^3$ respectively in 2013.

These observations are analogous to another study that also reported a similar trend.[20]

Seasonal Variation of WSIS during 2012 and 2013
Time series of WSIS from January 2012 to December 2013 are presented in Fig.6. The frequency of high peaks of WSIS was recorded during the winter months and low in monsoon months. This seasonal pattern might be due to change in meteorological parameters. K^+ showed a clear peak in both fine and coarse mode particles during the post-monsoon time, which suggested their relation with biomass/crop residue burning in near by states. Earlier studies

also suggested high K^+ concentrations during the biomass burning period. A higher concentration of other ionic species such as NH_4^+, Ca^{2+}, Mg^{2+}, NO_3^- and SO_4^{2-} was observed in the winter. Compared to other seasons, the high concentration trend in winter might be due to prevailing calm wind conditions and lower mixing height, restricting the dilution of WSIS in the atmosphere. High Ca^{2+} was noticed during the summer season, with higher levels observed in PM_{10} than $PM_{2.5}$. Ca^{2+} peaks in summer might be attributed to higher wind speed and temperature, which facilitate soil resuspension in the atmosphere. The only SO_4^{2-} showed some peaks in the monsoon season, which might be due to their formation in fine mode.
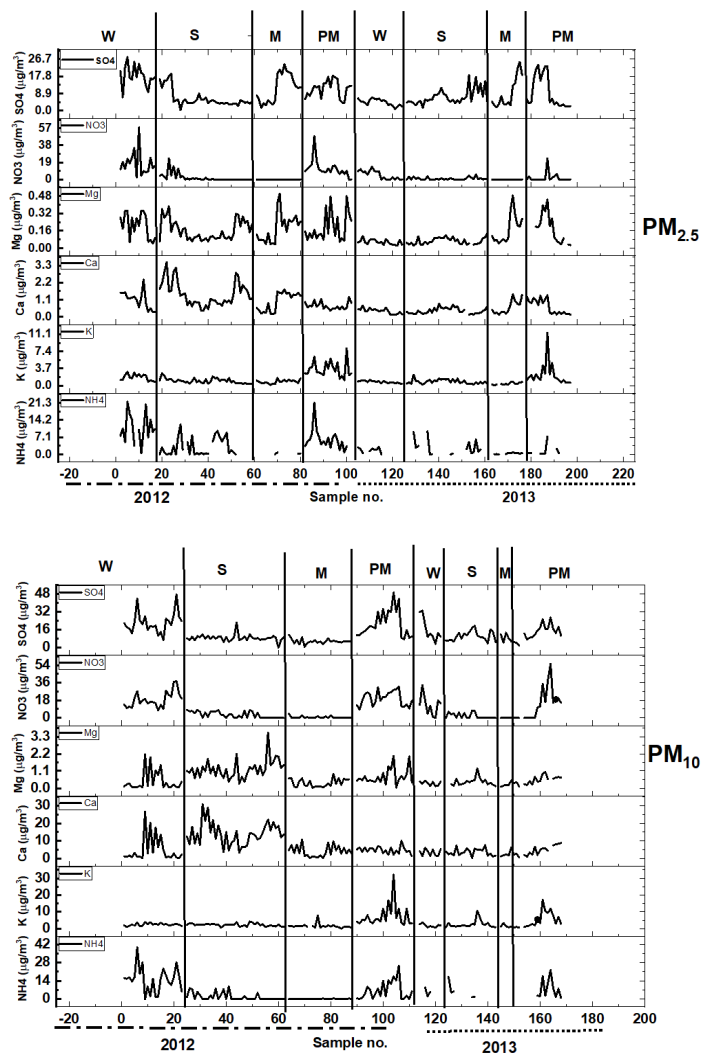

Fig. 6: Temporal variability in concentrations of WSIS in $PM_{2.5}$ and PM_{10}.

The concentration of Mg^{2+} has followed almost the same pattern of variation as Ca^{2+} in both $PM_{2.5}$ and PM_{10} during all seasons. However, in post-monsoon seasons, Mg^{2+} showed some extra peaks due to Firecrackers burning in the Diwali festival. Moreover, higher levels of NH_4^+, NO_3^- and SO_4^{2-} were observed during the post-monsoon and winter months.

