



Dry deposition fluxes of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ at a rural site of Indo-Gangetic Plain, India

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Abstract

The world's acute reactive nitrogen (Nr) deposition is chronically eroding the biospheric integrity and undermining earth system's resilience to be in an accommodatable state. The present study comprehensively attempts to decipher the dry depositions of atmospheric inorganic Nr along with other major ions through dustfall fluxes. Authentic atmospheric dust samples were collected by incorporating a surrogate-surface approach at an agriculturally intensive rural site in Indo-Gangetic plain of India over a year-long temporal scale from October 2017-September 2018. The mean ($\pm$ Standard Error) dry deposition fluxes of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ during the whole study period were observed as 0.41 ± 0.09 kg ha^{-1} yr^{-1} and 6.51 ± 1.58 kg ha^{-1} yr^{-1} , respectively. The total percent ionic contribution to the dustfall flux was observed 2.95% and the descending order of their percent contribution in total ionic fluxes were observed as SO_4^{2-} (31.46%) > Cl^- (15.74%) > K^+ (15.04%) > Ca^{2+} (13.97%) > Na^+ (10.23 %) > NO_3^- (7.06%) > Mg^{2+} (4.43%) > F^- (1.62%) > NH_4^+ (0.44%). The relative dominance of $\text{NO}_3^-\text{-N}$ over $\text{NH}_4^+\text{-N}$ fluxes was maintained in all seasons during the whole monitoring period which could be attributed to the competitive exclusion of $\text{NH}_4^+\text{-N}$ from acid-base neutralization reactions by other strong base cations in dustfall. Size-distribution and morphological analysis of dust particles from Scanning Electron Microscope images signified the anthropogenic involvement in shaping the dominant mode of particle-size distribution in dust fall fluxes which culminated into the dominance of fine-mode fraction over course-mode in dustfall.

Material and Methodology

- Dustfall samples were collected at an agriculturally intensive rural site in the Indo-Gangetic plain of India (Fig.1) on a 15 days interval using a pre-weighted surrogate surface dust fall collector (Tiwari et al., 2016). A total of 24 samples were collected during the entire sampling period.
- Before analyzing dustfall samples gravimetrically, they were desiccated for 48 hours and then weighted for final weight using weighing balance machine (Mettler Toledo-ME 204) and dustfall fluxes (DF) were calculated (in Kg ha^{-1} yr^{-1}) using the following equation (Katz, 1969)

$$\text{Dustfall fluxe (DF)} = W / (A \times T)$$

Where W denotes the sample weight (in Kg), A is the area (in hectare) and T is denoting the sampling duration (in year).

- The water soluble fraction of dustfall samples was extracted by washing the petri plate with 30 mL of ultrapure Milli-Q water followed by its ultrasonication for 30 min at a working frequency of 1 Hz. The extracts were filtered through 0.2- μm nylon syringe filter and were analyzed for its major cations (K^+ , NH_4^+ , Na^+ , Ca^{2+} , and Mg^{2+}) and anions (F^- , Cl^- , NO_3^- , and SO_4^{2-}) with the help of ion chromatography (Metrohm 883 basic plus model).

