

Spatio-Temporal Variation of Atmospheric Gaseous and Particulate Reactive Nitrogen Over Northern India

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Abstract

The present study reports spatio-temporal distribution pattern of major gaseous (NH_3 and NO_2) and particulate water soluble total nitrogen (pWSTN) in the ambient air to explore the seasonal variation, major interactions and dominating sources. Considering the major hotspot of atmospheric reactive nitrogen (N) emission, three sites in Indo-Gangetic plain (IGP) were selected based on different local source parameters. Results have shown that gas phase reactive N contribute upto 90% of total analyzed reactive N, where NH_3 imparted highest at all the three sites. Prayagraj, a fast growing urban site, has shown highest concentrations of NH_3 ($72.0 \mu\text{g m}^{-3}$), followed by Madhupur rural site ($57.7 \mu\text{g m}^{-3}$) and Delhi, an urban megacity site ($35.8 \mu\text{g m}^{-3}$). As compared to previous studies conducted at different sites of IGP, NH_3 concentrations were reported to be the highest at the former two sites. However, unlike NH_3 , NO_2 levels were recorded lower at Madhupur ($3.1 \mu\text{g m}^{-3}$) and Prayagraj ($9.4 \mu\text{g m}^{-3}$) sites as compared to Delhi ($13.4 \mu\text{g m}^{-3}$). Similarly, pWSTN concentrations were in the order of Madhupur ($6.6 \mu\text{g m}^{-3}$) < Prayagraj ($10.0 \mu\text{g m}^{-3}$) < Delhi ($10.1 \mu\text{g m}^{-3}$). A strong correlation of NO_2 with pWSTN at urban sites has shown the crucial role of NO_2 in the formation of nitrogenous aerosols. Significant spatial variation can be attributed to varying local emission sources ranging from microbial emission from improper sewage treatment and open waste dumping at Prayagraj, agricultural activities at Madhupur and vehicular exhausts at Delhi site.



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Introduction


When the neo-Malthusians were busy in predicting the impending food crisis across the world due to burgeoning levels of population, little did they conceive of a situation where the food production would outstrip the rate of population growth. This

has been made possible in large measure due to the increased production of the variegated nitrogenous inputs that have served to amplify the levels of food production.¹ A direct consequence of this has been the intensification in nitrogen (N) cycles across the world which, in turn, has

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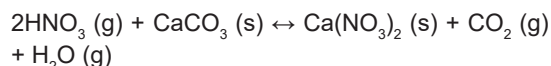
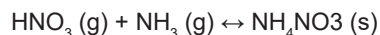
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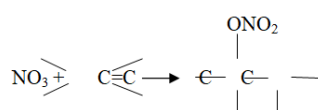
spawned a host of environmental problems ranging from deterioration in air quality levels to aquatic scares such as eutrophication and acidification.^{2,3} Nitrogenous components are one of the key players of atmospheric multi-phase chemistry, which significantly alters biogeochemical N cycle.⁴ Studies have shown rising concern over multi-fold increase in the emission of reactive N gases, mainly NH₃ and NO_x, which undergo multiple transformations due to various atmospheric processing. Most of the primary emissions of oxidized component of N (NO_x) are in the form of nitric oxide (NO), which soon gets oxidized into nitrogen dioxide (NO₂) through gas phase photochemistry. Photochemical oxidation reactions dominate the atmospheric chemistry of N compounds. Major atmospheric oxidants include OH, O₃, NO₃, HO₂ and Cl, which play a crucial role in the gas to particle conversion of atmospheric N. The magnitude and abundance of reactive particulate N are dependent on the number of conditions such as availability of precursor gases such as NH₃, NO₂, VOCs, ozone, etc., light availability, temperature and relative humidity (RH).

Due to the polar nature, gaseous N compounds get dissolved into the aqueous phase present in the atmosphere in the form of cloud, fog or water droplets.^{5,6} However, unlike NH₃ which is highly soluble gas, NO₂ is not readily soluble in water and its particle phase conversion depends on the kinetics of the reactants. If the reactant concentration gets lowered, NO_x oxidation from gas to particle get slowdown dramatically due to its lower range of Henry's law constant.⁷ It was found that insoluble gases have values around 10⁻³ mol L⁻¹ atm⁻¹ and highly soluble is in the order of 10⁵ mol L⁻¹ atm⁻¹. The rate of aqueous phase oxidation of NO_x drops off steeply with the concentration of the gases involved, even in the highly polluted areas and not significantly contributing to the aqueous phase acidity.⁸ In short, NO_x uptake by water droplets in the atmosphere is not believed to contribute to particulate N formation rather its photochemical oxidation into gaseous HNO₃ become the major source of particulate nitrate in the atmosphere.⁹ NH₃ as a major gaseous base in the atmosphere effectively neutralizes NO_x components and undergoes to both wet and dry deposition. Since neutralization is an equilibrium reaction, it does not necessarily imply to the permanent removal from

the atmosphere and remain in gas-particle-gas equilibrium, thus it degrades air quality and visibility.



Nitrogen oxides also readily react with atmospheric organic compounds, primarily VOCs and get reduced. VOCs/NO_x ratio strongly affects the gas particle partitioning of atmospheric reactive N and led to the formation of organic nitrates.¹⁰



Organic nitrogenous aerosols are mostly produced by the photochemical oxidation of VOCs by NO_x and NO_y species. Final products of such reactions include the formation of peroxy acetyl nitrates (PANs), alkyl nitrates (RONO₂), amines (RNH₂), hydrazines (RNHNNH₂), etc. However, the rate of formation and decomposition of such products highly dependent on the dynamics of NO and NO₂. Aliphatic amines are also emitted from a variety of sources, including sewage treatment, waste dumping, industrial activities, etc., along with NH₃.¹¹ However, most of the other organic N aerosols are product of VOCs- NO_x photochemical interactions.

