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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-ICS-3000, 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 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 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 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.

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