Relative contributions of \( \text{NH}_3 \), \( \text{NO}_2 \), \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) to dry deposition of Nitrogen at an agricultural site in the Indo-Gangetic Plain of India

**Saumya Singh**, Anshu Sharma and U.C. Kulshrestha

School of Environmental Sciences
Jawaharlal Nehru University
New Delhi
India
Nitrogen gas (N₂) accounts for more than 99.99% of all the nitrogen present in the atmosphere, while of the rest, again 99% is accounted for by nitrous oxide (N₂O) (Wallace and Hobbes, 2006). Other N species are thus only present in trace concentrations, but nonetheless play a vital role in atmospheric chemistry.

- It includes all biologically, chemically, and or photochemically active N compounds in the environment.

- Different forms of reactive N occurring under natural conditions are (NH₃), (NH₄⁺), (NO), (NO₂), (HNO₃), (N₂O), and (NO₃⁻) and organic compounds (urea, amines, nucleic acids and proteins).
Estimated total reactive nitrogen deposition from the atmosphere (wet and dry) in early 1990s, and projected for 2050.

Fig: Spatial patterns of total inorganic nitrogen deposition in (a) early 1990s, and (b) 2050 (unit in mg N/m²/yr) (Galloway et al., 2004).
Motivation

Fig: Nr deposition in India indicating IGP as a hotspot (a) Spatial distribution of total N (Kg N/ha/yr) for 2000 (left) and 2030 (right) (Bleaker et al., 2011) (b) NO\textsubscript{x}–N + NH\textsubscript{3}-N (Kg N/ha/yr) obtained from the 16 HTAP NO\textsubscript{x} models 7HTAP NH\textsubscript{3} models (Vet et al., 2014) (c) Concentration of NH\textsubscript{4}\textsuperscript{+} in rain (µeq/l) (Kulshrestha et al., 2005).
Study site

Mai Village, Jaunpur, Uttar Pradesh (rural site)
25°62’N and 82°51’E

- Approximately 62 % area is used for agricultural purpose.
- Urea and DAP fertilizer
Sample collection

Dry deposition

- Gases (NH₃, NO₂) & Particulates
- Impinger method
- Handy Sampler
- Monthly basis
- Monsoon 2013
Sample collection procedure and analysis

1. Gaseous Samples: (NH₃ & NO₂)

✓ Gaseous samples (NH₃ and NO₂) were collected on **8 hour basis** together with aerosol samples at a **flow rate of 1 LPM** on monthly basis. On an average 7 days sampling was done in a month on day-night basis.

✓ Absorbing solution

   - NH₃ - 25 mM H₂SO₄ solution
   - NO₂ - 0.1 M NaOH solution

✓ All gaseous samples were stored at 4°C before chemical analysis.

   Gaseous NH₃ was analysed by Blue Indophenol method and NO₂ was estimated colorimetrically by using spectrophotometer.
2. Particulate Phase Sampling:

Fine aerosol samples were collected using handy sampler (Envirotech make) covering all the seasons, with flow of 1 LPM using Teflon filters (25mm dia).

3. Analysis of major ions:

Major anions (Cl\(^-\), F\(^-\), NO\(_3\)^- and SO\(_4^{2-}\)) and cations (Na\(^+\), K\(^+\), NH\(_4^+\), Ca\(^{2+}\) and Mg\(^{2+}\)) were determined in the water soluble extracts of aerosols and rain water by using ion chromatograph (IC).

Ion balance method was adopted for the quality check of samples.
Instruments used for analysis

(a) Ion chromatograph

(b) UV-Vis Spectrophotometer

(c) pH meter
Deposition Flux calculation

✓ Dry deposition flux was calculated as the product of the atmospheric concentration and deposition velocity of a given compound. (Roberage et al., 2002; Horii et al., 2005; Shen et al., 2013).

\[ F = V_d \times C \]

Where \( V_d \) is deposition velocity of gas or aerosol and \( C \) is concentration (µg/m³) in ambient atmosphere.

For gaseous \( \text{NH}_3 \), \( V_d \) is taken as 0.2 cm/sec while for \( \text{NH}_4^+ \) the value was 0.15 cm/sec. (Kulshrestha et al., 2005; Zhang et al., 2012).

✓ Wet deposition fluxes (kg/ha/yr) of \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) were calculated on the basis of following formula

\[ \text{Flux} = \text{Concentration of species (C)} \times \text{precipitation amount (P)} \]
Results
Dry Deposition

Gas phase (µg/m³)

Aerosol Phase (µg/m³)

Total concentration of N in DD= 26.90 (µg/m³)

Fractions %
Oxidized = 5.83
Reduced = 94.17
Gas = 97.73
Aerosol = 2.27

Concentrations

Samples
Dry Deposition Flux

- Dry deposition flux was calculated as the product of the atmospheric concentration and deposition velocity of a given compound. (Roberage et al., 2002; Horii et al., 2005; Shen et al., 2013).
  \[ F = V_d \times C \]

  Where \( V_d \) is deposition velocity of gas or aerosol and \( C \) is concentration (\( \mu g/m^3 \)) in ambient atmosphere.

- For gaseous Nr, \( V_d \) is taken as 0.2 cm/sec while for aerosol Nr the value was 0.15 cm/sec. (Kulshrestha et al., 2005; Zhang et al., 2012).

**DD flux (KgN/ha/yr)**

- \( N-NH_3 = 15.78 \)
- \( N-NO_2 = 0.77 \)
- \( N-NH_4^+ = 0.14 \)
- \( N-NO_3^- = 0.15 \)

**Total Dry Deposition Flux = 16.84 KgN/ha/yr**

* 98 % of dry deposition occurred in gas phase at this site.
Total Dry inorganic N deposition Flux

Relative Contribution

N- DD Flux = 16.84 KgN/ha/yr

Reduced N = 94.54 %
Oxidized N = 5.46 %

N-NH₃ (g) = 93.70 %
N-NO₂ (g) = 4.57%
N-NH₄⁺ (p) = 0.8%
N-NO₃⁻ (p) = 0.9 %
Conclusions

• Total dry deposition flux of inorganic nitrogen at the site was 16.84 KgN/ha for the monsoon period.

• Relative contribution of reduced N deposition was much higher (94.5 %) that oxidized N deposition.

• Contribution of Gaseous NH\(_3\) was highest in total Nr dry deposition at the site with 93.7 %.

• The results of this study are highly important not only to strengthen our understanding about Nr deposition in India but also for necessary abatement measures and with these future outlook.....

✓ Due to higher deposition of Nr in Indo-Gangetic plain and its related adverse effect, the research of Nr in atmosphere become very significant.

✓ There is a gap between atmospheric Nr understanding in Indian research community, because of less data available from past, research in field of Nr needs urgent attention of scientific community in India.
Thank you !!

😊😊

Suggestions/Questions/Comments

Contact: Dr. Saumya Singh
E-mail id- saumya.8singh@gmail.com

Reduce your N Print