Organic nitrogen (ON), as one of the important sub-component, is known to play a crucial role in the atmospheric chemistry and global N cycle, which have been significantly altered by human activities.¹² Due to the slower scavenging process of organic N as compared to inorganic N compounds (NH₄⁺ and NO₃⁻), they tend to be transported through long distances and hence are the key agents in the global N transport system.¹³⁻¹⁵ Through dry and wet deposition, inputs of total N plays a crucial role in soil acidification, nutrient enrichment, eutrophication and tropospheric ozone formation on land and aquatic environments. Over the urban areas nitrogenous compounds also help in the haze and smog formation, especially during winters, causing the visibility reduction and severe health implications.¹⁶ However, observations of total atmospheric N through dry and wet depositions, published in the last few years have presented the relative significance

of ON in the atmosphere and thus its importance has been globally recognized.¹² Therefore, it can be inferred that the present estimate of the atmospheric reactive N budgets underestimates the total soluble reactive N in the atmosphere by virtue of their singular focus on the inorganic N viz. NH_4^+ , NO_3^- and NO_2^- .¹⁷ This requires a comprehensive study of reactive N, inclusive of both inorganic as well as its organic forms, and spatial and temporal variation in the scavenging process to enhance the scientific understanding of this aspect of the N cycle. Thus, the present study focuses one year long observation of NH_3 and NO_2 along with particulate water soluble total nitrogen (pWSTN) over the densely populated IGP region of the northern India.

Methodology

Sampling Sites

Being a major hotspot of air pollutants, Indo-Gangetic plain (IGP) is known for their very high population density and stationary sources of N emission in the atmosphere, which explains its selection as the spatial focus of this study.¹⁸ IGP region can be categorized under humid subtropical climate. Within IGP three different sites were selected based on the differential local sources and land use pattern (Figure 1). Prayagraj ($25^\circ 54' \text{N}$, $81^\circ 85' \text{E}$) as an urban site, formerly known as Allahabad, is located in

the southeastern part of Uttar Pradesh and central part of IGP region. Due to continuous development of its suburbs, in 2011, it was ranked the world's 130th fastest-growing city. Local brick kiln units, unregulated solid waste burning, vehicular exhausts from diesel powered and old vehicles are the major emission sources. Madhupur village ($25^\circ 54' \text{N}$, $82^\circ 00' \text{E}$) in Pratapgarh district, which is adjacent to the Prayagraj district, was selected as rural site. Madhupur site located is 70 km away in the north eastern side of Prayagraj. The city comes under one of the most backward districts of India. Primarily, as an agrarian district, Pratapgarh has risen in ranks as the top producer of Aonla or Amla fruit, which is used as herbal medicine. The village is poorly developed as hardly any roads pass across the area, having a very low vehicle density and high vegetation cover. Biomass burning, soil re-suspension and the agricultural activities are the main source of the pollution in the area. Delhi, representing megacity characteristics, is located at the upwind side of the IGP. Thus, it is highly affected by the long range transportation of pollutants. Vehicular emission, soil re-suspension, construction activities, bioaerosols and roadside dust are the major local sources. The sampling was conducted approximately at 15 meters above the ground, on the rooftop of the residential buildings at each site.

