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SHORT COMMUNICATION

# Long-Term (2013–2018) Relationship of Water-Soluble Inorganic Ionic Species of $PM_{2.5}$ with Ammonia and Other Trace Gases in Delhi, India

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## Abstract

Water-Soluble Ionic Components ($NH_4^+$, $SO_4^{2-}$, $NO_3^-$ and $Cl^-$) of $PM_{2.5}$ and trace gases ($NH_3$, NO, $NO_2$, $SO_2$, $HNO_3$) were monitored simultaneously to examine the relationship of ambient $NH_3$ in the formation of secondary aerosols in Delhi, India from January 2013 to December 2018. During the monitoring period, the average levels of $NH_3$, NO, $NO_2$, $SO_2$ and $HNO_3$ were 19.1 ± 3.8, 20.8 ± 4.3, 17.9 ± 4.2, 2.45 ± 0.47 and 1.11 ± 0.35 ppb, respectively. The levels of all trace gases ($NH_3$, NO, $NO_2$ and $SO_2$) were higher during the post-monsoon season (except $HNO_3$ which was higher in the winter season), whereas the concentrations of ionic components ($NH_4^+$, $SO_4^{2-}$, $NO_3^-$, $Cl^-$, $Ca^{2+}$ and $Na^+$) in $PM_{2.5}$ were estimated higher in the winter season. Significant annual variation in mixing ratio of $NH_3$ was observed during the study period with maxima (24.4 ± 4.5 ppb) in 2014 and minima (15.9 ± 9.1 ppb) in 2016. The correlation matrix of trace gases reveals that the ambient $NH_3$ neutralises the acid gases (NO, $NO_2$ and $SO_2$) at the study site. The study reveals the abundance of particulate $NH_4^+$ present in $PM_{2.5}$ samples at the study site neutralised the $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ particles during most of the seasons. The result reveals that the formation of $NH_4NO_3$ was higher during winter season due to favourable meteorological condition (lower temperature and higher relative humidity) and forward reaction of $NH_3$ and $HNO_3$.

**Keywords** $PM_{2.5}$ · WSIC · Trace gases · Ion balance · Acid gases

## 1 Introduction

Ammonia ($NH_3$) is an alkaline nitrogen gas and prominent constituents of nitrogen cycle which plays a vital role in the neutralisation of acidic species and the formation of secondary aerosols in the atmosphere (Stockwell et al. 2000; Aneja et al. 2009; Saraswati et al. 2019a, b; Aneja et al. 2001; Huang et al. 2010, 2011; Seinfeld and Pandis 2006). The formation of secondary aerosols [$(NH_4)_2SO_4$, $NH_4NO_3$ and $NH_4Cl$] in the atmosphere influenced by reaction rate of $NH_3$ which depends on the favourable meteorological condition (relative humidity and temperature) and level of acid gases (Ianniello et al. 2010, 2011; Meng et al. 2011; Saraswati et al. 2019b). These ammonium-containing aerosols constitute the major fractions of $PM_{2.5}$ in the atmosphere which have major effect on human health (Matsumoto and Tanaka 1996; Sharma and Behra 2010; Updyke et al. 2012). Agricultural activities, livestock, transport and industrial activities majorly contribute $NH_3$ to the atmosphere (Sutton et al. 2000; Li et al. 2006; Sharma et al. 2010a, b, 2011; 2016; Sutton et al. 2013; Xu and Penner 2012; Yang et al. 2011).

Fine fraction of particulate matter i.e. $PM_{2.5}$ (diameter ≤ 2.5 µm) is considered as one of the major pollutants having a negative impact on atmospheric chemistry (Pant and Harrison 2012; Sharma et al. 2021). The anthropogenic activities contribute significantly to the mass concentration of total $PM_{2.5}$ loading through gas-to-particle conversion (Huang et al. 2014). Secondary aerosols contribute to a major fraction of $PM_{2.5}$ concentrations which is mainly formed from $NH_3$ and its co-pollutants such that $NO_x$ and $SO_x$ (Sharma and Behra 2010; Saraswati 2019b; Singh et al. 2017). $NH_3$ as a primary alkaline gas neutralises the acid gases (mainly $HNO_3$ and $H_2SO_4$) and forms the secondary particulates ($NH_4NO_3$ and $(NH_4)_2SO_4$) (Pinder 2007; Sharma et al. 2014b), which are the major fractions of airborne fine particles (Chow et al. 1994; Aneja et al. 2001; Huang et al. 2011).

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In recent past, several studies on temporal and spatial changes of ambient $NH_3$, NO, $NO_2$, CO and $SO_2$ have been carried on short-term basis as well as year-long basis at the urban and sub-urban locations of India (Khemani et al. 1987; Singh and Kulshrestha 2014; Kulshrestha et al. 1996; Parasar et al. 1996; Parmar et al. 2001; Sharma et al. 2010a, b; 2012a, 2012b, 2012c; 2014a, b, c, d; 2017; Saraswati et al. 2018; 2019a, b); however, Long-Term study on seasonal basis as well as gas-to-particle conversion is inadequate. In this paper, we report the annual and seasonal changes of ambient $NH_3$, NO, $NO_2$, $SO_2$ and $PM_{2.5}$ measured for the period of 2013–2018. We also emphasise the role of ambient $NH_3$ and other trace gases (NO, $NO_2$, $SO_2$ and $HNO_3$) in the formation of secondary aerosols in Delhi, India.

## 2 Methodology

### 2.1 Study Site

Ambient $NH_3$, NO, $NO_2$, and $SO_2$ were monitored at CSIR-National Physical Laboratory (CSIR-NPL; 28° 38′ N, 77° 10′ E), New Delhi from January 2013 to December 2018 (Fig. 1). 24 h periodic sampling (2 samples/week) of $PM_{2.5}$ was also performed during this period. Monitoring site represents as a typical urban location surrounded by nearby road traffic and ICAR-Indian Agricultural Research Institute (ICAR-IARI), New Delhi. Delhi experienced four distinct seasons i.e. winter (January–February), summer (March–May), monsoon (June–September) and post-monsoon (October–December) as per meteorological classification. In Delhi region, winter months are chilly (temperature: ~ 2 °C) and noticeable intense fog and haze, whereas summers are generally very hot & dry (temperature: 47 °C) and experience repeated dust storms. A brief information about the study site is available in our previous paper (Sharma et al. 2021).

### 2.2 Monitoring of Trace Gases and $PM_{2.5}$

Ground-based analyzers were used to continuous measurement of trace gases ($NH_3$, NO, $NO_2$ and $SO_2$) at 10 m height from the surface level. In this study, $NH_3$ analyzer was used (Model: AC3M&CNH3, M/s. Environnment SA, France) to

