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Inter-annual Variation of Ambient Ammonia and Related Trace Gases in Delhi, India

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Abstract In this study, ambient NH_3, NO, NO_2, CO and SO_2 were measured continuously from February, 2008, to December, 2016. The annual average mixing ratios (mole/mole) of NH_3, NO, NO_2, CO and SO_2 were 17.8 ± 3.4 ppb; 21.2 ± 2.3 ppb, 18.1 ± 3.2 ppb; 1.7 ± 0.3 ppm and 2.0 ± 0.3 ppb, respectively. All the trace gases (NH_3, NO, NO_2, CO and SO_2) showed significant annual variation during the study. A significant increasing trend in mixing ratios of ambient NH_3 and NO_2 were observed at the observational site of Delhi, whereas, increasing trend were recorded in case of NO, CO and NO_2 mixing ratios. The results emphasized that traffic could be one of the significant sources of ambient NH_3 at the urban site of Delhi, as illustrated by positive correlations of NH_3 with traffic related co-pollutants (NO and CO).

Keywords Trace gases · Ammonia · Meteorological parameters · Annual variation

Since the gaseous toxic air pollutants are normally associated with acute short-term and chronic long-term human health problems, the study of these pollutants is essential to understand their mechanism of occurrence (Behera et al. 2015; Saraswati et al. 2017). Ammonia (NH_3) is the third most abundant nitrogen containing gas in the atmosphere after N_2 and N_2O (Seinfeld and Pandis 1998; Aneja et al. 2000). As a primary alkaline gas in ambient air, NH_3 can neutralize nitric acid and sulphuric acid gases to form ammonium nitrate and sulphate (Pinder et al. 2007; Sharma et al. 2012c, 2014, Saxena et al. 2017), which are important constituents of airborne fine particles or $PM_{2.5}$ (Chow et al. 2004; Kean et al. 2000; Aneja et al. 2001; Ram et al. 2010; Huang et al. 2011). The most recent consideration for NH_3 emissions on the global scale is linked to climate change based on its ability to form $PM_{2.5}$, specifically ammonium sulphate (Aneja et al. 2001). These aerosols can possibly increase the Earth's albedo (Sutton et al. 2000). The need to better understand the role of this particular air pollutant has been underscored in recent years as its atmospheric concentration increases. Effective management strategies are essential to mitigate the pollutants over public health concern and to enhance visibility (Brunekreef and Holgate 2002; Wang et al. 2012).

Major anthropogenic sources of ambient NH_3 are agricultural practices, livestock, transport and industrial activities (Sutton et al. 2000; Li et al. 2006; Sharma et al. 2010), along with natural sources like forest fires and emissions from soil (Olivier et al. 1998; Lee et al. 2005). Recent studies (Sutton et al. 1995, 2000; Wang et al. 2012) have established that reduction of NO compounds in three-way catalytic converters of automobile exhaust and industrial power stations emissions are significant contributors to atmospheric NH_3 in urban environments ($2NO + 2CO + 3H_2 \rightarrow 2NH_3 + 2CO_2$ or $2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O$) (Gandhi and Shelef 1991). Correlation matrix of ambient NH_3 with CO also suggested the dependency of NH_3 mixing ratio on the traffic intensity and air temperature (Perrino et al. 2002; Meng et al. 2011; Sharma et al. 2014). Li et al. (2006) observed spikes in the NH_3 time-series that was correlated with the spikes in the CO,

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and inferred that the NH_3 came from nearby traffic. In the previous study, we have reported the diurnal, seasonal and temporal variations in mixing ratios of ambient NH_3 and its interaction with other trace gases and reference theirein (Sharma et al. 2010a, b, 2012a, b, c, 2014; Saraswati et al. 2017). In this paper, we present the inter-annual variation in mixing ratios of ambient NH_3 and other related trace gases (NO, NO_2, CO and SO_2) in an urban area of Delhi.

Materials and Methods

Delhi, the capital of India is surrounded by four different climatic zones (Himalyas in the north, central hot plains in the south, the Thar desert in the west and the Indo Gangetic plain in the east), which influence its semi-arid climate consided as one of the most polluted megacites of the world. The mixing ratios (mole/mole or mole fraction) of ambient NH_3, NO, NO_2, CO and SO_2 were measured, along with meteorological parameters (temperature, relative humidity (RH), wind speed and wind direction) at the CSIR-National Physical Laboratory, New Delhi (28°38′N, 77°10′E; 218 m amsl) from February, 2008, to December, 2016. The observational site is amenable to free wind flow from all directions and represents a typical urban atmosphere, surrounded by huge roadside traffic (~100 m) and agricultural fields in the southwest direction (~500 m). The observational area is under the influence of air mass flow from north-east to north-west in winter and from south-east to south-west in the summer. The temperature of Delhi varied from maximum in summer to minimum in winter. Detailed descriptions of the sampling site including meteorology are available in Sharma et al. (2016a).

