

Project Completion Report



PHYSICOCHEMICAL CHARACTERIZATION OF AEROSOL AND SOURCE APPORTIONMENT IN THE MID-BRAHMAPUTRA PLAIN IN ASSAM: A MODELING APPROACH

Project Investigators

Dr. Raza R. Hoque Prof. K.P. Sarma Department of Environmental Science Tezpur University

Sponsored by

MINISTRY OF EARTH SCIENCE, Government of India Project No. MoES/16/16/10-RDEAS Title of the project: Physicochemical Characterization of Aerosol and Source Apportionment in the Mid- Brahmaputra plain in Assam: a modeling approach

Name of the PI: Dr. Raza Rafiqul Hoque

Associate Professor, Dept. of Environmental Science

Tezpur University

Name of Co-PI: Prof. K.P. Sharma

Professor, Dept. of Environmental Science Tezpur University

Implementing Institute: Tezpur University

Other Collaborating Institute: Nil

Acknowledgements

- Ministry of Earth Sciences (MoES), Government of India for sanctioning and funding the under the R &D in Earth and Atmospheric Sciences Programme.
- Tezpur University for ICP-OES and SEM-EDX analytical support. The SAIC (Sophisticated Analytical Instrumentation Centre), Tezpur University for emergency services on call.Dr Amit Prakash, Assistant Professor, Department of Environmental Science, Tezpur for the computation support.
- The administration of NERIWALM (Northeastern Regional Institute of Water and Land Management), Tezpur, Assam for providing us the space and required electricity for sampling. The Managing Director and concerned officials of Assam Cooperative Jute Mill Ltd, Silghat (Nagaon District, Assam) for space and electrical connections for sampling. Technical support received from mill staff Mr. Gogoi and Mr. Nurul Ahmed, Lohit Bhuyan and Mr. Bipul Sharma throughout the study has been acknowledged.
- ◆ Indian Statistical Institute (ISI), Tezpur campus for support during statistical analysis.
- NOAA Air Resource Laboratory (ARL) for providing free access to HYSPLIT model and related data. United States Environment Protection Agency (USEPA) for providing free downloadable CMB8.2 model and access to all other related support documents.

Date of Sanction & No: Date 9th March 2011, No MoES/16/16/10-RDEAS Duration of Project: 3 Years

Probable date of completion:

Original (as per sanction letter): 9th March 2014 Revised (give details of all revisions to date along with reasons for delay separately for each revision): 8th March 2015

Name of JRF/SRF/RA recruited under the project:

JRF/SRF: Pranamika Bhuyan (August 2011-March 8, 2014) Field attendant:

- Paramjyoti Borah (December 31st May 2012)
- Shahjahan Ali (June 2012 March 8 2014)

Total Project Cost: **Rs 69, 65, 300/-** (Rupees Sixty-nine Lakh Sixty-five Thousand Three Hundred Only)

Total Expenditure (2011-15): **Rs 65, 43, 123/-** (Rupees Sixty-five Lakhs Forty-three Thousand One Hundred Twenty-three Only)

• Index/table of contents-

•	Executive summary	I-VIII
•	Introduction	1-4
•	Review of Literature	. 5-9
•	Aim and Objective	. 10
•	Methods and Methodology	10-17
•	Summary of results	18-64
•	References	65-81

List of Tables

Table No. Title Page No. 1 Descriptive statistics of PM10 for results of mass concentration and measured parameters $(\mu g/m^3)$ for the whole study period and different seasons.....IV 2 Percent contribution of sources of aerosol over mid-Brahmaputra (Tezpur region) obtained from PCA-MLR analysis......VI The b_{ext} and standard visibility range (SVR) over Tezpur in the 3 mid-Brahamputra Valley......VII 1.2 5.4.1 Statistical results of annual and seasonal variation of mass concentration of PM10_____28 542 Statistical results of water soluble ions during the study period2012-14 and seasonal variation of concentrations(µg/m³)......29-30 5.4.3 Mean concentrations (μ g/m³) and other statistical results of carbonaceous fractions of 5.4.4 5.7 Spatial variation of mean mass concentration of PM10 and concentrations

	of its constituents ($\mu g/m^3$) in the Brahmaputra valley	38
5.9.1	Sea salt and non-sea salt fractions of different water soluble ions during the study	
	period and in different seasons	45
5.9.2	Correlation between various size fractions during Pre-monsoon, Monsoon and Post	<u>;</u> -
	monsoon45-	-46
5.10.1	Percentage frequency distribution of pH during the period 2012, 2013 and	
	2014	.47
5.10.2	Ionic composition of rainwater during the study period (2012-14) in μ eq/L	.48
5.11.2	Scavenging ratio (W, dimensionless), calculated as the relationship between	
	the ionic concentration in the precipitation and the aerosol	52
5.12.1	Ionic ratios and Enrichment factor with respect to sea for the water soluble ionic	
	composition of PM10	.53
5.12.2	Inter species correlation between the measured variables of PM10 for the period o	f
	2012-14	57
5.12.3a	Principal Component Analysis-Multiple linear regression	.59
5.12.3b	Percent contribution of sources of aerosol over mid-Brahmaputra (Tezpur region))
	obtained from PCA-MLR analysis	60
5.13.1:	Coefficients computed from ammonium sulphate growth curve - used to compute	e
	f(RH)	.63
5.13.2	bext and standard visibility range (SVR) over Tezpur in the mid-Brahan	mputra
	Valley	.64

List of Figures

Figure	No. Title	Page No.
1	Tri-Model distribution of seasonal particle number density	III
2	Percentage contribution of major sources by CMB model	VII
2.2	Schematic representation of the formation, growth, and processing of	
	atmospheric aerosols	

4.1	Map of study sites (Site 1-Tezpur university; Site 2-Silghat; Site 3- NERIWA (Source: Google maps)	ALM) 11
5.1	Monthly variation of relative humidity and temperature and windroses	
	for different seasons during the study period	18-19
5.2	Monthly backward trajectories for the whole study period (2012-14) at 500m above	'e
	ground level for 5days starting at 00.00hours	20
5.3.1a	SEM-EDX of Bulk atmospheric sample collected on glass fibre filter	21
5.3.1b	SEM EDX analysis of single aerosol particle	22
5.3.2a	Size distribution of PM10 during the day time around the year	23
5.3.2b	Size distribution of PM10 during the night time around the year	24
5.3.3a	Seasonal variation total aerosol number density	25
5.3.3b	Seasonal variation of aerosol number density in size range (0.265-0.900)µm	25
5.3.3c	Seasonal variation of aerosol number density in size range (1.150-2.250) μ m and	
	(2.750-9.250) µm	26
5.3.3d	Seasonal size distribution pattern	27
5.5.1	Seasonal variation of water soluble ionic concentrations of PM10	34
5.5.2	Seasonal variation of elemental composition of PM10	35
5.5.3	Seasonal variation of carbonaceous fraction of PM10	36
5.6	Spatial variations of particle size distribution	37
5.7.1	Spatial variation of water soluble ionic constituents ($\mu g/m^3$) in PM10	39
5.7.2	Spatial variation of elemental concentration of PM10 ($\mu g/m^3$) during	
	the study period	40
5.7.3	Spatial variation of carbonaceous fractions in PM10 during	
tl	he study period	41

5.8.1	Correlation between profiles rations of biomass smoke particles and aerosol of		
	Different seasons		
5.8.2	Incremental effect of episodic biomass burning on chemical species of PM10,		
	(average conditions of 3 consecutive years)		
5.10.2	Ionic balance and monthly variation of ionic concentration of cations and		
	anions		
5.11.1	Monthly variation of mean pH of rainwater with mean mass concentration of PM10		
	during the period 2012-14		
5.12.1	Enrichment factor of elemental composition of PM10 with respect to crust taking Al		
	as reference element		
5.12.3	Linear correlation between observed and model predicted total species		
	concentration(R ² =0.907)60		
5.12.4	Percentage contribution of major sources during the whole study period and in		
	different seasons by CMB model		

Abbreviation used:

Abbreviation	Full form
PM	Particulate matter
PCA-MLR	Principal Component Analysis-Multiple Linear
	Regression
CMB	Chemical Mass Balance
NERIWALM	Northeastern Regional Institute of water and Land
	Management
NEERI	National Environmental Engineering Research Institute
SEM	Scanning Electron Microscope
EDX	Energy dispersive X ray spectroscopy
ICP-OES	Inductively coupled Plasma-Optical emission
	Spectrometry
TOC	Total Organic Carbon
IC	Ion Chromatograph
СРСВ	Central Pollution Control Board
OC	Organic carbon
EC	Elemental carbon
WSOC	Water soluble organic carbon
WSIC	Water soluble inorganic carbon
TC	Total carbon
WSTC	Water soluble total carbon
NAAQS	National Ambient Air Quality Standard
EF	Enrichment Factor
SVR	Standard visibility range

SD	Standard deviation
US-EPA	United states Environmental Protection Agency
NAAQM	National Ambient Air Quality Monitoring
INDOEX	Indian Ocean Experiment
HYSPLIT	Hybrid single particle Lagrangian Integrated Trajectory
NOAA	National Oceanic and Atmospheric Administration
ARL	Air Resources Laboratory
GDAS	Global Data assimilation System
MDL	Method detection limit
BDL	Below detection limit
MBIE	Meji Burning Induced Enrichment
PC	Principal Component
µeqL ⁻¹	Micro equivalent per litre
µgm ⁻³	Micro gram per metre cube

Executive Summary

The project entitled "Physicochemical characterization of aerosol and source apportionment in mid-Brahmaputra plain in Assam: a modeling approach" is an attempt to understand the aerosol characteristics of mid-Brahmaputra plain. Since there was no such systematic study reported from this region explaining the possible major contributing sources of aerosol, this study was envisaged primarily to address basic issues of aerosol properties and their source apportionment in the Tezpur region of mid-Brahmaputra valley. Aerosol has bearing on the precipitation chemistry and, therefore, rainwater chemistry of the region was also studied.

The study involves physical and chemical characterization of aerosols to create a database for operation of two source apportionment receptor models namely Principal Component Analysis (PCA) and Chemical Mass Balance (CMB). The Physico-chemical data obtained was also used to model estimate the standard visibility rage (SVR) prevailing around the year in the study area.

To execute the objectives, we have chosen three sites in the mid-Brahmaputra plain namely Tezpur city (Urban), Tezpur University campus, Napaam (rural/ institutional) and Silghat (remote site) for over a year long cycle. [Tezpur and Napaam, District Sonitpur, are located on the north bank of Brahmaputra River and Silghat (District Nagaon), is located on the South bank]. Stations are centrally located along the length of Brahmaputra River in Assam.

Twenty-four hour grab sampling of PM10 was carried out by High volume sampler on Whatman glass fibre filter paper. GRIMM aerosol spectrometer was used to monitor size and number density of aerosol. To get the morphology of single particle a vacuum pump system was used in which both the glass as well as membrane filters of 25 mm diameter taken in a filter holder. Air mass was sucked through the filters at constant flow rate of 1.4 lt/min for 1 hr. Rainwater samples were collected manually using high density polypropylene bottles and funnel (Rastogi and Sarin, 2005)

For elemental analysis PM10 samples were digested using HNO₃ (Shah et al., 2006) and analyzed in ICP-OES (Perkin Elmer, OPTIMA-2100 DV). Morphological study was observed under a Scanning Electron Microscope (SEM) model JEOL JSM6390LV. Energy Dispersive

X-ray Spectrometer (EDX), INCAx Sight microanalysis system (Oxford Instruments, Model 7582), hyphenated with a Scanning Electron Microscope (SEM) (JEOL JSM 6390 LV).

Water soluble ions associated with the PM10 samples were extracted using ultra sonication. The ionic constituents of the extracted samples and rainwater were analyzed in Metrohm Ion Chromatograph (882 Compact IC professional). Analytikjena TOC analyzer was used for carbon analysis. Carbon of solid samples was analyzed using HT1300 module while water soluble carbon was analyzed by Multi N/C 2100 module. TC was analyzed by directly heating at the furnace while EC was determined following Lin and Tai, 2001 method.

Source apportionment of aerosol (PM10) was conducted using two receptor models namely Principal Component Analysis (PCA) and Chemical Mass Balance (CMB 8.2). The freely available model software of the CMB8.2 was obtained from the USEPA official website. The Standard Visibility Range (SVR) was estimated, the b_{ext} calculated from the light attenuating species of the PM10 using the model used in the IMPROVE programme of the USEPA (previously used by Singh et al., 2008)

The size distribution of some of the selected days from various seasons of the year a trimodeldistribution was observed (Fig 1). Various shapes of aerosol were found of combustion, crustal and biogenic origin (pollen). A particle suspected of diatom was also found in the study.





Table 1 represents the mean and other statistical results of major constituents of PM10 during the whole monitoring period and in different seasons. Followings are the major findings drawn from the monitoring period. It was observed that mean mass concentration of PM10 period was found 53.7±46 μ g/m³ which is within the national ambient air quality standard of 60 μ g/m³ (CPCB, 2009). The minimum PM10 was found during monsoon period and maximum during winter period. It was observed that water soluble ions constituted 17% of the total PM10 and followed the order SO₄²> Na⁺> K⁺> NH₄⁺> NO₃> CI> Ca²⁺> Mg²⁺> F⁻. Among ions SO₄²⁻ was found to be maximum for the whole study period having concentration 2.19±2 μ g/m³. Na⁺ was found to be dominating cation with concentration 1.12±1 μ g/m³ followed by K⁺.