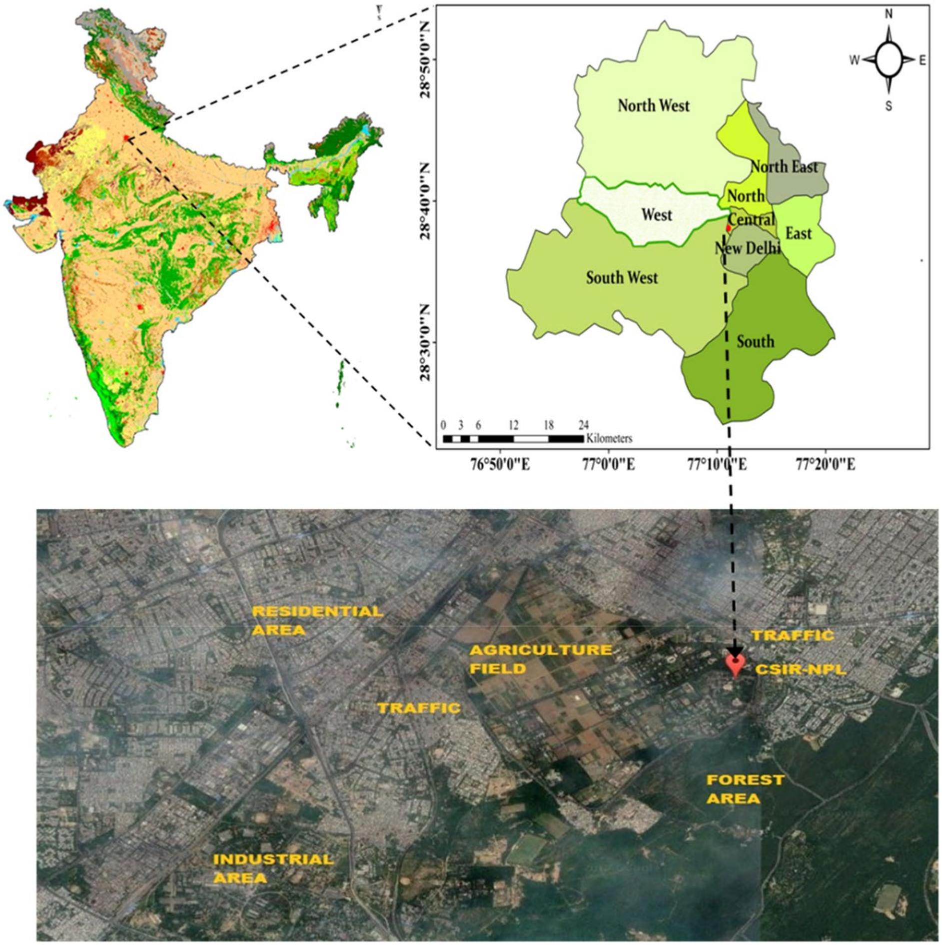

**Fig. 1** Map of the study site in Delhi (Source: Google maps)

measure the mixing ratios of $NH_3$, NO and $NO_2$ (working on chemiluminescence method with accuracy ± 1.0 ppb). Ambient $SO_2$ was used to measure $SO_2$ analyzer (Model: APSA 360A, M/s. Horiba Ltd., Japan) operating on ultraviolet fluorescence method (accuracy ± 0.5 ppb). Zero, span checks as well as periodic calibrations of these analyzers were performed using Zero Air Generator (Model: PAG-003, M/s. ECO Physics AG, Switzerland, accuracy ± 0.01 ppb) and NIST-certified respective reference gases (Saraswati et al. 2019b). The detailed principle of operations, calibration procedures and level of certified standard gases used are discussed in Sharma et al. (2014b). $HNO_3$ samples were collected using the standard impinger containing de-ionised water (25 ml) from November 2014 to December 2015 and analysed using Ion Chromatograph (DIONEX-ICS-3000, USA). Prebaked (at 550 °C for 5 h) and desiccated quartz microfiber filters (diameter: 47 mm) were used to collect $PM_{2.5}$ samples using fine particle sampler (APM 550, Make: M/s. Envirotech, India) for 24 h [at a flow rate of 1 $m^3\ h^{-1}$ (accuracy ± 2%)] from January 2013 to December 2018 (Saraswati et al. 2019b).

## 2.3 Chemical Analysis

To estimate the Water-Soluble Inorganic Components (WSICs) of $PM_{2.5}$, the collected filters were extracted in ultra-pure water for 90 min and extracted through 0.22 µm nylon filter. Cations ($Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Ca^{2+}$, and $Mg^{2+}$) and anions ($F^-$, $Cl^-$, $NO_3^-$ and $SO_4^{2-}$) of $PM_{2.5}$ concentrations were determined using Ion Chromatograph (DIONEX-ICS-3000, USA) with suppressed conductivity. The field blank filters were also analysed for blank correction. The detailed procedure of cations and anions analysis, calibration of ions, standards used and repeatability errors are available in our previous publication (Sharma et al. 2014b).

## 2.4 Meteorological Data

The ambient temperature (°C), relative humidity (RH; %), wind speed ($ms^{-1}$) and wind directions (degree) were also monitored using sensors placed on meteorological tower (5 stages tower of 30 m height). In this study, we used the meteorological data (temperature, RH, wind speed and wind direction) available at 10 m height (AGL) and summarised in Table 1 and Table S1 (see the supplementary information).

## 2.5 Estimation of $NH_4^+$ availability index (*J*) and conversion

For the observational site, $NH_4^+$ availability index (*J*) was estimated to explore the availability of $NH_4^+$ for neutralisation of acidic components of acid gases ($H_2SO_4$, $HNO_3$ and HCl) during the study period (Adam et al. 1999; Chu 2004) and is expressed as:

$$J = \frac{[NH_4^+]}{2\times[SO_4^{2-}] + [NO_3^-] + [Cl^-]} \times 100\% \tag{1}$$

When $J < 100\%$, it means it is an $NH_4^+$ deficit condition, which indicates that $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ are acidic. When $J = 100\%$, the particulate is neutral, indicating precise neutralisation of $SO_4^{2-}$, $NO_3^-$ and $Cl^-$. When $J > 100\%$, there is a sufficient $NH_4^+$ to fully neutralise acidic $SO_4^{2-}$, $NO_3^-$ and $Cl^-$.

In the present study, using the seasonal average of gaseous $NH_3$ and particulate ammonia of $PM_{2.5}$, the % fraction of $N–NH_4^+$ and $N–NH_3$ was computed for different seasons using the following equation:

$$\%N-NH_4^+ = \frac{\left[N-NH^+_{4(\text{Aerosol})}\right]}{\left[N-NH^+_{4(\text{Aerosol})}\right] + \left[N-NH_{3(\text{Ammonia})}\right]} \times 100\% \tag{2}$$

# 3 Results and Discussion

## 3.1 Mixing Ratios of Trace Gases and WSIC of $PM_{2.5}$

The annual average levels of trace gases ($NH_3$, NO, $NO_2$ and $SO_2$), WSICs and meteorology at the observational site of Delhi from January 2013 to 2018 are depicted in Table 1.

**Table 1** Annual mixing ratios of trace gases and meteorological parameters

| Details | Species | 2013 | 2014 | 2015 | 2016 | 2017 | 2018 |
|---|---|---|---|---|---|---|---|
| Gaseous species | $NH_3$ (ppb) | 16.4 ± 4.1 | 24.4 ± 4.5 | 18.5 ± 4.4 | 15.9 ± 9.1 | 20.4 ± 8.2 | 18.7 ± 6.3 |
| | NO (ppb) | 22.8 ± 9.7 | 19.2 ± 8.1 | 19.2 ± 7.4 | 16.46 ± 8.5 | 23.1 ± 8.6 | 20.4 ± 6.8 |
| | $NO_2$ (ppb) | 13.1 ± 4.9 | 21.8 ± 6.2 | 24.1 ± 8.6 | 19.61 ± 9.7 | 13.2 ± 5.1 | 13.9 ± 10.8 |
| | $SO_2$ (ppb) | 1.91 ± 0.41 | 1.8 ± 0.3 | 2.46 ± 0.82 | 2.59 ± 0.88 | 2.29 ± 0.76 | 2.50 ± 0.74 |
| Meteorological parameters | Temp (°C) | 24.2 ± 4.2 | 24.9 ± 2.6 | 25.2 ± 2.6 | 26.4 ± 5.6 | 22.7 ± 6.0 | 27.1 ± 6.0 |
| | RH (%) | 54.6 ± 10.9 | 53.4 ± 12.5 | 54.6 ± 12.4 | 53.4 ± 22.4 | 53.7 ± 10.0 | 54.2 ± 18.6 |
| | WS ($ms^{-1}$) | 1.49 ± 0.71 | 1.55 ± 0.70 | 1.56 ± 0.79 | 0.91 ± 0.18 | 0.88 ± 0.21 | 2.31 ± 0.5 |

During the entire study period (2013–2018), the average levels of $NH_3$, NO, $NO_2$, $SO_2$ and $HNO_3$ were 19.1 ± 3.8, 20.8 ± 4.3, 17.9 ± 4.2, 2.45 ± 0.47, 1.11 ± 0.35 ppb, respectively, whereas the levels of $NH_4^+$, $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ of $PM_{2.5}$ were 9.1 ± 3.5, 12.3 ± 4.1, 10.8 ± 4.8 and 9.3 ± 3.2 µg $m^{-3}$, respectively. The highest mixing ratio of ambient $NH_3$ was recorded in 2014 (24.4 ± 4.5 ppb) and the lowest level of $NH_3$ in 2016 (15.9 ± 9.1 ppb). The inter-annual variability in ambient $NH_3$, NO, $NO_2$, CO and $SO_2$ levels were discussed in detail in our previous publication and reference therein (Sharma et al. 2017). The annual concentrations of $PM_{2.5}$ estimated as 135 ± 45 µg $m^{-3}$ with a range of 35–451 µg $m^{-3}$. The annual concentration of $PM_{2.5}$ at the sampling site of Delhi exceeded more than 3 times of National Ambient Air Quality Standard (NAAQS; annual: 40 µg $m^{-3}$) of India and more than 25 times of World Health Organisation (WHO) guideline (5 µg $m^{-3}$).