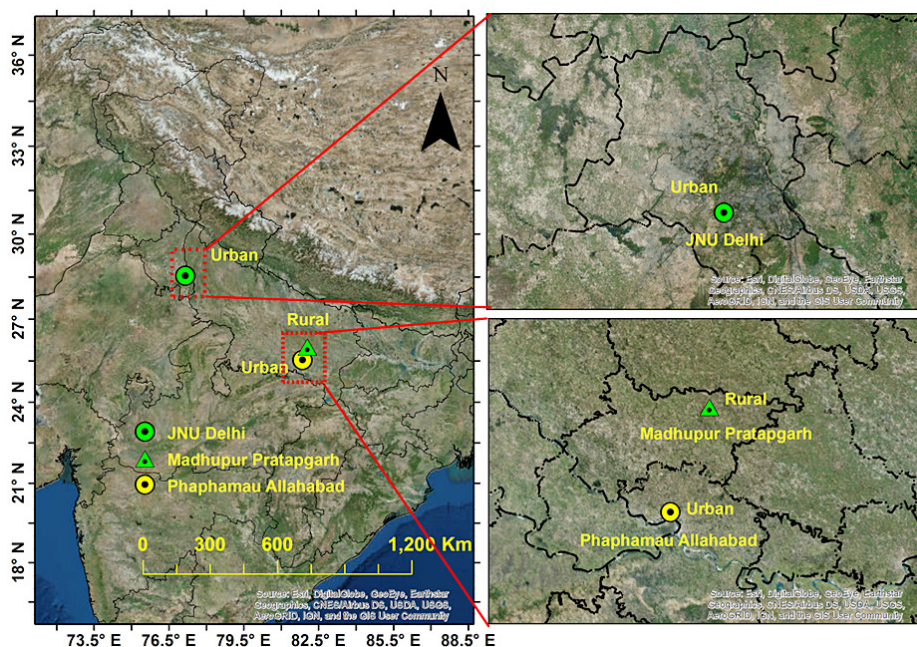


Fig.1: Schematic of three sampling sites in IGP selected for the study

Sampling Procedure

Eight hourly sampling (daytime) was conducted on every third day at the sampling sites for a year, starting from 1st December, 2016 to 30th November, 2017. The collection of gaseous (NH_3 and NO_2) and fine particulates sampling were conducted using a low volume sampling (LVS) unit, operated at a flow rate of 30 L min^{-1} (and regulated separately for gases at a flow rate of 1 L min^{-1}). The unit consisted a low volume vacuum pump which used to suck the ambient air through an open front at the another end. The particulates were filtered and collected on a 47mm (dia) Pallflex Tissuequartz 2500 QAT –UP microfiber filters using 47 mm filter holder at the open front side. The filtered air directly drawn to the impingers carrying absorbing solution for NH_3 and NO_2 . NH_3 samples were collected in a 20 ml of 2.5 mM H_2SO_4 absorbing solution and NO_2 samples were collected using 20 ml absorbing solution of sodium hydroxide and sodium arsenite mixture. The collected gaseous samples were transferred in polypropylene bottles and analyzed colorimetrically where the collection efficiency was observed to be 85% for NH_3 and 68% for NO_2 . The detailed sampling protocol along with the collection efficiency has been elaborated by Kulshrestha and coworkers.^{19,20} Both gaseous and particulate samples were stored in cool (-4°C) and dark place until the analysis. One field blank from each month was also analyzed in order to avoid over/under estimation during the sampling and analysis. A total of 102, 65 and 107 samples were collected from the Prayagraj, Madhupur (less number of filters due to the shortage of power supply in the village) and Delhi sites, respectively, for one year covering all the four seasons viz. Winter (Dec-Feb), Summer (Mar-Jun), Monsoon (Jul-Sep) and Post-Monsoon (Oct-Nov).

Analysis

Analysis of nitrogenous gaseous samples of NH_3 and NO_2 was performed using colorimetric method on UV–visible spectrophotometer (Perkin Elmer, USA). Gaseous NH_3 was analyzed using indo-phenol blue method where $(\text{NH}_4)_2\text{SO}_4$ used as a standard for the calibration. Calibration curve was plotted using serially diluted solution of blank, 0.5ppm, 1 ppm, 2.5 ppm, 5 ppm, 10 ppm standard with a regression coefficient (r^2) value of 0.998 at 630nm wavelength. The similar calibration curve was also plotted for

gaseous NO_2 samples at 540nm wavelength using Jacob and Hochheiser method. For NO_2 analysis, standards were prepared using blank, 0.25ppm, 0.5 ppm, 1 ppm and 2 ppm solution of NaNO_2 .

TOC/TN analyzer (Shimadzu model-TOC-LCPH E200 ROHS) was used for the analysis of WSTN. About one fourth of each filter ($\sim 3.14 \text{ cm}^2$ area) was soaked in 25ml MilliQ water for nearly 6–8 h, which was followed by ultrasonic treatment to disintegrate the soluble species from the filters. Then it was filtered through a Nylon fiber syringe filter (diameter: 25 mm) and transferred to a new vial for the analysis. The analytical procedure starts with injecting the sample into the furnace, which is maintained at a temperature of 720°C for TN analysis and followed by its oxidation using platinum catalyst. The evolved nitrogen monoxide (NO) was measured through oxidative combustion-chemiluminescence method. Potassium nitrate (KNO_3) standards (1, 10 and 50ppm) were used to calibrate WSTN in the samples. In order to get a coefficient of variation below 2% each analysis of WSTN was repeated two to three times.

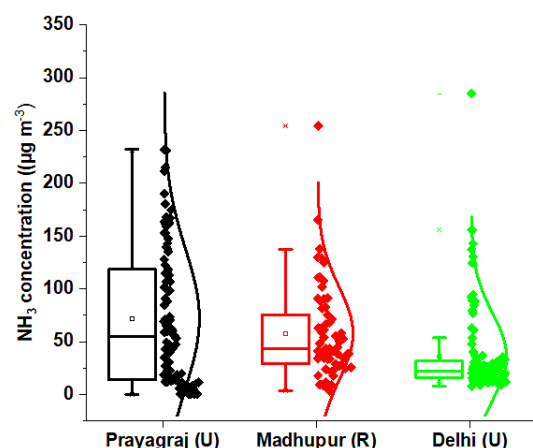


Fig.2: Annual distribution of NH_3 concentration at the three sites

(box plots are showing 25th and 75th percentile with the horizontal line inside representing the median value and the small square point stating the mean value. The vertically clustered dots are showing the concentrations of each sample along with their distribution curve corresponding to y-axis) (U =urban, R = rural).

Table 1: Reported concentrations of gaseous Nitrogen species at different sites

Site	Duration	NH ₃ (µg m ⁻³)	NO ₂ (µg m ⁻³)	References
Manhattan, US	Winter	3.7	-	27
Lahore, Pakistan	Winter	50.1	19.6	28
Singapore	Annual	2.5	1.7	29
Barcelona, Spain	Annual	6.9	-	30
Beijing, China	Annual	21.5	54.3	31
China	Summer	39.2	32.5	32
Pune (Urban)	Summer	2.0	1.9	33
Raichur (Nonurban)	Winter	0.9	3.8	33
Sarni (Industrial)	Summer	1.2	3.8	33
Delhi (Urban)	Annual	35.4	-	34
Rampur, UP (Rural)	Annual	6.7	7.3	35
Agra (Suburban)	Annual	10.5	5.4	36
Kanpur (urban)	Annual	17.1	21.3	37
Delhi (Urban)	Annual	29.4	-	19
Mai, UP (Rural)	Annual	50.5	24.4	21
Delhi (Industrial)	Annual	40.7	18.8	21
Delhi (Urban)	Annual	21.0	17.1	26
Delhi (Industrial)	Annual	-	26.0	38
Delhi (Urban)	Annual	19.6	19.7	39
Delhi (Urban)	Winter	35.4	15.8	20
Rohtak (Urban background)	Winter	14.6	6.1	20
Faridabad (Industrial)	Winter	39.2	24.9	20
Prayagraj, UP (Urban)	Annual	72.0	9.4	Present Study
Madhupur, UP (Rural)	Annual	57.7	3.1	Present Study
Delhi (Urban)	Annual	35.8	13.4	Present Study

