Rural versus urban gaseous inorganic reactive nitrogen in the Indo-Gangetic plains (IGP) of India

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Abstract
The present study reports on the abundance of reactive nitrogen (NH₃ and NO₂) at two sites, i.e. Okhla (urban site) in Delhi and Mai (rural site), located in the nearby state: Uttar Pradesh. The measurements were carried out during the period from October, 2012 to September, 2013 on a monthly basis. The average concentrations of NH₃ at Okhla and Mai have been recorded as 40.4 ± 16.8 and 51.57 ± 22.8 μgm⁻³, respectively. The average concentrations of NO₂ have been recorded as 24.4 ± 13.5 and 18.8 ± 12.6 μgm⁻³ at Okhla and Mai, respectively. Results show that the seasonal variation at Mai was more prominent where NH₃ concentrations varied at 72.0 μgm⁻³ during the winter, 47.2 μgm⁻³ during the summer and 30.7 μgm⁻³ during the monsoon season, whereas at Okhla the average NH₃ concentrations were almost equal during different seasons, namely 44.2 μgm⁻³ during the winter, 42.5 μgm⁻³ during the summer and 38.9 μgm⁻³ during the monsoon season. This is probably due to significant differences in crops and in the fertilizer amounts applied across the seasons in rural areas, while urban areas have almost constant sources throughout the year. Winter concentrations were highest at both sites, followed by summer and then the monsoon season. The average NO₂ concentrations were recorded as 39.6 μgm⁻³, 24.5 μgm⁻³ and 10.4 μgm⁻³ during the winter, summer and monsoon season at Okhla, whereas the average NO₂ concentrations were recorded as 27.5 μgm⁻³, 17.2 μgm⁻³ and 4.1 μgm⁻³ during the winter, summer and monsoon season, respectively. NO₂ emissions at Okhla may be attributed to various urban activities, such as vehicular traffic and industries, while NO₂ emissions at Mai may be attributed to biomass burning as a major source. However, NO₂ concentrations from vehicular traffic and nearby industries cannot be ignored at Mai.

Keywords: reactive nitrogen, agricultural sources, ammonia, nitrogen dioxide, Indo gangetic region

1. Introduction
Nitrogen (N) is an important constituent of human life and the earth system. N₂ gas constitutes 78.02% of the atmosphere. Like the saying, ‘water, water everywhere, but not a drop to drink,’ nitrogen surrounds us everywhere, but it cannot be directly utilized by plants and animals due to its inert nature. Plants and other organisms can utilize it only after its conversion to reactive nitrogen (Nr), which includes all chemically, biologically, photochemically and radioactively active compounds in the environment (Galloway et al 1995). Most of atmospheric N is contributed by N₂, with a minor contribution from N₂O (Gradel and Crutzen 1993), whereas traces of N are contributed by other N species such as NH₃ and NOₓ, etc. In the atmosphere, Nr is mainly released as NH₃, NOₓ, with small quantities of other gases such as HONO or organic N (Hertel et al 2012).
Due to anthropogenic activities, the natural biogeochemical cycle of nitrogen has been perturbed. Activities such as fertilizer application, animal husbandry, fossil fuel combustion, etc have contributed a huge amount of Nr species into the atmosphere (Galloway et al. 2008), resulting in their increased depositions onto the earth’s surface. According to research reports, elevated N deposition may lead to environmental problems such as eutrophication (Vitousek et al. 1997, Liu et al. 2011), biodiversity loss (Phoenix et al. 2006, Clark and Tilman 2008, Song et al. 2011, Li et al. 2012a), acidification of soil (Guo et al. 2010) and increased N2O emissions (Li et al. 2012b). Nr species have an adverse impact on air quality (Chan and Yao 2008, Kulshrestha et al. 2009, Shen et al. 2011, Aber et al. 1989, Bobbink et al. 1998, Fangmeier et al. 1994) and plants (Liu et al. 2011, Sutton et al. 2011).