Seasonal mixing ratios of $NH_3$, other trace gases (NO, $NO_2$ and $SO_2$) and concentrations of WSICs of $PM_{2.5}$ are depicted in Table 2, whereas the average seasonal variation in meteorology of observational site is summarised in Table S1 (in supplementary information). The monthly averages (pooled average from 2013 to 2018) of trace gases were also depicted in Fig. 2, whereas monthly average time series of these trace gases were also reported in Fig. S1 (in supplementary information). The ambient $NH_3$ indicated significant seasonal variation with highest mixing ratio during the post-monsoon season (22.2 ± 3.9 ppb) followed by the winter (20.9 ± 4.1 ppb), summer (19.4 ± 4.1 ppb) and monsoon (14.0 ± 2.5 ppb) seasons. The average levels of NO, $NO_2$ and $SO_2$ were also recorded highest during the post-monsoon and lowest during the monsoon season except $SO_2$ (Table 2). The average concentrations of $NH_4^+$ were recorded as 17.5 ± 2.8 µg $m^{-3}$, 9.3 ± 4.4 µg $m^{-3}$, 5.8±3.5 µg $m^{-3}$ and 3.9 ± 1.2 µg $m^{-3}$ during the winter, post-monsoon, summer and monsoon seasons, respectively. The higher concentration of $NH_4^+$ (17.5 ± 2.8 µg $m^{-3}$) during the winter season at the observational site of Delhi may be due to high RH (62.4 ± 12.6 %), low temperature (16.7 ± 3.6 °C) and higher $NH_3$ (20.9 ± 4.1 ppb) mixing ratio influenced the $NH_4^+$ aerosols formation (Khoder 2002). Similar seasonal concentrations of $SO_4^{2-}$ and $NO_3^-$ were also recorded with highest concentration during the winter season (Table 2). The higher source strength of mixing ratios of precursor gases, such as $NH_3$, $NO_x$ and $SO_2$, may lead to high concentrations of $NH_4^+$, $SO_4^{2-}$ and $NO_3^-$ during the winter season. The higher RH during the winter season also favours dissolution of significant fraction of $NH_3$ which increases the $NH_4^+$ formation (Ianniello et al. 2010).

In this study, the higher concentration of $HNO_3$ was estimated in the summer season followed by the winter, post-monsoon and monsoon seasons (Table 3). The more availability of $HNO_3$ in the summer at the study might be due

**Table 2** Seasonal variation in trace gases (in ppb) and WSIC of $PM_{2.5}$ (in µg $m^{-3}$) in Delhi during 2013–2018

| Seasons | $PM_{2.5}$ | $NH_3$ | $NO_2$ | NO | $SO_2$ | $Cl^-$ | $SO_4^{2+}$ | $NO_3^-$ | $NH_4^+$ | $Na^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Winter | 190 ± 82 | 20.9 ± 4.1 | 17.7 ± 4.5 | 18.1 ± 4.4 | 2.24 ± 0.37 | 15.6 ± 8.9 | 19.6 ± 6.9 | 22.7 ± 9.5 | 17.5 ± 2.8 | 3.2 ± 1.4 | 4.4 ± 2.6 | 1.27 ± 0.87 | 3.68 ± 1.46 |
| Summer | 92 ± 30 | 19.4 ± 4.1 | 19.1 ± 4.3 | 21.4 ± 5.4 | 2.25 ± 0.43 | 7.5 ± 3.1 | 8.5 ± 2.2 | 5.0 ± 2.8 | 5.8 ± 3.5 | 2.3 ± 0.6 | 2.6 ± 0.8 | 1.32 ± 0.90 | 2.65 ± 1.05 |
| Monsoon | 86 ± 33 | 14.0 ± 2.5 | 14.9 ± 3.7 | 20.4 ± 5.3 | 2.55 ± 0.26 | 6.2 ± 2.1 | 9.9 ± 1.9 | 4.7 ± 2.4 | 3.9 ± 1.2 | 2.1 ± 1.2 | 2.3 ± 0.9 | 2.24 ± 1.03 | 2.21 ± 0.08 |
| Post-Monsoon | 171 ± 72 | 22.2 ± 3.9 | 20.0 ± 4.2 | 23.3 ± 4.5 | 2.77 ± 0.36 | 7.8 ± 3.0 | 11.3 ± 3.4 | 10.9 ± 3.8 | 9.3 ± 4.4 | 2.1 ± 0.9 | 3.0 ± 1.1 | 2.37 ± 1.16 | 2.30 ± 1.07 |
| Average | 135 ± 45 | 19.1 ± 3.8 | 17.9 ± 4.2 | 20.8 ± 4.3 | 2.45 ± 0.47 | 9.3 ± 3.2 | 12.3 ± 4.1 | 10.8 ± 4.8 | 9.1 ± 3.5 | 2.4 ± 0.9 | 3.1 ± 1.2 | 1.81 ± 1.12 | 2.71 ± 1.21 |

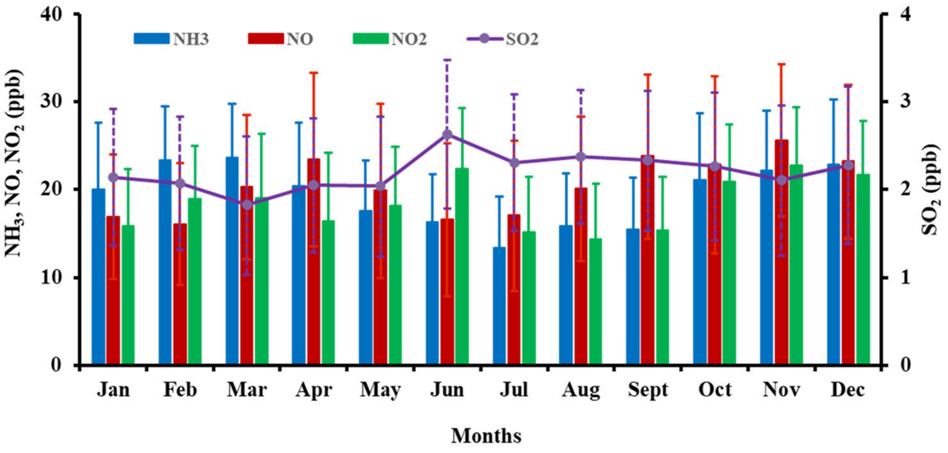

**Fig. 2** Monthly average (pooled average of 2013–2018) mixing ratios of $NH_3$, NO, $NO_2$ and $SO_2$ in Delhi, India

**Table 3** The measured concentration product ($K_m$) and theoretical equilibrium constant ($K_p$) of $NH_4NO_3$ formation during winter, summer and monsoon seasons during the measurement period at the study site

| Season | $NH_3$ (ppb) | $HNO_3$ (ppb) | $K_m$ ($ppb^2$) | $K_p$ ($ppb^2$) | 1000/T ($K^{-1}$) | Temp (K) | RH (%) | RHD (%) |
|---|---|---|---|---|---|---|---|---|
| Winter | 20.9 | 1.2 | 25.1 | 2.9 | 3.5 | 289 | 59.5 | 66.6 |
| Summer | 19.4 | 2.0 | 38.8 | 62.5 | 3.3 | 301 | 38.2 | 60.3 |
| Monsoon | 14.0 | 0.38 | 5.3 | 76.4 | 3.3 | 302 | 63.2 | 59.8 |
| Post-monsoon | 22.2 | 1.03 | 22.9 | 5.9 | 3.4 | 295 | 58.6 | 62.1 |

to increase photochemical activity and higher level of OH radical (Hoek et al. 1996; Wu et al. 2009) which increased the availability of $HNO_3$ from gaseous precursors gases ($NO_2 + OH = HNO_3$) (Behera and Sharma 2010; Liu et al. 2015). Sharma et al. (2007) also reported the 3 times higher $HNO_3$ level in summer than the winter at IIT Kanpur over the IGP region of India.