	Study	period	Pre- m	onsoon	Mons	soon	Post -n	nonsoon	Wi	nter
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PM10	53.73	46	52.29	45	22.38	14	43.95	31	97.07	49
F -	0.03	0.07	0.02	0.03	0.01	0.02	0.05	0.13	0.03	0.03
Cl ⁻	0.92	1.13	0.94	1.25	0.83	1.00	0.97	1.17	0.98	1.19
NO ₃	1.06	1.16	1.05	0.96	0.53	0.55	0.65	0.54	2.01	1.54
SO_4^{2-}	2.19	2.13	2.23	1.51	1.08	0.59	1.15	1.20	4.35	2.61
Na ⁺	1.85	1.12	1.96	1.31	1.59	0.89	1.71	0.86	2.18	1.35
$\mathrm{NH_4}^+$	1.12	1.20	1.11	0.92	0.54	0.48	0.65	0.37	2.21	1.66
K^+	1.35	1.28	1.35	0.94	0.77	1.06	1.07	0.98	2.24	1.51
Ca ²⁺	0.51	0.39	0.68	0.44	0.33	0.41	0.53	0.29	0.55	0.33
Mg^{2+}	0.07	0.05	0.09	0.06	0.04	0.03	0.07	0.05	0.08	0.05
Al	5.43	3.93	4.34	4.81	5.30	2.69	6.75	4.67	5.26	3.38
Cd	0.004	0.01	0.001	0.001	0.002	0.001	0.002	0.002	0.01	0.01
Со	0.003	0.01	0.002	0.002	0.002	0.002	0.003	0.003	0.005	0.02
Cr	0.06	0.10	0.05	0.05	0.03	0.02	0.06	0.13	0.11	0.14
Cu	0.03	0.05	0.01	0.02	0.01	0.01	0.02	0.03	0.07	0.09
Fe	1.54	3.39	1.00	1.18	0.52	0.87	0.75	1.31	3.81	5.88
Mn	0.04	0.09	0.03	0.05	0.02	0.08	0.02	0.02	010	0.15
Ni	0.06	0.17	0.03	0.02	0.03	0.12	0.03	0.05	0.16	0.28
Pb	0.07	0.14	0.05	0.06	0.02	0.02	0.04	0.04	0.17	0.24
WSOC	5.40	5.52	3.43	2.41	2.91	1.71	4.17	2.71	10.88	7.95
WSIC	0.90	0.84	0.65	0.45	0.68	0.83	0.94	0.74	1.37	1.01
WSTC	6.28	5.71	4.08	2.61	3.59	1.97	5.11	3.04	12.09	7.90
TC	18.96	19.30	13.28	10.37	10.53	20.69	16.61	13.59	34.50	18.53
EC	4.20	4.08	3.48	2.35	2.59	1.40	3.09	2.23	7.60	6.16
OC	14.76	17.37	9.80	9.03	7.94	20.70	13.52	11.90	26.91	16.18

Table 1: Descriptive statistics of PM10 for results of mass concentration and measured parameters $(\mu g/m^3)$ for the whole study period and different seasons

Concentrations of measured elements followed the order viz. Al>Fe>Pb>Ni>Cr>Mn>Cd>Co. It was observed that mostly crustal originated elements such as Al, Fe and Mn are abundant in the PM10 fraction. Concentrations of Pb and Ni were observed to be within the limit given by CPCB.

Carbonaceous fractions of PM10 for the study period 2012-14 were observed. Carbonaceous fraction has highest percentage contribution to the PM10 mass concentration which is 35% among all other parameters. The OC/EC ratios (Average 3.51) were found relatively high suggesting the dominance of emissions from biomass and biofuel burning as compared to lower OC/EC ratios from fossil fuel (Coal and vehicular exhaust) (Ram et al., 2012). The average WSOC/OC ratio was found 0.36 for the whole study period. This WSOC/OC ratios in the atmospheric aerosols have been used to indicate the extent of secondary aerosol formation and /or aging of aerosols during long range transport to remote locations (Aggarwal and Kawamura, 2009; Zhang et al., 2007).

The correlations between profile ratios of biomass smoke particles and aerosol over the study area was tested and it was found to be positive – monsoon (r = 0.65), post-monsoon (r = 0.68), winter (r = 0.70) and pre-monsoon (r = 0.72). This would mean that household biomass burning emissions have sufficient influence in aerosol properties over mid-Brahmaputra region.

The rainwater chemistry of the mid-Brahmaputra region is as per below:

There have been dominance of rainfall events with pH around 5.6 indicates cleaner atmospheric condition in the mid-Brahmaputra region as per literature. Rainwater samples were measured for ions viz. F⁻, Cl⁻, Br⁻, NO₃⁻, SO₄²⁻, Na⁺, K⁺, NH₄⁺, Ca²⁺ and Mg²⁺ for the year 2012-14. Concentrations of ionic constituents followed the order Ca²⁺>NH₄⁺>SO₄²⁻>Cl⁻> NO₃⁻> K⁺> Na⁺>Mg²⁺>F⁻>Br⁻. Among anions SO₄²⁻ was found to be maximum with concentration 90.90±113µeqL⁻¹ followed by Cl- with concentration 85.84±118 µeqL⁻¹.

To investigate dependency of rainwater chemistry on aerosol composition, we have drawn a relationship between pH and PM10 losing of each month during the study period 2012-14 considering rain events just after the PM10 sampling. It was observed that relation between mass concentration of PM10 and pH of rainwater showed negative correlation. The order of scavenging ratio (W) for the major ionic concentration was observed to be NO_3 - Ca^{2+} - Mg^{2+} - Cl^- > NH_4^+ > K^+ > SO_4^2 -> Na^+ . Primarily, a high W for NO_3^- ion was observed during the whole study period.

Enrichment factor of water soluble ions and trace elements were calculated with respect to sea and crust taking Na and Al as reference ion for marine and crust respectively. It was observed that ratio of SO_4^{2-} , K⁺ and Ca²⁺ with respect to sea is higher than unity. Higher EF is an indication of influence of anthropogenic input or other sources from nature like crustal input. Higher EF values with respect to crust were observed for Cr, Cu, Ni, Pb (10<EF<100) for the whole study period, whereas Ca and Mg showed very less enrichment. Trend was almost same for all the season.

Source apportionment was carried out using two models PCA and CMB. The identified sources by PCA were quantified by Multiple Linear Regression (MLR) Analysis. The summary of the PCA-MLR analysis has been given in Table 2 with the indentified sources of aerosol and respective percentage contribution.

Table 2: Percent contribution of sources of aerosol over mid-Brahmaputra (Tezpur region) obtained from PCA-MLR analysis (n=250)

Source (From PCA)	Percent contribution
Combustion – biomass burning, vehicular	56%
emission, coal burning, etc	
Street dust	16%
Construction dust	13%
Suspended Soil/Crustal dust	15%

The CMB model estimates explain that biomass burning, road dust and vehicular emissions are the major contributors of atmospheric aerosol over mid-Brahmaputra region. The source apportionment done by operating CMB gave the following output results (average of 200 nos. of 24 hr samples) shown in Fig 2:



Figure 2: Percentage contribution of major sources by CMB model

A Standard visibility range (SVR)> 19 km is considered very good visibility (Gomez and Smith, 1987). Model outcome showed that the visibility over mid-Brahmaputra valley is good throughout the year. There were of course events of lower visibility during months of Dec, Jan and Feb as per model estimates. Standard visibility range (SVR) along with b_{ext} over Tezpur in the mid-Brahamputra Valley is given in Table 3.

Table 3: The <i>b</i> _{ext} and stand	lard visibility rang	e (SVR) ov	er Tezpur in the	e mid-Brahamputra	Vallev
The stand		• (~ · · ·) • ·	•••••••••••••••••••••••••••••••••••••••		

Months	b_{ext} (Mm ⁻¹)			SVR (Km)		
	Mean	SD	Range	Mean	SD	Range
			356-			
Jan	656	223	1006	11	7	4.8-23
Feb	545	114	424-784	12	3	6.6-17
Mar	414	97	281-578	21	10	10.1-43
Apr	352	54	288-411	27	9	17.6-40
May	374	36	305-414	22	6	17.5-34
Jun	329	24	292-347	29	6	25-38
Jul	324	52	233-393	36	23	19-89
Aug	322	53	286-417	32	9	17-40
Sep	336	89	272-468	33	14	14-48
Oct	341	96	246-501	34	20	13-69
Dec	494	134	311-720	16	8	7.0-32

References

- Aggarwal, S. G.; Kawamura, K., 2009. Carbonaceous and inorganic composition in long-range transported aerosols over northern Japan: Implication for aging of water-soluble organic fraction. Atmos. Environ. 43 (16), 2532–2540.
- CPCB. 2009. Central pollution control Board, Government of India, <u>http://www.cpcb.nic.in/National Ambient Air Quality Standards.php</u> (as on 30-09-2015).
- Deka, P., Hoque, R.R., 2014. Diwali Fireworks: early signs of impact on PM10 properties of rural Brahmaputra valley. Aerosol Air Qual Res. 14, 1752-1762.
- Gomez, B., & Smith, C. G. (1987). Visibility at Oxford 1926–1985. Weather, 42,98–106.
- Lin, J.J., Tai, H.S., 2001. Concentrations and distributions of carbonaceous species in ambient particles in Kaohsiung City, Taiwan. Atmos. Environ. 35, 2627-2636.
- Ram, K., Sarin, M.M., Sudheer, A.K., Rengarajan, R., 2012. Carbonaceous and secondary inorganic aerosols during wintertime fog ad haze over urban sites in the Indo Gangetic plain. Aerosol Air Qual Res. 12, 359-370.
- Rastogi, N., Sarin, M.M., 2005. Chemical characteristics of individual rain events from a semi-arid region in India: three year study. Atmos Envrion. 39, 3313-3323.
- Shah, M.H., Shaheen, N., Jaffar, M., Khalique, A., Tariq, S.R., Manzoor, S., 2006. Spatial variations in selected metal contents and particle size distribution in an urban and rural atmosphere of Islamabad, Pakistan, J. Environ. Manage. 78 (2), 128-137.
- Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., Worsnop, D. R., 2007. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes.Geophys. Res. Lett. 34, L13801 DOI: 10.1029/2007GL029979
- Singh T, Khillare PS, Shridhar V, Agarwal T., 2008. Visibility impairing aerosol in urban atmosphereofDelhi.EnvironMonitAssess(2008)141:67–77

1. Introduction

Aerosols can be defined as dispersions/ suspension of solid or liquid in the atmosphere and are important constituent of atmosphere. The term particulate matter (PM) is commonly used to refer the solid phase suspension matter in the atmosphere. So, particulate matters are solid and liquid droplets present ubiquitously in the atmosphere and play vital role in the climate change. These particles are made up of a number of components, including acids (such as nitrates and sulfates), organic chemicals, metals, and soil or dust particles.

The size of particles is directly linked to their potential for causing health problems. Particles with diameter 10 μ m or smaller are the particles that generally pass through the throat and nose and enter the lungs and can affect the heart and lungs and causes serious health effects.

1.1 Classification

United states Environmental Protection Agency groups particles into two categories. These are

- Inhalable coarse particles which are larger than 2.5 μm and smaller than 10 μm in diameter. These are mainly associated with emissions from roadways, industries etc.
- Fine particles which are 2.5 μm in diameter and smaller. These particles are found in smoke and haze and can be directly emitted from sources such as forest fires, or they can form when gases emitted from power plants, industries and automobiles react in the air.

Again depending on their route of formation particulate matter can be divided into primary and secondary particles. Primary particles are emitted directly from a source, such as construction sites, unpaved roads, fields, smokestacks or fire. Secondary particles are formed in complicated reactions in the atmosphere of chemicals. These reactions are primarily photon driven. Some secondary particles include oxides of sulfur, nitrogen and organic carbons. Tropospheric aerosols contain sulfate, ammonium, nitrate, sodium, chloride, trace metals, carbonaceous materials, crustal elements and water.

1.2 Sources of Particulate matter

Sources of atmospheric particles may be natural or anthropogenic depending on their origin. Among natural sources of particles include soil and rock debris, volcanic emissions, sea spray, biomass burning and reaction between natural gaseous emissions. Human activities include burning of fossil fuels in vehicles, power plants and various industrial processes. Table 1.2 shows the range of emission estimates of particles generated from natural and anthropogenic sources, on global basis. Figure 1.2 shows the processes involved in the formation of aerosols.

Table 1.2: Global emission estimates for major aerosol classes (source- Atmospheric chemistry and physics)

Source	Estimated Flux, Tg/yr	References
Natural		
Primary		
Mineral dust		Zender et al., 2003
0.1-1.0	48	
1.0-2.5	260	
2.5-5.0	609	
5.0-10.0	573	
0.1-10.0	1490	
Seasalt	10,100	Gong et al., 2002
Volcanic dust	30	Kiehl and Rodhe, 1995
Biological debris	30	Kiehl and Rodhe, 1995
Secondary		
Sulfates from DMS	12.4	Liao et al., 2003
Sulfates from volcanic SO2	20	Kiehl and Rodhe, 1995
Organic aerosol from biogenic VOC	11.2	Chung and Seinfeld, 2002
Anthropogenic		
Primary		
Industrial dust (except black carbon)	100	Kiehl and Rodhe, 1995
Black carbon	12 ^a	Liousse et al., 1996
Organic aerosol	81 ^a	Liousse et al., 1996
Secondary		
Sulfates from SO2	48.6 ^b	Liao et al., 2003
Nitrates from Nox	21.3 ^c	Liao et al., 2004

a TgC

b Tg S

c Tg NO₃⁻



Figure 1.2: Schematic representation of the formation, growth, and processing of atmospheric aerosols (source: Zhang et al., 2015)

1.3 Effects of particulate matter

Particulate matter possesses two distinct effects on the environment, viz, direct and indirect effect. Depending on their composition, size and chemical behaviour, particulate matter behaves differently in different environmental conditions.

1.3.1 Health

The size of particulate matter is primarily linked with health problems. Smaller particles having diameter less than 10 micrometers pose serious health problems, because they can get penetrated into the lungs and ultimately to the bloodstream. Fine particles are mainly associated with respiratory problems in human. More over various scientific studies related to health issues revealed that fine fraction of particulate matters are responsible for various serious health issues in human beings. Long term exposure to these particles can cause premature death in people with heart or lung disease, nonfatal heart attacks, irregular heartbeat, aggravated asthma, decreased lung function and increased respiratory symptoms such as irritation of the airways, coughing or difficulty breathing.

1.3.2 Effect on ecosystem

Numerous studies have revealed that increase in the particle concentration in the atmosphere causes severe damage to the ecosystem. Vegetations are vulnerable to the particle pollution. Studies have reported that coating with dust may cause abrasion and radiative heating thereby reducing the process of photosynthesis by preventing essential photon flux to the photosynthetic tissues. Acidic and alkaline materials may cause leaf injury, stomata damage and while other materials may be taken up across the cuticle. PM deposited in the rhizosphere zone may affect the nutrient cycle of plant.

