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Abundance and distribution of gaseous ammonia and particulate ammonium at Delhi (India)

S. Singh and U. C. Kulshrestha

School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110067 India

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Correspondence to: U. C. Kulshrestha (umeshkulshrestha@gmail.com)

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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 postmonsoon seasons of the years 2010 and 2011. Average concentrations of gaseous NH_3 during premonsoon, monsoon and post monsoon seasons were recorded as 26.4, 33.2 and 32.5 $\mu g\,m^{-3}$, 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 $\mu g\,m^{-3}$ during premonsoon, monsoon and postmonsoon seasons, respectively. The percent fraction of particulate NH_4^+ was noticed highest during monsoon season due to increased humidity levels. On anaverage, 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

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rapidly with H_2SO_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. $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_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

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of various cafeteria 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_2SO_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 a 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.

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2.3 Analysis

Samples were analyzed immediately after the collection. Both gaseous NH_3 and particulate NH_4^+ 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 pentacyanonitrosylooferrete catalyzed phenol-hypochlorite reaction with NH_3 in alkaline solution. The colour intensity is directly proportional to the NH_4^+ present. The intensity of resultant NH_4^+ complex was determined at 630 nm. It is worth mentioning here that other common gaseous pollutants such as SO_2, O_3, NO_2 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 NH_3 and NH_4^+

Figure 3 shows the average concentrations and standard deviation of gaseous NH_3 and particulate NH_4^+. Gaseous NH_3 varied from 9.8 to 63.8 $\mu g\,m^{-3}$ with an average of 29.4 $\mu g\,m^{-3}$. Particulate 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 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 NH_3 and NH_4^+ 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 NH_3 depends on mainly source strength, atmospheric chemistry and temperature and humidity etc. As compared to NH_4^+, higher NH_3 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 NH_3 sources and relatively slow scavenging and NH_4^+ conversion processes.

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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 $\mu g\,m^{-3}$ with an average value of 28.9 $\mu g\,m^{-3}$ whereas the night time concentrations varied from 36.5 to 50.8 $\mu g\,m^{-3}$ with an average value of 41.07 $\mu g\,m^{-3}$. 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

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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 $\mu g\,m^{-3}$ whereas in monsoon period it was on an average 33.15 $\mu g\,m^{-3}$. In post monsoon (October/November), the average value of gaseous NH_3 was 32.5 $\mu g\,m^{-3}$. 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 $N\text{-}NH_3$ and $N\text{-}NH_4^+$ as follows-

$$\%\,N\text{-}NH_4^+\ \text{fraction} = \frac{N\text{-}NH_{4\,(Aerosol)}^+ \cdot 100\,\%}{N\text{-}NH_{4\,(Aerosol)}^+ + N\text{-}NH_{3\,(Ammonia)}} \quad (1)$$

The results show that particulate ammonia was always lower than the gaseous ammonia in all the seasons. The percent fraction of particulate $N\text{-}NH_4^+$ was 33.3 % of total N ($N\text{-}NH_4^+ + N\text{-}NH_3$). The percent fraction of particulate ammonia was noticed highest during monsoon season followed by pre monsoon and post monsoon. The highest $N\text{-}NH_4^+$ during monsoon may be due to higher relative humidity which results in faster NH_3-NH_4^+ conversion.

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4 Summary

Seasonal variation data showed that gaseous NH_3 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 NH_3. 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 NH_3 in all the seasons. The percent fraction of particulate N-NH_4^+ was noticed highest during monsoon season due to increased humidity levels. Gaseous NH_3 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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Table 1. Comparison of concentrations of gaseous ammonia with other studies.

Site	Characteristics of site	Concentration ($\mu g\, m^{-3}$)	Reference
Mumbai	Urban	35.0	Zutshi et al. (1970)
Yokahama	Urban	5.3	Yamamota et al. (1988)
Delhi	Urban	32.6	Kapoor et al. (1992)
Pune	Urban	2.0	Khemani et al. (1987)
Beijing	Urban	22.26	Ianniello et al. (2010)
Agra	Semi Urban	10.2	Singh et al. (2001)
Abbeville, LA, US	Rural	0.07	Cadle et al. (1982)
Richpur	Rural	0.9	Khemani et al. (1987)
Sinhagad (Rural)	Rural	0.	6 Khemani et al. (1987)
Pacific ocean	Marine	0.004	Quinn et al. (1988)
Arabian sea	Marine	1.6	Khemani et al. (1987)
Bay of Bengal	Marine	1.9	Khemani et al. (1987)
Delhi (Urban)		29.4	Present study