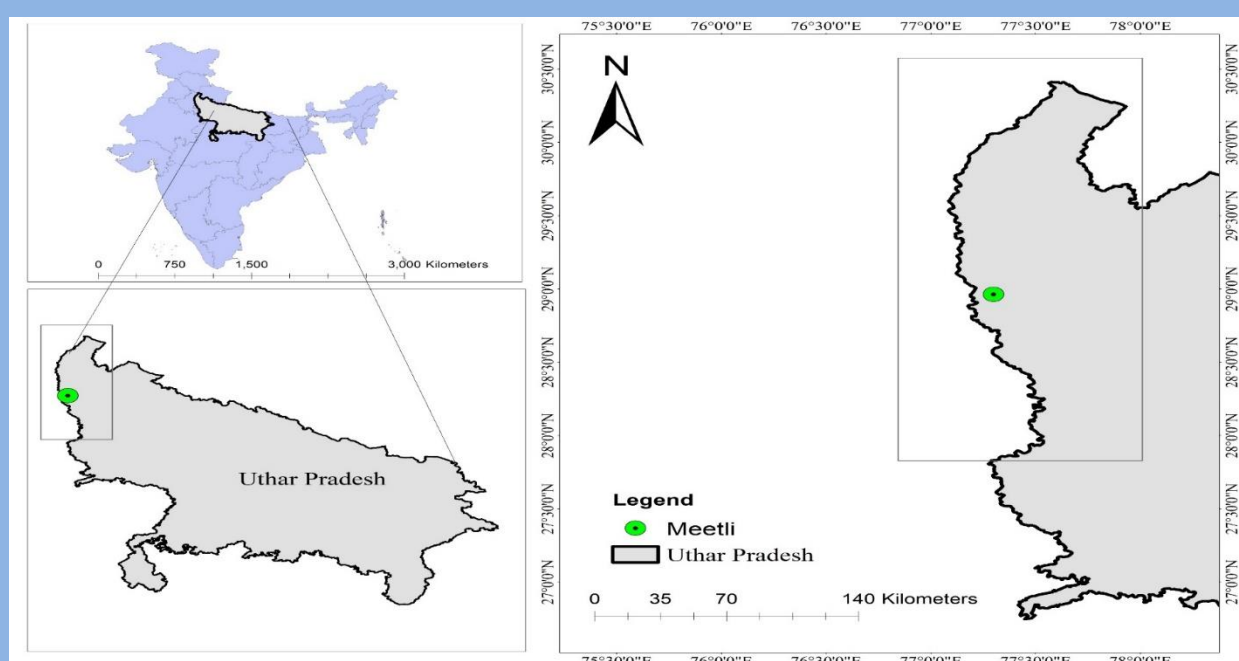


Fig.1. The geographical location of the sampling site.

- The dustfall samples were analyzed for its morphological characteristic using scanning electron microscopy (SEM; Carl Zeiss EVO 40, Germany).

- The images were further analyzed for its morphological features and size distribution with the help of ImageJ software (<https://imagej.nih.gov/ij/download.html>).

- To calculate back trajectories, HYSPLIT Model (<http://www.arl.noaa.gov/ready/hysplit4.html>) was used. These calculated trajectories, as an external link, are then loaded into an open-access GIS (geographic information system software) based software called TrajStat (version 1.4.4R4; http://www.meteothinker.com/products/trajstat_features.html) for further back trajectory cluster calculation. The cluster analysis of sampling-day's back trajectories were performed over a year-long temporal scale from October 2017-september 2018

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Results and discussion

- Dustfall samples' solutions were analysed for pH, electrical conductivity (EC) and total dissolved solids (TDS). All dustfall samples exhibited alkaline nature ($\text{pH} > 7.0$) and annual mean pH was found to be 7.39 ± 0.04 . The annual mean EC was found to be 388.28 ± 26.87 $\mu\text{S}/\text{cm}$, while annual mean TDS found to be 194.77 ± 13.47 ppm .

- SO_4^{2-} found to be the most abundant ion in the water soluble fraction of dustfall samples. K^+ replaced Ca^{2+} as most abundant depositing cation (Fig.2). This relative abundance of K^+ over Ca^{2+} can be attributed the intensive and ubiquitous use of traditional biomass **cookstove** (or *chulha*) at Meetli site. These stoves are daily used by approximately 2/3families (~0.16 billion households) of India. The annual mean dry deposition of dustfall was observed as 3118.5 kg ha^{-1} yr^{-1} (Fig.2).

