Abundance and distribution of gaseous ammonia and particulate ammonium at Delhi, India

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Abstract. This study reports abundance and distribution of gaseous NH$_3$ and particulate NH$_4^+$ at Delhi. Gaseous NH$_3$ and particulate NH$_4^+$ concentrations were measured during pre-monsoon, monsoon and post-monsoon seasons of the years 2010 and 2011. Average concentrations of gaseous NH$_3$ during pre-monsoon, monsoon and post-monsoon seasons were recorded as 26.4, 33.2 and 32.5 µg m$^{-3}$, respectively. Gaseous NH$_3$ concentrations were the highest during monsoon, thought to be due to decay and decomposition of plants and other biogenic material under wet conditions, leading to increased NH$_3$ emission. The results showed that particulate NH$_4^+$ was always lower than the gaseous NH$_3$ during all the seasons. The concentrations of particulate NH$_4^+$ were recorded as 11.6, 22.9 and 8.5 µg m$^{-3}$ during pre-monsoon, monsoon and post-monsoon seasons, respectively. The percent fraction of particulate NH$_4^+$ was noticed to be highest during the monsoon season, which is attributed to increased humidity levels favouring partitioning into the aerosol phase. On an average, 33.3 % of total N-NH$_x$ was present as particulate NH$_4^+$. Higher concentrations of NH$_3$ noticed during night time may be due to stable atmospheric conditions. The study highlighted that, as compared with rural sites, urban sites showed higher concentrations of gaseous NH$_3$ in India, which may be due to higher population density, human activities and poor sanitation arrangements.

1 Introduction

Recently, atmospheric research has been focused on the nitrogen cycle in order to understand the role of nitrogen in the atmosphere, ocean and terrestrial ecosystems. Reactive nitrogen plays an important role in the atmosphere. Ammonia and ammonium (NH$_x$) are important reactive nitrogen species in the atmosphere. Atmospheric ammonia has become an environmental concern because of two main reasons; firstly, because of its neutralizing nature and secondly, due to ecological consequences of its deposition on sensitive ecosystems, causing eutrophication (Sutton et al., 1998, 2009). Ammonia catalyzes the atmospheric reaction, i.e. oxidation of SO$_2$ in SO$_3$ and reacts rapidly with H$_2$SO$_4$, HNO$_3$. Neutralization results in submicron-sized NH$_4$ salts, i.e. (NH$_4$)$_2$SO$_4$, NH$_4$HSO$_4$ and NH$_4$NO$_3$ etc., which play an important role in radiative forcing. In spite of its initial neutralizing effect on atmospheric chemistry, the deposition of NH$_x$ leads to acidification of the soil similar to the acidic effect of SO$_2$ and NO$_x$ because of its oxidation in the soil to form nitrates (Jongebruer and Voorburg, 1992). Deposition of NH$_x$ from the atmosphere provides an excess N input to the ecosystem.

Sources of atmospheric NH$_3$ vary from region to region, Europe being the highest emitter, followed by the Indian subcontinent and China. Major sources of atmospheric NH$_3$ include domestic animals, biomass burning, oceans, human population and pets, use of synthetic N fertilizers, crops and soils under natural vegetation. Out of total global NH$_3$ emissions, about 50 % is contributed from Asia (Bouwman et al., 1997). Other environmental sources of ammonia include industrial emissions and coal gasification.

In India, reactive nitrogen measurements have not been attempted extensively. This study has been carried out to measure NH$_3$ and NH$_4^+$ concentration at an urban site in Delhi, with an emphasis given to quantifying and explaining differences in the partitioning between the particulate and gaseous fractions.
2 Methodology

