



# Relative contributions of NH<sub>3</sub>, NO<sub>2</sub>, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> 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









### **Reactive N**

- Nitrogen gas  $(N_2)$  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  $(N_2O)$  (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 (NH<sub>3</sub>), (NH<sub>4</sub><sup>+</sup>), (NO), (NO<sub>2</sub>), (HNO<sub>3</sub>), (N<sub>2</sub>O), and (NO<sub>3</sub><sup>-</sup>) and organic compounds (urea, amines, nucleic acids and proteins).









# Alarming threat..

Estimated total reactive nitrogen deposition from the atmosphere (wet and dry) in early 1990s, and projected for 2050.



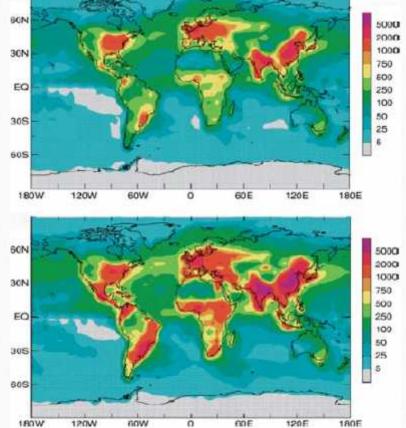


Fig: Spatial patterns of total inorganic nitrogen deposition in (a) early 1990s, and (b) 2050 (unit in mg N/m²/yr) (Galloway et al., 2004).









### **Motivation**

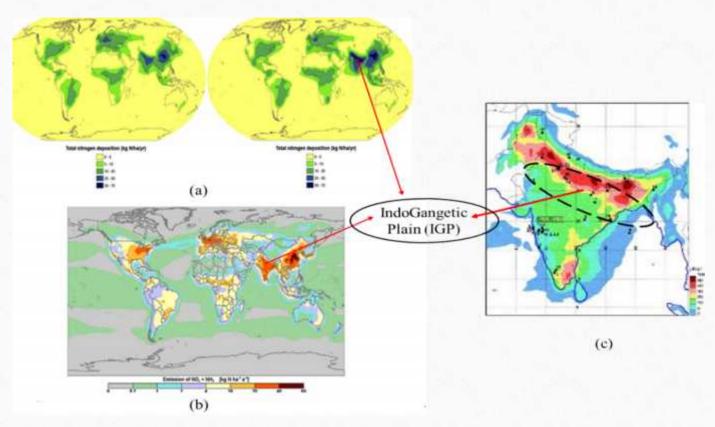


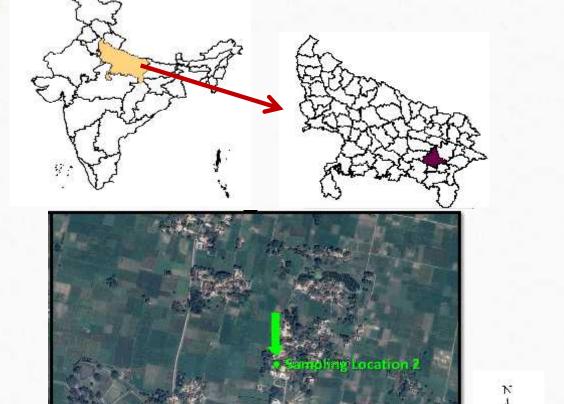
Fig: Nr deposition in India indicating IGP as a hotspot (a) Spatial distribution of total N (Kg N/ha/yr) for 2000 (left) and 2030 (right) (Bleaker et al., 2011) (b)  $NO_x - N + NH_3 - N$  (Kg N/ha/yr) obtained from the 16 HTAP  $NO_x$  models 7HTAP  $NH_3$  models (Vet et al., 2014) (c) Concentration of  $NH_4^+$  in rain (µeq/l) (Kulshrestha et al., 2005).











1,040

# Study site

Mai Village, Jaunpur, Uttar Pradesh (rural site) 25<sup>0</sup>62'N and 82<sup>0</sup>51'E

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



260

520



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1,560

2,080 Meter





# Sample collection

### Dry deposition

- Gases (NH<sub>3</sub>, NO<sub>2</sub>) & Particulates
- Impinger method
- Handy Sampler
- Monthly basis
- Monsoon 2013









### Sample collection procedure and analysis

- **1. Gaseous Samples:** (NH<sub>3</sub> & NO<sub>2</sub>)
- ✓ Gaseous samples (NH<sub>3</sub> and NO<sub>2</sub>) 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

NH<sub>3</sub> - 25 mM H<sub>2</sub>SO<sub>4</sub> solution

NO<sub>2</sub> - 0.1 M NaOH solution

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

Gaseous NH<sub>3</sub> was analysed by Blue Indophenol method and NO<sub>2</sub> 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<sup>-</sup>, F<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) and cations (Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) 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 a given compound. (Roberage et al., 2002; Horii et al., 2005; Shen et al., 2013).

$$F = V_d * C$$

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

For gaseous  $NH_{3}$ ,  $V_{d}$  is taken as 0.2 cm/sec while for  $NH_{4}^{+}$  the value was 0.15 cm/sec. (Kulshrestha et al., 2005; Zhang et al., 2012).

✓ Wet deposition fluxes (kg/ha/yr) of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> were calculated on the basis of following formula

Flux = Concentration of species  $(C)\times$  precipitation amount (P)





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# Results



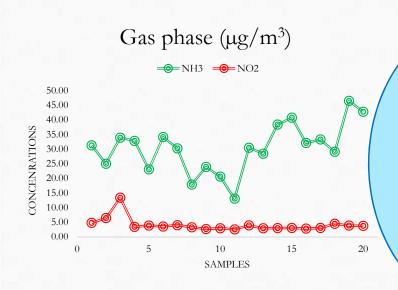


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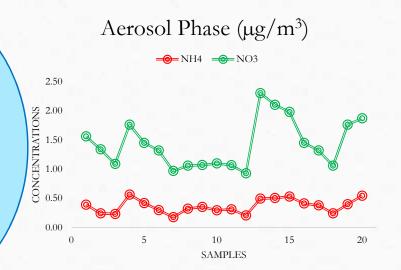


# **Dry Deposition**



Total concentration of N in DD= 26.90  $(\mu g/m^3)$ 

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







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$$F = V_d * C$$

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<sub>d</sub> is taken as 0.2 cm/sec while for aersol 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 %

 $N-NH_3(g) = 93.70 \%$ 

 $N-NO_2(g) = 4.57\%$ 

 $N-NH_4^+(p) = 0.8\%$ 

 $N-NO_3^-(p) = 0.9 \%$ 



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### **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<sub>3</sub> 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.





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### Thank you!!



# Suggestions/Questions/Comments

Contact: Dr. Saumya Singh

E-mail id- saumya.8singh@gmail.com







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