Mass concentration of $PM_{2.5}$ was recorded higher in the winter (190 ± 82 µg $m^{-3}$) followed by the post-monsoon (171 ± 72 µg $m^{-3}$), summer (92 ± 30 µg $m^{-3}$) and monsoon (86 ± 33 µg $m^{-3}$) seasons (Table 2). One of the reasons of the high level of $PM_{2.5}$ during winter could be the higher formation of secondary particles like $NH_4^+$ (17.5 ± 2.8 µg $m^{-3}$), $SO_4^{2-}$ (19.6 ± 6.9 µg $m^{-3}$), $NO_3^-$ (22.7 ± 9.5 µg $m^{-3}$) and $Cl^-$ (15.6 ± 8.9 µg $m^{-3}$) during the winter season (Table 2). During winter, the higher level of $Cl^-$ was recorded than other seasons (post-monsoon, summer and monsoon) due to enhanced fossil fuel combustion (Wang et al. 2005), whereas $K^+$ ion was higher due to biomass burning in Delhi and their surroundings (Sharma et al. 2014b). The higher concentrations of all the pollutants in the colder season may be due to the lower mixing height [100–250 m at sampling site as reported by Kumar et al. (2021)] by surface temperature inversion (Xu et al. 2016; Wang et al. 2014) and weak winds for lower dispersion of the pollutants. During all the seasons, mixing ratio of ambient $NH_3$ is negatively correlated with ambient temperature (winter: $r^2 = -0.49$, summer: $r^2 = -0.76$, monsoon: $r^2 = -0.69$, post-monsoon: $r^2 = -0.75$; $p < 0.05$), whereas positively correlated with the RH (winter: $r^2 = 0.54$, summer: $r^2 = 0.74$, monsoon: $r^2 = 0.75$, post-monsoon: $r^2 = 0.59$; $p < 0.05$). Similar correlations were also reported between these gases and meteorological parameters at other urban site (Makovic et al. 2008; Sharma et al. 2010a, b, c). The wind is one of the most important parameters for the transfer and dispersion of pollutants. The increase in wind speed indicates the increase in transport of pollutants which may result in lower pollutant concentration. In the present study, ambient $NH_3$ was negatively correlated with wind speed during all the season (winter: $r^2 = -0.67$, summer: $r^2 = -0.47$, monsoon: $r^2 = -0.75$, post-monsoon: $r^2 = -0.76$; $p < 0.05$). The highest $NH_3$ mixing ratio was observed during the lower wind speed (1–2 m $s^{-1}$) from downwind direction indicates the possible nearby sources and lowest $NH_3$ at high wind speed (5–6 m $s^{-1}$). The higher $NH_3$ mixing ratio was observed during the winter season may also be due to the lower wind speed which associated with local sources from nearby agricultural field.

## 3.2 Ionic Composition and Ionic Balance

$NH_3$ reacting with acid gases ($H_2SO_4$, $HNO_3$ and HCl) forms the $NH_4SO_4$, $NH_4NO_3$ and $NH_4Cl$ compounds which are referred as secondary inorganic aerosols (SIA). The secondary inorganic particulate components ($NH_4^+$, $SO_4^{2-}$, $NO_3^-$ and $Cl^-$) were dominant in $PM_{2.5}$ at the sampling location of Delhi. The secondary inorganic aerosol components i.e. $NH_4^+$, $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ manifested the highest levels in the $PM_{2.5}$ with an average level of 9.1 ± 3.5, 12.3 ± 4.1, 10.8 ± 4.8 and 9.3 ± 3.2 μg $m^{-3}$ during the study period (2013–2018). The $NH_4^+$, $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ were the major portions of the total soluble ions (Table 2). In winter, nitrates availability was significant due to possible reduction in $SO_2$ oxidation rates in response to lower level of OH radical (Walker et al. 2004). A relationship of particulate $NH_4^+$ with $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ during all the seasons supports the hypothesis (Fig. 3).

The molar ratios of $NH_4^+$ with $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ of $PM_{2.5}$ were also computed and summarised in Table 4, whereas charge balances are depicted in Fig. 4. It is to be noted that the molar ratio of $NH_4^+/SO_4^{2-} < 2$ indicates the $NH_4^+$ poor condition and > 2 indicates the $NH_4^+$ rich condition at the sampling site. The highest average molar ratio of $NH_4^+$ to the $SO_4^{2-}$ during winter (4.86) followed by post-monsoon (4.38), summer (3.61) and monsoon (2.1) seasons indicated the complete neutralisation of $H_2SO_4$, abundance of $(NH_4)_2SO_4$ and $NH_3$-rich condition during the winter season (Saraswati et al. 2019b). Since $NH_3$ is the only alkaline