Results and Discussion

Spatio-Temporal Variation of Ambient NH₃

Large scale variation in NH₃ concentrations was recorded at all the three sampling sites, as shown in Figure 2. NH₃ concentration at Prayagraj site was found to be the highest ranging from 0.19 to 232.0 µg m⁻³ with an annual mean value of 72.0±6.5µg m⁻³. It was followed by Madhupur site where NH₃ concentration ranged from 3.5 to 245.4 µg m⁻³ with an annual mean of 57.7 µg m⁻³. Its concentration was recorded lowest at the Delhi site ranging from 7.8 to 285 µg m⁻³ with an annual mean of 35.8 µg m⁻³. The concentrations of NH₃ at Prayagraj and Madhupur sites is quite high since none of the previous studies have reported such a high value as shown in Table 1. However, in an annual observation conducted in 2013 by Singh and Kulshrestha (2014), the annual mean concentration was reported to be 50.5 µg m⁻³ at a rural site within IGP which stands closest to the present reported value of

the Madhupur rural site. The agriculture activities, including both NH₃ based fertilizers application and animal husbandry being the largest source of NH₃ emission, makes the abundance of NH₃ in rural areas quite distinct.²² However, despite having urban character, Prayagraj site has shown exceptionally high mean values, which can be attributed to the abundance of mixed sources such as high vehicular density, biomass burning, agriculture activities, waste dumping sites within the vicinity of sampling area, large scale local cattle rearing, etc. Additionally, microbial emission might also be accounted for NH₃ emission due to improper sewer drainage and subsequent pollution of river Ganges and Yamuna, flowing across the city.²² Also by virtue of being a growing urban centre, the city of Prayagraj has a very high population density, which in a way leads to a greater generation of human excreta thereby causing greater amounts of NH₃ emission in the region.^{23,24} Such kind of mixed sources was not

observed around the sampling site of Delhi, where the dominant sources are vehicular emissions, industrial activity and other biogenic emissions. Wang *et al.* have found a positive relationship between NH_3 concentrations and vehicular density and reported that vehicular density contributes up to 25% of total NH_3 emission in urban areas.²⁵ A study conducted in 2010-11 at the same site in Delhi (JNU campus) have also reported an annual mean of $29.4 \mu\text{gm}^{-3}$.¹⁹ Sharma *et al.* (2014) have also reported a mean concentration of NH_3 as low as $21.0 \mu\text{gm}^{-3}$ at an urban residential site of Delhi.²⁶

Seasonal contribution in the total annual NH_3 emission at Prayagraj site was in the order of winter (41%) \geq post-monsoon (40%) $>$ monsoon (11%) $>$ summer (8%). Contribution at Madhupur village was in the order of Post-monsoon (43%) $>$ monsoon (24%) $>$ winter (21%) $>$ summer (12%). At the Delhi site, the observed order is Post-monsoon (49%) $>$ winter (24%) $>$ monsoon (15%) $>$ summer (12%). Despite having higher volatilization rates in hot summers, NH_3 concentrations were recorded lowest in the summer months as compared to other seasons at all three sites. Previous studies carried out over IGP also reported higher ambient NH_3 levels in winters as compared to summers.^{21,39} This anomaly can be explained by the higher mixing height and wind speed, which allows diffusion and dispersion of the atmospheric components, leading to their lower ambient levels. However, in the monsoon season, additional NH_3 emission might be contributed by decay and decomposition of organic matter under wet conditions.

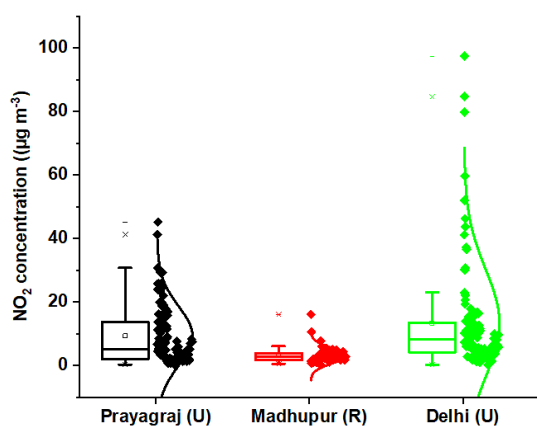


Fig.3: Annual distribution of NO_2 at all the three sites (U =urban, R = rural)

Spatio-Temporal Variation of NO_2

Variation in NO_2 concentrations at all the three sites has been shown in Figure 3. NO_2 levels were recorded the highest in Delhi, where it varied from 0.2 to $94.5 \mu\text{g m}^{-3}$ with an annual mean of $13.4 \mu\text{g m}^{-3}$. It was followed closely by Prayagraj with values ranging from 0.4 to $45.2 \mu\text{g m}^{-3}$ with an annual mean of $9.4 \mu\text{g m}^{-3}$. The Madhupur site predictably, owing to its rural character, reported lowest concentrations of NO_2 with the least variation ranging from 0.6 to $16.1 \mu\text{g m}^{-3}$ and an annual mean of $3.1 \mu\text{g m}^{-3}$.