2.1 Sampling site

Sampling was carried out in Delhi. The sampling site was located at the building of the School of Environmental Science (SES), Jawaharlal Nehru University, and New Delhi. The JNU campus lies extremely south of Delhi, (latitude 28°31′30″–28°33′30″ N and longitude 77°9′–77°11′ E) near a small forest area of around 400 ha, which lies 500, 700, 1500 and 1100 m to the N, E, S, and W, directions, respectively. The air was sampled from the top floor of the SES building by extending tubing through a window (height ∼15 m). The campus is located away from any industrial activities. The nearest two busy roads run north–south, 1 km east and 1 km west to the site, respectively. The traffic density of these roads is of the order of 10^6 vehicles per day. On the JNU campus, no major air pollution sources exist except vehicles like cars and bikes used by the students, faculty, visitors and the kitchens of various cafeterias existing in different hostels and buildings. It is likely that suspended particulate matter contamination may occur from the construction work going on near the School of Environmental Science. Flying planes also pass through the site to the south to land at IGI airport, which is around 5 km away to the west of the sampling site. Figure 1 shows the location of sampling site.

2.2 Sample collection

Gaseous NH$_3$ and aerosol samples were collected using a low volume pump (flow rate = 1 LPM). Air was sucked directly through an open-face filter pack without using sampling inlet tubing. Filter pack was connected to the impinger through silicon tubing. Samples were collected between April 2010 and July 2011. In the months of April and November 2010, NH$_3$ was collected by passing air through 25 mM H$_2$SO$_4$ (20 mL) in a standard impinger for 5 h. The particulate NH$_4^+$ was collected on Whatman 41 cellulose filters (dia = 47 mm) which was placed upstream of the impinger. On an average, the collection efficiency of impinger technique for NH$_3$ was estimated at 83 %. Collection efficiency of the method was checked by using two impingers in series and it was estimated only for the NH$_3$ by using the following formula:

\[
\text{Collection efficiency} = \frac{\eta_2^{*100}}{(\eta_1 + \eta_2)},
\]

where '\eta_1' and '\eta_2' are the values of optical density in impingers 1 and 2, respectively.
Such correction did not affect aerosol concentrations. These calculations indicated that without using efficiency correction, aerosol fraction is overestimated by $\sim 2\%$.

In total, 91 samples of gaseous $\text{NH}_3$ and 72 samples of particulate $\text{NH}_4^+$ were collected out of which 80 and 60 samples were found useful for $\text{NH}_3$ and $\text{NH}_4^+$, respectively. During the day, sampling was performed between 08:00 a.m. and 01:00 p.m., and at night between 06:00 p.m. and 11:00 p.m. Each aerosol sample represented the duration of two gaseous $\text{NH}_3$ samples collected during day and night. In order to collect samples with better efficiency, from May–July 2011, gaseous samples were collected using mist chambers instead of impingers at similar flow rate. This technique has been found more useful for $\text{NH}_3$ collection (efficiency $> 99\%$). Particulate $\text{NH}_4^+$ was extracted immediately by shaking with deionized water (10 mL) for 30 min in a ultrasonic bath.

**Sampling train setup**

The sampling unit consisted of two standard impingers, one pump, flow meter, connecting tubes (Fig. 2). The filter holder was exposed to outside air for the collection of aerosols. Impinger No. 2 was used to find out the efficiency of collection.

**2.3 Analysis**

Samples were analyzed immediately after the collection. Both gaseous $\text{NH}_3$ and particulate $\text{NH}_4^+$ were determined colorimetrically with the help of UV-Vis spectrophotometer (Perkin Elmer, USA) using the indophenol blue method. In this method, a blue indophenol dye is formed in the sodium pentacyanonitroferrate catalyzed phenol-hypochlorite reaction with $\text{NH}_3$ in alkaline solution. The color intensity is directly proportional to the $\text{NH}_4^+$ present. The intensity of resultant $\text{NH}_4^+$ complex was determined at 630 nm. It is worth mentioning here that other common gaseous pollutants such as $\text{SO}_2$, $\text{O}_3$, $\text{NO}_2$ at their normal atmospheric levels do not interfere with this method. However, other reduced N compounds such as amines have cross sensitivity during color development.

