

**WET SCAVENGING OF AIR POLLUTANTS AND ITS  
ACIDIFICATION IMPLICATIONS AT SELECTED  
SITES IN NORTH-WESTERN AND CENTRAL  
HIMALAYAN REGION OF INDIA**

**THESIS SUBMITTED TO**

**JAWAHARLAL NEHRU UNIVERSITY  
FOR THE AWARD OF THE DEGREE OF**

**DOCTOR OF PHILOSOPHY**

**BABLU KUMAR**



**SCHOOL OF ENVIRONMENTAL SCIENCES (SES)  
JAWAHARLAL NEHRU UNIVERSITY (JNU)  
NEW DELHI-110067, INDIA**

**2017**



जवाहरलाल नेहरू विश्वविद्यालय  
Jawaharlal Nehru University  
SCHOOL OF ENVIRONMENTAL SCIENCES

New Delhi-110067

Tele. 011-26704303, 4304

CERTIFICATE

This is to certify that the research work embodied in this thesis entitled “Wet Scavenging of Air Pollutants and Its Acidification Implications at Selected Sites in North-Western and Central Himalayan Region of India” has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. This work is original and has not been submitted in part or full for any other degree or diploma to any institute or university.

**Dr. F. A. Lone**  
(Co-Supervisor)  
Group Leader  
Centre for Climate Change  
and Mountain Agriculture,  
Shalimar Campus

**Bablu Kumar**  
(Candidate)

**Prof. S. Mukherjee**  
(Dean)

**Prof. U.C. Kulshrestha**  
(Supervisor)



**Prof. Saumitra Mukherjee**  
Dean  
School of Environmental Sciences  
Jawaharlal Nehru University  
New Delhi-110067

## **ACKNOWLEDGEMENT**

First and foremost, I would like to express my sincere gratitude to my mentor and supervisor Prof. U. C. Kulshrestha for accepting me in your esteemed lab for my Ph. D. study. He has been a source of inspiration and a guiding light for me throughout my work. His constructive criticism and careful guidance ensured better approach in problem solving. I would like to thank you for encouraging my research and for allowing me to grow as a research scientist. Your advice and view on both scientific research and various dimensions of social issues have been priceless.

I am deeply grateful for the continuous support, insight and patience of my co-supervisor Dr F. A. Lone. Thank you very much sir for helping me to complete my doctoral work. For this Ph. D. work, I would like to thank my doctoral research committee members: Dr. Monika J. Kulshrestha and Prof Dinesh Mohan for their time, interest, and valuable suggestions.

I extend my gratitude towards Prof. S. Mukherjee, present dean, and former deans Prof. I. S. Thakur and Prof. A. K. Atri for their support and suggestions. I am also hugely appreciative to Shahid, Samsulhaq, Kushal, Hippy and Ankush for helping me in sampling and fixing instruments at the sampling sites. I want to thank Prof. Dinesh Mohan's lab members Dr. Ankur, Hemant, Shalini and Rupa for assisting me in chemical analysis.

I want to thank present and former lab members Dr. Pallavi, Dr Sudha, Dr Gyan, Dr Saumya, Yashpal, Disha, Anita, Shabana, Kopal, Anshu, Saurabh, Manisha, Reema, Sudesh, Aizaz, Nasheem, Urjashvi, Mudita, Ankita, yogender, Suraj, Sunaina, Chanthingla, Akanksha and Rasna for sharing their knowledge and ideas with great support and care. I also want to thank them for fun, gossips and discussions on various dimensions. I want to thank lab assistant Ishwar Ji for his great support.

I would like to thank all my friends and classmates for their help. I extend my sincere thanks to SES office staff and all CIF members for their support and generous nature.

Finally, but by no means least, I would like to thank all family members who has always supported, encouraged and believed in me, in all my endeavors with love and unselfishly.

## TABLE OF CONTENTS

<b>Chapters</b>	<b>Page No.</b>
Certificate	
Acknowledgement	
List of Tables	
List of Figures	
List of Acronyms	
<b>Chapter 1 : Introduction</b>	<b>1-19</b>
1.1. Emission of air pollutants	
1.1.1. Particulate matter	
1.2. Transport of pollutants	
1.2.1. Air mass trajectory	
1.3. Deposition of air pollutants	
1.3.1. Factors affecting dry deposition	
1.3.1.2. dustfall	
1.3.2. Wet deposition	
1.3.2.1. Factors affecting wet deposition	
1.3.2.2. Different types of precipitation	
1.4. Snow and snowfall	
1.4.1. Shapes of snow crystal	
1.4.2. Properties of snow	
1.4.3. Different types of snowfall	
1.4.4. Chemistry of snow cover	
1.5. Acid rain	
1.5.1. cause of acid rain	
1.5.2. Effect of acid rain	
1.5.2.1. Acid rain and eutrophication	
1.5.2.2. Effect on soil chemistry	
1.5.3. Acid rain neutralizing agents	

**Chapter 2 : Literature Review** 20-31

2.1. International studies

2.2. National studies

2.3. Motivation of the study

2.4. Significance of the study

**Chapter 3: Material and Methods** 32-43

3.1. Study area

3.1.1. Kothi (North—western Himalaya)

3.1.2. Gulmarg (North—western Himalaya)

3.1.3. Mkteshwar (Central Himalaya)

3.2. Sample collection

3.2.1. Snowfall samples

3.2.2. Aerosol samples

3.2.3. Soil samples

3.2.4. Dustfall samples

3.3. Chemical analysis of snowfall samples

3.3.1. pH, EC and  $\text{HCO}_3^-$  of samples

3.4. QA/QC of data

3.5. Calculation of air mass trajectories

3.6. Statistical analysis

**Chapter 4 : Snow Chemistry** 44-67

4.1. pH of snowmelt samples

4.1.1. Frequency distribution of pH of snowmelt in north western and central Himalaya

4.1.2. Comparison with other study

4.2. Chemical composition of snowmelt

4.2.1. Quality check of data

4.2.2. Major ions of snowmelt

4.2.3. Relative percent of ions

4.2.4. Variation of major ions

- 4.2.5. Comparison of the present study with previous study at the same site
- 4.3. Geographic comparison of ions
- 4.4. Wet deposition fluxes
- 4.5. Acidity of snowmelt and Sources of neutralization
  - 4.5.1. Fractional acidity
  - 4.5.2. Neutralization factor

## **Chapter 5 : Chemical characteristics of aerosol and dustfall**

68-88

- 5.1. Chemistry of aerosol
  - 5.1.1. Chemical composition of aerosol and its relative contribution
    - 5.1.1.1. Major anions
    - 5.1.1.2. Major Cations
    - 5.1.1.3. Relative contribution of water soluble ions
  - 5.1.2. Sources influencing composition of aerosol
    - 5.1.2.1. Marine and non-marine contribution
    - 5.1.2.2. Crustal Influences
  - 5.1.3. Relationship between ionic composition of snow and aerosol
    - 5.1.3.2. Scavenging ratios
- 5.2. Chemistry of dustfall
  - 5.2.1. pH, Concentration and annual dustfall fluxes
    - 5.2.1.1. pH of dustfall samples
    - 5.2.1.2. Concentration of major ions ( $\mu\text{eq}/\text{m}^2/\text{day}$ ) of dustfall
    - 5.2.1.3. Annual deposition fluxes
  - 5.2.2. Ionic ratios in dustfall samples
  - 5.2.3. Neutralization capability of basic components in dustfall samples
    - 5.2.3.1. Neutralization ratios
    - 5.2.3.2. Regression analysis of acidic vs basic cations

## **Chapter 6 : Source identification (Local vs Long Range Transport)**

89-124

- 6.1. Marine and Non-marine influences
  - 6.1.1. Marine contribution

- 6.1.2. Non-marine contribution
- 6.1.3. Average contribution of different source categories
- 6.2. Clusterwise chemical composition of snowmelt
  - 6.2. 1. Sectorwise distribution of airmasses and its pH with major ions at Kothi
  - 6.2.2. Sectorwise distribution of airmasses and its pH with major ions at Gulmarg
- 6.3. LCLUC and its influence on snow chemistry
- 6.4. Statistical approach for source identification
  - 6.4.1. Kothi site
    - 6.4.1.1. Correlation analysis
    - 6.4.1.2. Principal component analysis
  - 6.4.2. Gulmarg site
    - 6.4.2.1. Correlation analysis
    - 6.4.2.2. Principal component analysis

## **Chapter 7: Soil chemistry and its relationship to snowmelt**

125-144

- 7.1. Soil characteristics
  - 7.1.1. Spatial distribution of soil pH
  - 7.1.2. Electrical conductivity of the soil
  - 7.1.3. Variability of soil CEC
  - 7.1.4. Major chemical components of the soil
    - 7.1.4.1. Soil nitrogen
    - 7.1.4.2. Soil sulphur
    - 7.1.4.3. Soil chloride
    - 7.1.4.4. Divalent cations of the soil
    - 7.1.4.5. Monovalent cations of the soil
- 7.2. Changes in soil nutrients level after snowmelt
  - 7.2.1. Factors influencing soil nutrient levels
  - 7.2.2. Possibility of nutrient leaching due to snowmelt pH
  - 7.2.3. Soil nutrients and role of CEC of soil
- 7.3. Relative deposition of dry deposition and wet deposition
  - 7.3.1. Calculation of relative percent deposition fluxes

7.3.2. LULCC effect on the spatial variability of deposition fluxes

<b>Chapter 8 : Conclusion</b>	145-150
<b>Refernces</b>	151-167
<b>Appendices</b>	
<b>List of Publications and Presentations</b>	



## LIST OF TABLES

S. No.	Title	Page No.
<b>Table 3.1</b>	Operating conditions employed for the analysis of ions by Ion Chromatograph.	38
<b>Table 3.2</b>	Calibration equation, correlation coefficient and analytical precision for different ionic species.	39
<b>Table 3.3</b>	Relative percent ion difference to check quality of data (WMO, 1994).	42
<b>Table 4.1</b>	Geographical comparison of pH of snowmelt samples.	47
<b>Table 4.2</b>	Average concentration $\pm$ SD of major ions along with pH, EC of snowmelt samples.	50
<b>Table 4.3</b>	Geographical comparison of major ions of snowmelt samples.	63
<b>Table 4.4</b>	Average wet deposition fluxes at Kothi, Gulmarg and Mukteshwar ( $\mu\text{eq}/\text{m}^2/\text{day}$ ).	65
<b>Table 5.1</b>	Concentration of major ions ( $\text{nmol}/\text{m}^3$ ) of aerosol.	69
<b>Table 5.2</b>	Geographical comparison of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ at various sites.	71
<b>Table 5.3</b>	Na ratios in aerosol sample at all sites.	75
<b>Table 5.4</b>	Scavenging ratios for major ions of concurrent aerosol and snowfall sample.	78
<b>Table 5.5</b>	Concentration of major ions ( $\mu\text{eq}/\text{m}^2/\text{day}$ ) of dustfall.	80
<b>Table 5.6</b>	Annual deposition fluxes of water soluble dustfall samples ( $\text{meq}/\text{m}^2/\text{anum}$ ).	82

<b>Table 5.7</b>	Regression coefficients of major base cations vs $\text{nssSO}_4^{2-} + \text{NO}_3^-$ at all sites (* denotes significant correlation).	88
<b>Table 6.1</b>	Sodium ratios of snowmelt and percent Sea salt fraction (ssf) and non sea salt fraction (nssf) of major ions in snowmelt at Kothi (a), Gulmarg (b) and Mukteshwar (c).	90
<b>Table 6.2</b>	Percent contribution of Marine Fraction, Crustal Fraction (CF) and Anthropogenic Fraction (Anthro) of various ionic species at Kothi (a), Gulmarg (b) and Mukteshwar (c).	95
<b>Table 6.3</b>	Average of pH and major ions ( $\mu\text{eq/l}$ ) in snow for trajectory classes at Kothi.	102
<b>Table 6.4</b>	Average concentrations ( $\mu\text{eq/l}$ ) of major ions and pH during different clusters at Gulmarg.	111
<b>Table 6.5</b>	Correlation coefficients of major ions in snowmelt samples at Kothi.	118
<b>Table 6.6</b>	Principal component analysis of major ions in snowmelt samples at Kothi.	120
<b>Table 6.7</b>	Correlation coefficients of major ions in snowmelt samples at Gulmarg.	122
<b>Table 6.8</b>	Principal component analysis of major ions in snowmelt samples at Gulmarg.	124
<b>Table 7.1</b>	CEC (cmol/kg) of soil at different sites of different categories in India.	128
<b>Table 7.2</b>	Major ions of soil (g/ton) before and after snowmelt (Kb- Kothi sample before snowmelt, Ka- Kothi sample after snowmelt, Gb- Gulmarg sample before snowmelt, Ga- Gulmarg sample after snowmelt, Mb- Mukteshwar sample before snowmelt, Ma- Mukteshwar sample after snowmelt) (n=4).	129
<b>Table 7.3</b>	Relative percent loss of soil nutrients after snowmelt.	136

## LIST OF FIGURES

S. No.	Title	Page No.
<b>Fig. 1.1</b>	Primary and secondary air pollutants ( <a href="https://www.sepa.org.uk">https://www.sepa.org.uk</a> ).	2
<b>Fig. 1.2</b>	Size distribution of airborne particulate matter (Mathys et al., 2001).	3
<b>Fig. 1.3</b>	Application of air mass trajectories in various fields (Kulshrestha and Kumar, 2014).	5
<b>Fig. 1.4</b>	Role of dust in processes affecting climate (Rodriguez et al., 2012).	7
<b>Fig. 1.5</b>	Conceptual Framework of wet deposition processes (Seinfeld and Pandis, 2006).	8
<b>Fig. 1.6</b>	Different shapes of ice crystal.	11
<b>Fig. 1.7</b>	SEM images of snow crystal showing different snowflake formation ( <a href="https://nsidc.org">https://nsidc.org</a> , Agricultural Research Service, United States Department of Agriculture).	13
<b>Fig. 1.8</b>	Chemical and physical processes governing the transformation of composition of snowcover (Pomeroy et al., 2005).	15
<b>Fig. 1.9</b>	Diagram showing possible pathway of acid rain formation (Botkin and Keller, 2010).	16
<b>Fig. 1.10</b>	Below cloud scavenging of pollutants by dust particles (Kulshrestha, 2007).	19
<b>Fig. 2.1</b>	Measured average annual S deposition in precipitation for 2005-2007 ( $\text{Kg S ha}^{-1}\text{a}^{-1}$ ) (Vet et al., 2014).	21
<b>Fig. 2.2</b>	Measured average annual N deposition in precipitation for 2005-2007 ( $\text{Kg N ha}^{-1}\text{a}^{-1}$ ) (Vet et al., 2014).	22
<b>Fig. 2.3</b>	$\text{SO}_4^{2-}$ Concentration ( $\mu\text{eq/l}$ ) in rain. The measurement values of 2000 year at various rural and suburban site of India are compared with the concentration obtained through MATCH model (Kulshrestha et al., 2005).	26
<b>Fig. 2.4</b>	$\text{NO}_3^-$ Concentration ( $\mu\text{eq/l}$ ) in rain. The measurement values of 2000	27

year at various rural and suburban site of India are compared with the concentration obtained through MATCH model (Kulshrestha et al., 2005).

<b>Fig. 2.5</b>	Spatial distribution of annual trends in temperature in the greater Himalayan region for 1970–2000 periods (Eriksson et al., 2009).	29
<b>Fig. 2.6</b>	Rapid retreat of glaciers of greater Himalaya comparing with the global average (Eriksson et al., 2009).	30
<b>Fig. 3.1</b>	Sites of sample collection.	33
<b>Fig. 3.2</b>	pH meter.	36
<b>Fig. 3.3</b>	Ion Chromatograph model Metrohm 883 used for the determination of ions in this study.	37
<b>Fig. 3.4</b>	Chromatogram of anions (a) and cations (b) for standard (2 ppm). (Retention time is shown above the peak).	40
<b>Fig. 3.5</b>	Ion Chromatogram of a (a) sample (anions) and (b) sample (cations).	41
<b>Fig. 4.1</b>	Percent frequency distribution of pH of snowmelt (a) Kothi (b) Gulmarg (c) Mukteshwar.	45
<b>Fig. 4.2</b>	Scatter plot showing ion balance between sum of anions and cation.	49
<b>Fig. 4.3</b>	Scatter plot showing conductivity balance between measured conductivity and calculated conductivity.	49
<b>Fig. 4.4</b>	Centre line indicates median, box plot shows 25 - 75 <sup>th</sup> percentile and bar indicates minimum & maximum values. Stars and circle denote the outliers.	52
<b>Fig. 4.5</b>	Percent contribution of major ions (a) Kothi (b) Gulmarg (c) Mukteshwar.	54
<b>Fig. 4.6</b>	Variation of Ca <sup>2+</sup> , SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> and NH <sub>4</sub> <sup>+</sup> in snowmelt samples at Kothi, Gulmarg and Mukteshwar.	56
<b>Fig. 4.7</b>	Comparison of the present study with previously reported 1986-87 values by Naik et al. (1995).	59
<b>Fig. 4.8</b>	Relative % increase in the concentrations of major ions since 1986-87.	60
<b>Fig. 4.9</b>	Neutralization factor at present sites.	66
<b>Fig. 5.1</b>	Major anions in water soluble aerosol.	70
<b>Fig. 5.2</b>	Major cations in water soluble aerosol.	72

<b>Fig. 5.3</b>	Percentage distribution of major ions in aerosol.	74
<b>Fig. 5.4</b>	Enrichment factor of aerosol with respect to soil samples.	76
<b>Fig. 5.5</b>	pH of water soluble dustfall samples.	79
<b>Fig. 5.6</b>	Ionic ratios at the present sites in dustfall samples.	83
<b>Fig. 5.7</b>	Neutralization factor of major basic species in water soluble dustfall samples.	85
<b>Fig. 5.8</b>	Regression analysis of $\text{nssSO}_4^{2-} + \text{NO}_3^-$ vs $\text{nssCa}^{2+}$ and $\text{nssSO}_4^{2-} + \text{NO}_3^-$ vs $\text{nssMg}^{2+}$ .	87
<b>Fig. 6.1</b>	Schematic diagram showing the approach of differentiation of non-sea salt fractions into Anthro and crustal associated fractions (CF) of various ionic components. ( $x = \text{F}^-, \text{Cl}^-, \text{NO}_3^-, \text{SO}_4^{2-}, \text{Ca}^{2+}, \text{NH}_4^+, \text{Mg}^{2+}, \text{K}^+, \text{Na}^+$ ), $\text{ssf} = \text{sea salt fraction}$ , $\text{nss} = \text{non-sea salt fraction}$ .	93
<b>Fig. 6.2</b>	Average contributions of different source categories at Kothi (a), Gulmarg (b), Mukteshwar (c).	97
<b>Fig. 6.3</b>	(a-f). Typical examples of six different air mass trajectories arriving at Kothi site. NAO = North Atlantic Ocean origin, Af = African origin, ME = Middle East origin, Eu = European origin (Eu), InW = Western India origin, Np = Nepal origin .	99
<b>Fig. 6.4</b>	Percent frequency of snowfall events occurring during different trajectory clusters at Kothi.	100
<b>Fig. 6.5</b>	Variation of pH with (a) $\text{nssSO}_4^{2-}/\text{nssCa}^{2+}$ (b) $\text{NO}_3^-/\text{nssCa}^{2+}$ at Kothi.	104
<b>Fig. 6.6</b>	(a-f). Examples of six different air mass trajectories arriving at the site using HYSPLIT model at Gulmarg site. NAO = North Atlantic Ocean origin, Af = African origin, ME = Middle East origin, Eu = European origin (Eu), InW = Western India origin , Pk = Pakistan origin .	108
<b>Fig. 6.7</b>	Percent frequency of snowfall events occurring during different trajectory clusters at Gulmarg.	110
<b>Fig. 6.8</b>	Variation of pH with (a) $\text{nssSO}_4^{2-}/\text{nssCa}^{2+}$ (b) $\text{NO}_3^-/\text{nssCa}^{2+}$ at Gulmarg.	112
<b>Fig. 6.9</b>	LCLUC at Kullu district (Kothi site) in year of 1989 and 2005 (Vishwa et al 2013).	116
<b>Fig. 6.10</b>	Percent LCLUC at Kullu district in Himachal Pradesh (Source: Vishwa et al 2013).	117
<b>Fig. 7.1</b>	Average pH of soils before and after snowmelt (Kb- Kothi sample before snowmelt, Ka- Kothi sample after snowmelt, Gb- Gulmarg sample before snowmelt, Ga- Gulmarg sample after snowmelt, Mb-	126

	Mukteshwar sample before snowmelt, Ma- Mukteshwar sample after snowmelt) (n=4).	
<b>Fig. 7.2</b>	Average concentration of soil $\text{NO}_3^-$ and $\text{NH}_4^+$ before snowmelt (n=4).	130
<b>Fig. 7.3</b>	Average concentration of soil $\text{SO}_4^{2-}$ before snowmelt (n=4).	131
<b>Fig. 7.4</b>	Average concentration of soil $\text{Cl}^-$ before snowmelt (n=4).	132
<b>Fig. 7.5</b>	Average concentration of soil $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ before snowmelt (n=4).	133
<b>Fig. 7.6</b>	Average concentration of soil $\text{Na}^+$ and $\text{K}^+$ before snowmelt (n=4).	134
<b>Fig. 7.7</b>	Relative percent loss of major soil cations ( $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ ).	136
<b>Fig. 7.8</b>	Regression analysis between loss of soil cation and $\text{H}^+$ of snowmelt.	138
<b>Fig. 7.9</b>	Relationship between CEC of soil and loss of soil cations.	140
<b>Fig. 7.10</b>	Regression analysis between the loss of soil cations and change in soil pH.	141
<b>Fig. 7.11</b>	Relative percent deposition of aerosol, dust and snowmelt at the sampling sites.	143

## **LIST OF ACRONYMS**

<b>µeq/l</b>	Microequivalent per litre
<b>µm</b>	Micro metre
<b>µeq/m<sup>2</sup>/day</b>	Microequivalent per metre square per day
<b>ADF</b>	Annual Deposition Fluxes
<b>ANOVA</b>	Analysis of Variance
<b>CEC</b>	Cation exchange capacity
<b>CF</b>	Crustal Associated fractions
<b>CPCB</b>	Central Pollution Control Board
<b>EC</b>	Electrical Conductivity
<b>EF</b>	Enrichment Factor
<b>g/ton</b>	Gram per ton
<b>HYSPLIT</b>	Hybrid Single Particle Lagrangian Integrated Trajectory
<b>IC</b>	Ion Chromatograph
<b>l/min</b>	Litre Per minute
<b>LRT</b>	Long Range Transport
<b>LULCC</b>	Land Use and Land cover Change
<b>meq/m<sup>2</sup>/anum</b>	Milli equivalent per metre square per anum
<b>ml</b>	Milli litre
<b>NAAQM</b>	National Ambient Air Quality Monitoring
<b>nmol/m<sup>3</sup></b>	Nano mole per metre cube
<b>nss</b>	Non sea salt
<b>PC</b>	Principal Component
<b>PM</b>	Particulate matter
<b>SR</b>	Scavenging Ratios

*Chapter 1*  
*Introduction*



---

## INTRODUCTION

The introduction chapter starts with background information on emission of atmospheric pollutants by various natural and anthropogenic processes / activities. These pollutants might have impacted very far away from its sources so considering this point air mass trajectory of air pollutants has been discussed. Pollutants either local or transported will be deposited via two major mechanism dry deposition and wet deposition. Among wet deposition, snowfall is one of very effective mechanism for removal of atmospheric pollutants. Considering its importance, the properties and chemistry of snow crystals have been discussed. At the end of this chapter, acidic precipitation has been discussed including its cause, effect on various ecosystems along with major neutralizing agents.

### 1.1. Emission of Air Pollutants

Air pollutants can be emitted by various natural and anthropogenic sources. There are following major natural sources of pollutants-

- Volcanoes- Source of ashes, smoke, SO<sub>2</sub>, CO<sub>2</sub> etc.
- Ocean- Source of various sea salt sprays
- Land sources- Source of dust particles
- Forest fire- Source of CO<sub>2</sub>, NO<sub>2</sub>, SO<sub>2</sub> etc.

There are following main anthropogenic i.e. man made sources of pollutants-

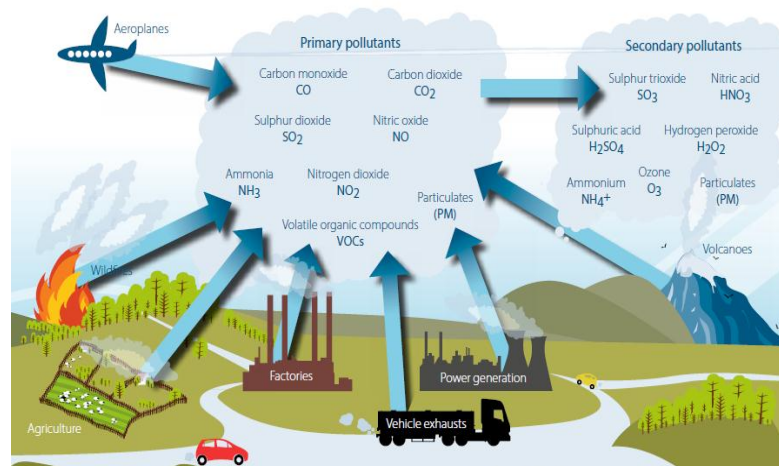
- Thermal power plant- Source of soot, SO<sub>2</sub> etc.
- Automobile – Source of CO, NO<sub>x</sub>, unburned hydrocarbon, O<sub>3</sub> etc.
- Agriculture- Source of NH<sub>3</sub>, CH<sub>4</sub> etc.

On the basis of its origin, air pollutants are classified into primary and secondary air pollutants (Fig. 1.1). Primary pollutants are those pollutants which are emitted directly from the sources in the atmosphere (Seinfeld and Pandis, 2006). There are following main primary pollutants-

- ❖ Compounds of nitrogen such as NO, N<sub>2</sub>O, NH<sub>3</sub> etc.
- ❖ Compounds of sulphur such as SO<sub>2</sub>, H<sub>2</sub>S etc.
- ❖ Compound of carbon like CO, CO<sub>2</sub>, CH<sub>4</sub>, VOCs.
- ❖ Compounds of halogen like CFCs
- ❖ Particulate matter

Those pollutants which are formed from primary pollutants under suitable meteorological conditions are called secondary pollutant. There are following main secondary pollutants-

- ❖ NO<sub>2</sub> and HNO<sub>3</sub> from NO.
- ❖ SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> from SO<sub>2</sub>.
- ❖ O<sub>3</sub> from VOCs and NO<sub>2</sub>.
- ❖ SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> aerosol.
- ❖ Particulate matter (PM).

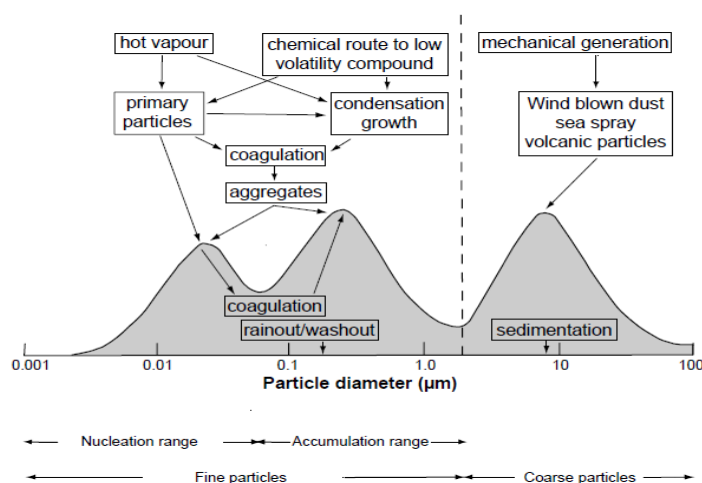


**Fig. 1.1:** Primary and secondary air pollutants (<https://www.sepa.org.uk>).

### 1.1.1. Particulate matter

Particulate matter is solid or liquid particles suspended in air. It consists of wide range of particles of different sizes, sources and chemical composition. These particles are generated by various natural and anthropogenic processes. The major man made processes/activities include emissions from smelter, power plants, mining operation and other combustion process.

The size of particles varies from 0.001 to 100  $\mu\text{m}$  (Fig. 1.2). The size of particle is very important parameter related to its transport, deposition with environmental and health effects. On the basis of size, it is broadly classified into two types- fine and coarse particles. Those particles having aerodynamic diameter less than 2.5  $\mu\text{m}$  are called fine particles while those having size larger than 2.5  $\mu\text{m}$  are called coarser particles (Pacyna, 1995). Generally, fine mode particulates are formed from anthropogenic process and chemically they are nitrate, sulphate, metals etc. whereas coarse mode particulates mainly generated from natural sources made of Ca, carbonates, Si, Fe etc. (Pilinis and Pandis, 1995). The fine modes of particles are further divide into nucleation and accumulation mode. Generally, nucleation mode of aerosols is formed by gas to particle conversion or condensation of hot vapours while accumulation mode of aerosols is generated from nucleation mode by coagulation or condensation processes. PM falling in coarser modes are generally generated by mechanical processes include wind blow dust, sea particles, volcanic particles etc.



**Fig. 1.2:** Size distribution of airborne particulate matter (Mathys et al., 2001).

## 1.2. Transport of air pollutants

Once air pollutants in form of either gaseous or particulate emitted in the atmosphere it might have impact very far away also. The long range transport of pollutants complicate the effort of policy maker to control air pollution since it is very difficult to distinguish local vs long range transported pollutants. But now a days air mass trajectory technique is used which is very helpful in differentiating local and transported pollutants.

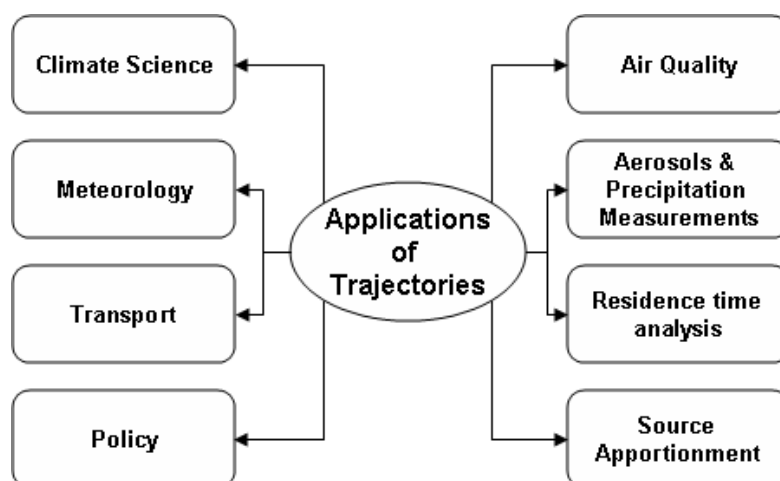
### 1.2.1. Air mass trajectory

A trajectory can be defined by a differential equation-

$$dr/dt=v[r(t)]$$

where  $r(t)$  is position vector at time  $t$ ,  $v$  is the velocity field.

Airmass trajectory is calculated to show the pathway of an infinitesimally air parcel through a centerline of an advected airmass having vertical and horizontal dispersion. Tracing of the pathway followed by an air parcel upwind from the selected coordinates is termed as 'backward air trajectory' while calculation of best possible pathway to be followed downwind from the selected coordinates in due course of time is called as 'forward trajectory'. The calculation of backward air trajectory using Langrangian approach easier and computationally cheap as it excludes the influence of upwind on the receptor site. There are various models such as HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory), FLEXTRA (FLEXible TRAjectories) model etc. which has been used for the calculation of the trajectories



**Fig. 1.3:** Application of airmass trajectories in various fields (Kulshrestha and Kumar, 2014).

In the beginning, trajectories were used to find out the source region and transport processes of air pollution but with the advancement of knowledge, trajectories are found useful to address various aspects related to atmosphere and environment. As shown in Fig. 1.3 trajectories are applied in various fields such as meteorology (Riccio et al., 2007), climatology (Shadbolt et al., 2006), transport of pollutants (Rodhe et al., 1981; Draxler and Taylor 1982), air quality (Gebhart et al., 2011; ), source apportionment (Harrison et al. 2000), residence time analysis (Escudero et al., 2011), aerosol measurements (Reddy et al., 2008), precipitation chemistry (Granat et al., 2002; Satyanarayna et al., 2010) and policies (Dvorska et al., 2009) etc.

### 1.3. Deposition of air pollutants

Deposition of air pollutants is the process by which pollutants are collected or deposited on to the surfaces such as ground, road, vegetation, mountains and water bodies etc. The pollutants are deposited via two processes viz dry and wet deposition. In general very large particles are settled quickly through sedimentation which is an important dry deposition process (as in case of dust fall), while small particles are removed by diffusion.

## **1.3.1. Dry deposition**

Dry deposition is a major pathway by which trace gases and particles are removed from the atmosphere. It is the transport of gaseous pollutants from the atmosphere onto the surfaces without involving precipitation. Dry deposition of particles is also important especially in the region where dry weather conditions prevail.

### **1.3.1.1. Factors affecting dry deposition**

The relative importance of dry deposition of species depends on the following factors (Seinfeld and Pandis, 2006)-

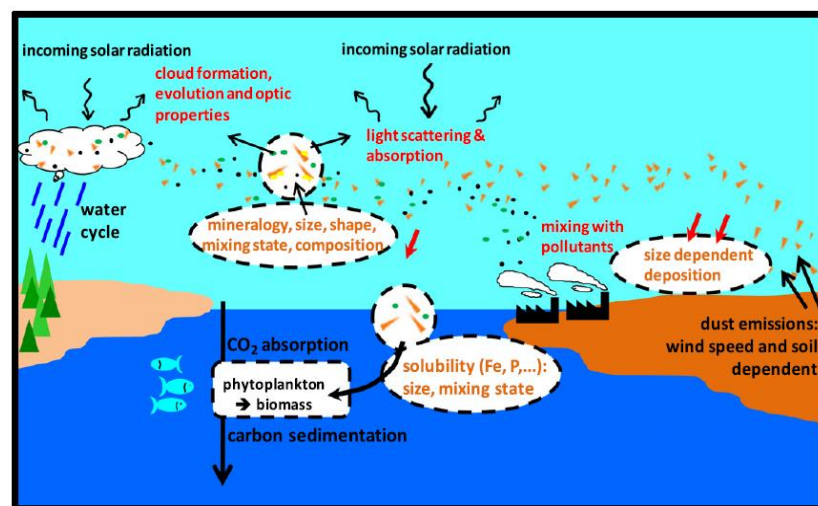
- i. Physical state and chemical properties of the species.
- ii. Size and shape of particles.
- iii. Turbulence and metamorphic factor.
- iv. Solubility of the species in water.
- v. Surface characteristics.

The level of turbulence in the atmosphere governs the rate at which species are settled down to the surface. Solubility and chemical reactivity of gases may affect their uptake at the surfaces, whereas size, density and shape may determine the deposition. The surface smoothness/roughness is very important factor in dry deposition of gases and particles.

### **1.3.1.2. Dustfall**

Those solid particles in the atmosphere which settle down due to its own weight are called as atmospheric dust. They are of varying size and classified as ultrafine ( $<0.1 \mu\text{m}$ ), fine ( $0.1-1 \mu\text{m}$ ) and coarse particles ( $> 1 \mu\text{m}$ ) (Rodriguez et al., 2012). It can be emitted by natural as well as anthropogenic sources by primary or secondary origin.

Dust is one of the most important components in the atmosphere influencing air quality, climate and biogeochemical cycle of the earth (IPCC, 2007) (Fig. 1.4). It can scatter as well as absorb radiations which depend on its size, shape and mineralogical composition (Redmond et al., 2010). Dust particles can act as ice and cloud condensation nuclei thus it is associated with formation of clouds (Herich et al., 2009). Dusts deposited in ocean play an important role in primary productivity and thus help in sequestration of atmospheric CO<sub>2</sub> (Mills et al., 2004). Poor air quality in cities due to dust coming from desert are responsible for increasing respiratory and other diseases which enhances mortality rate (Lee et al., 2010; Rodriguez et al., 2012).



**Fig. 1.4:** Role of dust in processes affecting climate (Rodriguez et al., 2012).

### 1.3.2. Wet deposition

The process of removal of materials by cloud, fog, drops, rain and snow from the atmosphere is known as wet deposition. In wet deposition, atmospheric hydrometeors scavenge aerosol particles.

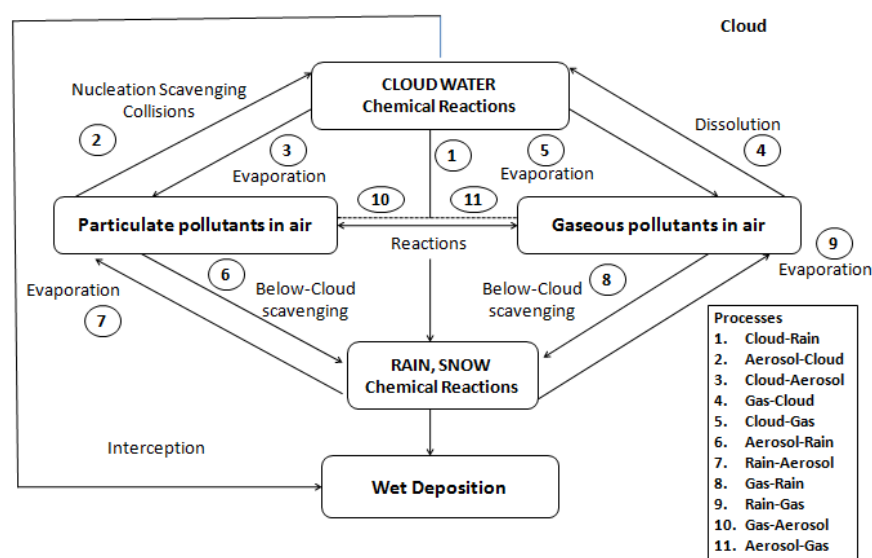
Figure 1.5 shows conceptual framework of the wet deposition process. It highlights three major steps for wet deposition-

- i. Species in the atmosphere come in contact with condensed water

- ii. Then the species are condensed by hydrometeors.
- iii. Finally, these are deposited onto the earth surface. It is likely that both gaseous and aerosol species compound may undergo chemical transformations during these steps.

### 1.3.2.1. Factors affecting wet deposition

Wet removal pathways depend on multiple and composite processes involving numerous physical phases (Seinfeld and Pandis, 2006). Above figure indicates that the variety of factors influence wet removal process. Figure 1.5 represents a set of complex reversible processes operating under suitable meteorological conditions leading to wet deposition. It is evident that aerosol phase in the form of pollutant is an important part that provides a way for gaseous pollutants to undergo wet deposition. Both the types in-cloud and below-cloud scavenging are necessary, which are grown by chemical and physical transformations and include evaporation, dissolution and set of chemical reactions.



**Fig. 1.5:** Conceptual Framework of wet deposition processes (Seinfeld and Pandis, 2006).

Wet deposition is broadly classified into two types-



## **In-cloud scavenging**

Scavenging of gases and aerosols by clouds and raindrops inside the clouds is called in-cloud scavenging. Pollutants are trapped and dissolved into the cloud and droplets inside the raining clouds and become part of cloud water system (Fig. 1.5). During cloud formation, gaseous species such as SO<sub>2</sub>, HNO<sub>3</sub> vapors and NH<sub>3</sub> etc. are effectively removed by dissolution into cloud water drops. Deliquescent aerosols (e.g. sea salt aerosols) are also favorably scavenged during cloud formation.

## **Below –cloud scavenging**

Removal of gases and particles (present below the clouds) by falling raindrops is called as below cloud scavenging. During rain, soluble gases and aerosols are dissolved into falling raindrops and are deposited onto the ground. Below cloud removal is influenced by the factors such as intensity of rain, size of rain drop and physical and chemical properties of scavenged species. Scavenging coefficient depends upon the size of the rain drop. Smaller rain drops scavenge more efficiently.

Below cloud scavenging is considered as an effective removal process for particulate matter in Indian conditions. In general in India, the loadings of soil dust in the atmosphere are too high due to which average total suspended particulates (TSP) in air is observed as high as 500-700 µg m<sup>-3</sup>. When it rains, the suspended particulate matter is removed by the droplet which drastically reduces TSP levels in air. Some pollutants are accumulated in air during non-rainy period which are also scavenged by rain through below cloud scavenging process.

### **1.3.2.2. Different types of precipitation**

There are following types of precipitation (Ahrens, 2007)-

1. **Drizzle**- A form of precipitation in which tiny water drops fall slowly having diameter less than 0.5mm (Ahrens, 2007).

2. **Rain**- Precipitation in which liquid water drop fall with diameter greater than 0.5 mm.
3. **Snow**- Precipitation in complex hexagonal ice crystal which generally join to form snowflake.
4. **Sleet** – An ice pellet which forms when cold rain drops or partially melted snowflake falls in deep subfreezing layer.
5. **Freezing rain or Glaze**- Falling super cooled liquid drops in relatively shallow subfreezing layer which forms ice immediately on striking a cold object.
6. **Rime or Hoarfrost**- An accumulation of white granular ice which forms when super cooled cloud or fog droplets strikes an object having temperature below freezing.
7. **Snow grains**- A small white opaque ice particles with diameter less than 1 mm and neither shatter nor bounce on striking a hard surface.
8. **Graupel or snow pellets**- A brittle white opaque ice particles with diameter less than 5 mm in the form of shower which bounce after string a hard surface.
9. **Hail** – Transparent or partially opaque ice crystals in round shape or irregular lumps with the largest form of precipitation having diameter of  $\frac{3}{4}$  inches or greater.

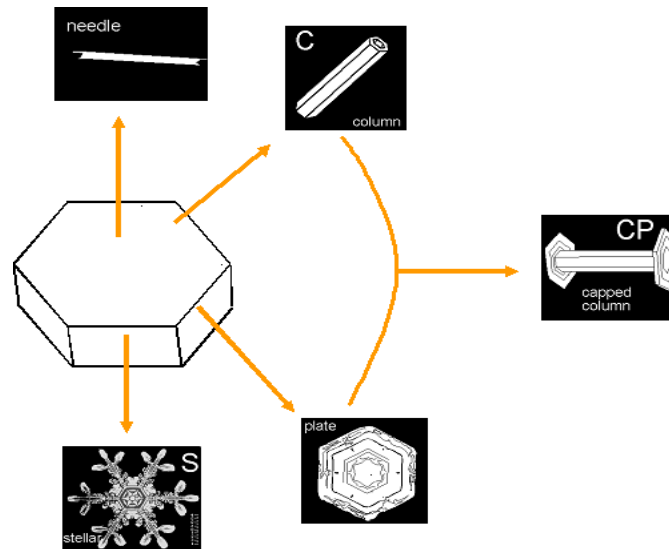
### 1.4. Snow and snowfall

Crystals of ice form on ice nuclei in subfreezing air. Particles which serve as ice nuclei are generally clay minerals, bacteria and even existing ice crystal. Snow is a complex hexagonal shape of packed ice crystal (Ahrens, 2007). Generally, snow joined together to form snowflakes. Snowfall occurs in certain region of world only but it influences regional weather to great extent. The snow pack can contain records that include climate proxies, deposition rate of aerosol contamination and photochemical alterations.

#### 1.4.1. Shapes of snow crystal

Snow crystal may take different shapes like dendrite, column, plate, needle etc. (Fig. 1.6). The shape of crystal is depending on relative humidity and air temperature (Ahrens, 2007).

The most common dendritic shape of snow generally form when temperature is around  $-12$  to  $-16^{\circ}\text{C}$ .



**Fig. 1.6:** Different shapes of ice crystal.

### 1.4.2. Properties of snow

There are following unique properties of snow-

1. **Physical state**- Below  $0^{\circ}\text{C}$  water exist primarily as solid i.e. ice while above  $0^{\circ}\text{C}$  it exists as liquid or vapour. At  $0.01^{\circ}\text{C}$  and  $4.58\text{ mm}$  of Hg, water exist in three forms i.e. ice, liquid and vapour which is called triple point.
2. **Latent heat**- The latent heat of fusion of snow is approx.  $3.33 \times 10^5\text{ J/Kg}$ . It is heat released during freezing of water into ice. The latent heat of vaporisation of snow is quite large i.e.  $2.83 \times 10^6\text{ J/Kg}$ .
3. **Thermal conductivity**- The thermal conductivity of ice cover is very low in comparison to the soil surface. It varies with the depth of ice cover, density and content of liquid water in ice. On an average, snow cover provides high insulation compared to soil surfaces which makes it a good habitat for those animals and plants which need protection from extreme cold weather during winter season (Palm and Tveitereid, 1979). The insulation of snow is due to its porous nature with large air content.

4. **Albedo**- The albedo of fresh snow is very high approximately 0.8-0.9 (Pomeroy et al., 2005) compared to vegetation and soil surfaces. The albedo of fresh snow decreases with age i.e. it can drop upto 0.4 (Hall and Martinec, 1985). These values can further drop if snow is contaminated with dust particles having soot. Apart from the nature of surface, the degree of reflection of radiation also depends upon the wavelength of incident radiation. In general for any surface, short wave incident radiations have higher albedo than long wave radiations (Male, 1980). Its reflection of radiations having shorter wavelength than longer wavelengths is very important factor influencing global climate system.
5. **Sound**- Fresh snow absorbs sound better than old snow probably due to difference in snow temperature (Ahrens, 2007). Thus after snow melting and refreezing sound waves will be more reflected than fresh snow fall (<https://nsidc.org>).
6. **Snow depth and temperature**- The temperature of snow surface is very much influenced by air blowing above it (<https://nsidc.org>). The colder air makes colder snow surface of top layer approximately upto 45 cms. In deeper snowpack, snow touching the ground is warmer due to warm ground and insulation provided by snow.
7. **Snow water equivalent (SWE)**- Snow consists mostly air with frozen water crystals (<https://nsidc.org>). SWE is basically amount of water produced due to melting of snow. On an average, 10:1 ratio of snow to water is observed but it varies with meteorological conditions prevail that area.

### 1.4.3. Different types of snowfall

Snow crystals grow in the atmosphere by absorbing water droplets on its surface. The snowflakes which fall on the earth surface are accumulation of ice crystals (Fig. 1.5).



**Fig. 1.7:** SEM images of snow crystal showing different snowflake formation

(<https://nsidc.org>, Agricultural Research Service, United States Department of Agriculture).

There are various types of snowfall-

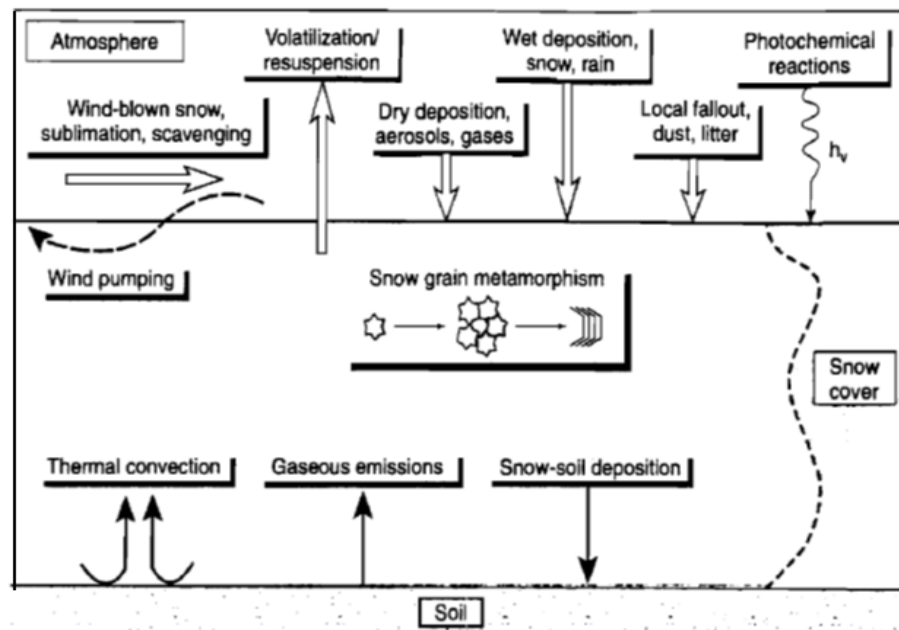
- i) **Blizzard**- It is a combination of blowing and drifting snow (Ahrens, 2007).  
Blowing snow is snow particles raised with greater height while drifting snow upto 2 meters above the surface. It is violent winter storm characterized by strong wind and low temperature with fine, dry and blowing snow which restricts visibility to less than  $\frac{1}{2}$  km (<https://nsidc.org>).
- ii) **Snowstorm**- It is characterized by snowfall with larger amounts.
- iii) **Snow flurry**- It features light showers of snow that falls for short durations intermittently with light accumulations (Ahrens, 2007).
- iv) **Snow squall** – It is an intense snowfall with short duration but heavy amount of snowfall causing poor visibility.

- v) **Snowburst**- It is characterized by a very intense snow shower usually of short time span with rapid snow accumulation and restricting visibility (<https://nsidc.org>).

#### 1.4.4. Chemistry of snow cover

During cold weather condition, snow on the ground changes to consolidated snow cover. The study of snow cover is very important since the change in snow cover plays an important role in climate and distribution of water across the globe. Chemically, it is heterogeneous in nature due to spatial and temporal variation in chemical constituents of snowfall (Pomeroy et al., 2005). Snow covers are further subjected to transformations by chemical and physical processes which further changes the chemical composition of snowfall (Jones and Stein, 1990; Pomeroy et al., 2005). The main reactions/ processes which is associated with transformation of composition of snow cover are following (Fig. 1.4)-

- Redistribution of snow by vegetation and wind.
- Metamorphism of snow grain within snow cover.
- Exchange of chemical components at the interface of snow and atmosphere.
- Chemical reactions occurring at surface and subsurface.
- Exchange of chemical components at the interface of soil and snow.



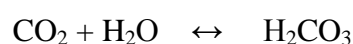
**Fig. 1.8:** Chemical and physical processes governing the transformation of composition of snowcover (Pomeroy et al., 2005).

## 1.5. Acid rain

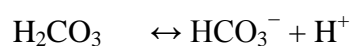
Precipitation of lower pH i.e. high acidity in the form of rain, snow, or hail is known as acid rain. Robert Smith discovered acid rain in 1852 and the term ‘acid rain’ was used in the year 1872.

### 1.5.1. Cause of acid rain

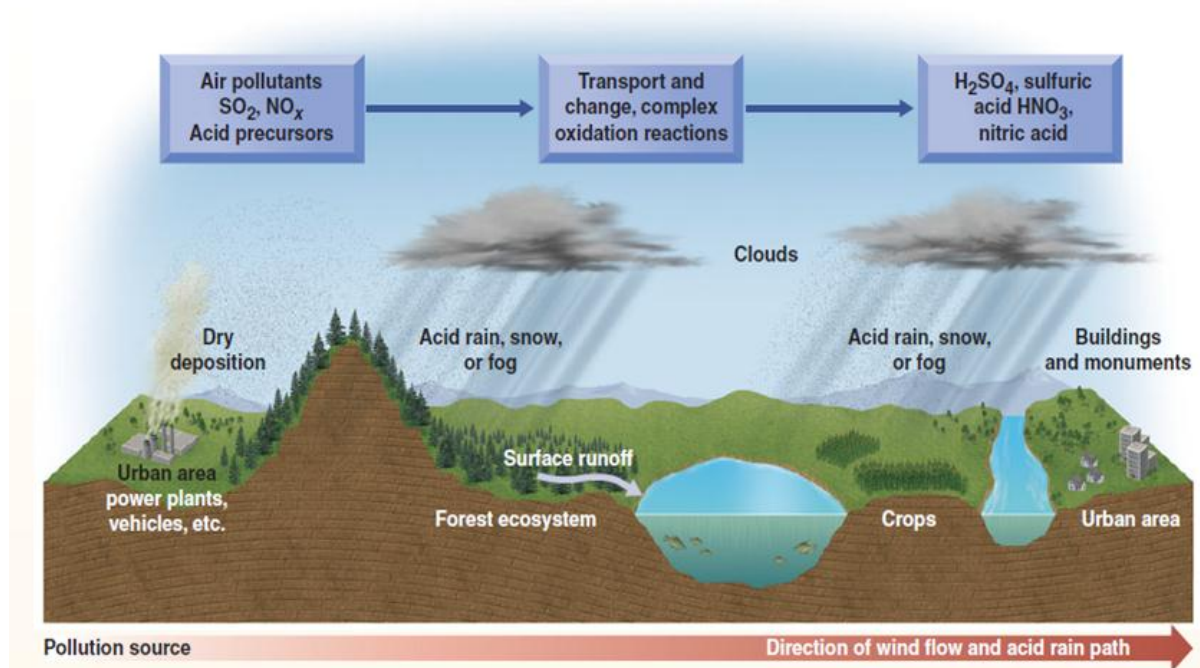
Rainwater in remote and unpolluted atmospheres has pH around 5.6 because of the presence of carbonic acid formed due to the dissolution of atmospheric  $\text{CO}_2$  in cloud water.



Carbonic acid dissociates to form bicarbonate ion in the water:

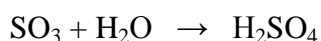
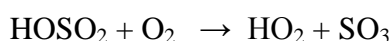
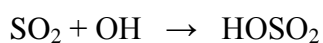


Further decrease in pH of rainwater up to 5.2 in unpolluted areas is due to the presence of organic acids. But oxidation of  $\text{SO}_2$  and  $\text{NO}_2$  to sulfuric and nitric acid in the atmosphere is the reason for the anthropogenic acid rain. Homogeneous and heterogeneous oxidation of

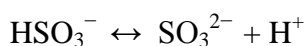
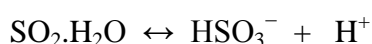
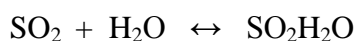


**Fig. 1.9:** Diagram showing possible pathway of acid rain formation (Botkin and Keller, 2010).

these precursor gases are the two possible oxidation reactions. Reaction with OH radicals initiates the gas-phase oxidation of these gases.



Homogeneous aqueous-phase oxidation of  $\text{SO}_2$  takes place by its dissolution and dissociation in water:



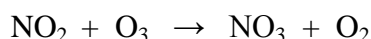
Gas-phase oxidation of  $\text{NO}_2$  is faster than  $\text{SO}_2$  by one order of magnitude:



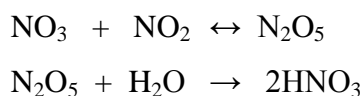


Also, significant formation of nitric acid takes place through ozone and  $\text{NO}_3$  radical reactions.

During daytime,  $\text{NO}_3$  radical is formed as follows:



$\text{NO}_3$  radical formed in day time reacts with  $\text{NO}_2$  at night time, resulting in the formation of  $\text{HNO}_3$ :



At ambient levels of  $\text{NO}$ , its aqueous-phase oxidation is very slow due to its low solubility in water and also the dependence on  $\text{NO}_2$  concentrations. It can be faster at higher  $\text{NO}_2$  levels. However, the reaction undergoes as follows:



Gas-particle reactions of  $\text{SO}_2$  and  $\text{NO}_2$  undergo heterogeneous oxidation.  $\text{SO}_2$  is rapidly converted into sulphate by  $\text{H}_2\text{O}_2$  in the liquid phase. On the surface of freshly emitted soot particle  $\text{SO}_2$  oxidises to sulphate but the afterwards reduction in the rate of oxidation takes place due to the saturation of surface of soot particle. In dusty regions, oxidation of  $\text{SO}_2$  onto soil dust particles leads to the formation of  $\text{CaSO}_4$  instead of  $\text{H}_2\text{SO}_4$ . Oxidation of  $\text{NO}_2$  on particle surface for example,  $\text{NaCl}$  from sea salt forms  $\text{NaNO}_3$ . However, with time reaction rate becomes slower due to saturation of surface.

## 1.5.2. Effect of acid rain

### 1.5.2.1. Acid rain and eutrophication

Eutrophication is the continuous enrichment of water by the addition of excessive amount of nutrients such as N and P resulting in increasing growth of aquatic life. Atmospheric deposition (example in the form of acid rain) can also affect nutrient concentration in water,

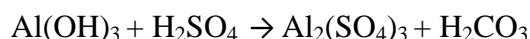
especially in highly industrialized regions. Thus, excess N and P deposition from air pollution including the overuse of fertilizers in agricultural activities results in eutrophication of waterways. Hence, eutrophication leads to depletion of oxygen due to the increase in algal blooms (Fig. 1.9).

In western countries, the lakes are primarily polluted by acid rain while in a developing country like India; lakes are in danger mainly due to eutrophication *i.e.* excessive plant growth caused by sewage, pesticide, fertilizer runoff and open air pollution. Most of the lakes near big urban places in India are highly (Vijayvergia, 2008; Kaur and Singh, 2012).

#### **1.5.2.2. Effect on soil chemistry**

Leaching is a process in which the essential nutrients such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$  are removed from the top soil and penetrate deep into the sub soil. Due to leaching, they are no longer available as nutrients or fertilizers needed for the growth of plant and trees.

The leaching occurs due to the addition of  $\text{H}^+$  from acidic deposition.  $\text{H}_2\text{SO}_4$  undergoes neutralization reaction with  $\text{Al}(\text{OH})_3$  as follows (Brady and Weil, 2000):



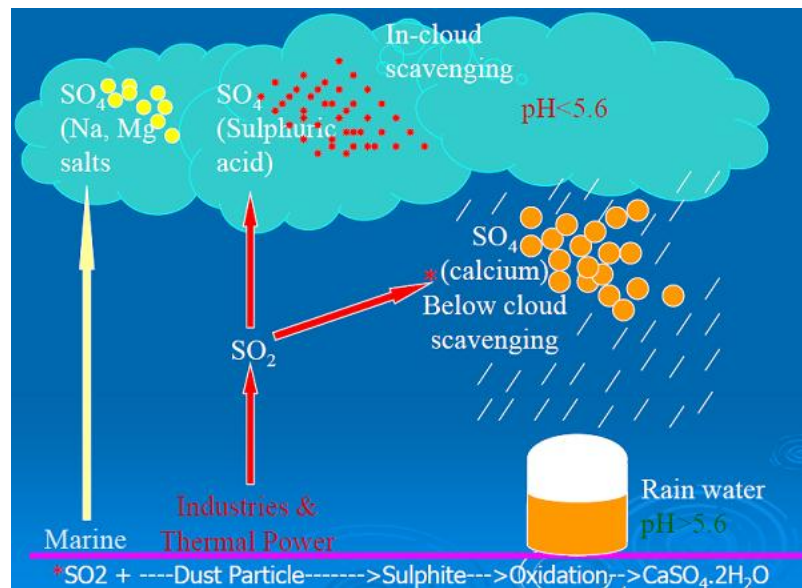
Since aluminium sulphate ( $\text{Al}_2(\text{SO}_4)_3$ ) is soluble in water so it is released from the soil particles. Low pH and high  $\text{Al}^{3+}$  concentration lead to soil toxicity and which adversely affects the populations of soil microorganisms. Due to this reason, the bacterial population unable to break down the dead and decaying leaves and other debris on the forest floor and leading to less availability of essential soil nutrients for plant growth.

#### **1.5.3. Acid rain neutralizing agents**

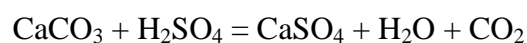
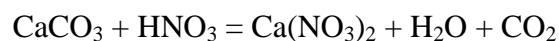
Acids *i.e.*  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  generated in acid rain are neutralized by  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{NH}_3$  etc. before their deposition on the earth surface (Elsom, 1987). The neutralization of acids

depends upon the availability of basic species in the atmosphere. These neutralization reactions tend to decrease in acidity of rain water.

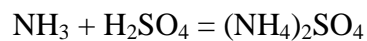
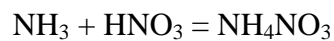
$\text{Ca}^{2+}$  is mainly emitted from soil surfaces and principal agent of neutralization in India (Kulshreshtha, 2007) leading to higher pH of rain water (Fig. 1.9).



**Fig. 1.10:** Below cloud scavenging of pollutants by dust particles (Kulshreshtha, 2007).



$\text{NH}_3$  is mainly produced by agricultural activities, biomass burning etc. It is also involved in reaction with acid and generate  $\text{NH}_4^+$  aerosol.



*Chapter 2*  
*Literature Review*

---

## LITERATURE REVIEW

This chapter presents a review of literature related to emission of atmospheric pollutants, dry and wet deposition, atmospheric dust composition and its importance, acid rain and its effect on various environments including soil system. At the end of chapter, significance of the study has been discussed along with objectives of PhD work. To compile, review of literature in systematic manner, it has been divided into two major headings i.e. international and national studies.

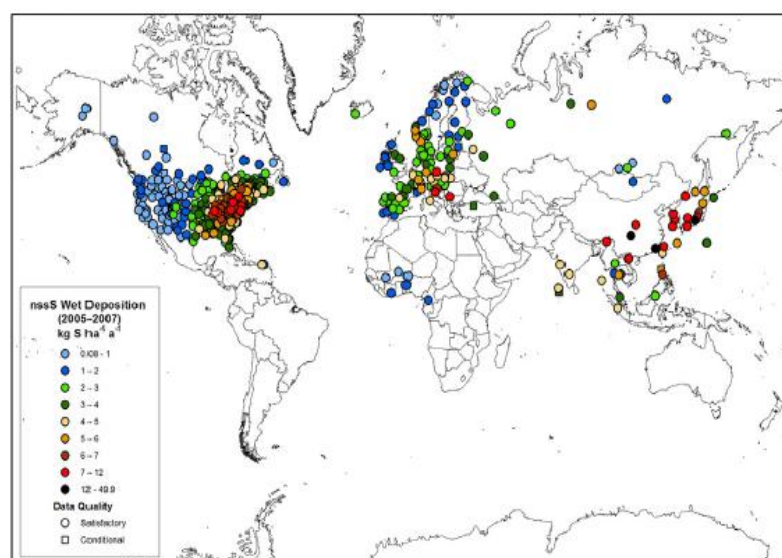
### 2.1 International studies

There has been a growing concern about the effect of human activities on continuous increase in gaseous and aerosol pollutants playing an important role in climate change produced several reports (Andreae and Crutzen, 1997; Ramanathan et al., 2001; IPCC, 2007). The increase in level of air pollutants and climate change is intrinsically connected since greenhouse gases and other air pollutants are emitted by one of the most significant anthropogenic source i.e. fossil fuel combustion (Jacob et al., 2009; Dennekamp et al., 2010). The combustion of fossil fuel generates both greenhouse gases like CH<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub>O etc along with air pollutants like SO<sub>2</sub>, NO<sub>2</sub>, PM etc. Apart from climate change, the increase in aerosol concentrations has significant impact on composition of ecosystem, visibility and human health (WHO, 1996; IPCC, 2014).