1.3.3 Effect on visibility

This is a direct effect of aerosols in the atmosphere. Visibility impairment is an important aspect of atmosphere. Fine particles (PM2.5) have been found to be associated with the reduced visibility. This recognizable effect of air pollution in the atmosphere is caused by the scattering and absorption of light by particles and gases in the air (US EPA 1999). Particulate matter that generally causes visual effects such as smog consists of sulphur dioxide, nitrogen oxides, carbon monoxide, mineral dust, organic matter, and elemental carbon or black carbon. The particles are hydroscopic due to the presence of sulphur, and SO₂ is converted to sulphate when high humidity and low temperatures are present. This causes the reduced visibility and yellow colour.

1.3.4 Effect on climate

Atmospheric aerosols affect the climate system by altering the radiation budget of the earth attenuating the incoming solar radiation and retaining outgoing through absorption of long wave radiation.. These effects may be of direct, indirect or semi direct. Direct effect of aerosol is associated with the scattering and absorption of solar radiation. Sulfate particles are responsible for global cooling effect due to its light scattering properties. Again carbonaceous particles such as soot, black carbon or elemental carbon are responsible for absorption of solar radiation keeping the earth warm. Moreover, aerosols also have indirect effect on climate by acting as cloud condensation nuclei. Fine particles or accumulation mode particles act as CCN and thereby change the earth's radiative budget due to the modification of clouds. An increase in the CCN leads to an increase in the number of cloud droplets and this leads to more scattering of solar radiation.

2. Review of literature & rationale for study

Presence of high levels of air pollutants in the ambient air affect the human health, health of ecosystems and other vital earth processes process. In India, aerosol studies have been carried in a program mode during last 5 decades only since International Geophysical Year (IGY) in 1957. Later on, Monsoon Experiment (MONEX), IMAP and most recently INDOEX were done to better understand Indian aerosols (Mitra and Sharma, 2002). The Indian Ocean Experiment (INDOEX) conducted a few years ago was the most ambitious research project so far in this field in India. Itmainly concerned with the haze over south Asia and the adjacent Indian Ocean (Ramanathan et al., 2002). INDOEX resulted in new understanding of aerosols above the Indian Ocean but not of urban aerosols in India (Monkkonen et al., 2004). In India, studies on particulate matter having aerodynamic diameter ≤ 10 has been added by governmental agencies like National Environmental Engineering Research Institute and Central Pollution Control Board (CPCB) by the end of 2000 (World Bank 2001; TERI, 2001).

Increasing concentrations of Particulate matters in the atmosphere has been drawing attention of the researchers due to their effect on environment as well as health of ecosystem. Researchers have found out that atmospheric aerosols have an impact on climate, both positive and negative, as well as hydrological cycle and human health (Pavuluri et al., 2011; Menon et al., 2002; Ackerman et al., 2000; Ramanathan et al., 2001). These particles affect Earth's radiation balance by scattering and absorbing solar and terrestrial radiation (Charlson et al., 1992). Particulate matters act as a cloud condensation nuclei thereby affecting cloud formation and cessation and also regulate heat transfer in the atmosphere which eventually contributes to the climate change (Tiwari et al., 2014). When we talk about aerosol pollution and its impact, it is worth mentioning that impact of aerosols does not confine to sources rather its impact can be felt across national boundaries and soon becomes a matter of global interest (Mitra and Sharma 2002; Nair et al., 2006). Issues related to particulate matter of various size fractions has been being studied extensively in various environments of the world (Kyotani and Iwatsuki 2002; Shi et al., 2003; Dan et al., 2004; Samburova et al., 2005; Johnson et al., 2006; Chonga et al., 2002; Han et al., 2005; Gomiscek et al., 2004; Anttila and Salmi, 2006; Borredy et al., 2015). It was observed during recent years that due to rapid growth of industries, vehicles, population, and anthropogenic activities, aerosol concentrations have been increased in megacities of rapidly developing countries in Asia (Menon et al., 2002; Akimoto, 2003). In India, studies on particulate matter having aerodynamic diameter ≤ 10 has been added by governmental agencies like

National Environmental Engineering Research Institute and Central Pollution Control Board (CPCB) by the end of 2000 (World Bank 2001; TERI, 2001). An extensive study on particulate matter has been in progress with different objectives related to its chemical constituents. These are some of the studies at different environments Kumar et al., 2001; Guazzotti et al., 2003; Sharma and Maloo, 2005; Chowdhury et al., 2007; Rengarajan et al., 2007; Sharma et al., 2007; Kothai et al., 2008; Khare and Baruah, 2008, 2009; Badarinath, et al., 2009; Chakraborty and Gupta, 2009; Fu et al., 2009, 2010; Pavuluri et al., 2010; Rastogi and Sarin, 2009, Khare et al., 2011; Deka and Hoque, 2014a; Deka and Hoque, 2014b and references therein.

Atmospheric particles are a mixture of various chemical components because of their multiple origins (Ward and Lincoln 2006; Saitoh et al., 2008; Deshmukh et al., 2011). Major anthropogenic contributors of these particles are traffic, industry, agriculture and forestry, households, construction, quarrying and mining, cement plants and ceramic industries, fossil fuel power plants etc. On the other hand, main natural contributors include the sea spray, soil re-suspension, volcanic eruption, biological particles, debris etc (Yadav et al., 2014). Tiwari et al., 2009 reported that major sources of particles in India are windblown dust, secondary aerosol, bio and fossil fuel combustion, traffic exhaust and biomass burning. Inorganic ions along with carbonaceous particles have been found to be associated with particles in the atmosphere. Most of the primary particulates act as precursors for large amount of inorganic and organic secondary aerosols (Rastogi et al., 2015). Secondary aerosol formation over a given region may vary depending upon the meteorological conditions such as solar radiation, temperature, wind speed, wind direction etc. Many water soluble ionic species (Na⁺, K⁺, NH₄⁺, Mg²⁺, Ca^{2+} , Cl^{-} , NO_{3}^{-} and SO_{4}^{2-}) constitutes large fraction of atmospheric particle mass and associated with adverse effects on human health and acidification of the environment (Grantz et al. 2003; Jung and Kim 2006). Kulshrestha et al., 2009 reported that most of the ions present in the troposphere gets easily dissolved by water in nature.

In S. Asia and N. Africa, the large north-south gradient in the aerosol dimming has altered both the north-south gradients in sea surface temperatures and land–ocean contrast in surface temperatures, which in turn slow down the monsoon circulation and decrease rainfall over the continents. On the other hand, heating by black carbon warms the atmosphere at elevated levels from 2 to 6 km, where most tropical glaciers are located. BC is thought to be the prime cause of melting of Hindu Kuch-Himalayan-Tibetan (HKHT) glaciers. Again, 50% of the observed retreat in arctic sea ice may be due to BC forcing (Ramanathan and Feng, 2009). Therefore, studies on black carbon levels are a vital

component. For, biomass burning is an inevitable phenomenon in the northeast India, high probabilities are there that atmospheric black carbon in this region would be high. Carbonaceous particles are important constituents of ambient aerosol. These particles are found in different forms in the atmosphere viz. primary including elemental, organic and secondary organic compounds (Sannigrahi et al., 2006). Carbonaceous aerosols are dominant component of fine particles contributing up to 10-70% to the total mass concentration and having different chemical and thermodynamic properties (Tsapakis et al., 2002). It was also reported that water soluble organic carbon may potentially act as cloud condensation nuclei and contributes significantly to the carbonaceous aerosol thereby contributing to the total carbon (TC up to 30%) and organic mass (more than 50%) (Kiss et al., 2002; Mader et al., 2004). Many researchers have reported that smoke from household fuel burning also act as an important source of atmospheric pollutants and has a significant impact on human health (Mumford et al., 1987), ambient environment (Nel et al., 2005), atmospheric chemistry (Ramanathan et al., 2001; Deka and Hoque, 2015) and climate change (Menon et al., 2002). Along with carbonaceous aerosols, ions such as SO_4^{2-} , Ca^{2+} , Cl^- are also important components of smoke from households. Water soluble fractions of organic carbon compounds have both primary and secondary sources and also one of the major routes to investigate secondary organic aerosol. Water soluble organic carbon is a complex mixture likely composed of oxygenated C functional groups such as COOH, COH, COC, CONO₂, CNO₂ and CNH₂ (Saxena et al., 1995).

Heavy metals are the metals with a specific gravity greater than about 5.0. They have a high atomic number and high atomic weight. Heavy metals, mainly the particulate form of atmospheric pollutants are persistent in nature and known for their toxicity when taken in excess (Sharma et al., 2008). The toxic trace metals generally show inverse relationship with wind speed, relative humidity and temperature (Karar et al., 2006).

Natural emissions such as crustal minerals, forest fires and oceans, traffic and industrial emissions such as combustion of fossil fuel and industrial metallurgical processes are the principal sources of heavy metals in the ambient air. The possible sources of Cr, Zn, Pb, Cd, Ni, Mn and Fe in PM10 particulates can be comprised of solid waste dumping, vehicular traffic with the influence of road dust, road dust and soil dust at residential site while vehicular traffic with the influence of soil dust, road dust, galvanizing and electroplating industry, and tanning industry at industrial site (Karar et.al. 2006). Naturally derived trace metals are usually found in coarse particles (Lee and Hieu, 2011). Zinc, copper and lead are three of the most common heavy metals emitted by vehicle traffic, totaling

at least 90% from the total emitted quantity (Popescu C. G. 2010). Heavy metals from air eventually deposit on the ground surface depending on wind patterns and ultimately increase their concentrations in adjacent areas. Atmospheric deposition of heavy metals increases their concentrations in soil and consequently in food chain (Sharma et.al. 2008).

The concentration of heavy metals in the air can be higher in spring. This may be due to the differences in wind direction in the spring (Lee and Hieu, 2011). The crustal enrichment factor has commonly been used as a primary tool to evaluate the relative strength between crustal and noncrustal sources in a given area. These EF factor predicts which metal in the atmosphere is likely to be increased by human activity. Pb and Cd are considered relatively volatile metal and because they are mainly transported through the atmosphere, they have been termed as Atmophile elements. In contrast Cr and Ni have been termed as lithophile element because of their mass principally transported by streams (Khillare et.al. 2004). The correlation matrix indicates that the heavy metals are showing a significant correlation with each other. This indicates their common source either vehicular or industrial emission (Khillare et.al. 2004).

The varying degree of metal concentration in SPM has a great significance because of the toxicity to the living organisms (Khillare et.al. 2004). The measurement of metal concentration levels in inhalable particles is important in determining their potential impacts on human health (Park et.al. 2010).

Numerous studies are there focusing on physical properties of aerosol and their effect on environment and climate. These studies have been mainly related to the size distribution of particulate matters in the atmosphere and their effects on human health and climate (Grimm and Eatough, 2009; Xu et al., 2002; McFiggans et al., 2006) It is important to measure the concentration and composition of particulate matter in the atmosphere on a real time basis. Since these particles are important with respect to human health and earth's radiation budget. In India various studies have been reported from different environments on physical properties of aerosol and its effect on radiative forcing (Jayaraman et al., 2006; Das and Jayaraman, 2011; Das et al., 2009; Singh et al., 2015; Kharol and Badarinath, 2006; Ganguly et al., 2006; Mohan and Payra et al., 2009; Ganguly et al., 2005; Pant et al., 2006; Massey et al., 2012). Among physical properties morphological studies of different components of particulate matter are important to assess their characteristics. Many researchers have studied morphological characteristics of different components of particulate matter using SEM, SEM-EDX, TEM etc. (Posfai et al., 1998; Zhang et al., 2008; Li et al., 2003; Li et al., 2009; Loh et al., 2012; Slowik et al., 2004). In India, various studies on morphology of aerosol particles have been reported from different environments (Agarwal et al., 2011; Tiwari et al., 2015; Durga et al., 2015; Pipal et al., 2011; Shandilya and Kumar, 2010; Chithra and Nagendra, 2013; Attri et al., 2001; Sarkar et al., 2010)

Study of aerosol and rainwater interaction has become an interesting phenomenon for the researchers to understand the processes involved. Many researchers have studied mechanism involved in the removal of aerosol by wet deposition (Chate et al., 2003; Kulshrestha et.al., 1999; He and Balasubramanian, 2008; Maria and Russell, 2005; Tsai et al., 1990; Encinas et al., 2004; Tang et al., 2005).

In India, a few studies are carried out to identify the sources of particulate matter specifically for the particulates with size less than 10 (PM10) and 2.5 (PM_{2.5}) μ m. Receptor modeling techniques such as enrichment factor (EF) analysis, chemical mass balance (CMB), factor analysis (FA), empirical orthogonal function (EOF), multiple linear regression, neural networks, edge detection and cluster analysis are used for source apportionment studies. The CMB model is most trusted for the coarse and fine particle source apportionment (USEPA, 1997). In Indian context, source apportionment by CMB is limited and factor analysis is widely used (Chelani et al., 2008)

a. Importance of the proposed project

There are limited research studies on aerosols in North-East India. To arrive at a national status of aerosols, data from northeast region of India cannot be ignored. Also, it is worthy to mention that polluting sources of the region is unique compared to major cities of India. So, it is imperative to carry out a source apportionment study of aerosols.

To understand the climate implications and other environmental effects aerosol better, physical and chemical properties of aerosols are essential. Large set of data which is expected from the study would be very handy for modeling studies in the future for us and many other groups working in the field. The outcome of the project would add up to the national status of aerosol that would be useful to researchers and planners.

3. Aims & Objectives (Objectives as approved/Deviation made from original objectives if any, while implementing the project and reasons thereof)

Followings are the major objectives of the project

- 1. Physicochemical characterization of atmospheric aerosols of central Assam region with the following major initiatives:
- o Morphological studies and size distribution
- o Estimation of mass density and number
- Elemental composition
- Ionic composition
- Organic and inorganic carbon
- 2. Spatial and seasonal variability of aerosols mass and number density and composition. Influence of biomass burning and monsoon on the aerosol characteristics would also be looked into.
- 3. Rainwater characterization over the year. Enumeration of relationship between rainwater chemistry and aerosols.
- 4. Modelling-
- o Source apportionment by CMB and PCA models
- o Model estimation of visibility impairment on the basis of mass scattering and absorption efficiencies

4. Methodology (Giving full details of study design, methods adopted, data collected supported)

4.1 Sampling sites

Monitoring of aerosols (aerodynamic diameter $\leq 10\mu m$ or PM10) at three stations namely Tezpur University campus, Napaam (Rural, Site 1), Silghat (Rural industrial site, Site 2) and Tezpur city (Urban, Site 1), and was carried out for the period of 2012-2014 (Figure 4.1). Tezpur and Napaam, District Sonitpur, are located on the north bank of Brahmaputra River and Silghat, District Nagaon, is located on the South bank. Stations are centrally located along the length of Brahmaputra River in Assam; Tezpur is Geographical position of Tezpur is at 26°37′N and 92°50′E and Silghat is at $26^{0}37'N$ 92°56′E. Within the Tezpur town sampling was carried out at North Eastern Regional Institute of Water and Land Management (NERIWALM) situated between the coordinates $26^{\circ}64$ 'N and $92^{\circ}81$ 'E.



