Wet Deposition of Total Dissolved Nitrogen in Indo-Gangetic Plain (India)

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Research Article

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Abstract

Very limited information on the magnitude and environmental impacts of both inorganic as well as organic forms of Nitrogen (N) wet deposition is available in India. Molar concentrations of inorganic (NH_4^+ and NO_3^-) and organic N in rainwater were monitored at three different land-use sites in Indo-Gangetic Plain (IGP) during the monsoon period (June-September) of 2017. It has been observed that dissolved organic N (DON) contributed significantly to the total dissolved N (TDN) ranging from 5–60%. Dissolved inorganic N (DIN = $NH_4^+ + NO_3^-$) concentration was recorded as high as 221.0 μmol L^{-1} at urban site to as low as 65.9 μmol L^{-1} at the rural site. A similar pattern was also observed for DON. NH_4^+ contribution to TDN had the order: urban megacity (65%) > urban (70%) > rural (75%). Agriculture and animal husbandry are the primary sources of NH_4^+ emissions in the rural site. However, NO_3^- has shown a contrasting trend at these sites (25%, 15% and 8%, respectively). Wet deposition fluxes of atmospheric TDN was observed to be higher at urban sites. This can attributed to a variety of local sources such as vehicular emission, microbial emissions, biomass burning, human excreta due to higher population density, and transportation from surrounding areas, as observed from concentration weighted trajectories (CWT) model and cluster analysis. Upwind region of IGP has experienced major influence of air mass transported from agriculturally rich northwest part of India. However, both the downwind sites have experienced by-and-large the influence of south-westerly air-masses originated over the Arabian Sea. Study has found that the DON contributes significantly to TDN and need to be included for budget assessment in South Asia.

Introduction

The demand for food and energy supply of growing human population might not have been sustained efficiently in the unavailability of nitrogenous fertilizers produced from industrial Haber-Bosch process. All forms of N utilized for food production are directly or indirectly added to the atmospheric reactive N, very much similar to the nitrogen pollutants emitted from fossil fuel and biomass burning. Together, these both kind of anthropogenic emissions adds more N to the atmosphere (160 TgN yr^{-1}) as compared to natural N fixation (125 TgN yr^{-1}) (Gruber and Galloway 2008). Further, the chemical transformations of reactive N from the biosphere and geosphere to the atmosphere have shown to have a cascading impact on the environment. Such as, their role in photochemical smog formation, air quality degradation, stratospheric ozone loss, health impacts, acidification and eutrophication of aquatic bodies and so on. In a study of 42 different sites of North America and Europe Bergström and Jansson (2006) have reported that significant increase in the phytoplankton biomass is particularly associated with elevated inorganic N deposition in lakes, which, in turn, resulting into the eutrophication of lakes in the northern hemisphere. There could be as high as 50% increase in the atmospheric N deposition from 1990 to 2050 over 33 world biodiversity hotspots (Phoenix et al. 2006). 11% of world's natural vegetation are receiving excess of nitrogen critical loads, having more than 1000 mgN m^{-2} yr^{-1} where most affected regions are Europe and Asia (Dentener et al. 2006). Fossil fuel emissions in the form of NOx has been dwarfed by the increasing agriculture emissions. They have reported that 80% of reactive N produced from crops are consumed by livestocks (11.8 TgN yr^{-1}). In comparison, human consume a much smaller amount of reactive N (2 TgN yr^{-1}) utilized in food production in European region (Sutton et al. 2011). Galloway and coworkers (1995; 2004; 1998; 2000) established the fact that global anthropogenic emissions of N (150 TgN yr^{-1}) have been increased manifold as compared to natural reactive N production (90–130 TgN yr^{-1}) and observed that growing population in the developing regions of Asia and Africa is going to be the major hotspot of reactive N emissions. But their sink for denitrification is not expanding in the same way.

Atmospheric deposition of reactive N for past, present and future, as calculated from RCP6.0 database for the year 2005, has shown a total N deposition is between 125 and 132 TgN yr^{-1} where organic N contribute about 20–30% of total N (TN) deposition (Kanakidou et al. 2016). The model predicted that anthropogenic activities are responsible for upto 50% of total organic N deposition. Zhang and Anastasio (2003) have reported that DON accounted for 4 ~ 28% of total dissolved nitrogen (TDN) in fog water in California. On contrary, Pacheco et al. (2004) have shown that WSON contribute as high as 90% of TDN over a tropical forested unpolluted site, claiming the natural origin of ON. Despite being ubiquitous in air, studies have suggested large variability in the occurrence of ON with time and space (Violaki et al. 2010; Cape et al. 2011). Rainwater samples collected in a coastal city of Taiwan have shown that DON accounted for up to 42% of TDN (Chen et al. 2015). Zhang et al. (2012) has simulated the results of DON in rainwater at 32 monitoring sites in China and reported that DON contributes from 7–67% of TDN, with the largest fraction been reported from the remote forest site.