NO_2 concentrations were recorded low at all the three sampling sites and much below the prescribed limits of National Ambient Air Quality Standards (NAAQS) by CPCB, which is $80 \mu\text{g m}^{-3}$ annual for residential areas. An annual mean of $26 \mu\text{g m}^{-3}$ was also reported previously at a site near the industrial area in Delhi.³⁸ Light-duty vehicles are the primary sources of NO_2 in urban areas. Being the megacity and national capital region (NCR) the vehicular density is increasing manifold in the Delhi, which probably lead to the higher concentration of NO_2 in Delhi as compared to Prayagraj urban site.^{20,21,39} However, as compared to previous studies carried out in Delhi, as shown in Table 1, the present study has shown the lowest value, which might be due to the relatively less number of vehicle movement in the vicinity of the JNU sampling site. Prayagraj site was dominated by both light-duty and heavy-duty vehicles contributing to the NO_2 emission. In contrast, rural areas are primarily characterized by lower vehicular movement due to poor road construction and infrastructure in the villages. No major roads were constructed around the 5 km^2 area of the sampling site, except a narrow one-lane road, which connects the village with the city. The biomass burning sources, primarily, can be attributed to the abundance of NO_2 in the rural site.

At these sites, the sources of NO_2 emissions are primarily vehicular exhausts and remains more or less constant throughout the year. In such conditions, changing meteorological conditions could be the major factor affecting their ambient levels. Seasonal contribution in the total annual NO_2 emission at Prayagraj site was in the order of winter (47%) \geq post-monsoon (32%) $>$ summer (13%) $>$ monsoon (8%) and at Delhi was in the order of Post-monsoon (58%) $>$ winter (24%) $>$ summer (12%) $>$ monsoon (6%). Higher contribution in winter

and post-monsoon season at both these urban locations can be corroborated with NH_3 abundance pattern owing to the calm weather conditions and the lower mixing height and vice-versa for summer lower concentrations.^{35,40} Exceptionally, higher values in post-monsoon season at Delhi can also be attributed to the crop residue burning incidents in the northwestern region of IGP and its transportation to the downwind regions, since none of the other local activity changes were observed.⁴¹ Seasonal contribution at Madhupur village was totally different from the urban locations. The pattern was in the order of Summer (41%) > monsoon (24%) > post-monsoon (23%) > winter (12%), suggesting the local factors which might be impacting the distribution pattern. One of the major causes of the higher NO_2 emission in summers is the use of diesel-powered generators in the villages, particularly due to the shortage of electricity supply and relatively larger social gatherings for local ceremonies in summers. This ultimately leads to the frequent use of diesel generators and causes a spike in NO_2 values during the summer. However, the lowest concentration in winter season could be attributed to higher rates of gas to particle conversion in humid conditions, which will be further investigated by its relation with particulate WSTN.

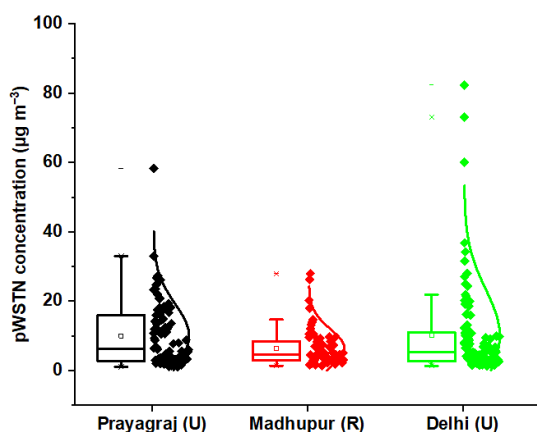


Fig.4: Annual distribution of pWSTN at the selected sites (U = urban, R = rural)

Spatio-Temporal Variation of Particulate Water-Soluble Total Nitrogen (Pwstn)

Studies have reported that Asian aerosols contribute up to 40% of nitrogenous compounds, which exists in water-soluble phase.^{42,43} Due to their polar characteristics, nitrogenous compounds are

highly reactive in nature and also dominate the atmospheric chemistry and aerosol formation. Thus, we investigated the annual distribution of water soluble total nitrogen in the particle phase (pWSTN) in ambient air at all the selected sites as shown in Figure 4.

As the figure clearly shows, the large scale variation was observed at both the urban sampling sites as compared to the rural site. The pWSTN concentration in fine aerosols found highest at the Delhi site, ranging from 1.3 to 82.4 $\mu\text{g m}^{-3}$ with an annual mean of 10.1 $\mu\text{g m}^{-3}$. It was closely followed by Prayagraj site, where the values ranged from 1.1 to 58.2 $\mu\text{g m}^{-3}$ with an annual mean of 10.0 $\mu\text{g m}^{-3}$. Concentration varied within smaller scale at the Madhupur, ranging from 1.3 to 27.9 $\mu\text{g m}^{-3}$ with the lowest annual mean value of 6.4 $\mu\text{g m}^{-3}$. The pWSTN contribution to the total particulates was found highest at Delhi, about 7% annually. It is followed by Prayagraj, where pWSTN contributed annually about 6%. The lowest contribution was observed at the Madhupur rural site, with an annual mean of 5%. Reports have shown that inorganic N aerosols contribute upto 90% of total atmospheric N in the polluted urban atmosphere. Some of the studies over South Asia have attempted to characterize the total atmospheric N deposition.^{42,44-49} A strong correlation between WSON and NH_4^+ in fine mode marine aerosols over the western North Pacific and East China Sea were observed, thereby, suggesting their contribution from anthropogenic sources.⁴⁴ The results of total N at 32 monitoring sites in China have shown that ON contributes, significantly, from 7% to 67% of WSTN.⁴⁶ Similar results were also observed by Srinivas *et al.* in the study of $\text{PM}_{2.5}$ and PM_{10} over Bay of Bengal.⁴⁷ Significant concentrations of gaseous and particulate nitrogen species were also reported over north India, suggesting the IGP as a major hotspot of N emission.^{21,50-52} NH_4^+ and NO_3^- contribute about 91% of total N at a coastal site in South India, despite the least influence of local anthropogenic sources.⁴³ This is primarily attributed to the transportation of their precursor gases from distant sources. NH_3 and NO_2 are the primary precursors of these aerosols and their gas to particle conversion highly influence the distribution and abundance pattern of nitrogenous aerosols.