Figure 4.1: Map of study sites (Site 1-Tezpur university; Site 2-Silghat; Site 3- NERIWALM) (Courtesy: Google maps)

According to the 2011 census, population of Sonitpur district is 2.0 million with a population density of 365per square km (Census of India 2011). The State of Assam has over 1.8 million registered

vehicles for transport and non-transport purposes as on 31st March 2012. The region is underdeveloped in terms of industrial growth. There are no heavy industries around the sampling station yet most tea estates have processing units of their own. The region as a whole has a few petroleum refineries, cement and paper industries and mines. Conventional biomass burning for cooking and some other household activities are prevalent in this region. Vast majority of the population in the region is dependent on solid biomass like wood, cow dung, crop residue and bamboo to deal with daily energy needs. Forest fires and agricultural biomass burning are seen during the months preceding the monsoon.

The whole year is divided into four distinct periods according to India Meteorological Department (IMD), i.e. Pre-monsoon (March-May), Monsoon (June- September), Post-monsoon (October-December) and winter (January-February). Pre-monsoon period and monsoon period receives highest rainfall. In summer the temperature rises up to 38.6°C and during winters the temperatures may drop to 12°C. Pre-Monsoon season starts from the month of March to May and this experience severe Nor'wester wind locally known as *"Bordoichila"* including the West Bengal region (Kaal Baishakhi). The effect of *Bordoichila* is experienced by the whole Assam region. This thunderstorm is accompanied by the lightning flashes, torrential rainfall, strong wind gust, hail and occasional tornadoes develops due to intense convection. A significant number of active brick kiln industries are there surrounding the study site. These industries get activated during the dry season i.e. during Postmonsoon to winter season and continue before it starts raining. Settlements surrounding the study area depend on wood, sticks made of cowdung, bamboo etc as fuel for their daily requirement in household activities.

4.2 Sampling of PM10

1. PM10 samples were collected on Whatman Glass microfiber (GF/A; size $8"\times10"$) by Respirable Dust Sampler (NEERI designed). Samplers were placed about 10-20m above ground at all three sites. Sample collection frequency was once per week with duration of 24 hour from 2012 to October 2014. At Site 2 and Site 3 samples were collected upto August 2013. A total of 200 numbers of valid samples were collected from three sites (Site 1=122, Site 2=42, Site 3=38). Sample collections were avoided during rainy days.

2. Near real time particle number concentration and size distribution of near surface aerosol was carried out using optical sizing technique of particle in a volume controlled flow. Optical particle counter (OPC) detects light scattered by the aerosol particles passing through a laser beam with known flow parameters of air mass. The aerodynamic optical diameter, the size distribution and the total number concentration of particle can be calculated from the intensity of scattered light. A Grimm optical particle counter (OPC), model-1.109, which gives description at 32 different size bins ranging from 0.265µm to 34µm was use for sampling at constant flow rate 1.4lt/min. Sampling was carried out for two days in a week from February, 2014 to May, 2015. Sampling was done at top of the department of Environmental Science building about 20mtr above the ground.

3. To get the morphology atmospheric particulate, air mass was sampled through glass fibre and membrane filter at constant flow using two different techniques. Bulk sampling was done using glass fibre filter in a high volume sampler for 24 hr. To get the morphology of single particle a vacuum pump system was used in which both the glass as well as membrane filters of 25 mm diameter taken in a filter holder. Air mass was sucked through the filters at constant flow rate of 1.4 lt/min for 1 hr. All the sampling was done above 20mtr above the ground at Tezpur University premises.

4.3 Sampling of rain

Rainwater was collected on event basis for the period of 2012 to 2014 at Tezpur University. A total of 234 (number of samples 2012=113, 2013=104, 2014=67) samples were collected from Tezpur. Collection of rainwater was done from site 1 only. Rainwater was collected manually and the collector consists of a funnel with diameter 20.3cm and a 2 Litre capacity bottle (Rastogi and Sarin, 2005). Both the funnel and bottle is made up of high density polypropylene material. The collector was placed at a height of 10 m above the ground and the collector height was maintained 1 m above the resting surface to avert contamination of samples from splashes. The collector bottle and the funnel were pre-cleaned with ultra-pure water (Milli Q of resistivity 18.2M Ω .cm) to avoid any contamination. The collector was placed just before the start of rain and removed just after the rain stopped. The sample was immediately transferred to the laboratory to measure its pH, conductivity (EC) and volume. The samples were filtered through filter paper (Whatman 1) to remove any insoluble fractions and were divided into two aliquots - one kept for determination of anions while other for cations. The samples were treated with chloroform to minimize microbial activities and stored in the refrigerator at about 4^oC (Akoto et al., 2011).

4.4 Chemical Analysis:

4.4.1PM10

4.4.1.1 Elements

An aliquot of PM10 sample was digested in concentrated HNO₃ (Shah et al., 2006; Chen and Ma, 2001) in a Teflon bomb at an oven temperature of 100°C for 8 hours. The final volume of the extract was made upto 30 ml and stored in pre washed polyethylene bottles maintain a pH of \approx 2. Elements Al, Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb, were analyzed in an ICP-OES (PerkinElmer, OPTIMA-2100DV).

4.4.1.2 Water soluble Ions

Aliquot of PM10 samples was extracted using ultra sonication method for 20minutes in ultrapure water and filtered (Deka and Hoque, 2014b). Sample volume was adjusted up to 10ml. Anions, F⁻, Cl⁻, NO₃⁻, SO₄²⁻ and cations, Na⁺, K⁺, NH₄⁺, Ca²⁺ and Mg²⁺ were analyzed by Ion Chromatography (Metrohm 882 Professional IC). Anions were analyzed using Metrosep A Supp 5 250/4.0 column and Metrosep A Supp 4/5 guard column with 3.2 mM Na₂CO₃ and 1.0 mM NaHCO₃ standard eluent at a flow rate of 0.7 ml/min. Cations were measured using Metrosep C4-150/4.0 and guard column Metrosep C4 Guard/4.0 with eluents as 1.7mmol/L HNO₃ and 0.7mmol/L Pyridin-2, 6-dicarboxylic acid at a flow rate of 0.9 ml/min.Before injection, the samples were filtered with 0.22µm pore size nylon filter paper (Make: Millipore).

4.4.1.3 Carbon

Total Carbon (TC) was determined directly by feeding the sample in to the heating furnace. To measure elemental carbon (EC), samples were preheated to remove OC and then fed into the heating chamber (Linand Tai, 2001). OC was obtained by subtracting EC from TC. There is a possible source of uncertainty in thermal separation of EC and OC. There is possible overestimation of EC due to presence of Humic like substances (HULIS) that are thermo-stable could interfere with the EC (Reisinger et al., 2008).

Water soluble organic carbon (WSOC) were extracted from the samples by ultra-sonication (Muranszky et al., 2011; Paglione et al., 2014) and analyzed in TOC analyzer (Analytikjena multi N/C 2100)

4.5 Morphology

For morphological study samples were taken (section of size 1x1 mm) and observed under a Scanning Electron Microscope (SEM) model JEOL JSM6390LV. Platinum metal coating of the sample was done before analysis under SEM. EDX analysis was done to get compositional information of the particle using Oxford EDX attached with the SEM.

4.6 Rainwater

A pH meter with (Make: Sartorius Model: portable pH meter PT 10) a glass electrode was used for pH measurement. The pH meter was calibrated before each measurement with standard buffer solutions of pH 4 and 7. EC was measured using a conductivity meter (Make: Systronics; Mode: Conductivity meter 304). Conductivity meter was periodically calibrated with 0.1N KCl (aqueous) solution.

Major anions (F^- , CI^- , NO_3^{2-} and SO_4^{2-}) and cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ and NH_4^+) were analyzed using Metrohm ion chromatograph (IC) model 882 Compact IC plus equipped with Conductivity detector. The anions were analyzed using MetrosepASupp 5 250/4.0 column appended with Metrosep A Supp 4/5 guard column and 3.2 mM Na₂CO₃ and 1.0 mM NaHCO₃ standard eluent with flow rate 0.7 ml/min. An inbuilt suppressor (MetrohmSupressor Module, MSM) was used for the anion analyses. The cations were measured using Metrosep C4-150/4.0 appended with a guard column Metrosep C4 Guard/4.0. The eluents were 1.7mmol/L HNO₃ and 0.7mmol/L Pyridin-2, 6dicarboxylic acid at a flow rate of 0.9ml/min.

4.7 Meteorology

Meteorological data such as temperature, relative humidity, wind direction and wind speed were obtained from Weather underground website (<u>http://www.wunderground.com</u>) for Tezpur station (Station ID-42451).

4.8 Backward trajectory Analysis

5 days backward trajectories were obtained arriving over the study site, at 500m above the ground level and time ending at 00.00 hrs, which were computed using the HYSPLIT model, developed by NOAA/ARL (http://ready.arl.noaa.gov/HYSPLIT.php) (Draxler and Rolph, 2003). The global meteorological data from the National Centres for Environmental Prediction's Global Data assimilation System (GDAS) were used for trajectory calculation. It has been observed by many researchers that most of the air –sea surface interactions takes place within the boundary layer of 500m (Zienlinski et al., 2014; Rozwadowska et al., 2010).

4.9 Statistical analysis

Descriptive statistics of the mass, number density, metals, ions etc. of aerosol and rain water will be calculated. Correlation matrix was evaluated to see the interrelationship between different elements and also to see the relationship between aerosols and meteorology.

4.10 Quality control

Before sampling of PM10 filter papers were conditioned properly to remove any artifacts. Whatman filter papers were desiccated using a desiccators (Silica gel coarse) for 24hours before sampling and after sampling to remove any traces of moisture associated with particulate matter. After 24 hour desiccation only pre and post sampling weight of the filter was taken. For estimation of anions Multielement Ion Chromatography Anion standard solution (Fluka Analytical) was used to calibrate the IC. For measurement of cation and TOC analyzer standards were prepared in the laboratory with analytical grade reagents. For all the parameters field blanks were analyzed and incorporated in the measurements.

Method detection limits (MDL) of both IC was calculated as the three times of half of standard deviation of seven analyses. Care was taken to minimize external contamination of sample due to handling and carrying of samples in various processes. To determine the detection efficiencies of the analytical instruments spiking with known standard concentrations were done with the help of ultrapure water.

The quality assurance/quality control (QA/QC) procedure was followed for precipitation chemistry monitoring. Samples contaminated with direct leaves fall or bird droppings were not taken into consideration. The bottles and funnels were pre-washed with ultrapure water (Ultrapure Type 1,

Simplicity, Millipore, resistivity 18.2M Ω .cm) before sampling. The collectors were placed just before the start of rain and removed just after the rain stopped. Field blanks were evaluated frequently and analyzed for all the parameters like the rain samples. Field blanks were taken by pouring ultra-pure water into the sampler and followed the procedure as mentioned above. Values of field blank were subtracted from the measured values of the samples. Replicate measurements were also conducted for the samples which showed RSD $\leq 5\%$ (n=8). In case of pH, the difference between replicate measurements were found to be less than 0.05 while for EC, it was less than 1µS/cm.

4.11 Source apportionment

Two models were applied for source apportionment (a) Principal component analysis (PCA) and (b) Chemical mass balance (CMB).

PCA is one of the popular data reduction model which is very widely used to understand hidden relationships between attributes. It aims at representing large amount of multidimensional data by transforming them into more intuitive low-dimensional representation. This transformation suppresses the dimensions deemed to contribute an insignificant percentage of the total variance present in the data.

The PCA analysis was performed using SPSS software for grouping of the data into principal components (PCs), each representing a source of the chemical attributes of aerosol. This was followed by Multiple Linear Regression (MLR) to quantitatively discriminate the percent strengths of individual identified sources.

Chemical mass balance (CMB) is a regulatory receptor model which is well documented and tested. The CMB8.2 model software, freely available at the USEPA website, was used to appreciate the source strengths using the source inventory of Central Pollution Control Board (CPCB), India. Given the number of sources, CMB model was run till the model converges with a maximum limit 20 runs for each sample. The source selections have been done by removing similar sources based on collinearity test.

5. Summary of the result (Detailed analysis of results indicating contributions made towards increasing the state of knowledge in the subject)

5.1 Meteorology

Figure 5.1 represents the variation of monthly meteorological parameters such as temperature, relative humidity and seasonal wind patterns. During the whole study period Northerly wind prevails with 71.17% calm condition. During Pre-monsoon (March-May) period wind directions were mostly from Northeasterly. Monsoon period experiences both southerly and northerly winds with calm conditions 76.96%. During post-monsoon and winter period dominant wind direction was observed to be northerly winds with calm conditions 75.72% and 75.28% respectively. It was observed that high humidity and high calm condition is the important characteristic of the study site, which is a favorable condition for the air pollutants to less dispersal and higher in situ secondary formation of pollutants during the study period.





Figure 5.1: Monthly variation of relative humidity and temperature and windroses for different seasons during the study period

5.2 Backward trajectory:

Backward trajectories were evaluated for the site 1 (Figure 5.2) for every months for the monitoring period 2012-14. It was observed that from January to February (i-ii) air parcel coming to the study site were mostly continental origins travelling over the Indo-Gangetic plain of India. From March to May (iii-v) air parcel starts its direction and during June to September (vi-ix) month study site receives air masses completely originated from sea i.e. Bay of Bengal. Again, from October to December (x-xii) wind starts originating from continents such as Middle East, Indo-gangetic plain, Bangladesh. It was observed that study site experiences air mass coming from different geographical
locations along with regionally originated air mass in different period of time. This air mass can be carrier of different air pollutants from different geopolitical boundary surrounding the Brahmaputra valley.