These air pollutants emitted locally or transported finally settle down. Atmospheric deposition is an important mechanism controlling the fate of toxic airborne pollutants and their transfer from the atmosphere to the surfaces. Atmospheric deposition is broadly divided into two type i.e. wet and dry deposition. Long term study of wet deposition can be used to notice the changes in oxides of N & S content thereby relating to coal & petroleum energy consumption patterns. Precipitation chemistry in general, provides information about the deposition fluxes of various air pollutants to different ecosystems. Hence, rain and snow chemistry become very important to know the sources of pollution and their possible effects on ecosystems and environment.

The highest precipitation weighted average concentration of sulphur globally in 2005-2007 and 2000-2002 were observed in Europe (Ireland and Croatia), Asia (China, India, Taiwan and Japan) and North America ranged from 12-49.82 kg S ha<sup>-1</sup>a<sup>-1</sup> and 12-34.90 kg S ha<sup>-1</sup>a<sup>-1</sup> and respectively (Vet et al., 2014). The lowest precipitation weighted average S deposition values observed were 0.08 kg S ha<sup>-1</sup> a<sup>-1</sup> and 0.05 kg S ha<sup>-1</sup> a<sup>-1</sup> in 2005-2007 and 2000-2002 respectively in western U.S (Vet et al., 2014). High SO<sub>4</sub><sup>2-</sup> deposition was estimated in central Europe, northeastern India, Bangladesh, northeastern North America, and East Asia (southeastern China) over the last decade (Bouwman et al., 2002; Rodhe et al., 2002; Dentener et al., 2006).

Anthropogenic emissions of sulphur changed remarkably in Europe, North America and Asia from 2000 to 2007. The major increase in S emission occurred in India, China and other parts of East and South Asia while reduction occurred mainly in the U.S., Europe and Canada (IJC, 2010; EANET, 2011; EMEP/CEIP, 2012).

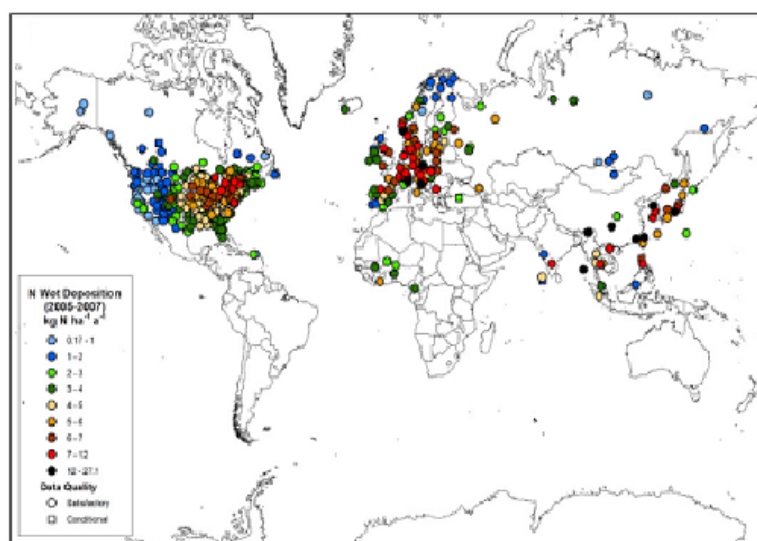


**Fig. 2.1:** Measured average annual S deposition in precipitation for 2005-2007 (Kg S ha<sup>-1</sup>a<sup>-1</sup>) (Vet et al., 2014).

Globally, the pattern of very high nitrogen deposition is very similar to sulphur deposition as observed by models (Bouwman et al., 2002; Rodhe et al., 2002; Dentener et al., 2006). The deposition of reactive nitrogen deposition is mainly dominated by domestic emissions with some contribution from long range transport. The areas of high N deposition include

southeastern China, large parts of Europe, northeastern India, northeastern North America and Bangladesh with the highest deposition of reactive nitrogen is in parts of Europe, North America with South and East Asia (Vet et al., 2014).

The highest precipitation weighted average concentrations of nitrogen were observed 1.50 - 1.93 mg N L<sup>-1</sup> and 1.50-1.88 mg N L<sup>-1</sup> in 2005-2007 and 2000-2002 periods respectively (Vet et al., 2014). In both 3 year periods, the highest values 1.93 and 1.88 mg N L<sup>-1</sup> were recorded at Chongqing Jinyunshan in eastern China and Ust Vym in western Russian Federation (Vet et al., 2014). N concentrations in precipitation samples more than 1.50 mg N L<sup>-1</sup> were observed in Russian Federation, China and Italy. The highest measured wet deposition of N were located at Asia and Europe ranged from 12.00-27.07 kg N h<sup>-1</sup> a<sup>-1</sup> and 12.00-24.55 kg N h<sup>-1</sup> a<sup>-1</sup> in 2000-2002 and 2005-2007 respectively (Fig. 2.2). Globally, the lowest concentrations of N were measured at Malaysia and United States (including Hawaii) ranging from 0.03 to 0.04 mg N L<sup>-1</sup>.



**Fig. 2.2:** Measured average annual N deposition in precipitation for 2005-2007 (Kg N ha<sup>-1</sup>a<sup>-1</sup>) (Vet et al., 2014).

Due to its significance, snowfall chemistry has been studied extensively throughout the world (Mayewski et al., 1983; Valsecchi et al., 1999; Wang et al., 2000; Marinoni et al., 2001; Kang et al., 2004; Marinoni et al., 2005; Niu et al., 2013; Xu et al., 2013; Zhang et al., 2013;

Kulshrestha and Kumar, 2014). Fresh snow chemistry in Himalaya ranges had shown relatively low concentration of air borne pollutants are representative of remote site (Marinoni et al., 2001; Shrestha et al., 2002; Kang et al., 2004). The ionic content in Himalayan snow is highly affected by the impact of long range transport of anthropogenic sources of air pollutants (Kulshrestha and Kumar, 2014). Snow chemistry at Shanghai in China suggested that fossil fuel combustion and biomass burning is the major source of air pollution (Zhang et al., 2013).

Generally, snow composition varied from site to site depending upon sources, type of sampling site, elevation from sea level, meteorological conditions, methods of sampling, regional and global scale transport of pollutants in relation to airmasses etc (Marinoni et al., 2005). Comparison of fresh snow chemistry and sources from central Himalayas revealed that both seasonality and geographical locations play an important role in the determination of chemical composition of snow (Marinoni et al., 2001). In another study from Central Himalayan region, the dominance of dissolved organic matter was noticed in snow samples (Xu et al., 2013). Zhang et al., 2013 have established the relationship between Mercury metal with secondary aerosols ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) and biomass burning in the snow samples collected at Shanghai in China.

In general, the sources of air pollution have been identified based on the data of precipitation chemistry using various statistical models. Air mass trajectory model is often used to identify possible sources of origin of pollutants contributing to atmospheric aerosols and precipitation as well as their impact on various ecosystems through deposition processes (Rodhe, 1972; Avila and Alacron, 1999; Harrison et al., 2000; Granat et al., 2002; Shrestha et al., 2002; Reddy et al., 2008; Calvo et al., 2010; Sathanarayana et al., 2010; Fleming et al., 2012; Kuniyal et al., 2013; Kulshrestha and Kumar, 2014). Trajectory calculations gained more importance when Rodhe (1972) plotted air mass trajectories and established that acid rain occurrence in northern Europe was mainly due industrial sources located in the south and west. Backward air mass trajectories upto 6500 m above the ground level have been used to explain the role of various dust storms originated from different deserts and measured at Hongkong (Lee et al., 2010).



Acid deposition has been a serious problem in North America, Europe and Japan (Rodhe and Granat, 1984; Hara and Akimoto, 1993; Sverdrup et al., 1994; Galloway, 1995; Menz and Seip, 2004). It causes loss of fish populations, loss of soil nutrients, activation of few heavy elements, and modification in microbial community structure as well as changes in forest ecosystem (Brimblecombe et al., 2007). Schwesig et al. (2003) reported that the decrease in soil pH may result in impoverishment of nutrients and enhance potentially toxic metal solubility such as  $Al^{3+}$ . Acidic precipitation may damage mountain forest ecosystems more rapidly (Sverdrup et al., 1994). Comprehensive studies on acid deposition have been carried out by different workers globally (Galloway, 1995; Granat et al., 2002; Rodhe et al., 2002; Zhang et al., 2007a; Kulshrestha, 2013). Despite its importance, it is not taken seriously by Indian workers especially in ecologically sensitive Himalayan region.

Dusty atmosphere is a common feature of arid and dry regions. Hyper arid regions like Sahara and Thar contribute significant amount of dust. This dust is transported through troposphere (Carrico et al., 2003). Dust carried by wind can travel tens of thousands of kilometers before being deposited. Thus, even remote areas located far from source regions receive a regular flux of particulate dust. Furthermore, the accumulation of dust is now accepted as a control of biogeochemical cycling in many ecosystems (Derry and Chadwick, 2007). The main sources of atmospheric dust are winds blowing over dry fields (ploughed fields, deserts and roads), various combustion products, volcanic eruption, sea salt spray from the ocean, pollen and other material from plant and meteoric particles etc.

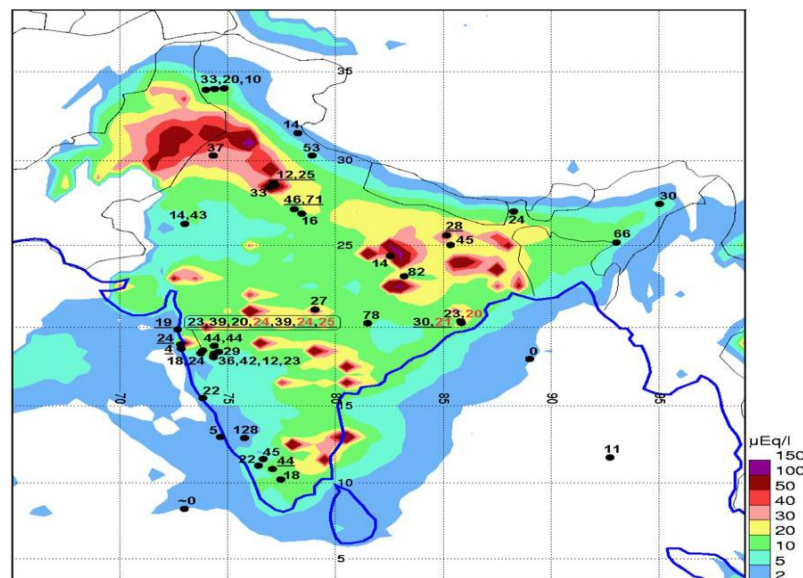
Mineral dust aerosols make up a large fraction of the tropospheric aerosol mass and therefore, impact the earth's climate and the atmospheric environment in several ways. Mineral dust particles scatter and absorb solar and terrestrial radiation and also alter cloud properties and thus are important climatic forcing agents (Anderson et al, 1996). The atmospheric mineral dust has potential to impact global atmospheric chemistry, cloud properties and precipitation development (Charlson et al., 1992; Dentener et al., 1996; Andreae and Crutzen, 1997; IPCC, 2014). Borys and Rahn (1981) have reported that the uptake of soluble species on dust alters the physical, chemical and optical properties and the overall ability of dust to act as cloud condensation and ice nuclei.

## 2.2 National studies

Wet deposition in terms of rain water chemistry has been studied at various sites in India. Several studies have been reported on rain chemistry mostly in urban areas (Khemani, 1989; Kumar et al., 1993; Kulshrestha et al., 1996; 2003; Safai et al., 2004; Kulshrestha et al., 2005; Tiwari et al., 2007; Singh et al., 2017) with few studies from rural sites (Mahadevan et al., 1989; Rao et al., 1990; Jain et al., 2000; Satyanarayana et al., 2010). A review of such studies has been reported by Kulshrestha et al (2005).

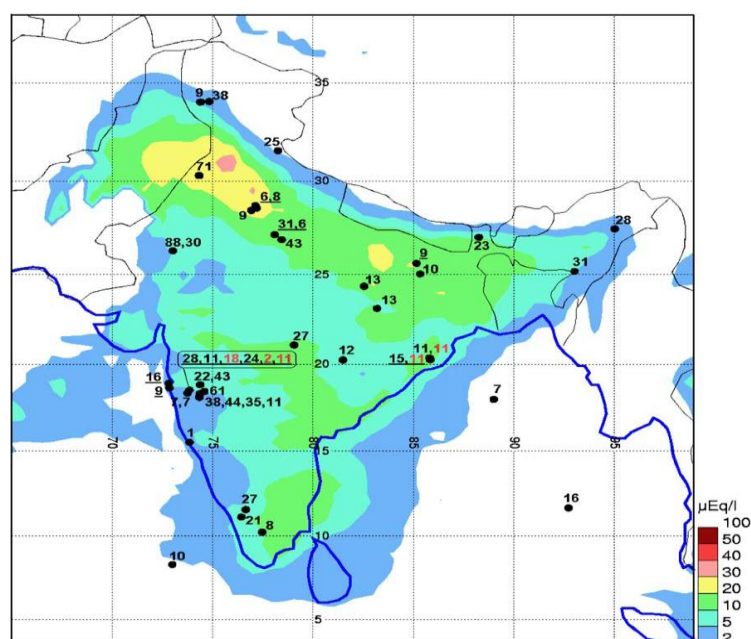
The median values for  $\text{SO}_4^{2-}$  in rain were 18  $\mu\text{eq/l}$  and 45  $\mu\text{eq/l}$  respectively in rural and urban sites (Kulshrestha et al., 2005). Higher values at urban site might be due to influence of urban and industrial sources. But very high values around very large cities as well as low values of  $\text{SO}_4^{2-}$  around western coast in Indian regions from MATCH model were not supported from measurement (Fig. 2.3). The discrepancy in simulated result from measurement values might be due to various reasons. One of the strongest reason of disagreement is due to the fact that model does not account for scavenging of  $\text{SO}_2$  by soil dust (Kulshrestha et al., 2003a).

However, India is reporting reduction in  $\text{SO}_2$  at many sites. A decreasing trend in  $\text{SO}_2$  levels in many cities like Delhi and Mumbai was reported by the Central Pollution Control Board's (CPCB, 2010) National Ambient Air Quality Monitoring (NAAQM) from 1995 to 2007. This decreasing trend was due to the use of LPG in place of coal as a domestic fuel and the reduction of the S content in gasoline from 0.1% to 0.05% in 2000 and in diesel fuel from 0.25% to 0.05% in 2005.



**Fig. 2.3:**  $\text{SO}_4^{2-}$  Concentration ( $\mu\text{eq/l}$ ) in rain. The measurement values of 2000 year at various rural and suburban site of India are compared with the concentration obtained through MATCH model (Kulshrestha et al., 2005).

No characteristic pattern is observed and there is no resemblance to the emission field for anthropogenic  $\text{NO}_x$  or to the concentration of  $\text{NO}_3^-$  from the MATCH model (Kulshrestha et al., 2005). Compared with the MATCH model, a few stations have similar values, in particular data from wet-only collectors at the rural stations near Bhubaneswar and near Panjim in Goa. For several other stations there seems to be an additional amount superimposed on the amount derived from  $\text{NO}_x$  emissions given by the model. This additional nitrate is quite randomly distributed, but is especially high at Jodhpur, which may reflect an influence from soil dust.



**Fig. 2.4**  $\text{NO}_3^-$ : Concentration ( $\mu\text{eq/l}$ ) in rain. The measurement values of 2000 year at various rural and suburban site of India are compared with the concentration obtained through MATCH model (Kulshrestha et al., 2005).

A number of studies of precipitation chemistry in the mountainous regions worldwide have been reported during the last few decades (Schemenauer et al., 1995; Aiuppa et al., 2003; Beiderwieden et al., 2005) but over Himalayan region, such studies are rare. Despite its great importance, with the increasing human perturbation, very limited studies have been reported so far on the changing aerosol composition and their wet scavenging ratios in western Himalayan ranges. The detailed and updated studies on fresh snowfall chemistry are even rare in rural areas of Himalayan region of India (Naik et al., 1995; Lone et al., 2010; Kulshrestha and Kumar, 2014). The ionic composition of rare muddy snowfall showed relatively high concentration of  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{SiO}_4^{2-}$  with low concentration of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  at Afarwat glaciers near Gulmarg of the Kashmir Himalaya, India (Lone et al., 2010). Naik and co-workers by analysis of 30 fresh snowfall at Gulmarg recorded that higher pH of snowfall might be due to high concentration of  $\text{Ca}^{2+}$ .

Unlike in Western countries, it is interesting to note that even at high  $\text{SO}_4^{2-}$  concentration, the pH of rain water has been observed to be very high in India. This may be due to the significant crustal interference (Kulshrestha et al., 2003b; 2009, Jain et al., 2000). In a study

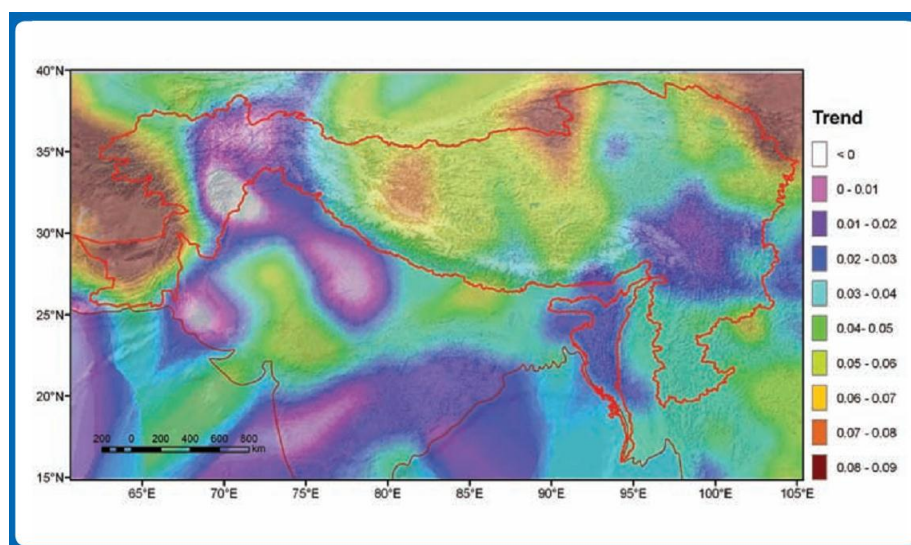
reported by Kulshrestha et al (1996) at New Delhi, the average pH of the rain water was 5.7 and its chemical composition was dominated by  $\text{NH}_4$  and  $\text{SO}_4$ . Calculation of sea salt fraction and enrichment factor revealed that this site was free for marine influence. The higher neutralization factors of Ca and Mg in bulk samples and highest dry deposition rates for Ca in comparison to other components indicated the positive interference of dust particles in neutralization (Kulshrestha et al., 1996).

During most part of the year, dry weather conditions prevail which determine the atmospheric deposition chemistry in India. Ambient concentrations of reactive gases are controlled by continuous input of atmospheric dust contributed by suspended soil. Hence, dustfall deposition is a significant removal mechanism in India as it provides very efficient sink for acidic gases such  $\text{SO}_2$  and  $\text{NO}_2$ . In India, atmosphere is full of dust which is rich in  $\text{CaCO}_3$ . The dust particles interfere with rains which results in rain water of higher pH. In true sense, dust particles control acidification at continental sites in Indian region (Kulshrestha et al., 1999, Khemani 1989). All these studies highlighted significant interference of atmospheric aerosol. In India, owing to its dusty nature, soil has been considered as a major contributor of particulates in the atmosphere (Mahadevan et al., 1989, Kulshrestha et al., 1995).

Dry deposition process has been studied extensively in the temperate mid-latitudes. But studies done in temperate region cannot be compared with that of tropical regions due to different meteorological conditions. Therefore, there is a need to study dry deposition fluxes or dustfall in the tropics where data is scanty. Kulshrestha et al (2003a) reported that the significant fraction of  $\text{SO}_4^{2-}$  in dust is contributed by  $\text{SO}_2$  oxidation. The alkaline nature of dustfall offers the preferable oxidation of acidic  $\text{SO}_2$  gas on the dust particles during suitable meteorological conditions. Dust particles control acidification at continental sites in Indian region (Rodhe et al., 2002 ; Kulshrestha et al., 2009). In India, atmosphere is full of dust which is rich in  $\text{CaCO}_3$ . The dust particles interfere with rains which results in rain water of higher pH. Derry and Chadwick (2007) showed that the accumulation of dust can be treated as a control of biogeochemical cycling in many ecosystems.

### 2.3 Motivation of the study

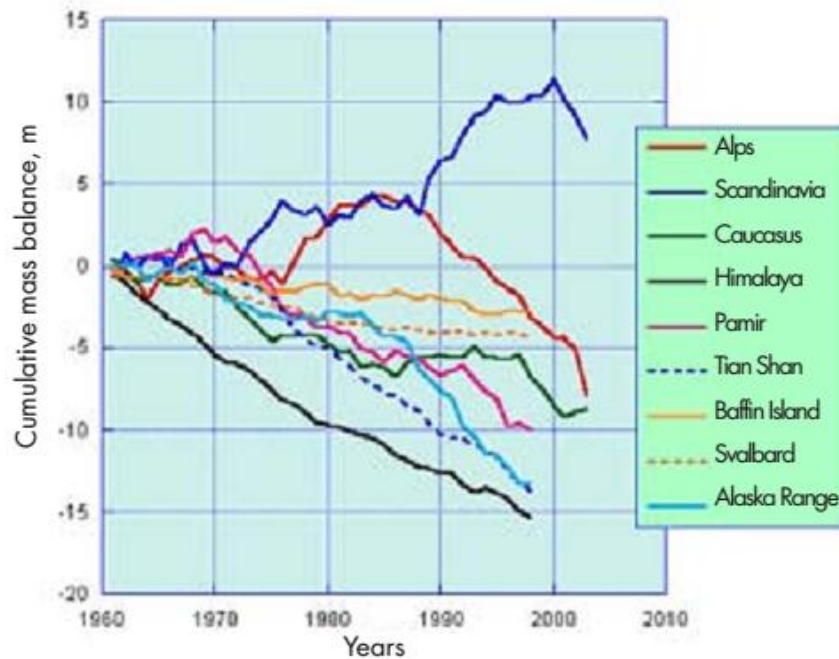
A few measurement experiments and simulated results from models indicated that extensive and continuous studies on sensitive ecosystem especially Himalaya is in urgent need. The Himalayan region is strongly impacted by climate change. Studies have proven that warming trend in the Himalayas over the last 100 years is much more than the global average of  $0.74^{\circ}\text{C}$  (Du et al., 2004; IPCC 2007). Studies have proven progressively higher warming with an increase in altitude over the whole of the greater Himalayan region (Eriksson et al., 2009) (Fig.2.3).



**Fig. 2.5:** Spatial distribution of annual trends in temperature in the greater Himalayan region for 1970–2000 periods (Eriksson et al., 2009).

Precipitation decrease in combination with temperature increase resulted in glacier retreat in the Himalayas. If the climatic warming and drying continue, the glacier contraction will speed up (Ren et al., 2003). Consequently, due to warming of Himalaya, snowmelt begins earlier and winter is shorter which ultimately affects the river regimes, water supplies, natural hazards and infrastructure and people's livelihoods mainly in basins regions such as the Tarim, which depends on the melting of the glaciers in summer. The health and extent of high altitude wetlands, green water flows from reservoirs, terrestrial ecosystems and sediment transport and water flow along rivers and in lakes are also affected. Today, retreating of Himalayan glaciers is faster than the world average (Eriksson et al., 2009) (Fig. 2.4).

Considering its importance and dearth of studies on atmospheric deposition in Himalaya, was motivation of the present study.



**Fig. 2.6:** Rapid retreat of glaciers of greater Himalaya comparing with the global average (Eriksson et al., 2009).

## 2.4 Significance of the study

Himalayan region, as very sensitive ecosystem regarding atmospheric deposition (Kuylenstierna et al., 2001) is being affected mainly by local sources as well as long-range transport of pollutants (Kulshrestha and Kumar, 2014). Local sources like tourist activities, transport and other human activities have an adverse impact on snow chemistry as well as aquatic and terrestrial ecosystems.

These pollutants are responsible for altering the atmospheric composition. Signatures of these activities are trapped in various forms of atmospheric depositions which can easily be revealed by the chemical characterization of aerosols and snowfall/rain. Since, the environment of western Himalaya is very sensitive from atmospheric deposition point of view (Kuylenstierna et al., 2001) studies on chemistry of aerosols and snowfall can be useful

for gathering information about the nature of these perturbations, interdependence and linkages of atmospheric constituents with terrestrial and aquatic components. The snow pack can contain records that include climate proxies, deposition rate of aerosol contamination and photochemical alterations. Hence, measurements of the chemical composition of atmospheric aerosols and their depositions via snow can be used to establish relationship between chemistry and sources of pollutant and further to plan developmental strategies.

In spite of its sensitivity, seasonal and annual depositions of various chemical species are not taken into account as they are not understood properly. There are very few papers on the rain water, aerosols and snow geochemistry in the Himalayas so far (Gajananda et al., 2005; Tiwari et al., 2012; Kuniyal et al., 2013). Also, the studies on the chemistry of fresh snowfall are limited in the western and central Himalayan region of India (Naik et al., 1995; Lone et al., 2010; Kulshrestha and Kumar, 2014) and impact of snowmelt on soil chemistry is rare.

Hence, the present work is an attempt to fulfil this knowledge gap in north western and central Himalayan region of India with the following objectives.

### **Objectives**

1. Determination of the chemical characteristics of precipitation (snowfall/rain) and dustfall at selected sites in western Himalayan ranges.
2. Identification of natural and anthropogenic sources and their relative contribution.
3. Establishing relationship between ionic content of precipitation and aerosols.
4. Estimation of relative contribution of sources of pollution through air mass trajectories
5. Comparison with other sites worldwide in order to find out inter-hemispheric differences.
6. Study of the effect of snowmelt on soil nutrient and its relation to human perturbation due to increased tourism activities at these sites.



*Chapter 3*  
*Material & Methods*

---

## MATERIAL & METHODS

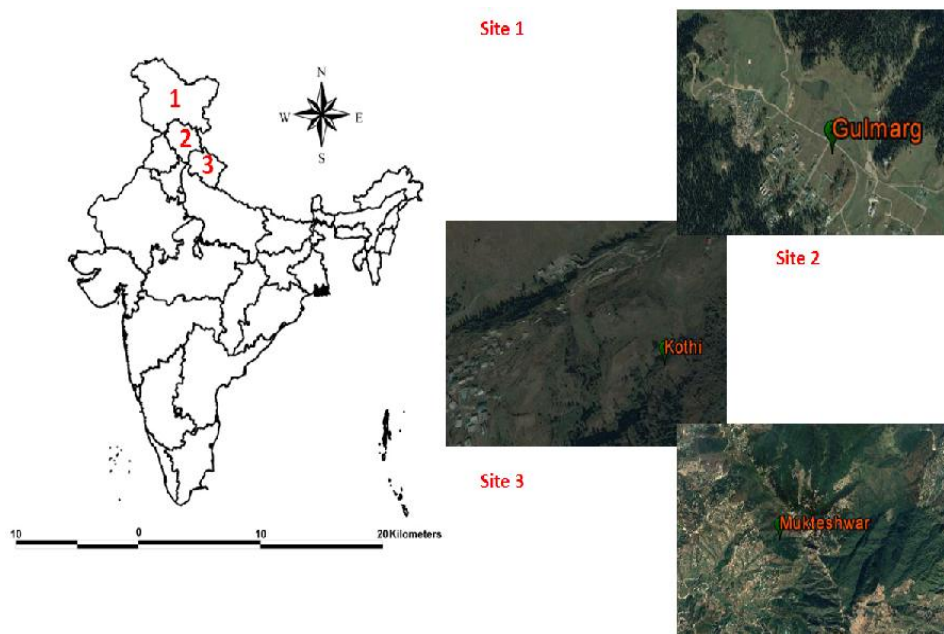
### 3.1 Study area

Three study areas i.e. Gulmarg, Kothi and Mukteshwar were selected for experiment in himalyan region of India. Gulmarg and Kothi are situated at north western Himalaya while Mukteshwar is located at central Himalaya in India.

#### 3.1.1 Kothi (North western Himalaya)

Kothi is a rural site located at 32.310 N and 77.200 E in north-western Himalayan ranges at ~ 2527m above sea level. It is situated at Kullu district in Himachal Pradesh state of India (Fig. 3.1). The site is located ~65km from north of Kullu which is the district headquarter of Kothi. There are no major industrial units around this village therefore; the site represents high altitude rural characteristics. The major local sources of air pollution at this site include vehicular emissions, tourist activities and biomass burning. However, these emissions are minimum during snowfall period.

Kullu has witnessed a very fast growth in number of tourists during past decade (Fig. 2). Human population of the Kullu district is increased by 45% from 1991 to 2011 (<http://www.census2011.co.in>). In the year 2012, around 3226445 tourists visited Kullu (<http://himachaltourism.gov.in/>) recording 108% increase between 2004 and 2013. In order to accommodate the surge of tourists, numbers of registered hotels is also increased by 37% from 1400 hotels in 1998 to 2010 hotels in 2008 (Vishwa et al., 2013) which can also contribute various anthropogenic components in precipitation.



**Fig. 3.1:** Sites of sample collection.

### 3.1.2 Gulmarg (North western Himalaya)

Gulmarg is a hill station located in Baramulla district in Jammu & Kashmir state of India (Fig. 3.1) at  $34.06^{\circ}\text{N}$  and  $74.38^{\circ}\text{E}$  in north-western Himalayan ranges at  $\sim 2690$  m above sea level. It is surrounded by Afghanistan and Pakistan to the north-west and Tibet to the north-east. Gulmarg is located 52 km to the south-west from Srinagar having  $\sim 730$  inhabitants in this hill station. Gulmarg is one of the most famous tourist spots which receive several thousand tourists every year. Snowfall occurs during winter and spring seasons (November – May). Gulmarg is very attractive in terms of the green vegetation and forest having trees of Birch, Christmas, apple etc. There are no major industrial units around this hill station hence the site represents high altitude rural characteristics. The major sources of air pollution at this site are tourist activities and emissions from electricity used in generators in various hotels. Most of the population use biomass as a source of energy for domestic heating and cooking purposes.

### 3.1.3 Mukteshwar (Central Himalaya)

Mukteshwar is located at 29.47°N 79.64°E in Nainital district of Uttarakhand state of India (Fig. 3.1). It is situated in the Kumaon Hills of central Himalaya at an altitude of 2286 meters. It lies approx 51 km NE of Nainital city, 51 km from Nainital, 72 km from Haldwani and 395 km from Delhi city. Mukteshwar is rich in scenic beauty, with magnificent views of the central Himalayas. It is one of the most famous tourist spots in north India which receive domestic as well as foreign tourists every year. The mean minimum temperature in this village ranges from -5 °C to 0 °C during January whereas the mean maximum temperature ranges from 25 °C to 30 °C during the month of June. There are no any major industrial units around this site. Most of the people use biomass as a source of energy for domestic heating and cooking purposes. The major sources of air pollution at this site include vehicular pollution used for tourist activities and emissions from agricultural activities.

## 3.2. Sample collection

### 3.2.1 Snowfall samples

Fresh snowfall samples were collected on event basis using prewashed plastic trays (20 cm diameter) during winter season (2012 – 2013). During this period, a total of 11, 35 and 48 snowfall samples were collected at Mukteshwar, Gulmarg and Kothi respectively. The tray was washed properly with high quality deionized water and dried before use. Sampler was placed at ~ 2 m height above the ground level. We have followed similar method which was used by Naik et al. (1995). The tray was kept outside just before the start of snowfall and was removed immediately after snowfall to avoid contamination. In order to get representative samples, collection was done in duplicate to observe any difference in two nearby samples. Random chemical analysis of such samples suggested no significant difference in the duplicate samples. The frozen snow was transferred from tray into pre-cleaned polypropylene bottles using polyethylene gloves and stored at 4 °C which were then transported to the laboratory for their chemical analysis. The precautions were taken to avoid any contamination (Mayewski et al., 1983; Kang et al., 2004). These samples were stored in the refrigerator at the site which was later transferred to the laboratory as soon as possible

latest by one month from the collection time. Samples were later processed for analysis of pH, EC,  $\text{HCO}_3^-$  and major ions.

### 3.2.2 Aerosol samples

Fine aerosol samples were collected during snowfall event for calculation of scavenging ratios. The aerosol samples were collected on Whatman 41 cellulose filters (Dia=47 mm) using a low volume pump (40l/min). A rotameter was fit in the line to measure the flow rate. The sampling duration varied according to snowfall event. A total of 11, 19 and 14 samples were collected during this period at Kothi, Gulmarg and Mukteshwar respectively. Precautions were taken to avoid contamination both in the laboratory and in the field (Kulshrestha et al., 2009). A field blank was also collected in the same manner. The samples were stored in polypropylene bags and refrigerated. The method of extraction of filters and analysis of aerosol samples was used as reported by Singh et al (2014).

### 3.2.3 Soil samples

The surface soil samples were collected from the depth of 5 cm, after clearing off the grasses, litter and other plant residues from the undisturbed land. The undisturbed soils were chosen for this purpose with a view to avoid the effects of different cultivation and fertilization practices. Soil samples were collected in quadruplicate manner before and after snowfall at each site. The surface soil so collected was stored in plastic bags. These samples were air dried ground with the help of pestle and mortar. These ground samples were sieved using a sieve of pore size 2 mm. Then 2 g of soil was dissolved in 10 ml water in centrifuge tubes. The samples were then sonicated for half an hour in 1 hertz ultrasonicator. This was done to make the sample solution homogeneous. This homogenous solution was further processed for chemical analysis.

### 3.2.4 Dustfall samples

Samples of dustfall were collected during 2012-13 at Mukteshwar (n=15), Gulmarg (n=14) and Kothi (n=11) at the study sites. For the collection of dustfall, a plastic tray of 6 inch diameter was used. These trays were cleaned, properly washed with distilled-deionised water and dried before the exposure of dustfall samples. Polypropylene petri plates were used for dustfall collection since it is chemically inert to inorganic and organic species of the dustfall

fluxes. A number of studies have proved that polypropylene plate is a very good material for collection of falling atmospheric dust (Saxena et al., 1992; Tiwari et al., 2016). The petri plates were kept at approx. 2 meter height to avoid any interference from local surface/soil or secondary fugitive dusts (Zhao et al. 2010; Alahmr et al. 2012). This tray was exposed in air for 10 days. The deposited material was dissolved into. 50 ml of high quality deionised water. The dissolved water soluble fraction of dustfall samples were analysed for pH, EC and major ions.

### 3.3. Chemical analysis of snowfall samples

#### 3.3.1 pH, EC and $\text{HCO}_3^-$ of samples

The electrical conductivity and pH of collected snow samples were measured immediately after their receipt in the laboratory. pH and EC were also measured for soil and water soluble dustfall samples. The electrical conductivity of samples was measured with Thermo Orion 5Star conductivity meter (fig. 3.3 a), calibrated with standard KCl solution. The pH of samples was measured with EUTECH pH meter (fig. 3.3 b), calibrated with standard buffer solutions of pH 4, 7 and 10. Electrodes were washed with distilled water and wiped after every analysis for maintaining the accuracy and correctness of the results.



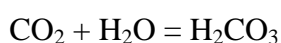
**Fig. 3.2:** pH meter.

Manual titration method was used for estimation of  $\text{HCO}_3^-$  in snow as well as water soluble dustfall and soil samples using 0.01639 N  $\text{H}_2\text{SO}_4$  (AWWA-WEF-APHA, 1998).

$\text{HCO}_3^-$  in snow and dust samples in indian region might be due to interference of soil-derived  $\text{CaCO}_3$ . Dissolution of  $\text{CaCO}_3$  in rain water results in  $\text{HCO}_3^-$  as follows:



$\text{HCO}_3^-$  can also be contributed due to dissolution of atmospheric  $\text{CO}_2$  into water forming  $\text{H}_2\text{CO}_3$  which is further dissociated to give  $\text{H}^+$  and  $\text{HCO}_3^-$ .



### 3.3.2 Ionic analysis

Prior to chemical analysis, all samples were filtered through nylon syringe filter (pore size of 0.2  $\mu\text{m}$ ). The major cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) and major anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) were analyzed by ion chromatograph (Metrohm 883 Basic IC Plus). Metrohm ion chromatograph instrument has been shown in Fig.3.4.



**Fig. 3.3:** Ion Chromatograph model Metrohm 883 used for the determination of ions in this study.

The anions were determined by using Metrosep A SUPP 4, 250/4.0 column and an eluent of 1.8 mmol/L Na<sub>2</sub>CO<sub>3</sub> and 1.7 mmol/L NaHCO<sub>3</sub> at a flow rate of 1.0 ml/min with Metrohm suppressor technique. The cation separation was achieved with the Metrosep C4-100/4.0 column and an eluent of 1.7 mmol/L Nitric acid and 0.7 mmol/L Dipicolinic acid at a flow rate of 0.9 ml/min without suppressor. Detailed information about the instrument and chemical used are given in table 3.1.

**Table 3.1:** Operating conditions employed for the analysis of ions by ion chromatograph.

Conditions	Anion	Cation
<b>Column</b>	Metrosep A SUPP 4, 250/4.0	Metrosep C4-100/4.0
<b>Sample Volume</b>	20 µl	20 µl
<b>Flow rate</b>	1.0 ml/min	0.9 ml/min
<b>Eluent</b>	1.8 mmol/L Na <sub>2</sub> CO <sub>3</sub> and 1.7 mmol/L NaHCO <sub>3</sub>	1.7 mmol/L Nitric acid and 0.7 mmol/L Dipicolinic acid
<b>System pressure</b>	4.6 MPa	5.22 MPa
<b>Detector setting</b>	Metrohm suppressor	Without suppressor

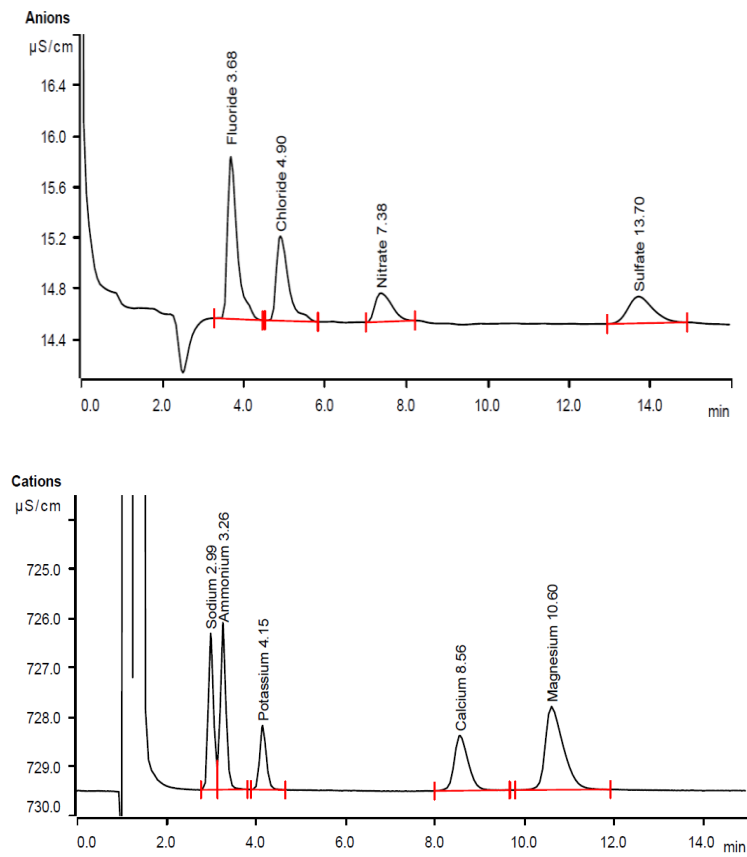
Calibration of methods and quantification of components were carried out using MERCK reference standards (CertiPUR). In the case of anions, 1, 2 and 5 ppm standards were used to achieve the calibration curve of each component, whereas the calibration curve of each cation was achieved by using 2, 5 and 10 ppm standards, respectively (Fig. 3.5a and 3.5b). The calibration equations along with precision and values of correlation coefficients ( $r^2$ ) for all the components are given in Table 3.2.



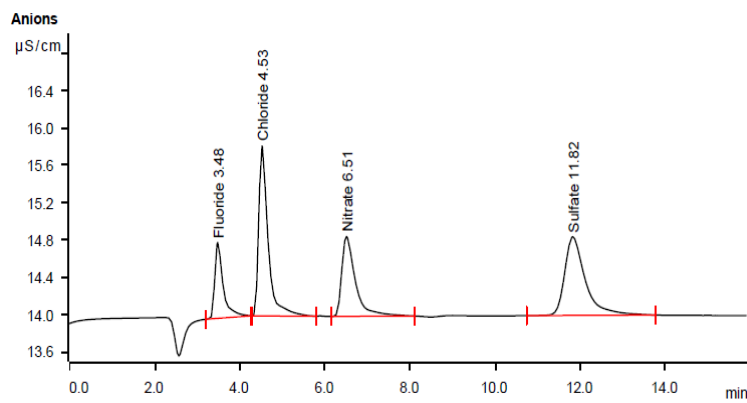
**Table 3.2:** Calibration equation, correlation coefficient and analytical precision for different ionic species.

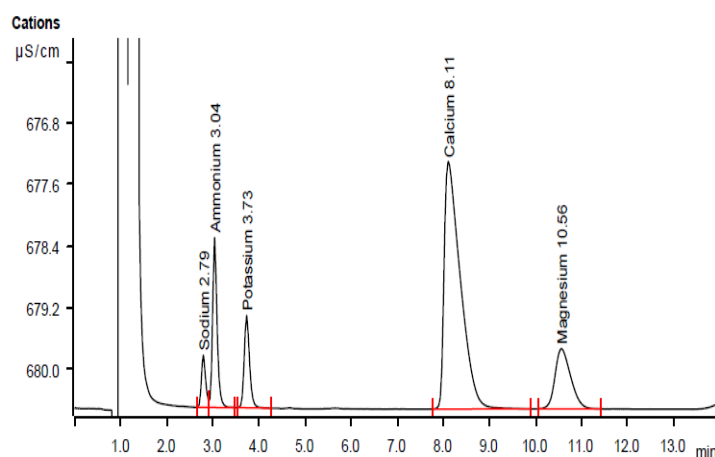
Major ions	Calibration equation	Correlation coefficient ( $r^2$ )	Precision
$F^-$	$y = 0.1368x + 0.0481$	0.9999	1.06%
$Cl^-$	$y = 0.1081x + 0.0035$	0.9998	3.37%
$SO_4^{2-}$	$y = 0.0858x + 0.0008$	0.9999	3.07%
$NO_3^-$	$y = 0.0552x - 0.0066$	0.9998	1.14%
$Na^+$	$y = 0.2138x - 0.0008$	0.9999	2.59%
$K^+$	$y = 0.1172x + 0.0025$	0.9999	4.08%
$Ca^{2+}$	$y = 0.2527x - 0.0100$	0.9999	0.41%
$NH_4^+$	$y = 0.2527x - 0.0100$	0.9999	2.84%
$Mg^{2+}$	$y = 0.3924x + 0.0088$	0.9999	2.80%

The Ion chromatograph column was equilibrated for 30 mins before analysis. Standards were used after every eight analytical run in order to check the calibration of the instrument for its variation that should not be more than  $\pm 5\%$ . Chromatogram of 2ppm standard solution of anions and cations has been shown in Fig. 3.5a and 3.5b, respectively. Fig. 3.6a and 3.6b shows the typical chromatogram of sample for anions and cations, respectively.



**Fig. 3.4:** Chromatogram of anions (a) and cations (b) for standard (2 ppm). (Retention time is shown above the peak).





**Fig. 3.5:** Ion Chromatogram of a (a) sample (anions) and (b) sample (cations).

### 3.4. QA/QC of data

Ionic data of samples were subjected to ion balance and conductivity balance checks to ascertain the quality of data (Gillett and Ayers, 1991, WMO, 1994, Ayers, 1995). A significant correlation observed between sum of anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ ) and sum of cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) indicates that almost all major cations and their counter anions were analyzed in the samples.

Ion balance was further supported by the calculation of the percent relative ion balance as below -

$$\text{Relative ion balance \%} = (\sum\text{C} - \sum\text{A}) \times 100 / (\sum\text{C} + \sum\text{A})$$

where,  $\sum\text{C}$  and  $\sum\text{A}$  are the sum of cations and anions (unit:  $\mu\text{eq/l}$ ).

**Table 3.3:** Relative percent ion difference to check quality of data (WMO, 1994).

Anions + Cations (ueq/l)	Acceptable ion difference (%)
$\leq 50$	$\leq \pm 60$
50 - 100	$\leq \pm 30$
100 - 500	$\leq \pm 15$
$> 500$	$\leq \pm 10$

The average percent ion difference within the acceptable range (WMO, 1994, Ayers, 1995, Kulshrestha et al., 2003) indicates good quality of data (Table 3.3). The strong correlation between measured conductivity and calculated conductivity also used further to confirm the high quality of dataset.

### 3.5. Calculation of air mass trajectories

In order to understand the contribution of airmasses approaching from different directions, 5-days backward trajectories were calculated by using the HYSPLIT model from NOAA (Draxler and Rolph, 2003) in himalyan region of India. In this study, we tried to see the movement of airmasses from various heights above ground level starting from 500 m to 5000m. The lower height above ground level creates the greatest uncertainty in air mass trajectories (Segura et al., 2013). Hence, higher heights are used to avoid complicated local topography effect on the back trajectories (Calvo et al., 2010). Lee and co-workers (2010) have used 6500m height for 315 hr backward air mass trajectories to explain the role of deserts on PM10 composition in Hong Kong. Since, north western Himalayan region receives heavy snowfall mostly during winters due to western disturbances (Naik et al., 1995) through high altitude winds, therefore, we have calculated the trajectories at 5000m height above ground level in the present study.

120 h backward trajectories of 5000m above ground level were calculated for all snowfall samples using the HYSPLIT model from NOAA (Draxler and Rolph, 2003). Kuniyal et al (2013) have also used the similar height to explain the composition of airmasses in this geographical region. In this model, trajectories are computed for every 6 hour for the location with GDAS (Global Data Assimilation System) meteorological data.

### **3.6. Statistical analysis**

In order to know the distribution and the relationship of various components between and within the site, statistical analyses were performed using Statistical Package for Social Sciences (SPSS Ver.16). Data values have been presented in tabular form as “means  $\pm$  Standard error”. The correlation and regression analyses were attempted to estimate relationship, cause and effects of the variation in ionic components. In order to explain the relationship between chemical components and their source, principal component analysis was also applied to the ionic dataset using SPSS 16.0 software. Graphs were plotted with the help of Sigma plot and MS-Excel 13.

One way ANOVA test was applied to the whole data set of different air clusters. The calculations show that most of the components have significant differences between air clusters suggesting that each airmass trajectory plays an important role in determining the chemical composition and pH of snow.

*Chapter 4*  
*Snow Chemistry*

---

## SNOW CHEMISTRY

This chapter mainly focuses upon the chemical characterization of snowfall at Kothi, Gulmarg and Mukteshwar in north western and central himalyan region of India. It discusses in detail about the variation of pH with comparison to other sites worldwide. The ionic compositions of snowfall are discussed including its sources and comparison to other tropical and temperate ecosystems. Wet deposition fluxes of major ions are also discussed and calculated in this chapter at the present sites. The sources of neutralization of acidity for snowmelt are also discussed in the end of this chapter.

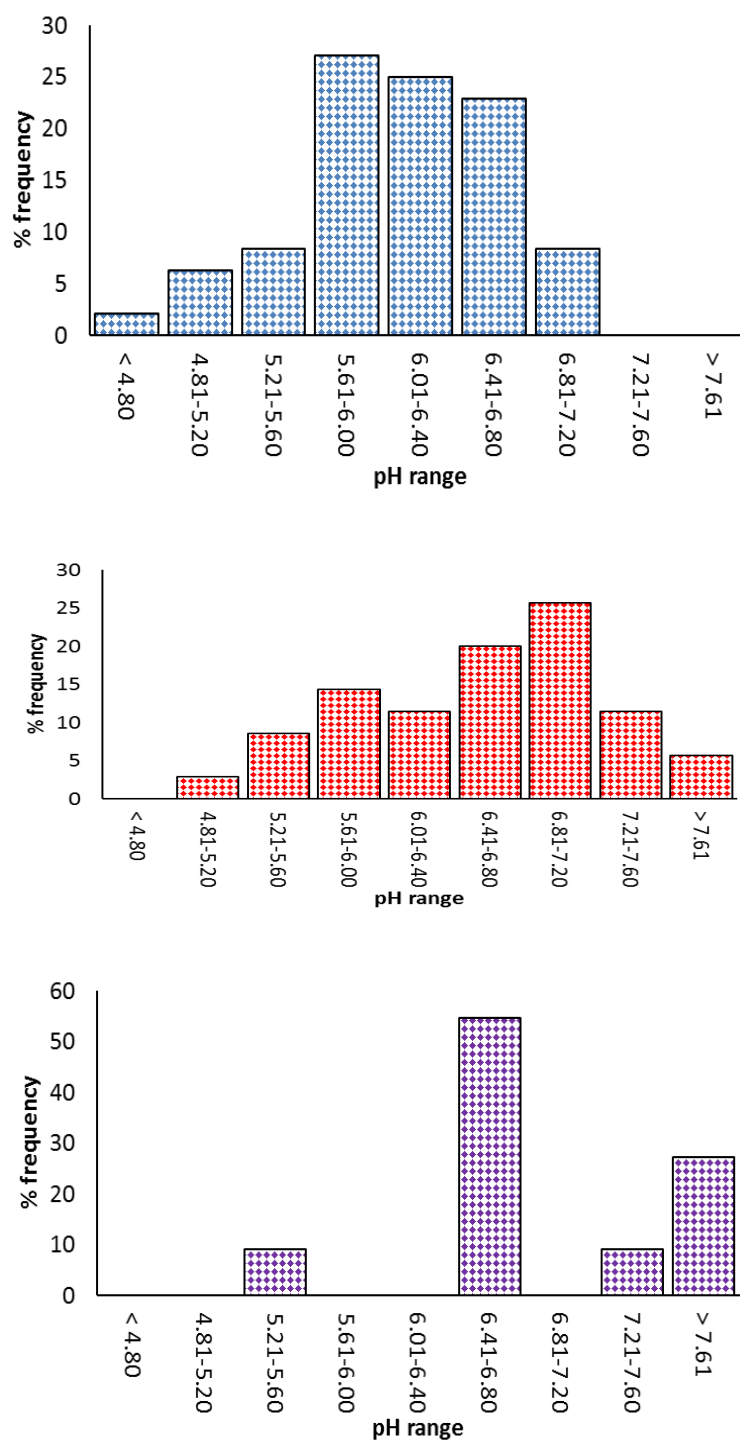
### 4.1. pH of snowmelt samples

#### 4.1.1. Frequency distribution of pH of snowmelt in north western and central Himalaya

In general, pH of the snowmelt samples at Kothi varied from 4.75 to 6.98 with an average value of 5.69 while Gulmarg site varied from 5.16 to 7.68 with an average value of 5.90. The pH of snowmelt samples at Mukteshwar ranged from 5.47 to 7.95 with an average of 6.37.

The pH value of 5.6 is considered as the natural pH of cloud water due to equilibration of atmospheric CO<sub>2</sub> (Charlson and Rodhe, 1982). Precipitation samples having pH value more than 5.6 have been termed as alkaline precipitation (Kulshrestha et al., 2005). Similar range of pH values of precipitation has been reported at higher altitude in Indian region (Naik et al., 1995; Tiwari et al., 2012; Budhavant et al., 2014a).

Fig. 4.1 (a-c) shows the percent frequency distribution of pH of snowfall samples at the sampling sites. Maximum number of samples had pH between 5.61- 6.00 (27%) followed by 6.01- 6.40 (25%), 6.41 – 6.80 (23%), 5.21 – 5.60 = 6.81 – 7.20 (11%) and the lowest percentage was for 4.41- 4.80 at Kothi while Gulmarg site followed the order- 6.81 – 7.20 (26%) > 6.41 – 6.80 (20%) > 5.61 – 6.00 (14%) > 6.01 - 6.40 = 7.21 – 7.60 (11%) > 5.21 - 5.60 (9%) > 7.61 -8.00 (6%) > 4.81 -5.20 (3%).



**Fig. 4.1:** Percent frequency distribution of pH of snowmelt (a) Kothi (b) Gulmarg (c) Mukteshwar.



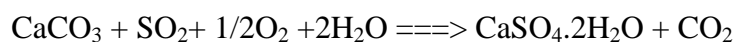
The maximum number of samples of snowmelt at Mukteshwar had pH between 6.41 and 6.80 (55%) followed by 7.61 – 8.00 (27%) and 5.21 – 5.60 = 7.21 -7.60). 16%, 12% and 9% snowfall samples were found acidic at Kothi, Gulmarg and Mukteshwar Himalayan region of India. Acidic precipitation has been reported at few other sites in Indian region (Kumar et al., 1993; Kulshrestha et al., 2005; Kulshrestha et al., 1999; Kulshrestha and Kumar, 2014). According to Das et al. (2005), 43 % of precipitation samples were observed to be acidic in nature at state botanical garden in Bhubaneswar, India while 18 % and 7% samples of rain water were found to be acidic rain at Delhi and Hyderabad respectively (Kulshrestha et al., 1996; 2003). Total 16 out of 42 EANET sites showed pH < 5 with the maximum number from China, Japan, Malaysia and Thailand (EANET, 2011).

#### 4.1.2. Comparison with other study

Table 4.1 shows the geographical comparison of pH of snowmelt samples of the present sites with other sites in the world. The differences in pH of precipitation might be due to differences in ionic composition of snowmelt. Acidic components such as  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  etc. decrease the pH of snowmelt while basic components such as  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$  helps in enhancing the pH of snowmelt samples. The lower pH reported at USA and European sights might be due to dominance of acidic sources over alkaline sources. The detailed discussions of ionic composition of various sites of the world have been given in section 4.3.

It is very clear from the Table 4.1 that pH of the snowmelt at the present sites are higher than other sites of the world. Slightly alkaline snowmelt has been reported at himalya in Indian region (Lone et al., 2010; Tiwari et al., 2012, Kulshrestha and Kumar, 2014; Kumar et al., 2016). Relatively high pH of snowfall in this area is due to the buffering effect of local soil dust which is rich in  $\text{CaCO}_3$ . The conditions which determine the pH of precipitation in acidified and Indian regions have been described by Rodhe et al (2002). Scavenging of  $\text{SO}_2$

onto the dust particles forming calcium sulphate in India has been demonstrated as follows (Kulshrestha, 2013)-



Formation of calcium sulphate does not contribute acidity in precipitation rather enhances the pH of solution.

**Table 4.1:** Geographical comparison of pH of snowmelt samples.

Sampling site	Country	pH	Reference
<b>Kothi, Himachal Pradesh</b>	India	<b>5.69</b>	Present study
<b>Gulmarg, Jammu &amp; Kashmir</b>	India	<b>5.90</b>	Present study
<b>Mukteshwar, Uttarakhand</b>	India	<b>6.37</b>	Present study
<b>Gulmarg, Jammu &amp; Kashmir</b>	India	<b>6.70</b>	Naik et al., 1995
<b>Afarwat glacier Kashmir, Himalaya</b>	India	<b>6.90</b>	Lone et al., 2010
<b>Central and Southern Californis</b>	USA	<b>5.20</b>	Gunz and Hofmann, 1990
<b>Mid Wales</b>	Ceredigion and Powys	<b>4.50</b>	Reynolds, 1983
<b>Scottish Catchment</b>	Europe	<b>4.20</b>	Tranter et al., 1967
<b>Larsemann Hills</b>	Antartica	<b>5.63</b>	Budhavant et al., 2014b
<b>Xixabangma Peak, Central Himalaya</b>	Tibet	<b>5.96</b>	Kang et al., 2002

## 4.2. Chemical composition of snowmelt

### 4.2.1. Quality check of data

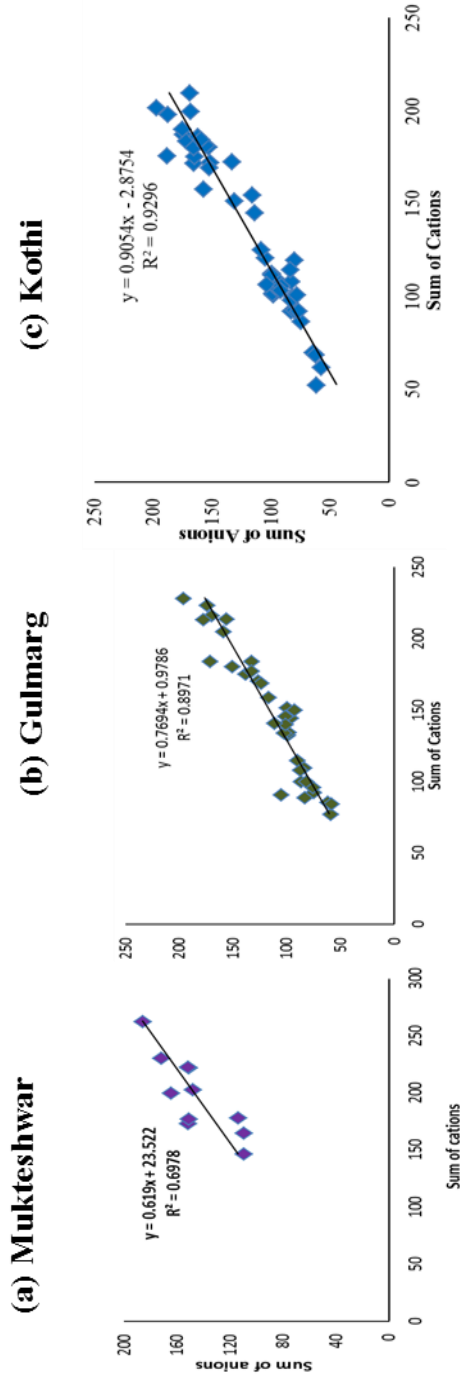
Snow chemistry data was subjected to ion balance and conductivity balance checks to ascertain the quality of data (Gillett and Ayers, 1991, WMO, 1994, Ayers, 1995). At Mukteshwar, a significant correlation ( $R^2 = 0.70$ ) was found between sum of anions ( $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$  and  $HCO_3^-$ ) and sum of cations ( $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ ) suggesting that almost all major cations and their counter anions were analyzed in the samples (Fig. 4.2a). Similar to Mukteshwar, a significant correlations between major cations and major anions were observed for Gulmarg ( $R^2 = 0.90$ ) and Kothi ( $R^2 = 0.93$ ) (Fig. 4.2 b-c). Ion balance was further supported by the calculation of the percent relative ion balance as below-

$$\text{Relative ion balance \%} = (\sum C - \sum A) \times 100 / (\sum C + \sum A)$$

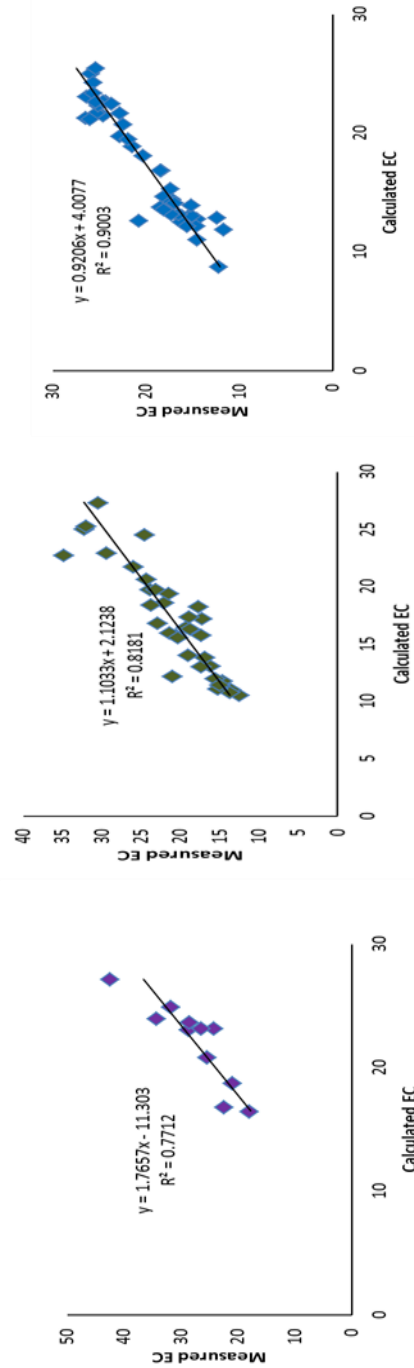
Where,  $\sum C$  and  $\sum A$  are the sum of cations and anions (unit:  $\mu\text{eq/l}$ ).

At Kothi, The average 6 % of ion difference has been observed for total ion sum 258  $\mu\text{eq/l}$ , which has been within the acceptable range (WMO, 1994, Ayers, 1995, Kulshrestha et al., 2003). Similar to Kothi, the percent ion difference were in acceptable range at Gulmarg and Mukteshwar.

The strong correlation noticed between measured conductivity and calculated conductivity ( $R^2 = 0.77$ ) further confirmed the high quality of dataset at Mukteshwar (Fig. 4.3a). Similar to Kothi, very good correlation between measured electrical conductivity (EC) and calculated conductivity were observed at Gulmarg ( $R^2 = 0.82$ ) and Kothi ( $R^2 = 0.90$ ) (Fig. 4.3 b-c).



**Fig. 4.2:** Scatter plot showing ion balance between sum of anions and cation.



**Fig. 4.3:** Scatter plot showing conductivity balance between measured conductivity and calculated conductivity.

### 4.2.2. Major ions of snowmelt

The average concentrations of major ions along with statistical deviations are given in Table 4.2 for all sites. At Kothi, the average concentration of ions followed the order-  $\text{Ca}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{SO}_4^{2-} = \text{HCO}_3^- > \text{NH}_4^+ > \text{NO}_3^- > \text{Mg}^{2+} > \text{K}^+ > \text{F}^-$ . The average amount of ions in  $\mu\text{g/l}$  at Gulmarg followed the order-  $\text{Ca}^{2+} > \text{Na}^+ > \text{Cl}^- > \text{NH}_4^+ > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^- > \text{Mg}^{2+} > \text{K}^+ > \text{F}^-$  while Mukteshwar site followed the following order-  $\text{Ca}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NH}_4^+ > \text{NO}_3^- > \text{Mg}^{2+} > \text{K}^+ > \text{F}^-$ .