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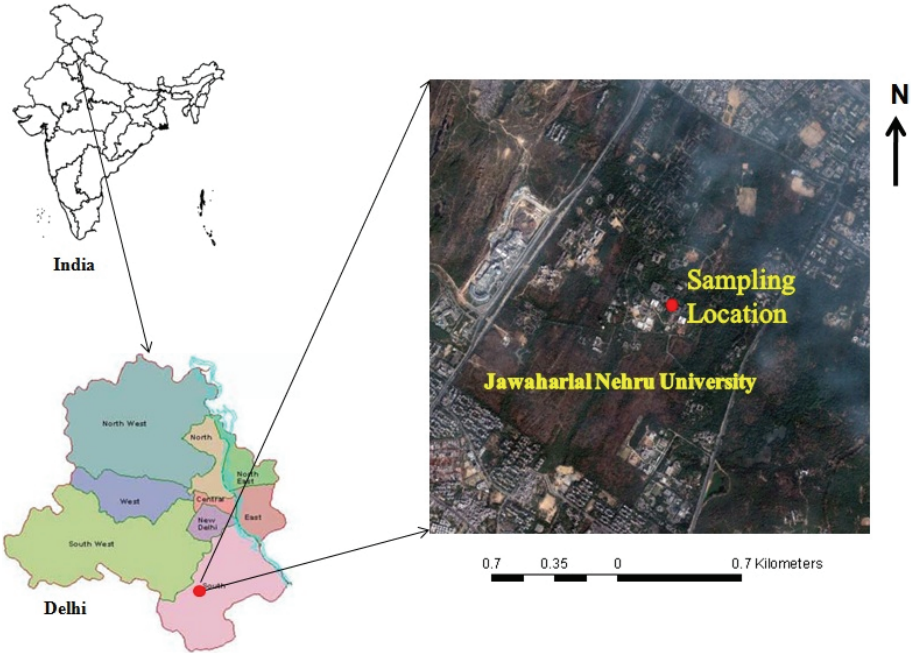

Fig. 1. Map showing sampling site and surroundings.

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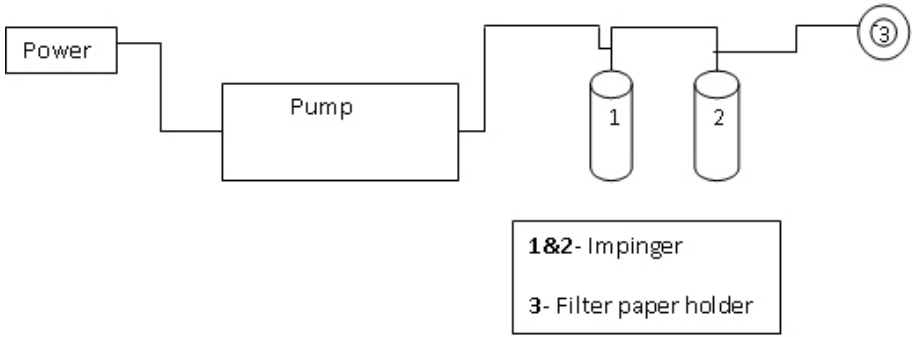

Fig. 2. Flow diagram of sampling assembly.

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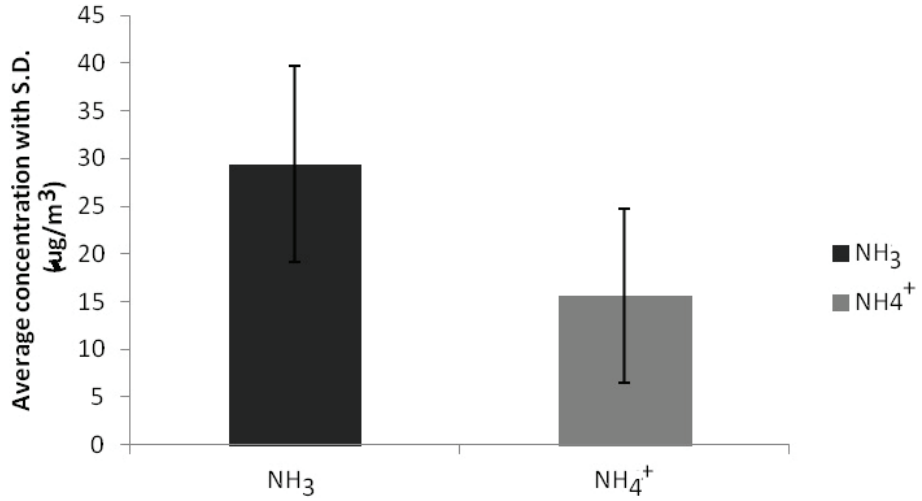

Fig. 3. Average concentration of gaseous NH_3 and particulate NH_4^+. Error bar shows standard deviation (S.D.).