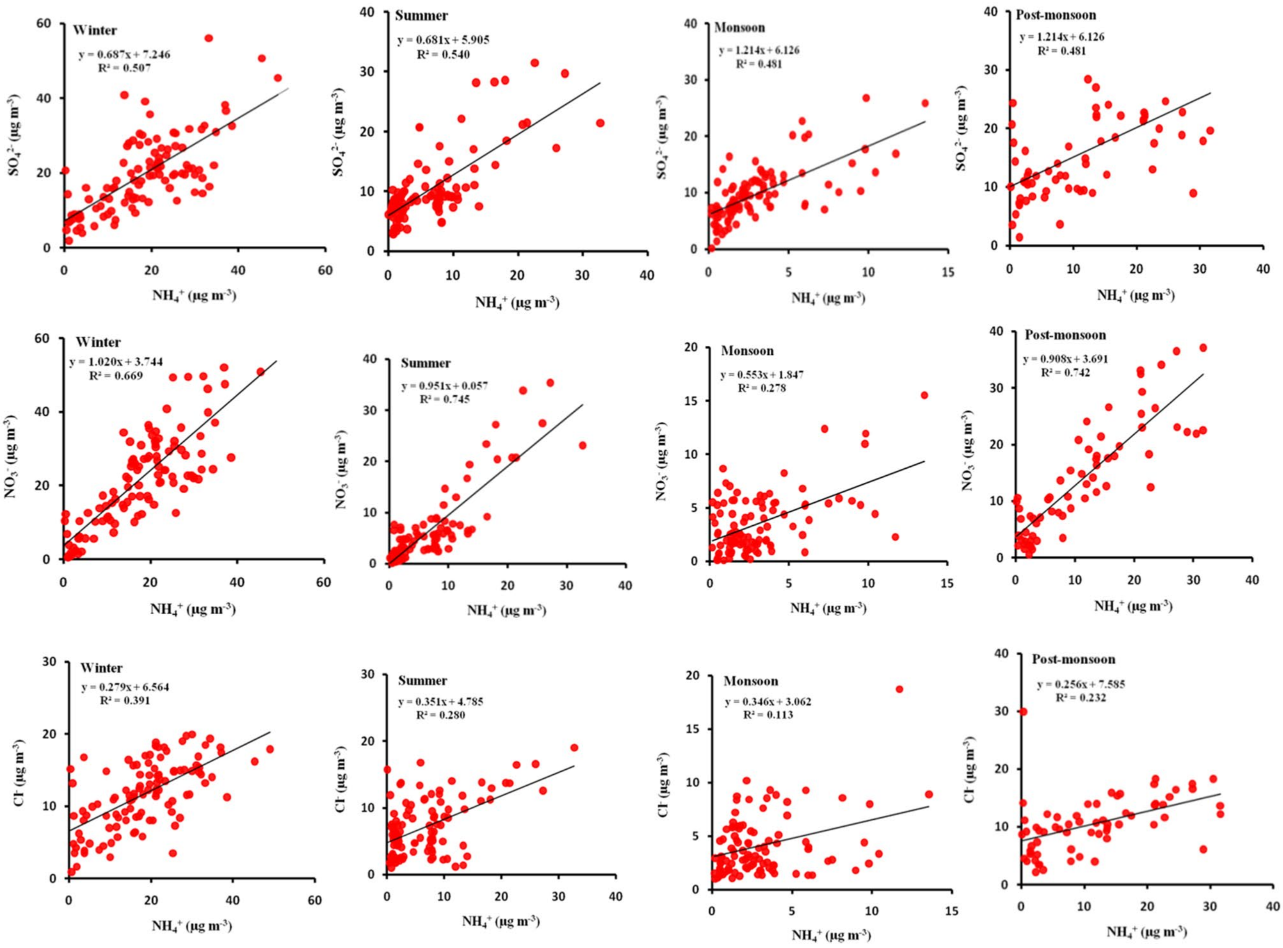

**Fig. 3** Scatter plots between $NH_4^+$ vs. $SO_4^{2-}$, $NH_4^+$ vs. $NO_3^-$, and $NH_4^+$ vs. $Cl^-$ of $PM_{2.5}$ in Delhi during winter, summer, monsoon and post-monsoon seasons

**Table 4** Model ratios $NH_4^+$ with other ionic species

| Parameters | Winter | Summer | Monsoon | Post-monsoon |
|---|---|---|---|---|
| $NH_4^+/SO_4^{2-}$ | 4.86 | 3.61 | 2.10 | 4.38 |
| $NH_4^+/NO_3^-$ | 2.64 | 3.62 | 2.82 | 2.94 |
| $NH_4^+/Cl^-$ | 2.22 | 1.53 | 1.24 | 2.35 |
| $NH_4^+/(SO_4^{2-}+NO_3^-)$ | 1.71 | 1.89 | 1.21 | 1.76 |
| $NH_4^+/(SO_4^{2-}+NO_3^-+Cl^-)$ | 0.97 | 0.85 | 0.61 | 1.01 |

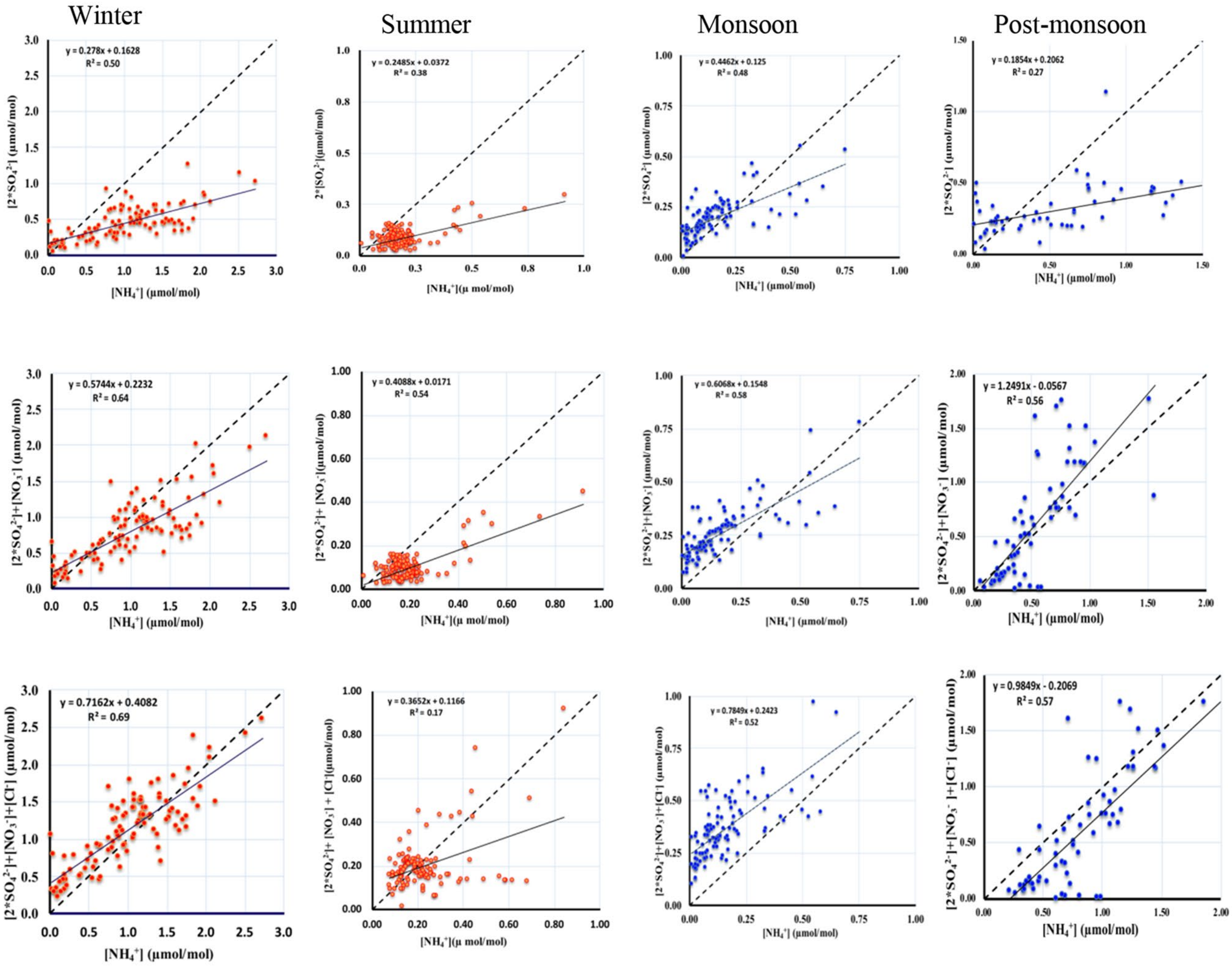

**Fig. 4** Charge balance: **a** between $SO_4^{2-}$ vs. $NH_4^+$, **b** between $SO_4^{2-} + NO_3^-$ vs. $NH_4^+$ and **c** between $SO_4^{2-} + NO_3^- + Cl^-$ vs. $NH_4^+$ during winter, summer, monsoon and post-monsoon in Delhi

gas in the atmosphere with adequate level to neutralise a significant portion of $SO_4^{2-}$, $NO_3^-$ and $Cl^-$, therefore, the aerosol electro-neutrality relationship ($NH_4^+$ availability index: *J*) between $NH_4^+$ and $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ ions can be computed (Chu 2004; Behra and Sharma 2010). During the winter (125.8%), post-monsoon (125.6%) and summer (102.2%) seasons, the average value of *J* was > 100% at the sampling site of Delhi. So there was enough $NH_4^+$ present in $PM_{2.5}$ samples to neutralise the $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ (Behra and Sharma 2010; Adam et al. 1999).

In the present case, the particulate $NH_3$ (in $PM_{2.5}$) had been lower than the gaseous $NH_3$ during all the seasons except the winter (54%) season (summer: 29%, monsoon: 28% and post-monsoon: 37%). Similar results were also reported by Singh and Kulshrestha (2012) at the other urban location of Delhi. The % fraction of (N-$NH_4^+$) was higher in the winter (54%) than all the other seasons. The higher N–$NH_4^+$ fraction during the winter may be due to favourable meteorological condition (lower temperature and higher RH) and abundance of $NH_3$ at sampling site, which results in faster $NH_3$ to $NH_4^+$ conversion (Saraswati et al. 2019b).