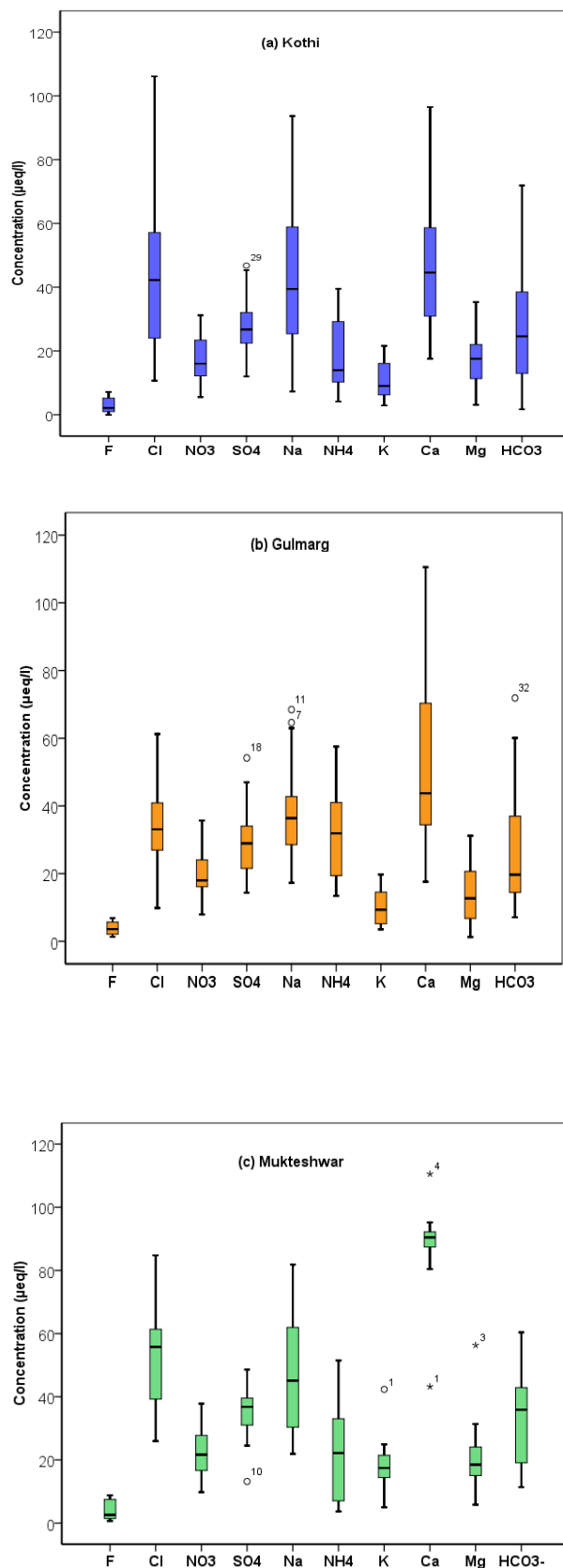
**Table 4.2:** Average concentration  $\pm$  SD of major ions along with pH, EC of snowmelt samples.

	Kothi	Gulmarg	Mukteshwar
<b>F-</b>	3.0 $\pm$ 2.3	3.8 $\pm$ 1.8	4.0 $\pm$ 3.3
<b>Cl-</b>	46.0 $\pm$ 25.4	34.7 $\pm$ 13.0	52.5 $\pm$ 18.7
<b>NO<sub>3</sub><sup>-</sup></b>	17.4 $\pm$ 7.3	19.0 $\pm$ 6.9	22.5 $\pm$ 9.0
<b>SO<sub>4</sub><sup>2-</sup></b>	27.4 $\pm$ 8.3	29.1 $\pm$ 9.1	34.7 $\pm$ 9.6
<b>Na<sup>+</sup></b>	43.7 $\pm$ 22.6	37.7 $\pm$ 13.4	46.9 $\pm$ 21.4
<b>NH<sub>4</sub><sup>+</sup></b>	18.4 $\pm$ 10.8	32.1 $\pm$ 13.7	23.7 $\pm$ 17.5
<b>K<sup>+</sup></b>	10.9 $\pm$ 5.7	9.8 $\pm$ 5.1	18.9 $\pm$ 9.6
<b>Ca<sup>2+</sup></b>	47.1 $\pm$ 21.1	52.6 $\pm$ 25.1	87.2 $\pm$ 16.3
<b>Mg<sup>2+</sup></b>	17.00 $\pm$ 7.7	14.1 $\pm$ 7.7	21.6 $\pm$ 13.5
<b>HCO<sub>3</sub><sup>-</sup></b>	27.4 $\pm$ 17.6	26.8 $\pm$ 17.5	32.4 $\pm$ 15.6
<b>pH</b>	6.07 $\pm$ 0.55	6.48 $\pm$ 0.78	6.96 $\pm$ 0.73
<b>EC</b>	19.8 $\pm$ 4.5	20.5 $\pm$ 6.2	27.6 $\pm$ 6.8

In general, the concentrations of all ions were recorded higher at Mukteshwar than Gulmarg and Kothi sites (Table 4.2). The highest concentration was observed for  $\text{Ca}^{2+}$  in comparison to all ions at the present sites. At Kothi, the concentration of  $\text{Ca}^{2+}$  varied from 17.6 to 96.5  $\mu\text{eq/l}$  with an average of 47.1  $\mu\text{eq/l}$  (Fig. 4.4).  $\text{Ca}^{2+}$  ranged from 17.6 to 110.6  $\mu\text{eq/l}$  with an average of 52.6  $\mu\text{eq/l}$  at Gulmarg site.  $\text{Ca}^{2+}$  being the most abundant ion varied from 43.2 to

110.6 with an average of 87.2  $\mu\text{eq/l}$  at Mukteshwar in central himalyan region of India (Fig. 4.4). Similar to our results, the highest concentrations of  $\text{Ca}^{2+}$  in snowmelt samples were reported by other workers also in Himalayan region of India (Naik et al., 1995; Lone et al., 2010; Kumar et al., 2016). After  $\text{Ca}^{2+}$  and  $\text{Na}^+$ , very high concentration of  $\text{NH}_4^+$  was observed in snowmelt samples at these sites.  $\text{NH}_4^+$  being one of the most dominant cation have been reported in precipitation samples in indian region (Jain et al., 2000; Kulshrestha et al., 2005; Singh et al., 2015).

Among anions, a significant amount of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  has been recorded at these sites in snowmelt samples. The concentration of  $\text{SO}_4^{2-}$  at these sites followed the order- Mukteshwar > Gulmarg > Kothi. The concentration of  $\text{SO}_4^{2-}$  at Kothi ranged from 12.0 to 46.8 with an average of 27.4  $\mu\text{eq/l}$  (Fig. 4.4). At Gulmarg, the concentration of  $\text{SO}_4^{2-}$  varied from 14.4 to 54.2 with an average of 29.1  $\mu\text{eq/l}$  while it ranged from 13.2 to 48.6 with an average of 34.7  $\mu\text{eq/l}$  at Mukteshwar site (Fig. 4.4). Similar to our result, a significant amount of  $\text{SO}_4^{2-}$  has been reported in snowmelt samples in Himalyan region of India by Naik and coworkers (1995). Spatial variations have been found for  $\text{NO}_3^-$  with an average of 17.4, 19.3 and 22.5 at Kothi, Gulmarg and Mukteshwar respectively in Himalayn region of India.

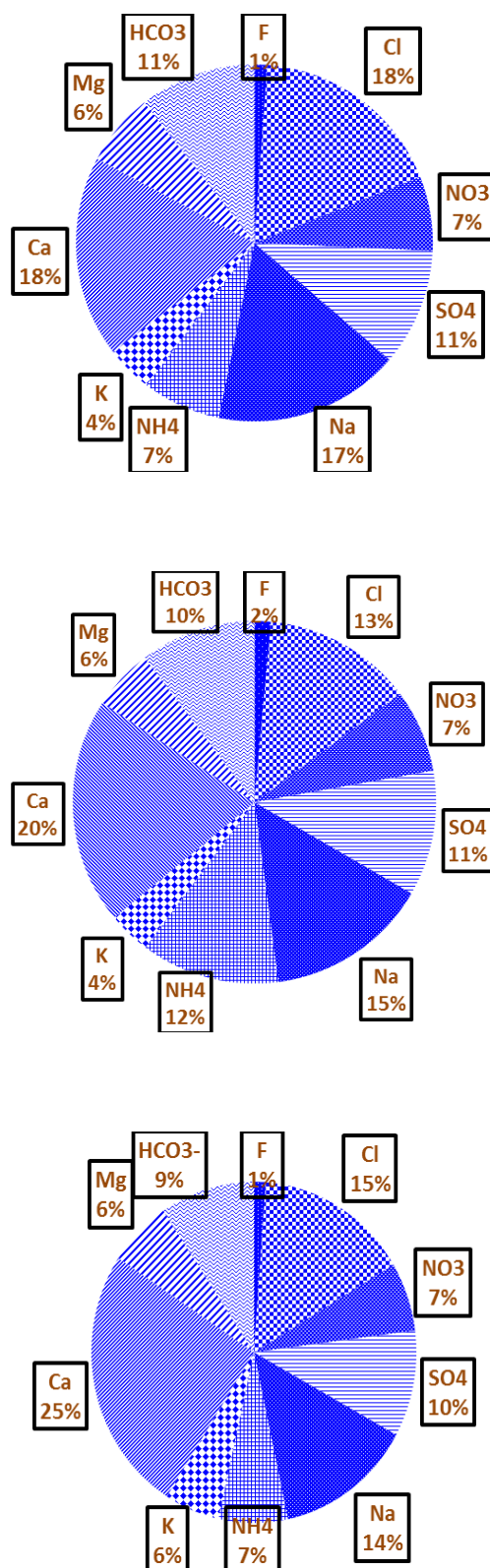


**Fig. 4.4:** Centre line indicates median, box plot shows 25 - 75<sup>th</sup> percentile and bar indicates minimum & maximum values. Stars and circle denote the outliers.

### 4.2.3. Relative percent of ions

The relative percent contribution of ions in the snowmelt samples at Kothi, Gulmarg and Mukteshwar have been shown in Fig. 4.5 (a-c). The most abundant ion was found to be  $\text{Ca}^{2+}$  at these sites with 18%, 20% and 25% among the total ions at Kothi, Gulmarg and Mukteshwar respectively. Very high percent of  $\text{Ca}^{2+}$  at these sites indicate the dominance of crustal influence in Indian region. Similar to our result, very high percent contribution of  $\text{Ca}^{2+}$  has been recorded in precipitation samples at other sites in India (Jain et al., 2000; Kulshrestha et al., 2005, Satyanarayana et al., 2010; Singh et al., 2015). Very high percent of  $\text{NH}_4^+$  has been observed at these sites with the following order- Gulmarg (12%), > Mukteshwar (7%) ~ Kothi (7%). This spatial variations of  $\text{NH}_4^+$  at these sites have been discussed in detail in the next section. A significant percent contribution of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  has been recorded in snowmelt samples at these sites (Fig. 4.5 a-c).

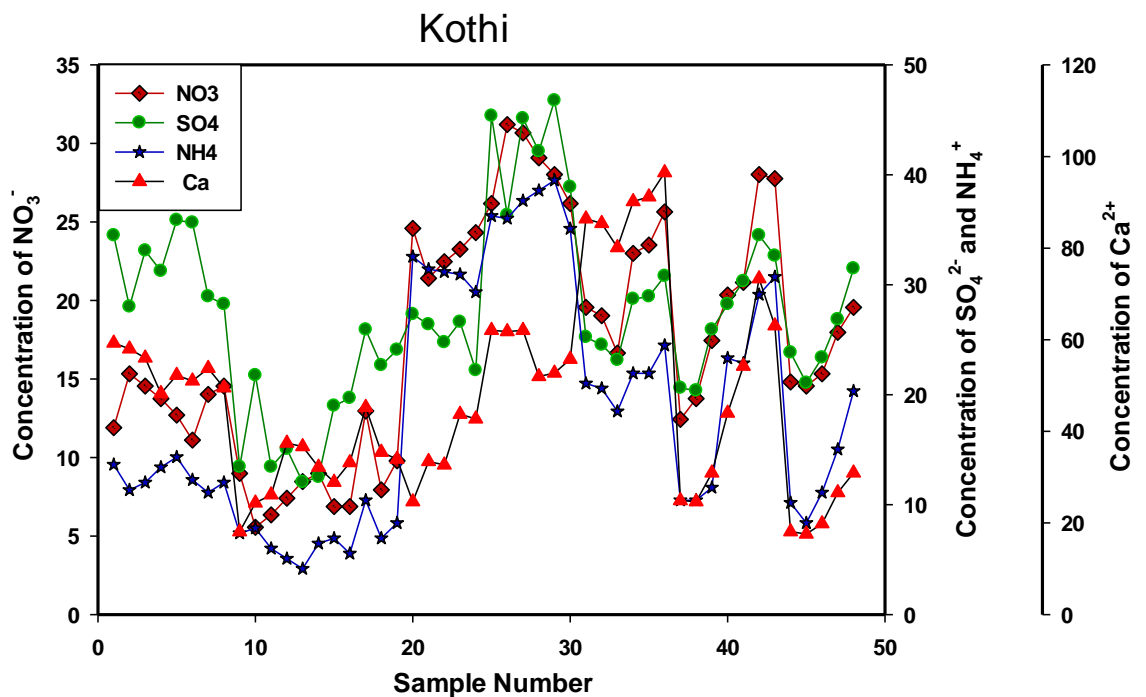


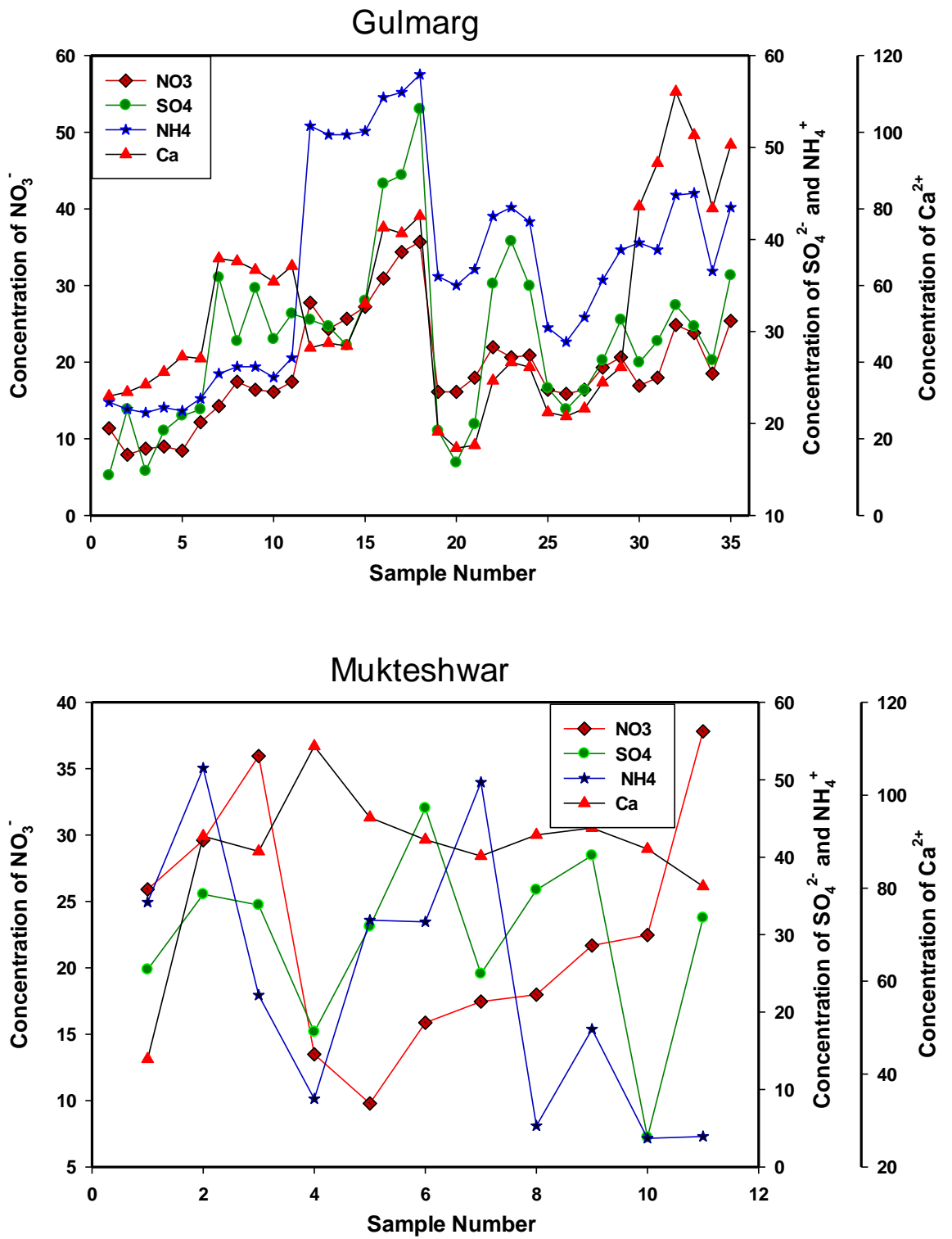


**Fig. 4.5:** Percent contribution of major ions (a) Kothi (b) Gulmarg (c) Mukteshwar.

#### 4.2.4. Variation of major ions

It is an established fact that the chemical nature of precipitation is greatly influenced by chemical components such as  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in Indian region (Jain et al., 2000; Kulshrestha et al., 2005). Hence, it is very important to discuss their variations in snowmelt samples at Himalayan region of India. The variation of these significant ions at Kothi, Gulmarg and Mukteshwar have been shown in Fig. 4.6 (a-c).





**Fig. 4.6:** Variation of Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> in snowmelt samples at Kothi, Gulmarg and Mukteshwar.

The most abundant ion was  $\text{Ca}^{2+}$  at the present sites. The highest concentration of  $\text{Ca}^{2+}$  indicating the dominance of crustal and marine sources which has been discussed in section 3.3. High levels of  $\text{Ca}^{2+}$  due to local as well as transported dust have been reported in precipitation (Satyanarayana et al., 2010; Budhavant et al., 2012). The suspended soil dust might be significant local source for  $\text{Ca}^{2+}$  since the soil in this region are loosely bound in the earth crust. Since, the site is very fascinating place for tourists attracting its scenic beauty. The ongoing construction activities especially building resorts to accommodate the maximum number of tourists. Besides this, road dust also contributes  $\text{Ca}^{2+}$  in precipitation. These activities are considered as significant sources of  $\text{Ca}^{2+}$  (Rahn, 1976; Kulshrestha and Kumar, 2014). Very high concentration of  $\text{Ca}^{2+}$  due to suspended dust has been reported in Indian precipitation (Kulshrestha et al., 2005).

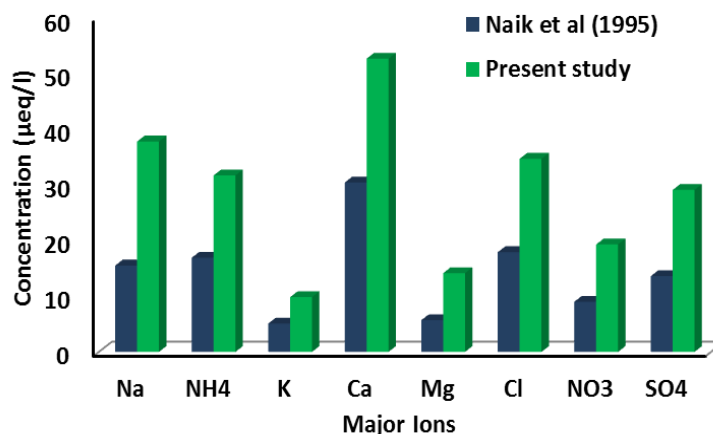
After  $\text{Ca}^{2+}$  and  $\text{Na}^+$ ,  $\text{NH}_4^+$  ion has been the most abundant. Very high concentration of  $\text{NH}_4^+$  among all cations indicated a significant influence of anthropogenic sources at Mukteshwar. The most important sources of  $\text{NH}_4^+$  are agriculture activities, livestock, excreta of human and animal etc. (Galloway, 1995; Singh and Kulshrestha, 2012). Local people in this region are dependent upon mainly agriculture activities for their livelihood. Due to this region, agriculture activities and livestock might be a significant source of  $\text{NH}_4^+$  at this site. Apart from these sources, local people as well as tourists reaching here also might be significant source for  $\text{NH}_4^+$  in this region. Singh and co-workers (2012) reported that humans are also a significant source of  $\text{NH}_3$ . Since many local people are forced to go in the open field for excretion since they don't have proper toilet facility. Open excreta of human and animal also might be a good source of  $\text{NH}_4^+$  at Mukteshwar. Apart from above mentioned sources, some contribution of long range transport can't be ruled out at this site which has not been discussed in this paper.

---

Among anions,  $\text{SO}_4^{2-}$  had the significant contribution in snowmelt samples at these sites. A comparison with other global data, we found that average concentration of  $\text{SO}_4^{2-}$  at this site was lower than Yulong snow (Zhu et al., 2012) but higher than Mt. Everest (Kang et al., 2004) and Mt. Logan Massif (Yalcin et al., 2006). Since, there is no any industrial activities at this site. Due to this reason, the maximum contribution of  $\text{SO}_4^{2-}$  might be due to transported  $\text{SO}_4^{2-}$  from other site in India or transboundary and long range transport  $\text{SO}_4^{2-}$ . Very similar range of  $\text{SO}_4^{2-}$  concentration has been reported worldwide (Avila and Alacron, 1999; Granat et al., 2002; Kulshrestha et al., 2003b; Tiwari et al., 2007; Satyanarayana et al., 2010; Budhvant et al., 2012). High concentration of  $\text{SO}_4^{2-}$  indicated a significant influence of anthropogenic sources emitting  $\text{SO}_2$ . Among local sources, diesel driven vehicular traffic might be the possible source of  $\text{SO}_4^{2-}$ . Vehicular flow due to increased tourist activities during winter season might be considered as a good source of  $\text{SO}_2$  at Mukteshwar.

$\text{NO}_3^-$  in snowfall samples might be due to emission of  $\text{NO}_x$  mainly from vehicular sources which is transformed into the atmosphere which give rise to  $\text{NO}_3^-$  in precipitation samples (Finlayson-Pitts and Pitts, 1986; Seinfeld and Pandis, 2006). Another local source might be biomass burning during winter season to produce heat by local people cannot be ruled out (Singh et al., 2014). Apart from local emissions, very high concentration of  $\text{NO}_3^-$  might be due to long range transport of  $\text{NO}_x$  /  $\text{NO}_3^-$  from various airmasses approaching at these sites.

## 4.2.5. Comparison of the present study with previous study at the same site



**Fig. 4.7:** Comparison of the present study with previously reported 1986-87 values by Naik et al. (1995).

Fig. 4.7 shows the comparison of ionic concentration of the present study (Gulmarg only) with the snowfall chemistry data of 1986-87 at Gulmarg as reported by Naik et al. (1995).

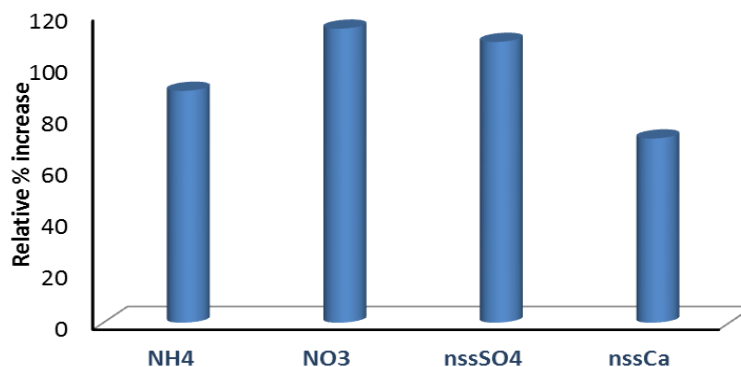
Fig. 4.8 shows that in a span of about 3 decades, there has been a remarkable percent increase in the concentrations of all the major ions. Relative percent increase has been calculated by the following formula-

$$\text{Relative \% increase} = (C_{\text{present}} - C_{\text{previous}}) * 100 / C_{\text{previous}}$$

Here,  $C_{\text{present}}$  = Concentration of the chemical species in the present study

$C_{\text{previous}}$  = Concentration of the same chemical species for the year 1986-87.)

In order to understand the effect of changes due to increased human activities during past three decades,  $\text{NSSO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  are considered as the major anthropogenic ions, their detailed discussion is given below.



**Fig. 4.8:** Relative % increase in the concentrations of major ions since 1986-87.

As compared to 1986-87 values,  $\text{NO}_3^-$  showed a remarkable increase (114 %).  $\text{NO}_3^-$  at this site is mostly contributed by anthropogenic activities such as vehicular traffic which is increased exponentially emitting significant amount of  $\text{NO}_x$ . Gulmarg has witnessed a very fast growth in number of tourists during past three decades. The number of tourists visited was reached to more than 15 lakhs in 2012 (<http://www.greaterkashmir.com>) which is very high number as compared to previous years. In addition, increased consumption of diesel in electricity generator sets by various hotels and Gondola during power failures (<http://ww2.gulmargalpine.com/>). Several fold increase in  $\text{NO}_3^-$  concentration in precipitation due to increased vehicular emissions during past two decades has been noticed by Singh and co-workers (2015).

The concentration of  $\text{NH}_4^+$  in the present study has been noticed 87% higher than the value reported from 1986-87. Significant increase in  $\text{NH}_4^+$  in snowfall may be attributed to direct input of ammonia from various biogenic and anthropogenic sources which have increased during past three decades. It is supported from the fact that the number of horses used for tourists activities have increased and reached to 3000 in 2013 (<http://www.greaterkashmir.com>). Piles of horse-dung are littered in every corner of Gulmarg creating sanitation problem which might be a significant source of ammonia. Apart from

these, humans are also considered as a good source of  $\text{NH}_3^+$  (Singh and Kulshrestha, 2012). From 2001-2011, human population of the Baramula district in which Gulmarg is situated has increased by 19.45 % (<http://www.census2011.co.in/>). In 2011, Baramula had population of 1,008,039. Open dispose of garbage and excreta from various hotels contribute high amount of  $\text{NH}_3$  in the air. Recently, state court has given order to treat properly effluents coming from various hotels (<http://www.risingkashmir.com>) which might control the emission of ammonia in coming future.

Among anions,  $\text{SO}_4^{2-}$  which is contributed by the oxidation of  $\text{SO}_2$  showed 2 fold increase in concentrations as compared to the values recorded in 1986-87. Diesel driven vehicular traffic is an important source of oxides of sulphur in Gulmarg area. Since, there is no major industry nearby, long range transport is an additional source of  $\text{SO}_4^{2-}$  at the site which is discussed in the Chapter 6.

The present study showed 5.9 as average pH at Gulmarg which is 0.8 unit lower the pH of snowmelt (6.7) reported during 1986-87. The decrease in pH is possibly due to the increase in acidic species such as nss  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . It can also be explained on the basis of elevated ratios of nss  $\text{SO}_4^{2-}/\text{nss Ca}^{2+}$  and  $\text{NO}_3^-/\text{nssCa}^{2+}$  (Jain et al., 2000). However, precipitation chemistry has very high spatial and temporal variations. Hence, comparison of the present study has some uncertainties. Future studies would be able to confirm the trends of decreasing pH and increasing acidity due to increasing concentrations of oxides of sulphur or nitrogen at the site.



---

### 4.3. Geographic comparison of ions

The differences in pH level in snowmelt samples worldwide have been discussed in detail in section 4.1.2. These differences in acidity of snowmelt are determined primarily by the interaction of acidic and basic species in the atmosphere. Acidic species are dominated by  $\text{SO}_2$  and  $\text{NO}_x$  which is precursor of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  respectively in precipitation samples. On the other hand, alkaline species ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$ ) help in enhancing pH of precipitation. The main source of alkaline species is atmospheric dust which is made up of carbonates and bicarbonates of Ca and Mg (Rahn, 1976; Kulshrestha et al., 2003; Kulshrestha, 2013).

In order to discuss the differences in pH level of snowmelt samples worldwide, it is important to compare the concentration of these species at the present sites with other geographical region of the world. Table 4.3 compares the concentration of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$  in snowmelt at himalayn region of India with other reported values globally.

It is very clear from Table 4.3 that the concentration of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are higher at himlayan region of India than other geographic regions of the world. Despite very high concentration of acidic species, pH of snowmelt samples in Indian region is on higher side. Unlike America and Europe, it is interesting that higher pH of precipitation is reported in India even at higher  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentration which might be due to huge amount of dust in the atmosphere (Kulshrestha, 2013). Very high concentration of  $\text{Ca}^{2+}$  at Indian sites in comparison to other sites of the world reflected the dominance of dust in Indian atmosphere.

**Table 4.3:** Geographical comparison of major ions of snowmelt samples.

Sampling site	Country	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Ca <sup>2+</sup>	References
Kothi, Himachal Pradesh	India	27.4	17.4	18.4	47.1	Present study
Gulmarg, Jammu & Kashmir	India	29.1	19.3	32.1	52.6	Present study
Mukteshwar, Uttarakhand	India	34.7	22.5	23.7	87.2	Present study
Gulmarg, Jammu & Kashmir	India	13.6	9.0	16.9	30.4	Naik et al., 1995
Afarwat glacier Kashmir, Himalaya	India	-	3.3	2.8	42.6	Lone et al., 2010
Central and Southern Californis	USA	4	5.1	-	4	Gunz and Hofmann, 1990
Mid Wales	Ceredigion and Powys	16	11	-	4	Reynolds, 1983
Scottish Catchment	Europe	26.5	12	-	-	Tranter et al., 1967
Larsemann Hills	Antartica	2.1	0.2	0.7	2.7	Budhavant et al., 2014b
Xixabangma Peak, Central Himalaya	Tibet	1.03	1.53	3.02	2.6	Kang et al., 2002

#### 4.4. Wet deposition fluxes

Fluxes of annual wet deposition flux (F) of all ionic species through snowfall were calculated by the following formula-

$$F = \frac{C \times V}{A}$$

Here F = Annual deposition flux in meq/m<sup>2</sup>/yr

C = Average concentration of ionic components in µeq/l

V = Volume of snowmelt in equivalent litres of water. Snowfall depth was converted to equivalent water using the formula-

$$V = A \times H / 1000$$

Where,

$$A = \text{Area of tray (314 cm}^2\text{)}.$$

H = Height of water melted from snow in cm (It is calculated by assuming 10: 1 conversion of snow into liquid) (Doesken and Judson 1996). Total annual snowfall of 1400 cm (14m) over Gulmarg was taken for calculation.

Table 4.4 represents the annual wet deposition fluxes for all samples. From the table, it is very clear that the annual wet deposition fluxes for snowmelt samples at Kothi followed the order-  $\text{Ca}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{SO}_4^{2-} = \text{HCO}_3^- > \text{NH}_4^+ > \text{NO}_3^- > \text{Mg}^{2+} > \text{K}^+ > \text{F}^-$ . The average fluxes of ions at Gulmarg followed the order-  $\text{Ca}^{2+} > \text{Na}^+ > \text{Cl}^- > \text{NH}_4^+ > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^- > \text{Mg}^{2+} > \text{K}^+ > \text{F}^-$  while Mukteshwar site followed the following order-  $\text{Ca}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NH}_4^+ > \text{NO}_3^- > \text{Mg}^{2+} > \text{K}^+ > \text{F}^-$ . The highest value of wet deposition fluxes was recorded for  $\text{Ca}^{2+}$  at all sites which may be due to crustal influence. Very high wet deposition fluxes for  $\text{Ca}^{2+}$  have been reported in India and other regions of the world (Parashar et al., 1996; Jain et al., 2000; Kulshrestha et al., 2003; Das et al., 2005; Zhang et al., 2007a). Elevated deposition fluxes for  $\text{Na}^+$  and  $\text{Cl}^-$  might be due to marine aerosols deposited at the site. Acidic species like  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are lesser in comparison to  $\text{Ca}^{2+}$  suggesting alkaline nature of precipitation which is very common in Indian region.

**Table 4.4:** Average wet deposition fluxes at Kothi, Gulmarg and Mukteshwar ( $\mu\text{eq}/\text{m}^2/\text{day}$ ).

Major Ions	Kothi	Mukteshwar	Gulmarg
$\text{Na}^+$	47	11	313
$\text{NH}_4^+$	20	82	266
$\text{K}^+$	12	65	81
$\text{Ca}^{2+}$	50	301	436
$\text{Mg}^{2+}$	18	75	117
$\text{F}^-$	3	14	31
$\text{Cl}^-$	49	181	287
$\text{NO}_3^-$	19	78	160
$\text{SO}_4^{2-}$	29	120	241
$\text{HCO}_3^-$	29	112	222

#### 4.5. Acidity of snowmelt and Sources of neutralization

##### 4.5.1. Fractional acidity

The capacity of neutralization of acidic components in precipitation was estimated by calculation of fractional acidity (FA). It was calculated by the following formula (Balasubramanian et al., 2001) -

$$\text{FA} = [\text{H}^+] / [\text{NO}_3^-] + [\text{SO}_4^{2-}]$$

If this ratio is equal to 1 then it is considered that acidity in precipitation sample is not neutralized at all. FA at all three sites were very less than 1 indicating almost complete neutralization of acidity in snowmelt samples. It is supported by alkaline pH of snowmelt at these sites.

$[\text{NO}_3^-] / [\text{NO}_3^-] + [\text{SO}_4^{2-}]$  ratio was used to calculate relative contribution of acidity generated by  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  (Zhang et al., 2012). The ratios at these sites were 0.39, 0.40 and 0.39 at Kothi, Gulmarg and Mukteshwar respectively. These values indicated that approximately only 39%, 40% and 39% acidity was generated by  $\text{NO}_3^-$  at Kothi, Gulmarg and Mukteshwar respectively indicating acidity contributed by  $\text{H}_2\text{SO}_4$  was higher than  $\text{HNO}_3$ . Similar ratios have been reported at other sites in India (Kulshrestha et al, 2005; Satyanarayana et al., 2010, Singh et al., 2015).

#### 4.5.2. Neutralization factor

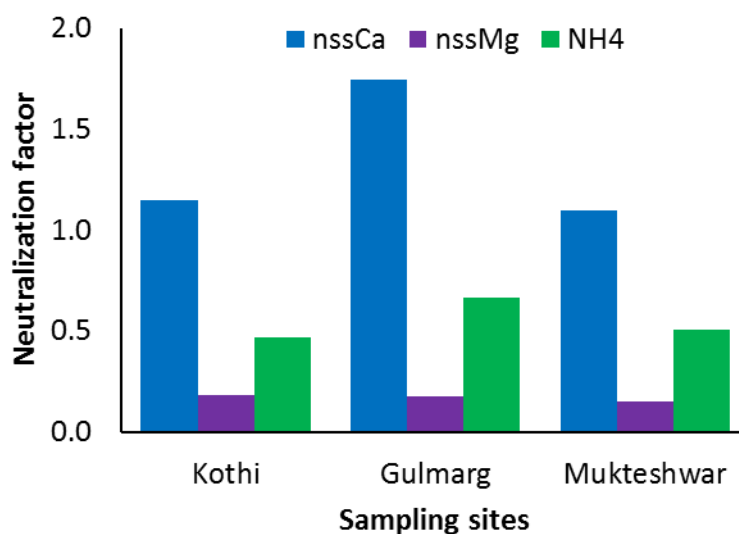
It is well known that  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are the major acidic species while  $\text{nss Ca}^{2+}$ ,  $\text{nss Mg}^{2+}$  and  $\text{NH}_4^+$  are the major alkaline species in precipitation samples. Due to this fact,  $\text{nss Ca}^{2+}$ ,  $\text{nss Mg}^{2+}$  and  $\text{NH}_4^+$  are mainly considered for calculation of neutralization factor.

The neutralization factor of these species were calculated by the following formula-

$$\text{NF}_{\text{Xi}} = \frac{[\text{X}_i]}{[\text{NO}_3^- + \text{nss SO}_4^{2-}]}$$

Where  $[\text{X}_i]$  = The concentration of desired ionic species i.e.  $\text{nss Ca}^{2+}$ ,  $\text{nss Mg}^{2+}$  and  $\text{NH}_4^+$  in ueq/l.

Using the above mentioned formula, the neutralization factor of  $\text{nss Ca}^{2+}$ ,  $\text{nss Mg}^{2+}$  and  $\text{NH}_4^+$  was calculated and are given in Fig. 4.9.



**Fig. 4.9:** Neutralization factor at present sites.

The neutralization factor for these species followed the order-  $\text{nss Ca}^{2+} > \text{NH}_4^+ > \text{nss Mg}^{2+}$ . The maximum neutralization of snowfall acidity at the present sites occurs by  $\text{nssCa}^{2+}$  which might be due to suspended soil dust rich in  $\text{CaCO}_3$  in Indian atmosphere (Jain et al., 2000). These soil dusts might be contributed significantly by long range transport. The importance

of transported dust in the neutralization of acidic components in precipitation samples has been observed globally (Satyanarayana et al., 2010; Budhavant et al., 2012). Similarly, very high value of neutralization factor for  $\text{nssCa}^{2+}$  and  $\text{NH}_4^+$  has been reported in precipitation samples globally (Saxena et al., 1991; Kulshrestha et al., 2003b; Das et al., 2005; Zhang et al., 2007a; Calvo et al., 2010; Satyanarayana et al., 2010).

*Chapter 5*  
*Chemical characteristics of aerosol*  
*and dustfall*

---

## CHEMICAL CHARACTERISTICS OF AEROSOL AND DUSTFALL

This chapter starts with the chemical composition of aerosol (section 5.1) at the present sites i.e. Kothi, Gulmarg and Mukteshwar in Himalayan region of India. It discusses the sources of aerosol including marine and crustal contribution. This chapter also deals with scavenging of aerosol by snowfall at these sites. The 2<sup>nd</sup> part of chapter (section 5.2) deals with the pH and ionic composition of water soluble fraction of dustfall at all three sites. The chapter also discusses annual deposition fluxes of dustfall. Ionic ratios have been calculated to find out the interrelationship between these ions. At the end of the chapter, neutralization of acidic anions such as  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  by major cations has been discussed.

### 5.1. Chemistry of aerosol

#### 5.1.1. Chemical composition of aerosol and its relative contribution

Table 5.1 gives the average concentration of major inorganic ions in aerosol samples at Kothi, Gulmarg and Mukteshwar site. On an average, the ionic concentration at Mukteshwar sites followed the order-  $\text{NH}_4^+ > \text{Cl}^- > \text{SO}_4^{2-} > \text{Na}^+ > \text{Ca}^{2+} > \text{NO}_3^- > \text{Mg}^{2+} > \text{K}^+ > \text{F}^-$  while the chemical components at Kothi and Gulmarg site followed the order -  $\text{NH}_4^+ > \text{Cl}^- > \text{Na}^+ > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+} > \text{F}^-$ . On an average, it is very clear from table 5.1 that the concentration of all water soluble ions were higher at Mukteshwar than Gulmarg and Kothi.

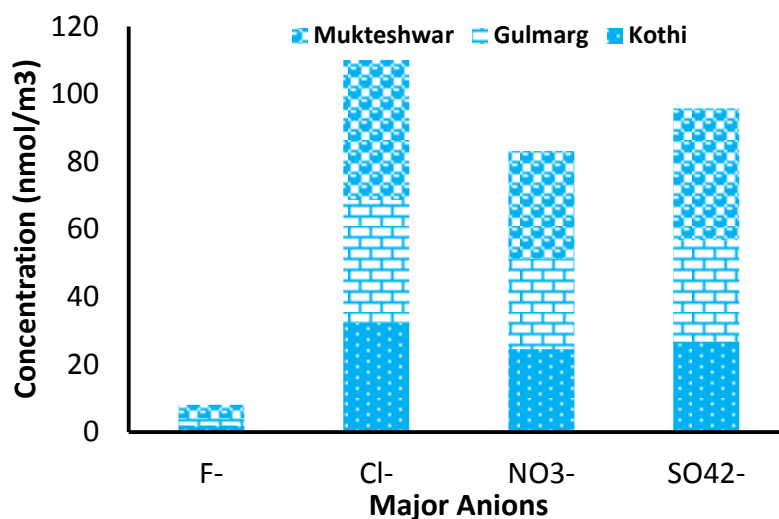


**Table 5.1:** Concentration of major ions (nmol/m<sup>3</sup>) of aerosol.

		F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
<b>Mukteshwar</b>	Mean	2.8	41.4	31.8	39.1	35.9	46.5	14.6	33.4	18.0
	SD	2.4	6.4	3.4	4.2	4.1	8.1	2.7	3.0	4.8
	Min	nd	30.8	27.2	33.3	29.7	29.0	9.9	28.9	7.0
	Max	6.5	50.5	36.8	45.7	41.7	57.2	18.9	38.6	23.1
	Median	2.7	40.1	31.4	38.1	36.3	45.4	14.0	32.7	18.8
	SE	0.6	1.7	0.9	1.1	1.1	2.2	0.7	0.8	1.3
<b>Gulmarg</b>	Mean	1.4	36.3	26.9	29.9	33.0	40.5	10.5	23.1	8.1
	SD	1.2	6.0	3.2	4.3	5.7	7.0	2.3	3.1	3.2
	Min	nd	26.7	22.2	23.3	24.2	29.2	7.3	18.3	3.4
	Max	3.2	46.0	32.2	37.1	42.7	51.8	14.8	28.9	13.5
	Median	1.6	35.3	27.7	30.6	33.8	39.6	10.9	23.1	7.4
	SE	0.3	1.4	0.7	1.0	1.3	1.6	0.5	0.7	0.7
<b>Kothi</b>	Mean	1.1	32.3	24.5	26.8	28.9	37.6	12.7	19.9	6.8
	SD	1.1	10.5	2.5	3.1	4.3	9.8	1.9	2.3	2.3
	Min	nd	11.3	21.0	22.3	22.9	15.1	9.2	16.2	2.1
	Max	3.2	46.8	28.3	32.0	35.3	49.7	15.5	22.9	10.3
	Median	1.3	35.3	24.3	26.1	28.4	41.0	12.4	19.5	6.8
	SE	0.3	3.0	0.7	0.9	1.2	2.8	0.5	0.6	0.7

### 5.1.1.1. Major anions

Among water soluble inorganic ions in aerosol samples, anionic composition is found to be dominated by  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  after  $\text{Cl}^-$  at these sites (Fig. 5.1). The average concentration of  $\text{SO}_4^{2-}$  at the present study sites followed the order- Gulmarg < Kothi < Mukteshwar.



**Fig. 5.1:** Major anions in water soluble aerosol.

Significant amount of  $\text{SO}_4^{2-}$  might be due to abundance of their precursor gases i.e.  $\text{SO}_2$  at the present sites. Studies on aerosol samples have proved that  $\text{SO}_4^{2-}$  in the atmosphere is formed by the oxidation of their gaseous precursors i.e.  $\text{SO}_2$  emitted from various anthropogenic sources (Finlayson-Pitts and Pitts, 1986). These precursor gases have emitted locally or long range transported. Apart from industrial emissions, diesel driven vehicles is one of the most important source of  $\text{SO}_2$  (Kumar et al., 2016) at these tourist sites. During electric failure, many hotels use diesel generator to fulfil demand of electricity. Similar range of concentration of  $\text{SO}_4^{2-}$  has been reported at Himalaya in Indian region (Kuniyal et al., 2013). The Concentrations of anthropogenic  $\text{SO}_4^{2-}$  at these sites were lower than cities like Agra (Kulshrestha et al., 1995), Raipur (Deshmukh et al., 2012) and Delhi (Chelani et al., 2010) in India and Xian (Shen et al., 2009), Beijing (Wang et al., 2006) and Wuhan (Huang et al., 2016) in China but comparable to Pokhara, Nepal (Tripathee et al., 2016) (Table 5.2). Such a result suggested relatively lesser pollution at Himalaya in comparison to other sites in south and east asia. However, the increasing level of air pollution is alarming globally including sensitive ecosystem like Himalaya.

**Table 5.2:** Geographical comparison of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  at various sites.

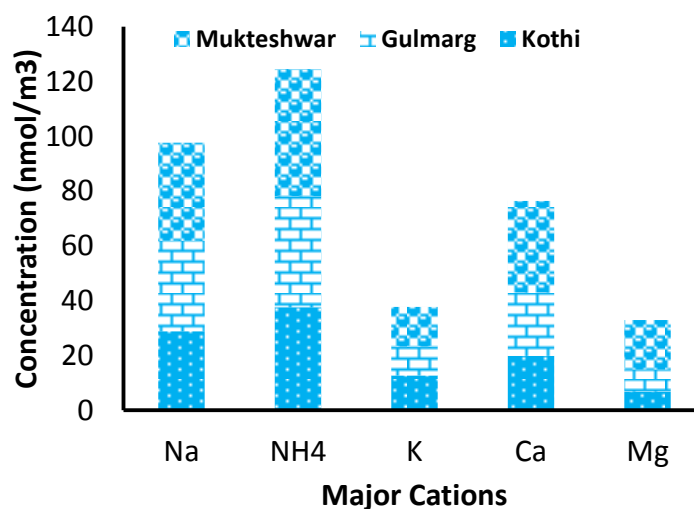
Sampling site	Country	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	References
<b>Pokhara</b>	Nepal	44.1	31.3	Tripathee et al., 2016
<b>Beijing</b>	China	283.9	367.1	Wang et al., 2006
<b>Xi'an</b>	China	354.2	259.7	Shen et al., 2009
<b>Wuhan</b>	China	174.8	181.9	Huang et al., 2016
<b>Raipur</b>	Inida	104.0	89.0	Deshmukh et al., 2012
<b>Delhi</b>	Inida	174.4	244.0	Chelani et al., 2010
<b>Sinhagad</b>	Inida	8.2	9.2	Khemani, 1989
<b>Silent valley</b>	Inida	24.3	19.5	Safai et al., 1993
<b>Agra</b>	Inida	205.2	159.8	Kulshrestha et al., 1995
<b>Kothi</b>	Inida	26.81	24.48	Present tudy
<b>Gulmarg</b>	Inida	29.89	26.87	Present tudy
<b>Mukteshwar</b>	Inida	39.10	31.81	Present tudy

The average concentration of  $\text{NO}_3^-$  followed the order- Kothi < Gulmarg < Mukteshwar. High Concentration of  $\text{NO}_3^-$  might be due to abundance of their precursor gases at the present sites. Studies have proved that that  $\text{NO}_3^-$  in the atmosphere are formed by the oxidation of their gaseous precursor  $\text{NO}_x$ , emitted from various anthropogenic sources (Finlayson-Pitts and Pitts, 1986). Among anthropogenic emissions, Vehicular flow due to increased tourist activities during winter season might be considered as a good source of  $\text{NO}_x$  at these tourist places (Finlayson-Pitts and Pitts, 1986; Seinfeld and Pandis, 2006). Another local source might be biomass burning during winter season to produce heat by local people cannot be ruled out (Singh et al., 2014). Apart from local emissions, very high concentration of  $\text{NO}_3^-$

might be due to long range transport of  $\text{NO}_x / \text{NO}_3^-$  from various airmasses (transboundary as well as long range transported) approaching at these sites. Similar range of concentration of  $\text{NO}_3^-$  has been reported at Himalaya in Indian region (Kuniyal et al., 2013, Kumar et al., 2016). The Concentrations of anthropogenic  $\text{NO}_3^-$  at these sites were lower than cities like Raipur (Deshmukh et al., 2012), Agra (Kulshrestha et al., 1995) and Delhi (Chelani et al., 2010) in India and Xian (Shen et al., 2009), Beijing (Wang et al., 2006) and Wuhan (Huang et al., 2016) in China but higher than Sinhagad (Khemani, 1989) (Table 5.2).

### 5.1.1.2. Major Cations

Among water soluble inorganic cations, the abundance of  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$  was very high at these sites (Fig. 5.2).  $\text{NH}_4^+$  was the most dominating cation among all ions in Himalayan region of India. The concentration of  $\text{NH}_4^+$  was the highest at Mukteshwar site followed by Gulmarg and Kothi.  $\text{NH}_4^+$  at these site is lower than Agra (Kulshrestha et al., 1995), Raipur (Deshmukh et al., 2012) and Delhi (Chelani et al., 2010) in India and Xian (Shen et al., 2009), Beijing (Wang et al., 2006) and Wuhan (Huang et al., 2016) in China but higher than Sinhagad (Khemani, 1989) and Silent valley (Safai et al., 1993). High concentration of  $\text{NH}_4^+$  among all cations indicated a significant influence of anthropogenic sources at these sites. Among anthropogenic sources, discharge from hostels, agriculture activities and animal excreta are major sources. The most important sources of  $\text{NH}_4^+$  are agriculture activities, livestock, excreta of human and animal etc. (Galloway, 1995; Singh and Kulshrestha, 2012). Apart from these sources, local people as well as tourists reaching here also might be significant source for  $\text{NH}_4^+$  in this region (Singh and Kulshrestha, 2014).

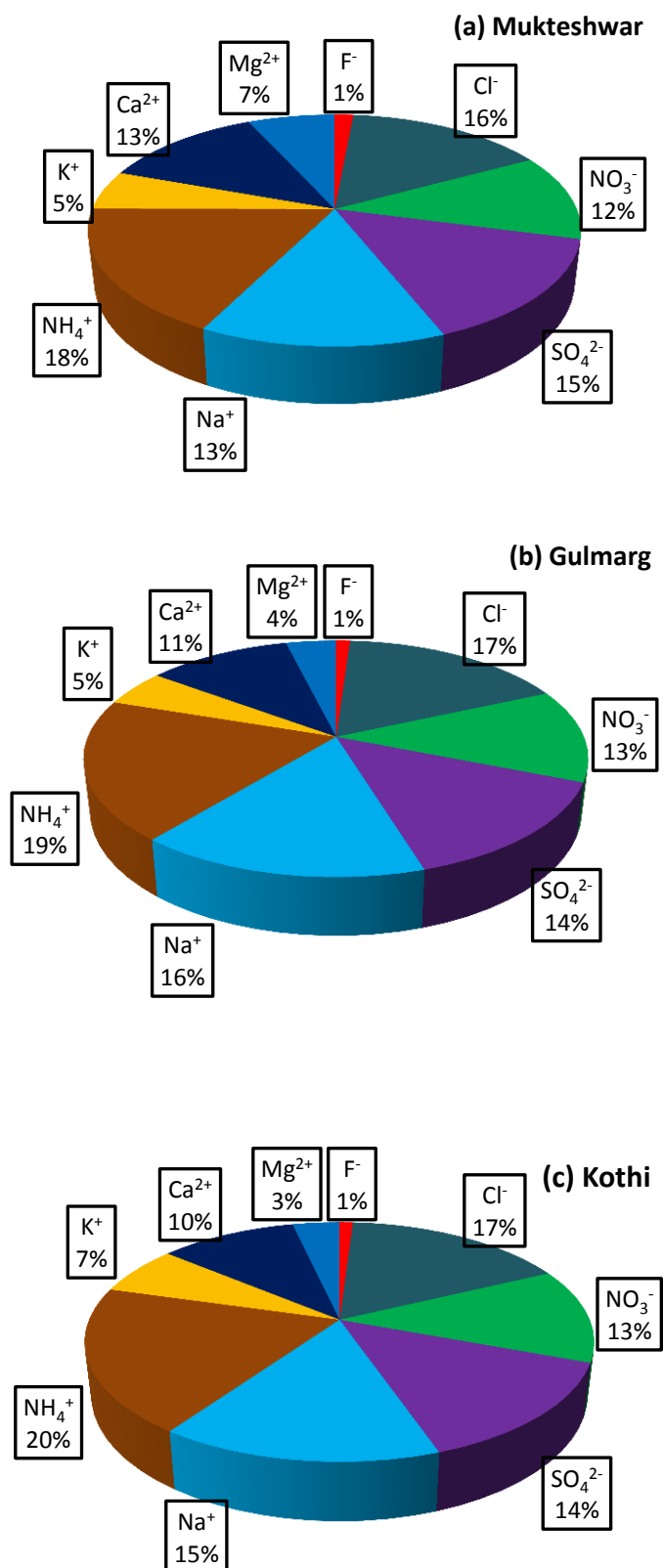


**Fig. 5.2:** Major cations in water soluble aerosol.

The average  $\text{Ca}^{2+}$  concentration followed the order- Mukteshwar > Gulmarg > Kothi.  $\text{Ca}^{2+}$  accounted for 9, 11 and 13 % among all ions for Kothi, Gulmarg and Mukteshwar site respectively (Fig. 1).  $\text{Ca}^{2+}$  at these site are higher than Sinhagad (Khemani, 1989), Silent valley (Safai et al., 1993) and Wuhan (Huang et al., 2016) but lower than Agra (Kulshrestha et al., 1995), Raipur (Deshmukh et al., 2012) and Delhi (Chelani et al., 2010) in India and Xian (Shen et al., 2009) and Beijing (Wang et al., 2006) in China. High concentration of  $\text{Ca}^{2+}$  at these sites suggested higher loadings of calcium rich dust particles which is very common in Indian atmosphere (Kulshrestha et al., 2009).

### 5.1.1.3. Relative contribution of water soluble ions

Fig. 5.3 (a-c) shows the relative percent abundance of water soluble inorganic ions in aerosol samples at Kothi, Gulmarg and Mukteshwar in himalayan region of India. The percent contribution was the highest for  $\text{NH}_4^+$  at these sites in comparison to other ions with 20%, 19% and 18% at Kothi, Gulmarg and Mukteshwar respectively. Very high percent of  $\text{NH}_4^+$  indicated the significant human perturbances at these sites. The various anthropogenic sources of  $\text{NH}_4^+$  have been discussed above in the section 5.1.1.1. Similar results with very high percent contribution of  $\text{NH}_4^+$  have been observed by other workers in India (Kulshrestha et al., 2009; Kuniyal et al., 2013). Very high percent contribution of  $\text{Cl}^-$  and  $\text{Na}^+$  at these sites indicated significant marine influences which have been discussed below in the next section. The significant anthropogenic perturbances is further confirmed by high percent contribution of  $\text{SO}_4^{2-}$  after  $\text{Cl}^-$  at these sites.  $\text{SO}_4^{2-}$  at these sites followed the order- Mukteshwar (15%) > Gulmarg (14%) ~ Kothi (14%). A significant percent of  $\text{Ca}^{2+}$  was also recorded at these sites.



**Fig. 5.3:** Percentage distribution of major ions in aerosol.

## 5.1.2. Sources influencing composition of aerosol

### 5.1.2.1. Marine and non-marine contribution

To understand marine and non-marine contribution of water soluble inorganic ions in atmosphere, sodium ratios were calculated as mentioned by Kumar and co-workers (2016). Sodium ratios were calculated by assuming Na in aerosol samples are of marine origin (Keene et al., 1986). Sea water ratios were taken findings from Keene and co-workers (1986). Sodium ratios for  $K^+$ ,  $Ca^{2+}$ ,  $Cl^-$ ,  $Mg^{2+}$ , and  $SO_4^{2-}$  at all three sites i.e. Kothi, Gulmarg and Mukteshwar were calculated and presented in Table 5.3.

**Table 5.3:** Na ratios in aerosol sample at all sites.

Na ratios	Kothi	Gulmarg	Mukteshwar
$Cl^-/Na^+$	1.12	1.10	1.14
$SO_4^{2-}/Na^+$	1.86	1.81	2.18
$K^+/Na^+$	0.44	0.32	0.41
$Ca^{2+}/Na^+$	1.38	1.40	1.87
$Mg^{2+}/Na^+$	0.47	0.49	1.01

It is very clear from the table that sodium ratios were much higher than sea water ratio for most of the ionic components.  $Cl^-/Na^+$  ratio was almost similar to sea water indicated the complete contribution of  $Cl^-$  from marine sources only. Similar result of  $Cl^-/Na^+$  ratios in atmospheric aerosol samples have been reported at other sites in India (Reddy et al., 2008; Kuniyal et al., 2013). Sodium ratios for K, Ca and  $SO_4$  were very high than sea water ratio indicated very significant contribution from non-marine sources. Ca in aerosol samples due to crustal influences have been reported at many sites in India (Reddy et al., 2008; Kumar et al., 2014) which has been discussed in detail in section 5.1.2.2. Very high percent of non-sea salt fraction of  $SO_4^{2-}$  confirm anthropogenic influences at these sites. Globally, researchers have proved by the experiments that  $SO_4^{2-}$  in aerosol samples come from the oxidation of  $SO_2$  emitted due to combustion of fossil fuel (Reddy et al., 2008; Kuniyal et al., 2013; Tripathee et al., 2016).

## 5.1.2.2. Crustal Influences

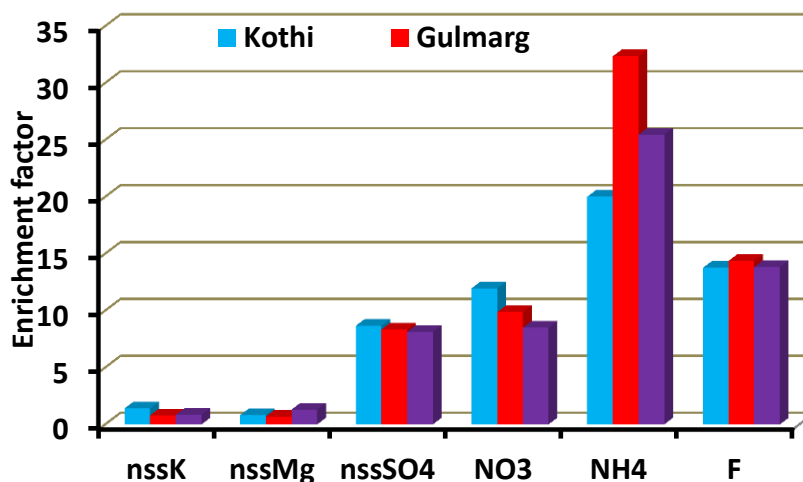


Fig. 5.4: Enrichment factor of aerosol with respect to soil samples.

As discussed above that non-marine sources had significant contribution at Himalayan sites in India. Further non-marine sources have been differentiated into crustal and anthropogenic fraction. The crustal fractions of major water soluble inorganic ions in aerosol samples have been calculated by considering  $\text{nssCa}^{2+}$  as reference element (Kulshrestha et al., 2003). To know the contribution of crustal sources, enrichment factor (EF) was calculated by the following formula-

$$EF_{\text{Soil}} = (y / \text{nss Ca}^{2+})_{\text{aerosol}} / (y / \text{nss Ca}^{2+})_{\text{Soil}}$$

Where,  $y$  is the nss concentration of ionic species ( $\text{nss SO}_4^{2-}$ ,  $\text{nss Ca}^{2+}$ ,  $\text{nss K}^+$ ,  $\text{nss Mg}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{F}^-$ ) in  $\mu\text{eq/l}$ .

$(y / \text{nss Ca}^{2+})_{\text{Soil}}$  is taken as standard ratio of local soils at the respective sites (Chapter 7).

The calculations of EF values for soil components have been presented in figure 5.4. EF at Mukteshwar site followed the order –  $\text{NH}_4^+ > \text{F}^- > \text{NO}_3^- > \text{nssSO}_4^{2-} > \text{nssMg}^{2+} > \text{nssK}^+$  while Kothi and Gulmarg site followed the order-  $\text{NH}_4^+ > \text{F}^- > \text{NO}_3^- > \text{nssSO}_4^{2-} > \text{nssK}^+ > \text{nssMg}^{2+}$ . From the fig. 5.4, it is very clear that the value of EF for  $\text{NH}_4^+$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$  and  $\text{nssSO}_4^{2-}$  is greater than 1 indicated its contribution in aerosol samples from anthropogenic sources mainly. The highest value of EF for  $\text{NH}_4^+$  at all three sites indicated its almost complete contribution from anthropogenic sources like biomass burning, agriculture activities etc.



A very high value of EF for nss  $\text{SO}_4^{2-}$  indicated significant anthropogenic perturbances mainly from fossil fuel combustion at these sites. High EF of nss  $\text{SO}_4^{2-}$  might be due to significant contribution from airmasses approaching at the present sites as mentioned in section 6.2 of chapter 6. There is no any major industry nearby sampling sites so contribution of  $\text{SO}_4^{2-}$  from airmasses coming from other sites in India and long range transport cannot be ruled out. Among local sources, diesel based generator used by various hotels during power failure might be one reason for high EF of  $\text{SO}_4^{2-}$  at these sites.

### 5.1.3. Relationship between ionic composition of snow and aerosol

#### 5.1.3.2. Scavenging ratios

The concurrent measurements of the chemical components of snowfall and aerosol help to understand aerosol removal by precipitation (Granat et al., 2002). Scavenging coefficients, scavenging rate, rain-out efficiencies and scavenging ratios are some reported parameters to demonstrate the scavenging of air pollutants (Hicks, 2005). In the present study, we have been estimated scavenging ratios (SR) assuming that the concentration of a chemical species in precipitation is related to its concentration in surface air using the following calculations (Granat et al., 2002; Kulshrestha et al., 2009)-

$$\text{SR} = (\text{C}_{\text{snowfall}} / \text{C}_{\text{aerosol}}) * \text{D}_a$$

Where  $\text{C}_{\text{snowfall}}$  = The concentration of a component in snowfall ( $\text{nmolKg}^{-1}$ )

$\text{C}_{\text{aerosol}}$  = The concentration of the same component in air ( $\text{nmolm}^{-3}$ )

$\text{D}_a$  = Density of air

This expresses SR in Kg of air per Kg of water

Table 5.4 gives SR for all ionic species at the present sites. SR at Kothi followed the order-  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{K}^+ > \text{SO}_4^{2-} > \text{NO}_3^- > \text{NH}_4^+$  while Gulmarg site followed the order-

$\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Cl}^- > \text{Na}^+ > \text{NO}_3^- > \text{NH}_4^+ > \text{SO}_4^{2-}$ . SR at Mukteshwar was in this order-  
 $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{Cl}^- > \text{K}^+ > \text{NH}_4^+ > \text{NO}_3^- > \text{SO}_4^{2-}$ .

