

# Chapter 9

## Atmospheric Deposition of Reactive Nitrogen in India

Umesh C. Kulshrestha, Monika J. Kulshrestha, Jetta Satyanarayana and Loka Arun K. Reddy

**Abstract** The increasing demand of food and energy of the global population is contributing excess reactive nitrogen ( $N_r$ ) in the atmosphere primarily in the form of ammonium and nitrate compounds. Subsequently, through wet and dry deposition processes, these compounds are deposited onto the ground, vegetation, soils, water bodies etc. enriching these systems with excess nitrogen (N). Knowledge about N deposition in North America and Europe is quite advanced because of systematic studies. But the present knowledge about N deposition in India and the south Asian region is very limited due to a lack of systematic measurements dedicated to nitrogenous compounds. Though a number of wet deposition studies have been reported by various groups for different sites and years in India, only a few of these are considered as having good quality data. This chapter reports quality controlled wet deposition fluxes of  $N_r$  at rural (2006–2008) and urban (2005–2008) sites in south India as part of the RAPIDC-CAD programme. The rural site Hudegadde is located in the reserve forest area of Western Ghats by the south-west coast of India while the urban site Hyderabad, the capital of Andhra Pradesh State is located in south-central India. In general, at both the sites, wet deposition of N through  $NH_4^+$  was observed to be higher than  $NO_3^-$ . Fluxes of  $NH_4^+$  showed an increasing pattern

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U. C. Kulshrestha (✉)

School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110067, India  
e-mail: umeshkulshrestha@yahoo.in

M. J. Kulshrestha

Radio and Atmospheric Sciences Division, National Physical Laboratory, New Delhi 110012, India  
e-mail: monikajk@yahoo.com

J. Satyanarayana

Analytical and Environmental Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India  
e-mail: satya\_ou@yahoo.com

L. A. K. Reddy

Air Quality Division, Environmental Diagnostics Research Department, National Institute of Environmental Research (NIER), Kyungseo-dong, Seo-gu 404-708, Incheon, Korea  
e-mail: arunloka2000@yahoo.com

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at Hudegadde, while those of  $\text{NO}_3^-$  showed an increasing pattern at Hyderabad. The possible reason for increasing  $\text{NH}_4^+$  at Hudegadde may be an increase in biomass burning and vegetation decay in the forest areas, which contribute higher ammonia to the atmosphere, together with transboundary pollution due to air-masses from nearby continental areas. The increasing pattern of  $\text{NO}_3^-$  fluxes at Hyderabad might be due to an increase in population, vehicular density and other urban activities. Projections using the MATCH model coupled with rain chemistry measurements showed that the Indo-Gangetic region experiences very high wet deposition of  $\text{NH}_4^+$  which might be due to a prevailing higher density of ammonia sources in the region. This chapter also highlights the importance of dry deposition of  $\text{N}_r$  species for the Indian region.

**Keywords** Ammonium fluxes • Dry deposition rates • Indian region • Reactive nitrogen • Wet deposition

## 9.1 Introduction

The primary reactive nitrogen ( $\text{N}_r$ ) species are  $\text{NH}_3$  and  $\text{NO}_x$ , which react further to produce other  $\text{N}_r$  species such as  $\text{HNO}_3$ ,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in the atmosphere. The major sources of  $\text{NH}_3$  are cattle, agricultural activities, fertilizer applications, fertilizer manufacturing, biomass burning, human excretion, and anaerobic activities in the soil system. The major sources of  $\text{NO}_x$  are vehicular exhaust, industrial combustion processes, and biomass burning. Emissions of  $\text{NO}_x$  result in the formation of nitric acid in the atmosphere. Ammonia ( $\text{NH}_3$ ) reacts with nitric acid or sulphuric acid forming ammonium sulphate and ammonium nitrate compounds. The presence of various phases of reactive nitrogen depends upon meteorological conditions, atmospheric acidity, temperature, humidity, and the scavenging processes.

In many countries, global emissions of nitrogen (N) and sulphur species are increasing due to the enhanced energy demands of a rapidly growing population. In the Indian region also, an upward trend of energy consumption has been recorded during the past two decades. Considering their importance, studies of wet and dry deposition have been carried out systematically in North America, Canada, Europe and East Asia. But in the Indian region, deposition fluxes have not been reported through a comprehensive and systematic network. The 'Composition of the Atmospheric Deposition' (CAD) program was an effort to study wet and dry deposition in Asia focusing upon quality of data ([www.sei-international.org/rapidc/networks-cad.htm](http://www.sei-international.org/rapidc/networks-cad.htm)).

This chapter presents some of the CAD findings, highlighting the wet deposition of nitrate and ammonium at a rural and an urban site in south India. At Hudegadde a rural site in south-west India, 3 years of data on wet deposition fluxes of nitrate and ammonium are discussed, while at Hyderabad, an urban site in south-central India, 4 years data are discussed. The deposition of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  at other Indian sites is also based on the compilations of Kulshrestha et al. (2003, 2005). The comparison of dry and wet deposition is also highlighted with reference to the Indian region.

## 9.2 Methods

### 9.2.1 Sampling Sites

As a part of the CAD program, samples of rain water were collected at two contrasting sites. The details of the sites are given below. Apart from this, data from about 100 locations as synthesized by Kulshrestha et al. (2003, 2005) are used to provide wet deposition flux estimates of  $\text{NO}_3^-$  and  $\text{NH}_4^+$ .

#### 9.2.1.1 Hudegadde—A Rural Site

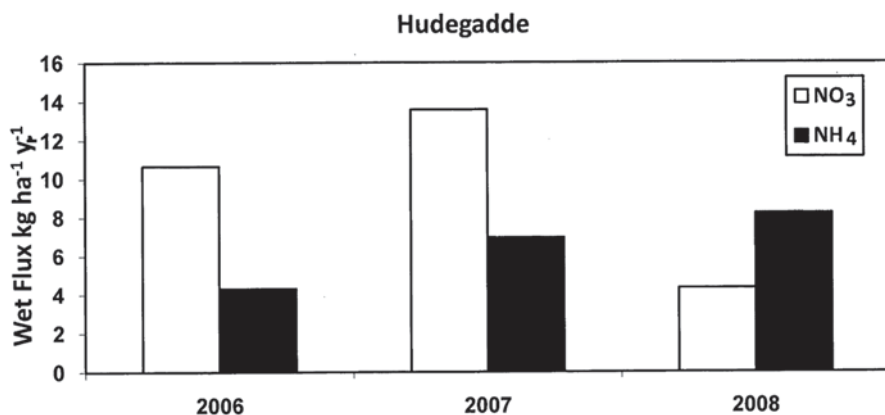
Hudegadde is a rural site located at  $14.36^\circ$  N and  $74.54^\circ$  E in Western Ghats by the south-west coast of India, in the Kannada district of Karnataka state (near the border of Kerala state). The site is located in a reserve forest in mountain ranges having dense green surroundings with thick forest and waterfalls. There are no residential houses nearby within a radius of 6 km. The site is located at 915 m above mean sea level (msl), and 145 km away from the coast of the Arabian Sea. The samples were collected using bottle and funnel on a rainfall event basis. The collector was installed just before the rain event to avoid any dustfall before the rain. The collector assembly was kept on the terrace of a house ( $\sim 5$  m above ground level), and at a height of 1 m from the base of the roof.

#### 9.2.1.2 Hyderabad—An Urban Site

Hyderabad ( $17.5^\circ$  N,  $78.5^\circ$  E) is the capital of Andhra Pradesh state of India. It is the fifth largest city in India with an area of  $260 \text{ km}^2$ . The land use is almost 93% urban (including industrial). The samples were collected at the terrace of the main building of our institute at a height of around 11 m above ground using a switch controlled rain water collector to avoid any contamination during sampling. The collector is opened whenever rain occurs and gets closed after the rain event with the help of a remote switch installed in the laboratory.

### 9.2.2 Sample Collection and Analysis

The samples were transferred into 60 ml polypropylene bottles and preserved by using a small quantity of thymol. The samples were kept in a refrigerator until they could be further analysed. The pH and electrical conductivity (EC) of these samples were measured by using a pH meter (Elico LI 612) and a conductivity meter (Elico CM 183), respectively. Both instruments were calibrated with a certified reference solution traceable to NIST. Determination of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  used ion chromatography (Metrohm 792 basic IC system). Separation of  $\text{NO}_3^-$  was performed with a Metrosep A supp 5-100 column, using a mixture of 3.2 mM



**Fig. 9.1** Wet fluxes of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> at rural site Hudegadde, in India

Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> as eluent at a flow rate of 0.7 ml/min. Separation of NH<sub>4</sub><sup>+</sup> was attempted by using a mixture of 4 mM tartaric acid (TA) and 0.75 mM of 2, 6-pyridine dicarboxylic acid (PDC) as eluent at a flow rate of 1.0 ml/min with the Metrosep C2-100 column.