According to Galloway et al. (1995), Nr is contributed by human activities at a rate of 140 Tg N per year globally in which 20 Tg, 80 Tg and 40 Tg are contributed by energy production, fertilizer production and the cultivation of legumes and other crops, respectively. An approximate 55–60% fraction of the total anthropogenically fixed N is redistributed back to the atmosphere as reduced N (NH3, NH3+NH4+) and oxidized N (NOx) (Galloway et al. 1995). The total (wet + dry) deposition of inorganic N in North America and Europe ranges at about 3–32 75 kg N ha−1 year−1 and 1–75 kg N ha−1 year−1, respectively (Nadelhoffer 2001). These concentration ranges are considered to be higher than the N deposition during the pre-industrial period (Holland et al. 1999).

The combustion of fossil fuel is primarily responsible for the anthropogenic emission of oxides of nitrogen (NOx). A significant amount of NOx is emitted by petrol and by diesel-based internal combustion engines from the transport sector. Around 30–40% of global nitrogen oxide emissions and 85% of regional emissions in North America are due to the combustion supply (Logan 1983). NOx is emitted into the atmosphere from both natural and anthropogenic sources such as fossil fuel combustion (Gadi et al. 2003), biomass burning (Lobert et al. 1990), the oxidation of atmospheric ammonia and lightning (Seinfeld and Pandis 1998). A higher concentration of NOx may damage human health and vegetation (Kinney 2008). Oxides of N form HNO3 and PAN in the atmosphere, which are important Nr species from an air quality viewpoint. The growing energy demand has resulted in the increased emission of NOx from coal combustion in thermal power plants and from petroleum combustion in the transport sector. In addition, biomass burning in traditional cooking and heating is also a significant source of NOx in the Indian region (Singh et al. 2014).

India has the second highest population in the world. Around 70% of the population lives in villages, taking care of agriculture to meet food supply demands. In order to get a higher yield of agriculture and of the food product, the increased practice of fertilizer application has added an extra load of nutrients, especially the Nr species. Most N is applied as urea or DAP fertilizers, which are considered significant sources of NH3. Urea and ammonia-based fertilizers contribute atmospheric NH3 due to volatilization. The elevated ambient temperature in tropical countries such as India plays an important role in NH3/NH4 equilibrium because of the greater volatilization of NH3 due to its higher vapour pressure (Asman 1992). The emission factor for the percent loss of N of urea and DAP are 15 and 5, respectively (Parashar et al. 1998). Other sources, such as decomposing excrement, inadvertent losses during the production of fertilizer and burning biomass, also contribute atmospheric NH3. In addition, shifting food habits from vegetarian to non-vegetarian (meat, milk and eggs diet, livestock production) are also responsible for increased atmospheric Nr.

Due to the population explosion and the exponential growth in agriculture, power generation and transport sectors in India, the emission of NH3 and NOx species are increasing and are expected to rise further, having an adverse impact on human health and on plants. Considering the implications of these two species (NH3 and NOx) in the changing N cycle, the present study was carried out in Indo-Gangetic plains at two sites of different characteristics (urban and rural) to study the emissions and atmospheric levels in relation to their sources and their role in the meteorological parameters.

2. Methodology

2.1. Monitoring sites

Two sites that have different land uses, land covers, sources and population densities in the Northern Indian plain were selected. The urban site has been referred to as Okhla, whereas the rural site has been referred to as Mai. Basic information regarding both sites has been given in table 1.

The location of both sites has been shown in figure 1. The map given in figure 1 also gives an idea of the land use, climate and population distribution in the study area.
land cover and housing density in the surrounding areas of the sites. As the major objective of the study was to observe reactive nitrogen chemistry at typical urban and rural sites, the Okhla and Mai sites were chosen. Okhla is a residential and industrial urban area that has a high population density with a mixed population of four wheelers and two wheelers, construction activities, congested road and streets indicating a very close livelihood due to which sanitation issue was always a concern during sampling. In contrast, the rural area of Mai has agricultural dominance, rural activities and a lesser population density, which has a lesser influence on industrial activities and transport pollution.

2.1.1. Okhla. Okhla was selected as an urban site, which is located in the South Delhi district. The site is dominated by heavy vehicular traffic and industries. Okhla had a population density of 10,935 inhabitants per square kilometre (28,320/sq mi), with a population growth rate of 20.59% during the decade of 2001–2011. The South Delhi district had a population of 2,733,752 in 2011, which is roughly equal to the total population of Jamaica or the US state of Nevada. The Okhla area is congested in terms of high-rise buildings, roads and other infrastructure. In the vicinity of the sampling site, there is a cremation ground, which can also contribute emissions of pollutants. Such waste also can be potential source of Nr. Table 2 gives the number of meat shops and their meat production in the Okhla locality.