Being a highly populated and an agriculturally rich country, the global assessments of reactive N have put India among the top contributor of N emission (Dentener et al. 2006). Intensive agricultural practices to meet the need of the food supply for the growing population have increased multifold emission of reactive N precursor gases such as NH_3 and N_2O. Aneja et al. (2012) have reported that livestock farming and agriculture emissions are primary sources of reactive N in India. Cattle rearing was found to contribute highest NH_3 emission in overall animal farming, whereas fertilizer application is primarily responsible for N emission among all agricultural practices. They estimated an emission of 1705 GgN yr^{-1} and 269 GgN yr^{-1} of NH_3 and 214 GgN yr^{-1} and 326 GgN yr^{-1} of N_2O from livestock and fertilizers, respectively for the base year 2003 (Aneja et al. 2012). Significant concentrations and dry deposition fluxes of inorganic and gaseous N species are also reported over North India, suggesting the Indo-Gangetic Plains as a major hotspot of N emission (Kulshrestha et al. 1996; Gupta et al. 2003; Sharma et al. 2007; Singh et al. 2017).

Wet deposition of inorganic reactive N has been extensively studied by various groups in India. Kulshrestha et al. (2005) compiled large data set of $NH_4^+$and NO_3^- depositional flux at four sites of different land-use pattern like industrial, urban, sub-urban and rural, where the highest mean NO_3-N depositional flux was found over urban sites and highest mean NH_4-N depositional flux found over industrial sites. The annual deposition of NO_3-N at the urban, suburban, rural and industrial site was found to be 4.48, 2.10, 4.06 and 3.92 kg ha^{-1}respectively. On the other hand, the annual deposition of NH_4-N at the urban, suburban, rural and industrial site was found to be 2.38, 2.10, 2.38 and 5.05 kg ha^{-1} respectively. The wet flux of total average NO_3-N and NH_4-N are estimated to be a 6.01kg ha^{-1} N deposition. For India, this value is equivalent to the wet deposition of 1.97 Tg N/yr. Studies in India have focused majorly on the inorganic forms of reactive N (Kulshrestha et al. 2003; Tiwari et al. 2007; Budhavant et al. 2011; Bhaskar and Rao 2017; Singh et al. 2017). Due to the slower scavenging

process of organic N (ON) as compared to inorganic N compounds (NH_4^+ and NO_3^-), ON tends to get transported through long distances and hence are also the key agents in the global nitrogen transport system (Gorzelska and Galloway, 1990; Neff et al., 2002; Matsumoto and Uematsu, 2005). Therefore, it can be infer that the present estimate of the atmospheric reactive N budget underestimates the total reactive N in the atmosphere by virtue of their singular focus on the inorganic N viz. NH_4^+, NO_3^- and NO_2^- (Cornell et al., 2011). This requires a comprehensive study of reactive N, inclusive of both inorganic as was well as its organic forms, and spatial and temporal variation in the wet scavenging process to enhance the scientific understanding of this aspect of the nitrogen cycle.

Methodology

Site description

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 (Phoenix et al., 2006). 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 (Fig. 1). *Prayagraj* (25°54'N, 81°85'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°54'N, 82°00'E) in Pratapgarh district, which is adjacent to the Prayagraj district, was selected as rural site. Madhupur site in Pratapgarh district located is 70 km away in the north eastern side of Prayagraj. The city comes under one of the most backward districts of India and can be considered primarily as an agrarian district. The village selected for the study 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.