- The annual mean dry deposition fluxes of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and total inorganic nitrogen (TIN) ($\text{NH}_4^+\text{-N} + \text{NO}_3^-\text{-N}$) were observed as 0.41 ± 0.09 , 6.51 ± 1.58 and 6.92 ± 1.57 kg ha^{-1} yr^{-1} , respectively. Thus, 94.08 % fraction of annual mean TIN is contributed by $\text{NO}_3^-\text{-N}$ (Fig.3) which could be attributed to the fact that nitrogen oxides readily undergoes heterogenous reactions with reactive surface of dust particles (Usher et al.,2003).

- The mean dry deposition fluxes of $\text{NH}_4^+\text{-N}$ during the Post-monsoon, Winter, Pre-monsoon and Monsoon period were observed as 0.91 ± 0.38 , 0.17 ± 0.03 , 0.23 ± 0.05 and 0.47 ± 0.14 kg ha^{-1} yr^{-1} , respectively (Fig.4a) while the mean dry deposition fluxes $\text{NO}_3^-\text{-N}$ during the Post-monsoon, Winter, Pre-monsoon and Monsoon period were observed as 7.50 ± 3.08 , 6.44 ± 0.40 , 3.57 ± 1.29 , and 8.27 ± 4.49 kg ha^{-1} yr^{-1} , respectively (Fig.4b). Moreover, the mean dry deposition fluxes of TIN during the Post-monsoon, Winter, Pre-monsoon and Monsoon period were observed as 8.41 ± 3.00 , 6.61 ± 0.41 , 3.80 ± 1.26 and 8.74 ± 4.45 kg ha^{-1} yr^{-1} , respectively (Fig.4c).

- During both annual and seasonal periods the wet deposition fluxes of $\text{NO}_3^-\text{-N}$ were found to be greater than the $\text{NH}_4^+\text{-N}$ (Fig.4) which could be attributed to the competitive exclusion of $\text{NH}_4^+\text{-N}$ from acid-base neutralization reactions by other strong base cations in dustfall.

- A diving into linear regression analysis between equivalent concentrations of different analyte alkaline cations (K^+ , NH_4^+ , Na^+ , Ca^{2+} , Mg^{2+}) and $\text{SO}_4^{2-} + \text{NO}_3^-$ disclosed the extent of statistical interconnectedness originated from the stoichiometric involvement of these variables in neutralization reactions that ultimately culminate into Nr scavenging through dustfall. Analyzing these linear regression also show the linear regression of $\text{SO}_4^{2-} + \text{NO}_3^-$ against all analyte alkaline cations gave positive R^2 values that were statistically significant ($p < 0.05$) for Na^+ , K^+ and Mg^{2+} and was statistically insignificant ($p > 0.05$) for NH_4^+ .

- These statistically significant and positive R^2 values manifesting the involvement of Na^+ , K^+ and Mg^{2+} in neutralization reaction, while a statistically insignificant R^2 value in case of NH_4^+ become suggestive towards virtual absence of NH_4^+ in the acid- base neutralization reactions of dustfall.

- Particle-size distributions were assessed by analysing SEM images of dustfall samples using ImageJ software (Tiwari et al., 2016). The data calculation from ImageJ showed that the fine-mode particles (aerodynamic diameter ≤ 2.5 μm) were showed 83.85% fraction, and the coarse-mode fraction (aerodynamic diameter $> 2.5 - \geq 10$ μm) shared 14.45% fraction in the dustfall samples. Large particles (aerodynamic diameter > 10 μm), on the other hand, contributed only 1.70% fraction (Fig.5).

- The transport paths of air mases reaching to the site during sampling days were delineated by backward trajectory analysis which showed that the Nr species at this site were contributed from both local and transboundary regions (Fig.6).

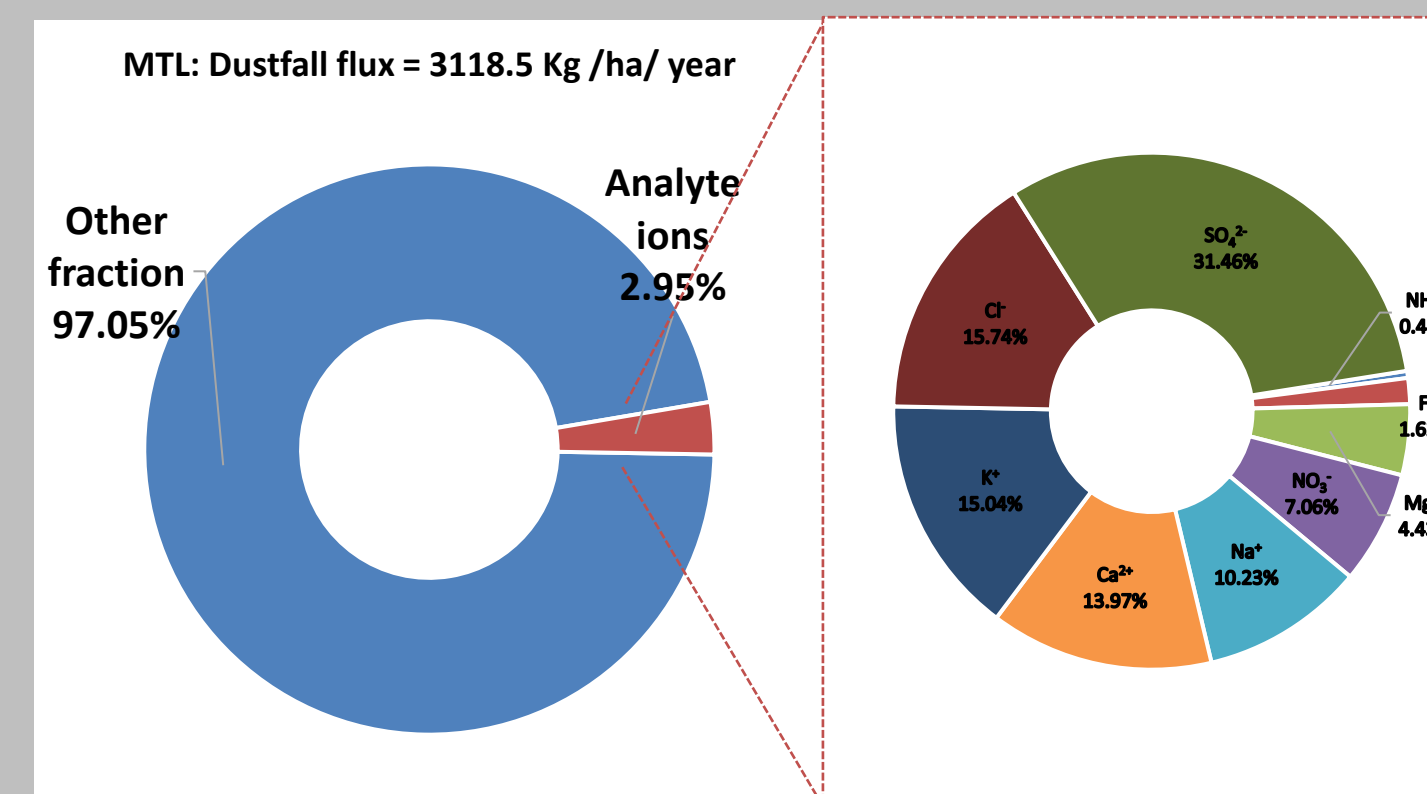


Fig.2 Contribution of major ions to the dustfall fluxes.