Figure 5.2: Monthly backward trajectories for the whole study period (2012-14) at 500m above ground level for 5days starting at 00.00hours.

5.3 Physical properties of Aerosol

5.3.1 Morphology

From bulk sample analysis (Fig 5.3.1a) it was observe that accumulation of atmospheric particle with various sizes and morphology occur. The particles in smaller size range are high in concentration. Agglomerates of small particles also observed. EDX analysis of bulk sample says about presences of Alumina silicate and Iron mineral in crustal type particle which may be come from dust. Carbon peak in the EDX spectrum tells about the presences of carbonaceous particle with regular shape originated from fuel burning.

Single particle analysis and compositional pattern (Figure 5.3.1b) confirm that particle in smaller range (less 1μ m) of crustal origin with irregular shape; particle with biogenic origin was also observed having spherical shape (pollen). Agglomerate of very small carbonaceous particle originated from anthropogenic source is seen. Some soot burning/ fly ash particle originated from anthropogenic activity with completely spherical shape was also observed.



Figure 5.3.1a: SEM-EDX of Bulk atmospheric sample collected on glass fibre filter



Figure 5.3.1b: SEM EDX analysis of single aerosol particle.

5.3.2 Diurnal variations of size and number density of aerosol

The size distribution of some of the selected days from various seasons of the year a **tri-model** distribution was observed. The distributions during the day and night time are given in fig 5.3.2a and 5.3.2b respectively. The variation in between the various size fractions is all most same for all the season. During post-monsoon the larger size fraction shows higher concentration compared to other season. The size distribution of monsoon shows lowest concentration in all size fractions.



Fig. 5.3.2a: Size distribution of PM10 during the day time around the year



Fig 5.3.2b: Size distribution of PM10 during the night time around the year

5.3.3 Seasonal variation of mass and number density of aerosol

Seasonal variation of aerosol number density of total $(0.265 - 34.000) \mu m$ and in the size range $(0.265-0.900) \mu m (1.150-2.250) \mu m$ and $(2.750-9.250) \mu m$ is shown in Fig. 5.3.3 (a-c). The number densities were high during winter and low during monsoon as compare to other seasons. The densities during pre-monsoon and post-monsoon remain the same. The main contributor of total atmospheric particulate in this region is in the size below 1 μm , which appears from the distribution.



5.3.3a : Seasonal variation total aerosol number density.



5.3.3b: Seasonal variation of aerosol number density in size range (0.265-0.900)µm.



5.3.3c: Seasonal variation of aerosol number density in size range (1.150-2.250) μm and (2.750-9.250) μm

The seasonal distribution of sizes of PM10 aerosols are shown in fig. 5.3.3d. The distribution through various seasons represent similarly with a tri-hump.



Figure 5.3.3 d: Seasonal size distribution pattern.

5.4 Chemical properties of Aerosol

5.4.1 Mass concentration of PM10 and seasonal variation

Table 5.4.1 represents the mass concentration of PM10 during the study period 2012-14. It was observed that annual mean mass concentration and standard deviation of PM10 was found to be 53.7±46 μ g/m³, lower than the standard of NAAQS (60 μ g/m³)given by CPCB. PM10 range was found to be 3.82-244.46 μ g/m³, having minimum during monsoon period and maximum during winter period. Minimum concentration of PM10 during monsoon period could be due to the washout of pollutants from atmosphere by high rainfall (Singh et al., 2010). Winter is mostly the dry period compared to other seasons. Burning of biomass both conventional and non conventional methods are larger emitter of particles during winter season along with anthropogenic activities. Both calm and subsidence condition of atmosphere favours the long residence time of particles during post-monsoon and winter season (Karar and Gupta, 2006). The concentrations of PM10 crossing the standard was observed in a very few events. Assam is a region rich in festivals mostly associated with agriculture. Both conventional and non-conventional (festivals like Magh Bihu, where Meji is burnt every year as a part of celebration) form of biomass burning celebrated post-harvest season(Deka and Hoque, 2014a), high wind gust during Norwester along with emissions from vehicles, brick kilns, festivals like Diwali (Deka and Hoque, 2014b)have been associated with higher concentration of PM10 during these events of high concentrations.

	Mean	SD	Maximum
2012-14 (n=250)	53.7	46	244.5
Pre-monsoon	52.3	45	197.5
Monsoon	22.4	13	66.9
Post-monsoon	44.0	31	178.0
Winter	97.7	49	244.5

Table 5.4.1: Statistical results of annual and seasonal variation of mass concentration of PM10

5.4.2 Ionic concentration of PM10

Mean concentrations and other statistical results are given in Table 5.4.2. Water soluble ions such as F⁻, Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺ were measured for the study period. It was observed that water soluble ions constituted 17% of the total PM10 and followed the order SO_4^{2-} $Na^+>K^+>NH_4^+>NO_3^->Cl^->Ca^{2+}>Mg^{2+}>F^-$. Among ions SO_4^{2-} was found to be maximum for the whole study period having concentration 2.19 $\pm 2 \mu g/m^3$. Presence of SO₄²⁻ ions in PM10 indicates the secondary formation of particulate SO_4^{2-} from the precursors like SO_2 by gas to particle conversion processes (Kulshrestha et al., 2009). Emissions from fossil fuel burning, biomass burning and long range transport may lead to increased level of SO_4^{2-} in the atmosphere. Na⁺ was found to be dominating cation with concentration $1.85 \pm 1 \ \mu g/m^3$. Marine contribution, re-suspension of soil dusts or crustal inputs have been major sources of Na⁺ during the study period. K⁺ was found to be second dominating cation with mean value $1.35\pm1.2 \,\mu g/m^3$. Abundance of K⁺ in PM10 is directly associated with the biomass burning as it reported by many researchers (Kleeman et al., 1999; Simoneit et al., 2004; Watson et al., 2008). Prevailing biomass burning in the region have contributed K⁺ in PM10. It has been observed that NO_3^- and NH_4^+ contributed to the PM10 mass during the study period. Presence of NO_3^- , a secondary product formed from the oxides of nitrogen, suggests the emissions from fossil fuel burning, biomass burning, NH_4^+ can be formed from the precursors like NH_3 emitted to the atmosphere by plants, animals, soil microorganisms and by various agricultural processes which include direct volatilization of solid NH₄NO₃ salts and fertilizers (Sutton et al., 2000; Li et al., 2006; Sharma et al., 2010).F was found to be minimum among all the ions. Presence of this ion could be due to the fossil fuel burning such as coal largely used in brick kiln, tea industries (Deka and Hoque, 2014b).

Table 5.4.2: Statistical results of water soluble ions during the study period 2012-14 and seasonal variation of concentrations (μ g/m³)

		F	Cl	NO ₃ ⁻	SO4 ²⁻	Na ⁺	$\mathrm{NH_4}^+$	K^+	Ca ²⁺	Mg ²⁺
	Mean	0.03	0.92	1.06	2.19	1.85	1.12	1.35	0.51	0.07
2012-14	SD	0.07	1.13	1.16	2.13	1.12	1.20	1.28	0.39	0.05
2012 11	Minimum Maximum	BDL 0.78	BDL 7 20	BDL 5 70	BDL 12 23	0.12 7.21	0.11 6.49	0.14 7.81	0.05	BDL 0.32
	Mean	0.02	0.94	1.05	2.23	1.96	1.11	1.35	0.68	0.02
Pre-monsoon	SD	0.03	1.25	0.96	1.51	1.31	0.92	0.94	0.44	0.06
	Minimum	BDL	BDL	BDL	BDL	0.70	0.22	0.25	0.14	0.02

	Maximum	0.16	5.96	4.64	5.86	7.21	3.74	3.58	1.79	0.23
	Mean	0.01	0.83	0.53	1.08	1.59	0.54	0.77	0.33	0.04
Monsoon	SD	0.02	1.00	0.55	0.59	0.89	0.48	1.06	0.41	0.03
WOUSDOIL	Minimum	BDL	BDL	BDL	0.04	0.47	0.13	0.14	0.05	BDL
	Maximum	0.08	5.23	3.94	2.65	6.28	3.16	7.81	3.03	0.20
	Mean	0.05	0.97	0.65	1.15	1.71	0.65	1.07	0.53	0.07
Post-	SD	0.13	1.17	0.54	1.20	0.86	0.37	0.98	0.29	0.05
monsoon	Minimum	BDL	BDL	BDL	0.10	0.31	0.14	0.19	0.06	0.01
	Maximum	0.78	4.17	3.40	6.64	4.20	1.65	5.30	1.16	0.28
	Mean	0.03	0.98	2.01	4.35	2.18	2.21	2.24	0.55	0.08
Winter	SD	0.02	1.19	1.54	2.61	1.35	1.66	1.51	0.33	0.05
w milei	Minimum	BDL	BDL	0.09	0.41	0.12	0.11	0.22	0.21	0.02
	Maximum	0.09	7.20	5.70	12.23	5.66	6.49	7.09	1.96	0.32

5.4.3 Elemental composition

Table 5.4.3 represents the mean concentration of elemental constituents of PM10. Concentrations of measured elements followed the order viz. Al>Fe>Pb>Ni>Cr>Mn>Cu>Cd>Co. It was observed that mostly crustal originated elements such as Al, Fe and Mn are abundant in the PM10 fraction. These elements can be originated from windblown dust or construction activities in the region. Elements constitute 14% of the total PM10 mass during the whole study period. Trace elements such as Cd, Cr, Cu, Pb, Ni and Co can be considered as partially natural origin and partially from anthropogenic activities. Presence of these elements in PM10 reveals the fact that this region is influenced by both natural and anthropogenic sources such as vehicular emission, industrial emission etc. Long range transport of fine fractions of these elements could be one of the reasons for their presence. Trace elements such as Pb and Ni were observed to within the limit of standard given by CPCB, Govt. of India. The mean Cr concentration $(0.06\mu g/m^3)$ in the study site was above the annual limit set by the World Health Organization $(0.0025 \mu g/m^3, WHO 2000)$.

Table 5.4.3: Elemental composition of PM10 and its seasonal variation

		Al µg/m ³	Cd µg/m ³	Co µg/m ³	Cr μg/m ³	Cu µg/m ³	Fe µg/m ³	Mn μg/m ³	Ni μg/m ³	Pb μg/m ³
	Mean	5.43	0.004	0.003	0.06	0.03	1.54	0.04	0.06	0.07
2012-14	SD	4	0.01	0.01	0.10	0.1	3	0.1	0.2	0.1
	Minimum	BDL								
	Maximum	30.43	0.05	0.06	0.89	0.37	31.03	0.78	1.63	1.30
Pre-monsoon	Mean	4.34	0.001	0.002	0.05	0.01	1.00	0.03	0.03	0.05

	SD	5	0.001	0.002	0.05	0.02	1	0.1	0.02	0.1
	Minimum	0.28	BDL	BDL	0.01	BDL	0.15	BDL	BDL	0.01
	Maximum	30.43	0.01	0.01	0.22	0.07	5.78	0.24	0.08	0.32
	Mean	5.30	0.002	0.002	0.03	0.01	0.52	0.02	0.03	0.02
Monsoon	SD	3	0.001	0.002	0.02	0.01	0.8	0.08	0.1	0.02
	Minimum	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Maximum	19.55	0.01	0.01	0.14	0.05	6.77	0.59	0.94	0.09
	Mean	6.75	0.002	0.003	0.06	0.02	0.75	0.02	0.03	0.04
Post-	SD	5	0.002	0.003	0.1	0.03	1	0.02	0.1	0.04
monsoon	Minimum	0.27	BDL	BDL	BDL	BDL	0.08	BDL	BDL	BDL
	Maximum	21.00	0.01	0.01	0.89	0.22	9.19	0.14	0.34	0.18
	Mean	5.26	0.01	0.005	0.11	0.07	3.81	0.10	0.16	0.17
Winter	SD	3	0.01	0.02	0.1	0.1	5	0.1	0.3	0.2
vv mitor	Minimum	BDL	BDL	BDL	BDL	BDL	0.06	BDL	BDL	0.01
	Maximum	16.92	0.05	0.06	0.71	0.37	31.03	0.78	1.63	1.30

5.4.4 Carbon

Table 5.4.4 presents the statistical results of carbonaceous fractions of PM10 for the study period 2012-14. Carbonaceous fraction has highest percentage contribution to the PM10 mass concentration which is 35% among all other parameters, during the whole study period. Among water soluble carbonaceous fraction water soluble organic carbon (WSOC) was found to be maximum with concentration $5.40\pm 5 \ \mu g/m^3$ followed by water soluble inorganic carbon (WSIC) with mean concentration $0.90\pm0.8 \ \mu g/m^3$. Presence of WSOC indicates secondary formation by photochemical reaction. The average concentration of OC was found $14.76\pm17 \ \mu g/m^3$ for the period 2012-14 and EC was found to be $4.20\pm4 \ \mu g/m^3$. Average TC (EC+OC) concentration was found to be $18.96\pm18 \ \mu g/m^3$ and ranges from 1.70 to $161.81 \ \mu g/m^3$. This reveals that the present site experiences severe pollution due to the high loading of carbonaceous particles. EC is emitted mainly from combustion sources such as vehicular emission, while OC can be emitted from both primary and secondary sources. Primary sources include gaseous organic carbon species in the atmosphere and secondary sources include chemical transformation of these gases in the atmosphere.

OC/EC ratio is a widely used method to determine the primary and secondary organic carbon present in the atmosphere (Rastogi et al., 2015). K^+/OC ratio is a good indicator of biomass burning. In our

study it was found to be 0.09 during the whole study period. This indicates the presence of agricultural waste burning emissions as reported from other parts of India and China (Ram et al., 2011; Andreae, 1983). The OC/EC ratios (Average 3.51) were found relatively high suggesting the dominance of emissions from biomass and biofuel burning as compared to lower OC/EC ratios from fossil fuel (Coal and vehicular exhaust) (Ram et al., 2012a, 2012b). Similar pattern of OC/EC ratio were observed during pre-monsoon, monsoon, post-monsoon and winter season.

