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Simultaneous Measurements of Ambient NH$_3$ and Its Relationship with Other Trace Gases, PM$_{2.5}$ and Meteorological Parameters over Delhi, India

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Abstract: In the present study, trace gases (NH$_3$, NO$_x$, CO and SO$_2$), PM$_{2.5}$ and meteorological parameters were carried out at 5 different monitoring sites [CSIR-National Physical Laboratory, New Delhi and other 4 air quality measurements (AQMS) sites (Anand Vihar, Mandir Marg, Punjabi Bagh and R.K. Puram) of Delhi Pollution Control Committee (DPCC)] of megacity Delhi, India, from January 2013 to December 2015 to estimate the spatio-temporal variation of pollutants over Delhi. The results showed large spatial and seasonal variations in mixing ratios of ambient trace gases and PM$_{2.5}$ concentration over Delhi. The average mixing ratios of NH$_3$, NO, NO$_2$, CO and SO$_2$ were 53.4 ± 14.9 ppb, 42.0 ± 14.6 ppb, 39.6 ± 13.0 ppb, 1.9 ± 0.4 ppm and 4.3 ± 1.0 ppb, respectively, whereas average concentration of PM$_{2.5}$ was 136.2 ± 49.6 μg m^{-3} during the entire study period. All the trace gases and PM$_{2.5}$ showed maxima during winter season followed by summer and monsoon seasons at all the sites. The 24-h average mixing ratios of the trace gases (NH$_3$, NO, NO$_2$, CO and SO$_2$) and PM$_{2.5}$ were recorded higher when compared with other sites of the country. The concentration of PM$_{2.5}$ is breaching the prescribed standard limit of National Ambient Air Quality Standards (NAAQS) of India.

Keywords: Ambient NH$_3$; Trace gases; PM$_{2.5}$; Correlation analysis; Sources; Meteorology

1. Introduction

Air pollution is rapidly increasing in India, due to various anthropogenic factors such as economic rise, population growth, huge consumption of fossil fuels, urbanization and increase in traffic flow [1]. As a consequence, atmospheric trace gases and particulate matter (PM) remain a nation-wide problem and result in regional photochemical smog and haze formation [2]. The ambient NH$_3$, SO$_2$ and NO$_x$ are primary precursor gases for the formation of fine particulate matter (PM$_{2.5}$) by gas to particle conversion process [3]. The ambient NH$_3$ as a dominant base plays an important role in atmospheric chemistry as well as ambient air quality [4]. NH$_3$ once emitted reacts with atmospheric acidic gases such as H$_2$SO$_4$ and HNO$_3$ which are oxidation products of SO$_2$ and NO$_2$, respectively, to form secondary particulate matter in the form of (NH$_4$)$_2$SO$_4$, NH$_4$HSO$_4$ and NH$_4$NO$_3$ [5–7]. Due to shorter residence time (1–3 days), NH$_3$ readily undergoes these reactions close to the source and contributes to increase in concentration of urban PM [8]. The fine particle NH$_4^+$ salts have impact on human health, visibility, ambient acidity, biodiversity of ecosystem and have implications for global radiation budget and transboundary air pollution [9, 10].

The major sources of ambient NH$_3$ are livestock waste and fertilizer application in the agricultural fields [11]. But, recent evidence suggests that human activities, industrial process, municipal waste and internal combustion in traffic are also major sources of ambient NH$_3$ at urban areas

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[12, 13]. There is a need to control NH_3, other trace gases (NO_x, SO_2) and $PM_{2.5}$ emission especially in urban areas where a complex mixture of harmful gases and particles of varying chemical composition are increasing and effecting the environment and human health [14]. Although the traffic contribution was thought to be small, several studies have reported a strong link between NH_3 emission and traffic [13, 15–17]. The introduction of three-way catalyst to reduce NO_x emission in gasoline vehicles in 1980 s and 1990 s increased vehicular NH_3 emission [18] in urban areas. NH_3 is now the dominant reactive nitrogen species emitted from vehicles after introduction of selective catalytic reduction (SCR) system in diesel vehicles [19]. The introduction of catalyst had increased the traffic source of NH_3 from 2 to 15% of total emitted NH_3 in Los Angeles area as reported in a roadway tunnel study [20]. Pierson and Brachaczek, [20], Fraser and Cass, [21], Moeckli et al. [22] suggested that on road vehicle NH_3 emissions increased significantly after the introduction of three-way catalytic converters. NH_3 mixing ratio in urban areas is comparable or even higher than that of rural areas as reported in various studies worldwide [23]. The ambient NH_3 is not routinely measured as compared to SO_2 and NO_x which have been regulated and going to decrease even further in many countries in coming years [24]. The vehicle emission standard to regulate NH_3 was also absent worldwide. It is a necessity to control emission of NH_3 with NO_x and SO_2 to reduce $PM_{2.5}$ concentration [24]. Pinder et al. [25] found that the NH_3 control technologies were most cost-effective as compared to SO_2 and NO_x. Wang et al. [26] reported that benefit of SO_2 reduction would be completely offset if NH_3 emission was allowed to keep their recent growth in order to reduce $PM_{2.5}$ concentration.

Delhi is the capital city of India and represents typical urban characteristics. The rapid urbanization and industrialization caused an increase in number of petrol and diesel vehicles which are added annually into Delhi; it is to be noted that the total number of registered vehicles in the city was of the order of 9.7 million in 2015–16 [27]. The condition worsens every winter as the city suffered by burning of crop residue in neighboring states and it records higher levels of air pollution [28]. Although a number of studies have been conducted on characteristics of aerosol, however, a limited attention has been paid to the factors which are responsible for the formation of secondary inorganic aerosols. A limited study has been done on the diurnal, seasonal and temporal variability of ambient NH_3 and its role in the formation of secondary inorganic aerosols at different parts of the India for limited period and at single monitoring station [13, 29–35]. In the present study, we report the mixing ratios of ambient NH_3 and other gases (NO_x, CO, SO_2) and $PM_{2.5}$ concentration at 5 different sites in Delhi from January 2013 to December

2015. Diurnal, seasonal and temporal variations of these trace gases and $PM_{2.5}$ were also reported and correlated with meteorological parameters (temperature, relative humidity, wind direction and wind speed) of all the observational sites.

2. Methodology

2.1. Description of Observational Sites

The measurements of trace gases (NH_3, NO, NO_2, CO and SO_2) and $PM_{2.5}$ were carried out at 5 different locations (Fig. 1) in Delhi, India, from January 2013 to December 2015. The detailed description of Delhi is available in our previous publication and reference therein [13]. Out of 5 observational sites CSIR-National Physical Laboratory (CSIR-NPL), New Delhi, is considered as a reference site and other 4 sites (AQMS: Anand Vihar, Mandir Marg, Punjabi Bagh and R.K. Puram) are operational under the DPCC, New Delhi, India. The diurnal, seasonal and temporal variations of ambient NH_3, NO, NO_2 and CO at CSIR-NPL (from January 2010 to December 2015) are already reported in our previous paper and reference therein [13, 36]. We have used these datasets (from January 2013 to December 2015) to compare the pollutants collected at 4 AQMS sites of DPCC, New Delhi. A brief description of these observational sites is given below:

1. CSIR-NPL (28°63′N, 77°17′E): is an urban/traffic site surrounded by agricultural fields of Indian Agricultural Research Institute (IARI) in W and SW direction and is under the influence of vehicular emission in SW, NW, NE and SE direction [13]. The site is encircled with roadside traffic and nearby road in N direction.

2. Anand Vihar (28°38′N, 77°18′E): site is near the Inter-State Bus Terminus (ISBT), which caters to the states of Uttar Pradesh, Uttarakhand and Himachal Pradesh, as shown in Fig. 1. Anand Vihar is a posh residential area and a fast developing commercial center in East Delhi. Sahibabad and Patparganj industrial areas are in close proximity. The study site may be defined as industrial-cum-commercial zone with less residential activities. However, due to proximity to ISBT, movement of traffic is relatively higher.

3. Mandir Marg (28°37′N, 77°12′E): site is located at NP Boys Senior Secondary School at Mandir Marg in Central Delhi. The observational site is surrounded by mainly ridge forest area and residential colony.

4. Punjabi Bagh (28°40′N, 77°7′E): monitoring site is located in Sarvodaya Kanya Vidyalaya No. 2 in Punjabi Bagh in West Delhi. This location is surrounded by major roadside traffic. The two major

opposite roads with heavy traffic are located at 500 m away from the monitoring site.

5. R.K. Puram (28°33′N, 77°11′E): site is located at Kendriya Vidyalaya, Sector 2, R.K. Puram in South Delhi near outer ring road with high traffic density.

2.2. Measurement Techniques

Measurements of mixing ratios of trace gases (NH_3, NO, NO_2, CO and SO_2) and $PM_{2.5}$ have been performed using USEPA-approved respective trace gas analyzers. A brief information about the instruments used, make, principle of operation and lower detection limit (LDL), etc., of all the instruments are listed in Table S1 (in supplementary information). The calibration of zero check (baseline calibration) of all the analyzers was performed using Pure Air Generator (PAG; accuracy ± 0.05 ppb). The measurement ranges of all the analyzers were calibrated (span calibration) periodically using respective traceable certified reference gases (NMI traceable). Calibration procedures (as well as traceability of standards used) of these analyzers are discussed in detail in our previous paper Sharma et al. [34]. Sampling inlets of all the analyzers were also placed at ∼ 10 m height (above the ground) at all the observational sites. These instruments were operated continuously (24 h) with uninterrupted and steady power supplies for more than 15–20 days in a month. The mixing ratios of NH_3, NO, NO_2, CO and SO_2 were measured at every 1-min interval by respective analyzers and calculated by hourly average values (the reported datasets have been used after omitting frequently detected sudden spikes and long gaps in the observations) for the entire sampling period.

Meteorological parameters were recorded by automatic weather station (AWS) at all the observational sites. The meteorological parameters such as temperature (°C), relative humidity (RH, %), wind speed (ms^{-1}) and wind direction (degree) were recorded simultaneously during the observational period [34]. The daily average visibility and rainfall data were downloaded from Weather Underground (http://www.wunderground.com).

3. Results and Discussion

3.1. Mixing Ratios of Trace Gases and Concentration of $PM_{2.5}$

Diurnal, seasonal and annual variations in mixing ratios of trace gases (NH_3, NO, NO_2, CO and SO_2) and concentration of $PM_{2.5}$ were analyzed and reported for 5 different observational sites in Delhi, India, during January 2013 to December 2015 (Table 1, 2). The annual average and seasonal variations in mixing ratios of all the trace gases, $PM_{2.5}$ concentration and meteorological parameters over Delhi are summarized in Table 1 and 2 (Fig S1 in supplementary information). The annual average mixing ratio of NH_3 varied from 16.1 ± 3.3 ppb (minima) at CSIR-NPL in 2013 to 71.0 ± 19.8 ppb (maxima) at Punjabi Bagh in 2014. The highest NH_3 mixing ratio was observed at Punjabi Bagh with annual average of 68.0 ± 18.9 ppb followed by 64.2 ± 20.8, 60.1 ± 16.0, 55.0 ± 15.4, 19.6 ± 3.5 ppb at Anand Vihar, Mandir Marg and R.K. Puram, NPL, respectively (Table 1). The overall annual average mixing ratio of ambient NH_3 was recorded as 53.4 ± 14.9 ppb over Delhi ranging from 19.8 ppb to 114.6 ppb. The average mixing ratio of ambient NH_3 was observed relatively higher in present case as compared to other cities of India and the world. Behera and Sharma [30] reported mixing ratio of ambient NH_3 as 38 ± 8 ppb at Kanpur, India; Tsai et al. [37] reported 45 ± 23 ppb at Kaohsiung, Taiwan, and Biswas et al. [38] reported 71 ± 24 ppb at Lahore, Pakistan. The annual mixing ratio of NO was recorded as 20.4 ± 6.2 ppb, 49.4 ± 17.1 ppb, 44.7 ± 15.4 ppb, 45.3 ± 15.3 ppb and 50.3 ± 19.5 ppb, at CSIR-NPL, Anand Vihar, Mandir Marg, Punjabi Bagh and R.K. Puram, respectively. The highest annual average mixing ratio of NO was recorded as 50.3 ± 19.5 ppb at R.K. Puram. The annual average mixing ratio of NO_2 and CO was varied from 13.4 ± 3.9 ppb in 2013 at NPL and 1.4 ± 0.4 ppm in 2015 at Mandir Marg to 51.4 ± 16.5 ppb at Punjabi Bagh in 2013 and 2.7 ± 0.6 ppm in 2015 at CSIR-NPL. The annual average mixing ratios of NO_2 and CO were recorded as 39.6 ± 13.0 ppb and 1.9 ± 0.4 ppm with nonsignificant spatial variability over Delhi. The time series and monthly average in mixing ratios of ambient NH_3, NO, NO_2, CO and SO_2 along with concentration of $PM_{2.5}$ are depicted in Figs. S2–S8 (in supplementary information).

The mixing ratios of NO and NO_2 were also observed higher in the present study as compared to other previous study at Delhi and other sites in the world [13, 32, 39]. The annual average mass concentration of $PM_{2.5}$ was reported highest (171.6 ± 63.1) μg m^{-3} at Anand Vihar and lowest as 105.6 ± 42.9 μg m^{-3} at NPL with overall annual average as 134.0 ± 49.6 μg m^{-3} over Delhi during the study period. The annual average concentration of $PM_{2.5}$ vary spatially over Delhi due to different anthropogenic sources strength and meteorological condition.

3.2. Diurnal Variation

Diurnal variation in mixing ratios of ambient NH_3, other trace gases and $PM_{2.5}$ concentration during winter, summer and monsoon seasons at various locations in Delhi are

Table 1 The year-wise annual average mixing ratios of ambient NH₃, other trace gases (NO, NO₂, CO, SO₂) and meteorological parameters during January 2013 to December 2015 at NPL, Anand Vihar, Mandir Marg, Punjabi Bagh and R.K. Puram in Delhi (± standard deviation)

Sites	Year	NH_3 (ppb)	NO (ppb)	NO_2 (ppb)	CO (ppm)	SO_2 (ppb)	$PM_{2.5}$ (µg m^{-3})	Temp (°C)	RH (%)	WS (m/s)	WD (deg)
NPL	2013	16.1 ± 3.3	23.2 ± 6.5	13.4 ± 3.9	1.9 ± 0.4	1.9 ± 0.4	107.6 ± 45.3	24.8 ± 2.1	53.5 ± 9.4	1.5 ± 0.4	158.3 ± 42.9
	2014	24.3 ± 3.6	19.1 ± 6.0	21.9 ± 5.4	1.9 ± 0.4	1.8 ± 0.3	120.1 ± 40.9	24.9 ± 2.4	50.5 ± 11.0	1.6 ± 0.4	179.6 ± 65.2
	2015	18.5 ± 3.6	18.9 ± 6.1	23.9 ± 6.6	2.2 ± 0.6	2.3 ± 0.5	123.0 ± 42.6	25.2 ± 2.4	54.7 ± 11.2	1.6 ± 0.5	88.6 ± 34.2
	Average	19.6 ± 3.5	20.4 ± 6.2	19.7 ± 5.3	2.0 ± 0.5	2.0 ± 0.4	116.9 ± 42.9	25.0 ± 2.3	52.9 ± 10.5	1.5 ± 0.5	142.2 ± 47.4
Anand Vihar	2013	69.3 ± 23.6	51.9 ± 20.6	46.0 ± 15.5	2.1 ± 0.5	5.0 ± 1.1	165.4 ± 63.6	25.5 ± 2.2	53.7 ± 7.9	1.5 ± 0.4	175.9 ± 52.2
	2014	58.4 ± 20.9	45.7 ± 15.4	50.0 ± 20.8	1.9 ± 0.4	4.9 ± 1.0	184.8 ± 69.4	25.3 ± 2.6	51.3 ± 9.7	1.5 ± 0.6	195.8 ± 56.3
	2015	64.9 ± 18.0	50.4 ± 15.4	44.4 ± 12.5	1.7 ± 0.4	5.4 ± 1.4	164.5 ± 56.3	26.4 ± 2.6	52.8 ± 9.4	1.6 ± 0.7	184.9 ± 58.6
	Average	64.2 ± 20.8	49.4 ± 17.1	46.9 ± 16.3	1.9 ± 0.4	5.1 ± 1.2	171.6 ± 63.1	25.7 ± 2.5	52.6 ± 9.0	1.5 ± 0.6	185.5 ± 55.7
Mandir Marg	2013	64.5 ± 14.6	44.1 ± 13.1	45.4 ± 13.2	1.7 ± 0.4	6.0 ± 1.1	125.2 ± 44.3	24.0 ± 2.2	59.0 ± 8.1	1.4 ± 0.5	207.5 ± 31.9
	2014	59.5 ± 18.9	44.4 ± 15.4	50.2 ± 19.1	1.5 ± 0.4	3.7 ± 1.1	124.6 ± 48.5	22.8 ± 2.5	56.9 ± 9.2	1.3 ± 0.5	214.8 ± 32.4
	2015	56.3 ± 14.6	45.7 ± 17.7	41.3 ± 14.3	1.4 ± 0.4	4.2 ± 1.1	106.1 ± 34.5	22.1 ± 2.6	58.9 ± 9.3	1.6 ± 0.5	211.7 ± 35.7
	Average	60.1 ± 16.0	44.7 ± 15.4	45.6 ± 15.5	1.5 ± 0.4	4.6 ± 1.1	118.6 ± 42.4	23.0 ± 2.4	58.3 ± 8.9	1.4 ± 0.5	211.3 ± 33.3
Punjabi Bagh	2013	68.4 ± 21.9	43.7 ± 13.8	51.4 ± 16.5	2.4 ± 0.5	5.3 ± 1.2	137.7 ± 52.4	24.6 ± 2.2	55.3 ± 8.2	1.2 ± 0.4	175.0 ± 31.3
	2014	71.0 ± 19.8	45.5 ± 15.0	52.2 ± 17.9	2.1 ± 0.4	5.2 ± 1.3	139.6 ± 51.1	23.8 ± 2.6	52.0 ± 10.0	1.3 ± 0.4	127.9 ± 22.6
	2015	64.4 ± 14.8	45.3 ± 15.3	43.5 ± 12.4	1.8 ± 0.4	4.8 ± 1.4	130.9 ± 43.2	23.3 ± 2.7	56.0 ± 10.5	1.3 ± 0.4	108.4 ± 20.0
	Average	68.0 ± 18.9	45.3 ± 15.3	49.0 ± 15.6	2.1 ± 0.5	5.1 ± 1.3	136.0 ± 48.9	23.9 ± 2.5	54.4 ± 9.6	1.3 ± 0.4	137.1 ± 24.7
R.K. Puram	2013	59.7 ± 19.0	46.1 ± 21.0	42.1 ± 10.8	1.7 ± 0.4	5.3 ± 1.0	145.9 ± 57.8	24.0 ± 2.2	59.1 ± 7.5	1.4 ± 0.5	192.4 ± 29.8
	2014	48.6 ± 14.1	50.7 ± 18.9	44.1 ± 13.1	1.5 ± 0.4	3.9 ± 0.9	140.3 ± 52.1	23.5 ± 2.5	55.6 ± 8.9	1.4 ± 0.5	199.3 ± 28.7
	2015	56.9 ± 13.0	54.1 ± 18.4	44.8 ± 12.3	1.7 ± 0.4	4.6 ± 1.1	128.2 ± 41.3	22.7 ± 2.6	57.0 ± 8.9	1.3 ± 0.5	200.4 ± 30.9
	Average	55.0 ± 15.4	50.3 ± 19.5	43.7 ± 12.1	1.7 ± 0.4	4.6 ± 1.0	138.2 ± 50.4	23.4 ± 2.4	57.3 ± 8.4	1.3 ± 0.5	197.4 ± 29.8
Overall average	2013	55.6 ± 16.5	41.8 ± 15.0	39.7 ± 12.0	2.0 ± 0.4	4.7 ± 1.0	136.4 ± 52.7	24.6 ± 2.2	56.1 ± 8.2	1.4 ± 0.4	181.8 ± 37.6
	2014	52.4 ± 15.5	41.1 ± 14.1	39.6 ± 15.3	1.9 ± 0.5	3.9 ± 0.9	141.9 ± 52.4	24.1 ± 2.5	53.1 ± 9.8	1.4 ± 0.5	183.5 ± 41.0
	2015	52.2 ± 12.8	42.9 ± 14.6	39.6 ± 11.6	1.9 ± 0.4	4.3 ± 1.1	130.5 ± 43.6	23.9 ± 2.6	55.9 ± 9.9	1.5 ± 0.5	158.8 ± 35.9
	Average	53.4 ± 14.9	42.0 ± 14.6	39.6 ± 13.0	1.9 ± 0.4	4.3 ± 1.0	136.2 ±49.6	24.2 ± 2.4	55.0 ± 9.3	1.4 ± 0.5	174.7 ± 38.2

Table 2 The average mixing ratios of ambient NH_3, NO, NO_2, CO, SO_2 along with $PM_{2.5}$ concentration during winter, summer and monsoon seasons at NPL, Anand Vihar, Mandir Marg, Punjabi Bagh and R.K. Puram in Delhi (values in parentheses are ranges)

Parameters		NPL		Anand Vihar		Mandir Marg		Punjabi Bagh		R.K. Puram	
Species	Season	Average ± SD	D/N	Average ± SD	D/N	Average ± SD	D/N	Average ± SD	D/N	Average ± SD	D/N
NH_3 (ppb)	Winter	25.3 ± 4.6 (4.2–56.4)	0.93	89.2 ± 24.7 (0.31–156.8)	0.91	85.1 ± 20.6 (0.87–145.6)	0.95	87.9 ± 23.1 (0.22–149.9)	0.95	76.1 ± 21.4 (0.52–157.0)	0.81
	Summer	19.6 ± 3.9 (1.7–53.7)	1.01	60.9 ± 19.0 (0.35–156.5)	0.9	52.2 ± 14.6 (2.06–145.7)	0.98	64.2 ± 17.5 (0.30–149.5)	1.02	46.4 ± 12.3 (0.17–149.7)	0.81
	Monsoon	13.8 ± 1.9 (2.80–40.6)	0.98	41.9 ± 18.0 (0.41–155.9)	0.93	40.3 ± 12.0 (3.37–143.9)	0.96	48.6 ± 15.0 (2.20–149.9)	1.31	39.8 ± 10.4 (4.09–143.4)	0.9
NO (ppb)	Winter	21.4 ± 7.2 (1.4–64.2)	0.88	72.8 ± 24.1 (0.15–247.8)	0.71	58.4 ± 19.6 (0.32–245.7)	0.67	59.7 ± 20.6 (0.13–252.0)	0.66	67.4 ± 23.8 (0.13–249.1)	0.71
	Summer	19.2 ± 5.9 (2.1–77.7)	0.87	46.6 ± 25.9 (0.13–247.9)	0.75	40.3 ± 15.4 (0.21–12.3)	0.68	41.2 ± 13.5 (0.13–240.2)	0.8	44.6 ± 19.2 (0.13–249.6)	0.62
	Monsoon	20.5 ± 5.5 (1.5–58.6)	0.79	40.5 ± 17.4 (0.16–247.0)	0.79	33.1 ± 10.2 (0.21–243.9)	0.76	32.2 ± 10.2 (0.13–132.9)	1.18	36.5 ± 15.0 (0.13–249.0)	0.77
NO_2 (ppb)	Winter	20.8 ± 5.9 (3.0–58.6)	0.98	61.3 ± 21.0 (0.12–236.6)	0.88	60.6 ± 19.9 (0.32–250.7)	0.7	66.3 ± 22.4 (0.97–255.5)	0.82	60.4 ± 17.0 (0.24–239.8)	0.66
	Summer	19.9 ± 5.6 (2.6–63.2)	0.9	42.3 ± 17.4 (0.16–195.2)	0.89	41.6 ± 14.5 (1.29–213.7)	0.7	44.9 ± 12.7 (0.13–189.6)	0.76	37.4 ± 11.0 (0.10–178.4)	0.72
	Monsoon	18.6 ± 4.4 (3.2–53.6)	0.98	32.2 ± 9.9 (0.13–220.2)	1.05	31.7 ± 11.1 (0.11–239.5)	0.72	33.6 ± 10.7 (0.16–203.1)	1.23	30.5 ± 7.4 (0.30–107.9)	0.74
CO (ppm)	Winter	2.2 ± 0.5 (0–20–4.34)	0.86	2.5 ± 0.4 (0.11–5.0)	0.83	2.5 ± 0.6 (0.10–5.0)	1.08	3.1 ± 0.6 (0.11–5.0)	0.92	2.4 ± 0.6 (0.10–5.0)	0.77
	Summer	2.0 ± 0.6 (0.23–3.56)	0.88	1.5 ± 0.4 (0.11–5.00)	1.25	1.2 ± 0.4 (0.10–4.93)	1.87	1.8 ± 0.5 (0.11–5.0)	0.92	1.3 ± 0.4 (0.10–4.96)	1.12
	Monsoon	2.0 ± 0.4 (0.22–3.99)	0.92	1.4 ± 0.3 (0.11–4.98)	0.91	0.8 ± 0.2 (0.10–4.80)	1.04	1.3 ± 0.2 (0.13–4.94)	2.08	1.1 ± 0.3 (0.11–5.0)	0.75
SO_2 (ppb)	Winter	1.9 ± 0.5 (0.6–4.2)	0.95	5.3 ± 1.2 (0.14 –10.44)	1.11	5.0 ± 1.3 (0.20–10.4)	1.17	5.2 ± 1.6 (0.13–10.4)	1.03	5.1 ± 1.1 (0.20–10.8)	1.03
	Summer	1.6 ± 0.5 (0.5–4.0)	0.98	4.7 ± 1.2 (0.13–10.4)	0.96	4.9 ± 1.3 (0.20–10.4)	0.94	4.9 ± 1.3 (0.13–10.4)	1.03	4.8 ± 1.1 (0.20–10.8)	0.88
	Monsoon	1.7 ± 0.5 (0.7–4.1)	0.99	5.1 ± 1.0 (0.14–10.4)	1.01	4.0 ± 0.8 (0.20–10.4)	0.97	5.2 ± 1.0 (0.13–10.4)	0.9	3.4 ± 0.7 (0.10–10.8)	0.88
$PM_{2.5}$ (µg m^{-3})	Winter	190.2 ± 67.3 (55.7–421.0)	–	266.0 ± 91.1 (1.0–798.0)	0.75	193.1 ± 66.7 (1.0–696.0)	0.84	212.3 ± 73.4 (4.0–828.0)	0.79	217.5 ± 75.0 (1.0–985.0)	0.75
	Summer	67.8 ± 27.9 (16.7–153.0)	–	136.0 ± 52.1 (1.0–795.0)	0.77	81.9 ± 28.2 (1.0–520.0)	0.89	111.6 ± 37.8 (1.0–680.0)	0.96	138.1 ± 47.3 (1.0–779.0)	0.83
	Monsoon	54.5 ± 34.3 (8.84–251.8)	–	84.9 ± 27.5 (1.0–792.0)	0.96	55.2 ± 16.9 (1–591.0)	0.92	62.9 ± 21.6 (1.0–396.0)	1.62	65.2 ± 25.8 (1.0–578.0)	0.95

depicted in Fig. 2. The ambient NH_3 reaches maximum during traffic hours and minimum during midday (1500–1600 h). We observe the NH_3 peak around 7:00–11:00 h in the morning and at around 17:00–20:00 h in the evening (Fig. 2). The increase in NH_3 mixing ratio during traffic hours (7:00–11:00) indicates traffic source at the observational sites of Delhi. Kirchner et al. [16] and Li et al. [40] also observed bimodal diurnal variation in NH_3 mixing ratio occurring during peak traffic hours which indicate vehicles as a significant source of NH_3. Meng et al. [41] and Zhao et al. [42] also observed the similar diurnal variation pattern of NH_3 mixing ratios at Beijing.

The NO and NO_2 levels are generally high during traffic hours with some values higher than 80 ppb. The photochemical process, emission–dilution balance of NO_x and O_3 and increased emissions of motor vehicles during morning
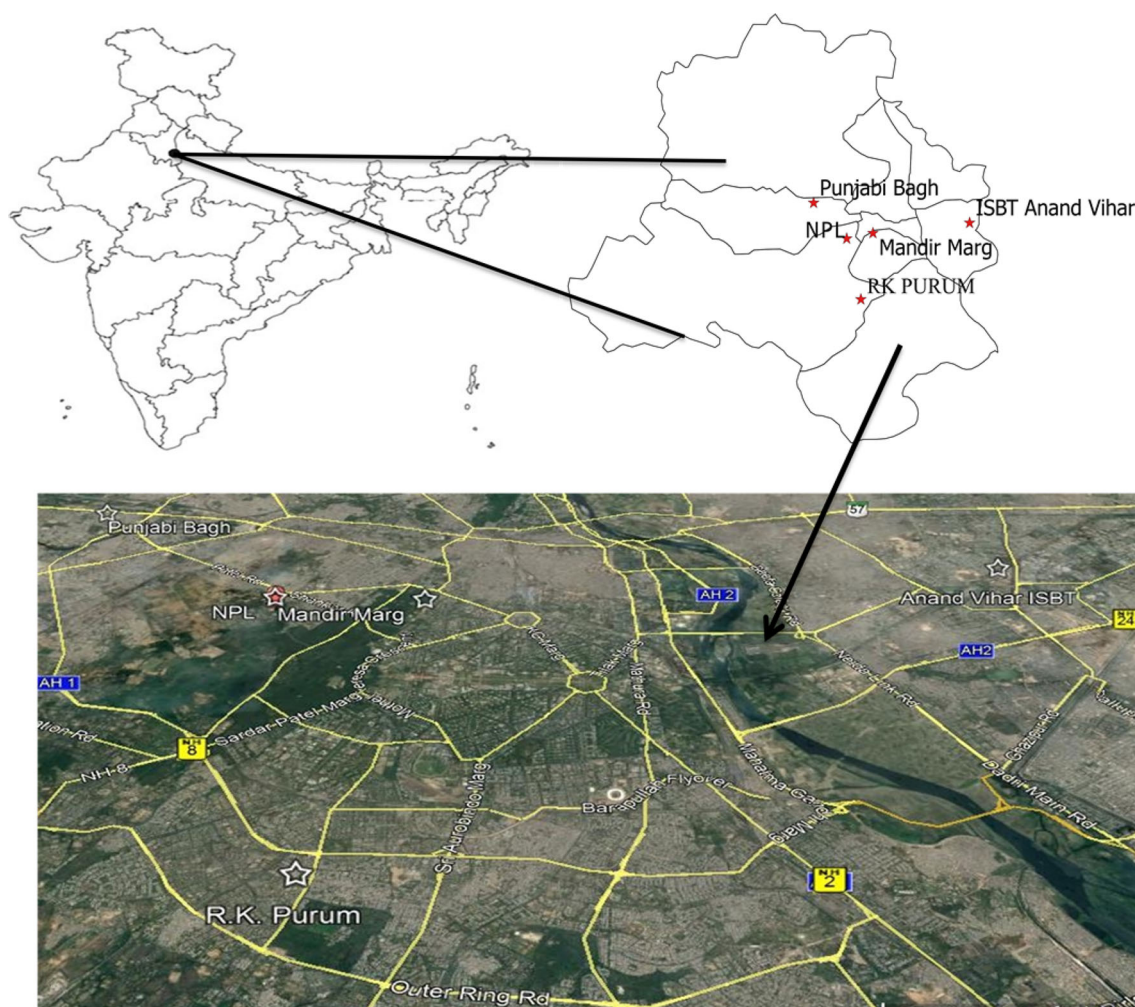
Fig. 1 Map of sampling locations

rush hour result in increase in early morning hour NO_x concentrations [43–45]. Varotsos et al. [46] also observed traffic rush-hour peak in NO_x concentration at Pattison an urban site of Greece. CO mixing ratio also shows double diurnal peak rather than single. The morning peak in CO mixing ratio was observed around 7:00–11:00 h and minima in the afternoon and again gradually increase after 5 h and reached maximum in the night. At all the 5 locations CO and NO_x mixing ratio also shows diurnal peak which may be due to the vehicular emissions [47]. The diurnal profile of NO_x ($NO+NO_2$) and CO shows clear signature of vehicular traffic [48–50] (as shown in the bimodal peak matching the traffic rush hour). The similar diurnal variations in mixing ratios of NO_x, CO were also observed at many urban sites in India and around the world [47, 51–55]. The diurnal variation of SO_2 with maxima during traffic hours was observed in winter due to lower boundary layer and less efficient oxidation to sulfate as compared to summer with distinct diurnal pattern and monsoon with no diurnal pattern. The

diurnal peak in the mixing ratio of NH_3, NO, NO_2 and CO was not only due to the vehicular source but also partially due to meteorological parameters (boundary layer, wind speed) and also due to photochemical formation of ozone from its precursors (NO_x and CO) [7, 53, 56–58].

During the study, both temperature and wind speed showed similar diurnal pattern characterized by high value during daytime and low values during nighttime in all the three seasons (Table S2; in supplementary information). As the midday wind speed is higher which results in dilution of pollutants as compared to morning and evening [59]. In the evening, the stability of atmospheric conditions starts increasing as wind speed and mixing height start decreasing which results in the increase in pollutants concentrations [39, 60]. Boundary layer height and wind speed were highest at noontime and increased the dilution of pollutants which results in lower concentrations [60]. The gradual increase of these gases and PM in the night can be attributed to the formation of nocturnal inversion layer [61, 62].
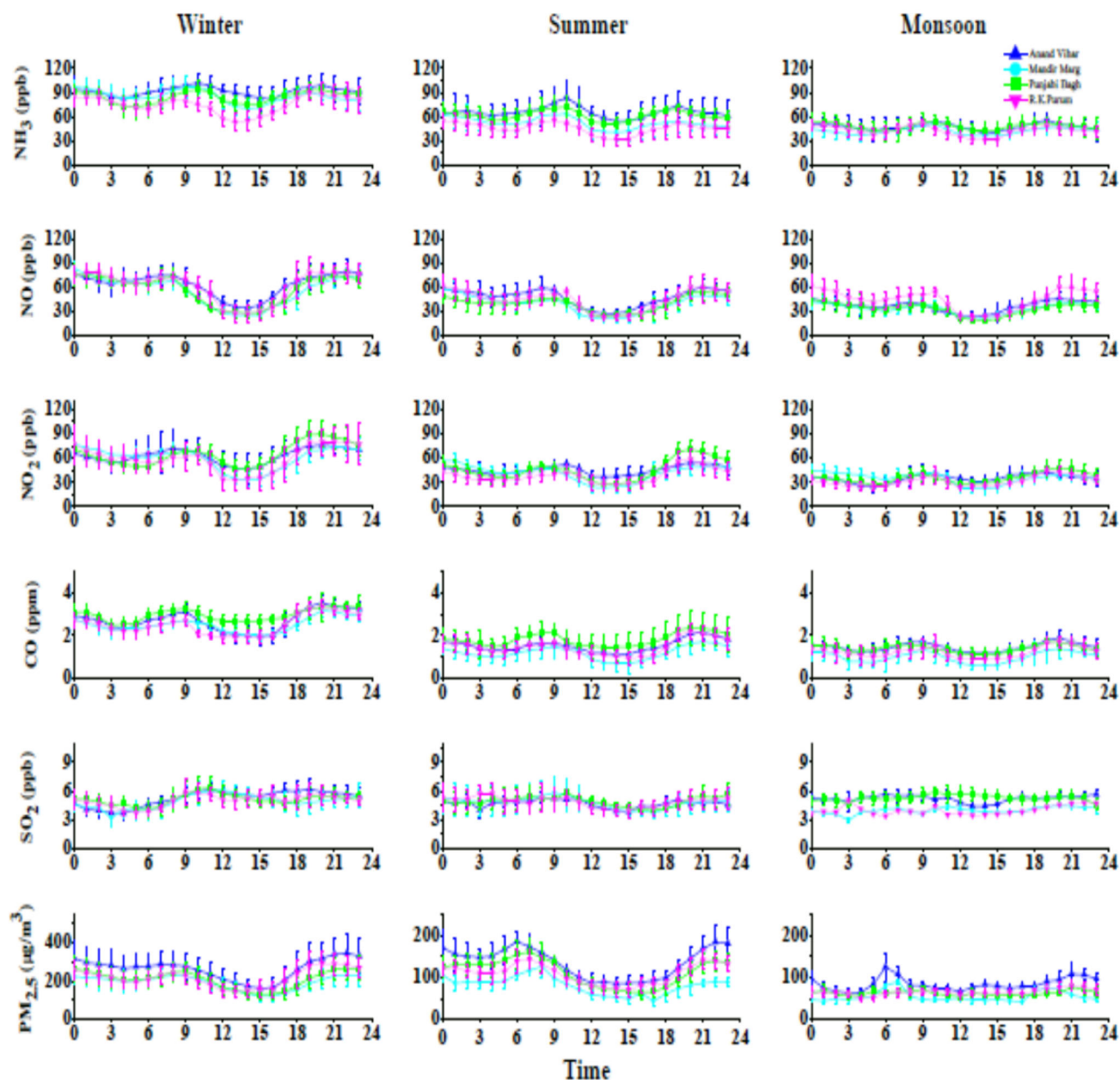
Fig. 2 Averaged diurnal variations in mixing ratios of ambient NH$_3$, NO, NO$_2$, CO, SO$_2$ and PM$_{2.5}$ concentration during winter, summer and monsoon seasons at Anand Vihar, Mandir Marg, Punjabi Bagh and R.K. Puram at Delhi

3.3. Seasonal Variation

We have analyzed the data according to three seasons, winter (November–February), summer (March–June) and monsoon (July–September) to observe the influence of meteorology on the mixing ratios of trace gases and PM$_{2.5}$ concentration. Table 2 and Table S1 (in supplementary information) show seasonal averaged values for all the parameters during the measurement period at the four sampling sites. Figure 3 also presents the mixing ratios of NH$_3$, other trace gases and PM$_{2.5}$ concentration at all the

sampling sites in Delhi in different season. Figure S8 (in supplementary information) shows the monthly statistics of NH$_3$, NO, NO$_2$, CO, SO$_2$ and PM$_{2.5}$ mixing ratio averaged over the 3-year period, measured at NPL and other four AQMS sites. The average mixing ratio of ambient NH$_3$ was 72.7 ± 19.0 ppb in winter followed by summer (48.7 ± 13.5 ppb) and monsoon (37.0 ± 11.5 ppb). The residue burning activities within Delhi and in surrounding agricultural area result in higher mixing ratio of NH$_3$ in winter season followed by summer and monsoon season [23, 29, 41, 63, 64]. The frequent temperature inversion in
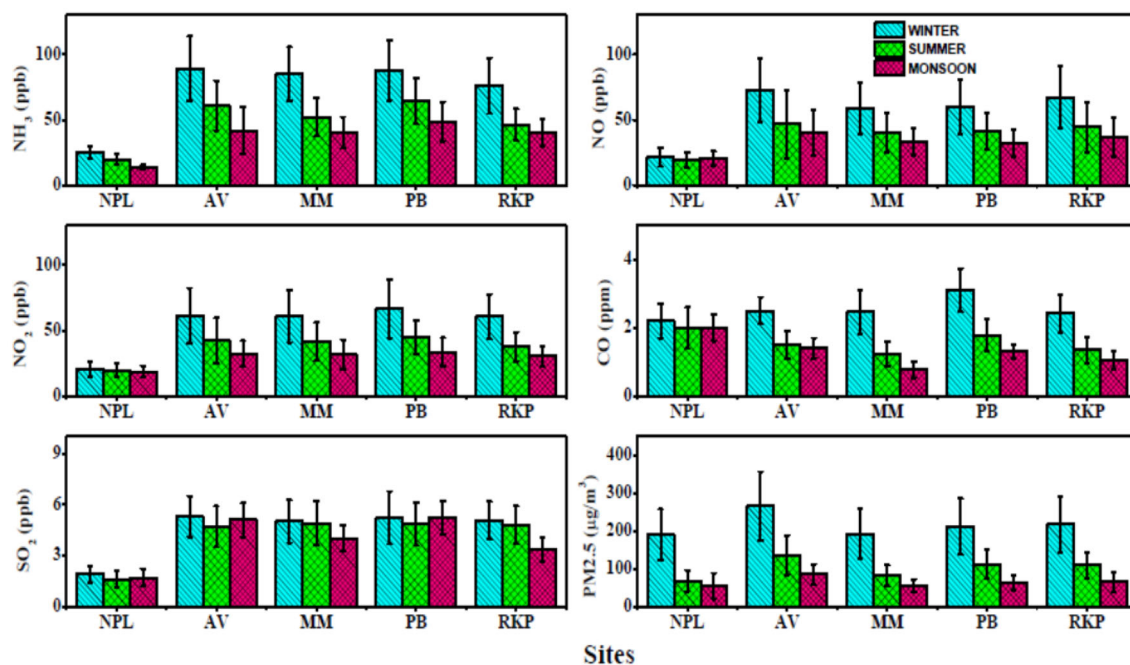
Fig. 3 Seasonal variations of mixing ratios NH_3, NO, NO_2, CO, SO_2 and concentration of $PM_{2.5}$ during January 2013 to December 2015 over Delhi

winter results in lower boundary layer which trapped the pollutants emitted from various anthropogenic and natural sources, while in the summer month, the greater photo-chemical reactions due to higher solar radiation and higher mixing height results in lower concentration [57, 58, 65, 66]. The frequent rainfall activity in the monsoon results in the lower concentrations of pollutant at the study site [45]. The concentration of $PM_{2.5}$ was also highest in winter (215.8 ± 74.9 μg m^{-3}) followed by summer (107.1 ± 38.7 μg m^{-3}) and monsoon (64.5 ± 25.2 μg m^{-3}) seasons. The concentration of $PM_{2.5}$ is exceeding the NAAQS (24 h average: 60 μg m^{-3}; annual average: 40 μg m^{-3}) in all seasons. It can be observed that the values of NH_3 and all other trace gases were higher in winter as compared to summer and monsoon. During the winter season, low wind speed and formation of lower stable boundary layer played an important role in slower dispersion of pollutants and localized emissions also increased due to enhanced biomass burning [23, 42, 67]. The variability in meteorological condition and different emission sources leads to large seasonal variability in mixing ratio of NH_3 and other trace gases and concentration of $PM_{2.5}$.

3.4. Temporal Variation of Trace Gases and $PM_{2.5}$

The monthly average plots of NH_3, other trace gases and $PM_{2.5}$ along with meteorological parameters were shown to understand their temporal variation at different timescales

(Fig. 4). Figures S2–S7 (in supplementary information) show the temporal variation in the mixing ratio of NH_3 and other trace gases, i.e., NO, NO_2, CO, SO_2, and $PM_{2.5}$ over Delhi during the measurement period (January 2013 to December 2015). The daily and monthly mean values of NH_3 varied from 19.8–114.6 ppb and 30.0–82.6 ppb, respectively with their annual mean 53.4 ± 14.9 ppb for the entire study period. The mixing ratio of NH_3 exhibited a similar trend, i.e., gradual increase from October to December, January and then gradual decrease from April to July, August at CSIR-NPL and other 4 AQMS sites of Delhi. The NH_3 mixing ratio reached maximum in December (114.6 ppb) and were minimum in July (21.5 ppb) over Delhi. NH_3 mixing ratio observed in this study was higher than of 14–91 ppb with annual average of 42 ppb observed by Singh and Kulshrestha [31] JNU (ur-ban site), Delhi, and comparable to the annual average value of 59 ppb at Okhla, Delhi, reported by Singh and Kulshrestha [68].

The temporal variation of NH_3 coincided with NO, NO_2 and CO indicating similar sources of traffic emission. The spikes in time series of NH_3 that correlate with spikes in CO time series were also observed by Li et al. [40] which indicate the emission of NH_3 from nearby vehicles. The overall time series shows that the local air circulations and changing meteorological conditions result in significant day-to-day variations in all the trace gases during the measurement period.
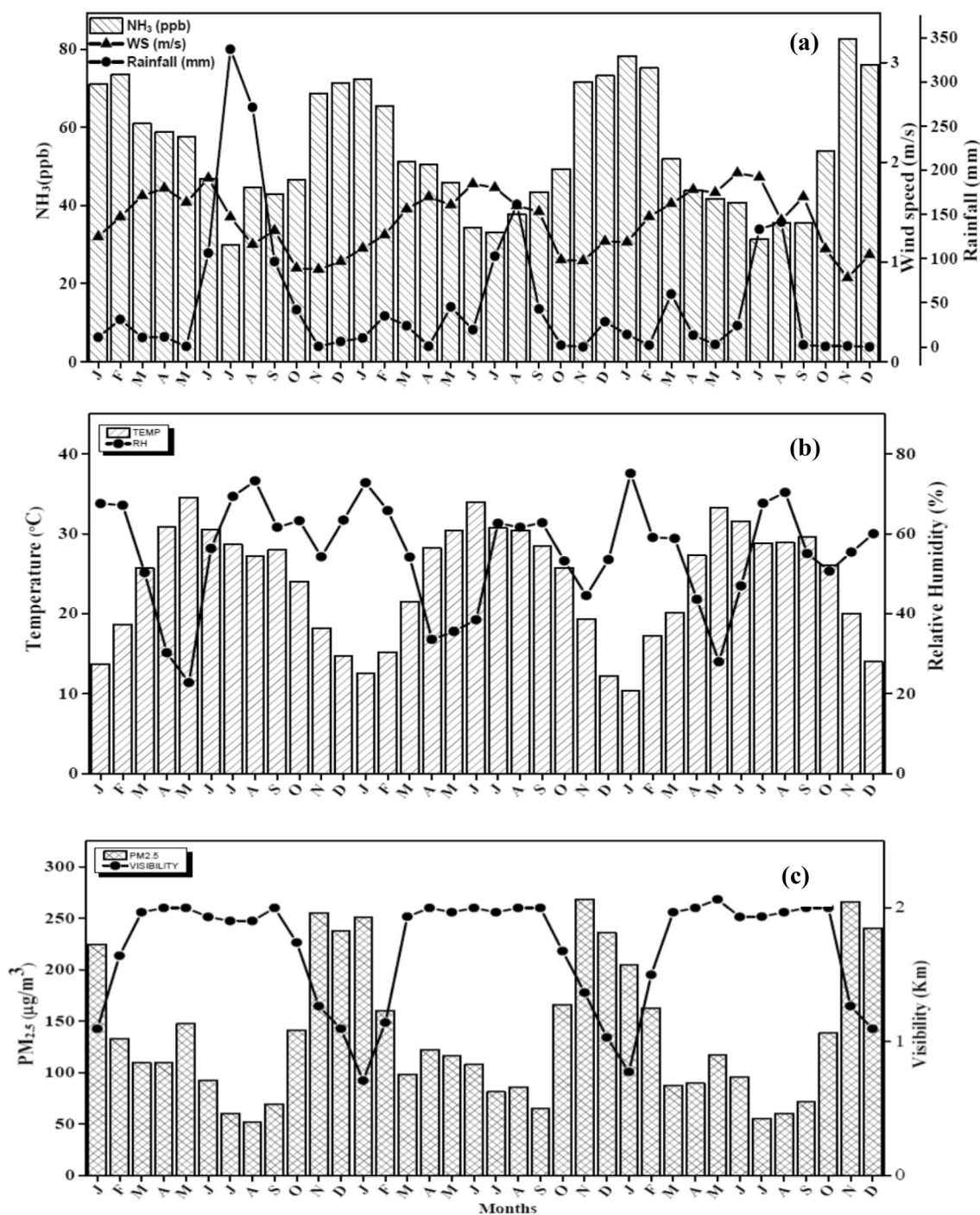
Fig. 4 Relationship between monthly **a** NH$_3$, wind speed and rainfall **b** temperature and relative humidity **c** PM$_{2.5}$ and visibility during January 2013 to December 2015 at Delhi