Sampling

Rain water samples were collected using an assembly of polyethylene funnel of about 30 cm diameter, attached to a 2L polyethylene bottle at all the selected sites. Since the whole IGP region receives maximum rainfall during the southwest monsoon, sampling was mainly conducted from May 2017 to September 2017. More than 80% of annual precipitation during this period controls most of factors of agriculture, ground water recharge and aquatic and terrestrial ecosystems (Gadgil and Rupa Kumar 2006). The samples were collected manually on an event basis using an assembly of pre-cleaned plastic bottles and funnels (Kulshrestha et al. 2003; Singh et al. 2017). The collection assemblies at each site were set up to coincide with rain, and were taken off immediately after the rain ceased. In order to avoid contamination of any sort, the assembly was meticulously cleaned every time with de-ionized water. Each time the volume of rain was measured carefully and the duration of rain was noted down to calculate rain intensity and fluxes. Samples that have been collected were stored in pre-washed PTFE bottles with a capacity of 120ml. Subsequently, a pinch of thymol was added in order to prevent the biological degradation in the samples (Gillett and Ayers 1991; Granat et al. 1992). A portion of sample of each event was stored separately for replicate measurements to improve data quality. A blank at each site was also analyzed to characterize data artifacts by thoroughly washing the collection assembly. All the blanks and samples were analyzed for reactive N analysis on Ion chromatography (for NH_4^+ and NO_3^-) and TOC analyzer (WSTN) and taken care of while calculations. A total of 89 samples (43, 30 and 16 from Prayagraj, Madhupur and Delhi sites, respectively) were collected and stored carefully at 4 ^oC in the refrigerator until the analysis.

Analysis

Inorganic reactive N (NH_4^+ and NO_3^-) in rainwater samples were analyzed using Ion Chromatography (Metrohm 883 Basic IC Plus). Cation column (Metrosep A SUPP4, 250/4.0) was used for the determination of cationa using mixture of 1.7mmol L^{-1} $NaHCO_3$ and 1.8 mmol L^{-1} Na_2CO_3 as eluent. Whereas, anion column (Metrosep C4-100/4.0) was used to determine anions using a mixture of 0.7 mmol L^{-1} dipicolinic acid and 1.7 mmol L^{-1} Nitric acid as eluent. MERCK certified standards for anions and cations were used for the calibration. Four standards of 1, 2, 5 and 10 ppm were used to draw the standard calibration curve for cations and anions. The correlation coefficient of standards was observed to be 0.99. Calibration curve was plotted every time the new eluent is prepared and quality was ensured by repeating the analysis of standards on regular interval. Replicate sample analysis has shown relative deviation lower than 10%. For quality assurance and quality control (QA/AC) procedure field blanks were collected at the start of each month sampling. Blanks and replicate samples were also handled and analyzed in the similar way as other samples.

TOC/TN analyzer (Shimadzu model-TOC-LCPH E200 ROHS) was used for the analysis of WSTN. About one fourth of each filter (~3.14 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^oC 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.

Results And Discussion

Spatial variation of total dissolved nitrogen (TDN)

Volume weighed concentration of TDN in rainwater was found to be highest at the Delhi site ranging from 47.9 to as high as 877.9 μmol L^{-1} with a mean value of 246.0 μmol L^{-1}, as given in Table 1. At Prayagraj TDN concentrations ranged from 21.6 to 271.2 μmol L^{-1} with a mean value of 100.1 μmol L^{-1}. The lowest range of variation was found at Madhupur where it remained within a scale of 7.6 to 155.2 μmol L^{-1} with a mean value of 79.0 μmol L^{-1}. Relatively higher concentrations at former two urban sites can be attributed to the variety of local sources such as vehicular exhausts, microbial emissions, biomass burning, and greater generation of human excreta due to higher population density, secondary aerosol formation and transportation from surrounding areas. Agriculture and animal husbandry are the primary sources of N emissions in the rural sampling site, since it has very low vehicular density. The order for TDN was found to be highest at Delhi followed by Prayagraj and lowest in Madhupur. This also supports the findings that wet scavenging at all the sites significantly remove the particulates from the ambient air. Further, as shown in Fig. 2, inorganic fraction dominance suggests that the TDN variation is highly dependent on the dissolved inorganic N (DIN) as compared to dissolved organic N (DON).

Table 1
Concentrations of different nitrogen fractions in rainwater at the sampling sites.

Components	Prayagraj (n = 29)		Madhupur (n = 16)		Delhi (n = 43)	
	Concentrations (in μmolL^{-1})					
	Mean ± SE	Range	Mean ± SE	Range	Mean ± SE	Range
TDN	100.1 ± 10.2	21.6-271.2	79.0 ± 9.4	7.6-155.2	246.0 ± 25.9	47.9-877.9
NH_4^+	70.5 ± 7.8	6.0-172.6	59.4 ± 9.7	6.1-143.3	160.6 ± 13.8	36.3-459.6
NO_3^-	14.8 ± 2.3	0.3–55.7	6.5 ± 0.7	0.5–12.3	61.4 ± 11.9	6.2-392.9
DIN	85.3 ± 8.9	16.5-228.2	66.0 ± 9.8	6.6-152.7	222.0 ± 24.2	42.6-852.5
DON	14.8 ± 2.1	0.7–43.0	13.1 ± 2.5	0.8–32.9	23.9 ± 3.7	0.0-102.8

Spatial Variability Of Dissolved Inorganic Nitrogen (DIN)

NH_4^+ and NO_3^- species are primarily accounted for dissolved Inorganic nitrogen (DIN) in the rain water. Reduced N (NH_4^+) concentrations were found higher than oxidized N (NO_3^-) in rainwater at all the sites, which can be attributed to the highly soluble and reactive nature of NH_3, the precursor gas of NH_4^+. As given in Table 1, DIN concentration was highest in Delhi followed by Prayagraj and lowest in Madhupur.

Reduced N or NH_4^+ concentration was recorded highest at Delhi ranging from 36.3 to 459.6 μmol L^{-1} with an average of 160.0 μmol L^{-1}. It was followed by Prayagraj, ranging from 6.0 to 172.6 μmol L^{-1} with an average of 70.5 μmol L^{-1}. Lowest value was found at Madhupur, where NH_4^+ ranged from 6.1 to 143.3 μmol L^{-1} with an average of 59.4 μmol L^{-1}. These results clearly suggest that NH_4^+ concentration is higher at urban sites as compared to rural site. Higher NH_4^+concentrations were also observed by Singh et al. (2017), whereNH_4^+ concentration was recorded four times higher at the Delhi site as compared to a rural site, located in the middle IGP region. Kulshrestha et al. (2005) found that growing population density is the primary reason for higher wet deposition of NH_4^+ in urban areas of north India. Galloway et al. (1995) reported that agricultural emissions are the major cause of higher NH_4^+ deposition in the Asian region. Delhi is surrounded by the agriculture intensive states Punjab, Haryana and western U.P., which impart a major share in food grain production in India. Most of the emissions from surrounding states get transported to the Delhi due to geographical conditions, which might be leading to the higher NH_4^+ concentrations in rainwater. Further, the spatial variation of NH_4^+ in rainwater was found contrasting to the gaseous NH_3concentrations, which was lowest in Delhi (35.8 μg m^{-3}) and higher at middle IGP sites, i.e. Prayagraj (72.0 μg m^{-3}) and Madhupur (57.7 μg m^{-3}). Lower ambient NH_3 and higher NH_4^+ suggest the presence of transported aged NH_4^+ particles in Delhi. However, local NH_3 sources are primarily responsible for NH_4 + concentration in rainwater at Prayagraj and Madhupur sites.

An oxidized N or NO_3^- concentrations was recorded the highest in Delhi followed by Prayagraj and Madhupur. It ranged from 6.2 to as high as 392.9 μmol L^{-1} in Delhi with an average of 61.4 μmol L^{-1}. At Prayagraj, NO_3^- ranged from 0.3 to 55.7 with an average of 14.8 μmol L^{-1}. It varied from 0.5 to 12.3 μmol L^{-1} with an average of 6.5 μmol L^{-1} at Madhupur site. Mean NO_3^- concentration in Delhi was found approximately four times higher than Prayagraj and ten times higher than Madhupur rural site. Delhi, being the national capital region (NCR), has a very high vehicular density, which is the primary source of NO_3^- (Goyal et al. 2013; Tiwari et al. 2015; Pant et al. 2015; Sharma et al. 2018). However, industrial emissions in Delhi also contributed to the very high NO_3^- in rainwater. Heavy duty and old vehicles are primary sources of NO_3^- at Prayagraj urban site. In the present study, rural site is least influenced by vehicular emissions, but the biomass burning is prominent in the village, which might be primarily contributing to NO_3^- levels (Singh et al. 2017).

Spatial Variability Of Dissolved Organic Nitrogen (DON)

Dissolved organic nitrogen (DON) was calculated from the difference of the molar concentration of TDN and DIN. Spatial variation of DON has been given in Table 1 and graphically represented in Fig. 2. DON concentration in rainwater was recorded highest in Delhi followed by Prayagraj and lowest in Madhupur. It ranged from 0.0 to102.8 μmol L^{-1} with an average value of 23.9 μmol L^{-1} in Delhi. At Prayagraj, it ranged from 0.7 to 43.0 μmol L^{-1} with an average of 14.8 μmol L^{-1}. It varied from 0.8 to 32.9 μmol L^{-1} with an average of 13.1 μmol L^{-1} at Madhupur site. Studies have found that due to higher residence time and lower scavenging process, DON in rainwater sometimes comes from the transported wind trajectories and emitted from distant anthropogenic sources

(Russell et al. 1998; Cape et al. 2001; Cornell et al. 2003). As compared to previous reported studies (Table 2) conducted at various developed urban sites around the world, the present results of urban sites have shown lower concentrations of DON but higher than marine coastal sites. Values were still close to agriculture/forest/grassland sites reported earlier, as shown in Table 2.