The average WSOC/OC ratio was found 0.36 for the whole study period. This WSOC/OC ratios in the atmospheric aerosols have been used to indicate the extent of secondary aerosol formation and /or aging of aerosols during long range transport to remote locations (Aggarwal and Kawamura, 2009; Zhang et al., 2007). A report from northern India during wintertime reported relatively low WSOC/OC ratio (~0.30-0.40) when biomass burning emissions are most dominant (Ram and Sarin, 2010). This suggests that emissions from biomass burning could be possible sources of these carbonaceous aerosols.

								OC/E	WSOC/
		WSOC	WSIC	WSTC	TC	EC	OC	С	OC
	Mean	5.40	0.90	6.28	18.96	4.20	14.76	3.51	0.36
2012-14	SD	5	0.8	6	18	4	17		
2012 14	Minimum	0.28	0.02	0.50	1.70	BDL	0.23		
	Maximum	40.62	5.49	40.64	161.81	29.42	160.36		
	Mean	3.43	0.65	4.08	13.28	3.48	9.80	2.81	0.35
Dra mangaan	SD	2	0.5	3	10	2	9		
Pre-monsoon	Minimum	0.94	0.15	1.28	3.03	0.54	0.92		
	Maximum	11.56	2.04	12.32	42.39	12.63	35.72		
	Mean	2.91	0.68	3.59	10.53	2.59	7.94	3.06	0.36
Monsoon	SD	2	0.8	2	20	1	20		
WIGHSOON	Minimum	0.28	0.02	0.50	2.04	BDL	0.26		
	Maximum	8.80	5.49	9.66	161.81	7.93	160.36		
	Mean	4.17	0.94	5.11	16.61	3.09	13.52	4.37	0.31
Post-	SD	3	0.7	3	13	2	11		
monsoon	Minimum	0.51	0.10	0.68	1.70	BDL	0.23		
	Maximum	15.07	3.94	15.43	53.14	10.34	45.22		
Winter	Mean	10.88	1.37	12.09	34.50	7.60	26.91	3.54	0.40
w miler	SD	8	1	7	18	6	16		

Table 5.4.4: Mean concentrations ($\mu g/m^3$) and other statistical results of carbonaceous fractions of PM10 along with mean OC/EC, WSOC/OC ratio

Minimum	1.22	0.24	1.46	4.61	0.21	0.94	
Maximum	40.62	3.64	40.64	85.35	29.42	79.24	

WSOC- Water soluble organic carbon; WSIC- water soluble inorganic carbon; WSTC- water soluble total carbon, OC- organic carbon; EC- Elemental carbon; TC-total carbon; SD-Standard deviation

5.5 Seasonal variation of chemical constituents of PM10

The whole sampling period can be divided into four distinct seasons according to the IMD (India Meteorological Department) viz. Pre-monsoon (March-May), Monsoon (June-September), Post-monsoon (October –December) and Winter (January- February). It is important to mention here that each season has been associated with different types of activities related to agriculture, industries of its own and such activities repeat year after year making a significant difference among the seasons. Therefore, we have calculated the seasonal variations of the chemical constituents by dividing whole study period into four distinct seasons.

The percentage contribution of ionic constituents during pre-monsoon, monsoon, post-monsoon and winter season were found to be 18%, 26%, 16% and 15% respectively. Maximum concentration of Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, K⁺ and NH₄⁺ were observed during winter season (Table 5.4.2). Among anions $SO_4^{2^-}$ showed maximum concentration during winter season with concentration $4.35\pm2 \ \mu g/m^3$. Presence of $SO_4^{2^-}$ during winter season reveals the fact that during this dry period some small scale industries like brick kilns become active and these industries are mostly coal fed. Therefore sufficient amount of SO_2 emission takes place which gets converted to secondary $SO_4^{2^-}$. More over biomass burning could also lead to formation of $SO_4^{2^-}$ in the atmosphere. Crustal originated ions such as Ca^{2+} and Mg^{2+} was found to be dominant during pre-monsoon period. Pre-monsoon season has been associated with high wind gust, comparatively drier weather and falls just after the winter period. Comparatively higher concentrations of Ca^{2+} and Mg^{2+} in this season can be attributed to the resuspension of soil dust or crustal input from the exposed surface soil. Again, long range transport could also carry mineral dusts containing Ca^{2+} salts from continental mass. Backward trajectory analysis (Figure 5.2 iii-v) showed the route of air mass travelled to this region.

 NH_4^+ was found during all the seasons. Presence of NH_4^+ in the study site may be due to the secondary formation from the precursor of NH_3 gas released from anthropogenic activities such as agricultural fields, animal excreta, pits, cattle farms etc and from biogenic emission. NO_3^- was also

found during the entire seasons and maximum during winter and minimum during monsoon period. Fossil fuel burning could be important source of NO₃⁻ in the atmosphere. It was observed that during monsoon period ionic concentrations were lowest among all other seasons. This could be due to scavenging by monsoonal rain. Monsoon season is the rainiest season and southwesterly winds carry moisture from Bay of Bengal. Among the measured ions Na⁺ showed maximum concentration $(1.59\pm0.89 \ \mu\text{g/m}^3)$. Na⁺ being the predominant ion reveals that long range transport of sea salts is an important phenomenon during this period. Among anion SO₄²⁻ was found to be predominant $(1.08\pm0.59 \ \mu\text{g/m}^3)$ during monsoon season, which could be due to the exchange of sulfur containing gases by Cl⁻ ion while travelling through long distances, commonly known as Cl⁻ depletion phenomenon (Harrison and Pio, 1983; Wall et al., 1988; Mamane and Gottlieb 1992; Sarin et al., 2010; Adachi and Buseck, 2015).



Figure 5.5.1: Seasonal variation of water soluble ionic concentrations of PM10

Trace elemental composition contributed 11%, 26%, 17% and 10% during pre-monsoon, monsoon, post-monsoon and winter season respectively to the total mass concentration of PM10.



Figure 5.5.2: Seasonal variation of elemental composition of PM10

It was observed that Al showed maximum concentration during all the seasons compared to other trace elements. Fe was found maximum during winter season. All elements originating from anthropogenic activities such as Cr, Cd, Co, Cu, Ni and Pb showed maximum mean concentration during winter season. Figure 5.5.2 present seasonal variation of trace elements. It was observed that during post-monsoon and winter period crustal elements such as Fe, Al showed higher concentration. This might be due to the uplift of crustal component due to strong winds and construction activities.

Carbonaceous fractions of PM10 also showed distinct seasonal variations (Fig 5.5.3). All the fractions of carbon viz. WSOC, WSIC, EC and OC concentrations were found to be higher during winter season. This could be associated with increasing amount of biomass burning in the study site and also due to the long range transport from Indo-Gangetic plain during winter seasons which was observed from backward trajectory analysis (Fig 5.2 i-ii).Total carbon contributed 25%, 47%, 38% and 35% to the total mass concentration of PM10 during pre-monsoon, monsoon, post-monsoon and winter season respectively. Like all other constituents, carbon was also found to be minimum during monsoon period due to washout process by rain.



Figure 5.5.3: Seasonal variation of carbonaceous fraction of PM10

5.6 Spatial variation of size distribution of PM10

The spatial variation of size distribution of aerosol was seen at three locations during three periods of the day – morning, mid-day and evening. The distributions of city area vary slightly than the ones in remote (Silghat) and rural (TU).



Fig 5.6: Spatial variations of particle size distribution

5.7 Spatial variation of PM10 and its composition

Table 5.7: Spatial variation of mean mass concentration of PM10 and concentrations of its constituents ($\mu g/m^3$) in the Tezpur region of mid-Brahmaputra valley

Те	zpur Univ	versity	S	ilghat	NER	IWALM
	Mean	SD	Mean	SD	Mean	SD
PM10	51.9	38	36.0	33	59.1	50
F ⁻	0.02	0.05	0.03	0.01	0.05	0.01
Cl ⁻	0.40	0.5	1.02	0.6	2.43	1
NO ₃ -	1.02	1	1.06	1	1.23	1
SO_4^{2-}	2.48	2	1.64	1	1.89	1
Na^+	1.38	0.6	1.37	0.4	2.68	1
$\mathrm{NH_4}^+$	0.95	1	0.94	1.05	1.17	1
K^+	0.97	0.8	0.98	0.8	2.15	2
Ca ²⁺	0.41	0.2	0.45	0.3	0.71	0.5
Mg^{2+}	0.06	0.05	0.05	0.04	0.09	0.05
Al	5.25	3	3.49	0.9	6.10	5
Cd	0.002	0.001	0.001	0.000	0.002	0.002
Co	0.002	0.002	0.002	0.001	0.003	0.002
Cr	0.03	0.04	0.04	0.04	0.05	0.08
Cu	0.01	0.01	0.01	0.01	0.01	0.02
Fe	0.66	0.8	0.52	0.6	0.85	1
Mn	0.02	0.06	0.01	0.01	0.03	0.03
Ni	0.03	0.09	0.02	0.02	0.03	0.04
Pb	0.03	0.03	0.03	0.02	0.05	0.06
WSOC	5.96	6	2.61	2	4.71	3
WSIC	0.85	0.7	0.50	0.2	1.00	1
WSTC	6.81	6	3.12	2	5.70	3
ТС	17.46	15	14.43	25	23.37	19
EC	4.15	4	2.52	1	5.05	3
OC	13.31	12	11.92	25	18.32	16

Mean mass concentration and standard deviation of PM10 was observed 51.9 ± 38 , 36.0 ± 33 , $59.1\pm50 \mu g/m^3$ in Site 1(Tezpur University campus), Site 2 (Silghat), and Site 3 (NERIWALM) respectively. It was observed that Site 3, urban site experiences higher PM10 load compared to other two sites. The PM10mass concentration followed the order Site 3> Site 1> Site 2. High traffic density, more exposure to emissions from small scale industries and construction and demolition might have contributed enormous amount of particulate matters to this region. Site 1 and 2 are rurally situated places in the Brahmaputra valley, which showed comparatively lower loading of PM10.

Mean concentration of major water soluble ions were observed to be higher in Site 3 except $SO_4^{2^-}$. Site 1 showed maximum concentration of $SO_4^{2^-}$ among all the three sites $(2.48\pm2 \ \mu g/m^3)$. Mean concentration of ions followed the order $SO_4^{2^-}>Na^+>NO_3>K^+>NH_4^+>Ca^{2+}>CI>Mg^{2+}>F^-$ in Site 1. Site 2 followed the order of concentration $SO_4^{2^-}>Na^+>NO_3>CI->K^+>NH_4^+>Ca^{2+}>Mg^{2+}>F^-$ and Site 3 followed the order $Na^+>CI>K^+>SO_4^{2^-}>NO_3>NH_4^+>Ca^{2+}>Mg^{2+}>F^-$. Na+ was found to be dominant in all the three sites (Figure 5.7.1). It shows that at all the three sites cations with maximum concentrations were sodium, potassium and ammonium while predominant anions were sulphate, nitrate and chloride. This reveals that though all the three sites are geographically apart from each other still possess similar chemical nature of PM10 during the study period.



Figure 5.7.1: Spatial variation of water soluble ionic constituents ($\mu g/m^3$) in PM10

Trace elements also showed prominent spatial variation. Among all the trace metals Al showed maximum concentration in all the three sites. Mean concentration of Al was found $5.25\pm3 \ \mu g/m^3$, $3.49\pm0.9 \ \mu g/m^3$ and $6.10\pm5 \ \mu g/m^3$ in Site 1, Site 2 and Site 3 respectively. It was observed that mostly crustal originated metals such as Al, Fe showed comparatively higher concentration than the metals originated from anthropogenic activities. During the monitoring period the urban site (Site 3) experienced more loading of trace metals compared to the rural sites. This could be due to the emissions from anthropogenic activities, industries and automobiles prevalent in the urban site.



Figure 5.7.2: Spatial variation of elemental concentration of PM10 ($\mu g/m^3$) during the study period

Spatial variation of carbonaceous fractions of PM10 was found to be prominent during the study period. Mean concentration of OC was found to be higher in Site 3 followed the order Site3>Site>1>Site2 (Table 5.7). WSOC also showed higher concentrations in all the three sites than WSIC. Presence of WSOC in PM10 reveals that secondary formation is an important source of organic carbon in the study site. The differences in the concentrations of carbonaceous species is mainly attributed to the varying source strength of emissions from biomass burning, fossil fuel combustion and boundary layer dynamics (Ram et al., 2010, 2012). Compared to all the three sites, Site 1 has experienced maximum loading of water soluble organic carbon. Conventional use of biofuel such as wood, cow dung, sugarcane baggase etc. for cooking purpose or any other means of biomass burning could release tremendous amount of carbonaceous particle to the atmosphere.



Figure 5.7.3: Spatial variation of carbonaceous fractions in PM10 during the study period

5.8 Influence of Biomass burning on aerosol over Tezpur region

5.8.1 Influence of household biomass burning

To understand the relationship between household biomass burning emission and aerosol mass of the region profile rations of household biomass biomass smoke particles and aerosol of various reasons were computed.

To attain this, biomass smoke particles from rural kitchens were collected considering major biomass use types during two seasons. Twelve household participated in this campaign. Smoke particle samples of wet and dry seasons were chemically characterized for major ions, selected elements and carbon. The detail sampling and analytical methodology is provided in Deka and Hoque (2015). The profile rations were computed as per below:

Anions : $[A_i^-]/\Sigma A^-$, where $[A_i^-]$ is the concentration of anion i and ΣA^- is the sum of all manor anions considered. The profile ratios of SO₄⁻, NO₃⁻, Cl⁻ and F⁻ were computed.

Elements : $[X_i]/\Sigma X$, where $[X_i]$ is the concentration of the element i and ΣX is the sum of elements considered. The profile ratios of Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Zn, K and Na were computed.

Carbon: Profile rations of WSIC and WSOC were computed as [WSIC]/[WSTC] and [WSoC]/[WSTC].

Correlations of profile rations of kitchen biomass smoke and aerosols of different seasons are presented in Fig 5.8.1.



Fig 5.8.1: Correlations between profiles rations of biomass smoke particles and aerosol of different seasons

The correlations between profile ratios of biomass smoke particles and aerosol over the study area was found to be positive – monsoon ($r^2 = 0.42$), post-monsoon ($r^2 = 0.46$), winter ($r^2 = 0.49$) and pre-

monsoon ($r^2 = 0.52$). This would mean that household biomass burning emissions have sufficient influence in aerosol over mid-Brahmaputra region.