**Table 5.4:** Scavenging ratios for major ions of concurrent aerosol and snowfall sample.

Ions	Kothi	Gulmarg	Mukteshwar
$\text{Cl}^-$	1088	1130	1388
$\text{NO}_3^-$	386	458	527
$\text{SO}_4^{2-}$	452	375	412
$\text{Na}^+$	953	910	1438
$\text{NH}_4^+$	238	446	621
$\text{K}^+$	548	1180	1241
$\text{Ca}^{2+}$	1271	1488	1625
$\text{Mg}^{2+}$	1098	1439	1513

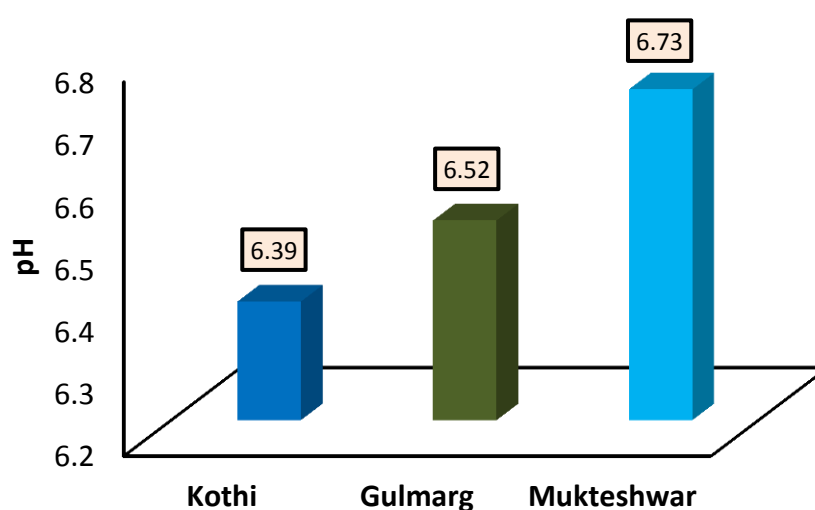
In general, scavenging ratio is the highest for  $\text{Ca}^{2+}$  in comparison to all ions at all three sites in himalayan region of India. The values of scavenging ratios were low for major anthropogenic ions such as  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . The differences in SR values of ions at these sites might be due to difference in particle size. Globally, researchers have proved that scavenging of aerosol particles are very much dependent on their sizes (Granat et al., 2002; Kulshrestha et al., 2009; Budhavant et al., 2014b). Kulshrestha et al (2009) observed the effective scavenging of coarser particles due to rain at Hyderabad in India. Budhavant and co-workers (2014b) have reported that coarser particles are removed easily than fine sized particles. Encinas and co-workers (2004) have suggested that particle size, and hygroscopicity, cloud type and rain intensity are the major factor affecting the scavenging ratios of aerosols. The differences in SR values also depend on the difference in origin of air masses at cloud forming level and the surface (Kulshrestha et al., 2009). Most of  $\text{Ca}^{2+}$  is scavenged by below cloud scavenging as reported by Kulshrestha et al., (2009). Below cloud

scavenging of crustal components in India is mainly responsible for alkaline precipitation (Kulshrestha et al., 2003).

## 5.2. Chemistry of dustfall

### 5.2.1. pH, Concentration and annual dustfall fluxes

#### 5.2.1.1. pH of dustfall samples



**Fig. 5.5:** pH of water soluble dustfall samples.

Fig. 5.5 gives the average value of pH of dustfall estimated at Mukteshwar, Gulmarg and Kothi. The average pH at these sites followed the order- Mukteshwar (6.73) > Gulmarg (6.52) > Kothi (6.39). At all the sites, pH is in the alkaline range and is comparable with other sites in Indian region (Jain et al., 2000; Kulshrestha et al., 2003a; Budhavant et al., 2012; Tiwari et al., 2016). These relatively high values of pH of dry deposition suggest the dominance of crustal components particularly, the presence of carbonates and bicarbonates of Ca (Khemani, 1989; Kulshrestha et al., 1996).

### 5.2.1.2. Concentration of major ions ( $\mu\text{eq}/\text{m}^2/\text{day}$ ) of dustfall

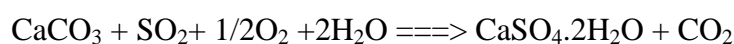
The average dustfall fluxes of the major water soluble anions and cations at the present sites are presented in Table 5.5. On an average, ionic fluxes at Mukteshwar site followed the order-  $\text{Ca}^{2+} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{Mg}^{2+} > \text{NO}_3^- > \text{Na}^+ > \text{NH}_4^+ > \text{K}^+ > \text{F}^-$ . The dustfall fluxes at Gulmarg site followed the order-  $\text{Ca}^{2+} > \text{HCO}_3^- > \text{Na}^+ > \text{SO}_4^{2-} > \text{Cl}^- > \text{Mg}^{2+} > \text{NO}_3^- > \text{NH}_4^+ > \text{K}^+ > \text{F}^-$ . The average ionic fluxes of water soluble ions at kothi site followed the order-  $\text{Ca}^{2+} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{Mg}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{NO}_3^- > \text{K}^+ > \text{NH}_4^+ > \text{F}^-$ . In general, ionic fluxes observed at Mukteshwar are higher in comparison to other two sites suggesting higher influence of anthropogenic and crustal sources which is discussed in detail in section 5.2.2.

**Table 5.5:** Concentration of major ions ( $\mu\text{eq}/\text{m}^2/\text{day}$ ) of dustfall.

(a) Mukteshwar										
	$\text{F}^-$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{HCO}_3^-$
<b>Mean</b>	1.5	42.6	22.0	29.5	41.0	10.4	8.1	86.2	24.8	59.3
<b>SD</b>	1.0	18.6	6.8	6.6	20.5	3.2	2.4	10.9	6.3	8.5
<b>Median</b>	1.6	50.5	25.0	29.8	47.0	11.2	9.4	86.2	26.2	57.6
<b>Min</b>	nd	13.3	9.9	19.3	3.7	4.7	3.4	65.3	14.3	44.9
<b>Max</b>	2.9	61.8	28.4	42.2	66.1	14.3	11.3	99.9	34.5	78.4
(b) Gulmarg										
	$\text{F}^-$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{HCO}_3^-$
<b>Mean</b>	1.0	22.5	18.3	27.5	29.1	8.6	5.1	69.4	25.4	50.9
<b>SD</b>	1.0	7.2	5.0	8.6	8.9	2.5	2.0	10.6	8.5	9.1
<b>Median</b>	1.2	22.7	19.6	30.0	32.4	9.2	5.5	73.1	28.7	51.8
<b>Min</b>	nd	8.7	7.9	11.5	13.6	4.1	1.1	48.7	10.2	34.7
<b>Max</b>	2.7	34.5	23.1	36.3	39.2	12.2	7.4	80.6	36.8	71.5
(c) Kothi										
	$\text{F}^-$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{HCO}_3^-$
<b>Mean</b>	0.8	19.1	12.1	16.2	24.5	4.7	9.6	46.7	13.6	31.6
<b>SD</b>	0.8	7.2	3.1	3.5	9.1	1.7	1.3	4.7	2.3	4.7
<b>Median</b>	0.8	22.8	13.2	17.8	28.5	4.9	9.6	47.0	14.4	33.2
<b>Min</b>	nd	5.8	5.4	8.5	8.9	1.6	7.6	36.1	7.9	22.1
<b>Max</b>	2.2	25.5	15.8	20.1	35.0	7.6	11.5	52.8	15.8	36.5

Among all ionic fluxes,  $\text{Ca}^{2+}$  is the highest at all sites.  $\text{Ca}^{+2}$  flux was the highest at Mukteshwar followed by Gulmarg and Kothi. This is a characteristic feature of Indian atmosphere. Dustfall deposition fluxes of  $\text{Ca}^{+2}$  have been reported the highest by other workers also at different sites in India (Kulshrestha et al, 2003a, Gupta et al., 2015; 2016; Tiwari et al., 2016). High concentrations of  $\text{Ca}^{+2}$  and high alkalinity indicated that soil derived  $\text{CaCO}_3$  dust particles have significant influence on atmospheric environment.

Dustfall at Mukteshwar has higher influence of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  compared to Gulmarg and Kothi indicating higher perturbation of anthropogenic influences. The deposition flux for  $\text{SO}_4^{2-}$  followed the order- Mukteshwar > Gulmarg > Kothi. The highest  $\text{SO}_4^{2-}$  flux at Mukteshwar might be due to increase in diesel driven vehicles, industrial emission and transboundary pollution from other states in India.  $\text{SO}_4^{2-}$  at these sites are lower than cities of India like Agra (Kulshrestha et al., 1995), Delhi (Kulshrestha, et al., 2003a) and Pune (Budhavant et al., 2012) indicating lesser anthropogenic perturbances at himlayan sites. However,  $\text{SO}_4^{2-}$  in any concentration at Indian sites generally does not contribute in acidity (Jain et al., 2000).  $\text{SO}_4^{2-}$  at these sites might have originated in the form of  $\text{CaSO}_4$  when  $\text{SO}_2$  reacted with particulate matter or could have deposited directly onto dust particles in the collecting vessel. In Indian weather conditions, atmospheric soil dust is effective scavenger of  $\text{SO}_2$ . (Kulshrestha et al 2003a). Scavenging of  $\text{SO}_2$  onto the dust particles forming calcium sulphate in India has been demonstrated as follows (Kulshrestha, 2013)-



Formation of calcium sulphate does not contribute acidity in samples rather enhances the pH of dustfall which is further supported by higher pH values of dustfall at these sites. In India high  $\text{SO}_4^{2-}$  concentrations associated with  $\text{Ca}^{+2}$  are reported (Kulshrestha et al, 1995, 1998).

The average dustfall flux of  $\text{NO}_3^-$  was the highest at Mukteshwar followed by Gulmarg and Kothi might be due to industries, vehicles and biogenic emission.  $\text{NO}_3^-$  at these sites is lower than Agra (Kulshrestha et al., 1993), Delhi (Parashar et al., 1996) and Pune (Budhavant et al., 2012) indicated relatively lesser  $\text{NO}_3^- / \text{NO}_2$  sources at Himalayas. Like  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  in Indian atmosphere might have reacted with Ca of dust.  $\text{NO}_3^-$  is often found on the surface of aged dust due to heterogeneous deposition of  $\text{HNO}_3$  (Kulshrestha et al., 1998; Kumar et al., 2008).



### 5.2.1.3. Annual deposition fluxes

**Table 5.6:** Annual deposition fluxes of water soluble dustfall samples ( $\text{meq/m}^2/\text{anum}$ ).

Ions	Kothi	Gulmarg	Mukteshwar
$\text{HCO}_3^-$	11.5	18.6	21.7
$\text{F}^-$	0.3	0.4	0.5
$\text{Cl}^-$	7.0	8.2	15.5
$\text{NO}_3^-$	4.4	6.7	8.0
$\text{SO}_4^{2-}$	5.9	10.1	10.8
$\text{Na}^+$	9.0	10.6	14.9
$\text{NH}_4^+$	1.7	3.1	3.8
$\text{K}^+$	3.5	1.9	2.9
$\text{Ca}^{2+}$	17.0	25.3	31.5
$\text{Mg}^{2+}$	4.9	9.3	9.0

The annual deposition fluxes (ADF) in  $\text{meq/m}^2/\text{anm}$  for each ion were calculated with the help of following formula-

$$\text{ADF} = [\text{D}_i \times 365] / 1000$$

Here  $\text{D}_i$  is the dustfall deposition fluxes of each ionic species in  $\mu\text{eq/m}^2/\text{day}$ .

ADF of major ionic species calculated by using the above formula have been presented in table 5.6.

The total annual deposition fluxes at Kothi site followed the order  $\text{Ca}^{2+} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{Mg}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{NO}_3^- > \text{K}^+ > \text{NH}_4^+ > \text{F}^-$  and  $\text{Ca}^{2+} > \text{HCO}_3^- > \text{Na}^+ > \text{SO}_4^{2-} > \text{Cl}^- > \text{Mg}^{2+} >$

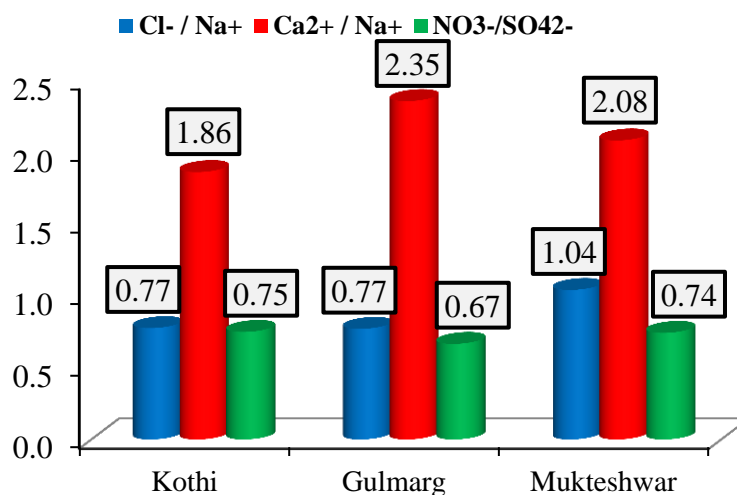
$\text{NO}_3^- > \text{NH}_4^+ > \text{K}^+ > \text{F}^-$  at Gulmarg in north western Himalayan region of India while Mukteshwar site in central himalya followed the order  $\text{Ca}^{2+} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{Mg}^{2+} > \text{NO}_3^- > \text{Na}^+ > \text{NH}_4^+ > \text{K}^+ > \text{F}^-$ .

In general, ADF were high at Mukteshwar followed by Gulmarg and Kothi. The total annual deposition fluxes for  $\text{Ca}^{2+}$  was the highest among all ionic species at all different sites in Himalayan region of India leading to higher values of pH of water soluble dustfall samples.

The annual deposition fluxes ( $\text{meq/m}^2/\text{ann}$ ) of 42 - 84 and 40 - 80 for  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  have been proposed to fresh water ecosystem. It is very clear from table 5.3 that  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  fluxes are very less from the range of proposed limits. In comparison to other sites in India, the value of deposition fluxes for  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were very low (Kulshrestha et al., 2003a; Tiwari et al., 2016). Kulshrestha and co-workers (2003) observed that higher  $\text{SO}_4^{2-}$  fluxes at Delhi in India are not a major problem for ecosystem since they are associated with crustal particles. But the same higher concentration of  $\text{SO}_4^{2-}$  at European sites may create many problems for various ecosystems due to its contribution in free acidity.

### 5.2.2. Ionic ratios in dustfall samples

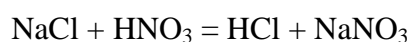
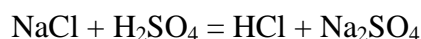
The ionic ratios have been estimated to know marine and non-marine influences in dustfall samples at the present sites. The ionic ratios of  $\text{Cl}^- / \text{Na}^+$ ,  $\text{Ca}^{2+} / \text{Na}^+$  and  $\text{NO}_3^- / \text{SO}_4^{2-}$  have calculated and presented in fig. 5.6.



**Fig. 5.6:** Ionic ratios at the present sites in dustfall samples.

$\text{Cl}^- / \text{Na}^+$  ratio is used to know marine influence in samples. In present case, these ratios are the highest at Mukteshwar indicating relatively more influence of marine components than other sites i.e. Kothi and Gulmarg. However,  $\text{Cl}^- / \text{Na}^+$  ratio at all sites are less than sea water ratio i.e. 1.16 indicated some depletion of chloride in atmosphere. This depletion might be due to reaction between sea salt and acids generated in the atmosphere (Keene et al., 1998).

The possible reaction is-



$\text{Ca}^{2+} / \text{Na}^+$  ratio was used to find the relative contribution of marine and crustal influences. At all sites, ratio is higher than 1 indicating strong crustal influence for  $\text{Ca}^{2+}$  than marine sources.

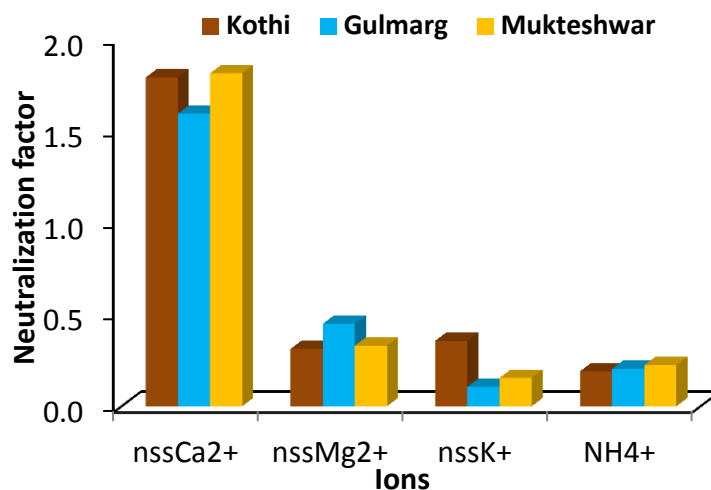
Among anthropogenic sources,  $\text{NO}_3^- / \text{SO}_4^{2-}$  ratios were used to know the relative contribution of stationary (biomass burning, coal combustion in industries) vs mobile (vehicular emissions) sources (Tiwari et al., 2016; Tripathy et al., 2016). If ratio of  $\text{NO}_3^- / \text{SO}_4^{2-}$  is less than 1 then it indicates more dominance of stationary sources over mobile sources. At all three sites in Himalayan region of India, we found the ratio is lesser than 1 indicated strong influence of stationary sources over mobile sources. The most probable dominant sources at these sites might be diesel based generator, brick kiln etc. Similar results have been observed by other workers in dustfall samples in Indian region (Jain et al., 2000; Kulshrestha et al., 2003; Tiwari et al., 2016).

### 5.2.3. Neutralization capability of basic components in dustfall samples

#### 5.2.3.1. Neutralization ratios

In dustfall samples, researchers have proved that  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{NH}_4^+$  are major neutralizing components of acidic species such as  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  (Kulshrestha et al., 2003; Satsangi et al., 2013; Tiwari et al., 2016). Therefore, neutralization ratios of the major cations  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{NH}_4^+$  were calculated from the same formula as mentioned in section 4.5 of chapter 4.





**Fig. 5.7:** Neutralization factor of major basic species in water soluble dustfall samples.

The calculations of neutralization factor for all three sites i.e. Kothi, Gulmarg and Mukteshwar has been presented in fig. 5.7. It is very clear from figure that the neutralization ratios at Kothi followed the order-  $nssCa^{2+} > nssK^{+} > nssMg^{2+} > NH_4^{+}$ . NF while Gulmarg and Mukteshwar site followed the order-  $nssCa^{2+} > nssMg^{2+} > NH_4^{+} > nssK^{+}$ .

The highest neutralization ratios were recorded for  $nssCa^{2+}$  at all three sites in Himalayan region of India. This observation might be due to suspension of soil dust in Indian atmosphere (Jain et al., 2000). Kulshrestha and co-workers (2003) have established that Indian soil dust is very rich in  $CaCO_3$ . A very similar result of high neutralization capability of  $nssCa^{2+}$  has been observed in dustfall samples of other sites in India (Jain et al., 2000; Budhawant et al., 2012; Tiwari et al., 2016). The lowest value of neutralization ratios for  $NH_4^{+}$  at Kothi sites and  $nssK^{+}$  at Gulmarg and Mukteshwar site indicated its negligible contribution in neutralization reaction at the sampling sites.

### 5.2.3.2. Regression analysis of acidic vs basic cations

The relative neutralization can be confirmed further by the regression plots of  $\text{nssSO}_4^{2-} + \text{NO}_3^-$  vs cation. To fulfil this purpose, regression plot has been drawn for two major neutralizing cations such as  $\text{nssCa}^{2+}$  and  $\text{nssMg}^{2+}$  at all sites. Regression analysis of  $\text{nssSO}_4^{2-} + \text{NO}_3^-$  vs  $\text{nssCa}^{2+}$  and  $\text{nssSO}_4^{2-} + \text{NO}_3^-$  vs  $\text{nssMg}^{2+}$  has been given in fig. 5.6. The extent of neutralization varied from site to site with different cations explaining different pH of water soluble dustfall samples as discussed in section 5.2.1.1. Most of the points in regression plots of  $\text{nssSO}_4^{2-} + \text{NO}_3^-$  vs  $\text{nssCa}^{2+}$  and  $\text{nssSO}_4^{2-} + \text{NO}_3^-$  vs  $\text{nssMg}^{2+}$  lying above 1:1 neutralization confirm its high presence in stoichiometric neutralization reaction (fig. 5.8). A very similar result has been recorded at other sites in dustfall samples (Kulshrestha et al., 2003; Tiwari et al., 2016).

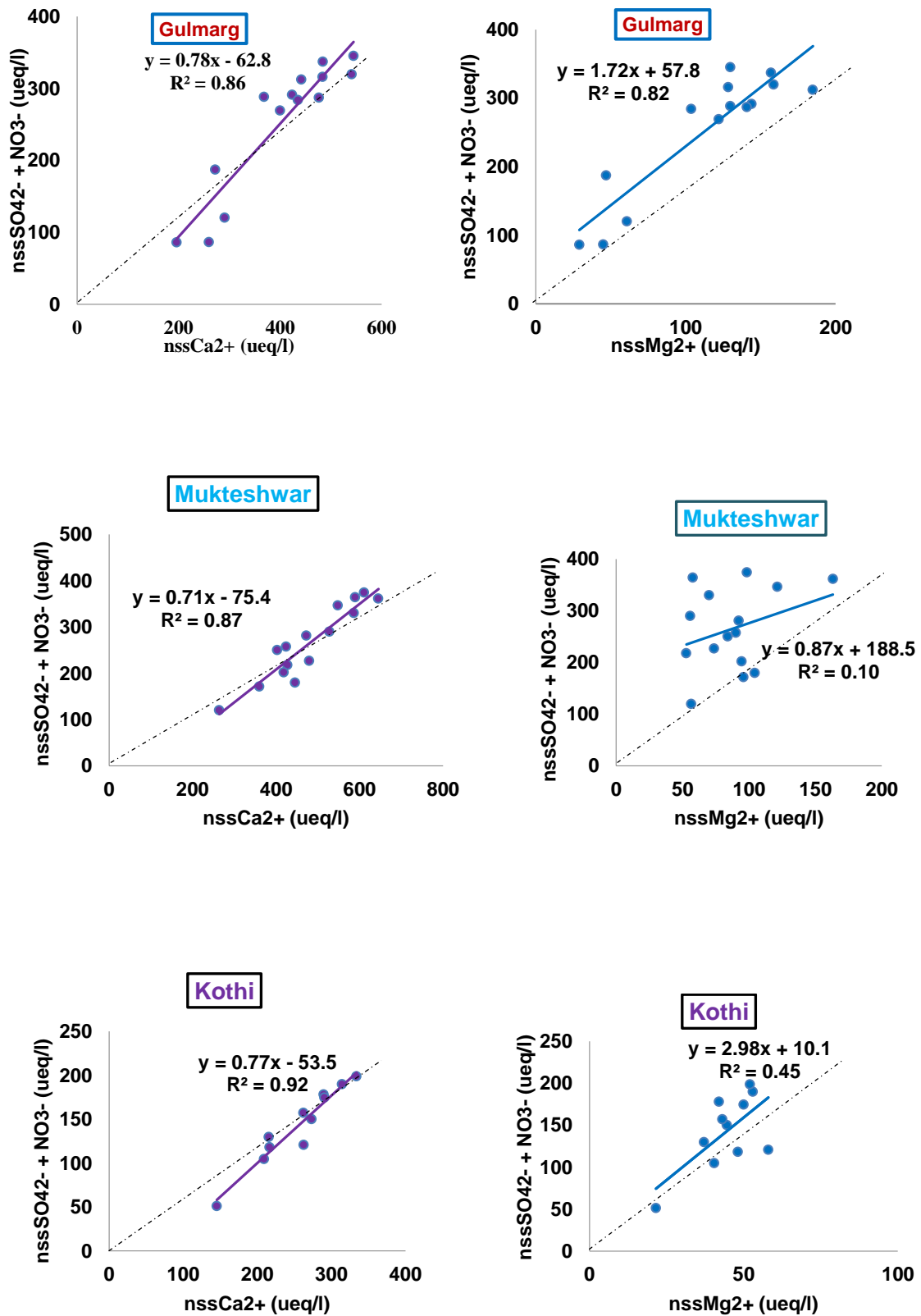


Fig. 5.8: Regression analysis of  $\text{nssSO}_4^{2-} + \text{NO}_3^-$  vs  $\text{nssCa}^{2+}$  and  $\text{nssSO}_4^{2-} + \text{NO}_3^-$  vs  $\text{nssMg}^{2+}$ .

The difference in neutralization of various cations is further confirmed from values of estimated regression coefficient presented in table 5.7. The difference in magnitude of  $\beta_1$  values confirmed difference in magnitude of dustfall scavenging at various site for all cations.

**Table 5.7:** Regression coefficients of major base cations vs  $\text{nssSO}_4^{2-} + \text{NO}_3^-$  at all sites (\* denotes significant correlation).

Site	Parameter	$\beta_1$ (Slope)	$\beta_0$ (Intercept)	p values
<b>Kothi</b>	$\text{nssCa}^{2+}$ vs $\text{nssSO}_4^{2-} + \text{NO}_3^-$	0.77	-53.5	0.00*
	$\text{nssMg}^{2+}$ vs $\text{nssSO}_4^{2-} + \text{NO}_3^-$	2.98	10.1	0.02*
	$\text{NH}_4^+$ vs $\text{nssSO}_4^{2-} + \text{NO}_3^-$	3.40	50.7	0.04*
	$\text{nssK}^+$ vs $\text{nssSO}_4^{2-} + \text{NO}_3^-$	3.44	32.3	0.01*
<b>Gulmarg</b>	$\text{nssCa}^{2+}$ vs $\text{nssSO}_4^{2-} + \text{NO}_3^-$	0.78	-62.8	0.00*
	$\text{nssMg}^{2+}$ vs $\text{nssSO}_4^{2-} + \text{NO}_3^-$	1.72	57.8	0.66
	$\text{NH}_4^+$ vs $\text{nssSO}_4^{2-} + \text{NO}_3^-$	4.61	15.4	0.63
	$\text{nssK}^+$ vs $\text{nssSO}_4^{2-} + \text{NO}_3^-$	6.63	74.5	0.34*
<b>Mukteshwar</b>	$\text{nssCa}^{2+}$ vs $\text{nssSO}_4^{2-} + \text{NO}_3^-$	0.71	-75.4	0.00*
	$\text{nssMg}^{2+}$ vs $\text{nssSO}_4^{2-} + \text{NO}_3^-$	0.87	188.5	0.06
	$\text{NH}_4^+$ vs $\text{nssSO}_4^{2-} + \text{NO}_3^-$	3.24	73.0	0.89
	$\text{nssK}^+$ vs $\text{nssSO}_4^{2-} + \text{NO}_3^-$	4.70	73.4	0.98

## *Chapter 6*

### *Source identification*

*(Local vs Long Range Transport)*

---

## SOURCE IDENTIFICATION (LOCAL VS LONG RANGE TRANSPORT)

This chapter is mainly focused upon the source identification (local vs long range transport) of snowfall at all three sites i.e. Kothi, Gulmarg and Mukteshwar in himalayan region of India. The present study focuses on quantification of relative contributions of marine and non-marine sources during winter season. Further, non-marine fractions have been quantified into crustal associated and anthropogenic sources. Airmass trajectories for different sectors have been calculated to find out the relative contribution of various ionic contents through long range transport. Further, it discusses about LCLUC impact on precipitation chemistry due to emission of crustal aerosols, increased tourist influx, population growth and other developmental activities. In order to explain the relationship between chemical components and their source, principal component analysis (PCA) and correlation analysis have been applied to dataset.

### 6.1. Marine and Non-marine influences

In order to find out the contribution of various sources categories, marine and non-marine fractions have been calculated at all sites i.e. Kothi, Gulmarg and Mukteshwar. Further non marine fraction has been calculated as crustal associated and anthropogenic fractions following the approach as reported by Kulshrestha et al (1997).

**6.1.1. Marine contribution:** Sea salt is made up of mainly  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{Mg}^{2+}$  with some fraction of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{K}^+$ . In order to estimate marine contribution, sodium ratios were calculated by assuming Na as a reference element for marine source (Keene et al., 1986). Sodium ratios for  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  at the present sites have been given in Table 6.1.

**Table 6.1:** Sodium ratios of snowmelt and percent Sea salt fraction (ssf) and non sea salt fraction (nssf) of major ions in snowmelt at Kothi (a), Gulmarg (b) and Mukteshwar (c).

<b>(a) Kothi</b>					
	<b>Cl<sup>-</sup></b>	<b>SO<sub>4</sub><sup>2-</sup></b>	<b>K<sup>+</sup></b>	<b>Ca<sup>2+</sup></b>	<b>Mg<sup>2+</sup></b>
<b>Sea water ratios (Keene et al., 1986)</b>	1.16	0.125	0.022	0.044	0.227
<b>Snowmelt ratios</b>	1.05	0.63	0.25	1.08	0.39
<b>EF (Sea water)</b>	0.91	5.03	11.30	24.51	1.72
<b>% ssf</b>	100	20	9	4	58
<b>% nssf</b>	0	80	91	96	42
<b>(b) Gulmarg</b>					
<b>Sea water ratios (Keene et al., 1986)</b>	1.16	0.125	0.022	0.044	0.227
<b>Snowmelt ratios</b>	0.92	0.77	0.26	1.39	0.37
<b>EF (Sea water)</b>	0.79	6.16	11.82	31.67	1.65
<b>% ssf</b>	100	16	8	3	61
<b>% nssf</b>	0	84	92	97	39
<b>(c) Mukteshwar</b>					
<b>Sea water ratios (Keene et al., 1986)</b>	1.16	0.125	0.022	0.044	0.227
<b>Snowmelt ratios</b>	1.12	0.74	0.40	1.86	0.46
<b>EF (Sea water)</b>	0.97	5.93	18.33	42.28	2.03
<b>% ssf</b>	100	17	5	2	49
<b>% nssf</b>	0	83	95	98	51

All ratios except  $\text{Cl}^-/\text{Na}^+$  were higher than standard sea water ratios of different components at the present sites. Average,  $\text{Cl}^-/\text{Na}^+$  ratio was very close to sea water value (1.16) indicating that  $\text{Cl}^-$  was completely contributed by marine sources. Almost similar  $\text{Cl}^-/\text{Na}^+$  ratios have been reported in snow/ice core samples globally (Marinoni et al., 2005; Yalcin et al., 2006).  $\text{Mg}^{2+}/\text{Na}^+$  ratios at these sites followed the order- Mukteshwar > Kothi > Gulmarg. These ratios were bit higher than the standard sea

water ratio reflecting dominance of marine contribution with some contribution from other source, probably crustal sources as discussed in the next subsection.  $\text{SO}_4^{2-}/\text{Na}^+$ ,  $\text{K}^+/\text{Na}^+$  and  $\text{Ca}^{2+}/\text{Na}^+$  were very high in comparison to standard sea salt values. Elevated ratios of  $\text{SO}_4^{2-}/\text{Na}^+$ ,  $\text{K}^+/\text{Na}^+$  and  $\text{Ca}^{2+}/\text{Na}^+$  might be due to higher contribution by non-marine sources. Similarly, elevated ratios for  $\text{SO}_4^{2-}/\text{Na}^+$ ,  $\text{K}^+/\text{Na}^+$  and  $\text{Ca}^{2+}/\text{Na}^+$  have been reported at various other sites (Jain et al., 2000; Zhang et al., 2007a).

Sea salt fraction (ssf) and non sea salt fraction (nssf) of each ionic species were calculated by the following formula-

$$\% \text{ssf} = 100 / \text{EF}_{\text{sea water}}$$

Enrichment factor is commonly used to estimate the origin of the chemical species in snow samples (Rahn, 1976; Keene et al., 1986; Kulshrestha et al., 1996). These calculations are based on ionic ratios between chemical species collected in precipitation samples and similar ratio present in a reference source. Generally, the reference material used for sea water is sodium while calcium or aluminium is used for continental crust. If the value of EF is not equal to 1 then it is believed to enrich ( $\text{EF} > 1$ ) or dilute ( $\text{EF} < 1$ ) as compared to the reference material.

Enrichment factor was calculated by the following formula-

$$\text{Here } \text{EF}_{\text{sea water}} = [\text{X}/\text{Na}^+]_{\text{snowfall}} / [\text{X}/\text{Na}^+]_{\text{Sea Water}}$$

Where, [X] is the concentration of desired ionic species in  $\mu\text{eq/l}$ .

$[\text{X}/\text{Na}^+]_{\text{Sea Water}}$  is the standard ratio of sea water (Keene et al., 1986).

% nssf of each chemical components were calculated by the following formula-

$$\% \text{nssf} = 100 - \% \text{ssf}$$

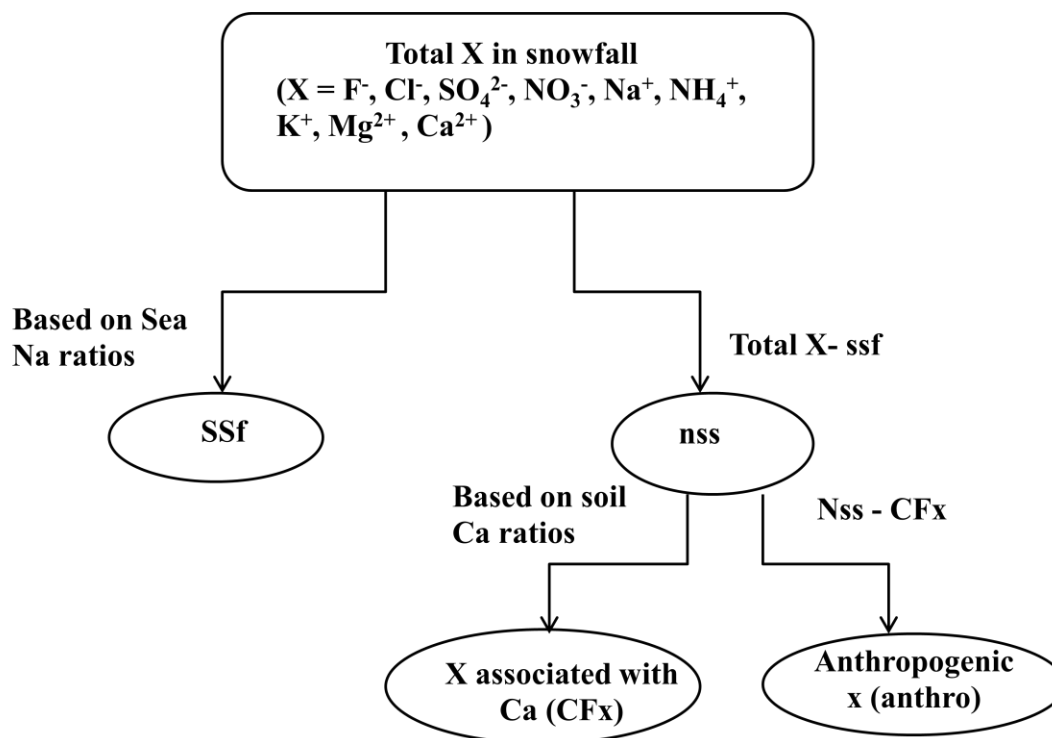
Table 6.1 presents the percent sea salt fraction and non sea salt fraction of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in snowfall samples at all three sites i.e. Kothi, Gulmarg and Mukteshwar. nssf of  $\text{SO}_4^{2-}$  at these sites followed the order – Kothi < Mukteshwar < Gulmarg while nssf of  $\text{K}^+$  was dominated at Mukteshwar followed by Gulmarg and Kothi. Almost complete fractions of  $\text{Cl}^-$  and  $\text{Mg}^{2+}$  are contributed by marine sources. Large fractions of nssf of  $\text{SO}_4^{2-}$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  at these sites indicated their origin from



non marine sources as discussed in the next subsection. Similar ranges of  $\text{nssSO}_4^{2-}$  and  $\text{nssCa}^{2+}$  have been reported at various sites in snow samples (Naik et al., 1995; Kang et al., 2004). High concentration of nssf of  $\text{SO}_4^{2-}$  has also been reported in precipitation samples over Indian Ocean during INDOEX (Kulshrestha et al., 1999; Granat et al., 2002). Similar range of  $\text{nssK}^+$  has been reported in precipitation samples at higher altitude sites in India (Naik et al., 1995).

### **6.1.2. Non-marine contribution**

Non- marine sources can be categorised into two major categories i.e. crustal and anthropogenic sources. Out of these two sources, anthropogenic sources mostly enhance the acidity of precipitation while crustal sources decrease the acidity by buffering of the acidifying species (Rodhe et al., 2002; Kulshrestha, 2013). Due to opposite characteristics in controlling acidity of precipitation, it is essential to quantify separately the non-marine fraction into crustal associated fractions and anthropogenic fractions. We have termed crustal associated fractions which has fractions of acidic components ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) present as salt of Ca i.e.  $\text{CaSO}_4$  or  $\text{Ca}(\text{NO}_3)_2$ . As illustrated in Fig. 6.1, we have followed the approach of Kulshrestha et al. (1997) and Jain et al. (2000) to calculate the contribution of crustal associated fraction and anthropogenic fraction of ionic species.



**Fig. 6.1:** Schematic diagram showing the approach of differentiation of non-sea salt fractions into Anthro and crustal associated fractions (CF) of various ionic components. ( $x = F^-, Cl^-, NO_3^-, SO_4^{2-}, Ca^{2+}, NH_4^+, Mg^{2+}, K^+, Na^+$ ), ssf= sea salt fraction, nss= non-sea salt fraction.

For the calculation of the crustal associated fraction (CF) of major ionic components,  $nss Ca^{2+}$  was considered as reference element in snowfall samples (Kulshrestha et al., 2003b). The presence of crustal components in the form of  $nss Ca^{2+}$  has been reported in precipitation globally (Rahn, 1976; Rodhe et al., 2002; Kulshrestha et al., 2003b; Budhavant et al., 2014a).

The percent contribution of CF was calculated by the following formula –

$$\% CF_x = 100 / EF_{Soil}$$

$$\text{Where, } EF_{Soil} = (y / nss Ca^{2+})_{snowfall} / (y / nss Ca^{2+})_{Soil} \quad \text{----- (iii)}$$

Where,  $y$  is the  $nss$  concentration of ionic species ( $nss SO_4^{2-}$ ,  $nss Ca^{2+}$ ,  $nss K^+$ ,  $nss Mg^{2+}$ ,  $NO_3^-$ ,  $NH_4^+$  and  $F^-$ ) in  $\mu eq/l$ .

$(y / nss Ca^{2+})_{Soil}$  is taken as standard ratio of local soils.

Then, the percent Anthro fractions of each component were calculated as follows-

$$\% \text{ Anthro}_x = \% \text{ nss}_x - \% \text{ CF}_x \quad \text{----- (iv)}$$

With the help of the above mentioned equation, the percent contribution of crustal fractions (CF) and anthropogenic fractions (Anthro) of each ionic species at these sites are given in Table 6.2.

CF  $\text{Ca}^{2+}$  at these sites followed the order- Mukteshwar > Gulmarg > Kothi. The crustal associated fraction of  $\text{SO}_4^{2-}$  was dominated at Mukteshwar site followed by Kothi and Gulmarg. Anthro  $\text{NO}_3^-$  at these sites followed the order- Mukteshwar > Gulmarg > Kothi. At all sites, the maximum fraction of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and F<sup>-</sup> was dominated by anthro fraction over CF.

The highest contribution of crustal  $\text{Ca}^{2+}$  might be due to contribution from local sources such as local soil, construction activities, road dust etc as well as long range transport of fine dusts. nss $\text{Ca}^{2+}$  has been reported in snow samples at Himalaya and Tibetan Plateau due to transported dust (Mayewski et al., 1983). Among nss  $\text{SO}_4^{2-}$ , high value of Anthro  $\text{SO}_4^{2-}$  might be due to significant contribution from various airmasses approaching at these sites as mentioned in section 6.2. This might be due to fossil fuel combustion at the origin of airmasses as well as picking it during the transport of airmasses before reaching at the site since there is no any significant source of  $\text{SO}_2$  nearby the sampling site. Apart from long range transport, contribution from local sources such as use of electric generators which are mostly operated on diesel can not be ruled out. Various hotels at these sites are forced to use these generators due to frequent power failure. The presence of Anthro  $\text{SO}_4^{2-}$  in the form of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$  has been reported in precipitation worldwide (Finlayson-Pitts and Pitts, 1986; Kulshrestha et al., 2003b). The crustal  $\text{SO}_4^{2-}$  at this site might be due to reaction of  $\text{SO}_2$  with  $\text{CaCO}_3$  rich dust particles forming Calcium Sulphate (Kulshrestha et al., 2003b; Kulshrestha, 2013) which is very common in Indian region.

**Table 6.2:** Percent contribution of Marine Fraction, Crustal Fraction (CF) and Anthropogenic Fraction (Anthro) of various ionic species at Kothi (a), Gulmarg (b) and Mukteshwar (c).

<b>(a) Kothi</b>									
	<b>F<sup>-</sup></b>	<b>Cl<sup>-</sup></b>	<b>NO<sub>3</sub><sup>-</sup></b>	<b>SO<sub>4</sub><sup>2-</sup></b>	<b>Na<sup>+</sup></b>	<b>NH<sub>4</sub><sup>+</sup></b>	<b>K<sup>+</sup></b>	<b>Ca<sup>2+</sup></b>	<b>Mg<sup>2+</sup></b>
<b>Marine</b>	0.0	100.0	0.0	19.9	100.0	0.0	8.9	4.1	58.2
<b>Crustal</b>	5.4	0.0	13.8	24.7	0.0	12.0	91.1	95.9	41.8
<b>Anthropo</b>	94.6	0.0	86.2	55.4	0.0	88.0	0.0	0.0	0.0
<b>(b) Gulmarg</b>									
<b>Marine</b>	0.0	100.0	0.0	16.2	100.0	0.0	8.5	3.2	60.6
<b>Crustal</b>	4.6	0.0	16.1	26.1	0.0	4.4	91.5	96.8	39.4
<b>Anthropo</b>	95.4	0.0	83.9	57.7	0.0	95.6	0.0	0.0	0.0
<b>(c) Mukteshwar</b>									
<b>Marine</b>	0.0	100.0	0.0	16.9	100.0	0.0	5.5	2.4	49.3
<b>Crustal</b>	9.1	0.0	21.6	34.0	0.0	10.0	94.5	97.6	50.7
<b>Anthropo</b>	90.9	0.0	78.4	49.1	0.0	90.0	0.0	0.0	0.0

At the present sites, NO<sub>3</sub><sup>-</sup> is found to be dominated by anthropogenic source in comparison to crustal sources (Table 6.2). Very high fraction of Anthro NO<sub>3</sub><sup>-</sup> might be due to the emissions of NO<sub>x</sub> from fossil fuel combustion and biomass burning. Among local sources, vehicles used by tourist might be the major source of NO<sub>x</sub>. Apart from local sources, Anthro NO<sub>3</sub><sup>-</sup> might be due to the emissions of NO<sub>x</sub> from fossil fuel combustion and biomass burning coming from various airmasses. NO<sub>3</sub><sup>-</sup> has been reported in airmasses due to long range transport in global precipitation (Avila and Alacron, 1999; Satyanarayana et al., 2010).

The maximum fraction of nssK<sup>+</sup> is contributed by crustal sources. Apart from biomass burning, nssK<sup>+</sup> due to crustal sources has been reported in precipitation (Zhang et al., 2007a). Sometimes local soils contain very high level of potassium (Jain et al., 2000).

Besides marine origin,  $Mg^{2+}$  is also contributed by crustal sources.  $Mg^{2+}$  has been reported in snow samples due to significant contribution from crustal sources (Kang et al., 2004). At the present sites,  $NH_4^+$  are contributed mainly by anthropogenic sources which might be due to significant contribution from local sources like animal and human excreta, effluents from various hotels with huge biomass burning/ biogenic sources with some contribution from long range transport.

### 6.1.3. Average contribution of different source categories

Marine, crustal and anthropogenic fractions of different ionic components were calculated to find out contribution of each source category.

The average % marine contribution in each air mass cluster was calculated as follows-

$$\text{Average marine \%} = \frac{\sum X_{\text{ssf}} \times 100}{\sum X_{\text{Total}}}$$

Here  $\sum X_{\text{ssf}}$  = Sum of concentration of all ssf values in each air mass cluster in  $\mu\text{eq/l}$ .

$\sum X_{\text{Total}}$  = Sum of concentration of all components in each air mass cluster in  $\mu\text{eq/l}$ .

The average crustal % for each air mass cluster was calculated as follows-

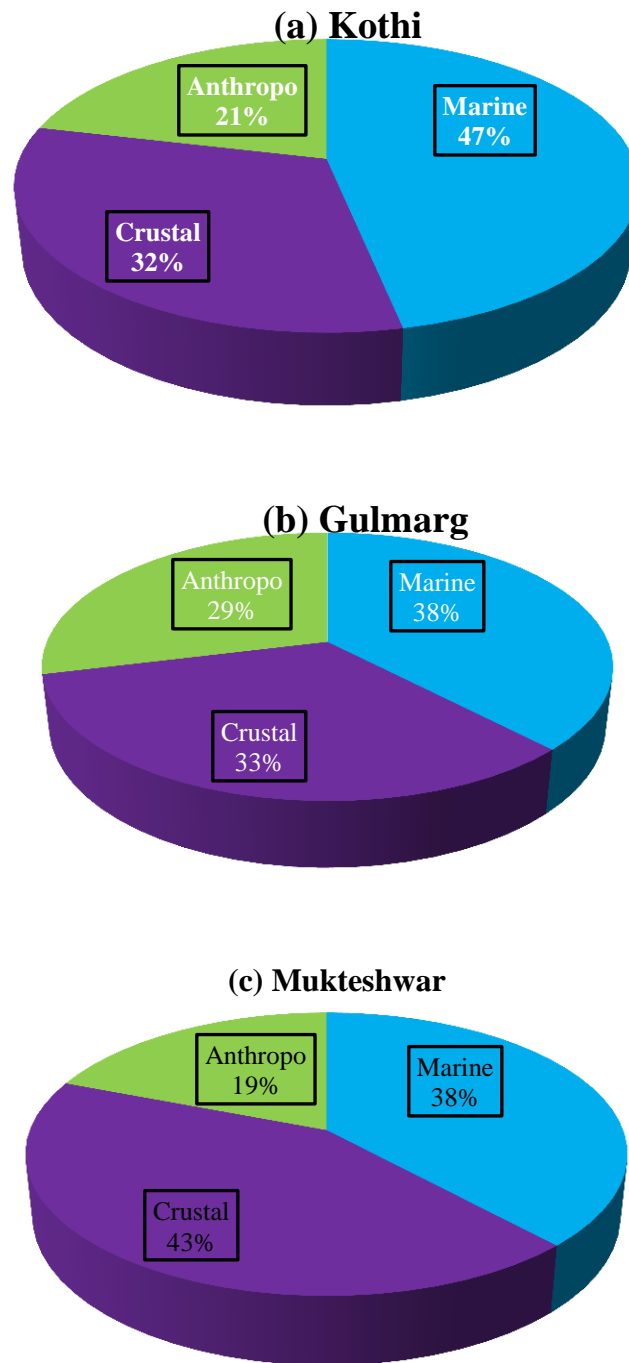
$$\text{Average crustal \%} = \frac{\sum X_{\text{CF}} \times 100}{\sum X_{\text{Total}}}$$

Here  $\sum X_{\text{CF}}$  = Sum of concentration of all CF values in each air mass cluster in  $\mu\text{eq/l}$ .

The average Anthro % for each air cluster air mass cluster was calculated as follows-

$$\text{Average Anthro \%} = 100 - \text{Average marine \%} - \text{Average crustal \%}.$$

Average percent contribution calculated from the above formula for different source categories i.e. marine, crustal and anthropogenic sources is given in fig. 6.2 (a-c). At Kothi, it is very clear from figure that the order of dominance has been Marine (47%) > Crustal (32%) > Anthropogenic (21%). These sources at Gulmarg site was dominated with marine (38%) followed by crustal (33%) and anthropogenic (29%) sources while Mukteshwar site followed the order – crustal (43%) > marine (38%) > anthropogenic (19%).



**Fig. 6.2:** Average contributions of different source categories at Kothi (a), Gulmarg (b), Mukteshwar (c).

Similar findings with dominance of marine and crustal over anthropogenic sources have been reported in precipitation samples by other workers globally (Zhang et al., 2007a; Budhavant et al., 2014a; Kumar et al., 2016).

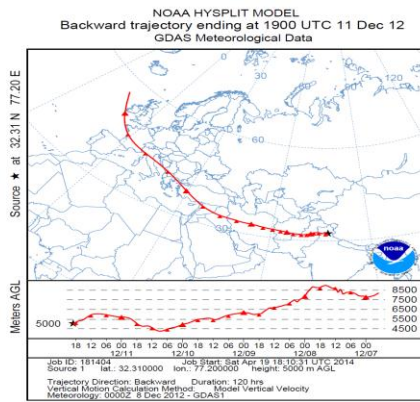
The significant contribution of crustal fraction has been observed in snow samples which might be due to local contribution with long range transport. The dominance of crustal fraction has been reported in snow samples worldwide (Mayewski et al., 1983; Shrestha et al., 2002). Anthropogenic contributions at these sites are mainly due to various airmasses reaching at these sites as discussed in section 6.2. However, the impact of anthropogenic sources is nullified significantly due to dominance of crustal contributions over anthropogenic contribution as reflected from the alkaline nature of snowmelt at these sites since sea salt don't play an important role in deciding pH of precipitation.

### **6.2. Clusterwise chemical composition of snowmelt**

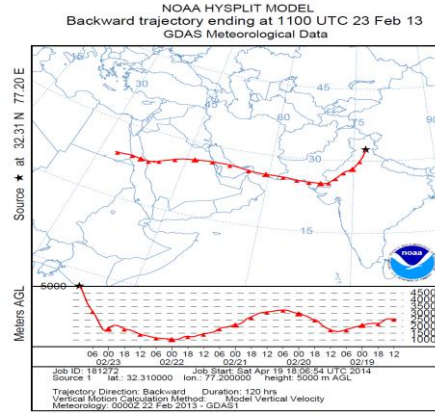
Backward air mass trajectories for 120 h of 5 000 m above ground level were calculated at Kothi and Gulmarg site using the HYSPLIT model from NOAA for all snowfall samples (Draxler and Rolph, 2003). HYSPLIT model were not applied at Mukteshwar site due to limited number of samples. Similar height has been applied by Kuniyal et al (2013) to study the composition and transport of aerosols in north western Himalayan region of India.

#### **6.2. 1. Sectorwise distribution of airmasses and its pH with major ions at Kothi**

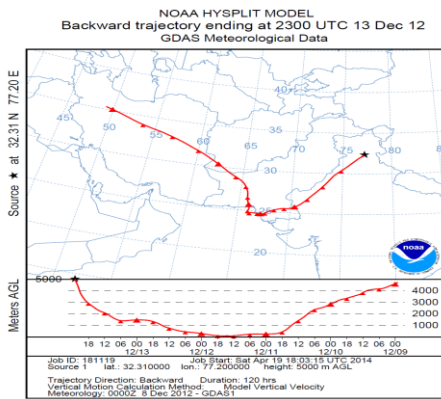
Total six clusters were identified viz. North Atlantic Ocean origin (NAO), African origin (Af), Middle East origin (ME), European origin (Eu), Western India origin (InW) and Nepal origin (Np). Typical example of each air mass trajectory has been shown in Fig. 6.3 (a-f). Percent occurrence of snowfall during each cluster is shown in Fig. 6.4. Table 6.3 gives the chemical compositions of major ionic species. The description of pH with its chemical composition for all six airmasses is given below.



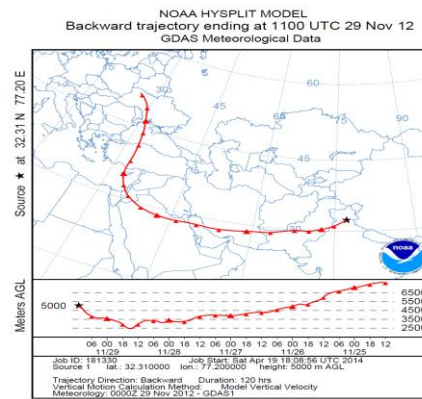
(a) pH = 6.35 (NAO)



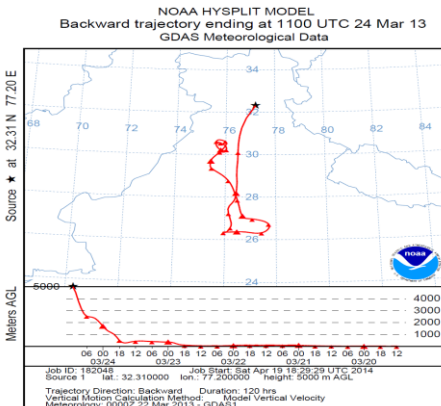
(b) pH = 5.72 (Af)



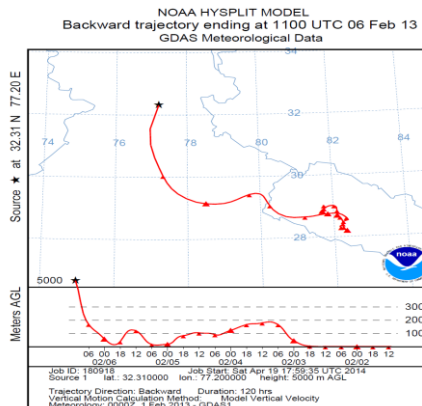
(c) pH= 4.96 (ME)



(d) pH = 5.48 (Eu)



(e) pH = 6.73 (InW)

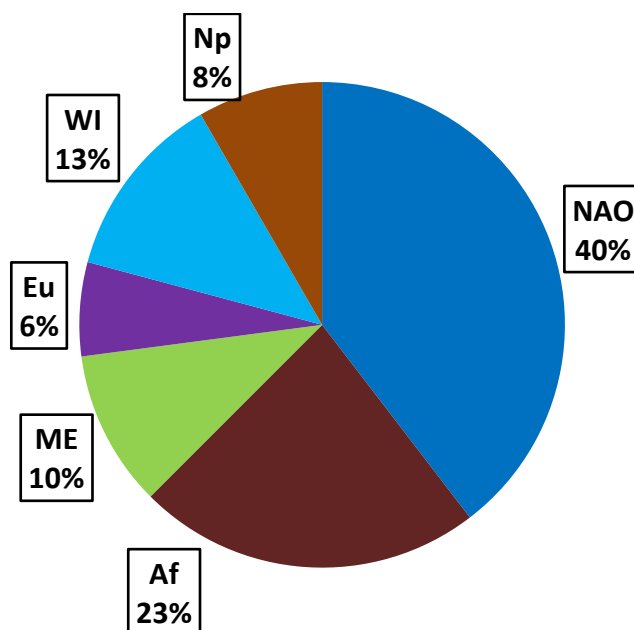


(f) pH = 6.01 (Np)

**Fig. 6.3:** (a-f). Typical examples of six different airmass trajectories arriving at Kothi site. NAO = North Atlantic Ocean origin, Af = African origin, ME = Middle East origin, Eu = European origin (Eu), InW= Western India origin, Np= Nepal origin .



**Cluster 1: North Atlantic Ocean origin (NAO)** - Airmasses originated from North Atlantic Ocean and passed over Europe to Afghanistan to Jammu & Kashmir and reached at the sampling site i.e. Kothi have been referred as NAO in Cluster 1. This cluster represented the highest number of events (40%). The average pH of the samples was noticed to be 6.35 which was the second highest among all the clusters. The average pH can be explained based on  $\text{nss SO}_4^{2-}/\text{nssCa}^{2+}$  and  $\text{NO}_3^-/\text{nssCa}^{2+}$  ratios given in Fig. 6.5. These ratios are very useful to explain acidity of precipitation (Jain et al., 2000; Satyanarayana et al., 2010). In this cluster, all the snow samples were having pH higher than 5.6 showing relatively alkaline nature of deposition. Such pH values of precipitation have been reported for oceanic airmasses globally (Calvo et al., 2010, Satyanarayana et al., 2010).



**Fig. 6.4:** Percent frequency of snowfall events occurring during different trajectory clusters at Kothi.

On an average, equivalent concentrations of ions in this clusters followed the following order –  $\text{Cl}^- > \text{Na}^+ > \text{Ca}^{2+} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{Mg}^{2+} > \text{NO}_3^- > \text{NH}_4^+ > \text{K}^+ > \text{F}^-$  (Table 6.3). The highest contribution of  $\text{Na}^+$  (24%) and  $\text{Cl}^-$  (26%) among all the ions clearly indicated the influence of marine sources. Obviously these airmasses are originated in

North Atlantic Ocean and carried sea salt which are deposited at the site. High concentrations of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  might be due to local and transported crustal influences. Sea salts also have small fraction of  $\text{Ca}^{2+}$  (Keene et al., 1986). The most of the  $\text{Ca}^{2+}$  is probably due to the crustal influence. The influence of Saharan dust has been reported in aerosol samples over North Atlantic Ocean during winter (Nakamae and Shiotani, 2013). The high concentrations of  $\text{SO}_4^{2-}$  might be due to both marine as well as anthropogenic contributions. Conversion of DMS into  $\text{SO}_4^{2-}$  over North Atlantic Ocean has also been reported as a source of  $\text{SO}_4^{2-}$  in precipitation (Andreae et al., 2003). European pick up of  $\text{SO}_2 / \text{SO}_4^{2-}$  during the transport of airmasses over Europe and Afghanistan can also result in high  $\text{SO}_4^{2-}$ . High concentrations of  $\text{SO}_4^{2-}$  in precipitation samples have been reported due to transport of airmasses over Spain even originated from North Atlantic Ocean before reaching at Montseny in North East Spain (Avila and Alacron, 1999).

**Cluster 2: African origin (Af)** - Airmasses originated from African continent and passed over Middle East/Gulf to Pakistan before reaching the sampling site have been termed as Af. This class represented 23 % of snowfall events. During these airmasses, the pH of snowfall samples varied from 5.41 – 6.15 having average value of 5.72. Its pH can also be explained in the same manner like NAO by ratios of  $\text{nss SO}_4^{2-} / \text{nssCa}^{2+}$  and  $\text{NO}_3^- / \text{nssCa}^{2+}$  (Fig. 6.5). Higher values of pH have been reported for precipitation samples in airmasses originated from African countries (Avila and Alacron, 1999, Budhvant et al., 2011).

On an average, equivalent concentrations of major components followed the following order –  $\text{Ca}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{NO}_3^- > \text{HCO}_3^- > \text{K}^+ > \text{Mg}^{2+} > \text{F}^-$  (Table 6.3). Very high concentrations of  $\text{Ca}^{2+}$  among all the ions indicated crustal dominance possibly influence of Saharan dust. Airmasses coming from African continents with very high concentrations of  $\text{Ca}^{2+}$  have been reported in global precipitation (Avila and Alacron, 1999, Satyanarayana et al., 2010, Budhvant et al., 2011). The highest concentrations of  $\text{SO}_4^{2-}$  in this cluster might be due to its sources in African region as well as further its addition from Middle East region during the transport.

**Table 6.3:** Average of pH and major ions ( $\mu\text{eq/l}$ ) in snow for trajectory classes at Kothi.

Air Clusters	NAO	Af	ME	Eu	InW	Np
pH	6.41	5.77	5.05	5.48	6.76	6.03
F <sup>-</sup>	1.4	5.1	0.9	0.5	5.1	6.7
Cl <sup>-</sup>	67.5	38.9	22.0	36.6	35.8	15.7
NO <sub>3</sub> <sup>-</sup>	10.4	26.1	16.4	14.5	21.2	24.3
SO <sub>4</sub> <sup>2-</sup>	24.0	34.7	25.3	22.3	26.9	31.4
nssSO <sub>4</sub> <sup>2-</sup>	16.0	30.3	22.4	17.7	22.6	29.4
Na <sup>+</sup>	63.6	35.5	23.5	36.8	34.4	16.1
NH <sub>4</sub> <sup>+</sup>	9.2	34.4	13.0	10.8	21.4	26.5
K <sup>+</sup>	6.7	18.6	6.0	6.6	15.8	11.4
nssK <sup>+</sup>	5.3	17.8	5.5	5.8	15.1	11.0
Ca <sup>2+</sup>	41.0	47.6	22.6	26.8	88.3	58.7
nssCa <sup>2+</sup>	38.2	46.0	21.6	25.2	86.8	58.0
Mg <sup>2+</sup>	20.3	15.1	12.6	16.3	17.3	12.6
nssMg <sup>2+</sup>	5.9	7.1	7.2	8.0	9.5	9.0
HCO <sub>3</sub> <sup>-</sup>	28.9	21.8	5.8	13.0	58.5	26.9
nssSO <sub>4</sub> <sup>2-</sup> /nssCa <sup>2+</sup>	0.42	0.66	1.04	0.70	0.26	0.51
NO <sub>3</sub> <sup>-</sup> /nssCa <sup>2+</sup>	0.27	0.57	0.76	0.58	0.24	0.42

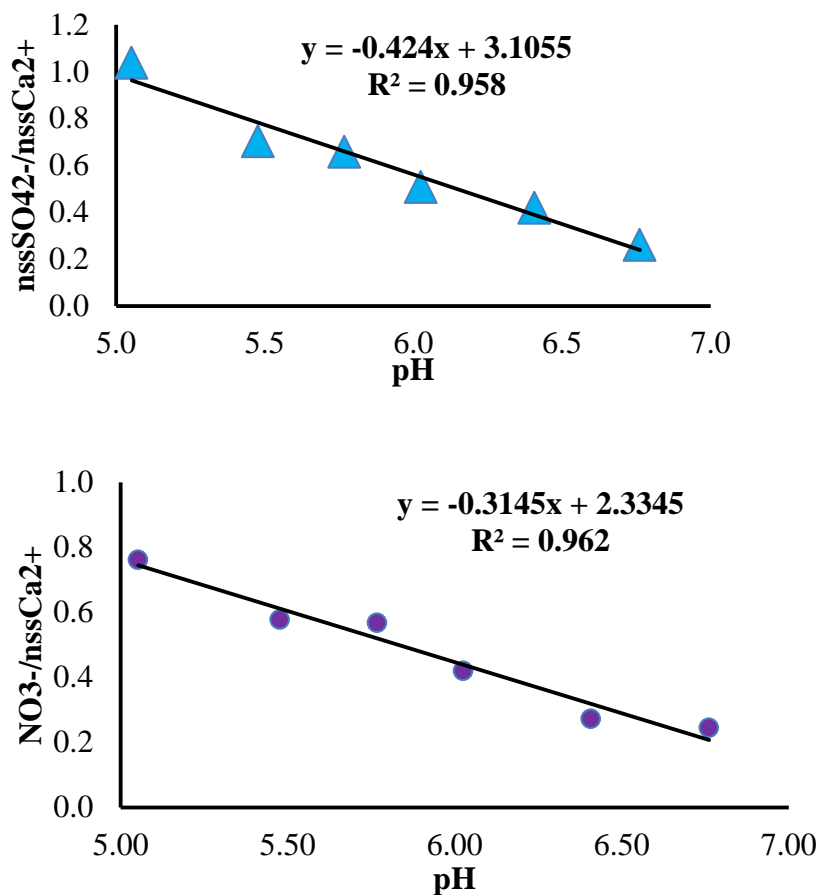
In various other reports, very high concentrations of SO<sub>4</sub><sup>2-</sup> have been reported in airmasses coming from African region in precipitation samples (Avila and Alacron, 1999, Reddy et al., 2008, Satyanaryana et al., 2010). NO<sub>3</sub><sup>-</sup> in Snow samples in this cluster might be contributed by the oxidation of NO<sub>x</sub> emitted from various sources such as combustion of fossil fuel, biomass burning and agricultural activities (Seinfeld and Pandis, 2006). The highest concentrations of NH<sub>4</sub><sup>+</sup> might be due to the influence of African biomass burning / agricultural activities. Very high concentrations of NH<sub>4</sub><sup>+</sup> with SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> indicated that the dominance of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub> which is generally reported for the acidified region (Shon et al., 2012). Biomass burning is a

significant source of atmospheric ammonia (Singh et al., 2014). The highest concentrations of  $K^+$  in these airmasses further corroborated the influence of biomass burning.  $K^+$  is considered as a tracer for biomass burning (Andreae, 1983, Kulshrestha et al., 2004). Biomass burning is a significant source of  $K^+$  in precipitation samples (Kulshrestha et al., 1999, Budhvant et al., 2011). Apart from biomass burning, very high percent contribution of  $Cl^-$  (14%) and  $Na^+$  (13 %) indicated a significant contribution from marine sources.