### 3.3 Gas to Particle Conversion

In the atmosphere, the acid gases ($HNO_3$ and $H_2SO_4$) formed by the reaction of $NO_x$ and $SO_x$ with hydroxyl radical (OH) and the particulate $NH_4^+$ were formed by the reaction of gaseous $NH_3$ with $HNO_3$ and $H_2SO_4$ acids gases (Heeb et al. 2008). In the present study, the role of atmospheric $NH_3$ in the formation of $NH_4NO_3$ and $NH_4SO_4$ was examined by estimating the significant positive correlation of $NH_3$ with $NO_x$ and $SO_2$ during the winter ($r^2 = 0.84$, $r^2 = 0.52$; $p < 0.05$), summer ($r^2 = 0.82$, $r^2 = 0.54$; $p < 0.05$), monsoon ($r^2 = 0.52$, $r^2 = 0.47$; $p < 0.05$) and post-monsoon ($r^2 = 0.79$, $r^2 = 0.58$; $p < 0.05$) seasons, respectively (Table S2 a–d, see the supplementary information). The positive correlation of

$NH_3$ with $NH_4^+$ also indicates the role of $NH_3$ in the transformation of $NH_4^+$ during all the seasons (winter: $r^2 = 0.77$; summer: $r^2 = 0.49$; monsoon: $r^2 = 0.52$; post-monsoon: $r^2 = 0.51$; $p < 0.05$). The gaseous ammonia was converted into particulate ammonia (of $PM_{2.5}$) and estimated as 54, 29, 28 and 37% during the winter, summer, monsoon and post-monsoon, respectively which further neutralised the $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ particulates. The average $NH_3/NH_4^+$ ratios varied from 1.19 to 3.58 with an average level of 2.62 during entire study period. The average $NH_3/NH_4^+$ ratio was computed as 1.19, 3.34, 3.58 and 2.38 during the winter, summer, monsoon, and post-monsoon, respectively. It was observed that the acidic gases ($HNO_3$ and $H_2SO_4$) were completely neutralised by the $NH_3$ gas during winter (as $NH_3/NH_4^+$ was close to 1). The higher ratio of $NH_3/NH_4^+$ during the summer, monsoon and post-monsoon suggested that the $NH_3$ gas was not neutralised completely (Meng et al. 2011) and $NH_3$ remained predominantly in the gas phase rather than aerosols phase (gaseous $NH_3$ to total $NH_x$ ($NH_x = NH_3 + NH_4^+ = 0.68$) (Gong et al. 2013). The higher seasonal $NH_4^+/NH_x$ ratios during all the seasons reflect the higher formation of $NH_4^+$ due to low temperature and higher RH (Saraswati et al. 2019b). Behera et al. (2013) also demonstrated the formation of particulate $NH_4^+$ from $NH_3$ at urban site of Kanpur, India.

The sulphur oxidation ratio [$SOR = SO_4^{2-}/(SO_4^{2-} + SO_2)$] and nitrogen oxidation ratio [$NOR = (PNO_3^- + GNO_3)/(NO_2 + PNO_3^- + GNO_3^-)$] are used as indicators of the secondary transformation process and sources of $SO_4^{2-}$ and $NO_3^-$, respectively (Khodar 2002; Baek and Aneja 2004; Behera and Sharma 2010). The higher SOR and NOR values were recorded in the winter (0.72, 0.43) followed by the post-monsoon (0.61, 0.27), summer (0.59, 0.22) and monsoon (0.58, 0.16) seasons at the sampling site (Table 5). Behera and Sharma (2010) had also obtained the higher level of SOR than NOR during the winter and summer seasons at Kanpur, India which demonstrates the low formation of $NO_3^-$ as compare to $SO_4^{2-}$. Saxena et al. (2017) also reported the higher level of SOR and NOR during winter in Delhi, whereas Sharma et al. (2007) showed the high NOR due to enhanced $NO_3^-$ formation during winter influenced by high humidity at Kanpur.

In the above section, the significant positive correlation of $NH_4^+$ with $SO_4^{2-}$ and $NO_3^-$ was observed which indicates the formation of $NH_4SO_4$ and $NH_4NO_3$ and their contribution to $PM_{2.5}$ (Table S2 a–d; in the supplementary information). We had also examined the reversible reaction of $NH_3$ and $HNO_3$ which results in the formation of particulate $NH_4NO_3$ as:

$$NH_3(g) + HNO_3(g) \leftrightarrow NH_4NO_3\ (S\ \text{or}\ aq) \quad (3)$$

**Table 5** Values of SOR and NOR during different seasons in Delhi

| Parameters | Winter | Summer | Monsoon | Post-monsoon |
|---|---|---|---|---|
| $NO_2$ (μg $m^{-3}$) | 33.3 | 35.9 | 28.1 | 37.6 |
| $NO_3$ (μg $m^{-3}$) | 22.6 | 4.9 | 4.6 | 10.9 |
| $GNO_3$ (μg $m^{-3}$) | 2.85 | 5.12 | 0.95 | 3.15 |
| $PNO_3 + GNO_3$ (μg $m^{-3}$) | 25.4 | 10.2 | 5.6 | 14.1 |
| $PNO_3/PNO_3 + GNO_3$ (%) | 88.9 | 48.1 | 82.1 | 77.3 |
| $GNO_3/PNO_3 + GNO_3$ (%) | 11.2 | 50.1 | 16.9 | 22.3 |
| NOR (%) | 42 | 22 | 16 | 27 |
| NOR | 0.42 | 0.22 | 0.16 | 0.27 |
| SOR (%) | 77 | 59 | 58 | 61 |
| SOR | 0.77 | 0.59 | 0.58 | 0.61 |

The equilibrium of $NH_4NO_3$ between gas and particulate phase depends on ambient temperature and RH (Wei et al. 2015). In this case, the product of measured concentration ($K_m = [NH_3] * [HNO_3]$) was computed and examined with the theoretically calculated equilibrium constant ($K_p$) at the same meteorological condition (Stelson and Seinfeld 1982; Saraswati et al. 2019b) and depicted in Table 3. The value of thermodynamic equilibrium constants calculated for the summer and the monsoon seasons indicated that $NH_4NO_3$ is not expected to be formed at the observational site (may be due to at most of the days as the product of $NH_3$ and $HNO_3$ were below the thermodynamically predicted dissociation constant) (Table 3). The conditions in the winter and the post-monsoon were more favourable for the formation of $NH_4NO_3$ as compared to summer and monsoon seasons (Behera and Sharma 2010).

## 4 Conclusion

In this paper, the Long-Term average seasonal mixing ratios of ambient trace gases ($NH_3$, NO, $NO_2$, and $SO_2$) and WSICs of $PM_{2.5}$ ($NH_4^+$, $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ etc.) were estimated at the observational site of Delhi, India (January 2013–December 2018) to examine the role of ambient $NH_3$ in the formation of secondary inorganic aerosols at the study site. The average levels of all trace gases ($NH_3$, NO, $NO_2$ and $SO_2$) were observed higher during the post-monsoon season, whereas the mass concentrations of WSICs of $PM_{2.5}$ were higher in the winter season. The correlation matrix of trace gases demonstrated that the ambient $NH_3$ neutralised all acid gases (NO, $NO_2$ and $SO_2$) at Delhi during the study period. Ion balance and molar equivalent ratios analysis of $PM_{2.5}$ also indicated that the abundance of particulate $NH_4^+$ at the study site to neutralise the $SO_4^{2-}$, $NO_3^-$, $Cl^-$ particles during all seasons, whereas the formation of $NH_4NO_3$ was higher during the winter due to favourable meteorological condition and forward reaction of $NH_3$ and $HNO_3$.