4. Relationship Among Trace Gases and PM$_{2.5}$

4.1. Bivariate Correlation Analysis

The ambient NH$_3$ is only primary alkaline gas present in the atmosphere that reacts with acidic gases and act as a precursor for secondary aerosol. The main source of ambient NH$_3$ is agriculture, but at urban area other sources include industries, landfills, waste burning and motor vehicles [15, 69]. Since the introduction of three-way catalyst in the vehicles, transport sector is believed to be the largest contributor in influencing NH$_3$ in the urban area [69–72]. A correlation analysis was employed to analyze the relationship of NH$_3$ with traffic-related
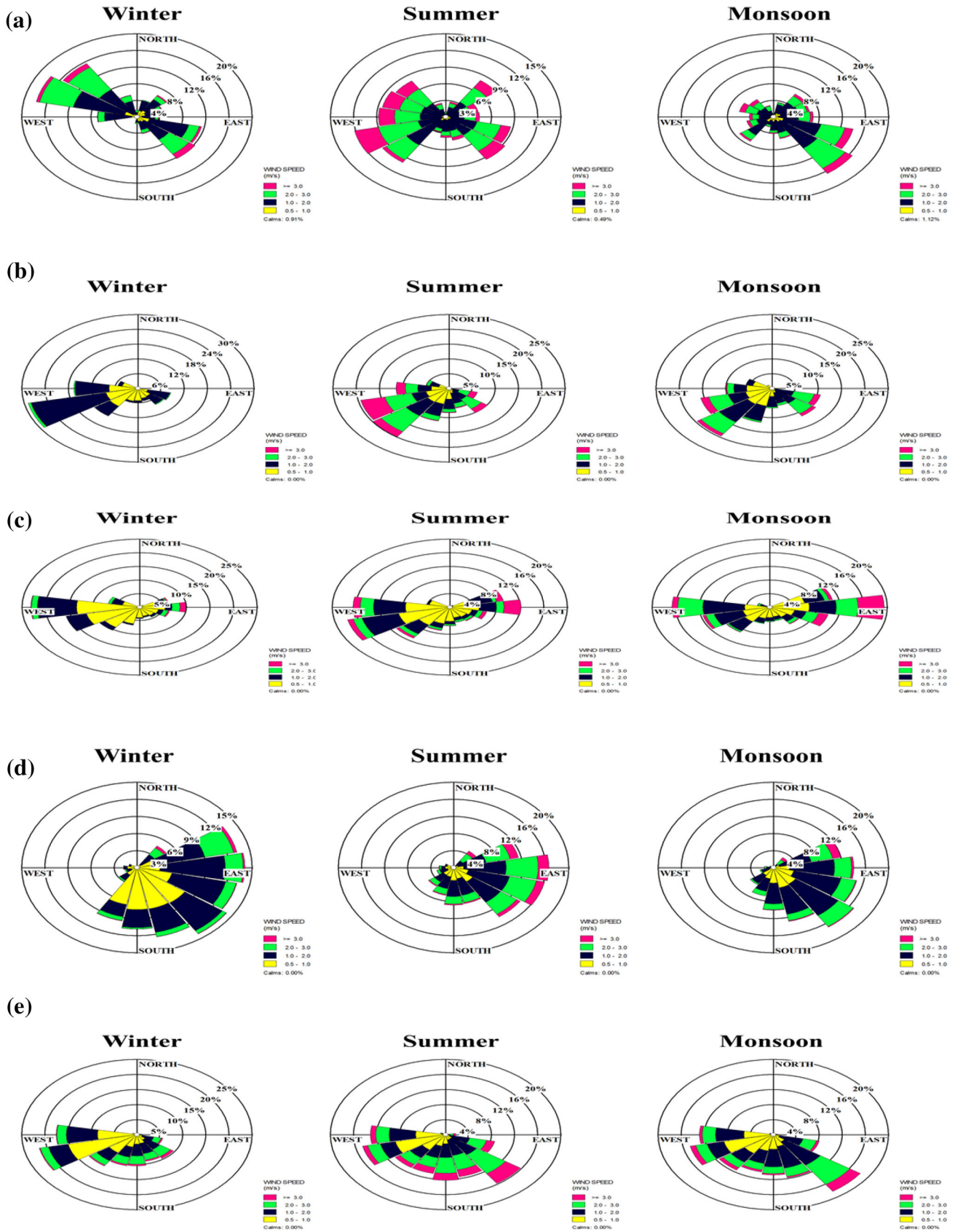
(a)

(b)

(c)

(d)

(e)

pollutant in different seasons (Table S3; in supplementary information). A study in Beijing found vehicular emission contributes to 74% of the ground NO_x, while power plants and industrial sources contributed only 2% and 13%, respectively. In case of CO, vehicles contribution was estimated to be more than 80% in Beijing and Guangzhou [73]. The bivariate correlation analysis was performed using hourly measured data from January 2013 to December 2015 over Delhi. The mixing ratio of NH_3 shows good correlation with all the traffic-related pollutant in all the seasons (Table S3; in supplementary information). It supports the hypothesis of contribution of traffic to the NH_3 mixing ratio at the urban area [17, 18, 74]. In the summer season, NH_3 shows weaker correlation with traffic-related pollutant as compare to winter which suggests other NH_3 sources not link to traffic are also significant (Table S3; in supplementary information). The correlation of NH_3 with SO_2 in summer and monsoon seasons also indicates non-traffic sources. The higher temperature in summer and monsoon increased NH_3 emission from soil and human waste and increased wind speed result in long-range transport sources [7, 75]. The increased temperature dissociates the particulate ammonium nitrate and results in volatilization of NH_3 from aerosol phase which mask correlation of NH_3 with traffic-related pollutants [76].

4.2. Meteorological Effects on Trace Gases and PM₂.₅

The meteorological parameters recorded during the measurement period (January 2013–December 2015) at 4 AQMS sites of DPCC and CSIR-NPL in Delhi are summarized in Table 1. The variations in local meteorological condition such as temperature, relative humidity (RH), wind speed, wind direction and rainfall play an important role in formation of air pollutant, dispersion, transport and dilution which can affect the temporal, diurnal and seasonal variations in gaseous pollutants (NH_3, NO_x, CO, SO_2) and PM₂.₅ [77]. The local and regional causes of particulate pollution can be understood by analyzing the influence of meteorology on trace gases concentration and PM. The monthly average mixing ratios of ambient NH_3, other trace gases and PM₂.₅ determined within selected range of meteorological parameters, i.e., temperature, RH, wind speed, rainfall and visibility over Delhi, are depicted in Fig. 4 and Table S5 (in supplementary information).

The highest average mixing ratio of NH_3 with a value of 91.6 ppb occurs at temperature less than 10 °C ($\leq$ 10 °C). At higher temperature, i.e., greater than 30 °C, the mixing

ratio of NH_3 is 45.4 ppb. This shows that the mixing ratio of NH_3 decreased with the increase in temperature. The negative correlation of NH_3 with temperature from June to December, January and also for the yearly value explained the decrease of NH_3 with increase in temperature (Table S4, in supplementary information). The other trace gases and PM₂.₅ also show decreasing trend with the increase in temperature. All other trace gases also show negative correlation with temperature in the months of winter season except NO_2 and SO_2 which shows positive correlation with temperature in January (Table S4, in supplementary information). The lowering of boundary layer in the winter season is the main reason for the trapping of pollutants emitted from anthropogenic activities and formed by gas to particles conversion which results in their higher concentration [78]. PM₂.₅ shows positive correlation with temperature from months of March to September which indicates the photochemical formation of PM₂.₅ species, i.e., SO_4^{2-} and NO_3^- from their precursor gases SO_2 and NO_x [79, 80].

RH plays important role in photochemical reaction and in the production of wet aerosols [81]. The average mixing ratio of NH_3 increased with increasing RH. Mixing ratio of NH_3 is 50.0 ppb at RH equal to or below 40% and increased to 62.9 ppb at RH greater than 80%. All other trace gases (NO_x and CO) also show same increasing trend. The concentration of PM₂.₅ and SO_2 mixing ratio increases with the RH range rising from < 40% to 60–80%; then their concentration drops slightly when RH is higher than 80%. The positive relationship of PM₂.₅ with RH in month of November and December is the result of favorable condition of higher RH and lower temperature in this season for the formation of PM₂.₅ from its precursor gases (NH_3, NO_x and SO_2) [82]. The higher RH is observed on windless, cloudy and hot days which are favorable for accumulation and chemical reactions of pollutants [83, 84].

The mixing ratio of ambient NH_3 decreases steadily when wind speed increases from $\leq$ 1 to 3.1–4.0 ms^{-1}. The mixing ratio of NH_3 is 68.1 ppb when wind speed is $\leq$ 1 ms^{-1} and decreases to 45.2 ppb when wind speed range is between 3.1–4.0 ms^{-1}. The other trace gases and PM₂.₅ also show the same decreasing trend with increasing wind speed. Ambient NH_3, other trace gases and PM₂.₅ show significant negative correlation with wind speed for every month and yearly value [85]. The significant negative correlation of ambient NH_3 and other trace gases with wind speed indicates decrease in mixing ratio with increasing wind speed because the pollutants are drifted vertically as well as horizontally through turbulent transfer mechanism under high wind speed and results in reduction in their concentration in the atmosphere [8]. The gaseous pollutants and fine particles tend to remain over the region of origin under low wind speed and results in

increase in concentration of pollutants [79]. In the winter season, the average wind speeds were lower at all the sampling sites as compared to summer and monsoon. This suggests local sources of emission of trace gases as stronger wind increase the dispersion of local air pollutants [39].

The daily average mixing ratio of NH_3 was higher, i.e., 59.8 ppb when there is no rainfall, and decreases to 38.3 ppb when daily average precipitation is greater than 50 mm (Table S5, in supplementary information). Results also show the lower monthly average concentration of ambient NH_3 when monthly rainfall was higher and vice versa. The other trace gases (NO, NO_2, CO, SO_2) and $PM_{2.5}$ concentration were also observed higher (45.0 ppb, 44.0 ppb, 1.9 ppm, 4.5 ppb) and 161.6 µg/m^3, respectively at < 0.1 mm precipitation and decrease to (33.8 ppb, 31.7 ppb, 1.3 ppm, 4.4 ppb) and 54.1 µg/m^3, respectively, at rainfall > 50 mm (Table S5, in supplementary information). The influence of precipitation on pollutants concentration can be observed by comparing the concentrations of monsoon season with winter and summer. The concentration of all pollutants (NH_3, NO, NO_2, CO, SO_2 and $PM_{2.5}$) was also calculated on precipitation (the amount of daily precipitation > 0.1) and non-precipitation days (Figure S9, in supplementary information) and decrease in mixing ratio from non-precipitation days to precipitation days was shown. All the observed pollutants show negative correlation with rainfall for most of the months and yearly value (Table S4, in supplementary information). It indicates the decrease in concentration of pollutant with increase in rainfall.

The average values of all the pollutants (NH_3, NO, NO_2, CO, SO_2 and $PM_{2.5}$) were also determined within selected range of visibility. The observed daily average concentrations of the pollutants were higher at visibility ≤ 0 km and lower when visibility was greater than 3 km. The concentration of $PM_{2.5}$ was 328.5 µg m^{-3} at visibility ≤ 0 and decreases to 81.7 µg m^{-3} when visibility was higher than 3 km. Ambient NH_3 and other trace gases also shows the same trend. We have observed that when concentration of $PM_{2.5}$ was higher then visibility is lower and vice versa. The trace gases NH_3, NO_x and SO_2 are the precursor gases for the $PM_{2.5}$. $PM_{2.5}$ is also showing significant negative correlation with visibility during the study period.

The distributions of average surface wind speed with the wind direction at CSIR-NPL and other 4 AQMS of Delhi are depicted in Fig. 5. In winter season, the wind mainly comes from the NW to SW direction across all the sites. The prevailing wind directions in summer were NW, NE, SW and SE. In monsoon season, wind mainly comes from the SE direction.

5. Conclusions

The ambient air quality of 5 different monitoring sites of megacity Delhi was examined using continuous observations of trace gases (NH_3, NO, NO_2, CO and SO_2), $PM_{2.5}$ and meteorological parameters (temperature, RH, wind speed and wind directions etc.,) from January 2013 to December 2015. All the observed parameters showed seasonal variation with higher peaks in the winter season due to increase in fuel burning, stagnant air conditions and less photochemical activity. The diurnal variation in ambient NH_3 and other trace gases shows a bimodal pattern characterized by higher mixing ratios during traffic hours and night and lower mixing ratios during noon and afternoon. The correlation of NH_3 with traffic-related pollutants (NO_x, CO) and bimodal diurnal cycle of NH_3 synchronized with traffic rush hour indicate the traffic emission as a significant source of NH_3 mixing ratio at the study sites. The photochemical reactions and air pollutants dispersion were influenced by diurnal variation in boundary layer stability and other meteorological parameters. This study can contribute to better understanding of particulate pollution in relation to trace gases at highly populated and urbanized megacity Delhi. The tremendous growth in Delhi and surrounding areas results in increased emission of primary pollutants, particulate matter and production of secondary pollutants, which cause further deterioration in the air quality of Delhi. The higher concentration of air pollutant affects human health and environment significantly over Delhi. These results suggest that more strict reductions in emissions of pollutant will be needed in order to significantly improve the air quality.

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