**Fig. 2.** Flow diagram of sampling assembly.

**Fig. 3.** Average concentration of gaseous $\text{NH}_3$ and particulate $\text{NH}_4^+$. Error bar shows standard deviation (S.D.) ($n = 91$ for $\text{NH}_3$ and $n = 72$ for the $\text{NH}_4^+$).

**3 Results and discussion**

**3.1 Average variation of $\text{NH}_3$ and $\text{NH}_4^+$**

Figure 3 shows the average concentrations and standard deviation of gaseous $\text{NH}_3$ and particulate $\text{NH}_4^+$. Gaseous $\text{NH}_3$ varied from 9.8 to $63.8\mu g m^{-3}$ with an average of $29.4\mu g m^{-3}$. Particulate $\text{NH}_4^+$ varied from 1.4 to $39.4\mu g m^{-3}$ with an average of $15.56\mu g m^{-3}$. Values of gaseous $\text{NH}_3$ in the similar order of magnitude have been reported two decades back by Kapoor et al. (1992) at Delhi ($32.6\mu g m^{-3}$) and Zutshi et al. (1970) at Mumbai ($35\mu g m^{-3}$). Both $\text{NH}_3$ and $\text{NH}_4^+$ varied, covering large ranges of concentration, which can be attributed to the various activities taking place in the surroundings, vegetation cover, land use patterns and meteorological factors. The concentration of $\text{NH}_3$ depends mainly on source strength, atmospheric chemistry and temperature and humidity etc. Bowman et al. (1997) and Goebes et al. (2003) have reported higher emission of $\text{NH}_3$ due to fertilizer application during spring and fall because high temperature increases volatilization of $\text{NH}_3$. Volatilization is temperature-dependent and varies significantly over day and seasons (Skjoth et al., 2004). In tropical regions, the effect of high temperatures can enhance the volatilization, thus contributing to higher amounts of $\text{NH}_3$. This might be one of the possible reasons for higher $\text{NH}_3$ concentrations at Indian sites (Kulshrestha et al., 2009; Singh et al., 2001). As compared to $\text{NH}_4^+$, higher $\text{NH}_3$ concentrations at Indian sites might be due to large contribution from $\text{NH}_3$ sources and relatively slow scavenging and $\text{NH}_4^+$ conversion processes.

It is worth mentioning here that $\text{NH}_3$ measurements have uncertainty due to various reasons. The use of Whatman 41 cellulose prefilter for $\text{NH}_3$ collection raises the possibility of $\text{NH}_3$ capture on the prefilter during humid conditions. However, in the United Kingdom, such interaction has not been found significant (Sutton et al., 1993) but under Indian conditions, such an effect may be more relevant and needs to be investigated. In addition, the uncertainty in $\text{NH}_3$ estimation due
to the impinger technique can be reduced by using denuder technique where the NH$_3$ is trapped first and the remainder is captured on a filter (Sutton et al., 2001b).

### 3.2 Comparison of Gaseous NH$_3$ concentration with other studies

Table 1 gives comparison of NH$_3$ reported by various workers at different sites worldwide. Interestingly, there are sufficient data available for NH$_4^+$ in rainwater at remote rural, urban, semiurban and marine sites worldwide (Lenhard and Gravenhorst, 1980; Likens et al., 1987; Galloway et al., 1987; Galloway, 1988; Khemani et al., 1989; Possanzini et al., 1988; Tuncel and Unger, 1996; Parashar et al., 1996; Khare et al., 1996; Kulshrestha et al., 2005; Satyanarayana et al., 2010). But very few studies report NH$_3$ and NH$_4^+$ in air (Table 1). The comparison shows that at most Indian sites, gaseous NH$_3$ concentrations are reported higher than at other sites. Within India, urban sites show higher gaseous NH$_3$ than that of rural sites. Higher concentration at urban...
sites may be due to increased population density, various activities and poor sanitation arrangements. Another possible reason of higher gaseous NH$_3$ in India is due to strong source contribution and inefficient wet deposition. In addition, alkaline atmospheric conditions due to soil-derived particles do not encourage NH$_3$ (an alkaline gas) to get adsorbed onto the particles in air. Figure 4 shows how alkaline soil dust is responsible for higher NH$_3$ concentrations in India. The soil dust, which is rich in CaCO$_3$, is mainly contributed by resuspension of soils from the nearby Thar desert and open agricultural fields. The high dust content in the atmosphere is a typical feature of Indian continental region (Kulshrestha et al., 2005).