The concentration of each season during both daytime and nighttime was estimated to observe the seasonal mean variation for both years (Fig. 7). In the winter day time, $\sum$cations and $\sum$anions were observed as 5.69 and 17.40 $\mu g/m^3$ in $PM_{2.5}$ and 15.08 and 32. 29 $\mu g/m^3$ in PM_{10} respectively. Whereas in monsoon season, the concentration

was as low as 1.88 and 10.62 µg/m³ in $PM_{2.5}$ and 6.07 and 7.55 µg/m³, in PM_{10} respectively. Results indicated that during winter, cations concentration in $PM_{2.5}$ rises 3 times than that of monsoon, while in PM_{10}, the rise was only up to 2.5 times. Significantly higher concentrations of cations during daytime in winters than monsoon indicated accumulation of particles transported from the long-range area and local sources like biomass burning, transport, brick kiln, etc. The highest concentration of pollutants during the winter months was also reported in previous studies owing to the lowering of boundary layer height and effect of source strength.[9,25] The concentration of Ca^{2+} during daytime summer (10.33 µg/m³) was noticed much higher compared to monsoon (4.39 µg/m³) in PM_{10}, while in $PM_{2.5}$, the concentrations in both seasons observed in a similar range (0.89 and 0.86 µg/m³ respectively). The higher Ca^{2+} was also reported in summer months (3.5 µg/m³) compared to winter (2.0 µg/m³) in PM_{10} aerosols at Kanpur.[29] During monsoon, a significant reduction of Ca^{2+} concentration in PM_{10} might be due to efficient washout due to coarse mode existence and efficiently settling down of these particles during rain. Moreover, the higher average value of Ca^{2+} observed in daytime summer compared to winter might be due to high wind flow that carries a large amount of soil dust whereas, during winter and monsoon, meteorological conditions suppressed dust resuspension (Fig. 7). In the present study, NO_3^- and SO_4^{2-} also showed significant seasonal variations in $PM_{2.5}$ and PM_{10}. A sharp reduction in the concentration of NO_3^- was observed in daytime summer just after winter in both $PM_{2.5}$ and PM_{10} aerosols. For the winter and summer seasons, NO_3^- concentrations were observed as 7.51 and 1.16 µg/m³ in $PM_{2.5}$ and 13.49 and 2.08 µg/m³ in PM_{10}, respectively. The sharp reduction in daytime summer concentration NO_3^- might be due to the photochemical oxidation process of NOx consumed to form secondary atmospheric pollutants. A different seasonal variation was noticed in SO_4^{2-} in different size particulate matter, where daytime maximum concentration was observed in the rainy season (10.62 µg/m³) in $PM_{2.5}$ and in winter (18.79 µg/m³) in PM_{10}. Higher SO_4^{2-} in monsoon might be due to their preferable formation in fine mode. An earlier study has also reported a higher percentage of SO_4^{2-} in monsoon than pre-monsoon during both day and nighttime.[26] In the daytime, K^+ showed the highest level during post-monsoon in $PM_{2.5}$ and PM_{10},

i.e., 2.14 and 4.40 µg/m³, respectively. The rise of K^+ concertation in post-monsoon was attributed to large-scale crop residue burning by farmers in nearby states.

At nighttime, the seasonal variation of all WSIS followed an almost similar trend with a slight difference in magnitude. The ∑cations and ∑anions levels in nighttime winter were observed 8.09 and 24.73 µg/m³ in $PM_{2.5}$ and 15.95 and 37.18 µg/m³ in PM_{10}, respectively. NH_4^+ was observed as the highest in nighttime winter while the lowest in monsoon in $PM_{2.5}$ (5.81 and 0.17 µg/m³ respectively) and PM_{10} (11.42 and 0.03 µg/m³) respectively. During summer and post-monsoon, NH_4^+ levels were observed as 1.72 and 3.33 µg/m³ in $PM_{2.5}$ and 2.87 and 8.92 µg/m³ in PM_{10}, respectively. The higher nighttime concentration of NH_4^+ in winter, summer and post-monsoon might be due to lower mixing height compared to daytime (Fig.2). In nighttime, K^+ concentrations were observed the highest in post-monsoon and least in monsoon in $PM_{2.5}$ (3.79 and 0.67 µg/m³)and PM_{10} (9.39 and 1.58 µg/m³) respectively. On the contrary, Ca^{2+} levels were noticed as the highest in summer season (0.95 and 7.24 µg/m³) in both $PM_{2.5}$ and PM_{10} respectively. The highest level of K^+ in post-monsoon was attributed to biomass burning while the highest level of Ca^{2+} in summer attributed to more active crustal sources. In this study, summer nighttime Ca^{2+} was noticed slightly lower than daytime despite lower mixing height, which might be due to more soil resuspension in daytime. Similar to daytime, NO_3^- concentration during nighttime of summer observed with sharp reduction in its level compared to winter. Summer and winter nighttime levels of NO_3^- were observed as 1.71 and 12.64 µg/m³ in $PM_{2.5}$ and 3.04 and 17.64 µg/m³ in PM_{10}, respectively. Moreover, during nighttime of winter and summer seasons, SO_4^{2-} concentrations were observed as 12.09 and 6.89 µg/m³ in $PM_{2.5}$ and 19.54 and 8.86 µg/m³ in PM_{10}, respectively. SO_4^{2-} concertation in nighttime of monsoon were observed as 10.13 and 5.01 µg/m³ in $PM_{2.5}$ and PM_{10} respectively, suggesting the preferable formation of fine mode SO_4^{2-} compared to coarse mode.