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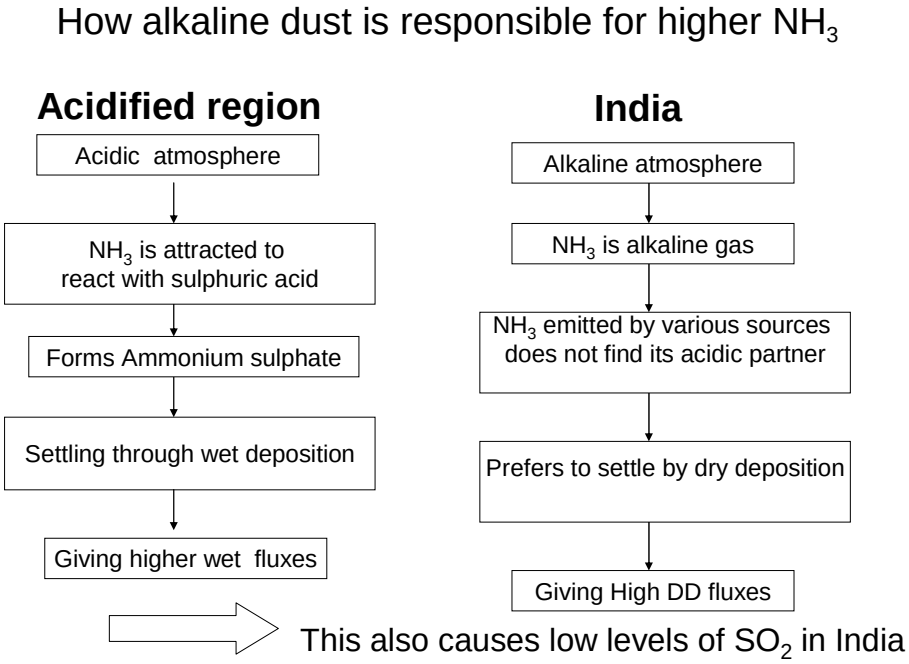

Fig. 4. Flow chart showing reason for higher NH_3 in Indian region.

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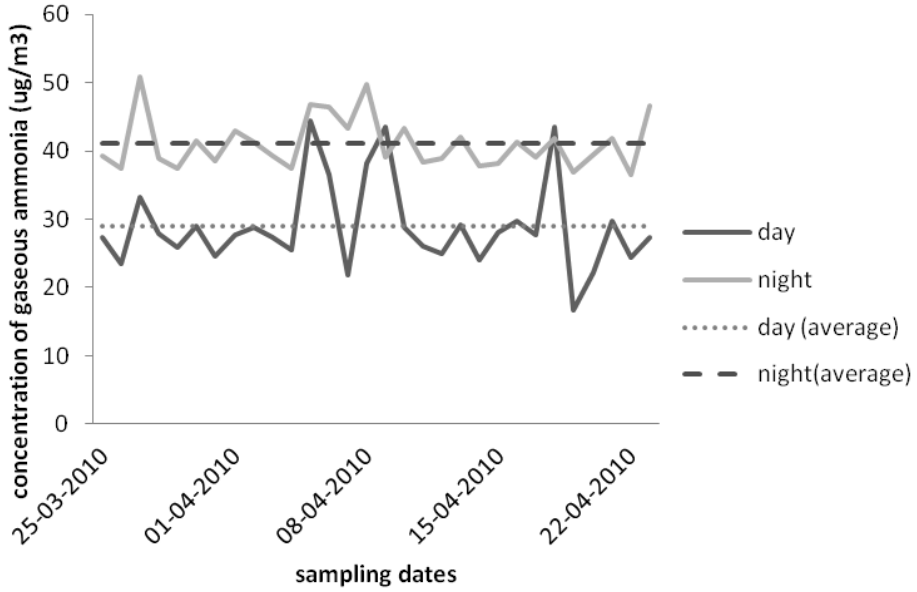

Fig. 5. Average diurnal variation of NH_3.

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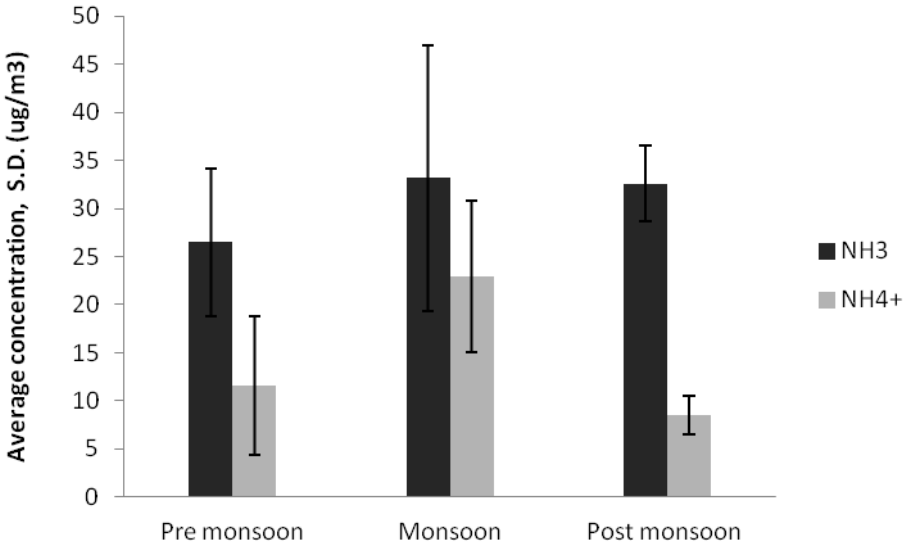

Fig. 6. Average concentration and standard deviation (S.D.) of gaseous NH_3 and particulate NH_4^+ during different seasons.

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