Ambient NH_3 mixing ratio was measured initially using an NH_3-analyzer (CLD88CYp, ECO Physics AG, Duernten, CH) operating (accuracy: ±0.5 ppb) on a chemiluminescence method (February, 2008, to December, 2012). From January, 2012, to December, 2015, the measurement of ambient NH_3 was carried out using an NH_3-analyzer (AC32M&CNH$_3$, Environment SA, Paris, FR), which also operates (accuracy: ±1.0 ppb) on the chemiluminescence method. NO and NO_2 were measured using a NO_x-analyzer (CLD 88p, ECO Physics AG, Duernten, CH) with a photocatalytic converter (Model: PLC 860 M/s. ECO Physics AG; accuracy: ±0.5 ppb). Carbon monoxide (CO) was observed continuously using a non-dispersive infrared (NDIR) gas filter correlation analyzer (Model 48 C; Thermo Fisher Scientific, Waltham, MA, USA). Sulphur dioxide was measured using a SO_2-analyser (APSA 360 A, Horiba Ltd, Japan). The detailed principle of operations, detection limits, calibration procedures, calibration standards used (traceable to NIST-USA)and repeatability etc., of all the respective analyzers are available in Saraswati et al. (2017). All the analytical instruments showed <2.0% repeatability error during the span calibration. The meteorological parameters (temperature, RH, wind speed and wind directions) were measured simultaneously using sensors at a meteorological tower, which was 100 m away from the observational site within the same campus (Sharma et al. 2010a, b, 2014).

Results and Discussion

The annual average mixing ratios of ambient NH_3, NO, NO_2, CO and SO_2 were 17.8 ± 3.4 ppb; 21.2 ± 2.3 ppb and 18.1 ± 3.2 ppb; 1.7 ± 0.3 ppm and 2.0 ± 0.3 ppb, respectively from February, 2008 to December, 2016 (Table 1). The highest annual average mixing ratio of ambient NH_3 was observed in 2014 (24.3 ± 3.6 ppb), whereas the minimum mixing ratio ambient NH_3 was recorded in 2010 (13.4 ± 4.2 ppb). Similarly, higher annual average mixing ratios of ambient NO and NO_2 were recorded in 2016 (25.6 ± 7.5 ppb) and 2015 (23.9 ± 6.6 ppb), respectively. Figure 1 showed the annual variation alongwith trend in mixing ratios of ambient NH_3, NO, NO_2, CO and SO_2 during 2008–2016. Mixing ratios of all the trace gases varied non-significantly, except for ambient NH_3 and NO_2 during the study. This may have been due to source strength of

Table 1 Annual average mixing ratios of trace gases alongwith inter-annual variations in Delhi

Species	Average	Annual differences from average								
		2008	2009	2010	2011	2012	2013	2014	2015	2016
NH_3	17.8 ± 3.4	−3.08[a]	1.88[a]	−4.38[a]	−1.48[a]	3.32[a]	−1.68[a]	6.58[a]	0.72[a]	1.92[a]
NO	21.2 ± 2.3	−2.05[a]	0.56[b]	1.35[b]	−1.95[a]	−0.35[b]	1.95[a]	−3.15[a]	0.75[b]	4.35[a]
NO_2	18.1 ± 3.2	−3.42[a]	−4.02[a]	0.38[b]	−2.92[a]	−0.32[b]	0.28[b]	0.78[a]	5.78[a]	3.28[a]
CO	1.68 ± 0.26	0.01[b]	−0.27[a]	0.03[b]	−0.17[a]	−0.07[b]	0.23[a]	0.13[a]	0.03[b]	0.13[a]
SO_2	2.01 ± 0.32	−0.68[a]	0.12[a]	0.04[b]	0.34[a]	0.24[a]	−0.16[a]	−0.26[a]	0.24[a]	0.14[a]

± Standard deviation

[a]Significantly different ($p < 0.05$)

[b]Not significantly different ($p > 0.05$)

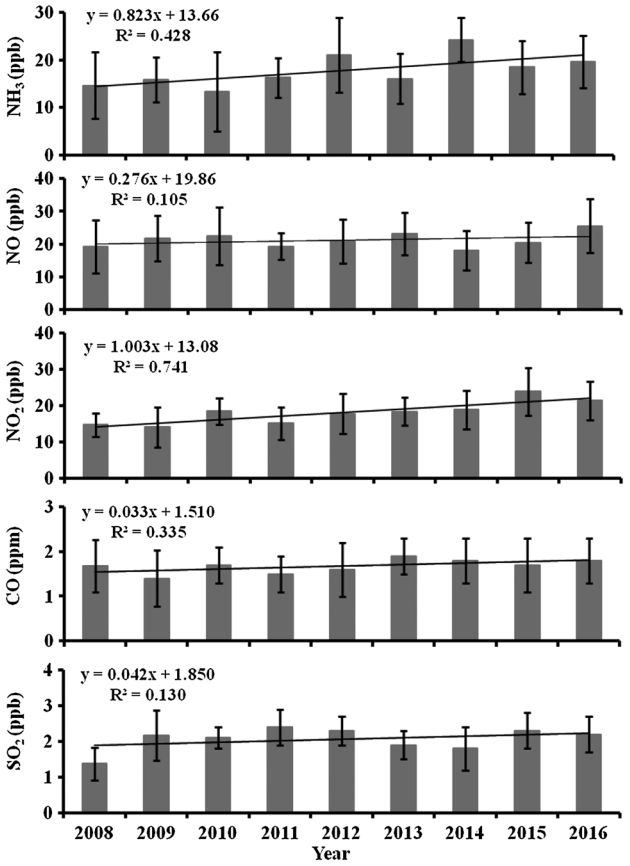

Fig. 1 Annual variation in mixing ratios of ambient NH_3, NO, NO_2, CO and SO_2 in Delhi, India

respective trace gases and prevailing meteorological conditions at the observational site in Delhi.