Seasonal contribution of the annual pWSTN concentration at Prayagraj site was in the order

of winter (49%) ≥ post-monsoon (25%) > summer (17%) > monsoon (9%) and at Delhi was in the order of Post-monsoon (56%) > winter (23%) > summer (12%) > monsoon (9%). Higher moisture content in winters provides for heterogeneous chemical reactions in the troposphere leading to the higher rate of particle conversion. The fog droplets processing significantly increase the particulate N compounds during winters over IGP.⁵³ Since most of the particulate N comes from agriculture activities, harvesting period in November and its coincidence with lower mixing height abruptly increase the aerosol ambient concentrations.⁵⁴ Same seasonal pattern at both the urban sites was also recorded for NO₂. This also suggests that NO₂ plays important role in particle formation at both the urban sites. However, the seasonal distribution was found insignificant at the Madhupur rural site and it was in the order of summer (28%) > post-monsoon (27%) > winter (26%) > monsoon (19%). Indiscriminately, lowest value of pWSTN was recorded in monsoon season at all the three sites owing to the washout effect

in monsoon season. Polar as well as the reactive nature of nitrogenous compounds lead to the wet removal of the aerosols and ultimately lowering of their ambient concentrations.⁵⁵ Unlike urban sites, rural site has shown highest concentration of pWSTN in summer months. The formation of WSON significantly increases ambient levels of pWSTN in the absence of rain events and contribute highest during summers owing to the greater photochemical oxidation and dust storms/ soil re-suspension influence.⁵⁶

Phase Partitioning of Gaseous and Particulate N along with their Relation with Meteorological Parameters

Scatter matrix and frequency distribution plot of gaseous and particulate N was used to analyze the phase partitioning of reactive N. There interlinkages and correlation with meteorological factors at the Prayagraj, Madhupur and Delhi sites have been shown in the Figure 5, 6 and 7, respectively.

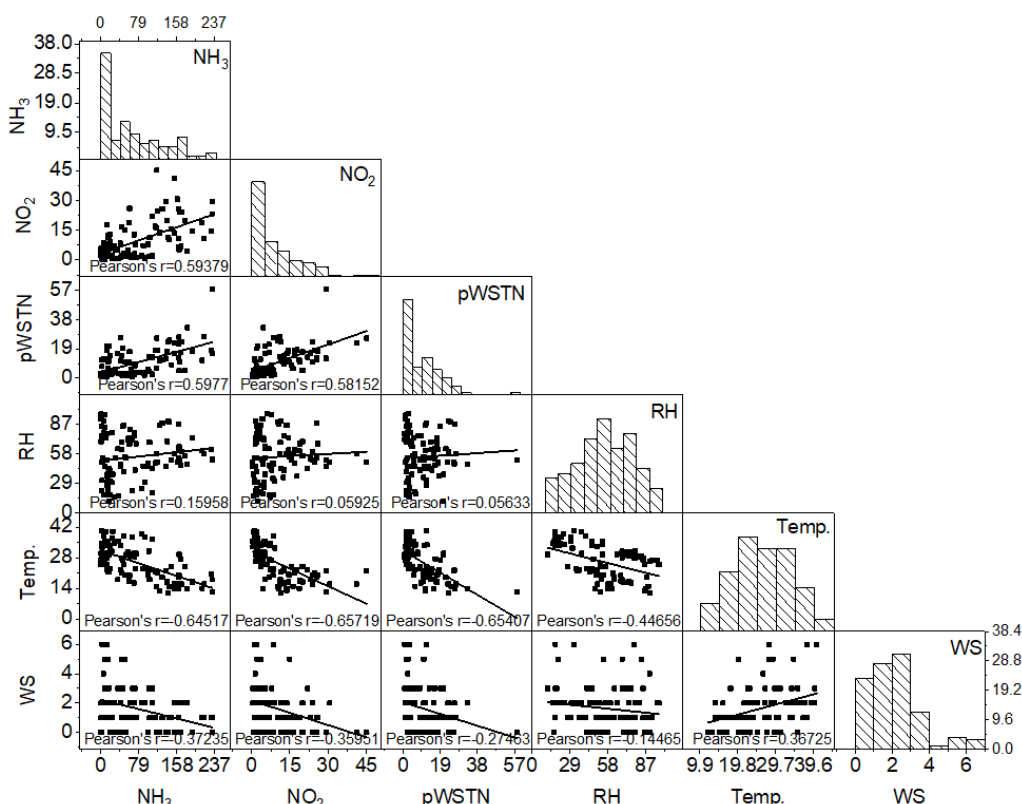


Fig.5: Frequency distribution and regression analysis of gaseous and particulate N with meteorological parameters at the Prayagraj site

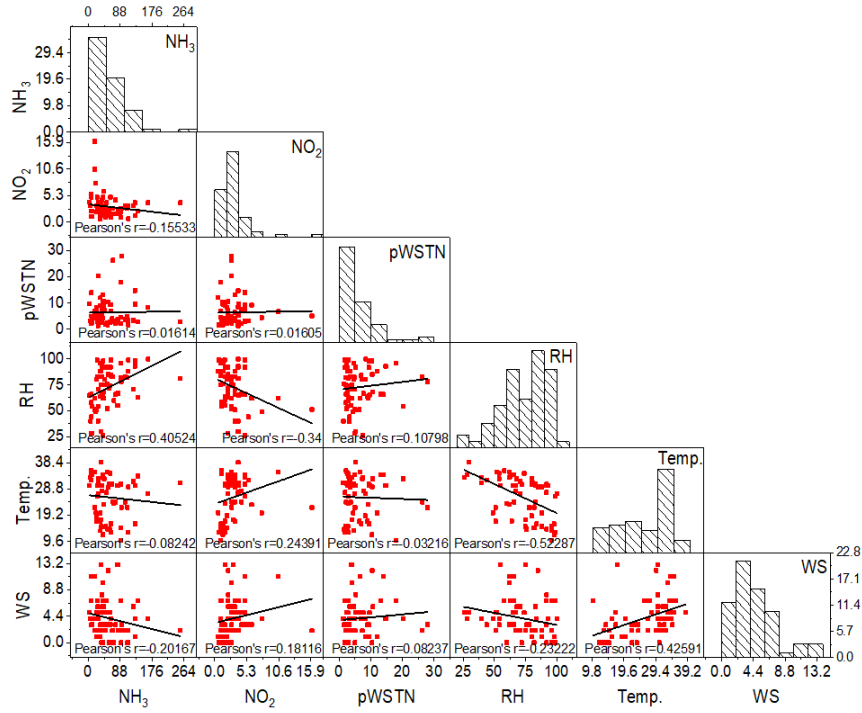


Fig.6: Frequency distribution and regression analysis of gaseous and particulate N with meteorological parameters at the Madhupur site

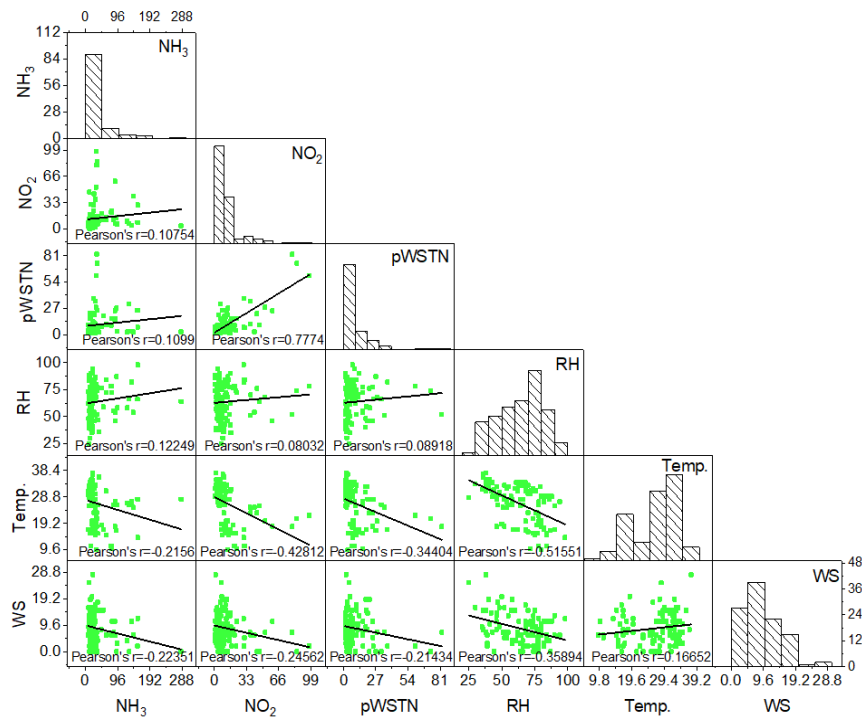
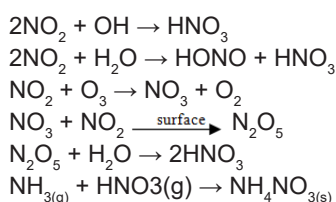


Fig.7: Frequency distribution and regression analysis of gaseous and particulate N with meteorological parameters at the Delhi site

Prayagraj

A good correlation was observed between N gases viz. NH_3 and NO_2 ($r = 0.59$), showing their common emission from biomass and fossil fuel burning in the urban areas. Alongside pWSTN has showed stronger correlation with NH_3 ($r = 0.60$) as compared to NO_2 ($r = 0.58$), indicating the higher contribution of NH_3 in the phase partitioning as compared to NO_2 . However, very close correlation (r) values of both the primary gases with pWSTN concentration, showing their simultaneous conversion into particle phase preferentially NH_4NO_3 .



This phase conversion is highly dependent on the precursor gases concentration and impact of meteorological parameters such as relative humidity (RH) and temperature. The frequency distribution of RH suggests that the value was less than a deliquescence point (<75%) for more than 75% of the sampling period. This indicates that NH_3 mostly remained in the gaseous phase for most of the days, which is substantiated by its positive correlation with RH. Unlike the previous studies, NH_3 has shown a negative correlation with temperature and wind speed, which is indicating that higher temperature and wind speed inhibiting the gaseous NH_3 concentrations. A similar case was also observed for NO_2 and pWSTN. This can be explained by the positive correlation of temperature and wind speed which might be allowing greater dispersion of the atmospheric pollutants and leading to their lower concentrations.

Madhupur

At the rural site, as shown in Figure 6, negative correlation between NH_3 and NO_2 ($r = -0.16$) was observed, showing their different emission sources. No correlation was found between gaseous and particulate nitrogen, indicating the gas phase oxidation of NH_3 and NO_2 . This is confirmed by the positive correlation of NH_3 and RH ($r = -0.41$), indicating dominance of NH_3 even at higher RH values. This anomaly can also be explained by their gas phase oxidation and least contribution

in particulate N formation. In contrast, NO_2 was negatively correlated with the RH and positively correlated with temperature, indicating towards their frequent oxidation at higher RH values and cooler atmosphere. However, insignificant correlation of pWSTN with RH and temperature is showing its independent formation with least impact of meteorological parameters at the rural site.