**Cluster 3: Middle East origin (ME)** - Airmasses originated from Middle East and reached to the sampling site via Pakistan and Haryana have been termed as Cluster 3. This group represented 10% of the total snowfall events. In this cluster, 80 % snowfall samples were observed to be acidic having pH below 5.6. During these airmasses, pH of the snowfall samples varied from 4.75 – 5.69 with an average of 4.94 pH which was the lowest among all the clusters due to the highest ratios of  $nss\ SO_4^{2-} / nssCa^{2+}$  and  $NO_3^- / nssCa^{2+}$  (Fig. 6.5). In another study, the occurrence of acidic rain has been reported when airmasses were coming from Gulf countries at Hudegade in Western Ghats located in south-west India (Satyanarayana et al., 2010).

On an average, equivalent concentrations of ionic species in these samples followed the following order -  $SO_4^{2-} > Na^+ > Ca^{2+} > Cl^- > NO_3^- > NH_4^+ > Mg^{2+} > K^+ > HCO_3^- > F^-$ . Among all the ions,  $SO_4^{2-}$  concentrations were the highest which might be due to fossil fuel combustion. Abdeen and co-workers (2014) reported that high concentration of  $SO_4^{2-}$  in aerosol samples over the middle east might be due to the dominance of industrial activities in this region. Very high concentrations of  $SO_4^{2-}$  have been reported in air masses coming from Gulf over Bay of Bengal and Arabian Sea during ICARB (Reddy et al., 2008). Such high levels of  $SO_4^{2-}$  have significantly lowered the pH contributing to the highest acidity in this cluster. Probably high concentrations of  $NO_3^-$  in this cluster can also be explained in the same manner. It is to be noted that the concentrations of  $Ca^{2+}$  were the lowest in these airmasses in comparison to all other air clusters. This feature is similar to that as reported by Satyanarayana and co-workers (2010) where very low concentration of  $Ca^{2+}$  has been reported in precipitation samples in airmasses coming from Gulf regions at Hudegade in Western Ghat, India. Similar

feature has been reported over Indian Ocean during INDOEX by Kulshrestha et al 1999.



**Fig. 6.5:** Variation of pH with (a)  $\text{nssSO}_4^{2-}/\text{nssCa}^{2+}$  (b)  $\text{NO}_3^-/\text{nssCa}^{2+}$  at Kothi.

**\Cluster 4: European origin (Eu)** - Airmasses originating from continental Europe and reached to the sampling site via Afghanistan and Jammu & Kashmir has been referred as Cluster 4. This class represented the least number of snowfall events (6 %). In this cluster, 67 % snowfall samples showed slightly acidic behaviour ( $\text{pH} < 5.6$ ). During these airmasses, pH of the snowfall samples varied from 5.35 – 5.66 with an average of 5.48 pH. Its pH can also be explained by ratios of  $\text{nss SO}_4^{2-}/\text{nssCa}^{2+}$  and  $\text{NO}_3^-/\text{nssCa}^{2+}$  (Fig. 6.5). European origin airmasses have been reported carrying acidic components. In a long term study, Avila and Alacron (1999) reported acidic precipitation in North East Spain when airmasses were coming from various sectors of Europe.

On an average, equivalent concentrations of ionic components followed the following order –  $\text{Na}^+ > \text{Cl}^- > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{Mg}^{2+} > \text{NO}_3^- > \text{HCO}_3^- > \text{NH}_4^+ > \text{K}^+ > \text{F}^-$ . Very high percent contribution of  $\text{Cl}^-$  and  $\text{Na}^+$  suggested that the marine sources had a significant contribution to these airmasses. Eu airmasses which are originated in Europe can have influence of Atlantic Ocean which might be the reason for the dominance of marine sources. Low pH and very high concentrations of  $\text{SO}_4^{2-}$  during these airmasses indicated that most of sulphate was of non-marine origin.  $\text{NO}_3^-$  concentrations were also found to be very high in these air masses. Significantly high concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in such airmasses have been reported in precipitation samples (Avila and Alacron, 1999).

**Cluster 5: Western India origin (InW)** - Airmasses originated in Western India in the state of Rajasthan and transported over Punjab and Haryana, finally, reaching to the sampling site have been grouped under cluster 5. This group represented 13% of the total snowfall events. During these airmasses, pH of the snowfall samples varied from 6.59 – 6.98 with an average of 6.73 which was the highest pH in comparison to all the clusters. The highest pH in this cluster compared to other airmasses might be due to the lowest ratios of  $\text{nss SO}_4^{2-} / \text{nssCa}^{2+}$  and  $\text{NO}_3^- / \text{nssCa}^{2+}$  (Fig. 6.5). Alkaline nature of precipitation is a typical feature in Indian region (Kulshrestha et al., 2005, Satyanarayana et al., 2010, Kulshrestha, 2013) due to  $\text{CaCO}_3$  rich dusty atmosphere.

On an average, equivalent concentration of ionic components followed the following order –  $\text{Ca}^{2+} > \text{HCO}_3^- > \text{Cl}^- > \text{Na}^+ > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{NO}_3^- > \text{Mg}^{2+} > \text{K}^+ > \text{F}^-$ . The equivalent concentrations of  $\text{Ca}^{2+}$  were the highest among all ions. In fact,  $\text{Ca}^{2+}$  was the highest among all the clusters providing the highest buffering of the acidity as indicated by the highest pH of snow. Very high concentrations of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  in this cluster clearly suggested the dominance of crustal sources. In India, the main source of  $\text{Ca}^{2+}$  is atmospheric dust (Khemani, 1989, Kulshrestha et al., 1996, Kulshrestha, 2013). The concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were also found to be high which might be due to adsorption of their respective gases ( $\text{SO}_2$  &  $\text{NO}_2$ ) onto the dust particles (Kulshrestha et al., 2003). Very high concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  have been reported in aerosol samples over western India (Rastogi and Sarin, 2009). Elevated concentrations of  $\text{NH}_4^+$

might be due to biomass burning contributions. Biomass burning is a common source for cooking and winter time heating (Singh et al., 2014).  $K^+$  which is a biomass burning marker also showed high concentration indicating biomass burning effect on snow composition. The particles of biomass burning in air masses originated from North West India have been reported in snow samples at Himalayan glacier (Xu et al., 2013).

**Cluster 6: Nepal origin (Np)** - Air masses originated from Nepal side reaching to the sampling site via Uttarakhand have been categorised as Cluster 6. This cluster represented the second lowest number of events (8 %). All samples in this air cluster were found to be alkaline in nature typically representing the feature of Indian region. During these airmasses, the pH of snowfall samples varied from 5.92 – 6.16 with an average pH of 6.01. Its pH can also be explained with the help of ratios of  $nss\ SO_4^{2-} / nssCa^{2+}$  and  $NO_3^- / nssCa^{2+}$  (Fig. 6.5). Similar range of pH has been reported in precipitation samples at Kathmandu valley in Nepal (Shrestha et al., 2013).

On an average, equivalent concentrations of ionic components followed the following order –  $Ca^{2+} > SO_4^{2-} > HCO_3^- > NH_4^+ > NO_3^- > Na^+ > Cl^- > Mg^{2+} > K^+ > F^-$ . Among all ions,  $Ca^{2+}$  had the highest concentrations. Similar to India, very high concentration of  $Ca^{2+}$  has been reported in precipitation samples at various sites in Nepal (Shrestha et al., 2013; Tripathee et al., 2014). Very high concentrations of  $SO_4^{2-}$  among all anions suggested a significant influence of anthropogenic sources. Diesel driven vehicles and brick kilns are the main sources of  $SO_2$  in Nepal (NESS, 1999). Huge growth of industries might be another reason for elevated concentrations of  $SO_4^{2-}$  during these airmasses (SOE 2001). Precipitation having high  $SO_4^{2-}$  content has been reported at various sites at Kathmandu valley in Nepal (Shrestha et al., 2013). Similarly, high concentrations of  $NO_3^-$  might be due to vehicular emissions mainly from Nepal and to some extent from Uttarakhand which are transported by Np airmasses to Kothi. Biomass burning can also be another source of influence having effect upto Himalayan glacier (Xu et al., 2013). Higher concentrations of  $NH_4^+$  in this cluster might be due to agricultural activities and biomass burning (Tripathee et al., 2014). Biomass burning might be one of the main reasons for very high concentrations of  $K^+$  too.

**6.2.2. Sectorwise distribution of airmasses and its pH with major ions at Gulmarg**

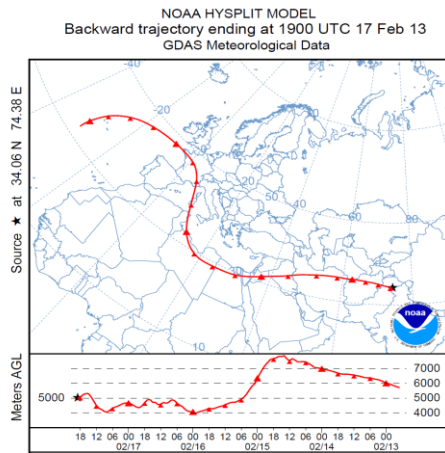
Air mass trajectories were calculated by methods as discussed above in the beginning of this section. Air mass trajectories revealed that Gulmarg was receiving snowfall through the airmasses originated from six major sectors which have been discussed below (Fig. 6.6). Percent occurrence of snowfall during each cluster is shown in Fig. 6.7.

The average pH and concentrations of ions of snow representing each air mass cluster are given in Table 6.4.

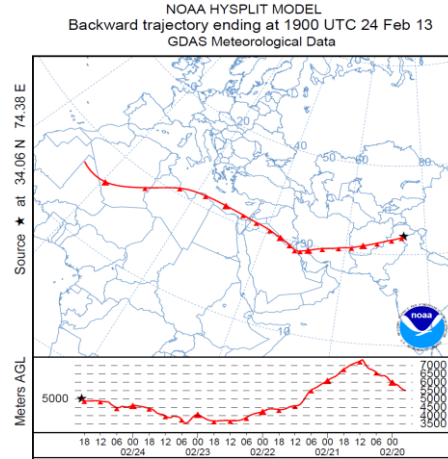
**North Atlantic Ocean origin (NAO)** - Airmasses coming from North Atlantic Ocean and passed over Europe to Afghanistan to Jammu & Kashmir have been referred as NAO (Fig. 6.6a). Among all air clusters, the highest numbers of events (31%) have represented by this cluster. The average pH of the samples during NAO airmasses was noticed as 6.96 (Table 6.4) which was the third highest among all the clusters.

Alkaline precipitation has been reported globally for airmasses originated from ocean (Sakihama et al., 2008; Satyanarayana et al., 2010). The average pH can be explained based on  $\text{nss SO}_4^{2-}/\text{nssCa}^{2+}$  and  $\text{NO}_3^-/\text{nssCa}^{2+}$  ratios given in Fig. 6.8. These ratios are very useful to explain acidity of precipitation (Jain et al., 2000; Satyanarayana et al., 2010). The highest concentration of  $\text{Na}^+$  among all cations and  $\text{Cl}^-$  among all anions clearly indicated the influence of marine sources. Very high  $\text{Ca}^{2+}$  is probably due to the crustal influence (Nakamae and Shiotani, 2013). High contribution of  $\text{SO}_4^{2-}$  in snow samples might be due to both marine as well as anthropogenic contributions. Airmasses originating from North Atlantic Ocean with high concentrations of  $\text{SO}_4^{2-}$  in precipitation samples have been reported at Montseny in North East Spain (Avila and Alacron, 1999).

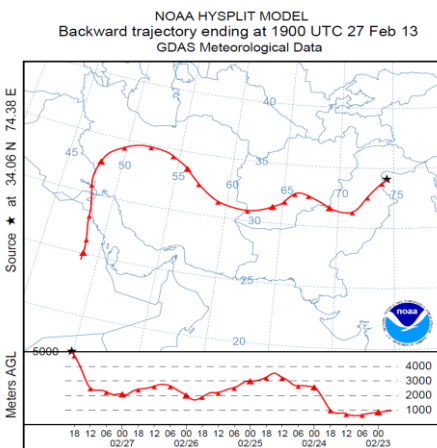




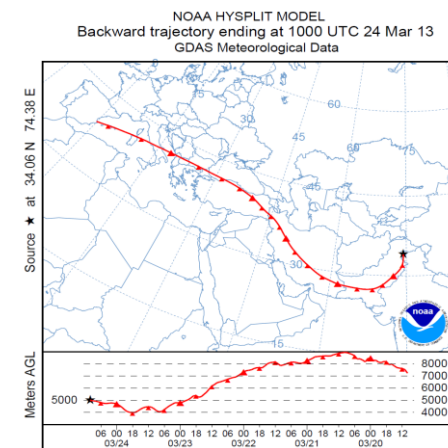
(a) pH= 6.96 (NAO)



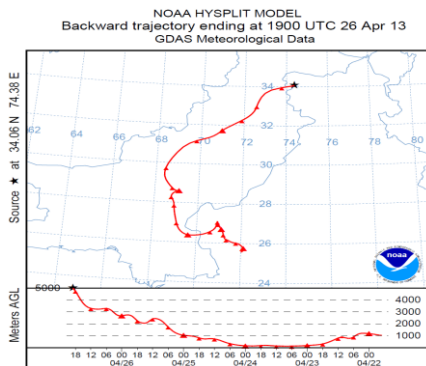
(b) pH = 6.54 (Af)



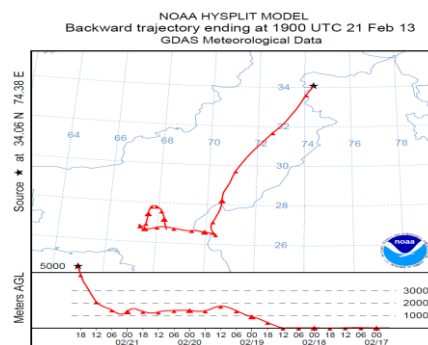
(c) pH= 5.21 (ME)



(d) pH = 5.52 (Eu)



(e) pH = 7.58 (InW)



(f) pH = 7.02 (Pk)

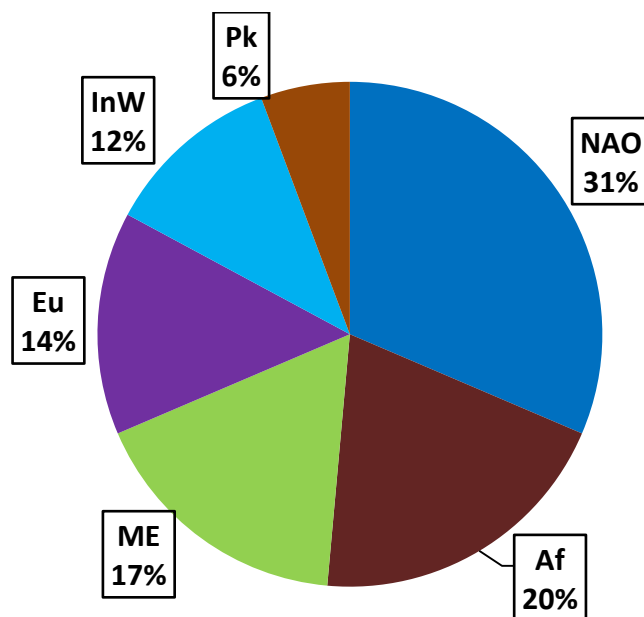
**Fig. 6.6:** (a-f). Examples of six different airmass trajectories arriving at the site using HYSPLIT model at Gulmarg site. NAO = North Atlantic Ocean origin, Af = African origin, ME = Middle East origin, Eu = European origin (Eu), InW= Western India origin , Pk= Pakistan origin .

**African origin (Af)** – Air masses coming from African continent and passed over Middle East to Pakistan before reaching the sampling site have been termed as Af (Fig. 6.6b). This class represented 20 % of snowfall events. During these air masses, the average pH was 6.54. Its pH can also be explained in the same manner like NAO by ratios of  $\text{nss SO}_4^{2-} / \text{nssCa}^{2+}$  and  $\text{NO}_3^- / \text{nssCa}^{2+}$  (Fig. 6.8).

Very high concentrations of  $\text{Ca}^{2+}$  among all the ions indicated crustal dominance possibly influence of Saharan dust. Abundance of  $\text{Ca}^{2+}$  has been reported in global precipitation in air masses coming from African continents (Avila and Alacron, 1999; Satyanarayana et al., 2010; Budhvant et al., 2011). The concentrations of  $\text{SO}_4^{2-}$  were noticed to be the highest in this cluster in comparison to all air masses which might be due to its sources in African region as well as further its addition from Middle East region during the transport. Air masses originating from African region with high concentrations of  $\text{SO}_4^{2-}$  have been reported in global precipitation (Avila and Alacron, 1999; Reddy et al., 2008; Satyanarayana et al., 2010). Very high concentration of  $\text{NO}_3^-$  might be due to oxidation of  $\text{NO}_x$  emitted from various sources such as combustion of fossil fuel, industrial activities, and biomass burning (Seinfeld and Pandis, 2006). Biomass burning and agricultural activities in this region might be responsible for the highest concentrations of  $\text{NH}_4^+$ . Further, enhanced concentrations of  $\text{K}^+$  in this air mass confirmed the influence of biomass burning. In general,  $\text{K}^+$  is considered as a tracer for biomass burning (Kulshrestha et al., 2004).

**Middle East origin (ME)** - Air masses coming from Middle East and reached to the sampling site via Pakistan have been termed as ME (Fig. 6.6c). This group represented 17% of the total snowfall events. The average pH (5.44) was the lowest in this cluster which is explained with basis of the highest  $\text{nss SO}_4^{2-} / \text{nssCa}^{2+}$  and  $\text{NO}_3^- / \text{nssCa}^{2+}$  ratios (Fig. 6.8).

The highest concentration of  $\text{SO}_4^{2-}$  among all anions might be due to fossil fuel combustion used for various purposes by Middle East countries. Similar to our study, Reddy et al (2008) reported very high concentrations of  $\text{SO}_4^{2-}$  in air masses coming from Gulf over Bay of Bengal and Arabian Sea during ICARB. Besides  $\text{SO}_4^{2-}$ , this cluster also showed high concentrations of  $\text{NO}_3^-$ . However, the concentrations of  $\text{Ca}^{2+}$  were the lowest in this cluster which resulted in the lowest pH.



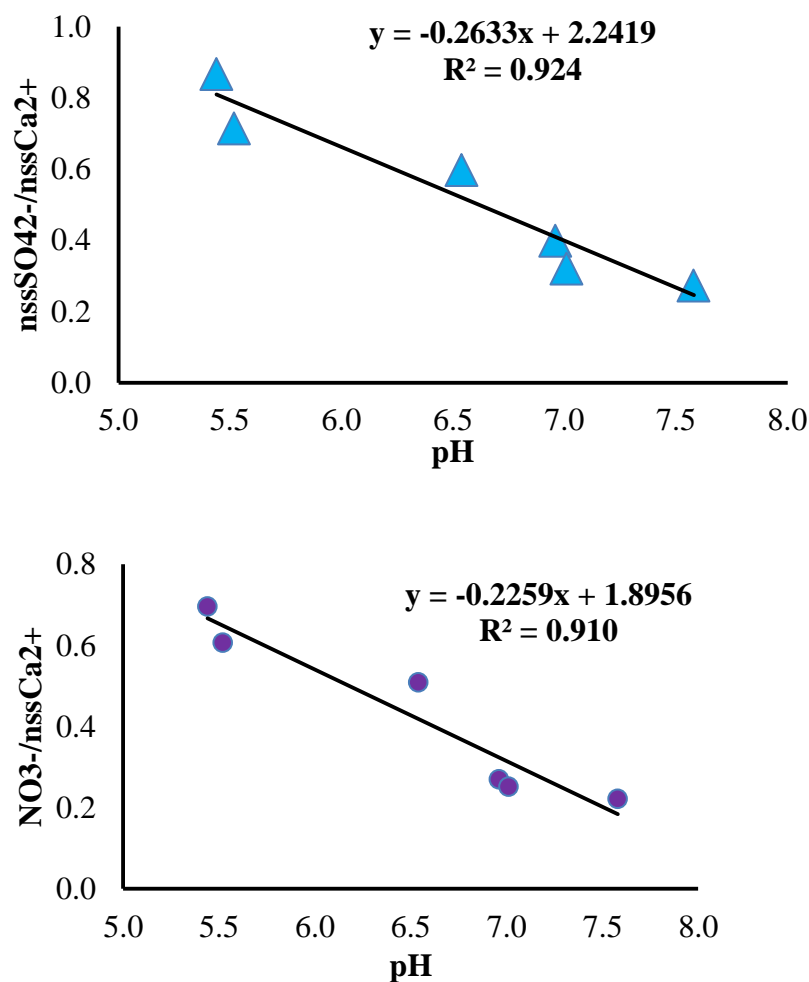
**Fig. 6.7:** Percent frequency of snowfall events occurring during different trajectory clusters at Gulmarg.

**Table 6.4:** Average concentrations ( $\mu\text{eq/l}$ ) of major ions and pH during different clusters at Gulmarg.

	NAO	Af	ME	Eu	InW	Pk
pH	6.96	6.54	5.44	5.52	7.58	7.01
F <sup>-</sup>	2.4	5.9	2.7	2.5	6.3	5.4
Cl <sup>-</sup>	44.3	35.6	18.9	35.6	33.2	26.3
NO <sub>3</sub> <sup>-</sup>	12.7	29.4	18.9	17.7	20.9	21.9
SO <sub>4</sub> <sup>2-</sup>	24.8	38.7	27.5	25.4	29.7	31.5
nssSO <sub>4</sub> <sup>2-</sup>	18.7	34.5	23.6	20.9	25.7	28.0
Na <sup>+</sup>	48.5	33.3	30.8	36.5	32.6	28.2
NH <sub>4</sub> <sup>+</sup>	16.4	52.5	35.2	27.7	38.5	36.0
K <sup>+</sup>	5.8	16.6	6.9	7.5	14.8	13.0
nssK <sup>+</sup>	4.7	15.9	6.2	6.7	14.1	12.4
Ca <sup>2+</sup>	49.2	59.3	28.6	30.8	95.6	88.4
nssCa <sup>2+</sup>	47.0	57.8	27.2	29.2	94.2	87.2
Mg <sup>2+</sup>	16.2	12.3	13.5	13.5	14.4	11.9
nssMg <sup>2+</sup>	5.2	4.8	6.5	5.2	7.0	5.5
HCO <sub>3</sub> <sup>-</sup>	26.1	27.6	11.4	16.3	56.5	41.1
nssSO <sub>4</sub> <sup>2-</sup> /nssCa <sup>2+</sup>	0.40	0.60	0.87	0.71	0.27	0.32
NO <sub>3</sub> <sup>-</sup> /nssCa <sup>2+</sup>	0.27	0.51	0.70	0.61	0.22	0.25

**European origin (Eu)** - Airmasses originating from continental Europe reaching to the sampling site via Afghanistan and Jammu & Kashmir have been referred as Eu (Fig. 6.6d). This class represented the third lowest number of snowfall events (14 %). The average pH of snowfall during these airmasses was observed to be slightly acidic (5.52). The second lowest pH value in these airmasses with respect to all other air clusters is justified from ratios of  $\text{nss SO}_4^{2-} / \text{nssCa}^{2+}$  and  $\text{NO}_3^- / \text{nssCa}^{2+}$  (Fig. 6.8).

The highest contribution of  $\text{Cl}^-$  and  $\text{Na}^+$  among all ions suggested that the marine sources had very significant influence on these airmasses (Fig. 6.6d). Very high concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  might be responsible for acidic pH during these airmasses. Similar to our observations, high concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  have been reported in airmasses originating from Europe in precipitation samples at Spain (Avila and Alacron, 1999).



**Fig. 6.8:** Variation of pH with (a)  $\text{nssSO}_4^{2-}/\text{nssCa}^{2+}$  (b)  $\text{NO}_3^-/\text{nssCa}^{2+}$  at Gulmarg.

**Western India origin (InW)** - Airmasses originated in Western India have been termed as InW (Fig. 6.6e). This group represented 12% of the total snowfall events. The average pH (7.58) of the snowfall was the highest in these airmasses with respect to all airmasses. Alkaline precipitation has been reported by many workers in Indian region (Kulshrestha et al., 2005; Satyanarayana et al., 2010; Kulshrestha, 2013). The lowest ratio of  $\text{nss SO}_4^{2-} / \text{nssCa}^{2+}$  and  $\text{NO}_3^- / \text{nssCa}^{2+}$  is justifying its highest pH value in comparison to all other air clusters (Fig. 6.8).

The concentration of  $\text{Ca}^{2+}$  was the highest in these airmasses in comparison to all the air clusters providing the highest buffering of the acidity as reflected from the highest pH. Very high concentration of  $\text{Ca}^{2+}$  might be due to atmospheric dust rich in calcium carbonate (Khemani, 1989; Kulshrestha, 2013). Significant amounts of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  might be due to adsorption of their precursor gases ( $\text{SO}_2$  &  $\text{NO}_2$ ) onto the dust components (Kulshrestha et al., 2003).

**Pakistan origin (Pk)** - Air masses originated from Pakistan reaching to the sampling site has been referred as Pk (Fig. 6.6f). This cluster represented the lowest number of events (6 %). The pH of snowfall samples was alkaline (7.01). Similar range of pH values has been reported in precipitation samples at various sites in Pakistan (Khattak et al., 2012; Shahid et al., 2013). The moderate pH value of this cluster can also be explained by moderate  $\text{nss SO}_4^{2-} / \text{nssCa}^{2+}$  and  $\text{NO}_3^- / \text{nssCa}^{2+}$  ratios.

Among all ions,  $\text{Ca}^{2+}$  had the highest concentrations. Very similar observations showing the dominance of transported dust in precipitation and aerosol samples have been reported at various sites in Pakistan (Begum et al., 2011; Khattak et al., 2012; Shahid et al., 2013). Very high concentrations of  $\text{SO}_4^{2-}$  among all anions suggested a significant influence of anthropogenic sources. Tremendous growth of industries and diesel driven vehicles might be responsible for elevated concentrations of  $\text{SO}_2$  which further affects  $\text{SO}_4^{2-}$  concentrations (Khattak et al., 2012). Similarly, high concentrations of  $\text{NO}_3^-$  might be due to  $\text{NO}_2$  emissions from vehicles in Pakistan. High

concentrations of  $\text{NH}_4^+$  in this cluster might be due to agricultural activities and biomass burning (Khattak et al., 2012). However, trajectory information has its limitations e. g. there is a possibility that materials originated from one site can be mixed with other. There is always a possibility that source regions identified based upon the air mass trajectories may contribute overlapping signatures as some of air masses are similar and pass over the same region. Hence, the firm inferences about the composition for different cluster should be taken with caution.

### **6.3. LCLUC and its influence on snow chemistry**

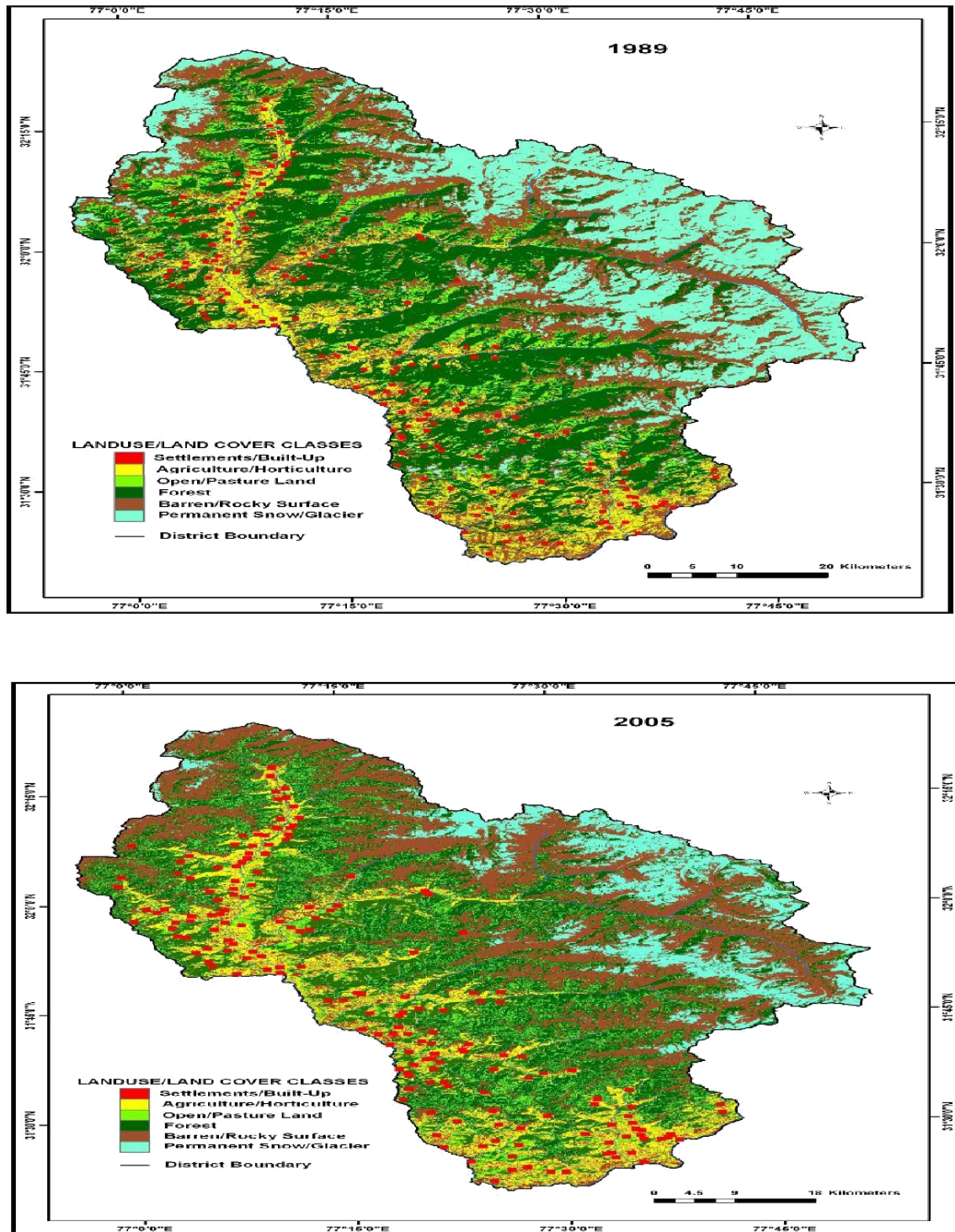
The spatiotemporal analysis of LCLUC provides important information about the process of development and environmental condition (Vadrevu et al 2013). LCLUC helps to understand the relationship among various components of the environment and climate change. LCLUC has significant impact on ecosystem services as it involves conversion of land from natural and agricultural areas to residential and urban uses (Vadrevu et al 2012, 2013). LCLUC is considered as a perturbing factor for regional climate change, biogeochemical cycle and water resources etc. in south Asia due to its growing population and economy (Madesn 2013). The changes due to LCLUC may alter biogenic emissions affecting gas to particle conversions having indirect influence on monsoon and hydrological cycles (Vishwa et al., 2013). It may alter emission patterns and amount of aerosols thus changing cloud formation and precipitation processes. Thus these changes may alter precipitation chemistry by affecting the exchange and removal of gaseous and aerosol pollutants. The change in meteorology due to LCLUC might be another reason affecting precipitation amount and its chemistry (Marini-Bettolo et al 1986). Keeping these advantages of LCLUC in mind, we have picked Kothi site out of three sites i.e. Kothi, Gulmarg and Mukteshwar for LCLUC study.

The change in land use land cover can be studied by satellite imageries. Among satellite images, the LANDSAT provide global record of the Earth's surface. LANDSAT imageries are very useful for first level of classification of rural as well as urban land cover. LCLUC was attempted at Kullu valley which is district of Kothi site in himalyan

region of India. LCLUC for 1989 and 2005 were taken from research findings of Vishwa et al (2013). During past two decades, the valley has gone through a major land cover and land use change. Report of Vishwa et al (2013) clearly indicated a decrease in snow cover and forest area, increase in rocky/barren surface and built up category in 2005 as compared to 1989 (Fig. 6.9). Fig. 6.10 shows that in Kullu district where the site is located, snow cover has decreased by 3.24% while rocky/barren surface has increased by 1.75%. The area under open land/pastures shows a considerable reduction (22.40%) indicating that large part of this area was converted to different settlement categories. The highest (52.38%) increase was seen for built up category to meet the demand of housing, infrastructures including transport and other amenities. Such high increase in built up area indicate a huge construction around the site and increasing road expansion which can be a significant source of aerosols.

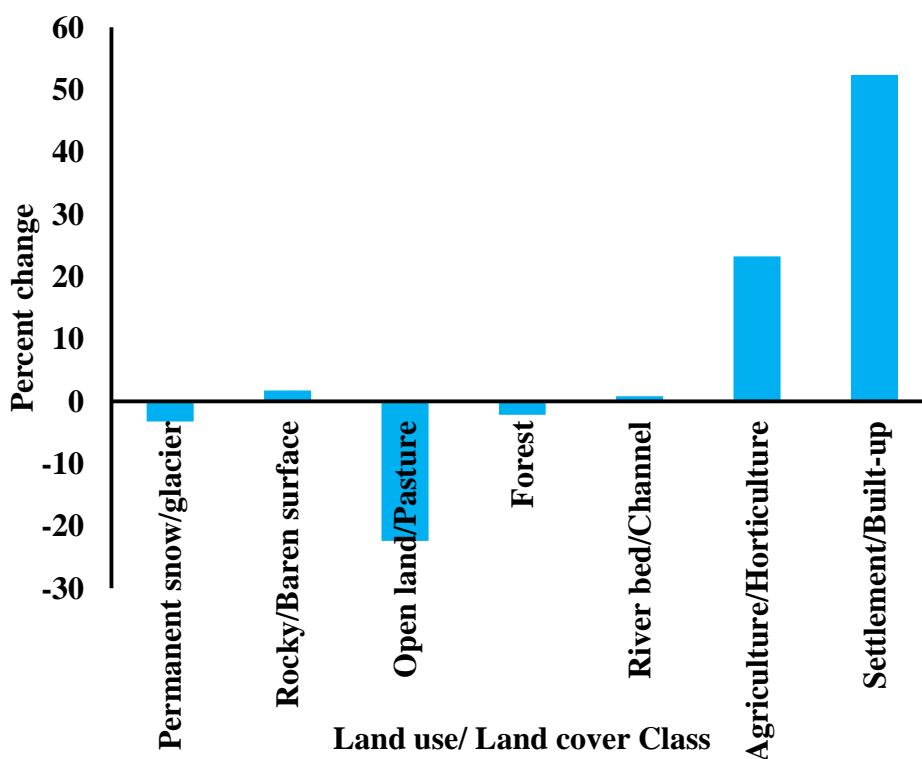
LCLUC has been reported a source of atmospheric dust which contributes to high levels of particulate matter (Kumar et al 2014). Elevated levels of Total Suspended Particulates (TSP) and aerosols have been attributed to soil dust in north India (Sharma and Kulshrestha 2014). The increase in local soil dust might be due to land cover land use change for urban expansion as experienced by this valley during last few decades. According to a study reported by Gajananda et al (2005), TSP at Mohal site in Kullu districts has increased significantly from 1996-2003. Kuniyal et al (2013) have reported high levels of PM<sub>10</sub> (314.7  $\mu\text{g m}^{-3}$ ) at Kothi violating the National Ambient Air Quality Standards (2013). Hence, LLUC can contribute crustal components such as Ca and Mg etc. Deforestation, land clearance, agriculture and urban expansion and crop residue burning contribute huge gases and aerosols in the atmosphere. LRT of oxides of S and N on reaction with the local crustal components gives rise to ions such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in precipitation (Kulshrestha 2013). This results in a combined signature of LCLUC ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and anthropogenic source influence (contributing  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) as recorded in our samples. These observations are further supported by the study of Singh and coworkers (2014b).





**Fig. 6.9:** LCLUC at Kullu district (Kothi site) in year of 1989 and 2005 (Vishwa et al 2013).

Singh and co-workers (2014b) have reported that due to decrease in green cover, increase in built urban, and construction activities for urban expansion of Delhi city.  $\text{Ca}^{2+}$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were noticed 8, 12 and 2 times high in 2010-11 as compared to 1994 value, clearly reflecting the mixed signatures of anthropogenic emission and LCLUC during past two decades.



**Fig. 6.10:** Percent LCLUC at Kullu district in Himachal Pradesh (Source: Vishwa et al 2013).

#### 6.4. Statistical approach for source identification

Statistical analysis is used to identify the relationship between major ions in snowmelt samples and their possible sources. For this purpose, correlation and principal component analysis (PCA) were applied using SPSS 16 software at Kothi and Gulmarg

site in Himalayan region of India. Due to lesser number of samples, these analyses were not applied at Mukteshwar site.

#### 6.4.1. Kothi site

##### 6.4.1.1. Correlation analysis

The correlation analysis between ions in precipitation samples is a useful statistical analysis to derive the relation among ions as well as the most probable sources of air pollutants. The correlation among major ions in snowfall samples at Kothi site is calculated using SPSS software and presented in table 6.5.

A strong correlations between  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  ( $r = 0.711$ ) in snowmelt samples are observed suggesting similar origin of these ions. It is well known that the combustion of fossil fuel generates  $\text{SO}_2$  and  $\text{NO}_x$  which oxidises to  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  respectively (Kulshrestha et al., 2005). Soil derived chemical components such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  showed significant correlation indicating their crustal origin.

**Table 6.5:** Correlation coefficients of major ions in snowmelt samples at Kothi.

	pH	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>
pH	1										
F <sup>-</sup>	.178	1									
Cl <sup>-</sup>	<b>.569**</b>	-.304*	1								
NO <sub>3</sub> <sup>-</sup>	-.141	<b>.863**</b>	-.303*	1							
SO <sub>4</sub> <sup>2-</sup>	.063	<b>.575**</b>	.296*	<b>.711**</b>	1						
Na <sup>+</sup>	.577**	-.348*	<b>.962**</b>	-.364*	.232	1					
NH <sub>4</sub> <sup>+</sup>	-.132	<b>.854**</b>	-.259	<b>.943**</b>	<b>.728**</b>	-.323*	1				
K <sup>+</sup>	.102	<b>.836**</b>	-.108	<b>.892**</b>	<b>.711**</b>	-.173	<b>.941**</b>	1			
Ca <sup>2+</sup>	<b>.672**</b>	<b>.676**</b>	.178	<b>.506**</b>	<b>.471**</b>	.152	<b>.425**</b>	<b>.608**</b>	1		
Mg <sup>2+</sup>	<b>.477**</b>	-.021	<b>.778**</b>	.034	<b>.493**</b>	<b>.718**</b>	-.021	.128	<b>.397**</b>	1	
HCO <sub>3</sub> <sup>-</sup>	<b>.813**</b>	<b>.405**</b>	<b>.387**</b>	.222	.298*	<b>.406**</b>	.137	<b>.368**</b>	<b>.881**</b>	<b>.495**</b>	1

\*\* . Correlation is significant at the 0.01 level (2-tailed).

\* . Correlation is significant at the 0.05 level (2-tailed).

Good correlations are observed between ions such as  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  ( $r = 0.506$ ),  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ( $r = 0.471$ ),  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ( $r = 0.493$ ). These strong correlations between these ions might be due to chemical reaction between crustal components rich in Ca and

Mg bicarbonates with the acids such as  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  generated in precipitation samples. These reactions enhance alkalinity of precipitation and decrease acidity of snow samples. These are further confirmed by strong correlation between pH and crustal components such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .

Interestingly,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  showed good correlation with  $\text{NH}_4^+$  derived from anthropogenic activities as well as crustal components such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . The strong correlations between these ions suggested the chemical reaction between these components. The formation of  $\text{NH}_4\text{HSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  in precipitation samples have been reported due to the reaction of ammonia in the atmosphere with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  (Kulshrestha et al., 2005, Seinfeld and Pandis, 2006). The strong correlations between  $\text{Na}^+$  and  $\text{Cl}^-$  ( $r = 0.962$ ),  $\text{Na}^+$  and  $\text{Mg}^{2+}$  ( $r = 0.718$ ) and  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  ( $r = 0.778$ ) suggesting their origin of marine components.

#### 6.4.1.2. Principal component analysis

In order to explain the relationship between chemical components and their source, principal component analysis has been applied to the dataset using SPSS 16.0 software. Since, it was not possible to apply PCA on each trajectory class due to statistically insufficient number of samples; we have attempted the analysis using whole dataset in order to find out relative contribution of sources to the total deposition. Varimax rotation at Eigen value 1 extracted three Principal Components (PC). These PCs accounted for 86% of the total variance (Table 6.6). The first PC had high loadings of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$  and  $\text{F}^-$  explained 39.1% of the total variance. Ions of PC1 are typically of anthropogenic characteristics e.g. fossil fuel combustion, vehicular pollution, biomass burning etc. (Kulshrestha et al., 1995, Kothai et al., 2008, Kuniyal et al., 2013). PC1 represents characteristics of the mixed acidic and alkaline pollutants.

**Table 6.6:** Principal component analysis of major ions in snowmelt samples at Kothi.

	PC1	PC 2	PC 3
Na <sup>+</sup>	-.182	<b>.929</b>	.133
NH <sub>4</sub> <sup>+</sup>	<b>.966</b>	-.199	.070
K <sup>+</sup>	<b>.906</b>	-.096	.299
Ca <sup>2+</sup>	.414	.132	<b>.880</b>
Mg <sup>2+</sup>	.166	<b>.841</b>	.246
F <sup>-</sup>	<b>.805</b>	-.259	.426
Cl <sup>-</sup>	-.107	<b>.956</b>	.108
NO <sub>3</sub> <sup>-</sup>	<b>.935</b>	-.208	.177
SO <sub>4</sub> <sup>2-</sup>	<b>.862</b>	.424	.040
HCO <sub>3</sub> <sup>-</sup>	.134	.320	<b>.920</b>
pH	-.118	.486	.005
Variance %	39.05	28.91	18.35
Cumulative %	39.05	67.96	86.31
Possible source	<b>Anthropogenic</b>	<b>Marine</b>	<b>Crustal</b>

The same components having the loadings of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> together, suggested their similar sources like fossil fuel combustion (industries and vehicular emissions), fertilizer applications etc. However, significant contribution of these components from soil in this region can not be ruled out (Kulshrestha et al., 1996). Ions such as SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> of PC1 can be considered as secondary pollutants since they are assumed to be produced from gas to particle conversion of SO<sub>x</sub>, NO<sub>x</sub> and NH<sub>3</sub>. The association of NH<sub>4</sub><sup>+</sup> with SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> in this PC might be due to neutralization of acidity generated by their precursor gases SO<sub>x</sub> and NO<sub>x</sub>. It seems that most of the airmasses arising from far distances carried H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> which interacted with NH<sub>3</sub> and crustal aerosols as soon as these airmasses arrived in Indian region.

As given in Table 6.3, NH<sub>4</sub><sup>+</sup>/SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>/NO<sub>3</sub><sup>-</sup> ratio values are significantly higher during InW, Af and Np airmasses as compared to the airmasses of far distances. Source of NH<sub>3</sub> in Indian region could be fertilizer applications, human excreta, biomass burning etc (Galloway et al., 2008; Singh and Kulshrestha, 2014). Reaction of NH<sub>3</sub> with these acidic components might have resulted in the formation of NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>

and  $\text{NH}_4\text{HSO}_4$ . Similar to our results, these combinations of  $\text{NH}_4^+$  have been reported by Naik and co-workers (1995) in the snow samples at Gulmarg, India. The presence of  $\text{NO}_3^-$  with  $\text{K}^+$  and  $\text{F}^-$  suggested biogenic sources and biomass burning which are very common during winters for domestic cooking and heating purposes in rural India (Singh et al., 2014). However, it is very difficult to quantify the fraction of biomass burning and agricultural activities. The strong influence of anthropogenic activities in the region has also been demonstrated by analysis of  $\text{PM}_{10}$  aerosols (Kuniyal et al., 2013).

The second PC explains 28.9% of the total variance having high loadings of  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{Cl}^-$  exhibiting typical characteristics of marine sources (Keene et al., 1986). The strong influence of sea salt components might be due to LRT by marine winds which have been discussed in next section. Apart from LRT, relatively small contribution from saline soil cannot be ruled out in this region (Kulshrestha et al., 1996). The influence of sea salt sources has been reported in rain water at this site (Tiwari et al., 2012).

The third PC has high loadings of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  explaining 18.4% of the total variance. This PC can be attributed to crustal sources. In India, atmospheric dust is reach in Calcium carbonate which is mainly responsible for alkaline precipitation (Kulshrestha, 2013). Apart from local sources, significant contribution by LRT from African region through LRT is also possible as detailed in the section 3.4.

### 6.4.2. Gulmarg site

#### 6.4.2.1. Correlation analysis

The correlation among ionic components in snowfall samples at Gulmarg site is calculated using SPSS software (Table 6.7). The strong correlations between major major sea salt components such as  $\text{Na}^+$  and  $\text{Cl}^-$  ( $r = 0.907$ ),  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  ( $r = 0.685$ ) and  $\text{Na}^+$  and  $\text{Mg}^{2+}$  ( $r = 0.769$ ) reflecting their origin from marine sources.

A good correlations are observed between  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  ( $r = 0.818$ ) in snowmelt samples suggesting similar sources of these ions. Globally, it is verified that  $\text{SO}_4^{2-}$  and

$\text{NO}_3^-$  in precipitation samples originate due to oxidation of their precursor gases  $\text{SO}_2$  and  $\text{NO}_x$  respectively from the combustion of fossil fuel (Jain et al., 2000; Rodhe et al., 2002; Kulshrestha et al., 2005; Zhang et al., 2007a; Kumar et al., 2016). A strong correlation between soil derived species such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  as well as  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  suggested their crustal origin. It is well know that the soil dust in indian atmosphere is rich in calcium and magnesium bicarbonates.

**Table 6.7:** Correlation coefficients of major ions in snowmelt samples at Gulmarg.

	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	pH
F <sup>-</sup>	1										
Cl <sup>-</sup>	.070	1									
NO <sub>3</sub> <sup>-</sup>	<b>.809**</b>	.080	1								
SO <sub>4</sub> <sup>2-</sup>	<b>.633**</b>	<b>.475**</b>	<b>.818**</b>	1							
Na <sup>+</sup>	-.115	<b>.907**</b>	-.023	.422 <sup>*</sup>	1						
NH <sub>4</sub> <sup>+</sup>	<b>.811**</b>	-.176	<b>.943**</b>	<b>.696**</b>	-.285	1					
K <sup>+</sup>	<b>.943**</b>	.161	<b>.908**</b>	<b>.778**</b>	-.028	<b>.881**</b>	1				
Ca <sup>2+</sup>	<b>.759**</b>	<b>.432**</b>	<b>.455**</b>	<b>.563**</b>	.289	.358 <sup>*</sup>	<b>.697**</b>	1			
Mg <sup>2+</sup>	.149	<b>.685**</b>	.244	<b>.568**</b>	<b>.769**</b>	.034	.241	.405 <sup>*</sup>	1		
HCO <sub>3</sub> <sup>-</sup>	<b>.599**</b>	<b>.465**</b>	.357 <sup>*</sup>	<b>.448**</b>	.362 <sup>*</sup>	.231	<b>.544**</b>	<b>.880**</b>	.346 <sup>*</sup>	1	
pH	<b>.466**</b>	<b>.569**</b>	.046	.252	.405 <sup>*</sup>	-.053	.366 <sup>*</sup>	<b>.819**</b>	.303	<b>.738**</b>	1

\*\* . Correlation is significant at the 0.01 level (2-tailed).

\* . Correlation is significant at the 0.05 level (2-tailed).

Similar to other reports in indian precipitation (Kulshrestha et al., 2003; Satyanarayana et al., 2010; Kumar et al., 2016), good correlations are observed between ions such as  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ( $r = 0.563$ ),  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  ( $r = 0.455$ ) as well as  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ( $r = 0.568$ ) at Gulmarg in Himalayan region of India. These correlations might be due to chemical reaction in atmosphere between soil dust rich in Ca and Mg bicarbonates with the acids such as  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . Due to these reactions, alkaline precipitation is observed at most of the sites in India (Jain et al., 2000; Kulshrestha et al., 2005; Kumar et al., 2016). Alakaline precipitation is further corroborated by strong correlation between pH and alkaline soil derived components ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ).

Surprisingly, sulphate and nitrate in snowmelt samples at Gulmarg showed good correlation with crustal components such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  as well as  $\text{NH}_4^+$  derived from anthropogenic activities such as agricultural practices, biomass burning etc. A good correlations between these ions suggesting the chemical reaction between sulphuric and nitric acid with sources rich in  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$ . The formation of compounds such as  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$  and  $\text{NH}_4\text{NO}_3$  in precipitation samples have been reported due to the reaction of  $\text{NH}_3$  with sulphuric and nitric acid (Kulshrestha et al., 2005, Seinfeld and Pandis, 2006).

#### 6.4.2.2. Principal component analysis

PCA is used to establish the relationship between ionic components of snowmelt samples and their sources at Gulmarg site. The ionic data were subjected to varimax rotation with eigen value greater than 1 in principal component analysis. Three PCs were extracted with 93% of the total variance (Table 6.8). The first factor (PC1) explained 52% of the total variance with high loadings of  $\text{F}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$  and  $\text{K}^+$ . PC1 implies the mixed characteristics of acidic and alkaline pollutants with dominance of anthropogenic sources such as fossil fuel combustion, industrial activities, biomass burning, vehicular pollution etc. A very similar finding with highly loaded PC of anthropogenic characteristics has been reported in precipitation samples at Himalayan region of India (Tiwari et al., 2012; Kumar et al., 2016). The association of  $\text{NH}_4^+$  with  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in PC1 might be due to interaction of  $\text{NH}_3$  with acids generated by precursor gases  $\text{SO}_2$  and  $\text{NO}_x$ . These neutralization reactions of  $\text{NH}_3$  and crustal components with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  might have resulted in alkaline snowmelt samples at these sites. The presence of  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{HSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  have been reported in precipitation samples globally (Kulshrestha et al., 2005; Tiwari et al., 2012; Kumar et al., 2016). The presence of  $\text{NO}_3^-$  with  $\text{K}^+$  and  $\text{F}^-$  suggested biogenic activities and biomass burning which is very common during winters for domestic cooking and heating purposes in rural region of India (Singh et al., 2014). The dominance of anthropogenic sources by analyzing aerosol samples has been demonstrated in himalayan region of India (Kuniyal et al., 2013).



**Table 6.8:** Principal component analysis of major ions in snowmelt samples at Gulmarg.

	<b>PC1</b>	<b>PC2</b>	<b>PC3</b>
<b>F</b>	<b>.807</b>	.540	-.106
<b>Cl</b>	-.039	.351	<b>.875</b>
<b>NO3</b>	<b>.978</b>	.066	.088
<b>SO4</b>	<b>.796</b>	.140	<b>.524</b>
<b>Na</b>	-.136	.177	<b>.954</b>
<b>NH4</b>	<b>.980</b>	.012	-.167
<b>K</b>	<b>.902</b>	.394	.034
<b>Ca</b>	.402	<b>.862</b>	.215
<b>Mg</b>	.193	.109	<b>.869</b>
<b>HCO3</b>	.262	<b>.844</b>	.241
<b>pH</b>	-.029	<b>.924</b>	.254
<b>Variance %</b>	51.65	27.67	13.14
<b>Cumulative</b>	51.65	79.31	92.46
<b>Possible sources</b>	<b>Anthropogenic</b>	<b>Crustal</b>	<b>marine</b>

PC2 with high loadings of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  explained 28% of the total variance. This PC indicates the presence of crustal sources in form of soil and road dust having local origin with significant contribution of long range transport. The presence of calcium carbonate in Indian atmosphere leading alkaline precipitation is very common (Jain et al., 2000; Kulshrestha et al., 2003b; 2005; Singh et al., 2015; Kumar et al., 2016).

The third PC which is highly loaded with  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  explaining 13% of the total variance suggested their origin from marine sources (Keene et al., 1986; Kulshrestha et al., 2005). The influence of sea salt components at this site might be due to LRT which has been discussed in this chapter only in section 6.2. Apart from LRT, some contribution from the soil in this region can't be ruled out (Kulshrestha et al., 1996).

## *Chapter 7*

# *Soil chemistry and its relationship to snowmelt*

---

## SOIL CHEMISTRY AND ITS RELATIONSHIP TO SNOWMELT

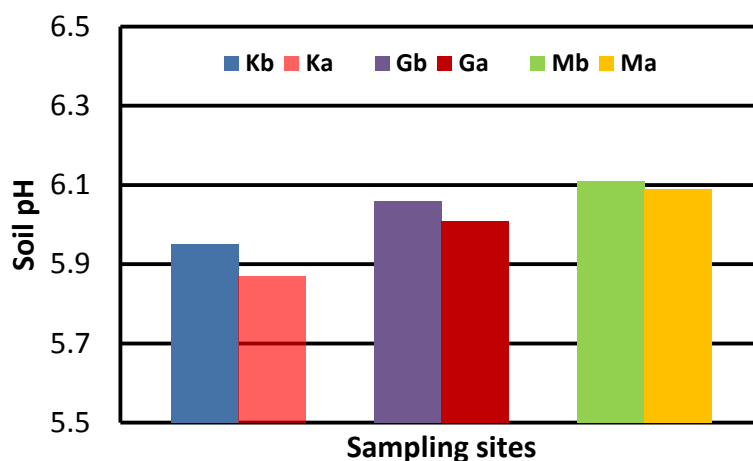
This chapter discusses the chemical composition of soil at three sampling sites i.e. Kothi, Gulmarg and Mukteshwar in himalayan region of India. It focuses upon change in soil nutrients after snowmelt during winter and post winter seasons. The change in soil composition after snowmelt has been reported in relation to pH of snowmelt as well as pH and cation exchange capacity of the soil. The chapter also discusses in brief, about the relative contribution of wet deposition of aerosols, dustfall and snowmelt.

### 7.1. Soil characteristics

#### 7.1.1. Spatial distribution of soil pH

It is well known that slightly acidic soil is very appropriate for the balanced nutrient supply to the plants (Leskiw, 1998). A range of pH 5.5 - 7.0 makes the essential soil nutrients available in a fertile soil. The forest plants grow suitably in the pH range of 4 – 7 while most of the crops like wheat, rice, maize, rice etc. grow better in a range of pH 5.5 – 7 (Foth, 1984). The average values of pH in the study area varied from 5.89 - 6.11 (Fig. 7.1). Thus, the observed pH values at the present sites in Himalayan region of India were found to be suitable for the maximum nutrient availability, growth of most of the forest plants and crops and, and microbial activity in soil.

The average pH values of soil at the present sites followed the order- Kothi < Gulmarg < Mukteshwar (fig. 7.1). Among all sites, the highest value at Mukteshwar might be due to the presence of base cations in higher concentration which is discussed later in this section. The soils of all present sites were recorded to be in range of slightly acidic to acidic. The acidic values of soil at the study sites might be due to the presence of decomposition of vegetation on the soil surface resulting in lowering of the pH values (Ashraf et al., 2012). The values of the pH in the present study are found to be in similar range to most other studies in the Himalaya (Rao et al., 1997; Raina and Gupta, 2009; Ashraf et al., 2012; Gairola et al., 2012) but lower than the values of pH reported for Kumaun Himalaya by some workers (Khera et al., 2001; Belwal and Mehta, 2014). The soils of all the present sites were recorded as slightly acidic which might be due to the presence of decomposed material of vegetation and plants on the soil surface resulting in lowering of the pH values (Ashraf et al., 2012).



**Fig. 7.1:** Average pH of soils before and after snowmelt (Kb- Kothi sample before snowmelt, Ka- Kothi sample after snowmelt, Gb- Gulmarg sample before snowmelt, Ga- Gulmarg sample after snowmelt, Mb- Mukteshwar sample before snowmelt, Ma- Mukteshwar sample after snowmelt) (n=4).

The decomposition of debris of plants and vegetation leads to the higher level of organic content in the soil and contributing in the soil acidity (Hodges, 1996) which is not estimated in the present study. Higher levels of organic matter are responsible for a larger number of cation exchange sites resulting in acidic soil (Naiman *et al.*, 1994). Like our study, the low pH values have been reported by others workers also worldwide due to higher content of organic matter level and the undisturbed nature of the soils in the study region (Robertson and Vitousek, 1981; Adams and Sidle, 1987). The lower pH values at the undisturbed sites might be due to accumulation and decomposition of organic matter of vegetation and forest debris, which releases acids (de Hann, 1977).

### 7.1.2. Electrical conductivity of the soil

The average value of electrical conductivity at three sites of our study area followed the order- Mukteshwar > Gulmarg > Kothi. A very similar range of electrical conductivity has been reported in soils of Himalayan region of India (Ashraf *et al.*, 2012; Belwal and Mehta, 2014). It is well known that higher electrical conductivity of soil solution means higher the concentration of ions in soil solution. The highest value of electrical conductivity of at Mukteshwar in comparison to Gulmarg and Kothi might be due to the presence of higher

levels of ions such as sodium, calcium, potassium and magnesium etc which has been discussed later in this chapter.

### **7.1.3. Variability of soil CEC**

The cation exchange capacity measures the magnitude of anionic sites on a soil that can retain cations like potassium, magnesium and calcium etc. by coulombic forces of attraction (Ross and Ketterings, 2011). The positively charged ions of CEC of a soil are easily exchangeable with cations of the soil solution. It means that a soil with lower CEC values has lesser capacity to maintain soil cations such as  $K^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$  than a soil with higher CEC values (Ross and Ketterings, 2011). In soils, cationic exchange sites are found mainly on the surfaces of organic matter (OM) and clay minerals. Higher content of clay i.e. higher CEC of soils have greater water holding capacity in comparison to low CEC soils (Ketterings et al., 2007).

CEC of soil was calculated by  $BaCl_2$  compulsive exchange method (Gillman and Sumpter, 1986). The average value of CEC (cmol/kg) of soil followed the order- Mukteshwar > Gulmarg > Kothi (table 7.1). The CEC value in the present study sites differed considerably from soil at other sites in north western and central Himalaya region of India (table 7.1). The differences in CEC among study sites might be due to variation in the level of organic carbon and clay content (Ross and Ketterings, 2011). The highest CEC values of Mukteshwar soils as compared to Gulmarg and Kothi might be due to higher content of organic carbon (Rao et al., 1997) which is not estimated in the present study.

**Table 7.1:** CEC (cmol/kg) of soil at different sites of different categories in India.

Nature of sites	Region	State	CEC (cmol/kg)	References
<b>Barren land</b>	Kemty, Garhwal Himalayas	Uttarakhand	28.97	Raina and Gupta, 2009
<b>Dalbergia sissoo forest</b>	Kemty, Garhwal Himalayas	Uttarakhand	29.92	Raina and Gupta, 2009
<b>Agriculture</b>	Bazeena, Kumaun Himalaya	Uttarakhand	12.5	Belwal and Mehta, 2014
<b>Pine Forest</b>	Bhetagad watershed, Kumaun Himalaya	Uttarakhand	8.68	Kothyari et al., 2004
<b>Rainfed agriculture</b>	Bhetagad watershed, Kumaun Himalaya	Uttarakhand	11.79	Kothyari et al., 2004
<b>Forest cover</b>	Shiwalik hills	Himachal Pradesh	5.67	Rao et al., 1997
<b>Cultivated land</b>	Shiwalik hills	Himachal Pradesh	10.99	Rao et al., 1997
<b>Undisturbed soil</b>	Kothi, North western Himalaya	Himachal Pradesh	9.44	Present study
<b>Undisturbed soil</b>	Gulmarg, North western Himalaya	Jammu and Kashmir	12.38	Present study
<b>Undisturbed soil</b>	Mukteshwar, Central Himalaya	Uttarakhand	14.27	Present study

#### 7.1.4. Major chemical components of the soil

The major ions of soils of the study sites have been reported in Table 7.2. The soil nutrients of Kothi followed the order-  $\text{Ca}^{2+} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{K}^+ > \text{Cl}^- > \text{Na}^+ > \text{Mg}^{2+} > \text{NO}_3^- > \text{NH}_4^+$ . The average concentration of Gulmarg soil followed the order-  $\text{Ca}^{2+} > \text{HCO}_3^- > \text{K}^+ > \text{SO}_4^{2-} > \text{Cl}^- > \text{Na}^+ > \text{Mg}^{2+} > \text{NO}_3^- > \text{NH}_4^+$  and Mukteshwar soil followed the same order as Gulmarg soil. On an average, cations dominated over anion at these sites which is very similar to a

feature noticed at other fertile soils in Indian region (Kulshrestha, 1993; Ashraf et al., 2012). The detailed description of major ions of soils has been given below in this section.