Table 2
DON concentrations in rainwater around the world.

Location	Ecosystem	DON (μmol L^{-1})	Reference
Prayagraj	Urban	14.8	Present Study
Delhi	Urban	23.9	Present Study
Madhupur	Rural	13.1	Present Study
UEA, UK	Urban	18	Cornell et al. 1995
Czeck Republic	Rural	7	Cornell et al. 1995
North Carolina, USA	Coastal	5.5	Peierls and Paerl, 1997
Mace Head, Ireland	Marine	3.3	Cornell et al. 1998
Chesapeake Bay, USA	Coastal	6.2	Russell et al. 1998
Finland	Forest	22.9	Piirainen et al. 1998
Hubbard Brook, USA	Forest	8.1	Campbell et al. 2000
Maracaibo, Venezuela	Urban	34.3	Morales et al. 2001
LaCeiba, Venezuela	Rural	35.0	Morales et al. 2001
Qahu, Hawaii	Marine	2.8	Cornell et al. 2001
Merlewood, England	Grassland	35	Cape et al., 2004
Bush, Scotland	Agriculture	15	Pacheco et al. 2004
Calabozo, Venezuela	Rural	24	Pacheco et al. 2004
Valencia, Venezuela	Urban	57	Pacheco et al., 2004
Altos de Pipe, Venezuela	Sub-urban	31	Pacheco et al., 2004
Thailand	Forest	14.3	Möller et al. 2005
Ravels, Belgium	Forest	25	Vandenbruwane et al. 2007
Mediterranean Basin	Remote Marine	23	Violaki et al. 2010
China	Mixed	77	Zhang et al. 2012a
China	Pristine	0.8	Jiang et al. 2013
China	Marine	57	Chen et al. 2015

Interactions Between DIN And DON Fractions Of Nitrogen

DIN have shown the strongest correlation with TDN at all the three sites, which suggests the strong dependence of total N to the inorganic fraction of N at this site, particularly with NH_4^+ owing to its very strong correlation with both DIN (r = 0.97, 0.95 and 0.99) and TDN (r = 0.92, 0.95 and 0.96 at Prayagraj, Delhi and Madhupur sites, respectively). TDN was also found to have good correlation with NO_3^- at both the urban sites (r = 0.70 and 0.92 at Prayagraj and Delhi, respectively), suggesting towards their contribution from vehicular emission and significant role of NO_3^- in wet deposition of reactive N (Fig. 3). Unlike urban sites, it was least correlated (r = 0.19) rural sites due to less combustion emission in rural areas. TDN in rainwater at the rural site is primarily governed by inorganic N-NH_4^+ and agriculture and animal husbandry are the primary sources of N in the rural areas. DON is the least explored fraction of TDN in rainwater in Indian region. It has shown strongest correlation with NO_3^- (r = 0.85) at Prayagraj, which conveys a very important information about its sources. Since vehicular emissions are primarily responsible for NOx abundance in urban areas and it has a crucial role in oxidizing the atmospheric organic aerosols which might be leading to the formation of organ nitrates (Rajput et al. 2018). Neff et al. (2002) have also found the formation of organo-nitrates in the polluted urban environments. However, it was less, but positively correlated with NH_4^+ (r = 0.32) indicating its contribution from farming activities too (Fig. 3). Unlike Prayagraj, DON has shown better correlation with NH_4^+ (r = 0.43) as compared to NO_3^- (0.29). This also suggest towards the common emission of NH_4^+ and DON from agriculturally rich northwest region of Delhi or natural sources. This also shows that DON may be dominated by reduced organic nitrogen species which are co-emitted with NH_3. At Madhupur site, no correlation was found between DON and NH_4^+ or NO_3^- i.e. independent of DIN, which suggests that DON might be contributed from a totally different sources, which need further analysis with other atmospheric species.