Percent Distribution of WSIS in $PM_{2.5}$ and $PM_{2.5-10}$
An analysis to observe the dominance of WSIS in $PM_{2.5}$ and $PM_{2.5-10}$ was done. In this analysis, $PM_{2.5}$ has been subtracted from PM_{10}, which gives $PM_{2.5-10}$. The percentage of Ca^{2+} in $PM_{2.5-10}$ was 89%

and 81% during day and nighttime, respectively (Fig.8). Whereas, percentage distribution study of SO_4^{2-} reveals their dominance in $PM_{2.5}$. The fine mode SO_4^{2-} was found 68% and 71% during day and

nighttime,respectively. A higher percentage in fine mode suggested their origin as secondary aerosol (via gas-to-particle conversion).
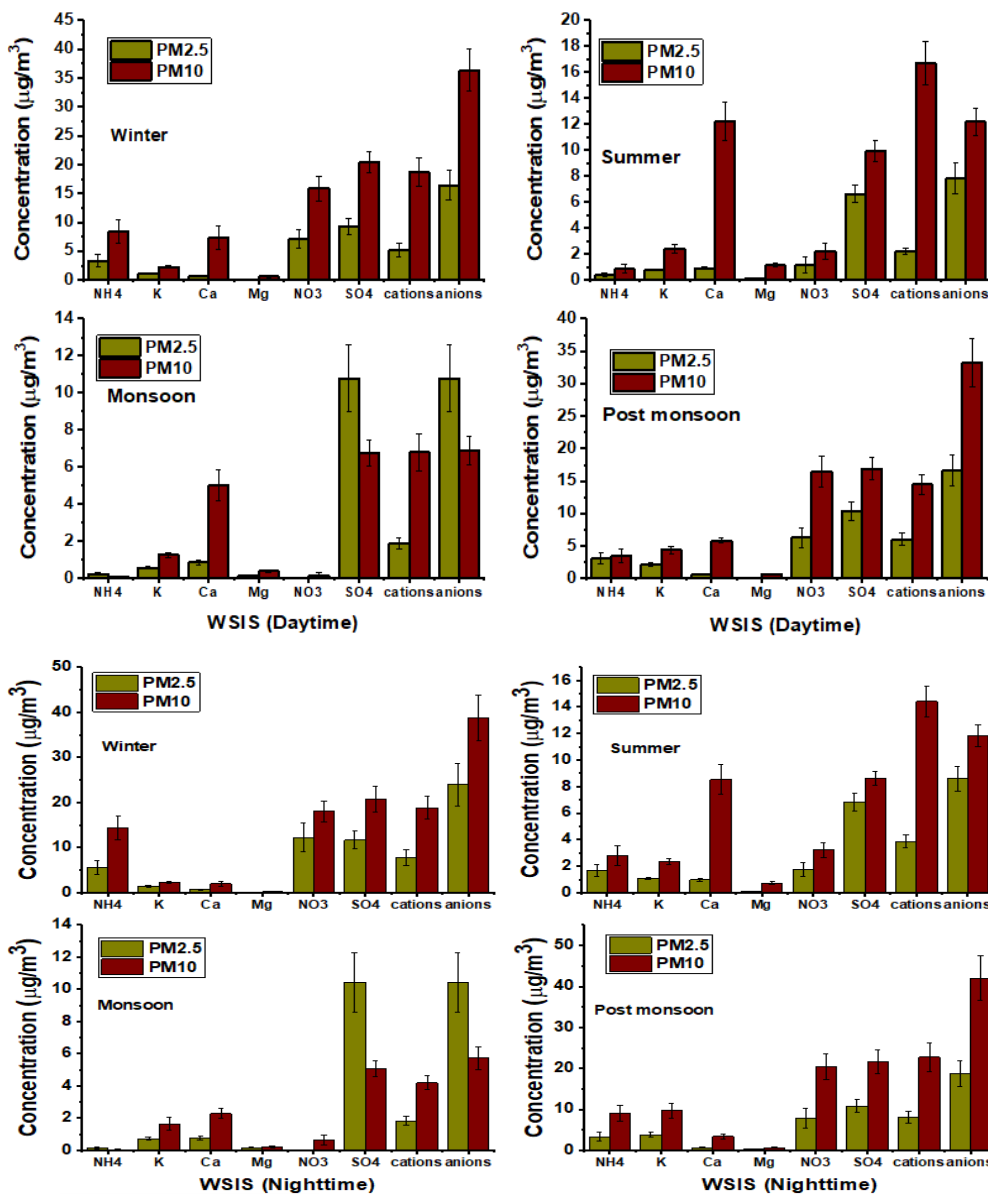

Fig. 7: Day time and night time variation of WSIS in $PM_{2.5}$ and PM_{10} during different seasons

A comparative study on the sum of all cations and anions suggested a higher percentage of cations in $PM_{2.5-10}$ in daytime (73%) and nighttime (63%) and a higher percentage of anions in fine mode in both daytime (59%) and nighttime (62%) respevtively. Earlier studies also suggested the cations such

as Ca^{2+} and Mg^{2+} of crustal origin and NO_3^- and SO_4^{2-} from anthropogenic sources. The fine mode existence of NH_4^+ was noticed higher in the daytime (63%) compared to nighttime (45%). At the same time, K^+ depicted a comparable percentage in fine mode during daytime (59%) and nighttime (56%).
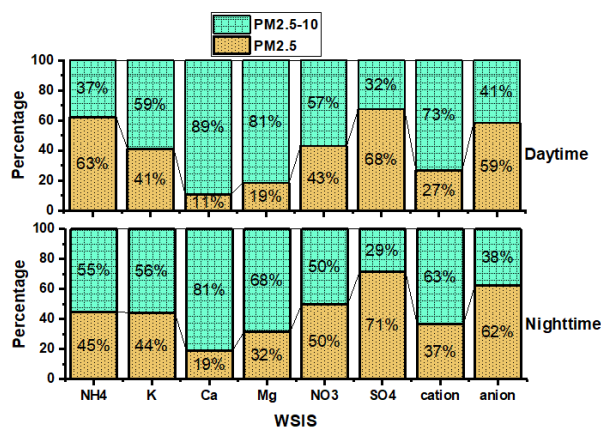
Fig. 8 The Percent distribution of WSIS in $PM_{2.5}$ and $PM_{2.5-10}$

NO_3^-/ SO_4^{2-} Mass Ratios in $PM_{2.5}$ and PM_{10}

The mass ratio of NO_3^-/SO_4^{2-} has been widely used by several researchers as a marker for the relative contribution of mobile vs. stationary sources of nitrogen and sulphur species in the atmosphere,[17,30] The mass ratios (NO_3^-/SO_4^{2-}) at the study site suggested the dominance of source type. Ratio values>1 indicate the prevalence of mobile sources, whereas the mass ratios value<1 suggests the dominance of stationary sources.[31] In this study, the seasonal average mass ratios of NO_3^-/SO_4^{2-}

in $PM_{2.5}$ and PM_{10} were observed in daytime and nighttime (Fig.9). The mass ratios were found in the range of 0.1-1.3 during different seasons of 2012 and 2013. In general, NO_3^-/SO_4^{2-} mass ratios showed comparatively higher values in winter and post-monsoon whereas least values in summer and monsoon period. The results of this ratio analysis suggested the dominance of stationary sources over mobile sources in the winter period, which might be facilitated by prevailing calm wind conditions.
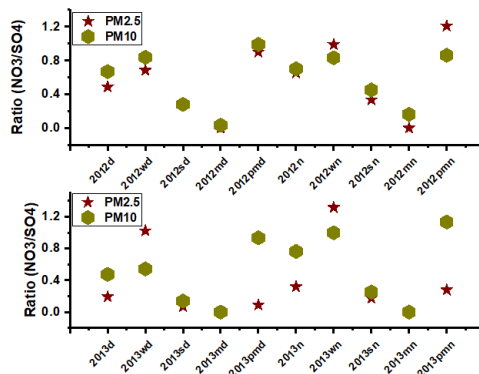