**Table 7.2:** Major ions of soil (g/ton) before and after snowmelt (Kb- Kothi sample before snowmelt, Ka- Kothi sample after snowmelt, Gb- Gulmarg sample before snowmelt, Ga- Gulmarg sample after snowmelt, Mb- Mukteshwar sample before snowmelt, Ma- Mukteshwar sample after snowmelt) (n=4).

	Kb	Ka	Gb	Ga	Mb	Ma
Cl <sup>-</sup>	29.8 ± 5.4	29.0 ± 6.5	34.4 ± 4.5	33.9 ± 8.0	31.4 ± 5.7	31.1 ± 7.9
NO <sub>3</sub> <sup>-</sup>	11.3 ± 3.5	10.7 ± 4.1	15.5 ± 3.9	14.9 ± 2.7	18.8 ± 2.3	18.5 ± 5.0
SO <sub>4</sub> <sup>2-</sup>	32.0 ± 6.2	29.5 ± 5.4	35.5 ± 4.2	33.6 ± 4.1	42.7 ± 4.1	42.0 ± 12.3
Na <sup>+</sup>	26.3 ± 3.8	24.6 ± 5.8	22.5 ± 4.1	20.6 ± 3.7	28.7 ± 6.4	27.4 ± 3.0
NH <sub>4</sub> <sup>+</sup>	3.1 ± 1.5	2.8 ± 0.6	2.1 ± 1.0	1.9 ± 0.5	2.7 ± 0.7	2.6 ± 0.9
K <sup>+</sup>	31.7 ± 4.5	28.7 ± 7.8	45.5 ± 6.6	42.9 ± 7.8	53.4 ± 6.2	52.1 ± 3.9
Ca <sup>2+</sup>	70.3 ± 5.4	65.6 ± 7.8	84.2 ± 9.2	79.2 ± 11.1	107.1 ± 17.5	105.2 ± 14.1
Mg <sup>2+</sup>	13.4 ± 3.6	10.9 ± 4.4	17.5 ± 5.5	14.9 ± 4.1	24.8 ± 6.7	23.3 ± 8.0
HCO <sub>3</sub> <sup>-</sup>	40.7 ± 5.8	36.5 ± 6.3	58.9 ± 9.4	57.3 ± 2.5	68.8 ± 5.8	68.8 ± 4.5

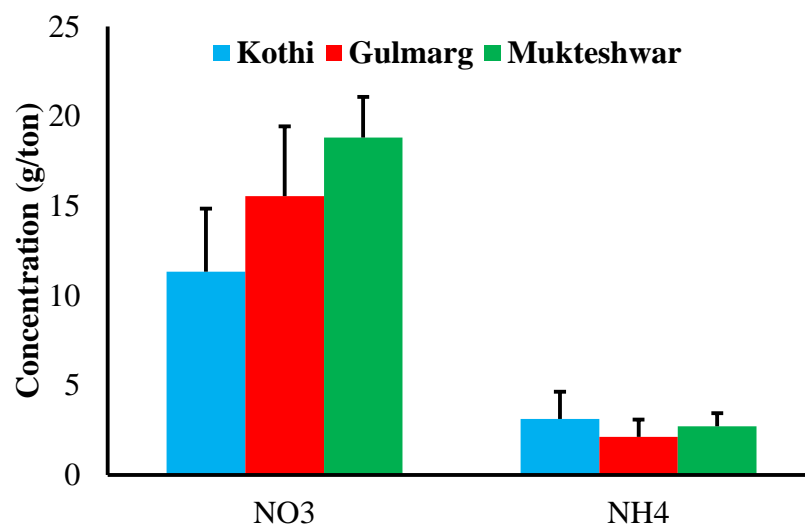
#### 7.1.4.1. Soil nitrogen

Nitrogen (NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) is an essential plant nutrient which is required for plant growth. If nitrogen is not available in adequate level in soil then the growth of various parts of plant remains undeveloped and stunted. Nitrogen in soil is one of the most limiting nutrients in tropical as well as temperate ecosystems (Fenn et al. 1998). Mitchell and Chandler (1939) have investigated that forest systems are limited by the amount of nitrogen available in the soil solution.

N in soil is available in the form of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> along with other forms of inorganic and organic nitrogen. NO<sub>3</sub><sup>-</sup> is the most dominating form of nitrogen which is taken up by plants from the soil. It is very mobile and easily transported with moisture in soil (Lowenfels and

Lewis, 2011). Therefore, it is easily taken up by plants for their growth. In contrast,  $\text{NH}_4^+$  is the most dominating form of inorganic nitrogen taken up by plants in acidic soil since the probability of acidification in that soil is very less (Brady and Weil, 2016). Proteins and amino acids are synthesised from  $\text{NH}_4^+$  therefore  $\text{NO}_3^-$  should be reduced to  $\text{NH}_4^+$ .

The values of total N as  $\text{NO}_3^-$  and  $\text{NH}_4^+$  varied significantly among study sites. The average N-  $\text{NO}_3^-$  value followed the order- Mukteshwar > Gulmarg > Kothi while the average N-  $\text{NH}_4^+$  value followed the order- Kothi > Mukteshwar > Gulmarg (Fig. 7.2). N as  $\text{NO}_3^-$  dominates over  $\text{NH}_4^+$  at the present sites.



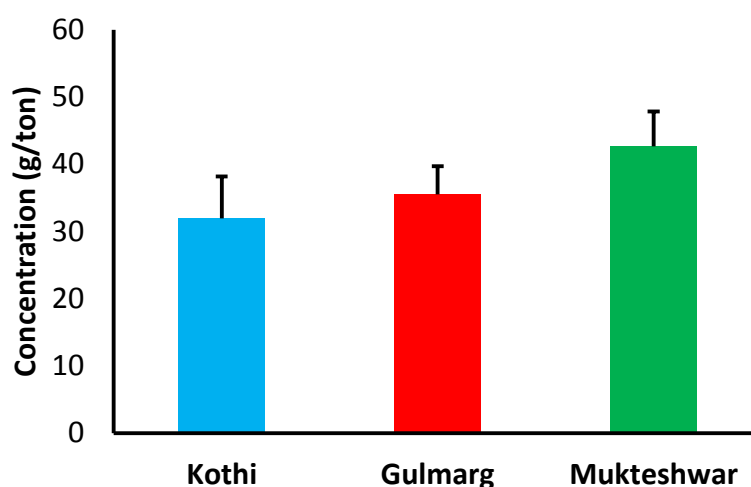
**Fig. 7.2:** Average concentration of soil  $\text{NO}_3^-$  and  $\text{NH}_4^+$  before snowmelt (n=4).

The variation in concentration of N level at these sites might be due to differences in the content of organic matter which comes from debris of vegetation, forests and animals (Aber and Melillo, 1991). The abundance and properties of organic matter decides the availability of nitrogen in the soil (de Hann, 1977). The abundance of organic matter is mainly responsible for the richness of N in top soil layer as compared to sub soil. On the basis of the concentration of  $\text{NO}_3^-$ , Cochrane and co-workers (1984) classified the soil system as follows- high > 20 g/ton, medium 10- 20 g/ton and low < 10 g/ton. The average  $\text{NO}_3^-$  concentration of all the soils at these sites were medium in  $\text{NO}_3^-$  level and do not need additional significant amount of nitrogen fertilizer.



#### 7.1.4.2. Soil sulphur

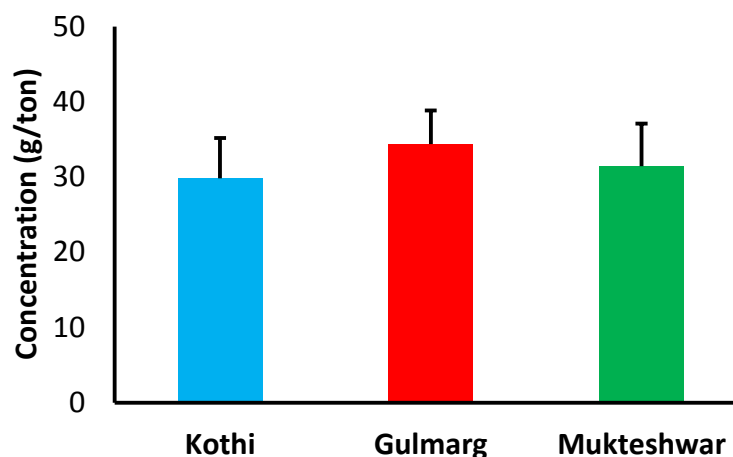
Sulphur is one of the most essential components of certain amino acids and thus help in the synthesis of essential plant proteins (Silva and Uchida, 2000). It is also involved in metabolism of vitamin B complex. Sulphur is very important in chlorophyll formation, seed production, stabilizing structure of proteins and nodule formation of legumes (McCauley et al., 2011). The  $\text{SO}_4^{2-}$  content was found the highest at Mukteshwar followed by Gulmarg and Kothi (fig. 7.3). The variation in S content of soil can also be explained might be due to variation in organic matter content as it was explained above for variation in nitrogen.



**Fig. 7.3:** Average concentration of soil  $\text{SO}_4^{2-}$  before snowmelt (n=4).

#### 7.1.4.3. Soil chloride

Chloride is an essential plant nutrient required for photosynthesis and leaf turgor. It is essential for the evolution of oxygen during photosynthesis (Silva and Uchida, 2000). Chloride increases the water level of plant tissues and osmotic pressure of the cell in plants (McCauley et al., 2011). The chloride content in the soil at the present sites varied considerably. The average content of chloride followed the order- Gulmarg > Mukteshwar > Kothi (fig. 7.4). An adequate amount of chloride in these soil might be due to input from various sources such as sea spray, dust, rainwater, air pollution along with fertilization and irrigation (White and Broadley, 2001).



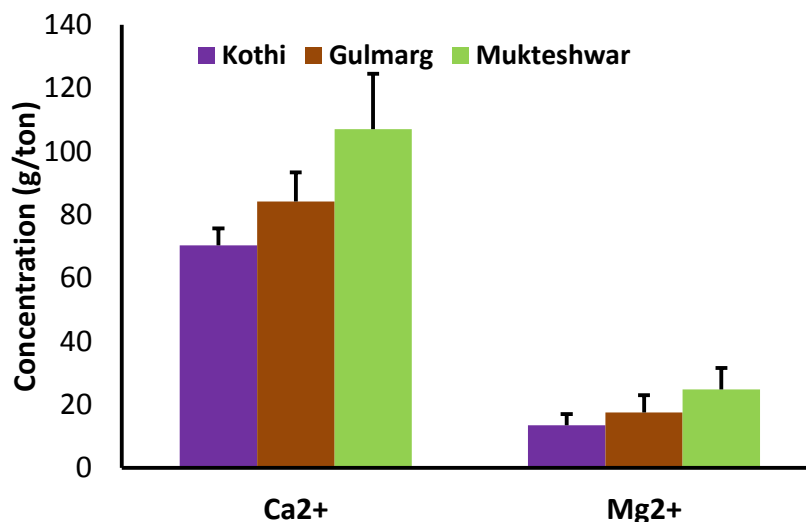
**Fig. 7.4:** Average concentration of soil Cl<sup>-</sup> before snowmelt (n=4).

#### 7.1.4.4. Divalent cations of the soil

Ca<sup>2+</sup> is the most essential plant nutrients which affects cell division by maintaining membrane permeability and cell integrity (Silva and Uchida, 2000). It plays a major agent in the synthesis of the cell wall and its plasticity (Silva and Uchida, 2000). It acts as an activator of various enzyme systems involved in the synthesis of protein and carbohydrate transfer. Calcium acts as an agent of detoxification in plants by neutralizing various organic acids (McCauley et al., 2011). It combines with several anions like nitrate, sulphate and phosphate etc. in soil and thus improving crop yield by increasing pH in acidic soil. It is an essential nutrient for production of seed in peanuts.

The concentration of calcium was the highest among all cations at the present sites (Table 7.2). The highest percentage of Ca<sup>2+</sup> than other cations like Na<sup>+</sup>, K<sup>+</sup>, and Mg<sup>2+</sup> etc. might be due to strong binding of Ca<sup>2+</sup> at cation exchange sites than other cations (Beckett, 1965). The presently investigated results lie within the range as reported by other workers (Malik et al., 2000; Ashraf et al., 2012).

The average concentration of Ca<sup>2+</sup> followed the order- Mukteshwar > Gulmarg > Kothi (fig. 7.5). The soil samples collected from Mukteshwar had the maximum concentration of Ca<sup>2+</sup> might be due to higher pH value of soil at Mukteshwar as compared to Kothi and Gulmarg soils.



**Fig. 7.5:** Average concentration of soil Ca<sup>2+</sup> and Mg<sup>2+</sup> before snowmelt (n=4).

Roy and co-workers (1981) have investigated by the field experiment that soil pH is one of the most important factor which affects the abundance as well as availability of Ca<sup>2+</sup> in the soil. On the basis of calcium content (g/ton), the soils classified by Cochrane and workers (1984) as follows- High > 80 g/ton, medium 8 - 80 g/ton, low < 8 g/ton. On the basis of above classification the soil at present sites exhibited medium to high concentration of calcium these sites.

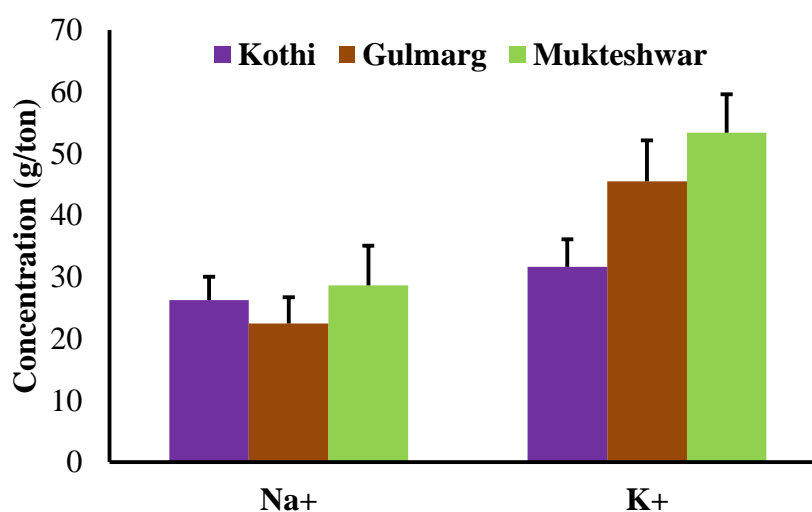
Magnesium is one of the essential components required for chlorophyll production and makes the central part of chlorophyll. It is a very important nutrient for the synthesis of ATP (Silva and Uchida, 2000). Magnesium showed lower concentrations at all sites during the study period. The magnesium was recorded with the minimum value at Kothi Site to the maximum value at Mukteshwar site. On the basis of Mg content (g/ton), the soils classified by Cochrane and workers (1984) as follows- High > 9.6 g/ton, medium 2.4-9.6 g/ton, low < 2.4 g/ton. The soil at present sites exhibited high concentration of magnesium so there is no need of extra Mg at these sites.

#### 7.1.4.5. Monovalent cations of the soil

The potassium is present in soluble forms in various parts of plants and responsible for the protein and carbohydrate synthesis. It activates different enzymes of the plants which are finally responsible for the metabolism of the plants, nitrate reduction, starch synthesis and also plays an important role in sugar degradation. The potassium also performs vital activities

like regulating respiration and transpiration and influencing actions of various enzymatic actions in the plant (Brady, 1996).

The average values of available potassium in the study area varied between 28.7 to 53.4 g/ton. The values of available K in the present study are similar to those observed by some other workers in other parts of the Himalaya, but in general differed considerably (Raina and Gupta, 2009; Gairola et al., 2012; Belwal and Mehta, 2014) might be due to difference in organic matter content.



**Fig. 7.6:** Average concentration of soil Na<sup>+</sup> and K<sup>+</sup> before snowmelt (n=4).

The differences in the concentration of K<sup>+</sup> of soil at these sites in Himalayan region of India might be due to variation in content of organic matter and clay. These variations also might be due to differences in the content of the parent rock. Malik and co-workers (2000) proved by the experiment that higher content of organic matter and clay are responsible for higher availability of potassium in nursery soil. It was corroborated by the investigation of Boruah and Nath (1992) and Basumatary and Bordoloi (1992) who showed that higher content of organic matter improves the abundance as well as retention of available potassium in the soil solution. On the basis of amount of K (g/ton), Rashid and Ahmad (1994) classified soil as follow as- high > 120 g/ton, medium 60-120 and low < 60. On the basis of this classification, soils at these sites were bit deficient in potassium and need potash fertilizer for better agriculture production in this region.

Sodium is an essential nutrient which is required for all higher plants (Silva and Uchida, 2000). In C4 plants, it helps in regeneration of phosphoenol pyruvate (PEP). Apart from potassium, it can help in regulation of stomatal closing and opening (McCauley et al., 2011). The highest value of sodium was recorded at Mukteshwar site followed by Gulmarg and Kothi site (Table 7.1). The differences in concentration of sodium at these sites might be due to difference in the level of clay and mineral contents of the soil (Brady and Weil, 2016).

## 7.2. Changes in soil nutrients level after snowmelt

### 7.2.1. Factors influencing soil nutrient levels

The loss of soil nutrients has been observed after snowmelt at all sites i.e. Kothi, Gulmarg and Mukteshwar in Himalayan region of India. The relative percent decrease of soil nutrient has been calculated by the following formula-

$$\text{Relative \% decrease} = (C_b - C_a) * 100 / C_b$$

Here,  $C_b$  = Concentration of soil nutrient before snowmelt

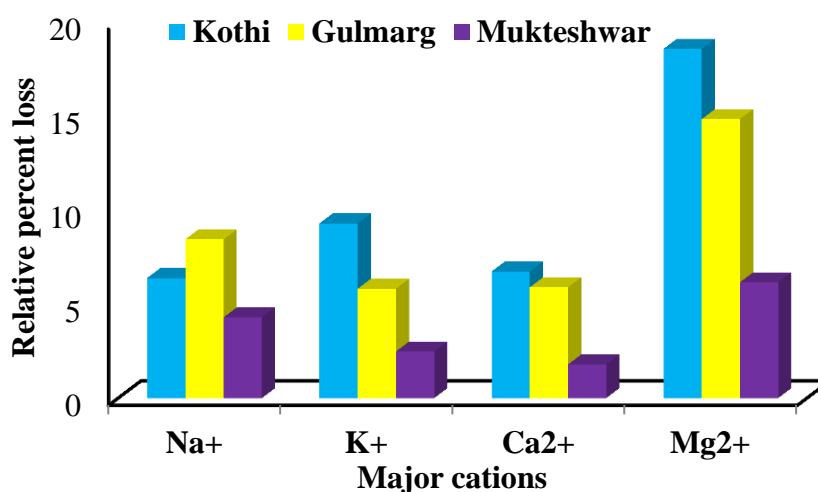
$C_a$  = Concentration of soil nutrient after snowmelt.

The result of calculation of the relative percent decrease has been given in Table 7.3. It is very clear from the table that the relative percent loss of ions except  $\text{Na}^+$  followed the order- Kothi > Gulmarg > Mukteshwar while the loss of  $\text{Na}^+$  followed the order- Gulmarg > Kothi > Mukteshwar. The loss of cations dominated over the loss of anions at these sites. Among anions, the loss of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  dominated at present sites. However, the loss of cations was dominated by  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  at the study sites with the highest loss at Kothi followed by Gulmarg and Mukteshwar (Fig. 7.7).

**Table 7.3:** Relative percent loss of soil nutrients after snowmelt.

	Kothi	Gulmarg	Mukteshwar
Cl <sup>-</sup>	2.7	1.3	0.9
NO <sub>3</sub> <sup>-</sup>	5.2	3.8	1.6
SO <sub>4</sub> <sup>2-</sup>	7.6	5.5	1.5
Na <sup>+</sup>	6.4	8.4	4.3
NH <sub>4</sub> <sup>+</sup>	11.7	9.3	4.5
K <sup>+</sup>	9.3	5.8	2.5
Ca <sup>2+</sup>	6.7	5.9	1.8
Mg <sup>2+</sup>	18.6	14.8	6.2
HCO <sub>3</sub> <sup>-</sup>	10.3	2.8	0.1

The decrease in soil nutrient at these sites after snowmelt might be due to various reasons such as dilution by snowmelt, leaching, percolation, infiltration and soil erosion etc. which has been discussed in this section. The loss of soil nutrients at these sites might be due to dilution by snowmelt. The concentrations of all components in snowmelt were lesser than the soil at the present sites. Ozawa et al (2001) indicated that the dilution effect by the large amount of snowmelt water whose concentration were lower than those of soil solutions lead to loss of soil nutrient levels.

**Fig. 7.7:** Relative percent loss of major soil cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>).

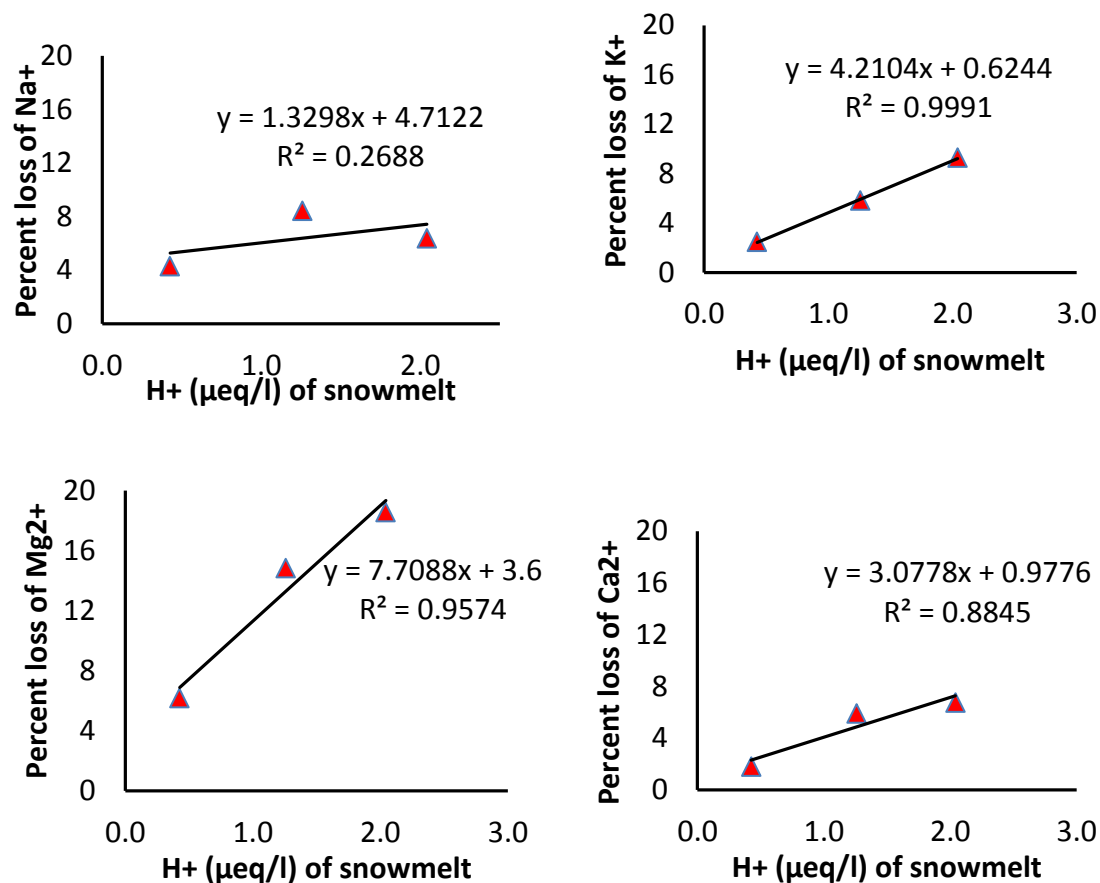
The loss of nutrients in top soil might be due to infiltration into deep soil. Ozawa et al (2001) found that a large amount of  $\text{NO}_3^-$  was leached from the soil during snowmelt period by extensive and rapid infiltration of meltwater into the soil. The loss of soil nutrients at these sites might be due to soil erosion also. The soil erosion may lead to the loss of top soil which might be responsible for the loss of soil components at these sites. Kothyari et al (2004) proved by the experiment that chemical components of the soil undergo erosion due to the action of rainfall and runoff. They found the annual soil loss varied between 0.06 and 5.47 tonnes/ha at different sites in Himalaya. The loss of organic matter due to soil loss might be one reason for drop in pH, CEC and loss of soil nutrients. Kothyari et al (2004) observed the loss of organic material in central Himalaya due to precipitation. They also found the annual loss of total N (6.24 kg/ha), total P (3.88 kg/ha) and total K (5.98 kg/ ha) from soil after rainfall. Similar to our investigation, the loss of soil nutrients has been reported in middle hills of Nepal Himalaya after precipitation (Collins and Jenkins, 1996).

The loss of major soil nutrients are of serious concern for terrestrial as well as aquatic ecosystems. Deficiency of essential soil nutrient from the top soil will eventually lead to agricultural loss and contamination of surface as well as ground water (Zhang et al., 2007b). A decrease in concentration of soil  $\text{K}^+$  will lead to loss of soil fertility and agricultural loss. The enrichment of potassium in ground water due to leaching will degrade the quality of water and ultimately become unfit for drinking purposes. Similar to  $\text{K}^+$ , loss of other macronutrients such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from the top soil also degrades the water quality of ground as well as surface water and decrease agricultural productivity (Zhang et al., 2007b).

### **7.2.2. Possibility of nutrient leaching due to snowmelt pH**

Apart from the above mentioned factor, pH of snowmelt also affects the soil nutrient which has been discussed in this section. The average pH of snowmelt at the present sites followed the order- Mukteshwar (6.37) > Gulmarg (5.90) > Kothi (5.69) which has been already discussed in detail in chapter 4. The different level of acidic snowmelt has been recorded at these sites. The frequency of acidic snowmelt reported at Kothi, Gulmarg and Mukteshwar were 17%, 12% and 5% respectively. The highest acidic precipitation at Kothi might be responsible for the loss of maximum cations in comparison to Gulmarg and Mukteshwar. Acidic precipitation would increase the concentration of the  $\text{H}^+$  ions in the soil solution. It results in the displacement of cations such as  $\text{K}^+$ ,  $\text{Ca}^{+2}$ , and  $\text{Mg}^{+2}$  from the soil with the  $\text{H}^+$

ions (Fig. 7.8). The loss of soil cation due to acid rain has been reported globally by other workers too (Likens et al., 1996; Lawrence et al., 1999; Minocha *et al.*, 2000; Zhang et al., 2007b). However, impacts of the acid rain on soil cation leaching depended not only on the acid rain pH level but also on the original soil pH level.



**Fig. 7.8:** Regression analysis between loss of soil cation and H<sup>+</sup> of snowmelt.

The difference in pH of soil and snowmelt might be one factor for the loss of nutrients at these sites. Zhang and co-workers (2007b) proved that the difference in pH of soil and rain can lead to loss of larger amount of cations (Zhang et al., 2007). On an average, the pH of snowmelt was lesser than the pH of soil at two sites i.e. Kothi and Gulmarg except Mukteshwar site. Due to this reason at these two sites leaching of cation might be one reason for the loss of soil nutrient. Zhang and co-workers (2007b) have investigated by simulation acid rain experiment that loss of K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> due to leaching were about 18.3%, 66.9%, 34.0%, and 46.0% respectively from the soil solution when pH of acidic precipitation



is low. Basumatary and Bordoloi (1992) recorded the loss of potassium due to leaching which results in the destruction of forest and vegetation.

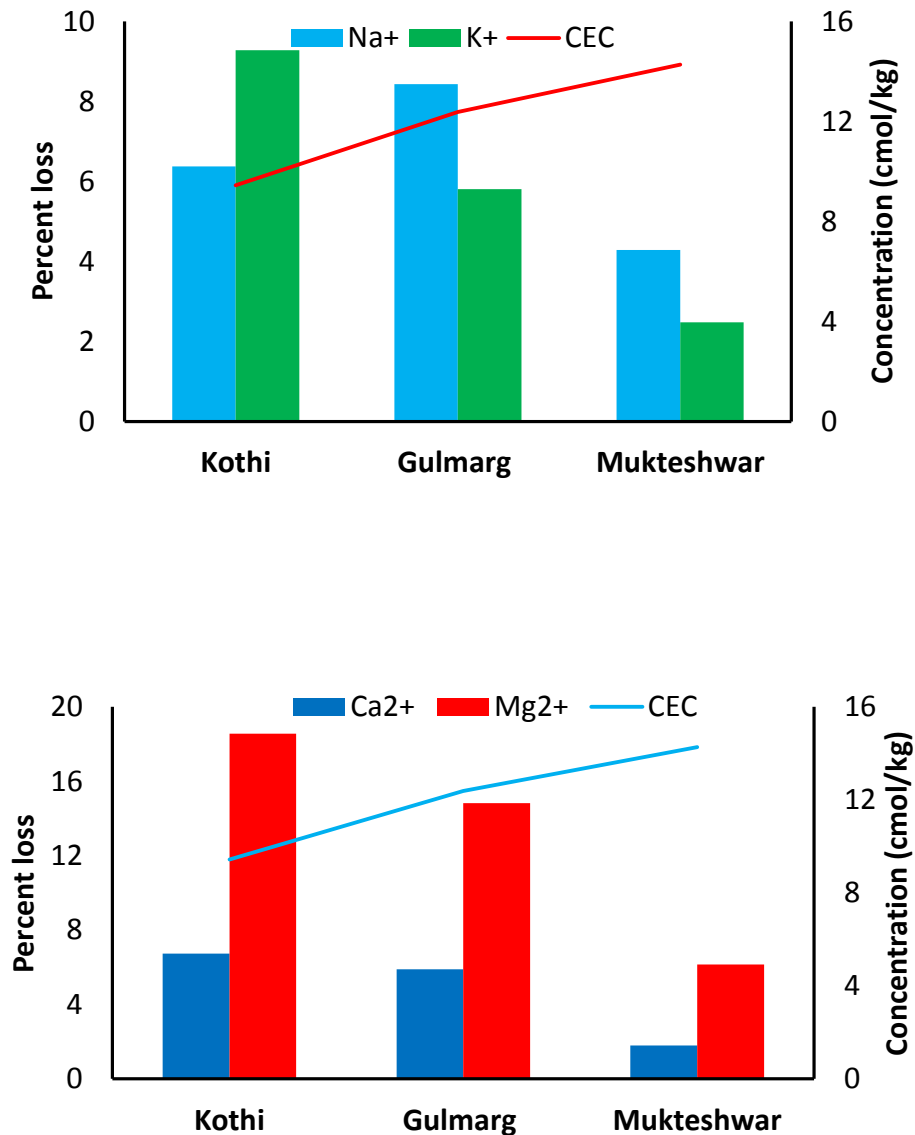
Any rain water having pH value below the pH of soil would lead to increase in concentration of  $H^+$  in the soil and ultimately result in leaching of  $Ca^{+2}$  from the soil solution (Zhang et al., 2007). After acidic precipitation, the soil pH decreases and it increases the level of  $H^+$  thus less anions were available in the soil solution (Zhang et al., 2007b). The availability of cations in the soil solution depends upon the abundance of negative charges of the soil (Zhang et al., 2007b). Due to this reason, essential soil cations such as  $K^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$  etc were removed from the soil system due to the cation exchange by  $H^+$ . Acidic precipitation may also generate complex aluminum hydroxide ions ( $Al(OH)_2^+$ ) in the soil due to lower pH value of the soil. These complex ions also reduce negative charges of the soil and remove the essential cations from the soil system.

In contrast to Kothi and Gulmarg sites, the pH of snowmelt was higher than the pH of soil at Mukteshwar site. The loss of major cations at Mukteshwar site might be due to abundance of  $OH^-$  after snowmelt. Any precipitation with pH value above the original soil pH would result in higher concentration of  $OH^-$  in the soil solution (Zhang et al., 2007b). These  $OH^-$  would then easily exchanges with other anions of soil such as  $Cl^-$ ,  $NO_3^-$  etc. The displaced anion from the soil can react with adsorbed Al in the soil and ultimately lead to the release of  $Al^{+3}$  in the soil solution due to anion effect (Bohn et al., 1979). Now, higher concentration of  $Al^{+3}$  in the soil solution can remove essential soil nutrients such as  $Mg^{2+}$ ,  $Ca^{2+}$  and  $K^+$  from the soil solution. Therefore, impacts of any precipitation on the loss of soil cations do not depend only on the pH level of rain but also on the pH value of the soil.

### 7.2.3. Soil nutrients and role of CEC of soil

The loss of soil nutrients level can be linked to CEC of soil apart from other factors such as pH of snowmelt, leaching, infiltration etc. which has been discussed above in the same section. The lowest loss of soil cations investigated at Mukteshwar might be due to higher CEC as compared to Gulmarg and Kothi soil (Fig. 7.9). Higher CEC of a soil are less likely to develop deficiencies of soil cations such as  $Ca^{2+}$ ,  $K^+$  and  $Mg^{2+}$  etc, while low CEC soils are more susceptible to leaching losses of soil cations (Ketterings et al., 2007; Ross and Ketterings, 2011). Therefore, a soil having higher the CEC values, pH of that soil solution

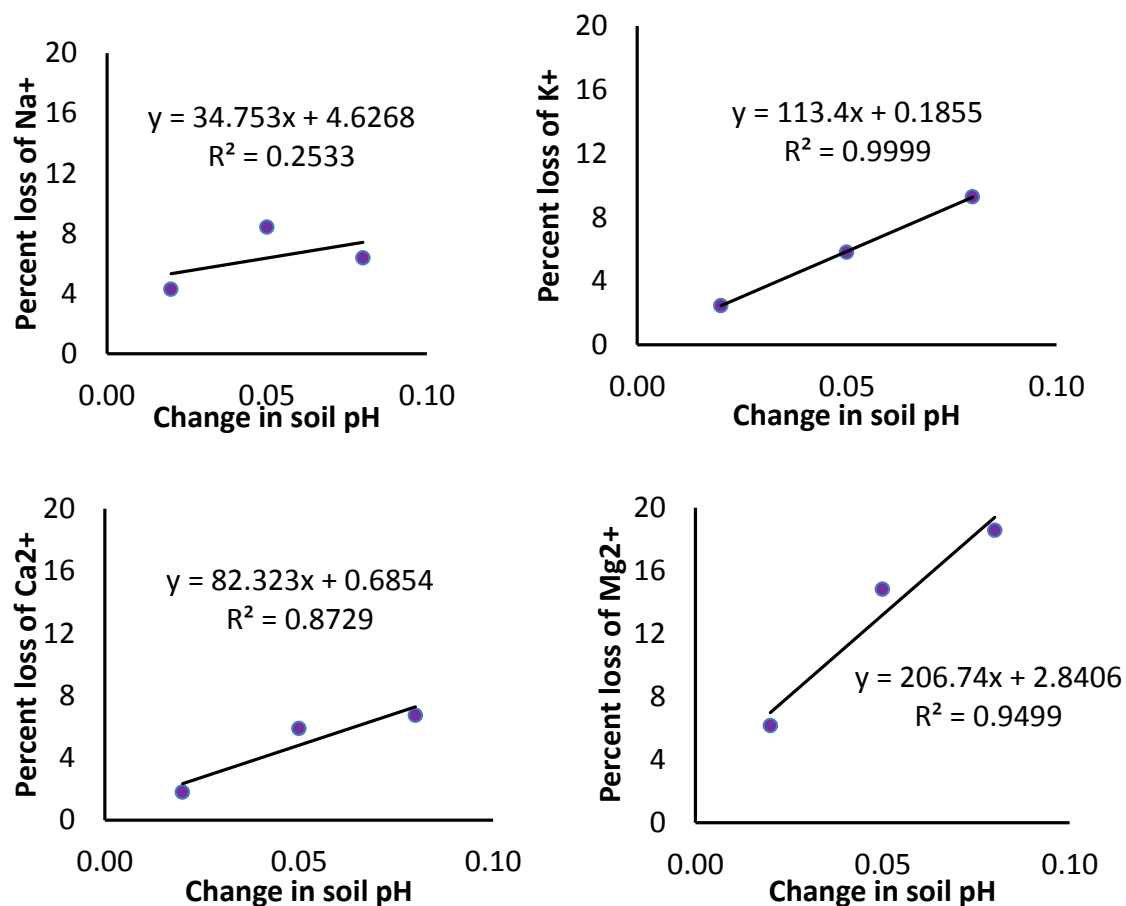
decrease slowly with time (Ketterings et al., 2007). If the drop of pH in soil solution is less than the loss of nutrient is likely to occur (Zhang et al., 2007b).



**Fig. 7.9:** Relationship between CEC of soil and loss of soil cations.

The lowest loss of soil cations observed at Mukteshwar after snowmelt might be due to the smallest drop in pH of the soil in comparison to Gulmarg and Kothi (Fig. 7.10). The lowest drop in pH of soil at Mukteshwar is due to higher CEC values. Very high CEC at Mukteshwar might be due to higher humous content and amount of organic matter which is not estimated in the present study. Higher content of humous level in soil increases the buffering capacity of the soil and restricts the drastic change in soil reaction (Raina and

Gupta, 2009). Although the small decrease in pH at these sites in himalayan region of India might be due to some loss of humous content and organic matter. The loss of organic matter might be due to various reasons such as leaching, percolation, soil loss etc (Zhang et al., 2007b) which has been discussed above in the same section. The decrease in pH of soil due to leaching of bases after high rainfall has been reported in Shiwalik hills of Himachal Pradesh (Rao et al., 1997).



**Fig. 7.10:** Regression analysis between the loss of soil cations and change in soil pH.

### 7.3. Relative deposition of dry deposition and wet deposition

#### 7.3.1. Calculation of relative percent deposition fluxes

This section describes the relative percent contribution of dry and wet deposition affecting the soil composition during snowmelt period in winter and post winter seasons. For this purpose, the contribution of major ions such as  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  has been investigated on the surface of soil by dustfall, aerosol and snowmelt samples. In order to

understand the effect of changes due to local and long range transport activities,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  are considered as the major anthropogenic ions along with  $\text{Ca}^{2+}$  as crustal component, their detailed discussion is given below.

The relative percent contribution of these ions were calculated by the following formula-

$$\% \text{ of any ion in dustfall/ aerosol/ snowmelt} = C_i * 100 / C_t$$

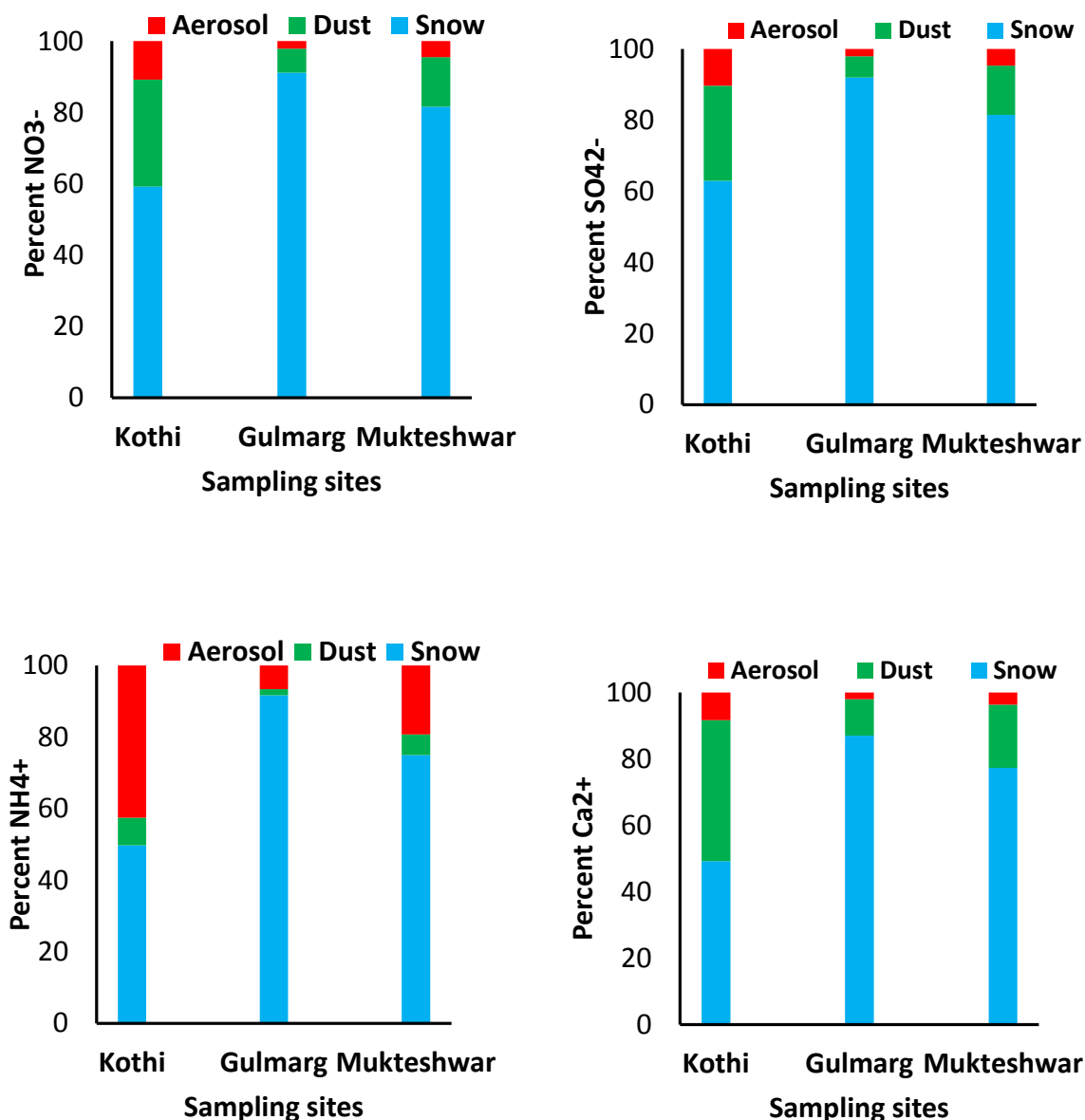
Here  $C_i$  = Concentration of ions ( $\text{SO}_4^{2-}$ /  $\text{NO}_3^-$ /  $\text{Ca}^{2+}$ /  $\text{Mg}^{2+}$ ) in dustfall/ aerosol/ snowmelt ( $\mu\text{eq}/\text{m}^2/\text{day}$ ).

$C_t$  = Total concentration of ions ( $\text{SO}_4^{2-}$ /  $\text{NO}_3^-$ /  $\text{Ca}^{2+}$ /  $\text{Mg}^{2+}$ ) in dustfall + aerosol+ snowmelt ( $\mu\text{eq}/\text{m}^2/\text{day}$ ).

The calculated relative contribution of ions has been presented in Fig. 7.11.

### 7.3.2. LULCC effect on the spatial variability of deposition fluxes

It is very clear from the Fig. 7.11 that the relative percent of  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in snowmelt samples is the highest at Gulmarg followed by Mukteshwar and Kothi while these ions in dustfall and aerosol samples is higher at Kothi than Gulmarg and Mukteshwar. The highest relative percent of  $\text{Ca}^{2+}$  in dust aerosol at Kothi indicating LULCC is one factor dominating at Kothi followed by Mukteshwar and Gulmarg. Satellite imagery reports (1989 vs 2005) around Kothi showed a significant decrease in snow cover (3.24%) and forests (2.17%) while increase in built up area (52.38%) and rocky/barren surface (1.75%) which can contribute suspended dust and elevated particulate levels in the atmosphere (Vishwa et al., 2013). However, the relative percent of  $\text{Ca}^{2+}$  in snow and aerosol indicating contribution of some fraction of  $\text{Ca}^{2+}$  from biomass burning, long range transport and marine sources as well as long range transport.



**Fig. 7.11:** Relative percent deposition of aerosol, dust and snowmelt at the sampling sites.

Very high percent of  $\text{NH}_4^+$  with  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in snowmelt samples at these sites indicating neutralization of acidity generated by their precursor gases  $\text{SO}_x$  and  $\text{NO}_x$ . It seems that  $\text{NH}_3$  has reacted with these acidic components resulted in the formation of  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$  which has been incorporated in snow deposition. This feature is similar to other reports worldwide indicating anthropogenic influence (Finlayson -Pitts and Pitts, 1986; Kulshrestha et al., 2003b; Seinfeld and Pandis, 2006). The increase in anthropogenic influence has been investigated by Kumar and co-workers (2014) at Gulmarg in north western Himalayan region of India. They noticed a drastic increase in the concentrations of anthropogenic components such as  $\text{nssSO}_4^{2-}$  (114%),  $\text{NO}_3^-$  (109%) and  $\text{NH}_4^+$  (90%) in three

decades. The increase in anthropogenic ions might be due to increase in LRT of pollutants as well as local activities such as tourism, vehicular traffic, diesel based electricity generator, biomass burning etc during past three decades.

*Chapter 8*  
*Summary & Conclusion*

---

## SUMMARY & CONCLUSION

Gaseous and particulate pollutants emitted by various natural and anthropogenic activities/processes into the atmosphere. Among anthropogenic activities, the increased industrialization and urbanization have caused serious environmental concern in remote areas too. Himalayan region is also not the exception. In addition, increasing tourist activities at these hilly places have resulted in increased emission of various gaseous and particulate pollutants.

These pollutants are responsible for altering the atmospheric composition. Signatures of these activities are trapped in various forms of atmospheric depositions which can easily be revealed by the chemical characterization of aerosols and snowfall/rain. Since, the environment of western Himalaya is very sensitive from atmospheric deposition point of view, studies on chemistry of dry and wet deposition can be useful for gathering information about the nature of these perturbations, interdependence and linkages of atmospheric constituents with terrestrial and aquatic components.

The present study is an attempt in this direction to fulfill this gap in Himalayan region of India. For this purpose, sampling was done at three sites i.e., Kothi and Gulmarg in north western Himalaya and Mukteshwar in central Himalayan region of India. The main focus of this study was to measure chemical composition of snowfall and its sources i.e., local and long range transport. The ionic compositions of fine aerosol and dustfall have been discussed at the present sites. This study also tried to understand the effect of snowmelt chemistry on chemical composition of soil.

The chemical characterization of snowmelt samples at Kothi, Gulmarg and Mukteshwar in Himalayan region of India has been discussed in **chapter 4**. The average pH of 5.69, 5.90 and 6.37 were reported at Kothi, Gulmarg and Mukteshwar respectively. Alkaline pH of snowfall in this area might be due to the buffering effect of local soil dust which is rich in  $\text{CaCO}_3$ .

The average concentration of major ions showed the highest concentration of  $\text{Ca}^{2+}$  in snowmelt samples at all three sites. The suspended soil dust, construction activities and road dust might be significant local source for  $\text{Ca}^{2+}$ . High concentration of  $\text{NH}_4^+$  at these sites indicated a significant influence of anthropogenic sources at these sites. The most important



sources of  $\text{NH}_4^+$  are agriculture activities, livestock, excreta of human and animal etc. Open excreta of human and animal also might be a good source of  $\text{NH}_4^+$  at these sites.

The maximum contribution of  $\text{SO}_4^{2-}$  might be due to transported  $\text{SO}_4^{2-}$  from other site in India or transboundary and long range transport  $\text{SO}_4^{2-}$ , since, there is no any significant industrial activities at this site. Among local sources, diesel driven vehicular traffic might be the possible source of  $\text{SO}_4^{2-}$ .  $\text{NO}_3^-$  in snowfall samples might be due to emission of  $\text{NO}_x$  mainly from vehicular sources and biomass burning during winter season to produce heat by local people. Unlike snowmelt samples of America and Europe, it is interesting that higher pH of precipitation at Himalaya even at higher  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentration might be due to huge amount of dust in the atmosphere.

$[\text{NO}_3^-] / [\text{NO}_3^-] + [\text{SO}_4^{2-}]$  ratios indicated acidity contributed by  $\text{H}_2\text{SO}_4$  was higher than  $\text{HNO}_3$ . However, fractional acidity at all three sites were very less than 1 indicating almost complete neutralization of acidity in snowmelt samples. The maximum neutralization of snowfall acidity at the present sites occurs by  $\text{nssCa}^{2+}$  which might be due to suspended soil dust rich in  $\text{CaCO}_3$  in Indian atmosphere.

In 3 decades, snowmelt samples at Gulmarg showed a remarkable increase in  $\text{NO}_3^-$  (114 %) might be due to anthropogenic activities such as vehicular traffic which is increased exponentially emitting significant amount of  $\text{NO}_x$ . Significant increase in  $\text{NH}_4^+$  (87%) in snowfall may be attributed to direct input of ammonia from various biogenic and anthropogenic sources which have increased during past three decades. Among anions,  $\text{SO}_4^{2-}$  which is contributed by the oxidation of  $\text{SO}_2$  showed 2 fold increase in concentrations as compared to the values recorded in 1986-87 might be due to increase in diesel driven vehicular traffic in Gulmarg area. The present study showed average pH 0.8 unit lower in 3 decades which might be due to elevated ratios of  $\text{nss SO}_4^{2-}/\text{nss Ca}^{2+}$  and  $\text{NO}_3^-/\text{nssCa}^{2+}$ .

This study also discussed a detailed chemical analysis of aerosol samples over Himalayan region of India in **chapter 5**. Among water soluble inorganic ions in aerosol samples, anionic composition is found to be dominated by  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  after  $\text{Cl}^-$  at these sites. Apart from industrial emissions, diesel driven vehicles and generator is one of the most important source of  $\text{SO}_2/\text{SO}_4^{2-}$  at these tourist sites. Apart from local emissions, very high concentration of  $\text{NO}_3^-$  might be due to long range transport of  $\text{NO}_x / \text{NO}_3^-$  from various airmasses (transboundary as well as long range transported) approaching at these sites. The result

suggested relatively lesser pollution at Himalaya in comparison to other sites in south and east asia. However, the increasing level of air pollution is alarming globally including sensitive ecosystem like Himalaya.

Among water soluble inorganic cations,  $\text{NH}_4^+$  was the most dominating cation in Himalayan region of India. Discharge from hotels, agriculture activities and animal excreta might be major anthropogenic sources of  $\text{NH}_4^+$ . Sodium ratios for K, Ca and  $\text{SO}_4$  at these sites were very high than sea water ratio indicated very significant contribution from non-marine sources. The value of enrichment factor of crustal sources for  $\text{NH}_4^+$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$  and  $\text{nssSO}_4^{2-}$  is greater than 1 indicated its contribution in aerosol samples from anthropogenic sources mainly.

Calculation of scavenging ratios (SR) by the concurrent measurements of the chemical components of snowfall and aerosol showed the highest for  $\text{Ca}^{2+}$ . The values of scavenging ratios were low for major anthropogenic ions such as  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . The differences in SR values might be due to difference in particle size.

The 2<sup>nd</sup> part of **chapter 5** discussed in detail about pH and ionic composition of water soluble dustfall samples. At all the sites, pH is in the alkaline range and suggested the dominance of crustal components particularly, the presence of carbonates and bicarbonates of Ca. Among all ionic fluxes,  $\text{Ca}^{2+}$  was the highest at all sites. This is a characteristic feature of Indian atmosphere. The annual deposition fluxes ( $\text{meq/m}^2/\text{anm}$ ) for  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  fluxes at these sites were very less from the range of proposed limits to fresh water ecosystem.  $\text{SO}_4^{2-}$  at these sites might have originated in the form of  $\text{CaSO}_4$  when  $\text{SO}_2$  reacted with particulate matter or could have deposited directly onto dust particles in the collecting vessel. Formation of calcium sulphate does not contribute acidity in samples rather enhances the pH of dustfall which is further supported by higher pH values of dustfall at these sites. Most of the points in regression plots of  $\text{nssSO}_4^{2-} + \text{NO}_3^-$  vs  $\text{nssCa}^{2+}$  and  $\text{nssSO}_4^{2-} + \text{NO}_3^-$  vs  $\text{nssMg}^{2+}$  lying above 1:1 neutralization confirm its high presence in stoichiometric neutralization reaction.

$\text{Cl}^- / \text{Na}^+$  ratio at all sites are less than sea water ratio i.e. 1.16 indicated some depletion of chloride in atmosphere. This depletion might be due to reaction between sea salt and acids generated in the atmosphere. At all three sites in Himalayan region of India,  $\text{NO}_3^- / \text{SO}_4^{2-}$  ratio is lesser than 1 indicated strong influence of stationary sources over mobile sources. The most probable dominant sources at these sites might be diesel based generator, brick kiln etc.

**Chapter 6** discussed about the source identification (local vs long range transport) of snowfall at all three sites in Himalayan region of India. In order to find out the contribution of various sources categories, marine and non-marine fractions have been calculated. In order to estimate marine contribution, sodium ratios were calculated by assuming Na as a reference element for marine source. Elevated ratios of  $\text{SO}_4^{2-}/\text{Na}^+$ ,  $\text{K}^+/\text{Na}^+$  and  $\text{Ca}^{2+}/\text{Na}^+$  might be due to higher contribution by non-marine sources.

Non-marine sources were categorised into two major categories i.e. crustal and anthropogenic sources. The highest contribution of crustal  $\text{Ca}^{2+}$  might be due to contribution from local sources such as local soil, construction activities, road dust etc as well as long range transport of fine dusts. Among nss  $\text{SO}_4^{2-}$ , high value of Anthro  $\text{SO}_4^{2-}$  might be due to significant contribution from various airmasses approaching at these sites. This might be due to fossil fuel combustion at the origin of airmasses as well as picking it during the transport of airmasses before reaching at the site. Apart from long range transport, some contribution from local sources such as use of electric generators which are mostly operated on diesel can not be ruled out. The crustal  $\text{SO}_4^{2-}$  at this site might be due to reaction of  $\text{SO}_2$  with  $\text{CaCO}_3$  rich dust particles forming Calcium Sulphate which is very common in Indian region. At the present sites,  $\text{NO}_3^-$  is found to be dominated by anthropogenic source in comparison to crustal sources. Very high fraction of Anthro  $\text{NO}_3^-$  might be due to the emissions of  $\text{NO}_x$  from fossil fuel combustion and biomass burning. At the present sites,  $\text{NH}_4^+$  are contributed mainly by anthropogenic sources which might be due to significant contribution from local sources like animal and human excreta, effluents from various hotels with huge biomass burning/biogenic sources with some contribution from long range transport.

On an average, the impact of anthropogenic sources is nullified significantly due to dominance of crustal contributions over anthropogenic contribution as reflected from the alkaline nature of snowmelt at these sites since sea salt don't play an important role in deciding pH of precipitation.

Backward air mass trajectories were calculated at Kothi and Gulmarg site using the HYSPLIT model from NOAA for all snowfall samples. At these sites, the lowest pH were recorded in Middle East origin (ME) cluster among all the clusters might be due to the highest ratios of  $\text{nss SO}_4^{2-} / \text{nssCa}^{2+}$  and  $\text{NO}_3^- / \text{nssCa}^{2+}$ . The highest pH in Western India origin (InW) cluster compared to other airmasses might be due to the lowest ratios of  $\text{nss SO}_4^{2-} / \text{nssCa}^{2+}$  and  $\text{NO}_3^- / \text{nssCa}^{2+}$ .

The change in soil nutrients after snowmelt in Himalayan region of India has been discussed in **chapter 7**. The soils of all the present sites were recorded as slightly acidic which might be due to accumulation and decomposition of organic matter of vegetation and forest debris, which releases acids. The observed pH values were found to be suitable for the maximum nutrient availability, growth of most of the forest plants and crops and, and microbial activity in soil.

Among soil nutrients, cations dominated over anions at these sites which is very similar to other fertile soils in Indian region. The variation in concentration of N and S level at these sites might be due to differences in the content of organic matter which comes from debris of vegetation, forests and animals. On an average, most of nutrients were medium to high level according to Cochrane and co-workers classification indicating sufficient level of essential components at these sites.

The loss of soil nutrients has been observed after snowmelt at the present sites. The relative percent loss of cations dominated over the loss of anions at these sites. The decrease in soil nutrient at these sites after snowmelt might be due to various reasons such as dilution by snowmelt, leaching, percolation, infiltration and soil erosion etc. The highest acidic precipitation at Kothi might be responsible for the loss of maximum cations in comparison to Gulmarg and Mukteshwar. Acidic precipitation would increase the concentration of the H<sup>+</sup> ions in the soil solution. It results in the displacement of cations such as K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> from the soil with the H<sup>+</sup> ions. The lowest loss of soil cations investigated at Mukteshwar might be due to higher CEC as compared to Gulmarg and Kothi soil. Higher CEC of a soil are less likely to develop deficiencies of soil cations such as Ca<sup>2+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> etc, since in this case pH of that soil solution decrease slowly with time. If the drop of pH in soil solution is less than the loss of nutrient is likely to occur.

The relative percent of Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in snowmelt samples is the highest at Gulmarg followed by Mukteshwar and Kothi while these ions in dustfall and aerosol samples is higher at Kothi than Gulmarg and Mukteshwar. The highest relative percent of Ca<sup>2+</sup> in dust aerosol at Kothi indicating LULCC is one factor dominating at Kothi followed by Mukteshwar and Gulmarg. Satellite imagery reports around Kothi showed a significant change in snow cover, forests, built up area and rocky/barren surface which can contribute suspended dust and elevated particulate levels in the atmosphere. However, the relative

---

percent of  $\text{Ca}^{2+}$  in snow and aerosol indicating contribution of some fraction of  $\text{Ca}^{2+}$  from biomass burning, long range transport and marine sources as well as long range transport.

### **Future Scope of work**

In this study, chemical composition of snowfall samples were analysed for major inorganic ions at three sites in Himalayan region of India. Since, it is very sensitive from atmospheric deposition point of view trace metals and organic species should also be analysed in order to find out sources of pollution more precisely. Sampling of snowfall should be performed for longer durations and at various sites in Himalayan region of India to determine factors affecting composition of snowfall in depth.

Findings of this study showed that acidity of snowmelt has been decreased in three decades at Gulmarg site. However, this opens up the scope of future research- (i) how long such composition of rain water will be retained (ii) at what rate the buffering capacity of the atmosphere is decreasing? Decreasing pH of snow due to anthropogenic components at Gulmarg is probably the first stage alarm which suggests continuous monitoring of acid deposition scenario in the Himalayan system in order to prevent disaster in near future.

Air mass trajectory model showed that acidity of snowmelt is affected by long range transport especially from Middle East and European region. However, the broad scope of this findings have opened a scope for policy makers and scientists to expand better understanding of long range transport of pollutants by combining chemical composition with meteorological data and concentration weighted trajectory at various sites in Himalaya.

Although, this work has shown that acidity of snowmelt affects soil nutrients which is new findings in this region. However, uncertainties remain about factors affecting composition of soil and at what extent since the limited number of samples have been used in this study. The inclusion of a long term observation by combining various sites in Himalaya will strengthen this type of study. The effect of dry deposition on soil composition should also be monitored at these sites. Additionally, field experiments should be performed at large scale to know the relationship between acidity of snowmelt and soil nutrients in Himalayan region of India.

# *References*

---

**REFERENCES**

- Abdeen Z., Qasrawi R., Heo J., Wu B., Shpund J., Vanger A., Sharf G., Moise T., Brenner S., Nassar K., Saleh R., Al-Mahasneh Q. M., Sarnat J. A., and Schauer J. J., (2014). Spatial and Temporal Variation in Fine Particulate Matter Mass and Chemical Composition: The Middle East Consortium for Aerosol Research Study. *The Scientific World Journal*, Volume 2014, Article ID 878704, 16 pages, <http://dx.doi.org/10.1155/2014/878704>.
- Aber J. D., Melillo J. M., (1991). *Terrestrial ecosystems*. Saunders College Publishing, Philadelphia.
- Adams P. W., Sidle R. C., (1987). Soil conditions in three recent landslides in southeast Alaska. *For Ecol Manag*, 18 (2) : 93–102.
- Ahrens C. D., (2007). *Meteorology today: Introduction to weather, climate, and the environment*. Eighth edition, Thomson's brooks/ cole.
- Aiuppa A., Bonfanti P., Alessandro W.D., (2003). Rainwater chemistry at Mt. Etna (Italy): natural and anthropogenic sources of major ions. *J. Atmos. Chem.* 46, 89–102.
- Alahmr F. O. M., Othman M., Wahid N. B. A., Halim A. A., Latif, M. T. (2012). Compositions of dust fall around semi-urban areas in Malaysia. *Aerosol Air Qual. Res.*, 12, 629–642, doi:10.4209/aaqr.2012.02.0027.
- Anderson J. R., Buseck P. R., Patterson T. L., Richard A., (1996). Characterization of the Bermuda tropospheric aerosol by combined individual-particle and bulk-aerosol analysis, *Environment Volume*, January Pages, 319-338.
- Andreae M. O., 1983. Soot carbon and excess fine potassium-long-range transport of combustion-derived aerosols. *Science*, 220, 1148-1151.
- Andreae M. O., Andreae T. W., Meyerdierks D., Thiel C., (2003). Marine sulfur cycling and the atmospheric aerosol over the springtime North Atlantic, *Chemosphere* 52 , 1321–1343.
- Andreae M. O., Crutzen P. J., (1997). Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry. *Science*, 276 (5315): 1052–1058.
- Ashraf M., Bhat G. A., Dar I, Y., Ali M., (2012). Physico-Chemical Characteristics of the Grassland Soils of Yusmarg Hill Resort (Kashmir, India). *Ecologia Balkanica*, Vol. 4, Issue 1 June 2012 pp. 31-38.
- Avila A., and Alacron M., (1999). Relationship between precipitation chemistry and meteorological situations at a rural site in northeastern Spain”, *Atmos Environ*, 33: 1663–1677.
- AWWA-WEF-APHA, (1998). *Standard Methods for the Examination of Water and Wastewater (Methods: 4500B. Electrometric Method; 2320B Titration Method)*.