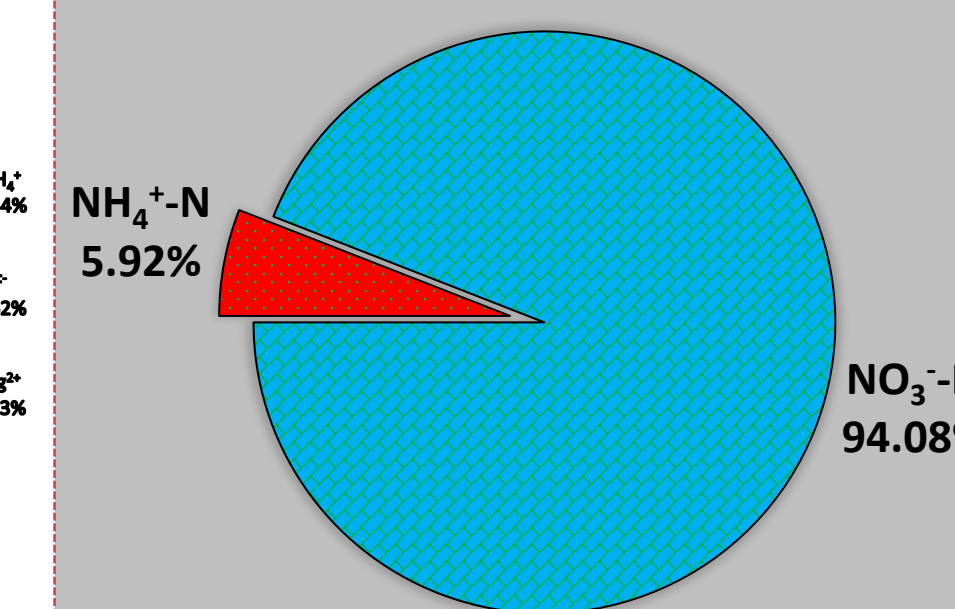


Fig.3. Percent contribution of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ to the total inorganic nitrogen

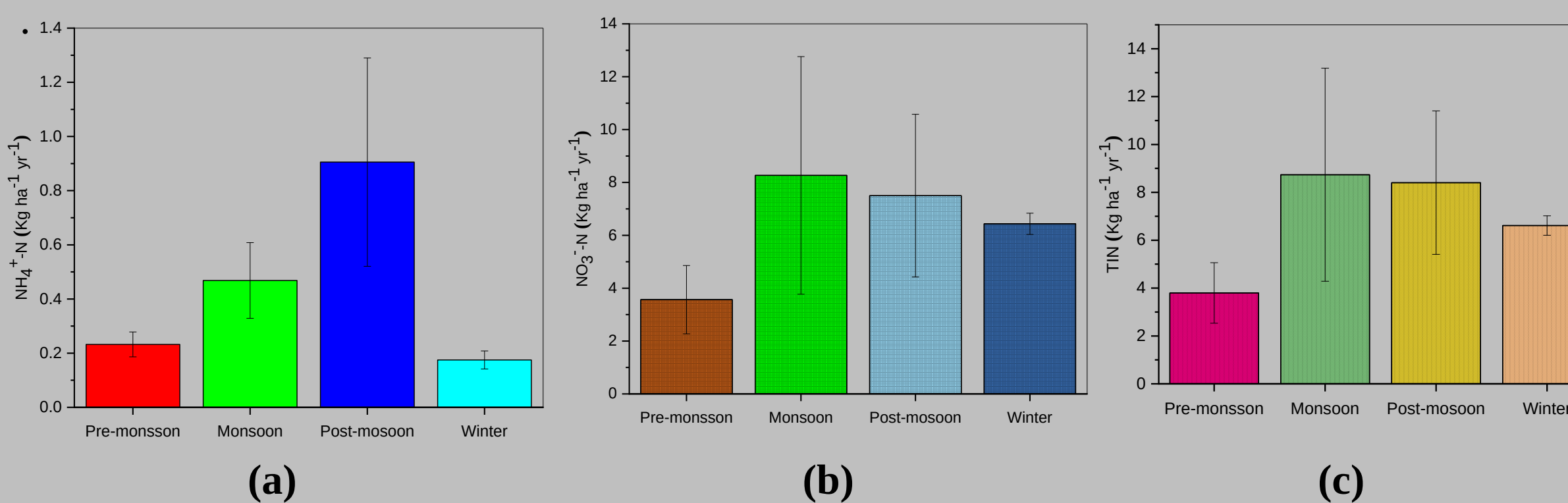


Fig.4. Dry deposition fluxes of (a) $\text{NH}_4^+\text{-N}$, (b) $\text{NO}_3^-\text{-N}$ and (c) TIN during different seasons.