Wet deposition fluxes of atmospheric dissolved nitrogen (DIN and DON) over IGP

Due to varying source contribution, the wet deposition fluxes of dissolved reactive N (TDN) has shown a large variation ranging from as high as 10 Kg N ha^{-1} yr^{-1} at Delhi site to 3.4 Kg N ha^{-1} yr^{-1} at Madhupur rural site. However, Prayagraj has recorded a moderate flux value of around 4.6 Kg N ha^{-1} yr^{-1}. The relative contribution of DIN and DON at each site has been represented in Fig. 4. As the figure clearly shows, NH_4^+ contributed the highest to the TDN at all the sites with highest share at Madhupur (75%; 2.5 Kg N ha^{-1} yr^{-1}) and lower at Prayagraj (70%; 3.2 Kg N ha^{-1} yr^{-1}) and Delhi (65%; 6.5 Kg N ha^{-1} yr^{-1}) sites. The percentage share of NH_4^+ and DON was found in the opposite trend of their spatial concentrations. DON contribution was also found highest at Madhupur (17%; 0.6 Kg N ha^{-1} yr^{-1}) followed by Prayagraj (15%; 0.7 Kg N ha^{-1} yr^{-1}) and lowest at Delhi (10%; 1.0 Kg N ha^{-1} yr^{-1}). However, NO_3^- has shown contrasting trend, which is the highest in Delhi (25%; 2.5 Kg N ha^{-1} yr^{-1}) followed by Prayagraj (15%; 0.7 Kg N ha^{-1} yr^{-1}) and lowest at Madhupur (8%; 0.3 Kg N ha^{-1} yr^{-1}). These patterns clearly indicate that the fossil fuel burning sources dominate the atmospheric N deposition in urban areas, whereas agriculture activities determine the atmospheric N levels in rural areas.

Long range transport and cluster analysis of TDN over selected sites

To understand the probable distant/local sources, air-mass backward trajectories (AMBTs) were simulated utilizing the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model with an input of GDAS Meteorological Data at an atmospheric height of 500 meters above mean sea-level (amsl.) (Draxler and Rolph 2003). Seven-days AMBTs were calculated for each rain event sampling. Furthermore, cluster analysis and concentration weighted trajectories of the TDN data set was also performed for each site based on a pre-existing algorithm of the nearest angle-distance function (Sirois and Bottenheim 1995). CWT analysis is a receptor modelling tool which is used widely to understand the spatial distribution of potential source regions of pollutants and details have been mentioned in previous studies (Bansal et al. 2019; Rai et al. 2020). The outputs of CWT and cluster analysis for TDN in rainwater are shown in Fig. 5.

In the present study, three major clusters were identified for Delhi site and two major clusters for both downwind closely located sites, which has explained the dominant pathways of TDN arriving at the study site through rainfall (Fig. 5). At Delhi, almost half of the TDN (cluster #2; 47%) showed association with trajectories originated from the northwestern part of India. Cluster #1 and #3 represents the influence of long-range transport from south east continental air mass (26%) and south west winds, originated from the Arabian Sea, respectively. This also suggests that TDN transported from agriculturally rich northwest region of Delhi could be one of the major factor of higher deposition fluxes over Delhi site. Both Prayagraj and Madhupur sites have shown similar path of two major trajectories i.e. southwest and southeast primarily due to south west monsoon winds which are primarily responsible for rainfall in north India from June to September. As shown in Fig. 5, both the clusters have contributed for TDN at Prayagraj site and each grids in the clusters have contributed to the deposition fluxes at the receptor site including both land and marine sources. However, bothe the clusters at Madhupur site and their CWT results have shown that local sources have contributed more for TDN at the receptor site with a major influence of south westerly marine/continental air mass (61%). Thus during monsoon period, the downwind sites of IGP experiences influence of air masses of mixed origins (continental/marine) whereas upwind site is relatively more influenced from northwesterly air mass.

Conclusions

There is an exponential increase in the anthropogenic emission of atmospheric reactive N as compared to natural sources from past few decades. Growing population and their demand for food and energy have significantly altered the natural nitrification-denitrification cycle through the heavy inputs of reactive forms of N (NH_4^+, NO_3^-, Amines, Hydrazines, etc.) which has led to serious implications on the sensitive ecosystems. Wet deposition is one of the important removal process which brings down most reactive soluble N forms to the natural surfaces. Considering its importance over highly populated IGP region, the present study was conducted at three sites to calculate the total N deposition fluxes and significance of organic N monitoring during monsoon season. Study has revealed that there is a large scale variation in the molar concentration of DIN and DON based on receptor site type and even higher at upper IGP as compared to centrally located sites. Higher levels at former site was also found to be associated with transported air mass from northwestern agriculturally rich region. DON has shown a good correlation with NO_3^- at urban sites, suggesting towards its crucial role in the formation of organic N or co-emitted with the fossil fuel combustion. Whereas, DON has shown no such relation at rural site, which accentuates the need of further investigation for its source receptor matrices. DON has been shown to have significant contribution in TDN at all the three sites, which suggests that organic forms of N cannot be ignored while assessing the atmospheric reactive N budget assessment.