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**Author contributions** Conception and design of the study were planned by SKS; Data collection (SKS) and analysis (chemical as well as data analysis) were performed by GK, SKS, TKM. The original first draft was written by GK. All the authors read and approved the final manuscript. The manuscript has been prepared in consultation with all co-authors.

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**Data availability** The datasets developed during the current study are available from the corresponding author on reasonable request.

## Declarations

**Conflict of interest** The authors declare that they have no conflict of interest.

**Ethical approval** Not applicable.

**Consent to participate** Not applicable.

**Consent to publish** Not applicable.

## References

Adam D, Schuhmacher P, Simmerer J, Häussling L, Siemensmeyer K, Etzbachi KH, Ringsdorf H, Haarer D (1999) Fast photoconduction in the highly ordered columnar phase of a discotic liquid crystal. Nature 371:141–153

Aneja VP, Agarwal A, Roelle PA, Phillips SB, Tong Q, Watkins N, Yablonsky R (2001) Measurements and analysis of criteria pollutants in New Delhi. India Environ Int 27(1):35–42

Aneja VP, Schlesinger W, Erisman JW (2009) Effects of agriculture upon the air quality and climate: research, policy, and regulations. Environ Sci Technol 43:4234–4240

Baek BH, Aneja VP (2004) Measurement and analysis of the relationship between ammonia, acid gases, and fine particles in Eastern North Carolina. J Air Waste Manag Assoc 54(5):623–633

Behera SN, Sharma M (2010) Investigating the potential role of ammonia in ion chemistry of fine particulate matter formation for an urban environment. Sci Total Environ 408(17):3569–3575

Behera SN, Betha R, Balasubramanian R (2013) Insights into chemical coupling among acidic gases, ammonia and secondary inorganic aerosols. Aerosol Air Qual Res 13(4):1282–1296

Chow JC, Watson JG, Fujita EM, Lu Z, Lawson DR, Ashbaugh LL (1994) Temporal and spatial variations of $PM_{2.5}$ and $PM_{10}$ aerosol in the Southern California air quality study. Atmos Environ 28(12):2061–80

Chu SH (2004) $PM_{2.5}$ episodes as observed in the speciation trends network. Atmos Environ 38(31):5237–5246

Gong L, Lewicki R, Griffin RJ, Tittel FK, Lonsdale CR, Stevens RG, Pierce JR, Malioy QGJ, Travis SA, Bobmanuel LM, Lefer BL, Flynn JH (2013) Role of atmospheric ammonia in particulate matter formation in Houston during summertime. Atmos Environ 77:893–900

Heeb NV, Saxer CJ, Forss AM, Brühlmann S (2008) Trends of NO, $NO_2$ and $NH_3$ emissions from gasoline-fueled Euro-3-to Euro-4-passenger cars. Atmos Environ 42(10):2543–2554

Hoek G, Mennen MG, Allen GA, Hofschreuder P, Van Der Meulen T (1996) Concentrations of acidic air pollutants in the Netherlands. Atmos Environ 30(18):3141–3150

Huang C, Chen C, Li L, Cheng Z, Wang H, Huang H, Streets D, Wang Y, Zhang G, Chen Y (2011) Emission inventory of anthropogenic air pollutants and VOC species in the Yangtze River Delta region, China. Atmos Chem Phy 11:4105–4120

Huang XF, He LY, Hu M, Canagaratna MR, Sun Y, Zhang Q, Zhu T, Xue L, Zeng LW, Liu XG, Zhang YH (2010) Highly time-resolved chemical characterization of atmospheric submicron particles during 2008 beijing olympic games using an aerodyne high-resolution aerosol mass spectrometer. Atmos Chem Phys 10(18):8933–8945

Huang RJ, Zhang Y, Bozzetti C, Ho KF, Cao JJ, Han Y, Zotter P (2014) High secondary aerosol contribution to particulate pollution during haze events in China. Nature 514(7521):218

Ianniello A, Spataro F, Esposito G, Allegrini I, Rantica E, Ancora MP, Zhu T (2010) Occurrence of gas phase ammonia in the area of Beijing (China). Atmos Chem Phys 10(19):9487–9503

Ianniello A, Spataro F, Esposito G, Allegrini I, Hu M, Zhu T (2011) Chemical characteristics of inorganic ammonium salts in $PM_{2.5}$ in the atmosphere of Beijing (China). Atmos Chem Phys 11(21):10803–10822

Khemani LT, Momin GA, Naik MS, Rao PP, Safai PD, Murty ASR (1987) Influence of alkaline particulates on pH of cloud and rain water in India. Atmos Environ 21:1137–1145

Khoder MI (2002) Atmospheric conversion of sulfur dioxide to particulate sulfate and nitrogen dioxide to particulate nitrate and gaseous nitric acid in an urban area. Chemosphere 49(6):675–684

Kulshrestha UC, Sarkar AK, Srivastava SS, Parasar DC (1996) Investigation into atmospheric deposition through precipitation studies at New Delhi (India). Atmos Environ 30:4149–4154

Kumar N, Soni K, Agarwal R (2021) Design and Development of SODAR Antenna Structure. MAPAN 36(4):785–793

Li Y, Schwab JJ, Demerjian KL (2006) Measurements of ambient ammonia using a tunable diode laser absorption spectrometer: characteristics of ambient ammonia emissions in an urban area of New York City. J Geophys Res Atmos 111:D10S02. https://doi.org/10.1029/2005JD006275

Liu X, Sun K, Qu Y, Hu M, Sun Y, Zhang F, Zhang Y (2015) Secondary formation of sulfate and nitrate during a haze episode in megacity Beijing, China. Aerosol Air Qual Res 15:2246–2257

Marković DM, Marković DA, Jovanović A, Lazić L, Mijić Z (2008) Determination of $O_3$, $NO_2$, SO2, CO and $PM_{10}$ measured in Belgrade urban area. Environ Monitor Asses 145:349–359

Matsumoto K, Tanaka H (1996) Formation and dissociation of atmospheric particulate nitrate and chloride: an approach based on phase equilibrium. Atmos Environ 30(4):639–648

Meng ZY, Lin WL, Jiang XM, Yan P, Wang Y, Zhang YM, Yu XL (2011) Characteristics of atmospheric ammonia over Beijing. China Atmos Chem Phys 11(12):6139–6151

Pant P, Harrison RM (2012) Critical review of receptor modelling for particulate matter: a case study of India. Atmos Environ 49:1–12

Parashar DC, Granat L, Kulshreshtha UC, Pillai AG, Naik MS, Momin GA, Rao PSP, Safai PD, Khemani LT, Naqavi SWA, Narverkar PV, Thapa KB, Rodhe H (1996) Report CM-90 September 1996. Department of meteorology Stockholm, University International Meteorological Institute in Stockholm, Sweden

Parmar RS, Satsangi GS, Lakhani A, Srivastava SS, Prakash S (2001) Simultaneous measurements of ammonia and nitric acid in ambient air at Agra (27° 10’ N and 78° 05’ E) (India). Atmos Environ 35:5979–5988

Pinder Robert W, Peter J Adams, Spyros N Pandis (2007) Ammonia emission controls as a cost-effective strategy for reducing atmospheric particulate matter in the eastern United States, pp 380–386

Saraswati Sharma SK, Mandal TK (2018) Five-year measurement of ambient ammonia and its interaction with other trace gases at an urban site of Delhi. India. Meteo Atmos Phys 130(2):241–257

Saraswati George MP, Sharma SK, Mandal TK, Kotnala RK (2019a) Simultaneous measurements of ambient NH3 and its relationship with other trace gases, $PM_{2.5}$ and meteorological parameters over Delhi, India. Mapan-J Metrol Soc India 34(1):56–69

Saraswati Sharma SK, Saxena M, Mandal TK (2019b) Characteristics of gaseous and particulate ammonia and their role in the formation of secondary inorganic particulate matter at Delhi, India. Atmos Res 218:34–49