5.8.2 Influence of episodic biomass burning

To appreciate the influence of episodic biomass burning festive *mej* burning period (mid-January each year) was considered for a study. PM10 samples were collected during consecutive three years viz., 2012, 2013 & 2014 during the *meji* burning period. (M*eji*, a temple like structure build of bamboo, leaves, rice straw, wood etc. which is lit at dawn after overnight feasting on the Bhogali Bihu festival each year).

The sampling protocol was as per following: First sample was collected two days prior the *meji* burning day, which has been considered as the background sample. The 2nd sample covered the *meji* burning episode and the 3rd and the 4th samples were collected covering 2 days that immediately followed the episode, as celebration continue with lesser intensity for the following two days too. The 5th and the 6th samples were collected one and two weeks after the *meji* burning day respectively. The samples are abbreviated as M1, M2, M3, M4, M5 and M6 respectively for 1st, 2nd,.....6th samples.

To see the effect of *meji* burning on PM10 loading we have calculated *Meji* Burning Induced Enrichment (MBIE) taking 1st sample as the background (Fig. 5.8.2). The incremental effect of *meji* burning was calculated as [Xij/Xi], where Xij is the mass concentration of the ith chemical species in the jth sample (j = 2-5) and Xi is the mass concentration of chemical species of the background sample. The increments are shown in Fig 5.8.2. An enrichment >1 is considered of having influence of *meji* burning. It was found that the incremental effect of *meji* burning was marginal, which was visible only on the meji burning day. The effect of *meji* burning dies down within a week.



Figure 5.8.2: Incremental effect of episodic biomass burning on chemical species of PM10, (average conditions of 3 consecutive years).

5.9 Effect of monsoon on aerosol

Monsoonal effect on aerosol can be evaluated by calculating sea salt contribution and non-sea salt contribution to the PM10. Since monsoon brings air masses originating from Bay of Bengal to this region. It was observed that during monsoon season sea salt fractions of Cl⁻, SO_4^{2-} and Ca^{2+} were almost equal to the standard ratios of corresponding ions with respect to Na as reference ion. This suggests that air mass travelling over the marine environment can carry a major portion of these ions. Backward trajectory analysis also revealed that during monsoon period direction of air mass travelled to this region was only originating from Bay of Bengal (Fig 5.2 vi-ix).Compared to monsoon season, sea salt fractions of other three seasons showed higher value than the standard corresponding ionic ratio (Table 5.9.1). This indicates presence of significant emission sources for these ions (Cl., SO_4^{2-} , K^+ , Ca^{2+} and Mg^{2+}) such as crustal input, anthropogenic activities and biomass burning.

Table 5.9.1: Sea salt and non-sea salt fractions of different water soluble ions during the study period and in different seasons

Sea salt fraction o	of PM10			
	ssCl	ssSO4 ²⁻	ssK^+	ssCa ²⁺
Seawater ratio	1.160	0.120	0.020	0.040
2012-2014	2.14	0.22	0.37	0.07
Pre-monsoon	2.28	0.24	0.39	0.08
Monsoon	1.85	0.19	0.32	0.06
Post-monsoon	1.98	0.21	0.34	0.07
Winter	2.53	0.26	0.44	0.09
Non sea salt fracti	ions of PN	/110		
		nssSO ₄ ²⁻	$nssK^+$	nssCa ²⁺
		1.97	1.31	0.43
Pre-monsoon		2.00	1.31	0.60
Monsoon		0.89	0.74	0.27
Post-monsoon		0.94	1.03	0.46
Winter		4.09	2.20	0.46

Correlations between various size fractions were tested for various seasons (Table 5.9.2). It was found that during the monsoon the fine fraction correlated better with the coarse fraction compared to their correlations during other seasons. This might point at the growth of aerosol size due to high relative humidity during the monsoon.

Table 5.9.2: Correlation between various size fractions during Pre-monsoon, Monsoon and Post-monsoon

Pre monsoon-2014	PM(0.265- 0.900)μm	PM(1.150- 2.250)μm	PM(2.750- 9.250)μm	PM(11.250- 34.000)μm
PM(0.265-0.900)µm	1.00			
PM(1.150-2.250)µm	0.73	1.00		
PM(2.750-9.250)µm	0.46	0.89	1.00	
PM(11.250-34.000)µm	0.12	0.56	0.70	1.00

Monsoon-2014	PM(0.265-	PM(1.150-	PM(2.750-	PM(11.250-
	0.900)µm	2.250)µm	9.250)µm	34.000)µm
PM(0.265-0.900)µm	1.00			
PM(1.150-2.250)µm	0.79	1.00		
PM(2.750-9.250)µm	0.78	0.91	1.00	
PM(11.250-				
34.000)µm	0.07	0.12	0.31	1.00

Post-Monsoon-2014	PM(0.265-	PM(1.150-	PM(2.750-	PM(11.250-
	0.900)µm	2.250)µm	9.250)µm	34.000)µm
PM(0.265-0.900)µm	1.00	0.56	0.32	-0.15
PM(1.150-2.250)µm	0.56	1.00	0.95	-0.03
PM(2.750-9.250)µm	0.32	0.95	1.00	0.06
PM(11.250-				
34.000)µm	-0.15	-0.03	0.06	1.00

5.10 Chemical characterization of Rainwater:

5.10.1 pH

Figure 5.10.1 presents the percentage frequency distribution of pH during the study period (2012, 2013 and 2014). Mean and standard deviation of pH was found to be 5.97 ± 0.58 , 5.76 ± 0.47 and 5.65 ± 0.41 during 2012, 2013 and 2014 respectively. This indicates the alkaline nature of rainwater in all the three years. Earlier studies on rainwater established that natural CO₂ dissolved into the rainwater may result in pH values of the rain in pristine atmosphere to be around 5.6 to 5.0 (Charlson and Rodhe, 1982; Galloway et al., 1993). In the case of rainwater showing pH below 5.0, there might be presence of natural H₂SO₄, weak organic acids like acetic acid, formic acid and succinic acid and/or anthropogenic emissions of H₂SO₄ and HNO₃. Rainwater having pH above 6.0 may be due to input of alkaline species (Han et al., 2011). This study has found that during 2012, total 50% of rainwater sample were in the range 5-5.6 and 5.6-6. In 2013 and 2014 total 61% of rainwater sample showed pH in the range of 5-5.6 and 5.6-6 in both the years. About 9%, 12% and 27% of rain events showed pH in the range 4.5-5 during 2012, 2013 and 2014 respectively (Table 5.10.1). Lowering of pH was observed when continuous rainfall occurred and in immediate subsequent rainfall. This dip in pH might be due to the absence of excess cation, thanks to removal by previous heavy rainfall that helps in the neutralization process (Pineiro et al., 2014; Sumari et al., 2009). In these events, as

neutralization did not happen in absence of cations, the observed pH could be the pH of cloud drifted from long distance elsewhere. A 3 year (2000-2002 and 2005-2007) study by Vet et al., (2014) reported that wet deposition of sulphur and mean concentration of sulphur in precipitation were highest in the eastern part of Asia which included northeast India.

An earlier study from Jorhat, upper Brahmaputra valley, about 200Km east of present study site reported 52% of rain events with pH 4.1-5.5 which they have reported as acidic events due to the weak capacity of soil to neutralize the acidity of rainwater in this region (Kulshrestha et al. 2014). So a long term study is required to appreciate this issue.

Table 5.10.1: Mean and Percentage frequency distribution of pH during the period 2012, 2013 and 2014.

рН	2012	2013	2014
Mean±SD	5.85±0.66	5.64±0.56	5.35±0.57
% frequency distribution (4.5-5)	9	12	27
% frequency distribution (5-5.6)	30	38	39
% frequency distribution (5.6-6)	20	23	22
% frequency distribution (6-6.5)	25	24	9
% frequency distribution (6.5-7)	15	2	3
% frequency distribution (7-7.5)	0	1	0
% frequency distribution (7.5-8)	1	0	0

5.10.2 Ionic constituents of rainwater

Rainwater samples were measured for ions viz. F-, Cl-, Br-, NO₃⁻, SO₄²⁻, Na⁺, K⁺, NH₄⁺, Ca²⁺ and Mg²⁺ for the year 2012-14 (Table 5.10.2). Concentrations of ionic constituents followed the order Ca²⁺>NH₄⁺>SO₄²>Cl⁻> NO₃^{->} K⁺> Na⁺>Mg²⁺>F⁻>Br⁻. Among anions SO₄²⁻ was found to be maximum with concentration 90.90±113µeqL⁻¹ followed by Cl- with concentration 85.84±118 µeqL⁻¹. As already mentioned in the earlier section 5.4.2, during the monitoring period SO₄²⁻ particles were more abundant in the study region and possible causes were also discussed. So, there has been a possibility of more scavenging of SO₄²⁻ ion by rainfall in the soluble form. Origin of SO₄²⁻ in rainwater could be from anthropogenic activities or long range transport as CCN. Anions such as Cl⁻

and NO_3^- were also found in rainwater samples with significant concentrations. Cl⁻ and NO_3^- has been found to be associated with biomass burning or any other combustion such as open waste burning as reported by many researchers (Patil et al., 2013). Therefore higher concentrations of Cl⁻ and NO₃⁻ during the study period might be due to the prevalent of profound combustion processes in the study region. Among cations Ca^{2+} was found maximum with concentration 152.95±108 µeqL⁻¹ followed by NH_4^+ with concentration 100.32±90 µeqL⁻¹ during the whole period of study 2012-14. Ca²⁺ ion is considered as a crustal component, which constitute major part of the ionic composition in rainwater. Though, Ca²⁺ was not a major cation in PM10 as mentioned in the earlier section, still our rainwater samples showed higher concentrations of this ion. This might be due to the long range transport of Ca²⁺ ion as CCN from arid regions of India (Fig 5.2).Emissions of N containing gases from the nitrogen-based fertilizer, biomass burning could lead to formation of NH₃ in the atmosphere which in turn converted to NH4⁺ by gas to particle conversion. (Aneja et al., 2001; Tripathee et al., 2013; Bouwman et al., 1997). These anthropogenic and natural sources contributed significant amount of NH_4^+ to the atmosphere. Presence of K⁺ in rainwater (66.26±89 µeqL⁻¹) indicates that the region has been influenced by biomass burning as it is considered as marker of biomass burning(Mouli et al., 2005; Viana et al., 2008). Rainwater acts as a scavenging factor for the precursor particles of major ions.

Table 5.10.2: Ionic c	omposition c	of rainwater	during the study	v period	(2012 - 14)) in L	lea/]	L
					(, r		

Major ions	Mean	SD
Li ⁺	0.07	0.07
Na^+	34.58	27
$\mathrm{NH_4}^+$	100.32	90
K^+	66.26	89
Ca ²⁺	152.95	108
Mg^{2+}	11.78	9
F	10.57	19
Cl	85.84	118
NO ₃ -	82.88	106
SO_4^{2-}	90.90	113

Figure 5.10.2 (a) represents ionic balance of rainwater constituents. Ionic balance between sum of anions and cations showed a good correlation with r value 0.880. This indicates the complete measurement of ionic constituents of rainwater during the study period. Fig 5.10.2 (b) represents the monthly variations of ionic constituents of rainwater. It was observed that from February to April month both the cations and anions showed increased level of concentrations and decreases from June to October. Since there was no rainfall or very less event of rainfall occurred during the months November, December and January (post-monsoon and winter). Therefore particles in the atmosphere were exposed for very long period of time and get accumulated. Whenever, there was a rain event during this period, it scavenged most of the particles present in the atmosphere, making the rain more ionic rich. Again, March, April and May (Pre-monsoon) have been associated with strong wind gust due to Nor'wester wind (locally known as Bordoichilla). Strong winds gust could help in the resuspension of surface soil, road dust to the atmosphere and eventually scavenged by rain. From June to September (monsoon) months this region receives rainfall due to southwesterly monsoon. During monsoon season highest rainfall occur which increases the dilution effect of ions. Scavenging of particles by continuous rainfall leads to decrease in the concentrations of ions in monsoon season (June-September).





Figure 5.10.2: (a) Ionic balance between \sum Anion and \sum Cation; (b) monthly variation of ionic concentration of cations and anions

5.11 Relationship of rainwater and aerosol

5.11.1 Relation between rainwater pH and mass concentration of PM10

To investigate dependency of rainwater chemistry on aerosol composition, we have drawn a relationship between pH and PM10 losing of each month during the study period 2012-14 considering rain events just after the PM10 sampling. It was observed that relation between mass concentration of PM10 and pH of rainwater showed negative correlation. As pollution aerosols, such as sulfate and nitrate that mostly exist in finer particles and the major contributor to acidity of the rainwater (Zeng et al., 2001; Tang et al., 2005), the acidity of the rainwater could increase with the increase of PM10 as shown in the Figure 5.11.1. Continuous rainfall could lead to more scavenging of aerosol particle from the atmosphere. The pH was observed to be decreasing during December and February month when there was no rainfall for a long period of time. This leads to increase in the mass concentration of PM10.



Figure 5.11.1: Monthly variation of mean pH of rainwater with mean mass concentration of PM10 during the period 2012-14

5.11.2 Scavenging ratio

The ratio between ionic concentrations in precipitation and in particulate fraction is known generally as scavenging ratio (Wx) (Jafffrezo and Colin 1988; Cadle et al., 1990; Harrison and Allen 1991). Scavenging ratio can be obtained from the following formula

 $Wx = (Xp)\rho a/Xa$(Eq 1)

Where Wx is the dimensionless scavenging ratio of X species, Xp and Xa are the X concentrations in the precipitation ($\mu g g^{-1}$) and in the aerosol ($\mu g m^{-3}$) respectively, and $\rho a= 1,290 g m^{-3}$, the density of air at 20⁰C and 760 mm Hg. All scavenging ratios were calculated following the above mentioned equation by which overall monthly averages of wet precipitation concentrations were divided by the overall monthly averages of the aerosol samples (Wx based on overall monthly averages).