Declarations

Ethics approval and consent to participate:

Not applicable.

Consent for publication:

Not applicable.

Availability of data and materials:

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Competing interests:

The authors declare that they have no competing interests.

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Authors' contributions:

Manisha Mishra: Analysis of samples; Interpretation of data; Drafting of manuscript.

Umesh Kulshrestha: Conception and design of the study; Interpretation of data; Critical revision of manuscript.

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Figures

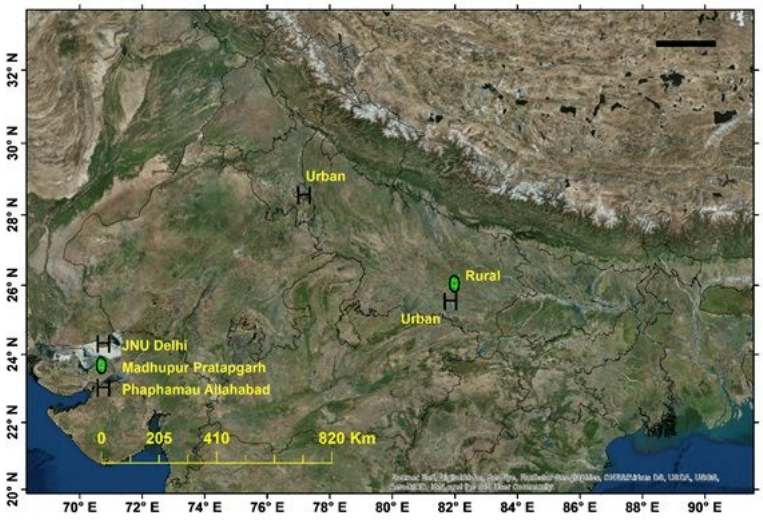

Figure 1

Description of three sampling sites in Indo Gangetic plains.

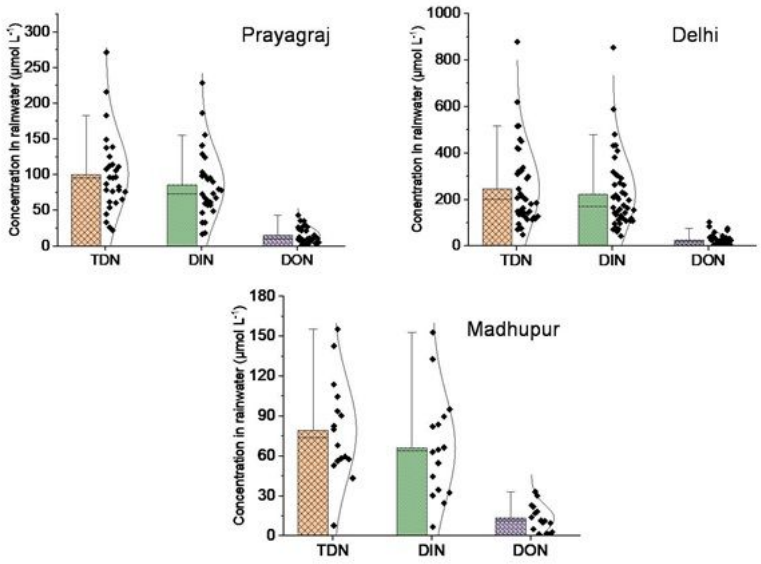

Figure 2

Volume weighed mean concentrations of TDN, DIN and DON in rainwater (with the horizontal line inside box representing the median value. The vertically aligned dots are showing the concentrations of each sample along with their distribution curve corresponding to y-axis).

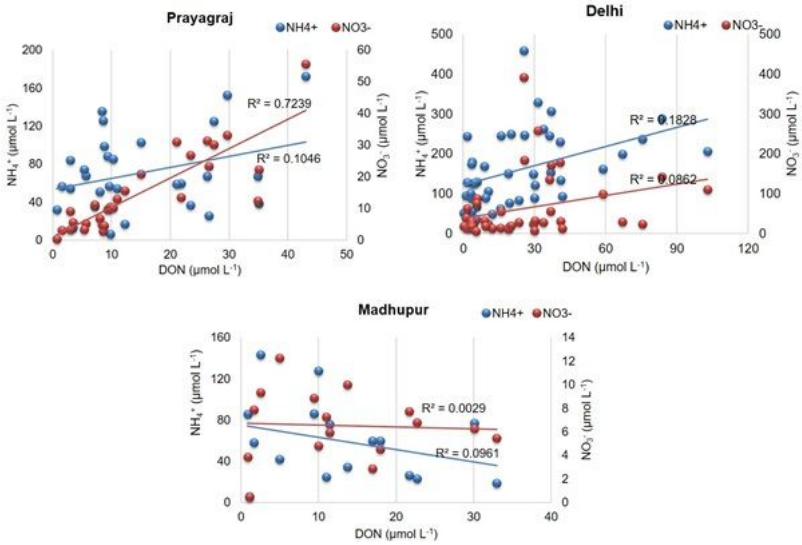

Figure 3

Regression analysis of DON with NH4+ and NO3- over the sampling sites.

