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# Study on the Relationship of WSIS of $PM_{2.5}$ with $NH_3$ and Other Trace Gases over Delhi, India †

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**Abstract:** The water soluble ionic species (WSIS) i.e., $NH_4^+$, $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ of $PM_{2.5}$ and trace gases ($NH_3$, NO, $NO_2$, $SO_2$, $HNO_3$) were measured to study the relationship of ambient $NH_3$ in the formation of secondary inorganic aerosols in Delhi, India from January 2013–December 2018. During the study period, the average concentrations of $NH_3$, NO, $NO_2$, $SO_2$ and $HNO_3$ were 19.1 ± 3.8 ppb, 20.8 ± 4.3 ppb, 17.9 ± 4.2 ppb, 2.45 ± 0.47 ppb, 1.11 ± 0.35 ppb, respectively. The concentrations of trace gases were higher during post-monsoon whereas the concentrations of WSIS in $PM_{2.5}$ were estimated higher in winter. The correlation matrix of trace gases reveal that the ambient $NH_3$ neutralize the acid gases (NO, $NO_2$ and $SO_2$) at the monitoring site. Study reveals that the abundance of particulate $NH_4^+$ at Delhi to neutralized the $SO_4^{2-}$, $NO_3^-$, $Cl^-$ particles during all the seasons.

**Keywords:** $PM_{2.5}$; aerosols; carbonaceous species; OC; IGP region

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## 1. Introduction

The formation of secondary aerosols in the atmosphere influenced by reaction rate of $NH_3$ which depends on the favorable meteorological condition and availability of acid gases in the atmosphere [1,2]. Fine fraction of particulate matter ($PM_{2.5}$) is considered as one of the major pollutants having a negative impact on atmospheric chemistry [3,4]. Secondary aerosols contribute to a major fraction of $PM_{2.5}$ mass concentration which is mainly formed from $NH_3$ and its co-pollutants such as $NO_x$ and $SO_x$ [5]. $NH_3$ as a primary alkaline gas neutralizes the acid gases ($HNO_3$ and $H_2SO_4$) and form the secondary particulates ($NH_4NO_3$ and $(NH_4)_2SO_4$), which are the major fractions of airborne fine particles [6]. 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 [7–11]. However, long-term study on seasonal basis as well gas-to-particle conversion is inadequate in Indian region. In this paper, we reported 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.

## 2. Materials and Methods

Ambient $NH_3$, NO, $NO_2$, and $SO_2$ were monitored at CSIR-National Physical Laboratory, New Delhi from January 2013 to December 2018. 24 h periodic sampling (2 samples/week) of $PM_{2.5}$ was also performed during this period on quartz filters. 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 [11]. The estimation of WSICs ($Na^+$, $NH_4^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, $NO_3^-$ and $SO_4^{2-}$) of $PM_{2.5}$ were determined using Ion Chromatograph (DIONEX, Sunnyvale, CA, USA) with suppressed conductivity [12].

## 3. Results and Discussion

During the study period (2013–2018), the average levels of $NH_3$, NO, $NO_2$, $SO_2$ and $HNO_3$ were 19.1 ± 3.8 ppb, 20.8 ± 4.3 ppb, 17.9 ± 4.2 ppb, 2.45 ± 0.47 ppb, 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 μg $m^{-3}$, 12.3 ± 4.1 μg $m^{-3}$, 10.8 ± 4.8 μg $m^{-3}$ and 9.3 ± 3.2 μg $m^{-3}$, respectively. Seasonal mixing ratios of $NH_3$, other trace gases (NO, $NO_2$ and $SO_2$) and concentrations of water soluble ionic components (WSICs) of $PM_{2.5}$ are depicted in Tables 1 and 2. The ambient $NH_3$ indicated significant seasonal variation with highest mixing ratio during post-monsoon season (22.2 ± 3.9 ppb) followed by winter (20.9 ± 4.1 ppb), summer (19.4 ± 4.1 ppb) and monsoon (14.0 ± 2.5 ppb) seasons.

**Table 1.** Seasonal variation in trace gases (in ppb) in Delhi during 2013–2018.

| Seasons | $NH_3$ | $NO_2$ | NO | $SO_2$ |
|---|---|---|---|---|
| Winter | 20.9 ± 4.1 | 17.7 ± 4.5 | 18.1 ± 4.4 | 2.24 ± 0.37 |
| Summer | 19.4 ± 4.1 | 19.1 ± 4.3 | 21.4 ± 5.4 | 2.25 ± 0.43 |
| Monsoon | 14.0 ± 2.5 | 14.9 ± 3.7 | 20.4 ± 5.3 | 2.55 ± 0.26 |
| Post-Monsoon | 22.2 ± 3.9 | 20.0 ± 4.2 | 23.3 ± 4.5 | 2.77 ± 0.36 |
| Average | 19.1 ± 3.8 | 17.9 ± 4.2 | 20.8 ± 4.3 | 2.45 ± 0.47 |

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

| Seasons | $PM_{2.5}$ | $Cl^-$ | $SO_4^{2+}$ | $NO_3^-$ | $NH_4^+$ |
|---|---|---|---|---|---|
| Winter | 190 ± 82 | 15.6 ± 8.9 | 19.6 ± 6.9 | 22.7 ± 9.5 | 17.5 ± 2.8 |
| Summer | 92 ± 30 | 7.5 ± 3.1 | 8.5 ± 2.2 | 5.0 ± 2.8 | 5.8 ± 3.5 |
| Monsoon | 86 ± 33 | 6.2 ± 2.1 | 9.9 ± 1.9 | 4.7 ± 2.4 | 3.9 ± 1.2 |
| Post-Monsoon | 171 ± 72 | 7.8 ± 3.0 | 11.3 ± 3.4 | 10.9 ± 3.8 | 9.3 ± 4.4 |
| Average | 135 ± 45 | 9.3 ± 3.2 | 12.3 ± 4.1 | 10.8 ± 4.8 | 9.1 ± 3.5 |

The higher concentration of $NH_4^+$ during winter season at the observational site of Delhi may be due to high (relative humidity) RH, low temperature and higher $NH_3$ mixing ratio influenced the $NH_4^+$ formation [13]. In winter, nitrates availability was significant due to possible reduction in $SO_2$ oxidation rates in response to lower level of hydroxyl (OH) radical [14]. A relationship of particulate $NH_4^+$ with $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ during all the seasons supports the hypothesis of gas-to-particle conversion. 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 neutralization of $H_2SO_4$, abundance of $(NH_4)_2SO_4$ and $NH_3$-rich condition during the winter season [11]. Since $NH_3$ is the only alkaline gas in the atmosphere with adequate level to neutralize a significant portion of $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ therefore the aerosol electro-neutrality relationship between $NH_4^+$ and $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ ions can be computed [15].

## 4. Conclusions

The average levels of all trace gases ($NH_3$, NO, $NO_2$ and $SO_2$) were observed higher during post-monsoon season whereas the mass concentrations of WSICs of $PM_{2.5}$ were higher in winter seasons. The correlation matrix of trace gases demonstrated that the ambient $NH_3$ neutralize all the acid gases (NO, $NO_2$ and $SO_2$) at Delhi during the study period.

**Author Contributions:** Conception and design of the study were planned by S.K.S.; Data analysis were performed by G.K., T.K.M. and S.K.S.; The original first draft was written by G.K. All authors have read and agreed to the published version of the manuscript.

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