2.1.2. Mai. The Mai village, which is located in the Jaunpur district of Uttar Pradesh state, was selected as the rural site. The total area of the village is 617 hectares, out of which 385 hectares (approximately 62%) are used for agricultural purposes. The area around the site is dominated by agricultural activities. A few industrial establishments are located at a distance of 13 km from the village, including one vegetable oil production factory. The combustion vapours and odour of this mill can be smelled in Mai. This region of Uttar Pradesh has three major crop seasons, namely i) Rabi (winter crops), ii) Kharif (monsoon crops) and Zaid (summer crops). The Rabi crop is dominated by corn, black gram, gram and mustard. The Kharif crop is dominated by rice, while the Zaid crop season is not cultivated much due to lack of water. Most fields remain open during the summer period. The farmers of Mai mainly apply DAP and urea fertilizers as a N supplement. The monthly variations of temperature and wind speed at both sites have been given in table 3.
2.2. Sampling and analysis

NH₃ and NO₂ samples were collected at a height of 15 m from the ground at both sites during October, 2012 to September, 2013 using a handy sampler (Envirotech model APM 821) at an average flow rate of 1 LPM. The handy sampler consisted of a battery-operated pump, which was used to suck air through impingers with an absorbing solution. The possibility of NH₄ aerosol in the absorbing liquid is remote as air was passed through a PTFE filter connected in the front of the sampling train (Singh et al. 2012). The sampling was carried out during the daytime and nighttime hours separately on an 8 hour basis. Daytime was considered as 10 am to 6 pm, while nighttime was considered between 10 pm to 6 am. The measurements were generally performed for 7 days during each respective month. However, the samples could not be collected during February, 2013 and April, 2013 at Okhla due to the breakdown of the sampler. There were no samples collected at Mai during February, 2013 due to the same cause. For the collection of gaseous NH₃, 25 mM H₂SO₄ was used as the absorbing solution, while NO₂ was collected using the arsenite method in which sodium hydroxide and sodium arsenite mixture are used as an absorbing reagent. The details of the methods are given elsewhere (Singh et al. 2014).

3. Results and discussion

3.1. Ammonia

3.1.1. Concentrations at the urban and rural sites. The average concentrations of NH₃ were recorded as 40.7 μg m⁻³ at the Okhla site and 51.6 μg m⁻³ at Mai.

Table 4 gives descriptive statistics of the NH₃ at the Okhla and Mai sites.

At the Okhla site, NH₃ concentrations varied from 20 to 126 μg m⁻³, with an average of 40.7 ± 16.8 μg m⁻³, although the daily average concentration of NH₃ did not show a large variation during each respective month. However, relatively higher average concentrations were recorded during the months of December (50.8 μg m⁻³), January (49 μg m⁻³) and May (50 μg m⁻³). At Okhla, the average NH₃ concentration did not show much difference during the different seasons. During winter (November-January), summer (May-June) and the monsoon (July-September) season, the average NH₃ concentrations were recorded as 44.3, 42.5 and 38.9 μg m⁻³, respectively. Such a seasonal pattern of NH₃ is very similar to the pattern reported by Singh and Kulshrestha (2012) at the JNU site of Delhi city.

At Mai, the NH₃ concentration varied from 13 to 127.8, with an average of 51.6 ± 22.8 μg m⁻³. At this site NH₃ concentration had more pronounced seasonality. The average concentrations of NH₃ during winter, summer and the monsoon season were recorded as 72.0, 47.2 and 30.7 μg m⁻³, respectively. The difference in NH₃ levels at the urban and the rural site may be attributed to the difference in source types and their strength. At Okhla, the possible sources of NH₃ are solid municipal waste, tissue waste, traffic, etc, which remain constantly active throughout the year, while at Mai, the major sources of NH₃ are agricultural activities and cooking. During the winter season, fertilizer application and other agricultural activities are at full swing, which emit NH₃. Gupta et al. (2003) also observed the highest NH₃ during the winter season due to maximum vegetation
growth and maximum fertilizer use during this period at the rural area.