Fig. 9: Seasonal variation of mass ratios of NO_3^-/SO_4^{2-} in $PM_{2.5}$ and PM_{10} during day and night time (d = day, n = night, w = winter, s = summer, m = monsoon, pm = post monsoon)

Behaviour of Reactive Nitrogen during Day and Nighttime in $PM_{2.5}$ and PM_{10}

The acidic species such as H_2SO_4 and HNO_3 are considered secondary air pollutants formed in the atmosphere via the oxidation process of their primary gaseous precursors (SO_2 and NOx) in the atmosphere.[32] The neutralization of these acidic species in the atmosphere is done by alkaline ions

such as NH_4^+ and Ca^{2+}. Therefore, the availability and correlation among these acidic and alkaline species decide the acidic/alkaline nature of dry/wet deposition.

Therefore, a correlation study between nitrogenous cation (NH_4^+) and anion (NO_3^-) in both during the day and nighttime in $PM_{2.5}$ and PM_{10}, was done (Fig.10).

In $PM_{2.5}$, the correlation coefficient (r) between NH_4^+ and NO_3^- was observed higher in daytime (r= 0.84) compared to nighttime (r=0.67). On the contrary, in PM_{10} higher correlation was observed between NH_4^+ and NO_3^- in nighttime (r=0.73) compared to daytime (r= 0.67). The result suggested that fine mode NH_4^+ has a higher affinity with NO_3^- in the daytime, whereas coarse mode NH_4^+ showed a higher affinity with NO_3^- in the nighttime. These results suggested that these ions were secondary in nature, and NH_4^+ mainly existed as $(NH_4)_2SO_4$ and NH_4NO_3 during the day and nighttime.
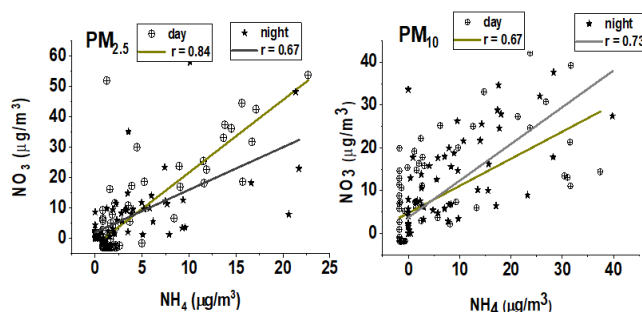

Fig. 10: Correlation between NH_4^+ and NO_3^- during day and night time in $PM_{2.5}$ and PM_{10}

Table 1: Principal Component Analysis of WSIS in $PM_{2.5}$ & PM_{10}

$PM_{2.5}$	Daytime			Nighttime			
	PC1	PC2	PC3	PC1	PC2	PC3	PC4
NH4	0.456	-0.387	0.302	0.393	-0.510	0.165	0.266
K	0.469	-0.129	-0.439	0.475	0.055	-0.620	0.090
Ca	0.235	0.570	0.546	0.278	0.469	0.649	0.405
Mg	0.308	0.572	0.002	0.362	0.576	-0.298	0.118
NO3	0.457	-0.371	0.390	0.453	-0.426	0.074	0.177
SO4	0.463	0.208	-0.515	0.454	0.062	0.271	-0.844
Eigen Value	2.793	1.821	0.55	2.607	1.47	0.856	0.553
% variance	46.54	30.35	9.17	43.46	24.5	14.27	9.21
Cumulative	46.54	76.89	86.05	43.46	67.96	82.23	91.44

PM_{10}	Daytime			Nighttime		
	PC1	PC2	PC3	PC1	PC2	PC3
NH4	0.489	-0.056	0.507	0.476	-0.127	0.512
K	0.353	0.354	-0.771	0.408	0.317	-0.645
Ca	-0.191	0.635	0.316	-0.205	0.600	0.533
Mg	-0.175	0.659	0.113	0.026	0.718	-0.078
NO3	0.552	0.127	0.015	0.527	-0.012	0.149
SO4	0.515	0.133	0.186	0.535	0.079	0.098
Eigen Value	2.736	1.860	0.650	3.064	1.828	0.617
% variance	45.600	31.000	10.840	51.06	30.47	10.28
Cumulative	45.600	76.610	87.440	51.06	81.53	91.810