Kapoor et al. (1992) reported the average NH_3 mixing ratio of NH_3 as 47.3 ± 13.6 ppb in Delhi, whereas, Sharma et al. (2010) reported the average mixing ratio of ambient NH_3 as 20.23 ± 2.71 ppb. Zutshi et al. (1970) reported the NH_3 mixing ratio as 50.7 ppb at Mumbai, whereas, Sharma et al. (2016b) reported the NH_3 mixing ratio as 43.4 ± 7.0 ppb at Kolkata, India. The diurnal, seasonal and day to day variations in mixing ratios of ambient NH_3 and other trace gases (O_3, NO, NO_2, CO and SO_2) at Delhi and other locations of India are already discussed in our previous studied (Sharma et al. 2010a, b, 2012a, b, c, 2014; Saraswati et al. 2017) and compared with other studies (Sharma et al. 2014).

Annual average mixing ratios and inter-annual variations in mixing ratios of NH_3, NO, NO_2, CO and SO_2 (from the average value of the study period) are summarized in Table 1. The maximum annual variation in mixing ratio of ambient NH_3 was in 2014 (6.58 ppb), whereas minumum in 2015 (0.72 ppb). The minimum and maximum inter-annual variations in mixing ratio of ambient NO were −0.35 ppb in 2012 and 4.35 ppb in 2016, respectively. Similarly, maximum (5.78 ppb) significant inter-annual variation in mixing ratio of NO_2 was observed during 2015. The mixing ratios of CO and SO_2 were also varying inter-annually during the study period (Table 1). The inter-annual variation in mixing ratios of NH_3, NO, NO_2, CO and SO_2 were observed may be due to source strength of respective traces and meteorological condition of the observational site.

Although agriculture has historically been the major source of ambient NH_3, however, the contribution of vehicles equipped with three-way catalytic converters has increased considerably at the urban sites (Sutton et al. 2000; Heeb et al. 2008). Therefore, in order to examine the contribution of traffic to NH_3, it may be useful to compare/correlate ambient NH_3 with those of primary pollutants mainly emitted by motor vehicle exhausts, such as NO and CO. Table 2 summarized the correlations among NH_3 versus NO, NH_3 versus NO_2, NH_3 versus CO and NH_3 versus SO_2 during 2008–2016, along with meteorological parameters at the study site.

The correlation matrix of hourly annual average mixing ratios of NH_3 with NO and CO during 2008–2016 showed positive correlation ($r = 0.53$ NH_3 vs. NO; $r = 0.66$ NH_3 vs. CO), supporting the hypothesis that traffic is also an important source of NH_3 at the observational site (Table 2). Meng et al. (2011) also reported a strong positive correlation ($r = 0.78$) between NH_3 and NO during winter at Beijing,

Table 2 Correlation matrix of trace gases and meteorological parameters during 2008−2016 in Delhi

Species	NH_3	NO	NO_2	CO	SO_2	Temp	RH	WS
NH_3	1							
NO	0.53*	1						
NO_2	0.41	0.32	1					
CO	0.66*	0.28	0.59*	1				
SO_2	0.32	0.29	0.29	–0.39	1			
Temp	0.44	–0.05	0.19	–0.41	0.65*	1		
RH	–0.58*	0.15	0.25	0.12	0.26	–0.31	1	
WS	0.12	0.35	0.43	0.33	–0.06	–0.46*	0.15	1

*Significant at $p < 0.05$

China, and considered traffic to be one of the sources of ambient NH_3 at there. The correlation coefficient of NH_3 versus CO was also reported as $r=0.71$ during winter in Beijing, China (Meng et al. 2011), further supporting the present study. SO_2 also reacts with the hydroxyl radical (OH) to form sulphuric acid (Seinfeld and Pandis 1998). Table 2 shows a positive relationship of between NH_3 and NO_2 ($r=0.41$), which indicates the formation of HNO_3 and simultaneously NH_4NO_3 in the atmosphere (Stockwell et al. 2000). During night time, the increased humidity and lowered temperature, along with a higher mixing ratio of NH_3, SO_2 and NO_2 may facilitate the formation of NH_4^+ aerosol in the atmosphere. Table 2 also shows the positive relationship between NH_3 and SO_2 during study ($r=0.32$) indicationg the possible formation of $(NH_4)_2SO_4$.

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