In general, N fertilizer application, increased livestock production, solid waste generation and high population density are the possible sources of NH₃ in India. Generally, 240 kg per ha per year DAP in basal dressing and 480 kg per ha per year urea in top dressing are applied in the field. However, the total fertilizer amount depends on the crop and season. According to the statistics, consumption of major fertilizers has increased in recent years. From 1999–2000 to 2011–2012, urea consumption increased by 44%, whereas DAP consumption increased by approximately 61%. According to data from the Fertilizer Association of India, out of the total national consumption, North India consumes around 38% of urea and 40% of DAP. However, less than 30% of the applied N fertilizer is absorbed by the crops. More than 20% is evaporated as ammonia emissions (Cai 1997). Around 20% of urea-N is lost into the atmosphere immediately after its application in the soil (Whitehead and Raistrick 1990) Factors such as soil moisture and temperature, soil texture and the form of nitrogen affect the intensity of NH₃ evaporation, controlling the efficiency of the fertilizer. Fertilizer N use efficiency can vary from one environment to another (Fennand Hossner 1985). In addition, the changing food habits of people also contribute to the increasing levels of atmospheric NH₃. However, NH₃ concentration is likely only representative of a small area as it is mainly influenced by low-level local sources, whereas for NOₓ, more remote sources also can play a role.

According to estimates, around 1175 Gg NH₃ is contributed by different kinds of fertilizer in India (Parashar et al 1998), with urea as the highest contributor. As shown in figure 2, around 94% NH₃ is contributed by urea fertilizer. The other major source of NH₃ is the livestock population, which contributes around 1433 Gg of NH₃. The livestock population is dominated by cattle, which emit a major fraction (~73%) of atmospheric NH₃ (Parashar et al 1998). It is important to mention that solid waste and human excreta, etc are also important sources of ambient NH₃ at Okhla. As mentioned earlier, the site is highly populated and has poor sanitation arrangements. In addition, according to recent reports non-agricultural sources, such as vehicles equipped with catalytic converters, also contribute NH₃ (Bari et al 2003). Such non-agricultural emissions influence NH₃ mixing ratios at urban locations and nearby roads (Sutton et al 2000, Heeb et al 2008, Ianniello et al 2010, Sharma et al 2014).

Meng et al (2011) also found traffic to be an important source of NH₃ in Beijing during the winters.

3.1.2. Day-night variations of NH₃ during different months. Figure 3 shows the day-night variations of NH₃ during
different months at Okhla and Mai. At Okhla, daytime concentrations of NH3 varied from 4.9 to 139.1 μg m⁻³, with an average of 38.7 μg m⁻³, while nighttime concentrations varied from 3.7 to 114.2, with an average of 42.6 μg m⁻³. The high concentrations during the nighttime can be attributed to atmospheric stability due to the trapping of gaseous NH3 near ground level at both sites (Burkhardt et al 1998, Cadle et al 1982, Singh et al 2001, Singh and Kulshrestha 2012).

Figure 3(b) shows the average concentrations of NH3 during the day and night times at Mai. Daytime concentrations of NH3 varied from 9.9 to 148.8 μg m⁻³, with an average of 49.8, while nighttime concentrations varied from 5.9 to 145.7, with an average of 53.4 μg m⁻³. Unlike Okhla, where NH3 concentrations were always recorded higher during the nighttime, at Mai, daytime concentrations were higher during the December, March, May and June months. Daytime high concentrations of NH3 are supported by Behera et al (2013) due to large evaporative emissions from various sources. It is possible that daytime higher NH3 concentrations are observed due to evaporation from fertilized fields since these months are typical months during which fertilizer is applied to most of the crops. In addition, agriculture residue burning during the summer season may also give rise to daytime higher concentrations of NH3 at Mai. To assess the difference between the daytime and nighttime levels of gaseous NH3, a paired t-test (two-tailed) was performed. The test showed that there was no significant diurnal difference at a 95% confidence level (P > 0.05) for both sites.

3.1.3. Comparison of concentrations of gaseous NH3 with other studies. Table 5 gives a comparison of NH3 concentrations at various sites worldwide. In general, NH3 levels at both sites are much higher than at temperate sites. This is probably due to the tropical climate. The high temperature of tropics helps in the higher evaporation of NH3 from agriculture fields, municipal waste dump yards and other sources. In addition, NH3, being an alkaline gas with an abundance of alkaline dust, also favours its gaseous existence (Singh and Kulshrestha 2012), while most temperate regions have an acidified atmosphere in which the dominance of sulphuric acid consumes gaseous NH3, forming NH4⁺ and SO4²⁻ aerosols (Kulshrestha 2013).

3.2. Nitrogen dioxide (NO2)

3.2.1. Concentrations of NO2 at Okhla and Mai. Table 6 gives descriptive statistics of NO2 at Okhla and Mai. The average concentration of NO2 at Okhla was recorded as 24.4 μg m⁻³, ranging from 5 to 63.6 μg m⁻³. At Mai, NO2 varied from 2.5 to 40.6, with an average of 18 μg m⁻³. Figure 4 shows the monthly variation of NO2 at Okhla and Mai. The seasonal mean NO2 concentrations at Okhla were recorded as 39.6, 24.5 and 10.4 μg m⁻³ during the winter, summer and monsoon season, respectively. At Mai, the mean NO2 concentrations during the winter, summer and monsoon season were recorded as 27.5, 17.2 and 4 μg m⁻³, respectively. The major source of NO2 in a rural area is biomass burning (wood, crop residue and dung cakes) during cooking and heating. (Singh et al 2014). Generally, around 621 tons of biomass are burnt by a typical village of around 200 families in North India, as reported by Singh et al (2014). Okhla, since it is an urban site, had higher NO2 than Mai. This is probably because the Okhla area is dominated by vehicular and industrial activities, which contribute significant amounts of NO2 in air. Gurjar et al (2004) observed that NOx emissions have risen significantly from 94 Gg in 1990 to 161 Gg in 2000. These results are almost in line with vehicular growth in the city. The number of vehicles in Delhi has increased from 243295 in 1994 to 6932706 in 2010 (DSHB 2011).
The possible reason for high NO\textsubscript{2} concentrations during the winter season is the formation of inversions in which pollutants are trapped in the boundary layer, whereas during the summer period, a higher mixing height allows dispersion in free tropospheric air, causing the dilution of the pollutants (Reddy \textit{et al} 2012). In addition, higher photochemical activity also helps in breaking down the pollutants into other simpler compounds. Higher concentrations of pollutants during the winter season is a typical feature in the India region. Gupta \textit{et al} (2003) have also reported higher concentrations of NO\textsubscript{2} during winters. A similar observation was reported by Kelly \textit{et al} (1989) and Barbiaux \textit{et al} (1992). However, the average concentrations observed in the present study are much higher than those reported in other studies for rural areas. Higher concentrations of NO\textsubscript{2} at Mai are probably due to NO\textsubscript{2} emissions from biomass burning during cooking and heating. In rural India, domestic cooking and heating is based on biomass burning (Singh \textit{et al} 2014). In addition, the burning of rice and wheat straw in the industrial units located at \textasciitilde13 km from the sampling site could also contribute NO\textsubscript{2} at Mai. Also, local vehicular traffic can also give rise to NO\textsubscript{2} in the atmosphere. NO\textsubscript{x} emissions into the atmosphere are dominated by the combustion of fossils fuels and biomass, which represent 75\% of total emissions, with more than 50\% of that from fossil fuels alone. NO\textsubscript{x} emissions are therefore strongly influenced by anthropogenic activities. Ammonia oxidation is a potential tropospheric source of NO\textsubscript{x}. The oxidation of ammonia in the atmosphere is initiated by the reaction with OH

\[ \text{OH} + \text{NH}_3 \rightarrow \text{NH}_2 + \text{H}_2\text{O} \]  

This reaction may play a very important role in controlling NH\textsubscript{3} concentrations, especially in tropics where OH concentrations are higher in the atmosphere (McConnell 1973). At lower NO\textsubscript{x} levels, NH\textsubscript{2} reacts with O\textsubscript{3}, forming the NH\textsubscript{2}O radical

\[ \text{NH}_2 + \text{O}_3 \rightarrow \text{NH}_2\text{O} – \text{NO} \]  

The NH\textsubscript{2}O radical reacts with oxygen and finally forms NO. Therefore, such a reaction sequence results in a source or a sink of nitrogen oxides, depending on ambient NO\textsubscript{x} concentrations (Delmas \textit{et al} 1997).