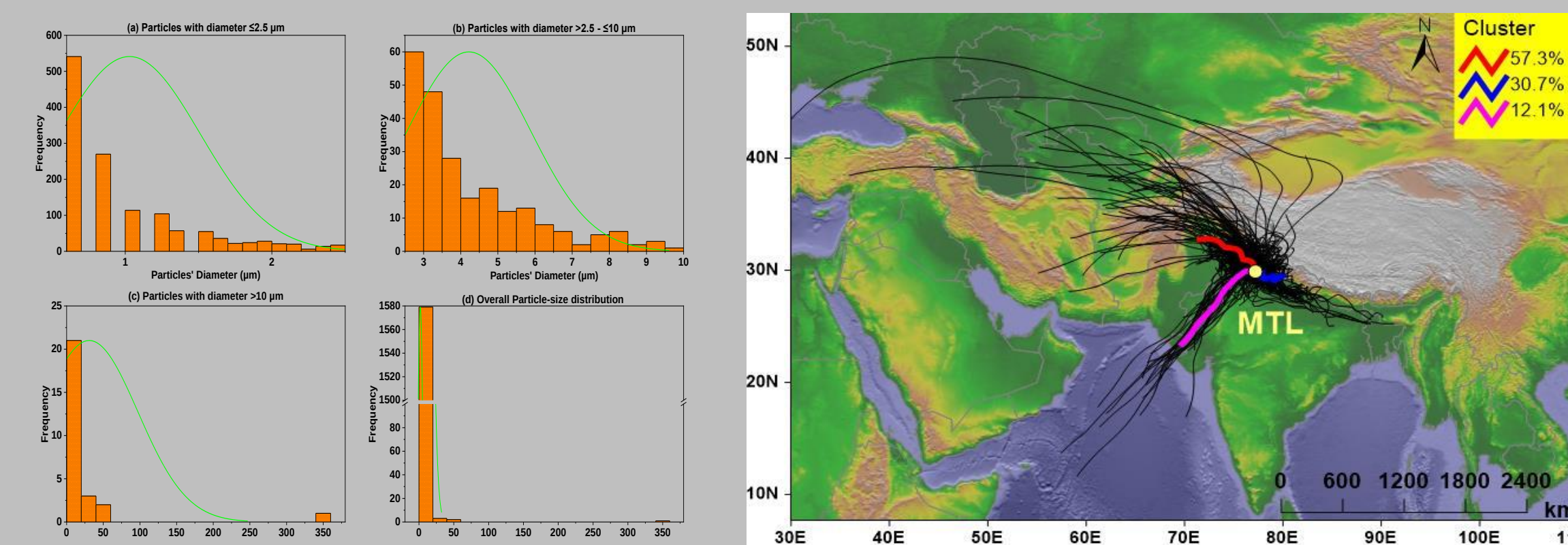


Fig.5. Histograms coupled with bell curves are depicting the distributional pattern of particle-size in dust fall fluxes at MTL site.