## 9.3 Results and Discussion

### 9.3.1 Increasing Patterns of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>

Wet deposition fluxes of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> at Hudegadde are shown in Fig. 9.1. These fluxes have been calculated for annual rainfall based on monsoon data, combined with the measured precipitation amount. It should be noted that non-monsoonal rains have higher concentrations of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> in samples and hence, the fluxes in this chapter represent conservative estimates.

Wet deposition fluxes of NO<sub>3</sub><sup>-</sup> at Hudegadde were observed to be 11, 14 and 4 kg ha<sup>-1</sup> year<sup>-1</sup> during 2006, 2007 and 2008 respectively. At Hudegadde, average NH<sub>4</sub><sup>+</sup> fluxes were estimated as 4, 7 and 8 kg ha<sup>-1</sup> year<sup>-1</sup> during 2006, 2007 and 2008 respectively. While at Hyderabad, NH<sub>4</sub><sup>+</sup> deposition fluxes were estimated as 6, 14, 36 and 15 kg ha<sup>-1</sup> year<sup>-1</sup> and that of NO<sub>3</sub><sup>-</sup> fluxes were estimated as 18, 44, 52 and 63 kg ha<sup>-1</sup> year<sup>-1</sup> during 2005, 2006, 2007 and 2008, respectively (Fig. 9.2).

Although the short-term data of the present study are not sufficient to predict any trends, these results suggest that NH<sub>4</sub><sup>+</sup> fluxes have an increasing pattern at Hudegadde, while NO<sub>3</sub><sup>-</sup> fluxes have an increasing pattern at Hyderabad. The possible reason for increasing NH<sub>4</sub><sup>+</sup> at Hudegadde may be due to an increase in biomass burning and vegetation decay in the forest areas, which contribute higher ammonia to the atmosphere. In addition, moving air-masses from nearby continental areas

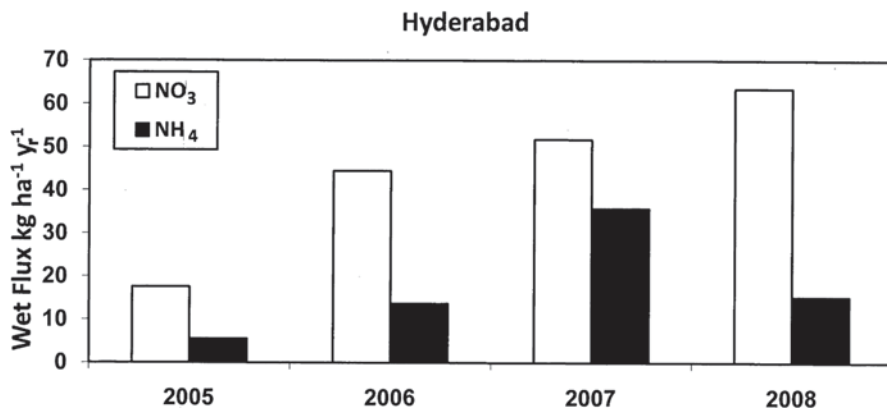


Fig. 9.2 Wet fluxes of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  at the urban site Hyderabad, India

also transport these fluxes to Hudegadde (Satyanarayana et al. 2010). The reason for the increasing pattern of  $\text{NO}_3^-$  fluxes at Hyderabad might be due to the growing size of the city, with an increase in population, vehicular density and industries etc. which contribute precursors of  $\text{NO}_3^-$  to the atmosphere. The decrease of  $\text{NO}_3^-$  at Hudegadde during 2008 and the decrease of  $\text{NH}_4^+$  at Hyderabad during 2008 needs to be investigated in terms of source strength and trajectory analysis for these sites and years. This also suggests a need to carry out long-term N deposition measurements in the Indian region to quantify the trends and to reduce uncertainties in the measurements.

### 9.3.2 Wet Deposition Concentration and Rates for Different Categories of Sites in India

In a developing country like India, deposition measurements are carried out sporadically. Recently, Kulshrestha et al. (2003, 2005) have synthesized the data reported by various workers for about 100 locations in 35 research papers throughout the country. This review indicated poor data quality associated with  $\text{NO}_3^-$  and  $\text{NH}_4^+$  values. In most of the studies, samples were not preserved properly. Also, delay in chemical analysis was found to be an important factor which is responsible for the decay of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in samples.