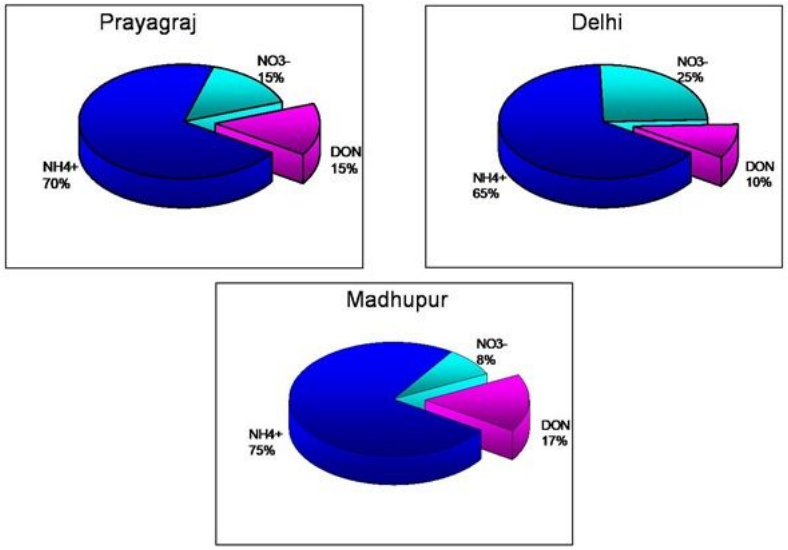

Figure 4

Relative contribution of DON in the TDN in the rainwater at each site.

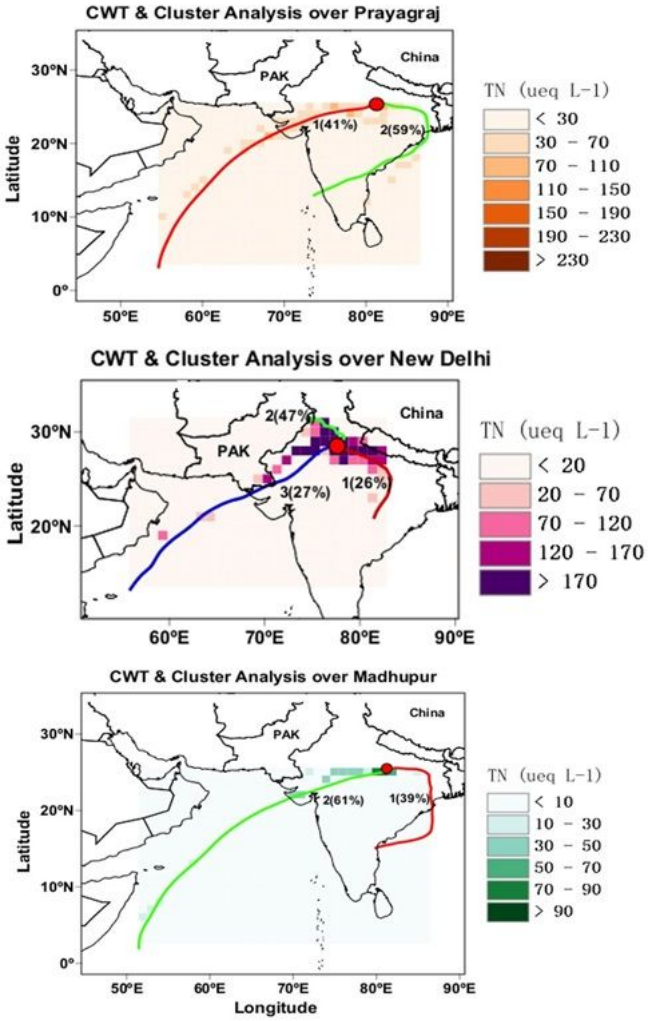

Figure 5

CWT and cluster trajectories analysis at the sampling site during monitoring period (May to September, 2017)