3.2.2. Day-night variation of NO\textsubscript{2} at Okhla and Mai during different months. Figures 5(a) and (b) show the variation of NO\textsubscript{2} at the Okhla and Mai sites during different months. The daytime concentrations of NO\textsubscript{2} varied from 5.0 to 72.6, with an average of 25.9 \(\mu\text{g/m}^3\), whereas nighttime concentrations of NO\textsubscript{2} varied from 5.0 to 66.2, with an average of 22.8 \(\mu\text{g/m}^3\). At Mai, daytime concentrations varied from 2.3 to 56.9, with an average of 19.8 \(\mu\text{g/m}^3\), while nighttime concentrations varied from 2.6 to 36.9, with an average of 17.7 \(\mu\text{g/m}^3\). Daytime higher concentrations of NO\textsubscript{2} at both sites are quite obvious due to various sources, such as industries, traffic, etc, which are more active during the daytime. A paired t-test (two-tailed) result showed the significant diurnal variation at a 95\% confidence level (\(P<0.05\)). In a study reported by NEERI (2008) at Delhi, during the summer season, the daytime NO\textsubscript{2} concentration
was recorded as 40 μg m⁻³, while at midnight, the NO₂ concentration was 30 μg m⁻³. During the winter season, the daytime concentration of NO₂ was recorded at about 60 μg m⁻³, which was higher than was recorded in summer and in the post-monsoon season. Contrary to the winter season, the NO₂ level increased gradually after sunset to about 80 μg m⁻³ by midnight. It is worth mentioning that unlike NH₃ levels, which are affected by local sources, NO₂ levels can be affected by more remote sources.

4. Conclusion

The present study reports the abundance of gaseous inorganic reactive nitrogen species (NH₃ and NO₂) at urban and rural sites in the Indo-Gangetic plains in India. The results showed significant differences in the NH₃ levels between the rural and urban sites due to different types of sources and their strength. High concentrations of gaseous NH₃ measured at the rural site can be attributed to fertilizers and biomass burning, whereas municipal waste, human excreta, vehicular traffic and tissue waste were found responsible for NH₃ emissions at the urban site. The seasonal variation of NH₃ at the rural site (Mai) was more significant, with NH₃ concentrations at 72 μg m⁻³ during the winter, 47.2 μg m⁻³ during the summer and 30.7 μg m⁻³ during the monsoon season due to agricultural patterns and the amount of fertilizer applied during different seasons. The average NH₃ levels during different seasons at Okhla were not very different, indicating that at the urban site, the sources of NH₃ are almost constant throughout the year. At Okhla, NH₃ concentrations were recorded as 44.2 μg m⁻³ during the winter, 42.5 μg m⁻³ during the summer and 38.9 μg m⁻³ during the monsoon season. Generally, at both sites, nighttime NH₃ was always higher than daytime NH₃ due to atmospheric conditions.

The average concentrations of NO₂ were 24.4 μg m⁻³ and 18.8 μg m⁻³ at Okhla and Mai, respectively. Seasonal average NO₂ concentrations at Okhla were recorded as 39.6, 24.5 and 10.4 μg m⁻³ during the winter, summer and monsoon seasons, respectively. The average concentrations of NO₂ were recorded as 27.5, 17.2 and 4 μg m⁻³ during the winter, summer and monsoon seasons, respectively, at Mai. The lower NO₂ concentrations during the monsoon season at both sites can be due to the washout effect of Monsoon rains. Generally, daytime NO₂ concentrations were higher than nighttime NH₃ at both sites, as the NO₂ sources are very active during the daytime. The study reveals that due to biomass burning, the rural site (Mai) showed high levels of NO₂. Such high levels of NO₂ are not generally expected at a rural site. The study reveals that both NH₃ and NO₂ are contributed by biomass burning at the rural site, suggesting that biomass burning emissions might have severe health effects in the long run, especially on females and children, who are most exposed in side houses where burning takes place. Therefore, there is a need to improve our understanding about Nr emissions and their chemistry at rural sites in order to prepare reliable estimates of Nr. This can be achieved by strengthening the monitoring of and modeling efforts about Nr in India. This will further help in understanding the potential health and environmental risks due to Nr.

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