Saxena M, Sharma A, Sen A, Saxena P, Saraswati Mandal TK, Sharma SK, Sharma C (2017) Water soluble inorganic species of $PM_{10}$ and $PM_{2.5}$ at an urban site of Delhi, India: seasonal variability and sources. Atmos Res 184:112–125

Seinfeld JH, Pandis SN (2006) Atmospheric chemistry and physics from air pollution to climate change. John Wiley, New York

Sharma M, Kishore S, Tripathi SN, Behera SN (2007) Role of atmospheric ammonia in the formation of inorganic secondary particulate matter: a study at Kanpur. India J Atmos Chem 58(1):1–17

Sharma SK, Datta A, Saud T, Mandal TK, Ahammed YN, Arya BC, Tiwari MK (2010a) Study on concentration of ambient $NH_3$ and interaction with some other ambient trace gases. Environ Monit Asses 162:225–235

Sharma SK, Datta A, Saud T, Saxena M, Mandal TK, Ahammed YN, Arya BC (2010b) Seasonal variability of ambient $NH_3$, NO, $NO_2$ and $SO_2$ over Delhi. J Environ Sci 22(7):1023–1028

Sharma SK, Mandal TK, Arya BC, Saxena M, Shukla DK, Mukherjee A, Bhatnagar RP, Nath S, Yadav S, Gautam R, Saud T (2010c) Effects of the solar eclipse on 15 January 2010 on the surface $O_3$, NO, $NO_2$, $NH_3$, CO mixing ratio and the meteorological parameters at Thiruvanthapuram, India. Annales Geophyscae 28: 1199–1205

Sharma SK, Saxena M, Mandal TK, Ahammed YN, Pathak H, Datta A, Saud T, Arya BC (2011) Variations in mixing ratios of ambient ammonia, nitric oxide and nitrogen dioxide in different environments of India. J Earth Sci Climate Change 1:102

Sharma SK, Singh AK, Saud T, Mandal TK, Saxena M, Singh S, Ghosh S, Raha S (2012a) Study on water soluble ionic composition of $PM_{10}$ and trace gases over Bay of Bengal during W_ICARB campaign. Meteo Atmos Phys 118:37–51

Sharma SK, Singh AK, Saud T, Mandal TK, Saxena M, Singh S, Ghosh S, Raha S (2012b) Measurement of ambient $NH_3$, NO, $NO_2$ and $SO_2$ over Bay of Bengal during W_ICARB campaign. Ann Geophys 30:371–377

Sharma SK, Saxena M, Saud T, Korpole S, Mandal TK (2012c) Measurement of $NH_3$, NO, $NO_2$ and related particulates at urban sites of Indo Gangetic Plain (IGP) of India. J Sci Indust. Res 71(5):360–362

Sharma SK, Harit RC, Kumar V, Mandal TK, Pathak H (2014a) Ammonia emission from rice-wheat cropping system in subtropical soil of India. Agril Res 3(2):175–180

Sharma SK, Mandal TK, Rohtash KM, Gupta NC, Pathak H, Harit RC, Saxena M (2014b) Measurement of ambient ammonia over the National Capital Region of Delhi, India. Mapan-J Metrol Soc India 29(3):165–173

Sharma SK, Mandal TK, Sharma C, Kuniyal JC, Joshi R, Dhayani PP, Rohtash SA, Ghayas H, Gupta NC, Arya BC, Kumar A, Sharma P, Saxena M, Sharma A (2014c) Measurements of particulate ($PM_{2.5}$), BC and trace gases over the northwestern Himalayan region of India. Mapan-J Metrol Soc of India 29(4):243–253

Sharma SK, Kumar M, Rohtash Gupta NC, Saraswati Saxena M, Mandal TK (2014d) Characteristics of ambient ammonia over Delhi, India. Meteo Atmos Phy 124:67–82

Sharma SK, Rohtash MTK, Deb NC, Pal S (2016) Measurement of ambient $NH_3$, NO and $NO_2$ at an urban area of Kolkata, India. Mapan-J Metrol Soc India 31(1):75–80

Sharma SK, Saraswati MTK, Saxena M (2017) Inter-annual variation of ambient ammonia and related trace gases in Delhi. India Bull Environ Contamin Toxicol 99(2):281–285

Sharma SK, Mukherjee S, Choudhary N, Rai A, Ghosh A, Chatterjee A, Vijayan N, Mandal TK (2021) Seasonal variation and sources of carbonaceous species and elements of $PM_{2.5}$ and $PM_{10}$ over the eastern Himalaya. Environ Sci Pollut Res 28:51642–51656

Singh S, Kulshrestha UC (2012) Abundance and distribution of gaseous ammonia and particulate ammonium at Delhi. India Biogeosciences 9(12):5023

Singh S, Kulshrestha UC (2014) Rural versus urban gaseous inorganic reactive nitrogen in the Indo-Gangetic plains (IGP) of India. Environ Res Lett 9(12):125004

Singh N, Murari V, Kumar M, Barman SC, Banerjee T (2017) Fine particulates over South Asia: review and meta-analysis of $PM_{2.5}$ source apportionment through receptor model. Environ Pollut 223:121–136

Stelson AW, Seinfeld JH (1982) Relative humidity and temperature dependence of the ammonium nitrate dissociation constant. Atmos Environ 16(5):983–992

Stockwell WR, Watson JG, Robinson NF, Steiner W, Sylte WW (2000) The ammonium nitrate particle equivalent of NOx emissions for wintertime conditions in Central California’s San Joaquin Valley. Atmos Environ 34:4711–4717

Sutton MA, Dragosits U, Tang YS, Fowler D (2000) Ammonia emissions from non-agricultural sources in the UK. Atmos Environ 34(6):855–869

Sutton MA, Reis S, Riddick SN, Dragosits U, Nemitz E, Theobald MR et al (2013) Towards a climate-dependent paradigm of ammonia emission and deposition. Philos Trans R Soc B Biol Sci 368(1621):13

Updyke KM, Nguyen TB, Nizkorodov SA (2012) Formation of brown carbon via reactions of ammonia with secondary organic aerosols from biogenic and anthropogenic precursors. Atmos Environ 63:22–31

Walker JT, Whitall DR, Robarge W, Paerl HW (2004) Ambient ammonia and ammonium aerosol across a region of variable ammonia emission density. Atmos Environ 38(9):1235–1246

Wang Y, Zhuang G, Tang A, Yuan H, Sun Y, Chen S, Zheng A (2005) The ion chemistry and the source of $PM_{2.5}$ aerosol in Beijing. Atmos Environ 39(21):3771–3784

Wang Z, Li J, Wang Z, Yang W, Tang X, Ge B, Wand W (2014) Modeling study of regional severe hazes over mid-eastern China in January 2013 and its implications on pollution prevention and control. Sci China Earth Sci 57(1):3–13

Wei L, Duan J, Tan J, Ma Y, He K, Wang S, Huang S, Zhang Y (2015) Gas-to-particle conversion of atmospheric ammonia and sampling artifacts of ammonium in spring of Beijing. Sci China Earth Sci 58(3):345–355

Wu Z, Hu M, Shao K, Slanina J (2009) Acidic gases, $NH_3$ and secondary inorganic ions in $PM_{10}$ during summertime in Beijing, China and their relation to air mass history. Chemosphere 76(8):1028–1035

Xu L, Penner JE (2012) Global simulations of nitrate and ammonium aerosols and their radiative effects. Atmos Chem Phys 12(20):9479–9504

Xu W, Wu Q, Liu X, Tang A, Dore AJ, Heal MR (2016) Characteristics of ammonia, acid gases, and $PM_{2.5}$ for three typical land-use types in the North China Plain. Environ Sci Pollut Res 23(2):1158–1172

Yang F, Tan J, Zhao Q, Du Z, He K, Ma Y, Duan F, Chen G (2011) Characteristics of $PM_{2.5}$ speciation in representative megacities and across China. Atmos Chem Phys 11(11):5207–5219