### 3.3 Diurnal variation

Full time series of all daytime measurements of NH$_3$ and NH$_4^+$ are shown in Fig. 5a. Figure 5b shows the variation of gaseous ammonia in day and night. It is very clear that the nighttime concentrations are higher than the daytime. The daytime concentrations of NH$_3$ varied from 16.6 to 44.3 µg m$^{-3}$ with an average value of 28.9 µg m$^{-3}$, whereas the nighttime concentrations varied from 36.5 to 50.8 µg m$^{-3}$ with an average value of 41.07 µg m$^{-3}$. The high NH$_3$ concentrations during nighttime are probably due to stable atmospheric conditions. Burkhardt et al. (1998) have also reported higher concentrations of NH$_3$ during nighttime due to stable atmospheric conditions, which results in the trapping of gaseous NH$_3$ near ground level. Similar observations have been reported by Cadle et al. (1982) and Singh et al. (2001).

### 3.4 Variation during pre-monsoon, monsoon and post-monsoon

Figure 6 shows that the gaseous NH$_3$ concentrations are the highest during monsoon season (July–September), a period of higher rainfall, whereas it is observed to be the lowest in the samples collected during pre-monsoon. The average concentration of gaseous NH$_3$ during pre-monsoon (March–June) was 26.47 µg m$^{-3}$, whereas in the monsoon period it was on an average 33.15 µg m$^{-3}$. In post-monsoon (October–November), the average value of gaseous NH$_3$ was 32.5 µg m$^{-3}$. The highest concentration of NH$_3$ during monsoon season may be due to decay and decomposition.
of plants and other biogenic material under wet conditions which emit NH₃. In addition, seasonality in agricultural source activity, like growing seasons and timing of manure application to fields, can also influence the seasonal concentration of NH₃. However, this influence may be more effective in rural areas as compared to the present site.

3.5 Estimation of percent fraction of gaseous and particulate ammonia

Based on average values of gaseous ammonia and particulate ammonia, percentage fraction was calculated for N-NH₃ and N-NH₄⁺ as follows:

$$\% \text{ N-NH}_4^+ = \frac{\text{N-NH}_4^+(\text{Aerosol}) \times 100}{\text{N-NH}_4^+(\text{Aerosol}) + \text{N-NH}_3(\text{Ammonia})}$$  \hspace{1cm} (2)

The results show that particulate ammonia was always lower than the gaseous ammonia in all the seasons. The percent fraction of particulate N-NH₄⁺ was 33.3 % of total N (N-NH₄⁺ + < N-NH₃). The percent fraction of particulate ammonia was most noticeable during monsoon season, followed by pre-monsoon and post-monsoon. The highest N-NH₄⁺ during monsoon may be due to higher relative humidity, which results in faster NH₃-NH₄⁺ conversion.

4 Summary

Seasonal variation data showed that gaseous NH₃ concentrations were the highest during the monsoon period, which might be due to decay and decomposition of plants and other biogenic material under wet conditions which emit NH₃. It might also be due to seasonality in agriculture sources and manure application, which might have higher influence at rural sites as compared to the present urban site. It was noticed that particulate NH₄⁺ was always lower than the gaseous NH₃ in all the seasons. The percent fraction of particulate N-NH₄⁺ was most noticeable during monsoon season due to increased humidity levels. Gaseous NH₃ levels were recorded to be higher during nighttime than daytime, which is consistent with higher atmospheric stability during nighttime and an associated reduced dispersion of this gas, which typically emitted from low-level sources.

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