Delhi

As shown in Figure 7, least but positive correlation between NH_3 and NO_2 ($r = 0.11$) was observed at this urban site, which shows that mostly their sources remain different throughout the year. A strong correlation was found between NO_2 and pWSTN ($r = 0.78$), indicating towards the oxidation of NO_2 playing key role in the particulate formation during the sampling period over urban site. Similar to the previous sites, gaseous and particulate N abundance was found independent of RH. However, their negative correlation with temperature and wind speed, showing greater dispersion of atmospheric components in hot and windy weather conditions at Delhi site also.

Relative Contribution of Atmospheric Gaseous and Particulate N

Figure 8 shows the relative contribution of NH_3 , NO_2 and particulate N in the ambient air at the selected sampling sites. Gas phase reactive N contributed upto 90% of total atmospheric N. NH_3 was found to contribute maximum and more than 60%, annually, of total atmospheric N at all the three sites with highest contribution at the rural site Madhupur (86%) followed by urban sites, Prayagraj (79%) and Delhi (60%). Agriculture emission, cattle rearing and biomass burning are the primary sources of NH_3 at the rural site and microbial emission, human excreta and combustion generated emissions are primary sources at the urban sites. In contrast, NO_2 was found to contribute higher at both the urban sites as compared to rural site, with highest percentage in Delhi (23%) followed by Prayagraj (10%) and lowest at Madhupur (5%). Vehicular emissions (both gasoline and diesel) are the primary source of NO_2 in the urban areas. Furthermore, the order of pWSTN contribution was observed higher at Delhi (17%) and Prayagraj (11%) and lower at Madhupur (10%) which can be corroborated with NO_2 distribution pattern and its strong correlation with particulate N abundance at the urban sites.⁵⁷

Seasonal meteorology has also shown its impact in the relative abundance of particulate N in ambient air at all the three sites. While, geographically, closely located sites, Prayagraj and Madhupur, have shown a similar seasonal abundance pattern, slightly a

different pattern was observed at Delhi, which can be attributed to the influence of long range transport of pollutants from upwind regions, which could be additionally affecting the relative abundance of atmospheric reactive N at the Delhi site.

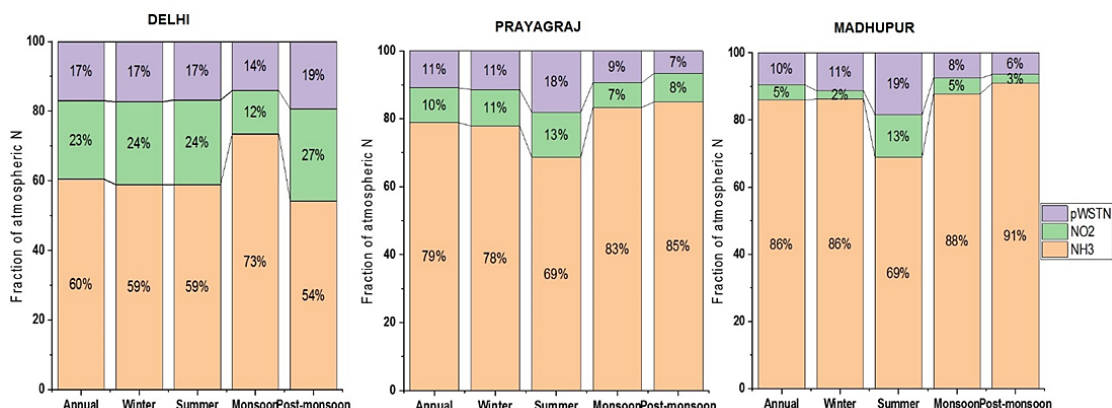


Fig. 8: Relative contribution of atmospheric reactive N in ambient air at three sites

Conclusion

Increasing emissions of atmospheric reactive N are considered as an important player in altering the N cycle. In this context, the present study conducted over highly populated IGP region has shown alarming levels of NH_3 with very high concentrations over the fast growing urban sprawls of Prayagraj. It was followed by Madhupur rural site owing to the livestock and agriculture sources, which are considered as the biggest source of NH_3 emissions in India. However, Delhi having urban megacity characteristics has shown to have least concentration of NH_3 . In contrast, due to less vehicular emission Madhupur has shown the lowest NO_2 concentrations followed by Prayagraj and highest at Delhi. Growing vehicular density and industrial emission are the primary sources of NO_2 over the urban areas. Similarly, particulate N was also observed to be lowest at Madhupur followed by Prayagraj and highest in Delhi. Seasonal distribution pattern of gaseous and particulate N have shown similar trends at both the urban sites where post-monsoon and winter months were found to contribute to the highest annual emissions. This can be attributed to the significant impact of changing meteorology on the abundance of atmospheric reactive N since the local sources over urban areas generally remains same throughout the year. However, the different trend

of NH_3 , NO_2 and particulate N were recorded at the rural site, which suggests more impact of local emission sources as compared to meteorology such as fertilizer application, biomass burning, microbial emission etc. A strong correlation of NO_2 with pWSTN has confirmed the role of NO_2 oxidation in the atmospheric nitrogenous aerosol formation over urban sites. Whereas, no correlation between NH_3 , NO_2 and pWSTN at rural site could be attributed to the least NO_x concentrations or alternatively organic N compounds might be contributing to the particulate N formation. Due to high levels, NH_3 was found to be actively involved in the particulate formation at the Prayagraj site. However, no correlation at Madhupur and Delhi has shown the gas phase oxidation of NH_3 . Seasonal meteorology has also shown its impact in the relative abundance of particulate N in ambient air at all three sites. The present study will be helpful in reducing uncertainties while assessing the effects of atmospheric N aerosols in degrading air quality, impacting regional climate and sensitive ecosystems.

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Conflict of Interest

The authors do not have any conflict of interest.

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