Based on the rain chemistry data, the sites have been classified into five categories, i.e. rural, suburban, rural and suburban, urban and industrial (Kulshrestha et al. 2003). Average wet deposition fluxes of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  have been calculated for these categories which are presented in Table 9.1.

Table 9.1 shows that fluxes of  $\text{NO}_3^-$  are always higher than  $\text{NH}_4^+$  at all categories of sites. Highest concentrations of  $\text{NO}_3^-$  are recorded for urban sites, which is obvious due to more vehicular emissions (contributing more  $\text{NO}_x$  as a precursor of  $\text{NO}_3^-$ ). A similar feature has been observed at Hyderabad as reported in the

**Table 9.1** Wet deposition flux of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  for different categories of sites in India as reported by Kulshrestha et al. (2003)

Site category	$\text{NO}_3^-$ $\text{kg ha}^{-1} \text{ year}^{-1}$	$\text{NH}_4^+$ $\text{kg ha}^{-1} \text{ year}^{-1}$
Rural	18	3
Suburban	9	3
Rural and suburban	15	3
Urban	20	3
Industrial	17	6

**Table 9.2**  $\text{NH}_4^+$  and  $\text{NO}_3^-$  deposition at different sites ( $\text{meq m}^2 \text{ year}^{-1}$ )

Site	Category	Type of deposition	$\text{NH}_4^+$	$\text{NO}_3^-$	Reference
Delhi	Urban	Wet	19	26	Khemani et al. (1989)
		Dustfall	4	4	
		DD aerosol	2	17	
Pune	Suburban	DD gases	115	3	
		Wet	17	18	Pillai et al. (2001)
		Dustfall	1	12	Pillai et al. (2001)
		DD aerosol	2	6	
Bhubaneswar /NK	Rural forest	DD gases	16	2	
		Wet	22	13	Granat et al. (2001)
		Dustfall	–	2	Granat et al. (2001)
Silent Valley	Rural forest	Wet	11	74	Rao et al. (1995)
		Dustfall			
		DD aerosol	3	6	
		DD gases	2	1	
Sinhadag	Rural forest	Wet	16	8	Pillai et al. (2001)
		Dustfall			
		DD aerosol	1	3	
		DD gases	2	2	
Agra, Dayalbagh	Suburban	Wet	30	4	Saxena et al. (1991)
		Dustfall	3	6	Kulshrestha (1993)
		DD aerosol		27	
		DD gases			

*DD* dry deposition

previous section, where increasing fluxes of  $\text{NO}_3^-$  have been noticed. The highest  $\text{NH}_4^+$  fluxes at industrial sites indicate that industrial areas also experience significant deposition of ammonia in India. Interestingly, suburban sites show minimum levels for both  $\text{NO}_3^-$  and  $\text{NH}_4^+$  deposition, indicating minimum influence of nitrogenous sources. It should be noted that higher  $\text{NO}_3^-$  fluxes at rural sites might be due to soil resuspension. Projections using the MATCH model coupled with rain chemistry measurements in India show that wet deposition of  $\text{NH}_4^+$  is the highest in the Indo-Gangetic region, which might be due to the prevailing higher density of ammonia sources in the region.

### 9.3.3 Importance of Wet and Dry Deposition in the Indian Region

In India, most of the rainfall occurs during the monsoon period (June–September) and the remaining period is dominated by dry weather conditions. Even during monsoons, there are gaps of several days when it does not rain. This highlights the importance of dry deposition of atmospheric constituents in the Indian region. According to Kulshrestha et al. (2003), dry deposition of gaseous ammonia is more significant than its wet deposition in India. Unfortunately, not many reports are available on dry deposition in India. Among the limited studies available, most of these consider dustfall as dry deposition without differentiating dry deposition of gases and particles. Table 9.2 shows estimated dry deposition of gas phase  $\text{NH}_3$ ,  $\text{NH}_4^+$  aerosols and  $\text{NH}_4^+$  dustfall based on the reported studies as referred to in the table. In an estimate based upon EMEP dry deposition velocities, Singh et al. (2001) found that dry deposition of  $\text{NH}_4^+$  was 9 times more significant than wet deposition at Agra. Wet deposition of  $\text{NH}_4^+$  has been reported as  $3.4 \text{ kg ha}^{-1} \text{ year}^{-1}$  as compared with  $39 \text{ kg ha}^{-1} \text{ year}^{-1}$  of dry deposition.

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