Principal Component Analysis of WSIS in $PM_{2.5}$ and PM_{10}

To study the origin and sources of major water-soluble inorganic species, Principal Component Analysis (PCA) was performed. PCA is a multivariate technique used to convert data into a small dataset of the independent variable or principal components (PCs).[33] Factor loading >0.50 was included for the

source apportionment. Data analysis for PM_{10} and $PM_{2.5}$ was performed during the day and nighttime for 2012-2013 (Table 1). For coarse fraction analysis, a total of 3 PCs were extracted, explaining 87.4% and 91.8% of data during the day and night time, respectively. In PM_{10}, no significant difference was observed during the day and nighttime PCA analysis. PC1 in both day and nighttime explained maximum emission, reflecting the significant contribution from anthropogenic sources of air pollution, i.e., SO_2 and NO_x, which eventually converts into secondary aerosol. PC_2 explained ~ 31% data and showed high correlations of Ca^{2+} and Mg^{2+}. Therefore, this PC indicates emissions from crustal sources or windblown dust. PC3 explained ~ 10% data during the day and nighttime with the correlation between NH_4^+, K^+, and Ca^{2+} indicating biomass burning and secondary aerosol formation. For the fine mode particles, a total of 3 & 4 PCs were extracted during the day and nighttime, respectively, explaining >80% data. The first PC explained maximum data with high correlations of SO_4^{2-} and NO_3^- with NH_4^+ and K^+ indicating anthropogenic emissions including vehicular and biomass burning and consecutive secondary aerosol formation. During the daytime, PC2 explained 30% data with high correlations of Ca^{2+} and Mg^{2+} indicating crustal sources. But during nighttime, PC2 showed a positive correlation of Ca^{2+} and Mg^{2+} and a negative correlation of NH_4^+ and NO_3^-. This suggested crustal sources and secondary aerosol formation at low temperatures in the fine mode particles. Similarly, PC3 showed a negative correlation between K^+ and SO_4^{2-} with Ca^{2+} during the daytime, whereas K^+ was negatively correlated with Ca^{2+} and SO_4^{2-} during nighttime in PC4. This suggested biomass burning and secondary aerosol formation. These results indicated that in the fine mode particles, secondary aerosol formations are more prominent than coarse mode, and at low temperature, SO_2 and NOx also participate in other chemical conversions than their sulphate and nitrate salts.

Conclusions
Two years of continuous study of water-soluble ionic species in $PM_{2.5}$ and PM_{10} at a site in central Delhi provides comprehensive data on the behaviour of these species during day and nighttime. The results showed that the mean levels of both ∑cations and ∑anions were higher in nighttime

than daytime in $PM_{2.5}$ and PM_{10}. Furthermore, it revealed the higher average concentration of Ca^{2+} and Mg^{2+} in the daytime compared to nighttime, while higher values of K^+, NH_4^+, NO_3^- and SO_4^{2-} in nighttime compared to daytime in $PM_{2.5}$ and PM_{10}. A higher daytime Ca^{2+} indicated the role of active crustal sources. While the lower daytime value of NO_3^- might be due to the photochemical oxidation process of NOx in the daytime. Moreover, the different levels in day and nighttime were noticed higher values in $PM_{2.5}$ compared to PM_{10}. Among anions, significant variation was observed in NO_3, showing ~49% higher values in the nighttime than daytime, while for SO_4^{2-} only ~9% higher values were noticed in the nighttime. The higher variation of NO_3^- level might be due to their active participation in the daytime photo-oxidation process. The higher day and nighttime difference of Ca^{2+} and Mg^{2+} were observed in PM_{10} compared to $PM_{2.5}$, suggesting their dominance in the coarse mode. In PM_{10}, the highest Ca^{2+} concentration was observed in daytime summer and least in nighttime monsoon, indicating the role of loose soil and meteorological conditions. The higher daytime SO_4^{2-} concentration in monsoon compared to summer indicated the preferable formation of secondary aerosols in fine mode. A high correlation was observed between NO_3^- and NH_4^+ in fine and coarse mode particles in the day and nighttime. Also, NH_4^+ levels were found to be in good correlation to SO_4^{2-} and NO_3^-, indicating the role of secondary aerosol formation. In both day and nighttime, NH_4^+ mainly existed as $(NH_4)_2SO_4$ and NH_4NO_3.

Conflict of Interest
The authors do not have any conflict of interest.

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