- Ayers G.P., (1995). Some practical aspects of acid deposition measurement. Presentation to the Third Expert Meeting on Acid Deposition Monitoring Network in East Asia, 14–16 November 1995, Niigata Prefecture, Japan, pp. 1–20.
- Balasubramanian R., Victor T., Chun N., (2001). Chemical and statistical analysis of precipitation in Singapore. *Water Air Soil Pollut* 130, 451–456.
- Basumatary A., Bordoloi P. K., (1992). Forms of potassium in some soils of Assam in relation to soil properties. *J Indian Soc Soil Sci*, 40(3):443–446.
- Beckett P. H. T., (1965). The cation exchange equilibrium of calcium and magnesium. - *Soil Science*, 100: 118-12.
- Begum B.A., Biswas S.K., Pandit G. G., Saradhi I.V., Waheed S., Siddique N., Seneviratne M.C.S., Cohen D.D., Markwitz A., Hopke P.K., (2011). Long-range transport of soil dust and smoke pollution in the South Asian region. *Atmos Pollut Res* 2 : 151-157.
- Beiderwieden E., Wrzesinsky T., Klemm O., (2005). Chemical characterization of fog and rain water collected at the eastern Andes cordillera. *Hydrol. Earth Syst. Sci.* 2, 863–885. [www.copernicus.org/EGU/hess/hessd/2/863/](http://www.copernicus.org/EGU/hess/hessd/2/863/).
- Belwal M., Mehta S. P. S., (2014). Physico-chemical properties of the main soil types of Ranikhet region of Kumaun (Uttarakhand), *Journal of Chemical and Pharmaceutical Research*, 6(4): 682- 688, ISSN: 0975-7384.
- Bohn H. L., McNeal B. L., O'Connor G. A., (1979). *Soil Chemistry*. John Wiley & Sons, New York, Toronto.
- Boruah H. C., Nath A. K., (1992). Potassium status in three major soil orders of Assam. *J Indian Soc Soil Sci* 40(3):559–561.
- Borys R. D., Rahn, K. A., (1981). Long-range atmospheric transport of cloud active aerosol to Iceland , *Atmospheric Environment*, Volume 15, Issue 8, Pages 1491-1501.
- Botkin D. B., Keller E. A., (2010). *Environmental science: Earth as a living planet*. Wiley Global Education
- Bouwman, A. F., Vuuren, D. P. V., , Derwent, R. G., & Posch, M. (2002). A global analysis of acidification and eutrophication of terrestrial ecosystems. *Water, Air, and Soil Pollution*, 141(1-4), 349-382.
- Brady N. C., & Weil R. R. (2000). *Elements of the nature and properties of soils* (No. 631.4 B733E.). Upper Saddle River, NJ, USA: Prentice Hall.
- Brady N. C., (1996). *The nature and properties of soil*, 10th edn. Prentice Hall, New Delhi.
- Brady N. C., Weil R. R., (2016). *The Nature and Properties of Soils*, 14th Edition, Publisher Pearson, ISBN -13: 978-0132279383.
- Brimblecombe P., Hara H., Houle D., Novak M., (2007). *Acid Rain - Deposition to Recovery*, Springer book archives, ebook.



- Budhavant K. B., Rao P. S. P., Safai P. D., (2014b). Chemical Composition of Snow-Water and Scavenging Ratios over Costal Antarctica, *Aerosol Air Qual Res*, 14: 666–676.
- Budhavant K. B., Rao P. S. P., Safai P. D., Ali K., (2011). Influence of local sources on rainwater chemistry over Pune region, India, *Atmospheric Research*, 100, 121-131.
- Budhavant K. B., Rao P. S. P., Safai P. D., Gawhane R. D., Raju M. P., Mahajan C. M., Satsangi P. G., (2012). Atmospheric wet and dry depositions of ions over an urban location in South- West India. *Aerosol Air Qual. Res.*, 12, 561–570, doi:10.4209/aaqr.2011.12.0233.
- Budhavant K. B., Safai P. D., Granat L., and Rodhe H., (2014a). Chemical composition of the inorganic fraction of cloud-water at a high altitude station in West India. *Atmos Environ*, 88: 59-65.
- Calvo A. I., Olmo F. J., Lyamani H., Alados-Arboledas L., Castro A., Fernández-Raga M., Fraile R., (2010) Chemical Composition of Wet Precipitation at the Background EMEP Station in Víznar (Granada, Spain) (2002-2006). *Atmos. Res.* 96: 408–20.
- Carrico C. M., Bergin M. H., Shreshtha A. B., Dibb J. E., Gomes, L., Harris J. M., (2003). The Importance of carbon and mineral dust to seasonal aerosol properties in the Nepal Himalaya,” *Atmos. Environ.* 37, 2811-2824.
- Charlson R. J., Schwartz S. E., Hales J. M., Cess R. D., Jr. Coakley J. A., Hansen J. E., Hofmann D. J. (1992). Climate forcing by anthropogenic aerosols. *Science*, vol. 255, no. 5043, pp. 423– 430.
- Charlson R. J., Rodhe, H., (1982). Factors controlling the acidity of natural rainwater. *Nature*, 295: 683-695.
- Chelani A., Gajghate D.; ChalapatiRao C., Devotta S., (2010). Particle size distribution in ambient air of Delhi and its statistical analysis. *Bull. Environ. Contam. Toxicol.* 85, 22–27.
- Cochrane T. T., Sanchez L. G., deAzevedo L. G., Porras J. A., Graver C. L., (1984). Land in tropical America, CIAT/EMBRAPA-CPAC, Call, Columbia.
- Collins R., Jenkins A., (1996). The impact of agricultural land uses on stream chemistry in the middle hills of the Himalayas, Nepal. *Journal of hydrology*, 185, 71 – 86.
- CPCB (Central Pollution control Board’s), (2010). Air Quality Monitoring, Emission Inventory and Source Apportionment Study for Indian Cities. CPCB, Govt. of India, New Delhi, India.
- Das R., Das S. N., and Mishra V. N., (2005). Chemical composition of rainwater and dustfall at Bhubaneswar in the east coast of India. *Atmos Environ*, 39: 5908–5916.
- de Hann S., (1977). Humus, its formation, its relation with the mineral part of the soil and its significance for soil productivity. In: *Organic matter studies*, vol 1. International Atomic Energy Agency, Vienna, pp 21–30.

- Dennekamp M, Carey M. (2010). Air quality and chronic disease: why action on climate change is also good for health. *N S W Public Health Bull* 21: 115-21.
- Dentener F. J., Carmichael G. R., Zhang Y., Lelieveld J., Crutzen P. J., (1996). Role of mineral aerosol as a reactive surface in the global troposphere. *Journal of Geophysical Research:Atmospheres*, vol. 101, no.D17, pp. 22869–22889.
- Dentener F., Drevet J., Lamarque J. F., Bey I., Eickhout B., Fiore A. M., Hauglustaine D., Horowitz L.W., Krol M., Kulshrestha U.C., Lawrence, M., Galy-Lacaux C., Rast S., Shindel, D., Stevenso, D., Van Noije T., Atherton C., Bell N., Bergman D., Butler T., Cofala J., Collins B., Doherty R., Ellingsen K., Galloway J., Gauss, M., Montanaro V., Müller J.F. , Pitari G., Rodriguez J., Sanderson M., Solomon F., Straha, S., Schultz M., Sudo K., Szopa S., Wild O., (2006). Nitrogen and sulfur deposition on regional and global scales: a multimodel evaluation. *Global biogeochemical cycles*, 20(4).
- Derry L. A., Chadwick O. A., (2007). Contributions from earth's atmosphere to soil. *Elements* 3, 333–338.
- Deshmukh D. K., (2012). Characterization of dicarboxylates and inorganic ions in urban PM10 aerosols in the Eastern Central India. *Aerosol Air Qual. Res.* 2012, 12, 592–607.
- Doesken N. J., Judson A., (1996). *The Snow Booklet: A Guide to the Science, Climatology, and Measurement of Snow in the United States*. Colorado State University Department of Atmospheric Science, 78pp.
- Draxler R. R., Rolph, G. D., (2003). HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model. NOAA Air Resources Laboratory, Silver Spring, MD. Model access via NOAA ARL READY Website <http://ready.arl.noaa.gov/HYSPLIT.php>.
- Draxler R. R., Taylor, A. D., (1982). Horizontal parameters for long-range transport modelling. *Journal of Applied Meteorology* 21, 367–372.
- Du M., Kawashima S., Yonemura S., Zhang X., Chen S. (2004). Mutual influence between human activities and climate change in the Tibetan Plateau during recent years. *Global and Planetary Change*, 41(3), 241-249.
- Dvorska A., Lammel G., Holoubek I., (2009). Recent trends of persistent organic pollutants in air in central Europe — air monitoring in combination with air mass trajectory statistics as a tool to study the effectivity of regional chemical policy”, *Atmospheric Environment*, 43, 1280–1287.
- EANET, (2011). Second Periodic Report on the State of Acid Deposition in East Asia (Part I) (Regional Assessment). Acid Deposition Monitoring Network in East Asia. Available from: [http://www.eanet.cc/product/PRSAD/2\\_PRSAD/2\\_PRSAD1.pdf](http://www.eanet.cc/product/PRSAD/2_PRSAD/2_PRSAD1.pdf).
- Elsom D., (1987). *Atmospheric Pollution-Causes, Effects and Control Policies*, Basil Blackwell Inc.
- EMEP/CEIP, (2012). EMEP Emissions Data. European Monitoring and Evaluation Programme/Centre on Emission Inventories and Projections. Available from: <http://webdab1.umweltbundesamt.at/>.

- Encinas D., Calzada I., Casado H., (2004). Scavenging ratios in an urban area in the Spanish Basque country. *Aerosol Sci and Tech* 38: 685–691.
- Eriksson M., Jianchu X., Shrestha A. B., Vaidya R. A., Nepal S., Sandström, K. (2009). The changing Himalayas: Impact of climate change on water resources and livelihoods in the greater Himalayas. International centre for integrated mountain development (ICIMOD).
- Escudero M., Stein A. F., Draxler R. R., Querol X., Alastuey A., Castillo S., Avila A., (2011). Source apportionment for African dust outbreaks over the Western Mediterranean using the HYSPLIT model”, *Atmospheric Reserach* 99, 518–527.
- Fenn M. E., Poth M. A., Aber J. D., Boron J. S., Bormann B. J., Johnson D. W., Lenly A. D., McNulty S. G., Ryan D. F., Stottlemeyer R., (1998). Nitrogen excess in North American ecosystems: predisposing factors, ecosystem responses and management strategies. *Ecol Appl* 8(3):706–733.
- Finlayson-Pitts J. B., Pitts J. J. N., 1986. *Atmospheric Chemistry: Fundamentals and experimental techniques*. A Wiley-Interscience publication John Wiley & Sons.
- Fleming Z. L., Monks P. S., Manning A. J., (2012). Review: Untangling the influence of air-mass history in interpreting observed atmospheric composition”, *Atmospheric Research*, 104-105, 1–39.
- Foth H. D., (1984). *Land in tropical America*. CIAT / EMBRAPA- CPAC. Call, Columbia
- Gairola S., Sharma C. M., Ghildiyal S. K., Suyal S., (2012). Chemical properties of soils in relation to forest composition in moist temperate valley slopes of Garhwal Himalaya, India. *Environmentalist*, DOI 10.1007/s10669-012-9420-7.
- Gajananda K., Kuniyal J. C., Momin G.A., Rao P. S. P., Safai P. D., Tiwari S., Ali K., (2005). Trend of atmospheric aerosols over the north western Himalayan region, India. *Atmos. Environ.* 39 (27): 4817–4825.
- Galloway J., Townsend A., Erisman J. W., Bekunda M., Cai Z., Freney J. R., (2008). Transformation of the nitrogen cycle: recent trends, questions, and potential solutions *Science* 320 889–92
- Galloway J. N., (1995). Acid deposition: perspectives in time and space. *Water Air Soil Poll.* 85: 15–24.
- Gebhart K. A., Schichtel B. A., Malm W. C., Barna M. G., Rodriguez M. A., and Jr. Collett J. L., (2011). Back-trajectory-based source apportionment of airborne sulphur and nitrogen concentrations at Rocky Mountain National Park, Colorado, USA”, *Atmospheric Environment* , 45, 621–633.
- Gillman G. P., Sumpter E. A., (1986). Modification to the compulsive exchange method for measuring exchange characteristics of soils. *Aust. J. Soil Res.* 24:61-66.
- Gillett R., Ayers, G., (1991). The use of thymol as a biocide in rainwater samples. *Atmos. Environ.* 24A, 2677–2681.

- Granat L., Norman M., Leck C., Kulshrestha U. C., Rodhe H., (2002). Wet scavenging of sulfur compound and other constituents during the Indian Ocean Experiment (INDOEX)", *Journal of Geophysical Research* 107, 8025, doi:10.1029/2001JD000499.
- Gunj D. W., Hoffmann M. R., (1990) Field investigation on the snow chemistry in central and southern California-I. Inorganic ions and hydrogen peroxide. *Atmos. Env.*, 24A,1661-71.
- Gupta G. P., Kumar B., Singh S., Kulshrestha U. C., (2015). Urban climate and its effect on biochemical and morphological characteristics of Arjun (*terminalia arjuna*) plant in NCR Delhi. *Chemistry and Ecology*, 0275-7540.
- Gupta G. P., Singh S., Kumar B., Kulshrestha U. C., (2016). Deposition and mpact of Urban Atmospheric Dust on Two Medicinal Plants during Different Seasons in NCR Delhi. *Aerosol and Air Quality Research*, x: 1–13, xxx. doi: 10.4209/aaqr.2015.04.0272.
- Hall D. K., Martinec J., (1985). Remote sensing of ice and snow. Chapman and Hall, New York, 189 pp.
- Hara H., Akimoto H., (1993). National level variations in precipitation chemistry in Japan. In *Proceedings of the International Conference on Regional Environment and Climate Changes in East Asia, Taipei*. November 30–December 3, 1993.
- Harrison R. M., Grenfell J. L., Peak J. D., Clemitshaw K. C., Penkett S. A., Cape J. N., McFadyen G. G., (2000). Influence of airmass back trajectory upon nitrogen compound composition', *Atmospheric Environment*, 34, 1519–1527.
- Herich H., Tritscher T., Wiacek A., Gysel M., Weingartner E., Lohmann U., Baltensperger U., Cziczo D. J., (2009). Water uptake of clay and desert dust aerosol particles at sub- and supersaturated water vapor conditions. *Physical Chemistry Chemical Physics: PCCP* 11, 7804–7809.
- Hick B. B., (2005). A climatology of wet deposition scavenging ratios for the United States. *Atmos Environ* 39: 1585–1596.
- Hodges S. C., (1996). Soil fertility basics: N.C. certified crop advisor training. Soil Science Extension, North Carolina State University. 75p.
- <https://nsidc.org>. National Snow and Ice Data Center, CIRES, 449 UCB, University of Colorado, Boulder, CO 80309-0449 USA.
- Huang T., Chen J., Zhao W., Cheng J., Cheng S., (20136). Seasonal variations and correlation analysis of water-soluble inorganic ions in PM<sub>2.5</sub> in Wuhan in 2013. *Atmosphere* 2016, 7, 49.
- IJC, (2010). Canada-United States Air Quality Agreement Progress Report 2010. Report, ISBN:978-1-100-17179-1.<http://www.epa.gov/airmarkets/progsregs/usca/docs/2010/report.pdf>.

- IPCC (Intergovernmental Panel on Climate Change), (2007). Climate change 2007: The physical basis. In: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., Miller, H.L. (Eds.), Contribution of the Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom.
- IPCC, (2014). Climate Change 2014: Synthesis report. Fifth assessment report (AR5) of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Jacob D. J., Winner D. A., (2009). Effect of climate change on air quality. *Atmospheric Environment*, 43: 51–63.
- Jain M., Kulshrestha U. C., Sarkar A. K., Parashar D. C., (2000). Influence of crustal aerosols on wet deposition at urban and rural sites in India. *Atmospheric Environment*, 34, pp 5129-5137.
- Jones H. G., Stein J., (1990). Hydrogeochemistry of snow and snowmelt in catchment hydrology. In process studies in hillslope hydrology. M. G. Anderson and T. P. Burt (Eds.). Wiley, Chichester, pp. 255-298.
- Kang S., Qin D., Mayewski P. A., Sneed S. B., Tandong Y., (2002). Chemical composition of fresh snow on Xixabangma peak, Central Himalaya, during the summer monsoon season. *Journal of Glaciology* 48 (161), 337–339.
- Kang S., Mayewski P. A., Qin D., Sneed S. R., Ren J., Zhang D., (2004). Seasonal differences in snow chemistry from the vicinity of Mt. Everest, central Himalayas. *Atmos Environ*, 38: 2819-2829.
- Kaur S., Singh I., (2012). Accelerated phosphate & nitrate level: factors to blame for 'eutrophication' in Yamuna river, Delhi, India. *International journal of plant, animal and environmental sciences*, Vol. 2, Issue-3, ISSN- 2231-4490.
- Keene W. C., Pszenny A. P., Galloway J. N., Hawley M. E., (1986). Sea salt corrections and interpretations of constituent ratios in marine precipitation. *J. Geophys. Res.* 91: 6647–6658.
- Keene W. C., Sander R., Pszenny, A. A. P., Vogt, R., Crutzen P. J., Galloway J. N., (1998). Aerosol pH in the marine boundary layer: A review and model evaluation, *J. Aerosol Sci.*, 29, 339– 356, 1998.
- Ketterings Q., Reid S., Rao R., (2007). Cation Exchange Capacity (CEC), Corneel university cooperative extension, College of agriculture and life sciences, Department of crop and soil sciences, Agronomy Fact Sheet Series, fact sheet- 22.
- Khattak M. I., Rehana K., Jana A., (2012). Chemical precipitation of aerosols particulates of rain waters reference to atmospheric pollution at Lahore / Pakistan, *Sci. Int.(Lahore)*, 24(1): 81-86.

- Khemani L. T., (1989). Physical and chemical characteristics of atmospheric aerosols. In: Cheremissionoff, P.N. (ed.) Air pollution control 2 Encyclopedia of Environmental control Techniques. Gulf publishing, USA.
- Khera N., Kumar A., Ram J., Tewari A., (2001). Plant biodiversity assessment in relation to disturbances in mid-elevational forest of Central Himalaya, India. *Trop Ecol* 42(1):83–95.
- Kothai P., Saradhi I. V., Prathibha P., Hopke P. K., Pandit G. G., Puranik, V. D., (2008) Source Apportionment of Coarse and Fine Particulate Matter at Navi Mumbai, India. *Aerosol Air Qual. Res.* 423-436.
- Kothyari B. P., Verma P. K., Joshi B. K., Kothyari U. C., (2004). Rainfall – runoff- soil and nutrient loss relationship for plot size areas of bhetagad watershed in central Himalaya, India. *Journal of hydrology*, 293, 137- 150.
- Kulshrestha M. J., Kulshrestha U. C., Parashar D. C., Vairamani M., (2003a). Estimation of SO<sub>4</sub> contribution by dry deposition of SO<sub>2</sub> onto the dust particles in India. *Atmospheric Environment*, 37 (22), 3057-3063.
- Kulshrestha U.C., (1993). A study on aerosol composition and deposition flux of selected pollutants at Agra. Ph.D. Thesis, Dayalbagh Educational Insitute, Agra.
- Kulshrestha U. C., (2007). Air quality assessment through atmospheric depositions: a comparison of measurements & model calculations for India. *Indian J of Environmental Management*, 34, 51-55
- Kulshrestha U. C., (2013). Acid rain, in *Encyclopedia of Environmental Management*, Taylor and Francis, Manila Typesetting Company.
- Kulshrestha U. C., Azhaguvel S. N., Rao T., Sekar R., (2004). Relationship of sulphate aerosols with natural and anthropogenic sources in south-central India Proceedings of 8th IGAC Conference, September 4–9, 2004. Christchurch, New Zealand.
- Kulshrestha U. C., Granat L., Engardt M., Rodhe H., (2005). Review of precipitation monitoring studies in India a search for regional patterns. *Atmos. Environ.* 39, 7403–7419.
- Kulshrestha U. C., Jain M., Mandal T. K., Gupta P. K., Sarkar A. K. Parashar D. C., (1999). Measurements of acid rain over Indian ocean and surface measurements of atmospheric aerosols at New Delhi during INDOEX pre-campaigns. *Curr. Sci.* 76, 968–972.
- Kulshrestha, U. C., Jain M., Saxena A. K., Kumar A., Parashar D. C., (1997). Contribution of sulphate aerosol to the rain water at urban site in India. In proceedings of IGAC international symposium on atmospheric chemistry and future global environment, Nagoya congress center, Nagoya, Japan, 11-13 November, 1997.
- Kulshrestha U. C., Kulshrestha M. J., Sekar R., Sastry G. S. R., Vairamani M., (2003b). Chemical characteristics of rainwater at an urban site of south-central India. *Atmos. Environ.* 37, 3019–3026.

- Kulshrestha U. C., Kumar B., (2014). Airmass Trajectories and Long Range Transport of Pollutants: Review of Wet Deposition Scenario in South Asia. *Adv in Meteor*, Volume 2014, Article ID 596041, 14 pages, <http://dx.doi.org/10.1155/2014/596041>.
- Kulshrestha U. C., Kumar N., Saxena A., Kumari K. M., Srivastava S. S., (1995). Identification of nature and source of atmospheric aerosols near Taj Mahal (Agra). *Environmental Monitoring and Assessment*, 34, 1-11.
- Kulshrestha U. C., Reddy L. A. K., Satyanarayana J., Kulshrestha M. J., (2009). Real-time wet scavenging of major chemical constituents of aerosols and role of rain intensity in Indian region. *Atmos Environ*, 43: 5123-5127.
- Kulshrestha U. C., Sarkar A. K., Srivastava S. S., Parashar D. C., (1996). Investigation into atmospheric deposition through precipitation studies at New Delhi (India). *Atmos. Environ.* 30, 4149–4154.
- Kulshrestha U. C., Saxena A., Kumar N., Kumari K. M., and Srivastava S. S., (1998). Chemical composition and association of size-differentiated aerosols at a suburban site in a semi-arid tract of India. *J. Atmos. Chem.*, 29, 109–118, doi:10.1023/A:1005796400044.
- Kumar A., Sarin M. M., Sudheer A. K., (2008). Mineral and anthropogenic aerosols in Arabian Sea-atmospheric boundary layer: Sources and spatial variability. *Atmos. Environ.*, 42, 5169–5181, doi:10.1016/j.atmosenv.2008.03.004.
- Kumar B., Kopal V., Kulshrestha U C., (2014). Deposition and Mineralogical Characteristics of Atmospheric Dust in relation to Land Use and Land Cover Change in Delhi (India). *Geography Journal*, Volume 2014, Article ID 325612, 11 pages, <http://dx.doi.org/10.1155/2014/325612>.
- Kumar B., Singh S., Gupta G. P., Lone F. A., Kulshrestha U. C., (2016). Long range transport and wet deposition fluxes of major chemical species in snow at Gulmarg in north western Himalayas (India). *Aerosol and air quality research*, x: 1–12, xxxx.
- Kumar N., Kulshrestha U. C., Saxena A., Khare P., Kumari K. M., Srivastava, S. S., (1993). Effect of anthropogenic formate and acetate level in precipitation at four sites in Agra. *Atmos. Environ.* 27B: 87–91.
- Kuniyal J. C., Sharma M., Chand K., Mathela C. S., (2013). Water soluble ionic components in particulate matter (PM10) during high pollution episode days at Mohal and Kothi in the north-western Himalaya, India. *Aerosol air qual res*, x:1-15,xxxx.
- Kuylenstierna J. C. I., Rodhe H., Cinderby S., Hicks K., (2001). Acidification in developing countries: Ecosystem sensitivity and the critical load approach on a global scale. *Ambio*, 30(1): 20-28.
- Lawrence G. B., David M. B., Lovett G. M., Murdoch P. S., Burns D. A., Stoddard J. L., Baldigo B. P., Porter J. H., Thompson A.W., (1999). Soil calcium status and the response of stream chemistry to changing acidic deposition rates. *Ecological Applications* 9, 1059–1072.

- Lee Y. C., Yang X., Wenig M., (2010). Transport of dusts from East Asian and non-East Asian sources to Hong Kong during dust storm related events 1996-2007. *Atmospheric Environment* 44, 3728-3738.
- Leskiw L. A., (1998). Land capability classification for forest ecosystem in the oil stands region. Alberia Environmental Protection, Edmonton.
- Likens G. E., Driscoll C. T., Buso D. C., (1996). Long-term effects of acid rain: response and recovery of a forest ecosystem. *Science* 272, 244–246.
- Lone F. A., Khan M. A., Qureshi N., Kirmani N. A., Sidiquee S. H., Shah R. A., (2010). Environmental chemistry of a rare muddy snowfall occurrence on Alpine zone glaciers of Gulmarg, Kashmir Himalaya, India. *Current World Environment* Vol. 5(2), 271-278.
- Lowenfels J., Lewis W., (2011). *Teaming with Microbes: The Organic Gardener's Guide to the Soil Food Web. Revised Edition (Science for Gardeners)*, pp. 49, 110. ISBN 978-1-60469-113-9.
- Madsen S. T., (2013). *State, Society and the Environment in South Asia* Routledge (2013)
- Mahadeven T. N., Negi B. S., Meenakshy V., (1989). Measurement of element composition of aerosol matter and precipitation from a remote continental site in India. *Atmospheric Environment* 23, 869-874.
- Male D. H., (1980). The seasonal snowcover. In *Dynamics of snow and Ice Masses*, S. Colbeck (Ed.). Academic Press, Toronto, pp. 305-395.
- Malik M. S., Abbasi M. K., Rahim N., (2000). Laboratory study of physical-chemical characteristics and the nutrient status of soils collected from Rawalakot Azad Jammu and Kashmir, *Pakistan Journal of biological sciences* 3(12), 2082-2086
- Marini-Bettòlo G. B., (1986). *Chemical Events in the Atmosphere and their Impact on the Environment* Studies in Environmental science 26 Elsevier
- Marinoni A., Polesello S., Smiraglia C., Valssecchi S., (2001). Chemical composition of fresh snow samples from the southern slope of Mt. Everest region (Khumbu-Himal region, Nepal). *Atmospheric Environment* 35, 3183-3190.
- Marinoni A., Polesello S., Smiraglia C., Valssecchi S., (2005). Chemical composition of fresh snow samples from the southern slope of Mt. Everest region, *Atmos. Environ.* 35: 3183-3190.
- Mathys P., Stern W. B., Oglesby L., Braun-Fahrländer C., Ackermann-Liebrich U., Jantunen M., Kynjli N., (2001). Elemental analysis of airborne particulate matter by ED-XRF within the European EXPOLIS study. *ICP Information Newsletter* 2001; 27(3):190-195.
- Mayewski P. A., Lyons W. B., Ahmad N., (1983). Chemical composition of a high altitude fresh snowfall in the Ladakh, Himalayas. *Geophys Res Lett* 10 (1): 105–108.
- McCauley A., Jones C., Jacobsen J., (2011). *Plant Nutrient Functions and Deficiency and Toxicity Symptoms*, Montana state university, College of Agriculture Dean, June 2011,



- Menz F. C., Sep H. M., (2004). Acid rain in Europe and the United States: an update. *Environmental Science & Policy*, 7, 253–265.
- Mills M. M., Ridame C., Davey M., La Roche J., Geider R. J., (2004). Iron and phosphorus co limited nitrogen fixation in the eastern tropical North Atlantic. *Nature* 429, 292–294.
- Minocha R., Long S., Magill A. H., Aber J., McDowell, W. H., (2000). Foliar free polyamine and inorganic ion content in relation to soil and soil solution chemistry in two fertilized stands at the Harvard Forest, Massachusetts. *Plant Soil*. 222: 119–137.
- Mitchell H. L., Chandler R. F., (1939). The nitrogen nutrition and growth of certain deciduous trees of Northeastern United States. *The Blackrock Forest Bulletin* no. 11. Cornwall-on-the-Hudson, NY.
- Naik M. S., Khemani L. T., Momin G. A., Rao P. S. P., Safai P. D., Pillai A.G., (1995). Chemical composition of fresh snow from Gulmarg, North India”, *Environ Pollut*, 87 (2): 167–171.
- Naiman R. J., Pinay G., Johnston C. A., Pastor J., (1994). Beaver influences on the long-term biogeochemical characteristics of boreal forest drainage networks.- *Ecology*, 75: 905–921. *Nutrient Management Module* No. 9.
- Nakamae K., and Shiotani M., (2013). Interannual variability in Saharan dust over the North Atlantic Ocean and its relation to meteorological fields during northern winter, *Atmos Res* 122: 336–346.
- NESS, 1999. Ambient Air Quality Monitoring of Kathmandu Valley, ADB TA 2847-NEP Project, unpublished report submitted to MoPE.
- Niu H., He Y., Zhu G., Xin H., Du J., Pu T., Lu X., (2013) Environmental implications of the snow chemistry from Mt. Yulong, southeastern Tibetan Plateau. *Quaternary International* 313-314, 168-178.
- Ozawa M., Shibata H., Satoh F., Sasa K., (2001). Effects of Surface Soil Removal on Dynamics of Dissolved Inorganic Nitrogen in a Snow-Dominated Forest, *Optimizing Nitrogen Management in Food and Energy Production and Environmental Protection: Proceedings of the 2nd International Nitrogen Conference on Science and Policy*, The ScientificWorld (2001) 1(S2), 527–533, ISSN 1532-2246; DOI 10.1100/tsw.2001.311
- Pacyna J. M., (1995). Sources, particle size distribution and transport of aerosols. In: Kouimtzis T, Samara C, editors. *Airborne particulate matter*. Berlin a.o.: Springer.
- Palm E., Tveitereid M., (1979). On heat and mass flow through dry snow. 3: *Geophys. Res.*, 84(C2), 745-749.
- Pomeroy J. W., Jones H. G., Tranter M. A. R. N. N., Lilbak G., (2005). 163: Hydrochemical Processes in Snow-covered Basins *Encyclopedia of Hydrological Sciences*. Edited by M G Anderson. 2005 John Wiley & Sons. Ltd.

- Rahn K. A., (1976). The chemical composition of the atmospheric aerosol, technical report, 265 pp., Grad. Sch. of Oceanogr., Univ. of R. I., Kingston.
- Raina A. K., Gupta M. K., (2009). Soil and vegetation studies in relation to parent material of Garhwal Himalayas, Uttarakhand (India). *Ann. For.*, 17(1): 71-82.
- Ramanathan V., Crutzen P. J., Kiehl J. T., Rosenfeld D., (2001). Aerosols, climate, and the hydrological cycle. *Science* 294: 2119-2124.
- Rao P. S. P., Momin G. A., Safai P. D., Pillai A. G., Naik M. S., Khemani L. T., (1990) Impact of Ca and SO<sub>4</sub> on pH of rain water in rural environment in India. *Indian J Environ Pollut* 10, 941–943.
- Rao R. V. S., Mahapatra S. K., Velma T. P., Sidhu G. S., Raila K. P. C., (1997). Characterization and classification of some soils of Shiwalik Hills in Himachal Pradesh. *Agropedology*, 7, 14-21.
- Rashid A., Ahmad N., (1994). Soil testing in Pakistan. Proceedings of FADINAP regional workshop on cooperation in soil testing for Asia and the pacific, held in Bangkok, Thailand, August, 16 to 18, 1993.
- Rastogi N., Sarin M. M., (2009). Quantitative chemical composition and characteristics of aerosols over western India: One-year record of temporal variability, *Atmospheric Environment* 43, 3481–3488.
- Reddy L. A. K., Kulshrestha U. C., Satyanarayana J., Kulshrestha M. J., Moorthy K. K., (2008). Chemical characteristics of PM<sub>10</sub> aerosols and air mass trajectories over Bay of Bengal and Arabian Sea during ICARB”, *Journal of Earth System Science*, 117, 345–352.
- Redmond H. E., Dial K. D., Thompson J. E., (2010). Light scattering and absorption by wind blown dust: Theory, measurement, and recent data. *Aeolian Research* 2, 5–26.
- Ren J. W., Qin D. H., Kang S. C., Hou S. G., Pu J. C., Jin Z. F., (2003). Glacier variations and climate warming and drying in the central Himalayas. *Chinese Science Bulletin* 48(23): 2478-2482.
- Reynolds B. (1983). The chemical composition of snow at a rural upland site in Mid-Wales. *Atmos. Environ.*, 17, 1849-51.
- Riccio A., Giunta G., Chianese E., (2007). The application of a trajectory classification procedure to interpret air pollution measurements in the urban area of Naples (Southern Italy), *Science of the Total Environment*, 376, 198–214.
- Robertson G. P., Vitousek P. M., (1981). Nitrification in primary and secondary succession. *Ecology* 62:376–386.
- Rodhe H., (1972). A study of the sulfur budget for the atmosphere over Northern Europe. *Tellus* 24, 128- 138.
- Rodhe H., Crutzen P., Vanderpol A., (1981). Formation of Sulphuric and Nitric acid in the atmosphere during Long Range Transport *Tellus* 33, 132.

- Rodhe H., Dentener F., Schulz M. (2002). The global distribution of acidifying wet deposition. *Environmental Science & Technology*, 36(20), 4382-4388.
- Rodhe H., Granat L., (1984). An evaluation of sulfate in European precipitation 1955–1982. *Atmos. Environ.* 1984, 18: 2627–263.
- Rodríguez S., Alastuey A., Querol X., (2012). A review of methods for long term in situ characterization of aerosol dust, *Aeolian Research* 6 (2012) 55–74.
- Ross D. S., Ketterings Q., (2011). Recommended Methods for Determining Soil Cation Exchange Capacity, Chapter 9, Cooperative Bulletin No. 493, Recommended Soil Testing Procedures for the Northeastern United States Last Revised 5/2011
- Roy H. F., Larry S. M., Roy H. D., (1981). *Fertilizers and soil amendments*. Prentice Hall, Inc., Englewood Cliffs, New Jersey.
- Safai P. D., Khemani L. T., Momin G. A., Rao P.S. P., Pillai A. G., (1993). Mass size distribution and chemical composition of aerosols at silent valley, India. *Indian J of Radio and space physics* 22, February, 56-61.
- Safai P. D., Rao P. S. P., Momin G. A., Ali K., Chate D. M., Praveen P. S., (2004). Chemical composition of precipitation during 1984–2002 at Pune, India. *Atmos. Environ.* 38, 1705–1714.
- Sakihama H., Ishiki M., Tokuyama A., (2008). Chemical characteristics of precipitation in Okinawa Island, Japan, *Atmos Environ* 42: 2320–2335.
- Satsangi A., Pachauri T., Singla V., Lakhani A., Kumari K. M., (2013). Water soluble ionic species in atmospheric aerosols: Concentrations and sources at Agra in the Indo-Gangetic Plain (IGP). *Aerosol Air Qual. Res.*, 13, 1877–1889, doi:10.4209/aaqr.2012.08.0227.
- Satyanarayana J., Reddy L. A. K., Kulshrestha M. J., Rao R. N., Kulshrestha, U. C., (2010). Chemical composition of rain water and influence of airmass trajectories at a rural site in an ecological sensitive area of Western Ghats (India)”, *Journal of Atmospheric Chemistry*, 66,101-116.
- Saxena A., Kulshrestha U. C., Kumar N., Kumari K. M., Srivastava S. S., (1992). Dry deposition of nitrate and sulphate on surrogate surfaces. *Environ. Int.*, 18, 509–513, doi:10.1016/0160-4120(92)90269-A.
- Schemenauer R. S., Banic C. M., Urquizo N., (1995). High elevation fog and precipitation chemistry in southern Quebec, Canada. *Atmos. Environ.* 29 (2235–2252), 1995.
- Schwesig D., Kalbitz K., Matzner, E., (2003). Effects of aluminium on the mineralization of dissolved organic carbon derived from forest floors. *Eur. J. Soil Sci.* 54: 311–322.
- Segura S., Estelle V., Esteve A. R., Utrillas M. P., Martí´nez-Lozano J. A., (2013). Analysis of a severe pollution episode in Valencia (Spain) and its effect on ground level particulate matter, *Journal of Aerosol Science* 56, 41–52.

- Seinfeld J. H., Pandis S. N., (2006). *Atmospheric Chemistry and Physics - From Air Pollution to Climate Change* (2nd Edition), John Wiley & Sons.
- Shadbolt R. P., Waller E. A., Messina J. P., Winkler J. A., (2006). Source regions of lower-tropospheric airflow trajectories for the lower peninsula of Michigan: a 40-year air mass climatology”, *Journal of Geophysical Reserach-Atmos.* 111.
- Shahid M. A. K., Awan M. S., Hussain K., Sabir R., (2013). Acidic rain probability and solid aerosol concentration in the atmosphere of Faisalabad (Pakistan). *Peak J Physical and Environ Sci Res* Vol.1(2): 12-22.
- Sharma D., and Kulshrestha U. C., (2014). Spatial and Temporal Patterns of Air Pollutants in Rural and Urban Areas of India *Environmental Pollution* 10.1016/j.env. pol. 2014.08.026
- Shen Z., Cao J., Arimoto R., Han Z., Zhang R., Han Y., Liu S., Okuda T., Nakao S., Tanaka S., (2009). Ionic composition of tsp and PM<sub>2.5</sub> during dust storms and air pollution episodes at Xi'an, China. *Atmos. Environ.* 43, 2911–2918.
- Shon Z., Kim K., Song S., Jung K., Kim N., Lee J., (2012). Relationship between water-soluble ions in PM<sub>2.5</sub> and their precursor gases in Seoul Megacity, *Atmospheric Environment*, 59 , 540-550.
- Shrestha S., Pandey V. P., Yoneyama Y., Shrestha S., Kazama F., (2013). An evaluation of rainwater quality in Kathmandu Valley, Nepal, *Sustain. Environ. Res.*, 23(5), 341-350, 341.
- Shrestha A. B., Wake C. P., Dibb J. E., Whitlow S. I., (2002). Aerosol and Precipitation Chemistry at a Remote Himalayan Site in Nepal, *Aerosol Sci and Tech* 36: 441–456.
- Silva J. A., Uchida, R., (2000). eds. *College of Tropical Agriculture and Human Resources, University of Hawaii at Manoa, ©2000. From: Plant Nutrient Management in Hawaii's Soils, Approaches for Tropical and Subtropical Agriculture. Chapter 3- Essential Nutrients for Plant Growth: Nutrient Functions and Deficiency Symptoms.*
- Singh S., Kulshrestha U. C., (2012). Abundance and distribution of gaseous ammonia and particulate ammonium at Delhi, *India Biogeosciences* 9 5023–9
- Singh S., Kulshrestha U. C., (2014). Rural versus urban gaseous inorganic reactive nitrogen in the Indo-Gangetic plains (IGP) of India *Environ. Res. Lett.* 9 (2014) 125004 (9pp)
- Singh S., Kumar B., Gupta G. P., Kulshrestha, U. C., (2014 b). Signatures of increasing energy demand of past two decades as captured in rain water composition and air mass trajectory analysis at Delhi (India), *J Energy, Environ and Carbon credits*, Vol. 4, Issue-3, ISSN: 2249-8621.
- Singh S., Gupta G. P., Kumar B., Kulshrestha U. C., (2014a). Comparative study of indoor air pollution using traditional and improved cooking stoves in rural households of Northern India, *Energy Sustain Dev* 19, 1–6.

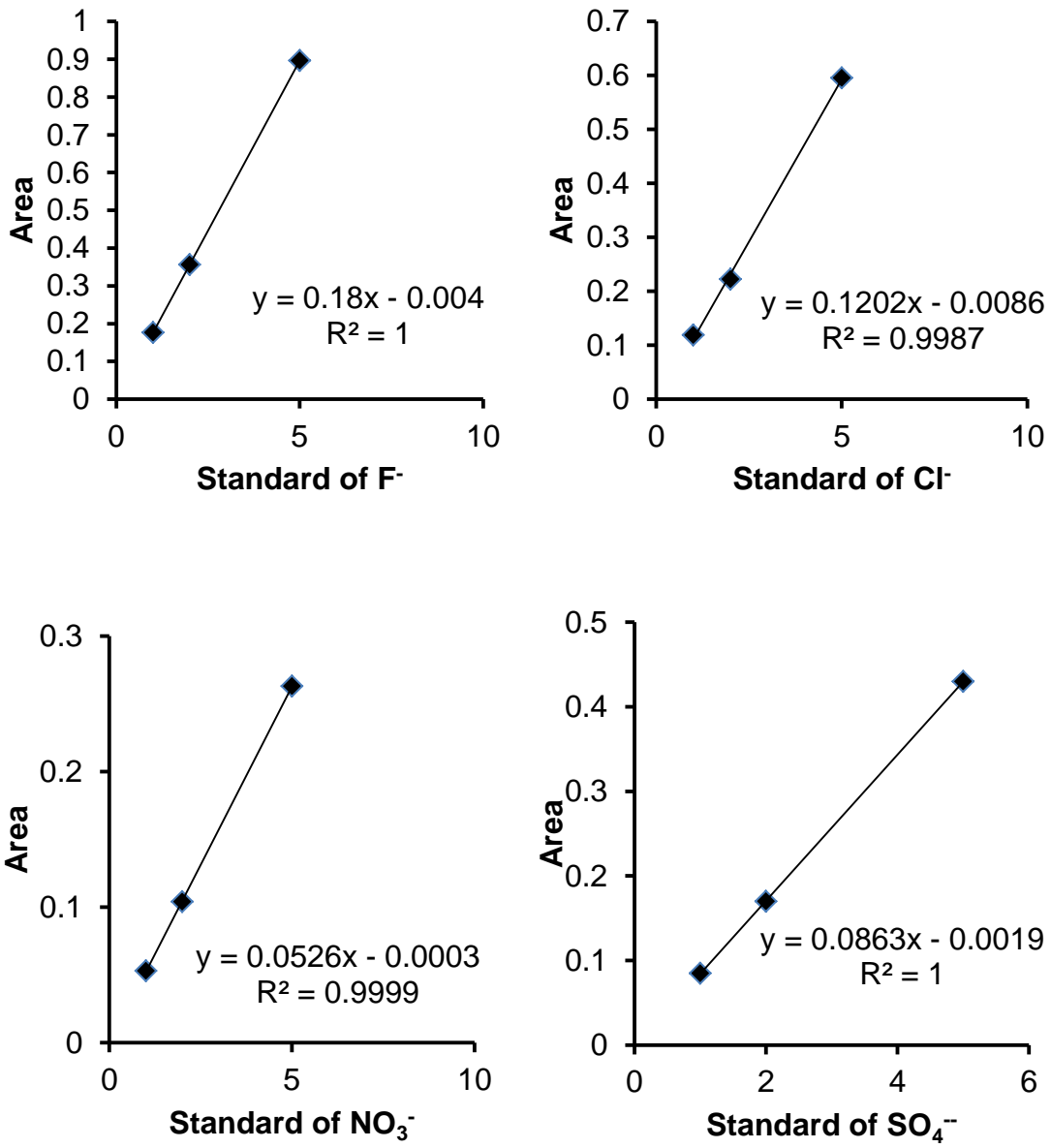
- Singh S., Sharma A., Kumar B., Kulshrestha U. C., (2017). Wet deposition fluxes of atmospheric inorganic reactive nitrogen at an urban and rural site in the Indo-Gangetic Plain. 2017. Atmospheric Pollution Research, <http://dx.doi.org/10.1016/j.apr.2016.12.021>.
- SOE, (2001). Report Nepal: State of the Environment, UNEP, ISBN: 92-807-2012-0.
- Sverdrup H., Warfvinge P., Nihlgard B., (1994). Assessment of soil acidification effects on forest growth in Sweden. *Water Air Soil Pollut* 1994;78:1, 36.
- Tiwari S., Chate D. M., Bisht D. S., Srivastava M. K., Padmanabhamurty B., (2012). Rainwater chemistry in the North Western Himalayan Region, India”, *Atmos Res*, 104-105: 128–138.
- Tiwari S., Gupta G. P., Kulshrestha U. C., (2016). Summer Time Dustfall Fluxes of Reactive Nitrogen and Other Inorganic Species over the Tropical Megacity of Indo-Gangetic Plains, *Earth Interactions*, Volume 20 (2016), Paper No. 23.
- Tiwari S., Kulshrestha U. C., Padmanabhamurty B., (2007). Monsoon rain chemistry and source apportionment using receptor modeling in and around National Capital Region (NCR) of Delhi, India. *Atmos. Environ.* 41, 5595–5604.
- Tranter M., Daveis T. D., Abrahams P. W., Blackwood I., Brimblecombe P., Vincent, C. E., (1967) Spatial variability in the chemical composition of snowcover in a small, remote, scotish catchment. *Atmos. Env.*, 21, 853-62.
- Tripathee L., Kang S., Rupakheti D., Zhang Q., Huang J., Sillanpää M., (2016). Water-Soluble Ionic Composition of Aerosols at Urban Location in the Foothills of Himalaya, Pokhara Valley, Nepal, *Atmosphere* 2016, 7, 102; doi:10.3390/atmos7080102
- Tripathee L., Kang S., Huang J., Sillanpää M., Sharma C. M., Luthi Z. L., Guo J., Paudyal R., (2014). Ionic composition of wet precipitation over the southern slope of central Himalayas, Nepal, *Environ Sci Pollut Res*, 21:2677–2687.
- Vadrevu K. P., (2013). Chris Justice, Prasad Thenkabail, Garik Gutman, 2013 Summary of the 2013 NASA Land Cover/Land Use Change Regional Science Meeting, South India *The Earth Observer* 25(2) 24-30
- vadrevu K. P., Ellicott E., Giglio L., Vermote E., Justice C., Lau W., ( 2012). Vegetation Fires in the Himalayan Region - Aerosol Load, Black Carbon Emissions and Smoke Plume Heights *Atmospheric Environment* 47 241–251
- Valsecchi S., Smiraglia C., Tartari G., Polesello S, (1999). Chemical composition of Monsoon deposition in the everest region, *science total Env.* 226: 187-199.
- Vet R., Artz R. S., Carou S., Shaw M., Ro C. U., Aas W., Baker A., Bowersox V.C., Dentener F., Galy-Lacaux C., Hou A., Pienaar J. J., Gillett R., Forti M. C., Gromov S., Hara H., Khodzher T., Mahowald N. M., Nickovic S., Rao P. S. P., Reid N. W., (2014). A global assessment of precipitation chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus. *Atmospheric Environment*, 93, 3-100.

- Vijayvergia R. P. (2008). Eutrophication: A Case Study of Highly Eutrophicated Lake Udaisagar, Udaipur (Raj.), India with regards to its Nutrient Enrichment and Emerging Consequences. In Proceedings of Taal2007: The 12th World Lake Conference (Vol. 1557, p. 1560).
- Vishwa B. S. C., Kaur B. K., Simrit K., (2013). Land Use/Cover change and its implications for Kullu District of Himachal Pradesh India International journal of Geomatics and Geosciences Vol.3 issue 3 pages 538-551
- Wang C., Zhu W., Wang Z., Guicherit R., (2000). Rare Earth elements and other metals in atmospheric particulate matter in the western part of the Netherlands. *Water Air Soil pollut.* 121, 109-118.
- Wang Y., Zhuang G., Sun Y., An Z., (2006). The variation of characteristics and formation mechanisms of aerosols in dust, haze, and clear days in Beijing. *Atmos. Environ.* 2006, 40, 6579–6591.
- White P. J., Broadley M. R., (2001). Chloride in Soils and its Uptake and Movement within the Plant: A Review, *Annals of Botany* 88: 967-988.
- WHO, (1996). Revised WHO Air Quality Guidelines. Copenhagen, World Health Organization, Regional Office for Europe.
- WMO, (1994). In: Mohnen, V., Santroch, J., Vet, R. (Eds.), Report of the workshop on precipitation chemistry laboratory techniques, Hradec Kralove, Czech Republic 17–21 October. WMO Report no 102.
- Xu J., Zhang Q., Li X., Ge X., Xiao C., Ren J., Qin D., (2013). Dissolved Organic Matter and Inorganic Ions in a Central Himalayan Glacier: Insights into Chemical Composition and Atmospheric Sources. *Environmental science and Technology*, 47, 6181-6188.
- Yalcin K., Wake C. P., Dibb J. E., Whitlow S. I., (2006). Relationships between aerosol and snow chemistry at King Col, Mt. Logan Massif, Yukon, Canada. *Atmos Environ* 40: 7152-7163.
- Zhang J., Ouyang, Y., Ling, D., (2007b). Impacts of simulated acid rain on cation leaching from the Latosol in south China. *Chemosphere*, 67, 2131–2137.
- Zhang M., Wang S., Wu F., Yuan X., Zhang Y., (2007a). Chemical Composition of Wet Precipitation and Anthropogenic Influence at a Developing Urban Site in Southeastern China. *Atmos. Res.* 84: 311–322.
- Zhang X., Jiang H., Zhang Q., Zhang X., (2012). Chemical characteristics of rainwater in northeast China, a case study of Dalian. *Atmospheric Research xxx* (2012) xxx–xxx.
- Zhang Y., Xiu G., Wu X., Moore C. W., Wang J. , Cai J., Zhang D., Shi C., Zhang R., (2013). Characterization of mercury concentrations in snow and potential sources, Shanghai, China, *Science of the total Environment*, 449, 434-442.

Zhao J., Peng P., Song, J., (2010). Research on flux of dry atmospheric falling dust and its characterization in a subtropical city, Guangzhou, South China. *Air Qual. Atmos. Health*, 3, 139–147, doi:10.1007/s11869-009 0062-y.

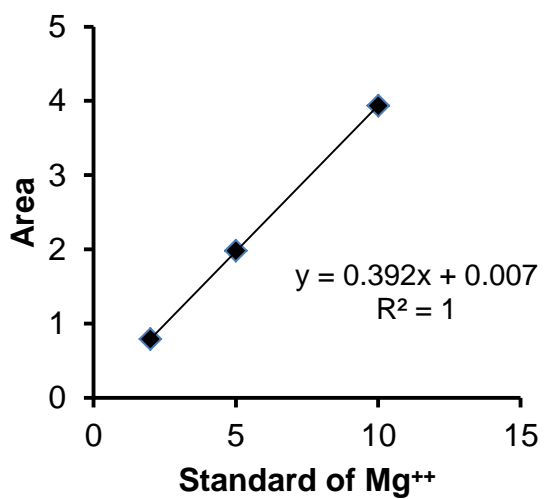
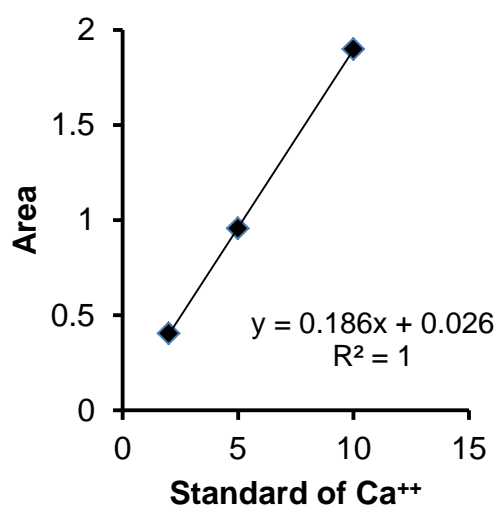
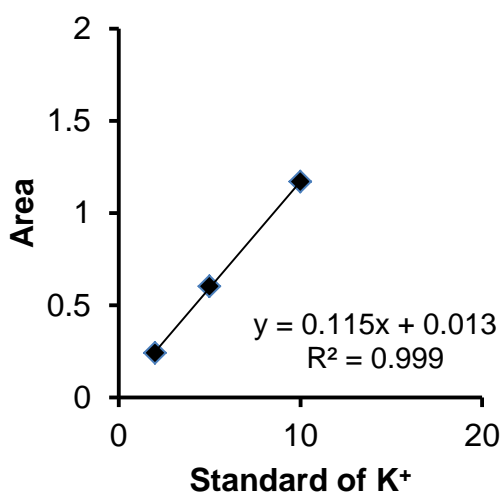
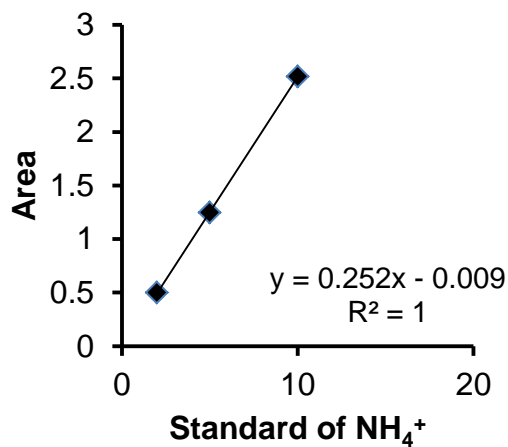
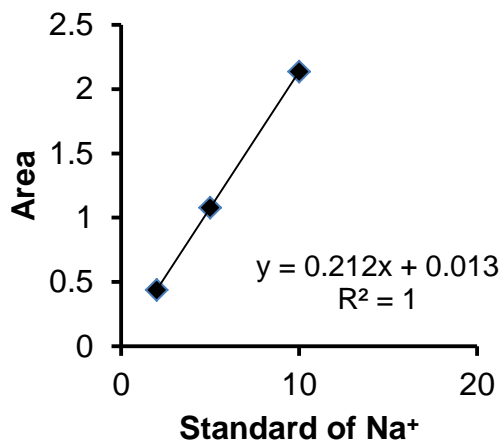
Zhu G. F., Pu T., He Y. Q., Shi P. J., Zhang T., (2012). Seasonal variations of major ions in fresh snow at Baishui Glacier No. 1, Yulong Mountain, China. *Environ Earth Sci.* 69, 1-10.

## APPENDICES



**Fig. a:** Calibration curve for anions (1, 2, 5 ppm concentrations).





**Fig. b:** Calibration curve for cations (2, 5, 10 ppm concentrations).



**Snowfall collection**

# *List of Publications & Conferences*

## List of Publications

1. Singh, S., Sharma, A., **Kumar B.**, and Kulshrestha, U. C., 2017. Wet deposition fluxes of atmospheric inorganic reactive nitrogen at an urban and rural site in the Indo-Gangetic Plain, **Atmospheric Pollution Research**, ISSN: 1309-1042, xxx, 1-9, <http://dx.doi.org/10.1016/j.apr.2016.12.021>.
2. **Kumar, B.**, Singh, S., Gupta, G. P., Lone, F. A., Kulshrestha, U. C., 2016. Long range transport and wet deposition fluxes of major chemical species in snow at Gulmarg in north western Himalayas (India). **Aerosol and Air Quality Research**, 16: 606–617, ISSN: 1680-8584 print / 2071-1409, doi: 10.4209/aaqr.2015.01.0056.
3. Gupta G. P., **Kumar, B.**, and Kulshrestha, U. C., 2016. Impact and pollution indices of urban dust on selected plant species for green belt development: mitigation of the air pollution in NCR Delhi, India. **Arabian Journal of Geosciences**, ISSN: 1866-7511, 9: 136. DOI 10.1007/s12517-015-2226-4.
4. Gupta G. P., Singh, S., **Kumar, B.**, and Kulshrestha, U. C., 2016. Deposition and impact of Urban Atmospheric Dust on Two Medicinal Plants during Different Seasons in NCR Delhi. **Aerosol and Air Quality Research**, ISSN: 1680-8584, 16: 2920–2932, doi: 10.4209/aaqr.2015.04.0272.
5. Singh, R., Kulshrestha, M. J., **Kumar, B.**, Chandra, S., 2015. Impact of anthropogenic emissions and open biomass burning on carbonaceous aerosols in urban and rural environments of Indo-Gangetic Plain. **Air Quality, Atmosphere and Health**, ISSN: 1873-9326, DOI 10.1007/s11869-015-0377-9.
6. **Kumar, B.**, Gupta, G. P., Singh, S., Lone, F. A., Kulshrestha, U. C., 2015. Snow Chemistry at Mukteshwar in Central Himalayan Region of India. **Modern Chemistry and applications**, ISSN: 2329-6798, 3:3, <http://dx.doi.org/10.4172/2329-6798.1000160>.
7. **Kumar, B.**, Singh, S., Gupta, G. P., Lone, F. A., Kulshrestha, U. C., 2015. Atmospheric Deposition of Reactive Nitrogen and Other Species in Relation with

Long Range Transport and Land Use and Land Cover Change in North Western Himalayas. **IORE Journal of Environmental Science**. IJENV Vol2.2 (2016).

8. Singh, S., **Kumar, B.**, Gupta G. P., and Kulshrestha, U. C., 2015. Signatures of increasing energy demand of past two decades as captured in rain water composition and air mass trajectory analysis at Delhi, India, **Journal of Energy, Environment and carbon credit**, ISSN 2249-8261, 3:3.
9. Gupta G. P., Singh, S., **Kumar, B.**, and Kulshrestha, U. C., 2015. Industrial dust sulphate and its effects on biochemical and morphological characteristics of Morus (Morus alba) plant in NCR Delhi. **Environmental Monitoring and Assessment**, , ISSN: 1573-2959, 187:67, 0617-6369.
10. Gupta G. P., **Kumar, B.**, Singh, S., and Kulshrestha, U. C., 2015. Urban climate and its effect on biochemical and morphological characteristics of Arjun (terminalia arjuna) plant in NCR Delhi. **Chemistry and Ecology**, ISSN 0275-7540, 2015, 1-17.
11. Kumari, A., **Kumar, B.**, Manzoor, S., Kulshrestha, U. C., 2015. Status of Atmospheric Mercury Research in South Asia: A Review. **Aerosol and Air Quality Research**, 15: 1092–1109, doi: 10.4209/aaqr.2014.05.0098.
12. Kulshrestha, U. C., **Kumar, B.**, 2014. Airmass Trajectories and Long Range Transport of Pollutants: Review of Wet Deposition Scenario in South Asia. **Advances in Meteorology**, ISSN: 1687-9309, Volume 2014, Article ID 596041, 14 pages, <http://dx.doi.org/10.1155/2014/596041>.
13. **Kumar, B.**, Verma, K., Kulshrestha, U. C., 2014. Deposition and Mineralogical Characteristics of Atmospheric Dust in relation to Land Use and Land Cover Change in Delhi (India). **Geography Journal**, ISSN: 1475-4959, Volume 2014, Article ID 325612, 11 pages, <http://dx.doi.org/10.1155/2014/325612>.
14. Singh, S., Gupta G. P., **Kumar, B.**, and Kulshrestha, U. C., 2014. Comparative study of indoor air pollution using traditional and improved cooking stoves in rural

households of Northern India. **Energy for Sustainable Development**, ISSN: 0973-0826 , 19 (1–6).

15. **Kumar, B.**, Meena, Y., Gupta G. P., Singh, S., and Kulshrestha, U. C., 2013. Identification of Nature and Sources of Dustfall at Mukteshwer in Kumaon Region of Central Himalaya, India. **International Journal of Chemistry and Chemical Engineering**. Volume 3, Number 3, (149-154).
16. **Kumar, B.**, Gupta G. P., Singh, S., and Kulshrestha, U. C., 2013. Study of abundance and characterization of culturable bioaerosol at Delhi, India. **International journal of Environmental Engineering and management**. Vol. 4, No. 3, 219- 226.
17. Kulshrestha, U. C., **Kumar, B.**, Gupta, G. P., and S Singh, 2012. Importance of bioaerosols, black carbon and trace gases- defining criteria for good habitats, **Indian Journal of air pollution and control**, 2012.

### **Book chapter**

**Kumar B.**, Sudesh, 2017. Atmospheric deposition and ecosystem sensitivity. Air Pollution and Climate Change in South Asia : Issues, Impact and Initiatives, Editor- prof. U. C. Kulshrestha, ISBN : 9781910390344, **Athena Academic Ltd.** 145-157 St. John Street, London, EC1V 4PW, United Kingdom.

## Conferences

1. **Kumar, B.**, Singh, S., Gupta G. P., and Kulshrestha, U. C., 2011. Measurement of fireworks gaseous emissions during Diwali festival festivals at Delhi. Presented in national conference on **science of climate change and Earth's sustainability: issues and challenges** during 12-14 september, 2011. Earth Science India, Lucknow, India.
2. **Kumar, B.**, Singh, S., Gupta G. P., and Kulshrestha, U. C., 2011. Effect of Fireworks Air Pollution on Microbial Population during Diwali Festival at Delhi, **EBI conference** during 30-31 December, 2011. JMI, New Delhi.
3. **Kumar, B.**, Meena, Y., Chauhan, A., Singh, S., Gupta G. P., and Kulshrestha, U. C., 2012. Geochemical and anthropogenic influence on snow composition in kumaon region of Himalaya. 49<sup>th</sup> annual convention "**Towards the energy security- exploration, exploitation and new strategies, IGU conference**, Gandhinagar, Gujrat.
4. **Kumar, B.**, Meena, Y., Chauhan, A., Singh, S., Gupta G. P., and Kulshrestha, U. C., 2012. Chemistry of snowfall in relation to air mass trajectory at Nainital site in Himalayan region, **IASTA conference**, Mumbai.
5. **Kumar, B.**, Singh, S., Gupta G. P., and Kulshrestha, U. C., 2012. Short term high level accumulation of air pollutants due to pyrotechnics: a case study during diwali festival, **national seminar on environmental pollution and bioremediation**, JNU, New Delhi.
6. **Kumar, B.**, Meena, Y., Gupta G. P., Singh, S., and Kulshrestha, U. C., 2013. Identification of Nature and Sources of Dustfall at Mukteshwer in Kumaon Region of Central Himalaya, India. International Conference on "**Chemical, Environmental and Bioprocess Engineering**" (**CEBE - 2013**) Krishi Sanskriti, JNU, 21-22 Dec, 2013.
7. **Kumar, B.**, Gupta G. P., Singh, S., and Kulshrestha, U. C., 2013. Study of abundance and characterization of culturable bioaerosol at Delhi, India. 2<sup>nd</sup> International

Conference on “**Agriculture, Food Technologies and Environment – New Approaches**” (AFTENA - 2013) On 19<sup>th</sup> and 20<sup>th</sup> October, 2013 at JNU, New Delhi.