	Feb	March	April	May	June	July	August	Sept	October	December	2012-14
Na ⁺	650.5	732.7	710.6	467.2	403.9	475.6	534.0	473.0	298.6	853.5	559.9±171
$\mathrm{NH_4}^+$	1933.7	4162.2	3248.1	2706.1	2080.6	1623.8	3096.0	3048.0	1675.7	5949.8	2952.4±1326
K^+	1549.3	2985.5	1712.1	1658.9	1453.8	1302.5	1369.7	1780.6	646.7	5756.8	2021.6±1435
Ca ²⁺	3987.6	3837.3	4956.3	3626.8	4229.2	3105.2	3976.6	3243.2	2874.0	7085.8	4092.2±1212
Mg ²⁺	4564.5	3484.9	3466.7	3030.9	3446.0	3708.4	3023.7	3088.1	2546.0	5793.4	3615.3±933
Cl ⁻	10488.0	9161.2	2153.6	1448.8	1174.1	1207.0	1034.9	1919.4	1689.1	1697.3	3197.3±3524
NO ₃ -	8006.6	8758.1	5565.1	5647.4	3348.2	2539.4	2712.2	4225.2	3560.8	9608.2	5397.1±2587
SO4 ²⁻	4346.2	2413.7	1833.2	1436.3	1321.4	1447.8	1064.4	1372.6	1304.4	3408.6	1994.8±1081

Table 5.11.2: Scavenging ratio (W, dimensionless), calculated as the relationship between the ionic concentration in the precipitation and the aerosol

The order of scavenging ratio for the major ionic concentration was observed to be $NO_3^- >Ca^{2+}>Mg^{2+}>Cl^->NH_4^+>K^+>SO_4^{2+}>Na^+$. Primarily, a high W for NO_3^- ion was observed during the whole study period (Table 5.10.2). For NO_3^- their substantial atmospheric fractions are usually in the gas phase which has not been considered for our study. As a result their scavenging ratios could be increased by the contribution of their corresponding gases (HNO₃) to rainwater concentrations through the efficient gas-washout process (Encinas and Casado 1999; Voisin et al., 2000). Crustal originated ions (Ca²⁺, Mg²⁺) showed higher scavenging ratio. Cl⁻ ion also showed high W, this could be due to the association of gaseous HCl into the rain droplets (He and Balasubramanian, 2008).

1.12 Source Apportionment of aerosol over the study area

5.12.1 Ionic ratios and Enrichment factor:

Table 5.12.1 represents the ionic ratio and enrichment factors of measured ion of PM10 with respect to sea taking Na as reference ion (Wilson, 1975). Although we have considered the assumption that sodium is originated from marine sources which may not be real, since present study site is an inland station far away from the oceanic region, but such an assumption gives an approximation for further interpretations (Tiwari et al., 2009). It was observed that Cl⁻/Na⁺ ratio was depleted during the study period from the ratio of seawater. Chloride depletion in sea salt particles has been explained by the reaction of gaseous or aqueous HNO₃ or H₂SO₄ with NaCl in sea salt particles or by the gaseous SO₂ by sea salt droplet later oxidized to sulphuric acid (Harrison and Pio, 1983; Wall et al., 1988; Mamane and Gottlieb 1992; Sarin et al., 2010). More over Souza et al., 2014 reported that depletion of Cl⁻indicates several acting sources for this ion beyond sea salt. Except Cl⁻, all other ions showed higher ratio with respect to Na, considering it as marine origin. This implies that ions such as SO₄²⁻, K⁺, Ca²⁺, Mg²⁺ can be originated from both anthropogenic activities and natural processes other than marine origin.

Table	5.12.1:	Ionic	ratios	and	Enrichment	factor	with	respect	to	sea	for	the	water	soluble	ionic
compo	osition o	fPM1	0												

Ionic ratio of PM10 with respect to sea								
	Cl ⁻ /Na ⁺	SO4 ²⁻ /Na ⁺	K ⁺ /Na ⁺	Ca ²⁺ /Na ⁺	Mg ²⁺ /Na ⁺			
Winter	0.45	2.00	1.03	0.25	0.04			
Pre-monsoon	0.48	1.14	0.69	0.34	0.05			
Monsoon	0.52	0.68	0.48	0.21	0.03			
Post-monsoon	0.57	0.67	0.62	0.31	0.04			
2012-14	0.50	1.19	0.73	0.27	0.04			
Seawater ^a	1.16	0.12	0.02	0.04	0.22			
Enrichment factor	r with respe	ect to sea						
	Cl	SO_4^{2-}	K^+	Ca^{2+}	Mg^{2+}			
2012-14	0.4	10	36	7	0.2			
Winter	0.4	17	51	6	0.2			
Pre-monsoon	0.4	9	34	9	0.2			
Monsoon	0.4	6	24	5	0.1			
Post-monsoon	0.5	6	31	8	0.2			

a Wilson, 1975

Enrichment factor of water soluble ions were calculated with respect to sea and crust taking Na and Al as reference ion for marine and crust respectively with the help of following formula

EFx = (X/Na)air/(X/Na)seawater...(Eq 2)EFx = (X/Al)air/(X/Al)crust...(Eq 3)

Where X is the ion of interest, $(X/Na)_{air}$ is the ionic ratios of aerosol, $(X/Al)_{air}$ is the ratio of elements with respect to Al. The ratios X/Na and X/Al for seawater and crust were taken from the literature by Wilson, 1975 and Taylor and McLennan, 1995. According to Azri et al. (2010) if the enrichment factor (EF) is less than 10, then slightly enriched condition. If EF> 1000, then highly enriched and in a condition where 10<EF<1000, then the ion can be considered as enriched. If EF values with respect to sea and crust were found near to unity then it signifies predominance of ions in particulate matter from respective sources. From Table 5.12.1 it was observed that ratio of SO₄²⁻, K⁺ and Ca²⁺ with respect to sea is higher than unity. Higher EF is an indication of influence of anthropogenic input or other sources from nature like crustal input.

Figure 5.12.1 presents the EF with respect to crust. The EF value of Fe, Mn, Na and K was observed to be almost equal to unity. Highest EF was observed for Cd (100<Cd<10000). Higher EF values were observed for Cr, Cu, Ni, Pb (10<EF<100) for the whole study period, whereas Ca and Mg showed very less enrichment. Trend was almost same for all the season. The elements with high enrichment factors generally showed rather low concentrations. On the contrary Na, Mg, K, Ca, Mn and Fe have rather high concentrations but low enrichment factor (<5), which indicates negligible contribution of anthropogenic sources and main origin from the airborne dust. Higher EF for Cd, Pb could be due to presence of potent anthropogenic sources such as the fuel combustion or metal smelting (Wang et al., 2006).



Figure 5.12.1 Enrichment factor of elemental composition of PM10 with respect to crust taking Al as reference element (source: Taylor and McLennan, 1995)

5.12.2 Interspecies Correlations

Table 5.12.2 presents the correlation matrix of the species measured to find out associations between variables for the period 2012-14. PM10 mass concentration showed significant correlation between major water soluble ions (Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺), trace elements (Cu, Mn) and carbonaceous fractions (WSOC, WSIC, EC, OC). Significant correlation indicates that these variables contributed major portion of PM10 in the atmosphere. Major water soluble ions showed significant correlation among each other and also with WSOC, OC, EC and TC. High correlation was found between NH₄⁺ and SO₄²⁻, NO₃⁻ and SO₄²⁻ and NH₄⁺ and NO₃⁻which shows the formation of ammonium sulphate, ammonium bisulphate (NH₄HSO₄) and ammonium nitrate (Gupta and Mandariya, 2013). Coal burning, vehicular emissions and industries are the common sources of NO₃⁻ and SO₄²⁻. Carbonaceous fractions viz. WSOC, WSIC, OC, EC, TC and WSTC showed significant
correlation among each other. Al is considered as crustal originated trace element in the PM10. It showed significant positive correlation with Na⁺ and K⁺, which indicate crustal input as possible sources of these ions. Like Al, other trace elements such as Cd, Cr, Fe, Mn, Ni, Mn and Pb showed significant positive correlation with ions such as Na⁺, K⁺, and NH4⁺. K⁺, tracer for biomass burning emissions, showed significant correlation with the major carbonaceous fractions which indicates that the biomass burning a potential emission source in this region.

	PM10	F-	Cl-	NO ₂ -	SQ4 ²⁻	Na ⁺	NH_{4}^{+}	K ⁺	Ca ²⁺	Mg ²⁺	Al	Cd	Со	Cr	Cu	Fe	Mn	Ni	Pb	WSOC	WSIC	WSTC	TC	EC	OC
PM10	1	-		,	2.04		4																		
F	0.028	1																							
Cl	256**	-0.019	1																						
NO3 ⁻	.688**	0.008	280**	1																					
SO4 ²⁻	.646**	0.058	.320**	.628**	1																				
Na ⁺	.325**	-0.012	.414**	.268**	.214**	1																			
$\mathrm{NH_4}^+$.616**	-0.033	.219**	.649**	.612**	.330**	1																		
К ⁺	.565**	-0.006	.366**	.521**	.348**	.709**	.728**	1																	
Ca ²⁺	.204**	-0.006	.451**	.182**	.407**	.510**	.211**	.368**	1																
Mg ²⁺	.168**	-0.007	.444**	.126*	.416**	.428**	.150*	.254**	.931**	1															
Al	0.053	-0.108	0.119	-0.015	228**	.492**	0.019	.230**	-0.052	-0.099	1														
Cd	0.112	-0.038	-0.084	0.026	0.024	.272**	.153*	.244**	-0.034	-0.033	.305**	1													
Co	0.007	-0.001	-0.042	-0.101	-0.048	0.104	0.012	0.027	-0.042	-0.047	.243**	.564**	1												
Cr	0.109	0.004	.127*	0.042	0.064	.291**	0.098	.176**	0.05	0.081	.248**	.655**	.344**	1											
Cu	.221**	-0.035	0.021	.126*	.132*	.332**	.208**	.289**	0.011	0.031	.268**	.636**	.153*	.768**	1										
Fe	0.12	-0.035	-0.016	0.108	0.086	.253**	.175**	.258**	0.012	0.027	.151*	.804**	.176**	.776**	.794**	1									
Mn	.166**	-0.035	-0.033	0.108	0.073	.206**	.174**	.243**	0.016	0.018	0.117	.703**	.137*	.620**	.699**	.865**	1								
Ni	0.087	-0.012	-0.001	0.052	0.04	.239**	0.095	.179**	-0.028	-0.012	.217**	.585**	.219**	.504**	.571**	.601**	.484**	1							
Pb	.149*	-0.059	-0.047	0.076	0.047	.272**	.179**	.270**	-0.031	-0.026	.240**	.897**	.359**	.717**	.696**	.890**	.795**	.528**	1						
WSOC	.562**	.181**	.309**	.529**	.832**	.211**	.600**	.365**	.348**	.384**	170**	0.102	-0.039	.126*	.199**	.148*	0.124	.149*	0.108	1					
WSIC	.327**	-0.102	.238**	0.086	.133*	.629**	.308**	.485**	.304**	.266**	.439**	.329**	.144*	.348**	.388**	.249**	.196**	.304**	.296**	.212**	1				
WSTC	.585**	.159*	.332**	.528**	.823**	.285**	.612**	.414**	.379**	.409**	-0.111	.141*	-0.02	.167**	.243**	.177**	.146*	.184**	.142*	.993**	.345**	1			
TC	.663**	0.077	.327**	.588**	.513**	.235**	.493**	.486**	.169**	.154*	-0.004	0.074	-0.076	0.094	.205**	.140*	.156*	0.12	0.111	.533**	.179**	.541**	1		
EC	.629**	0.002	.363**	.527**	.657**	.237**	.661**	.466**	.185**	.213**	0.067	0.097	0.094	.125*	.226**	0.089	0.11	.169**	0.104	.711**	.310**	.719**	.567**	1	
OC	.585**	0.084	.274**	.527**	.410**	.204**	.387**	.428**	.144*	0.12	-0.022	0.059	-0.109	0.074	.173**	.135*	.147*	0.092	0.099	.419**	.133*	.426**	.978**	.384**	1

Table 5.12.2: Inter species correlation between the measured variables of PM10 for the period of 2012-14	
--	--

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

5.12.3 Principal Component Analysis-Multiple Linear Regression (PCA-MLR)

Principal Component Analysis (PCA) was done after normalizing the data to see the contributing sources for the monitoring period. And, the estimation of source contribution was done by MLR. The Identified and quantified sources are confirmed by CMB.

PCA gives idea of potential sources which typically require a large robust dataset i.e. >100 samples (Cusac et al. 2013). Sample size is vital for a good PCA. Though Lawley and Maxwell (1971) suggested that at 51 more samples than the number of variables to support chi-square testing, Gorsuch (1983) and Kline (1979) recommended a sample size of at least 100. The PCA was done taking 250 samples. Outliers (those beyond 2SD) were removed and the dataset was normalized. By extracting the eigenvalues and eigenvectors from the correlation matrix, principal factors with eigenvalue>1 were chosen for Varimax rotation.

The PCA revealed 4 major components explaining 73.21% of variance (Table 5.12.3a). PC1 explained 23.68% of variance with high loading of K⁺, NO₃⁻, SO₄²⁻, EC, OC, WSOC and NH₄⁺. This indicates combustion sources - biomass burning (EC, OC and K), Vehicular emission (EC, OC, NO₃⁻) and coal combustion (EC, OC and SO₄²⁻). This factor could also explain secondary formation (NO₃⁻, SO₄²⁻, WSOC and NH₄⁺).

The PC2 is explained 21.66% of the variance with higher loadings Cu, Fe, Mn, Ni and Pb, which are typical of road dust. These metals are come to the roads from vehicular wear and tear. The PC3 explains 14.56% of the variance with high loading of Ca, Mg, Na and $SO_4^{2^-}$, Ca and Sulphate together points at gypsum, which is a construction material. These species are also associated cement. Therefore, this component is attributed to construction activities. PC4 explains 13.31% of the total variance and with high loading of Al, Na, K and WSIC, which points as feldspar. This factor may be attributed to crustal/ soil emission.

Rotated Component Matrix ^a PC1 PC 2 PC 3 PC 4										
	PC1	PC 2	PC 3	PC 4						
Al	-0.10	0.13	-0.17	0.81						
Cu	0.14	0.84	0.00	0.20						
Fe	0.07	0.96	0.02	0.05						
Mn	0.08	0.90	0.01	0.01						
Ni	0.06	0.69	-0.03	0.17						
Pb	0.06	0.90	-0.04	0.14						
Na	0.22	0.19	0.42	0.76						
NH ