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 due to decay and decomposition of plants and other biogenic material under wet conditions which emit NH$_3$. 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 highest during monsoon season due to increased humidity levels. 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. Study highlighted that as compared to 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 upon 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 ecosystem 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 $\text{H}_2\text{SO}_4$, HNO$_3$. In spite of neutralizing effect, its deposition leads to acidification of the soil similar to the acidic effect of acids of SO$_2$ and NO$_x$ (Jongebreur and Voorburg, 1992). 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 important role in radiative forcing. Deposition of NH$_x$ from the atmosphere provides an excess N input to the ecosystem. This may also affect NH$_3$/NH$_4^+$ ratios in the atmosphere. Sources of atmospheric NH$_3$ vary from region to region, Europe being the highest emitter followed by 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, 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 etc.

But 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 a urban site in Delhi. In this study, attempt has also been made to quantify particulate and gaseous fractions of ammonia.

2 Methodology

2.1 Sampling site

Sampling was carried out in Delhi. Sampling site was located at the building of School of Environmental Science (SES), Jawaharlal Nehru University, and New Delhi. JNU campus lies in extreme South of Delhi, (latitude 28°31′30″–28°33′30″ N and longitude: 77°9′0″–77°11′0″ E) having mini forest area in its surroundings. 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. In 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 School of Environmental Science. Flying planes also pass through southerly to the site for landing at IGI airport which is around 5 km away in the west from 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). Samples were collected between April 2010 and July 2011. In the months of April 2010 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 as 83%. In total, 91 samples of gaseous NH$_3$ and 72 samples of particulate NH$_4^+$ were collected. In day time, sampling was performed between 8 a.m. and 1 p.m. while in the night time, between 6 p.m. and 11 p.m. Each aerosol sample represented the duration of two gaseous NH$_3$ samples collected during day and night time. In order to collect samples with better efficiency, during May 2011–July 2011, gaseous samples were collected using mist chamber instead of impinger at similar flow rate. This technique has been found more useful for NH$_3$ collection (efficiency > 99%). Particulate NH$_4^+$ was extracted immediately by shaking with deionized water (10 ml) for 30 min in an ultrasonic bath.

#### 2.2.1 Sampling train setup

Sampling unit consisted of two standard impingers, one pump, flow meter, connecting tubes (Fig. 2). Filter holder was exposed outside in 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 NH₃ and particulate NH₄⁺ were determined colorimetrically with the help of UV-Vis spectrophotometer (Perkin Elmer, USA) using Indophenol blue method. In this method, a blue indophenols dye is formed in the sodium pentacyanonitrosylferrous catalyzed phenol-hypochlorite reaction with NH₃ in alkaline solution. The colour intensity is directly proportional to the NH₄⁺ present. The intensity of resultant NH₄⁺ complex was determined at 630 nm. It is worth mentioning here that other common gaseous pollutants such as SO₂, O₃, NO₂ at their normal atmospheric levels do not interfere in this method. However, other reduced N compound such as amines have cross sensitivity during colour development.

3 Results and discussion

3.1 Average variation of NH₃ and NH₄⁺

Figure 3 shows the average concentrations and standard deviation of gaseous NH₃ and particulate NH₄⁺. Gaseous NH₃ varied from 9.8 to 63.8 µg m⁻³ with an average of 29.4 µg m⁻³. Particulate NH₄⁺ varied from 1.4 to 39.4 µg m⁻³ with an average of 15.56 µg m⁻³. Values of gaseous NH₃ in the similar order of magnitude have been reported two decades back by Kapoor et al. (1992) at Delhi (32.6 µg m⁻³) and Zutshi et al. (1970) at Mumbai (35 µg m⁻³). Both NH₃ and NH₄⁺ varied covering large range 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 NH₃ depends on mainly source strength, atmospheric chemistry and temperature and humidity etc. As compared to NH₄⁺, higher NH₃ concentrations indicate an unique feature of atmospheric environment at Indian sites (Kulshrestha et al., 2009; Singh et al., 2001) which may be due to large contribution from NH₃ sources and relatively slow scavenging and NH₄⁺ conversion processes.
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 rain water at remote rural, urban, semiurban and marine sites world wide (Lenhard and Gravenhorst, 1980; Likens et al., 1987; Galloway et al., 1987; Galloway, 1988; Khemani et al., 1989; Possanzini et al., 1988; Vincent, 1995; 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). 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, 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.

3.3 Diurnal variation

Figure 5 shows the variation of gaseous ammonia in day and night. It is very clear that the night time concentrations are higher than day time. But patterns of NH$_3$ variation during day and night time are similar indicating higher NH$_3$ results in higher NH$_4^+$ and vice versa.

The daytime concentrations varied from 16.6 to 44.3 µg m$^{-3}$ with an average value of 28.9 µg m$^{-3}$ whereas the night time 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 night time are probably due to stable atmospheric conditions. Burkhardt et al. (1998) have also reported higher concentrations of NH$_3$ during night time due to stable atmospheric conditions which results in to 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 (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 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 NH$_3$. In addition, seasonality in agricultural source activity like growing season and timing of manure application to fields can also influence the seasonal concentration of NH$_3$. 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-NH$_3$ and N-NH$_4^+$ as follows-

$$
\% \text{ N-NH}_4^+ \text{ fraction} = \frac{\text{N-NH}_4^+ (\text{Aerosol}) \cdot 100 \%}{\text{N-NH}_4^+ (\text{Aerosol}) + \text{N-NH}_3 (\text{Ammonia})}
$$

The results show that particulate ammonia was always lower than the gaseous ammonia in all the seasons. The percent fraction of particulate N-NH$_4^+$ was 33.3 % of total N (N-NH$_4^+$ + N-NH$_3$). The percent fraction of particulate ammonia was noticed highest during monsoon season followed by pre monsoon and post monsoon. The highest N-NH$_4^+$ during monsoon may be due to higher relative humidity which results in faster NH$_3$-NH$_4^+$ conversion.
4 Summary

Seasonal variation data showed that gaseous NH₃ concentrations were the highest during 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 site as compared to the present urban site. It was noticed that particulate NH⁺₄ was always lower than the gaseous NH₃ in all the seasons. The percent fraction of particulate N-NH⁺₄ was noticed highest during monsoon season due to increased humidity levels. Gaseous NH₃ levels were noticed higher during night time than day time which might be due to higher atmospheric stability during night time.

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References


Table 1. Comparison of concentrations of gaseous ammonia with other studies.

<table>
<thead>
<tr>
<th>Site</th>
<th>Characteristics of site</th>
<th>Concentration (µg m(^{-3}))</th>
<th>Reference</th>
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</thead>
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<tr>
<td>Mumbai</td>
<td>Urban</td>
<td>35.0</td>
<td>Zutshi et al. (1970)</td>
</tr>
<tr>
<td>Yokahama</td>
<td>Urban</td>
<td>5.3</td>
<td>Yamamota et al. (1988)</td>
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<td>Delhi</td>
<td>Urban</td>
<td>32.6</td>
<td>Kapoor et al. (1992)</td>
</tr>
<tr>
<td>Pune</td>
<td>Urban</td>
<td>2.0</td>
<td>Khemani et al. (1987)</td>
</tr>
<tr>
<td>Beijing</td>
<td>Urban</td>
<td>22.26</td>
<td>Ianniello et al. (2010)</td>
</tr>
<tr>
<td>Agra</td>
<td>Semi Urban</td>
<td>10.2</td>
<td>Singh et al. (2001)</td>
</tr>
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<td>Abbeville, LA, US</td>
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<td>0.07</td>
<td>Cadle et al. (1982)</td>
</tr>
<tr>
<td>Richpur</td>
<td>Rural</td>
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<td>Khemani et al. (1987)</td>
</tr>
<tr>
<td>Sinhagad (Rural)</td>
<td>Rural</td>
<td>0.01</td>
<td>6 Khemani et al. (1987)</td>
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<tr>
<td>Pacific ocean</td>
<td>Marine</td>
<td>0.004</td>
<td>Quinn et al. (1988)</td>
</tr>
<tr>
<td>Arabian sea</td>
<td>Marine</td>
<td>1.6</td>
<td>Khemani et al. (1987)</td>
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<td>Bay of Bengal</td>
<td>Marine</td>
<td>1.9</td>
<td>Khemani et al. (1987)</td>
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<td>Delhi (Urban)</td>
<td></td>
<td>29.4</td>
<td>Present study</td>
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Fig. 1. Map showing sampling site and surroundings.
Fig. 2. Flow diagram of sampling assembly.
Fig. 3. Average concentration of gaseous NH$_3$ and particulate NH$_4^+$. Error bar shows standard deviation (S.D.).
How alkaline dust is responsible for higher NH₃

**Acidified region**
- Acidic atmosphere
- NH₃ is attracted to react with sulphuric acid
- Forms Ammonium sulphate
- Settling through wet deposition

**India**
- Alkaline atmosphere
- NH₃ is alkaline gas
- NH₃ emitted by various sources does not find its acidic partner
- Prefers to settle by dry deposition

Giving higher wet fluxes

Giving High DD fluxes

This also causes low levels of SO₂ in India

**Fig. 4.** Flow chart showing reason for higher NH₃ in Indian region.
Fig. 5. Average diurnal variation of NH₃.
Fig. 6. Average concentration and standard deviation (S.D.) of gaseous NH$_3$ and particulate NH$_4^+$ during different seasons.