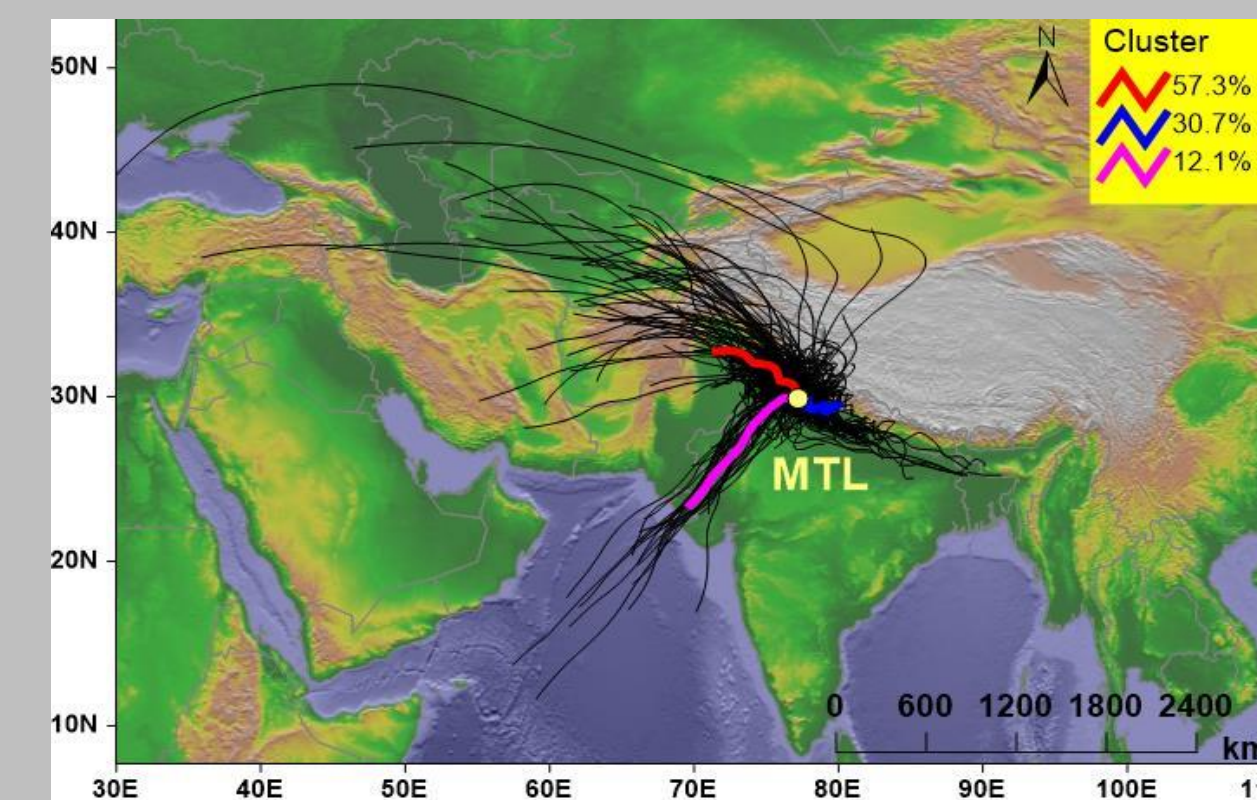


Fig.6 Seventy-two hours backwards-trajectories, computed at an arrival altitude of 0.5 km above ground level for each dust samples during entire sampling periods.

Conclusion

- All dustfall samples exhibited the alkaline nature which could be attributed to the fact that the study domain is a NH_3 emission hotspot and atmospheric dust in this region is rich in alkaline CaCO_3 , both of which can significantly neutralize the acidic fraction of dust aerosols.
- Sulphate found to be the most abundant ion in the water soluble fraction of dustfall samples. Apart from that, K^+ replaced Ca^{2+} as most abundant depositing cation which could be attributed to the intensive biomass burning in the tradition cookstoves specially during the daily meal preparation at this site.
- During both annual and seasonal period, the wet deposition fluxes of $\text{NO}_3^-\text{-N}$ were found to be greater than the $\text{NH}_4^+\text{-N}$, which could be attributed to the competitive exclusion of $\text{NH}_4^+\text{-N}$ from acid-base neutralization reactions by other strong base cations in dustfall.
- The fine-mode particles were found to be dominant to be representative dustfall samples which become suggestive toward the anthropogenic involvement in shaping the dominant mode of particle size in the dustfall fluxes.
- Nr species at this site were contributed from both local and transboundary source regions.