8. **Kumar, B.**, Gupta, G. P., Singh, S., Singh, S., and Kulshrestha, U. C., 2013. Dustfall Chemistry vis-à-vis influence of non-marine sources in central himalayan region of india. **National seminar on climate change, Environment and sustainable development** organized by NESAI and Jamia Hamdard, Held at Jamia Hamdard on 9-10 Dec, 2013.
9. **Kumar, B.**, Meena, Y., Gupta G. P., Singh, S., and KulshresthA, U. C., 2014. Deposition of mineral aerosols as dustfall components at Mukteshwer in kumaon region of central Himalayan, INDIA.50th annual convention on “**sustainability of earth system - the future challenges**”. IGU. 275, 2014.
10. **Kumar, B.**, Gupta G. P., Singh, S., and Kulshrestha, U. C., 2015. Deposition and transport of Acidic Constituents of Precipitation affecting Himalayas, **Acid rain conference**, Rochester, New York, USA.



HOSTED BY



Contents lists available at ScienceDirect

# Atmospheric Pollution Research

journal homepage: <http://www.journals.elsevier.com/locate/apr>

## Wet deposition fluxes of atmospheric inorganic reactive nitrogen at an urban and rural site in the Indo-Gangetic Plain

Saumya Singh, Anshu Sharma, Bablu Kumar, U.C. Kulshrestha\*

School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, 110067, India

### ARTICLE INFO

#### Article history:

Received 11 June 2016

Received in revised form

22 December 2016

Accepted 25 December 2016

Available online xxx

#### Keywords:

Wet deposition flux

Nitrogen

Indo-Gangetic Plain

Delhi

LULC

Agriculture

### ABSTRACT

Excess nitrogen deposition is a matter of concern for sensitive ecosystems. However, understanding the sources and transport of Nr species has been a challenge due to limited observations of atmospheric deposition of the key Nr species across India. In this study, wet deposition of atmospheric inorganic Nr species was investigated during the year 2013 at two regionally representative sites: Delhi (an urban site) and Jaunpur (a rural site). These sites are located in the Indo-Gangetic Plain (IGP) region, which is one of the most populated and fertile regions of India. The average  $\text{NH}_4^+$  concentrations in rain water were found to be  $25.4 \mu\text{eq l}^{-1}$  and  $98.5 \mu\text{eq l}^{-1}$  at the rural and urban sites, respectively, whereas average  $\text{NO}_3^-$  concentrations were  $12.4 \mu\text{eq l}^{-1}$  and  $28.7 \mu\text{eq l}^{-1}$  at the rural and urban sites (respectively). The annual average wet deposition fluxes of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  at Delhi were calculated as  $10.45$  and  $3.05 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  respectively, whereas at Jaunpur the fluxes were  $3.19$  and  $1.56 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  respectively. In order to assess the Nr deposition, our estimates showed 486% increase in  $\text{NO}_3^-$  (from  $0.52$  to  $3.05 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) while 283%  $\text{NH}_4^+$  ( $2.72$ – $10.44 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) between 1994 and 2013 at Delhi, clearly indicating the effect of urbanization and Land Use Land Cover (LULC) change. Reduced versus oxidized N deposition contribution was also estimated. This study provides key quantitative information to support regional nitrogen budget estimates in south Asia.

© 2017 Turkish National Committee for Air Pollution Research and Control. Production and hosting by Elsevier B.V. All rights reserved.

### 1. Introduction

Nitrogen oxides ( $\text{NO}_x$ ) and ammonia are the key reactive nitrogen (Nr) species in atmospheric chemistry and ecosystem productivity. Although the major source of ammonia in the atmosphere is agriculture, other sources can include industry, landfills, household products, biomass burning, motor vehicles, and even wild animals (Ianniello et al., 2010). Before 1995, the contribution of vehicles to non-agricultural  $\text{NH}_3$  emissions was negligible, but in recent times  $\text{NH}_3$  concentrations in urban environments have also increased due to the over-reduction of nitrogen oxide compounds in catalytic converters of automobile exhaust and industrial power stations (Sutton et al., 1995; Sutton et al., 2000). Fossil fuel emissions and intensive agricultural

activities have drastically accelerated the nitrogen (N) cycle, resulting in increasing deposition rates of N species (Galloway et al., 2008; Penuelas et al., 2012; Canfield et al., 2010). Increasing Nr deposition has many adverse effects on human health, vegetation health, air quality, soil acidification, eutrophication, and most importantly global climate change (Sutton et al., 1994; Sun et al., 2004; Ianniello et al., 2011). Further, it affects the global carbon cycle (Goulding et al., 1998; Galloway et al., 2004). Once the reactive nitrogen species are released into the atmosphere, their fate is decided by several processes such as transformation, transport, and deposition. Nr species are deposited either through dry deposition or wet removal processes. Despite a long history of precipitation composition measurements (almost 150 years), the spatial and temporal variations of atmospheric Nr deposition remain unclear due to the complexity of reactions during transport and deposition (Park and Lee, 2002). Nevertheless, the wet deposition of Nr species has been studied by a number of groups as part of acid deposition studies. Available research indicated N deposition reached  $70 \text{ Tg yr}^{-1}$  N and

\* Corresponding author.

E-mail address: [umeshkulshrestha@gmail.com](mailto:umeshkulshrestha@gmail.com) (U.C. Kulshrestha).

Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control.



## Long Range Transport and Wet Deposition Fluxes of Major Chemical Species in Snow at Gulmarg in North Western Himalayas (India)

Bablu Kumar<sup>1</sup>, Sudha Singh<sup>1</sup>, Gyan Prakash Gupta<sup>1</sup>, Farooq Ahmad Lone<sup>2</sup>,  
Umesh Chandra Kulshrestha<sup>1\*</sup>

<sup>1</sup> School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110067, India

<sup>2</sup> Centre for Climate Change and Mountain Agriculture, SKUAST Kashmir, Shalimar, Srinagar, 190025 (J&K), India

### ABSTRACT

The study reports snow chemistry and long range transport of pollutants at Gulmarg in north-western Himalayan region of India during winters of 2012–2013. The pH of snowmelt varied between 5.16 and 7.68 with an average of 5.90. The frequency distribution of pH of snowmelt showed that the maximum number of samples (31%) had pH between 6.81 and 7.20. However, 12% samples were observed to be acidic (below 5.6). Scavenging ratios (SR) values suggested that crustal components ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) are efficiently removed by snow. The study site has significant influence of non-marine sources. Wet deposition contributed 34, 27, 45, 71, 8 and 13  $\text{meq m}^{-2}$  fluxes of  $\text{nssSO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{nssCa}^{2+}$ ,  $\text{nssMg}^{2+}$  and  $\text{nssK}^+$  respectively. Both local emissions as well as long range transport (LRT) of pollutants were found to be the sources of these ionic species. Backward airmass trajectory calculations showed that this site received airmasses from six major sectors i.e., i) North Atlantic Ocean origin (NAO), ii) African origin (Af), iii) Middle East origin (ME), iv) European origin (Eu), v) Western India origin (InW), vi) Pakistan origin (Pk). The highest average pH (7.58) of the snowfall was noticed during InW airmasses which had the lowest ratios of  $\text{nssSO}_4^{2-}/\text{nssCa}^{2+}$  and  $\text{NO}_3^-/\text{nssCa}^{2+}$ . Very high pH has been observed in precipitation samples at Indian sites due to buffering of acidic components by atmospheric dust rich in  $\text{CaCO}_3$ . The lowest pH (4.94) was noticed for ME airmasses which had the highest  $\text{nssSO}_4^{2-}/\text{nssCa}^{2+}$  and  $\text{NO}_3^-/\text{nssCa}^{2+}$  ratios. Data of present study was compared with a study reported almost three decades ago. We noticed a drastic increase in the concentrations of anthropogenic components such as  $\text{nssSO}_4^{2-}$  (114%),  $\text{NO}_3^-$  (109%) and  $\text{NH}_4^+$  (90%). This is probably due to increase in LRT of pollutants as well as local activities during past three decades.

**Keywords:** Snow chemistry; Himalayan region; Acidic depositions; Wet fluxes; Airmass trajectories.

### INTRODUCTION

Rapid urbanization and industrialization processes during past few decades have led to global concern about various processes such as acid deposition, climate change, and monsoon modification etc. (Andreae and Crutzen, 1997; IPCC, 2014). If the present trend of growth rate are continued, Asian  $\text{SO}_2$  and  $\text{NO}_x$  emissions are expected to exceed that of European and North American emissions by 2020 (Galloway, 1995). Increasing emissions of aerosols are also going to affect air quality further affecting global and regional atmospheric phenomenon (IPCC, 2014). Deposition of such anthropogenic constituents via wet and dry removal processes has significant adverse impacts on terrestrial and aquatic ecosystems (Seinfeld and Pandis, 2006). Snowfall

which is considered as one of the most effective wet removal processes for air pollutants at high altitude sites, deposits significant amounts of biogeochemically important trace chemical species on various surfaces. Thereby, chemical composition of snowfall provides important information about air quality and sources of pollution. Data on chemical components of snow are important for other interpretations too including validation of regional and global transport models (Marinoni *et al.*, 2005; Budhavant *et al.*, 2014a).

Acid deposition has been a serious problem in North America, Europe and Japan (Hara and Akimoto, 1993; Galloway, 1995; Menz and Seip, 2004). It causes loss of fish populations, loss of soil nutrients, activation of few heavy elements, modification in microbial community structure and changes in forest ecosystem (Brimblecombe *et al.*, 2007). Comprehensive studies on acid deposition have been carried out by different workers globally (Galloway, 1995; Granat *et al.*, 2002; Rodhe *et al.*, 2002; Zhang *et al.*, 2007; Kulshrestha, 2013). There have been a number of studies on snow chemistry too (Valsecchi *et al.*, 1999; Kang *et al.*, 2004; Marinoni *et al.*, 2005; Kulshrestha and Kumar, 2014).

\* Corresponding author.

Tel.: 0091 11 26704320; Fax: 0091 11 2670 4320  
E-mail address: umeshkulshrestha@gmail.com

# Impact and pollution indices of urban dust on selected plant species for green belt development: mitigation of the air pollution in NCR Delhi, India

Gyan Prakash Gupta<sup>1</sup> · Bablu Kumar<sup>1</sup> · U. C. Kulshrestha<sup>1</sup>

Received: 10 August 2015 / Accepted: 20 October 2015 / Published online: 24 February 2016  
© Saudi Society for Geosciences 2016

**Abstract** This paper reports biochemical changes in foliar of four plant species due to deposition of atmospheric dust falling onto the foliar surface. The paper also reports air pollution tolerance index (APTI) and air pollution index (API) in order to categorize the selected plants into sensitive and tolerant species against air pollution and their usefulness for green belt development in National Capital Region (NCR) Delhi. Two sites and four plant species Arjun (*Terminalia arjuna*), Morus (*Morus alba*), Sheesham (*Dalbergia sissoo*), and Ashok (*Polyalthia longifolia*) were selected for this study. Results indicated that for all the plant foliar, the dustfall fluxes were more than two times higher at the industrial site (SB) than that at the residential site (JNU). Among major ions ( $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{-2}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ ),  $\text{Ca}^{++}$  and  $\text{SO}_4^{-2}$  had very high fluxes representing as major constituents of dustfall at both the sites. APTI values suggested that all the four species are sensitive species and can be used as biological indicators. API values suggested that Arjun and Morus are very good performers (API=5) whereas Sheesham and Ashok as only good performers (API=4) further suggesting that Arjun and Morus species can be used for green belt development in NCR Delhi. Since Sheesham and Ashok have their aesthetic as well as economic values and are good performers, these can also be planted for green belt development.

**Keywords** Dust · Dustfall fluxes · Foliar · Biochemical constituents · APTI · API · Green belt

This article is part of the Topical Collection on *DUST*

✉ U. C. Kulshrestha  
umeshkulshrestha@gmail.com

<sup>1</sup> Jawaharlal Nehru University, School of Environmental Sciences, Delhi 110067, India

## Introduction

Most of the developing as well as developed countries are facing the challenges of air pollution (Santos et al. 2015). Due to increasing number of industries, vehicular exhaust, and decreasing plant cover, coping with deteriorating air quality is becoming difficult. Hence, emission reduction is the major target of the governments for which air pollution control systems are installed at the source as a common practice. This can also be achieved by the technique called biofiltration which cleans the ambient air by absorption and reflection (Arndt and Schweizer 1991; Pathak et al. 2011; Dzierzanowski et al. 2011). In this regard, several studies have been published about the designing and implementation of air pollution treatment using biofiltration processes (Bhattacharya 1994; Millard 2000; Klumpp et al. 2004).

The abundance of atmospheric dust in India has been known for centuries but recently, the air pollutants emitted from various industries, transport, and other anthropogenic activities interact with ambient dust modifying its chemical properties (Kulshrestha and Sharma 2015; Kumar et al. 2014). Dust pollution is rising as a serious health hazard in urban areas, especially in north Indian cities where naturally high levels of dust interfere with anthropogenic emissions of  $\text{SO}_2$ ,  $\text{NO}_2$ , elemental carbon, and organic carbon etc. (Sharma and Kulshrestha 2014). Apart from soil suspension, atmospheric dust is also contributed by the vehicles, industries, and construction activities. Atmospheric dust is scavenged mainly by sedimentation process affecting the surfaces. In our previous study, we found that dustfall significantly affects the biochemical properties of plants further influencing the physiology of the plant (Gupta et al. 2015a, b). Dust particles clog the stomata, whereas  $\text{SO}_4^{-2}$  and  $\text{NO}_3^-$  content of the dustfall enhance the plant stress by increasing the foliar acidity.



## Deposition and Impact of Urban Atmospheric Dust on Two Medicinal Plants during Different Seasons in NCR Delhi

Gyan Prakash Gupta, Bablu Kumar, Sudha Singh, Umesh Chandra Kulshrestha\*

*Jawaharlal Nehru University, School of Environmental Sciences, Delhi 110067, India*

### ABSTRACT

This study reports dustfall deposition on foliar surfaces of two medicinally important plant species i.e., Arjun (*Terminalia arjuna*) and Morus (*Morus alba*) in relation with its impact on biochemical constituents and surfaces morphology of the foliar. The study was carried out at a residential (JNU) and an industrial site (SB) of National Capital Region (NCR) Delhi. The results showed that at the industrial site, the dustfall fluxes were almost 2.5 times higher than that at the residential site. Dustfall fluxes were noticed higher on Morus foliar than Arjun foliar as the roughness of Morus foliar is greater. Deposition fluxes of major anions ( $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ) and cations ( $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) ions were also calculated by analyzing aqueous extract of dustfall at both the site. The results showed that with the increase in dustfall fluxes on the foliar surfaces, the levels of photosynthetic pigments and soluble sugar decreased while the levels of ascorbic and proline amino acid were increased at both the sites for both the plants. Dustfall fluxes had distinct seasonality having the order of fluxes as winter > summer > monsoon. Surface morphological study revealed that dust deposition adversely affects the foliar surface, cuticle and epidermal layers. Dust particle deposition ruptures and blocks the stomatal pores. As compared to the residential site, the foliar samples collected from the industrial site showed a more significant impact of dust on biochemical constituents and surface morphology.

**Keywords:** Urban dust; Ionic fluxes; Biochemical constituents; Foliar surface; Stomata damage.

### INTRODUCTION

Generally, dry deposition of gaseous and particulate pollutants takes place through diffusion, Brownian movement and impaction (Finlayson-Pitts and Pitts, 1986). However, coarse particles which are generated through disintegration processes are primarily deposited via sedimentation commonly referred as dustfall in a region like India (Rao *et al.*, 1992; Kulshrestha *et al.*, 1995; Kulshrestha *et al.*, 2003; Gupta *et al.*, 2015). The major sources of dust pollution include suspension of soil, agriculture related activities, road dust, vehicular exhaust, power plants, construction activities, brick kilns and cement factories etc. (Karanasiou *et al.*, 2014; Upadhyay *et al.*, 2015). In addition, transboundary and long range transport also contributes a significant amount of atmospheric dust in the south Asian region (Begum *et al.*, 2011). Countries like India have high loading of soil derived dust in the atmosphere under prevailing dry weather conditions. The soil derived particulate matter is rich in  $CaCO_3$  and acts as an effective scavenger of atmospheric  $SO_2$  forming

$CaSO_4$  which is also removed through dustfall (Kulshrestha *et al.*, 2003; Kulshrestha, 2013; Gupta *et al.*, 2015). Deposition of such particulate matter on the foliar may lead to different phytotoxic effects depending on the characteristics of the deposited material. The sulphate, nitrate and heavy metals are the most commonly reported air pollutants responsible for phytotoxic effects (Sheppard, 1994; Reeves and Baker, 2000). Sulphate and nitrate being acidic species have higher aqueous affinity which allows these ions to mobilize into the foliar mesophyll cells creating stress (Fowler *et al.*, 1989; Grantz *et al.*, 2003; Buchner 2004; Gupta *et al.*, 2015). Dustfall having pH values  $\geq 9$  might cause direct or indirect injury to the foliar tissues (Vardak *et al.*, 1995; Auerbach *et al.*, 1997).

Deposition of dust on the foliar surface may alter its optical properties, particularly the foliar surface reflectance in the visible and near infrared region (Hope *et al.*, 1991; Keller and Lamprecht, 1995). Dustfall also alters optical properties of snow-cover which can lead to an increase in temperature of vegetation surface (Spatt and Miller 1981; Spencer and Tinnin, 1997), changes in grazing patterns of animal (Walker and Everett 1987; Auerbach *et al.*, 1997; Spencer and Tinnin, 1997). According to Sharifi *et al.* (1997), the deposition of road dust of  $40 \text{ g m}^{-2}$  can cause the 2–3°C increase in leaf temperature in desert environments. The species having stomata in grooves might be less affected

\* Corresponding author.

Tel.: 0091 11 26704320

E-mail address: umeshkulshrestha@gmail.com

# Impact of anthropogenic emissions and open biomass burning on carbonaceous aerosols in urban and rural environments of Indo-Gangetic Plain

Ruchi Singh<sup>1</sup> · Monika J Kulshrestha<sup>1</sup> · B Kumar<sup>2</sup> · S Chandra<sup>1</sup>

Received: 4 June 2015 / Accepted: 20 October 2015  
© Springer Science+Business Media Dordrecht 2015

**Abstract** Carbonaceous aerosols were studied at two locations, urban and rural, on day and night time basis for 1 year in the Indo-Gangetic Plain. Average OC and EC concentrations at the urban site were observed as 25.6 and 13.7  $\mu\text{g}/\text{m}^3$ , while at the rural site as 29.6 and 12.8  $\mu\text{g}/\text{m}^3$ . Exceptionally high OC and EC values were observed during November indicating the impact of large-scale open biomass burning, in the post-harvesting season, on carbonaceous aerosols in the region. The high OC and EC levels were observed during the winter season and low during the monsoon season. Estimated secondary organic carbon accounted for 44.4 and 39.5 % of OC at the urban site and 58.3 and 35.6 % of OC at the rural site during day and night time, respectively. A good correlation was observed between OC and EC indicating a common origin of these species at both the sites. OC/EC ratios mainly in the range 1–4 at the urban site suggested the influence of motor vehicle exhaust as the main emission source whereas at the rural site, an occurrence of OC/EC > 4 indicated the impact of residential wood smoke and biomass burning. PM<sub>2.5</sub> samples were analyzed for eight individual carbon fractions (OC1, OC2, OC3, OC4, EC1, EC2, EC3, and OP). Principal component analysis of eight carbon fractions indicated the influence of anthropogenic emissions at both the sites.

**Keywords** Organic carbon · Elemental carbon · Secondary organic carbon · Char · Soot

✉ Monika J Kulshrestha  
monikajk@yahoo.com

<sup>1</sup> CSIR-National Physical Laboratory, New Delhi, India

<sup>2</sup> Jawaharlal Nehru University, New Delhi, India

## Introduction

Fine particles are a complex mixture of various chemical species emitted into the atmosphere either directly or through gas to particle conversion processes (Turpin and Huntzicker, 1995). The study of particulate matter, especially fine particles, is important due to their deeper harmful effects on the respiratory system (Zhang et al. 2015; Mathew et al. 2015). Carbon is a major constituent of fine particulate matter. Hence, the study of carbonaceous aerosols becomes important to investigate their role in human health, climate change, visibility reduction, and radiation balance (Yubero et al. 2014). The carbonaceous aerosols mainly consist of organic carbon (OC) and elemental carbon (EC). The average PM<sub>2.5</sub> composition contains 12.7 to 14.2 % OC while 5.3 to 8.5 % EC in Shanghai (Feng et al., 2009). OC contains hundreds of individual organic compounds like aliphatic and aromatic hydrocarbons, acids, etc. (Feng et al. 2006) while EC is mainly carbon with graphite-like particles. OC is further classified into primary organic carbon (POC) and secondary organic carbon (SOC). POC is directly emitted by biogenic and combustion sources such as higher n-alkanes, PAHs, etc. while SOC is generated via oxidation of volatile organic compounds (VOCs) such as organic acids. EC is directly emitted by primary combustion sources such as biomass burning, vehicular exhaust, and coal combustion (Andreae et al. 2001).

According to classical understanding, OC cools the atmosphere by reflecting or scattering back sunlight while EC warms it by absorption of sunlight (Han et al. 2009). But recently, the role of OC in cooling or warming has become a matter of debate (Cazorla et al. 2013). The absorption of solar radiation by non-soot OC emitted from biomass burning may be comparable to EC at short wavelengths (Magi et al. 2009). OC also contains mutagenic and carcinogenic compounds like polycyclic aromatic hydrocarbons (Feng et al. 2006; 2009).

## Snow Chemistry at Mukteshwar in Central Himalayan Region of India

Bablu Kumar<sup>1</sup>, Gupta GP<sup>1</sup>, Sudha Singh<sup>1</sup>, Lone FA<sup>2</sup> and Kulshrestha UC<sup>1\*</sup>

<sup>1</sup>School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110067, India

<sup>2</sup>Centre for Climate Change, Mountain and Agriculture, SKUAST, Shalimar, Srinagar, 191123, Jammu & Kashmir, India

### Abstract

The present study reports snow chemistry and source apportionment at Mukteshwar in central Himalayan region of India during winter 2012-13. In this study, fresh snowfall samples were collected at Mukteshwar during winter season of 2012-13. The results showed that the pH of the snowmelt samples ranged from 5.47 to 7.95 with an average of 6.37 indicating alkaline nature of precipitation which is similar to the range reported. The concentration of ions followed the following order-  $\text{Ca}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NH}_4^+ > \text{NO}_3^- > \text{Mg}^{2+} > \text{K}^+ > \text{F}^-$ . Very high concentration of  $\text{Ca}^{2+}$  indicated the dominance of crustal sources. Source fraction calculations revealed that crustal, marine and anthropogenic sources contributed 40%, 38% and 22% ionic components in snowmelt, respectively. Since, Mukteshwar is remote site as compared to Delhi, values of  $\text{NO}_3^-$  were compared with the  $\text{NO}_3^-$  reported in the precipitation (rain water) of Delhi as  $\text{NO}_3^-$  is an indicator of vehicular pollution in urban areas. Such comparison of  $\text{NO}_3^-$  values suggested that though Mukteshwar precipitation had 1/3 of  $\text{NO}_3^-$  in precipitation as compared to Delhi, but considering it as a small town, precipitation at Mukteshwar is significantly influenced vehicular sources possibly due to Long Range Transport (LRT) of pollution.

**Keywords:** Himalaya; Precipitation; Vehicular pollution;  $\text{NO}_3^-$ ; Crustal sources

### Introduction

Air pollution is considered as one of the major environmental challenges. Huge amount of air pollutants is injected into the atmosphere due to rapid urban and industrial growth during past few decades. South East and South Asian are the major air pollution emitters due to rapidly increasing energy demand for their fast growing economy. Among south Asian countries, Indian emissions are significant. After China, India is the second biggest emitter of  $\text{SO}_2$  in Asia [1]. However, the levels of gas like  $\text{SO}_2$  are quenched by atmospheric dust in India resulting in very low ambient  $\text{SO}_2$  [2,3]. Nevertheless, emissions of atmospheric aerosols and gaseous pollutants have caused the problems of acid deposition, ozone depletion, climate change and monsoon modification etc. [4-6]. Once emitted, most of these pollutants are scavenged by removal processes. Wet deposition is one of the most effective deposition processes of airborne pollutants.

Long term study of wet deposition can be used to notice the changes in oxides of N & S content thereby relating to coal & petroleum energy consumption patterns. Hence, rain and snow chemistry become very important to know the sources of pollution and their possible effects on ecosystems and environment. Precipitation chemistry in general, provides information about the deposition fluxes of various air pollutants to different ecosystems. Due to its significance, snowfall chemistry has been studied extensively throughout the world [7-14]. Fresh snow chemistry in Himalaya ranges had shown relatively low concentration of air borne pollutants are representative of remote site [9,11,15]. The ionic content in Himalayan snow is highly affected by the impact of long range transport of anthropogenic sources of air pollutants [16]. Snow chemistry at Shanghai in China suggested that fossil fuel combustion and biomass burning is the major source of air pollution [14].

Acid deposition, a serious threat to terrestrial, aquatic and marine ecosystem has been studied comprehensively at various places in North America, Europe, Japan and other countries of the world [2,17-19]. Acidic precipitation is determined primarily by the interaction of acidic and basic species in the atmosphere. Acidic species are dominated by  $\text{SO}_2$  and  $\text{NO}_x$  which is precursor of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  respectively which are mainly emitted by fossil fuel combustion. On the other

hand, alkaline species ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$ ) help in enhancing pH of precipitation. The main source of these species is atmospheric dust which is made up of carbonates and bicarbonates of Ca and Mg [2,3,20]. Unlike North America and Europe, it is interesting that higher pH of precipitation is reported in India even at higher  $\text{SO}_4^{2-}$  concentration which might be due to huge amount of dust in the atmosphere [3].

In India, several studies have been reported on rain chemistry mostly in urban areas [2,21-26] with few studies from rural sites [27-30]. The detailed and updated studies on fresh snowfall chemistry are even rare in rural areas of Himalayan region of India [16,31,32]. Hence, this study was carried out to fill this knowledge gap about the chemical characteristics of snow in central Himalaya by selecting Mukteshwar as a rural representative site. The present study also focuses on quantification of relative contributions of marine and non-marine sources during winter season. Further, non-marine fractions have been quantified into crustal associated and anthropogenic sources. An attempt has been also made to highlight the extent of influence of vehicular pollution in urban area like Delhi vs. remote area like Mukteshwar by considering  $\text{NO}_3^-$  concentration as an indicator of vehicular pollution.

### Materials and Methods

#### Sampling site

Mukteshwar is located at 29.47°N 79.64°E in Nainital district of Uttarakhand state of India (Figure 1). It is situated in the Kumaon Hills of central Himalaya at an altitude of 2286 meters. It lies approx. 51 km NE of Nainital city, 51 km from Nainital, 72 km from Haldwani and 395 km from Delhi city. Mukteshwar is rich in scenic beauty,

\*Corresponding author: Kulshrestha UC, School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110067, India, Tel: 981-061-1857; E-mail: [umeshkulshrestha@gmail.com](mailto:umeshkulshrestha@gmail.com)

Received June 28, 2015; Accepted August 03, 2015; Published August 07, 2015

Citation: Kumar B, Gupta GP, Singh S, Lone FA, Kulshrestha UC, et al. (2015) Snow Chemistry at Mukteshwar in Central Himalayan Region of India. Mod Chem appl 3: 160. doi:10.4172/2329-6798.1000160

Copyright: © 2015 Kumar B, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

## Atmospheric Deposition of Reactive Nitrogen and Other Species in Relation with Long Range Transport and Land Use and Land Cover Change in North Western Himalayas

Bablu Kumar<sup>1</sup> G P Gupta<sup>1</sup> Sudha Singh<sup>1</sup> F A Lone<sup>2</sup> U C Kulshrestha<sup>1\*</sup>

<sup>1</sup>School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110 067

<sup>2</sup>Centre for Climate Change, Mountain and Agriculture, SKUAST, Shalimar, Srinagar, 191123 (J&K)

\*Corresponding Author: [umeshkulshrestha@gmail.com](mailto:umeshkulshrestha@gmail.com)

### Abstract

This paper discusses the influence of Land Use and Land Cover Change (LULCC) and transported sources on the reactive nitrogen species along with other ions and their variation in fresh snowfall at Kothi site which is located in north-western Himalayan region of India. In spite of its eco-sensitivity, Himalayan region of India has not been investigated from the view point of fresh snowfall chemistry research. This study is first of its kind which reports the influence of Long Range Transport (LRT) of pollution and local sources by analyzing snow chemistry in this region. The pH of snow varied between 4.75 and 6.98 (mean pH = 5.69). Trajectory analysis revealed that most of acidic events were recorded when air masses arrived from middle-east sector. Such air masses brought high concentrations of acidifying substances such as  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . However, reactive nitrogen ( $\text{NH}_4^+$ ) content was significantly high during African origin (Af), Western India origin (InW) and Nepal origin (Np) air masses. High  $\text{NH}_4^+$  deposition contributes excess N which has adverse effect on several ecosystems. Besides LRT, LULCC had also significant effect on snow chemistry through local developmental activities such as deforestation and construction of buildings etc. Biomass burning used for domestic heating and cooking purpose could be a source of influence as indicated by the presence of  $\text{K}^+$ . Principal Component Analysis also corroborated the dominance of anthropogenic sources.

**Keywords:** Snow Chemistry, Himalaya, LRT, Reactive Nitrogen, Tourist Activities

# Signatures of Increasing Energy Demand of Past Two Decades as Captured in Rain Water Composition and Airmass Trajectory Analysis at Delhi (India)

*Sudha Singh, Bablu Kumar, Gyan Prakash Gupta, U C Kulshrestha\**

School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, India

## Abstract

*This study reports chemical characteristics of rain water in Delhi during monsoon (2010–11) with a comparison to earlier reported values of 1994. The results showed that non-marine sources had significant influence on rain water composition. The pH of the samples varied from 5.24 to 7.48 with an average value of 6.52 showing an alkaline nature of rain water. However, the dominance of  $\text{NO}_3^-$  over  $\text{SO}_4^{2-}$  indicated higher influence of vehicular emissions over industrial sources at this urban site. Air mass trajectory analysis revealed that the easterly air masses were the most polluted which carried highest amount of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . The study highlighted that the difference in ion balance may be minimized by including measured  $\text{HCO}_3^-$  concentrations especially in Indian perspective where interference of soil-derived  $\text{CaCO}_3$  is reported very high. A comparison of this study with that of 1994 values reported earlier indicated a remarkable increase in the concentrations of various chemical components of rain water which might be due to the impact of industrial and urban expansion of the city since 1994. The maximum increase (~12 times) was noticed for  $\text{NO}_3^-$  concentrations, clearly reflecting the signatures of increased emissions of  $\text{NO}_x$  from various anthropogenic sources, especially, vehicular emissions which are drastically increased during past two decades. In spite of introduction of CNG vehicles, Bharat stage I–IV emission norms and metro rail etc., increase of  $\text{NO}_x$  suggests an immediate need of further stringent regulations.*

**Keywords:** Vehicular emissions, energy demand, rain chemistry,  $\text{NO}_x$ , airmass trajectory

\***Author for Correspondence** E-mail: umeshkulshrestha@gmail.com

## INTRODUCTION

Anthropogenic activities such as urbanization and industrialization are responsible for atmospheric accumulation of various gases and particulate matter which have significant influence on atmospheric chemistry [1, 2, 3, 4]. Gaseous and particulate pollutants emitted by such activities are removed by wet and dry deposition processes [5, 6, 7, 8, 9, 10]. Rain, dew, fog, hail and snow are the common wet removal pathways which scavenge aerosols and gases from the atmosphere [11]. Rain is the most effective wet removal process which scavenges pollutants via in-cloud and below cloud scavenging processes [12, 13, 14]. Hence, the chemical composition of rain water acts an indicator of the air quality of the region. Due to the difference in the characteristic of natural environment and

human activities, the composition of precipitation varies according to the geographical locations. Chemical composition of rain water carrying the impact of such characteristics has been reported worldwide by several workers [15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27].

A number of studies on precipitation chemistry have also been carried out at various urban locations in India too [28, 29, 30, 31, 32, 33]. Most of these studies have described marine, non-marine, industrial, vehicular and crustal contributions identifying sources of local importance. Rarely, long range transport of pollutants has been reported as a phenomenon in the region. Apart from local sources, Long Range Transport (LRT) of pollutants also affects rain water chemistry.



# Industrial dust sulphate and its effects on biochemical and morphological characteristics of *Morus* (*Morus alba*) plant in NCR Delhi

Gyan Prakash Gupta · Sudha Singh · Bablu Kumar · U. C. Kulshrestha

Received: 2 August 2014 / Accepted: 13 January 2015  
© Springer International Publishing Switzerland 2015

**Abstract** Abundance of  $\text{CaCO}_3$  rich soil dust is a typical feature of atmospheric environment in the Indian region. During prevailing dry weather conditions, dustfall is deposited onto the foliar surfaces of plant affecting their morphology, stomata and the levels of biochemical constituents. This study reports the chemical characteristics of dustfall, its effect on foliar morphology and biochemical constituents of a medicinal plant (*Morus alba*) at two sites which are differentiated on the basis of landuse pattern, viz., (i) residential, Jawaharlal Nehru University (JNU), and (ii) industrial, Sahibabad (SB), located in the National Capital Region (NCR) of Delhi. Dustfall was characterized for major anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) and cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{++}$  and  $\text{Ca}^{++}$ ). Biochemical parameters such as chlorophyll a, chlorophyll b, total chlorophyll, carotenoid, proline and ascorbic acid were determined in foliar samples. The results showed that the dustfall fluxes of all the major ions were found to be higher at the industrial site (SB) as compared to the residential site (JNU). Foliar analysis revealed that the levels of biochemical parameters were more affected at SB site due to higher levels of dust  $\text{SO}_4^{2-}$  contributed by various anthropogenic sources resulting in more stressful conditions affecting the biochemistry of the plant. The possible entry pathways for dust  $\text{SO}_4^{2-}$  into foliar cells

are also discussed in the paper. It was noticed that the deposition of urban dust was responsible for the damage of trichome, epidermis, cuticle and stomatal guard cells significantly affecting foliar morphology. SB exhibited more damage to these morphological parts suggesting that industrial dust is harmful to the plants.

**Keywords** Air pollution · Atmospheric dust · Sulphate · Foliar · Biomonitoring

## Introduction

Dust is considered as one of the most widespread air pollutants predominantly found in African and Asian regions (Tegen and Fung 1995). Very high loadings of atmospheric dust in the Indian region are responsible for high levels of particulate matter. Often these levels are recorded higher than the prescribed limits of National Ambient Air Quality Standards (NAAQS) of the Central Pollution Control Board (CPCB 2013; Kulshrestha et al. 1999, 2003; Kulshrestha 2013). Atmospheric deposition of particles to the earth's surface takes place via wet and dry deposition processes. Wet deposition generally takes place in the form of precipitation while dry deposition includes the uptake of gases at the surface as well as settling and impaction of particles. Dustfall which is an important phenomenon in the Indian region occurs mainly through sedimentation and impaction processes (Morselli et al. 1999; Yun et al. 2002; Kulshrestha 2013). Dust is primarily a mixture of suspended soil,

G. P. Gupta · S. Singh · B. Kumar · U. C. Kulshrestha (✉)  
School of Environmental Sciences, Jawaharlal Nehru  
University,  
Delhi 110067, India  
e-mail: umeshkulshrestha@gmail.com

# Urban climate and its effect on biochemical and morphological characteristics of Arjun (*Terminalia arjuna*) plant in National Capital Region Delhi

Gyan Prakash Gupta, Bablu Kumar, Sudha Singh and U C Kulshrestha\*

*School of Environmental Sciences, Jawaharlal Nehru University, Delhi 110067, India*

*(Received 18 November 2014; final version received 9 April 2015)*

This paper reports impacts of urban pollution on the biochemical and morphological characteristics of Arjuna (*Terminalia arjuna*) in particular the effects of urban industrial dustfall deposition on its foliar surface at a residential site (Jawaharlal Nehru University, JNU) and an industrial site (Sahibabad, SB) in Delhi region. Atmospheric dustfall fluxes were estimated for major anions and cations. Morphological analysis of foliar samples was carried out by using the scanning electron microscope. Biochemical parameters, namely chlorophyll a, chlorophyll b, total chlorophyll, carotenoids, total soluble sugar, proline amino acid and ascorbic acid were also analysed in foliar samples. Results showed that the dustfall fluxes of ( $\text{SO}_4^{2-} + \text{NO}_3^-$ ) at the industrial site were almost three times higher than that of the residential site. This can be attributed to the emissions of industrial activities and diesel-driven vehicular traffic in the area. It was observed that these elevated fluxes of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  had significant impacts on the biochemical constituents of the plant and foliar morphology. Concentrations of chlorophyll and carotenoids were recorded decreasing with increasing dustfall fluxes of ( $\text{SO}_4^{2-} + \text{NO}_3^-$ ), whereas proline and ascorbic acid were found to be increasing with the increase in the dustfall fluxes of ( $\text{SO}_4^{2-} + \text{NO}_3^-$ ) indicating the effect of pollution stress. The study showed that the deposition of dustfall was responsible for damage to stomata and leaf surface morphology, more significantly at the industrial site.

**Keywords:** air pollution; urban dust; dry deposition; biochemical parameters; stomatal damage

## 1. Introduction

It is widely accepted that high levels of atmospheric pollution can trigger severe environmental problems. Both gaseous as well as particulate pollutants play a very important role in various plant processes such as nutrient cycling, soil acidity and photosynthesis.[1] Different natural and industrial sources emit a considerable amount of particulate matter and gases such as  $\text{SO}_2$  and  $\text{NO}_2$ , which finally settle down through wet and/or dry deposition processes.[2] Air particulates have been reported to create serious environmental problems in industrial and urban areas.[3] According to WHO database, air pollution is a severe problem of low-income group countries including south Asian mega cities such as Delhi, Dhaka and Kathmandu.[4] Much of the air pollution in these cities is contributed by the transport sector due to large and continuously increasing density of the automobile vehicles. According to 2010 data, Delhi city has witnessed

---

\*Corresponding author. Email: [umeshkulshrestha@gmail.com](mailto:umeshkulshrestha@gmail.com)



## Review

# Status of Atmospheric Mercury Research in South Asia: A Review

Anita Kumari, Bablu Kumar, Shabana Manzoor, Umesh Kulshrestha\*

*School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110067, India*

---

## ABSTRACT

Mercury (Hg) is a highly toxic metal, which is known as a global pollutant due to its ability to undergo long-range transport in the atmosphere. Methylated mercury can pose serious adverse effects on human health and environment. Mercury is emitted into the atmosphere by various natural and anthropogenic sources. The largest anthropogenic source of mercury is coal combustion, which contributes ~62% of global emissions. Total global emissions of atmospheric mercury are estimated to be 5600 Mg/year from natural and anthropogenic sources, respectively, contributing around 37% and 63% of total atmospheric mercury. About 40% of global anthropogenic emissions are contributed by East and Southeast Asia with the largest emissions from China (75%) followed by South America and Sub-Saharan Africa. Latter regions are mainly responsible due to increase in artisanal and small scale gold mining. The present estimates of mercury emissions have large uncertainties in global budget, which are mainly due to lack of knowledge of mercury exchange between various components of ecosystem with its speciation in spatial and temporal distribution. Special efforts are needed in the regions of growing economy especially in South Asia where atmospheric mercury is almost unattempted. In order to reduce uncertainties and get more realistic emission figures, there is need to develop an extensive monitoring network to measure various forms of mercury in air, soil and aquatic systems in south Asia. Controlling the emissions of global atmospheric mercury is a big challenge to the scientists and policymakers. Probably, it can be achieved by focusing on implementation of the available technologies and by developing new technologies for mercury removal through developing an extensive partnership between industries and governmental organizations.

**Keywords:** Atmospheric mercury; Global mercury budgets; Coal emission; Mercury cycle; Mercury in south Asia.

---

## INTRODUCTION

Mercury is one of the most toxic heavy metals which is globally distributed in air, water and soil systems (Nriagu and Pacyna, 1988; Schroeder and Munthe, 1998; Downs *et al.*, 1998). It is also found in biota and other living organisms because of its bioaccumulative nature (Downs *et al.*, 1998; MDOMP, 2007). Despite the fact that mercury is very toxic having adverse effects on human health and the environment, it was not considered as a pollutant until 1950 when Minimata poisoning episode took place in Japan causing many deaths and neurological damage (Harada, 1995). Later on mercury poisoning episodes were also reported in Iraq in 1972 and in Canada in 1978 (USEPA 1997a). However, several efforts have been made afterwards to review environmental aspects of mercury (Nriagu, 1979), atmospheric mercury (Lindqvist and Rodhe, 1985), sampling and measurement techniques (Lu and Schroeder, 1999; Pandey, *et al.*, 2011), sources of mercury (Pirrone *et al.*, 2010; Rajaf, *et al.*, 2013) and harmful

effects of mercury pollution (Azimi and Moghaddam, 2013). Very few studies summarize overview of atmospheric mercury covering its all aspects (Schroedger and Munthe, 1998; Selin, 2009). Research on mercury has attracted significant scientific attention during past few years. There is no much concern has been raised to study various forms of atmospheric mercury with its spatial and temporal distribution in the world. However, recent launch of UN report on Global Mercury Assessment 2013 on atmospheric mercury has once again regenerated research momentum worldwide. Through this paper, we have attempted to review the status of understanding about the sources of atmospheric mercury, its occurrence in various forms, methods used for sampling and analysis by various researchers, transformations and fate of atmospheric mercury and its abundance in South Asia. Global mercury budget, global comparison of atmospheric mercury, its impact on environment and human health, abatement of atmospheric mercury and the existing policies related to mercury regulation have also been discussed and analyzed.

## ABUNDANCE AND SOURCES OF MERCURY

Mercury is a member of group 12 and period 6 of the

---

\* Corresponding author.

*E-mail address:* umeshkulshrestha@gmail.com

## Review Article

# Airmass Trajectories and Long Range Transport of Pollutants: Review of Wet Deposition Scenario in South Asia

**Umesh Kulshrestha and Bablu Kumar**

*School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110067, India*

Correspondence should be addressed to Umesh Kulshrestha; [umeshkulshrestha@gmail.com](mailto:umeshkulshrestha@gmail.com)

Received 24 April 2014; Revised 6 June 2014; Accepted 9 June 2014; Published 12 August 2014

Academic Editor: M. Ángeles García

Copyright © 2014 U. Kulshrestha and B. Kumar. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

This paper presents a review of airmass trajectories and their role in air pollution transport. It describes the concept, history, and basic calculation of air trajectories citing various trajectory models used worldwide. It highlights various areas of trajectory applications and errors associated with trajectory calculations. South Asian region receives airmasses from Europe, Middle East, Africa, and Indian Ocean, and so forth, depending upon the season. These airmasses are responsible for export and import of pollutants depositing in nearby states. Trajectory analysis revealed that soil is contributed by the dust storms coming from Oman through Gulf and Iran, while most of black carbon (BC) sources are located in India. A detailed review of trajectories associated with wet deposition events indicated that airmasses coming from Europe and Middle East carry high concentration of acidic pollutants which are deposited in Himalayan ranges. Similarly, trajectory analysis revealed that acidic pollutants from continental anthropogenic sources are transported to an ecosensitive site in Western Ghats in India and the outward fluxes of anthropogenic activities of Indo-Gangetic region are transported towards Bay of Bengal. Hence, transboundary and long range transport of pollutants are very important issues in South Asia which need immediate attention of scientists and policy makers.

## 1. Introduction

*1.1. Concept of Trajectories.* Air flow may be described in two different ways: (i) Eulerian (named after Swiss mathematician Leonhard Euler) and (ii) Lagrangian (named after French mathematician J L Lagrange) [1–3]. In the Eulerian approach, the air flows through the points fixed in the space whereas in the Lagrangian approach [3], individual air parcel is chosen and followed as it moves in time and space. Most of chemistry models are based on Eulerian approach as this is a useful tool to explain various chemical and physical processes. In the Eulerian model, chemical reactions are calculated based on the concentration of a pollutant diluted over the entire grid scale. Most of transport and dispersion models use Lagrangian approach due to some limitations in Eulerian model, for example, boundary layer in top entrainment and convective transport, and so forth [4, 5]. The advantage of Lagrangian approach is that it has minimum numerical diffusion [5]. Airmass trajectory is calculated to show the pathway of an infinitesimally air parcel through a centerline of an advected airmass having vertical and horizontal dispersion.

Tracing of the pathway followed by an air parcel upwind from the selected coordinates is termed as “backward air trajectory,” while calculation of best possible pathway to be followed downwind from the selected coordinates in due course of time is called “forward trajectory.” The calculation of backward air trajectory using Lagrangian approach is easier and computationally cheap as it excludes the influence of upwind on the receptor site. Lagrangian approach has also been applied in photochemical modeling [6, 7].

*1.2. History of Air Trajectories.* Trajectories were first computed by Petterssen in 1940 which were based upon graphic representation [8]. But with the advancement of computer in 1960s, people started isentropic analysis, trajectory calculations, and their graphic representation on computers [9]. Since then, trajectory calculations and their presentation have experienced gradual advancement in techniques and technologies. Trajectory calculations gained more importance when Rodhe plotted airmass trajectories and established that acid rain occurrence in Northern Europe was mainly due

## Research Article

# Deposition and Mineralogical Characteristics of Atmospheric Dust in relation to Land Use and Land Cover Change in Delhi (India)

**Bablu Kumar, Kopal Verma, and Umesh Kulshrestha**

*School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110067, India*

Correspondence should be addressed to Umesh Kulshrestha; [umeshkulshrestha@gmail.com](mailto:umeshkulshrestha@gmail.com)

Received 30 May 2014; Revised 31 July 2014; Accepted 31 July 2014; Published 26 August 2014

Academic Editor: Jaime Hart

Copyright © 2014 Bablu Kumar et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

This study highlights that the increasing urbanization and industrialization in Delhi are responsible for higher fluxes of atmospheric dust and its chemical constituents. Delhi has experienced a drastic change in land use and land cover area during the past two decades. Road lengths of the city have increased by 76% from 1985 to 2011. The number of mobile vehicles has reached 80,52,508 in 2014 from 24,32,295 in 1994. The industrial units in Delhi have increased by 39.54% in 2011 as compared to 1994 value. Atmospheric dust which is originated from soil in this region becomes carbon rich due to interaction of suspended soil with atmospheric pollutants. Emissions of carbonaceous aerosols from coal and petroleum combustions are mainly responsible for silica dominated soil dust transforming into carbon rich particulate matter. Such dust may play very important role in the atmosphere having significant influence on human health, global warming, climate change, radiative forcing, visibility, and cloud formation. It is expected that if the rate of development remains the same, green cover of the city invariably will be sized down in order to meet the demand of housing, transportation, industries, and so forth in proportion to the rising population.

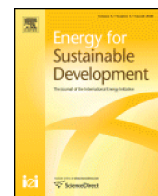
## 1. Introduction

Generally, atmospheric dust represents airborne particles in the size range  $<1\ \mu\text{m}$  to  $\sim 75\ \mu\text{m}$  [1, 2]. Atmospheric mineral dust is mainly emitted from arid and dry regions followed by its transportation to distant places through high speed winds. In addition, open land, grazing fields, ploughing, vehicle use, and unpaved roads, and so forth, are also important sources of dust [3]. According to Jickells and coworkers (2005), around one-third of the global land area is considered a potential source of atmospheric dust [4]. Global distribution of atmospheric dust has been thoroughly modelled by Tegen and Fung (1994; 1995) [5, 6]. The abundance of dust in the air is controlled by factors such as vegetation cover, precipitation, wind velocity, and soil moisture [7]. Dust mainly consists of loose particles contributed by soil erosion, road transport, industries, volcanic eruptions, and so forth.

The atmospheric mineral dust plays an important role in controlling various atmospheric processes such as radiative forcing, cloud characteristics, precipitation, and atmospheric

chemistry [8, 9]. Dust aerosols impact these processes according to their size distribution, origin, and lifetime in the atmosphere [5, 6, 10–12]. Mineral dust has significant influence on ecosystem, environment, and biogeochemical cycles through deposition of minerals and organic materials on terrestrial ecosystem [4, 13]. Deposition of dust can affect the nutrient levels in aquatic system [13, 14]. Also, it adversely affects human health when contaminated by carbonaceous materials, soluble and chelatable metallic salts, and pesticides [15, 16].

LULCC also plays an important role in dust emission. Mostly vegetation cover is reduced and built area is increased in urbanization processes. Due to rapid development, developing countries are facing drastic LULCC due to human activities. In the absence of integrated and holistic development in regional planning, developing countries are experiencing the problem of loss of agricultural land, open space, and protection of ecologically sensitive areas [17]. Development of peripheral or suburban areas near metropolitan cities is leading to sparse vegetation and encroachment on wetland



# Comparative study of indoor air pollution using traditional and improved cooking stoves in rural households of Northern India



Sudha Singh, Gyan Prakash Gupta, Bablu Kumar, U.C. Kulshrestha \*

School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110067, India

## ARTICLE INFO

### Article history:

Received 21 October 2013

Revised 22 January 2014

Accepted 23 January 2014

Available online xxx

### Keywords:

Indoor air pollution

Biomass burning

Traditional cooking stove (TCS)

Improved cooking stoves (ICS)

Fine aerosols

## ABSTRACT

A major fraction of the rural population of India still burns biomass for domestic cooking and heating. Biomass materials such as wood, dung cakes and crop residues are burnt to produce energy for cooking. These are major sources of aerosol and gaseous pollutants in the atmosphere. Indoor measurements of gaseous species and chemical characteristics of aerosols contributed by burning biomass in traditional cooking stoves (TCS) vs. improved cooking stoves (ICS) are reported in this paper. Samples were collected from a village called Khairatpur, located in Sultanpur district of Uttar Pradesh state. The concentrations of aerosol components and gases in the indoor air during the operation of ICS were found to be lower as compared to TCS. On an average, total concentrations of major ions were lower by 32% during ICS operation. The most significant difference was observed for  $\text{SO}_4^{2-}$  aerosols (lower by 47%). Among  $\text{SO}_x$ ,  $\text{NO}_x$  and  $\text{NH}_3$  gases,  $\text{SO}_x$  showed maximum reduction (lower by 55%). Estimates of consumption of different types of biomasses showed that 621 t biomass is burnt annually by the villagers during cooking with TCS as compared to 365 t during ICS cooking. A social survey in the form of a questionnaire revealed that most of the women in the village of this study found ICS better than the TCS in terms of handling, reduced emissions, easier cooking and time & fuel efficiency.

© 2014 International Energy Initiative. Published by Elsevier Ltd. All rights reserved.

## Introduction

Burning of biomass results in the emission of a complex mixture of pollutants in the form of gases and aerosols and is a major source of air pollution. Most of the population in most of the developing countries uses biomass energy, especially in rural areas. People in rural areas have very limited access to modern energy resources but different types of biomass fuels are often available to them from local sources. The price of using biomass energy is simply the labor required in collecting it (WHO, 2006; World Bank, 1996a, b). Air pollution contributed by the combustion of these biomasses has significant impacts on climate change and human health (Andreae and Merlet, 2001; Dockery et al., 1993; Samet et al., 2000) especially, in rural areas in India where traditional stoves are used for cooking. In the traditional stove called 'Chullah' dung cakes, crop residues and woods are burnt to produce energy. It is a stove with an open fire with low efficiency. It emits a significant amount of air pollutants. Some of these pollutants have longer residence time depending upon the ventilation in the house. This results in high risk of lower respiratory infections, tuberculosis, asthma, cancer of the upper airways and cataracts (Bruce et al., 2000; Smith et al., 2004). It is particularly problematic for the women who are normally responsible for cooking and for the young children who spend time around their mothers near the cooking area. The Indo-Gangetic Plains (IGP) region in South Asia is one of the most densely populated regions

in the world and also a major source of air pollutants from cooking with biomass fuels. Knowledge of the indoor environment is limited and is of great importance as the majority of the people have been found to spend about 80–90% of their time indoors in many countries (Delgado-Saborit et al., 2011; Koistinen et al., 2001; Scapellato et al., 2009). Latest Global Burden of Disease (2012) reports 3.5 million premature deaths per year from HAP (household air pollution) and another 0.5 million premature deaths from ambient air pollution originating from households (Lim et al., 2012). It is now recognized that climate change is a major threat and combustion of biomass in households is a contributor with significant emission of greenhouse gases. In addition, biomass combustion emits other pollutants such as black carbon which reduce crop yields and may contribute to the melting of glaciers and disruption of the monsoon (Venkataraman et al., 2010).

The concentrations of indoor air pollutants originating from the burning of solid fuels depend on a number of factors such as fuel type, housing characteristics and methods of cooking. Depending on cooking activities, the extent of pollution can vary between days and within the day (Ezzati et al., 2000; He et al., 2005). Comparison of pollution level using traditional and improved cook stoves has been reported globally by various researchers (Armendáriz-Arnez et al., 2010; Kar et al., 2012; Singh et al., 2012). To the best of our knowledge, these studies have mainly focused upon CO,  $\text{PM}_{2.5}$  and black carbon without including inorganic aerosol components and their precursor gases. The present study has been carried out as a part of project 'Surya' of the United Nations Environment Programme (UNEP). In this paper, we present a comparison of chemical components of fine aerosols and gaseous

\* Corresponding author. Tel./fax: +91 11 26704320.

E-mail address: umeshkulshrestha@gmail.com (U.C. Kulshrestha).

## **Identification of Nature and Sources of Dustfall at Mukteshwer in Kumaon Region of Central Himalaya, India**

**Bablu Kumar\*, Y. Meena, G.P. Gupta, S Singh and U.C. Kulshrestha**

*School of Environmental Sciences, Jawaharlal Nehru University,  
New Delhi-110067 INDIA.*

### **Abstract**

The wind-driven transport and deposition of dust particles can cause considerable physical and chemical changes to the atmospheric environment. Recently it has been realized that dust aerosol are very important and these play an important role in radiative forcing and acid rain. During most part of the year, prevailing dry weather conditions increase the significance of dustfall deposition. Ambient concentrations of reactive gases such as SO<sub>2</sub> and NO<sub>2</sub> etc. are controlled by continuous input of atmospheric dust contributed by suspended soil. Despite evidence of the ecological importance of dust deposition, the studies on chemistry of dustfall and their sources are not extensively carried out through space and time in Indian region especially in hilly region. Hence, the present work is aimed to study chemical composition of dustfall at Mukteshwer in Kumaun region of central Himalaya to find out their association with anthropogenic and crustal sources. High pH (7.14) at this site indicating the alkaline nature of dustfall and high alkalinity may be due to Soil derived aerosols which are rich in CaCO<sub>3</sub>. Among anions, SO<sub>4</sub><sup>-2</sup> concentration was the highest which were associated with Ca<sup>+2</sup> similar to other reports in Indian region. This is primarily because SO<sub>2</sub> adsorb onto dust particles resulting in the formation of Calcium Sulphate. Very high SO<sub>4</sub><sup>-2</sup> concentration could be due to long range transport since nearby no any significant source of SO<sub>2</sub> exit. Higher concentration of NO<sub>3</sub><sup>-</sup> can be attributed to high vehicular emissions due to increased tourist activities with long range transport of aerosol, which becomes integral part of dust. Among cations, dustfall extract showed very high K<sup>+</sup> after Ca<sup>+2</sup> indicating wood burning used for cooking and heating purposes. Calculation of marine influxes and crustal contribution

## **Study of Abundance and Characterization of Culturable Bioaerosol at Delhi, India**

**Bablu Kumar, Gyan Prakash Gupta, Sudha Singh and U.C. Kulshrestha\***

*School of Environmental Sciences, Jawaharlal Nehru University,  
New Delhi 110067 INDIA.*

### **Abstract**

Air particulates associated with biological origins are termed as bioaerosols. Bioaerosols consist of different species of bacteria and fungi including viruses, pollen, spores etc. Airborne bacteria and fungi can be toxigenic, allergenic and infectious. Infection can be caused by complete microorganisms as well as by its fragments or byproducts. The higher presence of bioaerosol can cause asthma and rhinitis, hypersensitivity pneumonitis, sick-building syndrome and organic dust toxic syndrome. This study reports the abundance of culturable airborne bacteria during monsoon and winter seasons at a site in Jawaharlal Nehru University campus, south Delhi. The results showed that the average concentrations of bacteria were higher during rainy season in comparison to winter season. The abundance is relatively higher than reported from temperate regions, which may be due to favourable climatic conditions of tropics. It was found that the percentage of Gram +ve bacteria dominated over Gram -ve bacteria during both the seasons. Among Gram +ve bacteria, cocci shape dominated over rod shape. Strong positive correlation of temperature with CFU indicated that the abundance of bacteria is largely controlled by ambient temperature.

**Keyword:** Bioaerosols, culturable bacteria, temperature, CFU, Gram +ve and Gram -ve.



## Defining Criteria for Good Habitats - Importance of black carbon, bioaerosols and trace gases

U. C. Kulshrestha<sup>1</sup>, B. Kumar<sup>1</sup>, G. P. Gupta<sup>1</sup>, Sudha Singh<sup>1</sup> and M. J. Kulshrestha<sup>2</sup>

<sup>1</sup>School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110067

<sup>2</sup>Radio and Atmospheric Science Division, National Physical Laboratory, New Delhi 110012

(Email: umeshkulshrestha@gmail.com)

### Abstract

Clean air is necessary for good health and environment. The quality of air is monitored and assessed by setting up standards of limits by selecting certain parameters for a defined habitat. Based on scientific assumptions, these defined limits act as criteria for good air quality. At present, Central Pollution Control Board has defined national criteria for SO<sub>2</sub>, NO<sub>x</sub>, RSPM, PM<sub>2.5</sub>, NH<sub>3</sub>, etc. limiting to their ambient air levels. However, with the advancement of scientific understanding about various aspects of air pollution, certain pollutants such as bioaerosols, black carbon, organic carbon also need to be considered as important parameters for assessing the quality of air. In India, urban aerosols are composed of carbon as major element (C >50% of total particulates). Around 10-20% of that is sometimes black carbon. Till now, most of our studies have been focused upon chemical pollution and air quality. But this study highlights when air is chemically cleaner during monsoon season due to wash out effect, it is the most polluted biologically due to the presence of bioaerosols. The results showed that the average concentration of bacteria during monsoon season was four times higher than the winter season. With the increasing energy consumption, combustion of fossil fuel in the urban areas and biomass in the rural areas is rapidly increasing which contributes large quantity of black carbon (BC) and organic carbon (OC). These two parameters (BC and bioaerosols) are quite sensitive to assess air quality. In addition, we need to define indoor permissible limits for trace gases such as NO<sub>2</sub>, CO and SO<sub>2</sub> etc. in order to provide good health to the people.

**Key words:** Air quality, bioaerosols, black carbon, organic carbon, criteria, good habitat.

### 1. Introduction

Clean air is a need of our healthy life, which is generally believed to be free from unwanted constituents. Gases such as SO<sub>2</sub>, NO<sub>x</sub>, CO etc. are considered as typical chemical air pollutants for which regular air quality monitoring is carried out by different agencies. Recent focus of research has found carbonaceous aerosols as the important chemical pollutants which affect human health and climate. These carbonaceous aerosols which include black carbon (BC) and organic carbon (OC) are not much discussed in terms of defining criteria for indoors. The concentrations of most of the chemical pollutants are noticed the lowest during monsoon season indicating cleaner air due to wash out effect of rains. But sometimes this information may be misleading about good air quality because when the ambient air levels of chemical pollutants are low, the atmosphere is contaminated by bioaerosols. Hence, air quality needs to be assessed on the basis of chemical and biological aspects.

Bioaerosols are defined as the microorganisms or particles, gases, vapours, or fragments of biological origin that exist in the air. Bacteria, fungi and viruses are the common bioaerosols found in the atmosphere. These airborne microorganisms can be toxigenic, allergenic and infectious. The presence of bioaerosols in ambient air may cause asthma and rhinitis (Beaumont, 1988), hypersensitivity pneumonitis (Sistered et al., 1993), sick-building syndrome (Dales et al., 1991) etc. Bioaerosols are generated by a variety of sources. The most significant sources of bioaerosols are soils, plants, vegetables, water bodies, sewage sludge, animal feeding, fermentation process, agricultural activities and human beings etc.

The abundance of bioaerosols has been reported by various authors at many places worldwide in different conditions (Giorgio et al., 1995; Kim et al., 2009; Wang et al., 2010; Kumar and Kulshrestha, 2011). Both outdoor and indoor environments are found rich in bioaerosols. It is to

# Atmospheric Deposition and Ecosystem Sensitivity

*Bablu Kumar\* and Sudesh*

*School of Environmental Sciences,*

*Jawaharlal Nehru University, New Delhi-110067*

*\*Corresponding author: bablukumarjnu@gmail.com*

## Abstract

Increasing emissions of anthropogenic atmospheric pollutants mainly from fossil fuel combustion and urbanization during past few decades have led to global concern about various processes such as acid deposition, climate change, and monsoon modification. The global trend of Anthropogenic S emissions indicated that reductions occurred in Canada, the U.S., and Europe while major increases occurred in China, India and other parts of east and south Asia. The areas of high N deposition include southeastern China, northeastern India and Bangladesh, large parts of Europe, and northeastern North America. Once they are released in the atmosphere their fate depends upon their physical state, particle size, and chemical reactivity. The pollutants are deposited *via* two processes *viz.* dry and wet deposition. Dry deposition is a pathway by which trace gases and particles are removed from the atmosphere onto the surfaces without involving precipitation. Wet deposition occurs *via* two mechanisms *viz.* in-cloud and below-cloud scavenging. In-Cloud scavenging is important in temperate regions like Europe, North America where measured acidity of rain water is very high due to high emissions of SO<sub>2</sub> and NO<sub>x</sub> and low loading of soil-derived particulate matter in the atmosphere. Unlike temperate region, below cloud scavenging is important in tropics and subtropics like India and China, since the surface layer of the atmosphere has higher concentration of soil-derived particulate matter both at rural and urban sites. The soil derived particulate matter is rich in Ca and Mg which buffers the acidity of rain water. The differences in chemical composition of the deposited atmospheric constituents are responsible for different consequences on terrestrial and aquatic ecosystems in temperate and tropics. The direct effects of wet and dry deposition of acidic substances on terrestrial vegetation in the temperate zone appear to be significant. Due to acidic deposition on soil, pH becomes low thereby reducing cation exchange capacity (CEC) which ultimately lead to depletion of essential soil nutrients like Ca<sup>2+</sup>, Mg<sup>2+</sup> *etc.* affecting various ecosystem in different manner. Sensitive ecosystem like Himalaya,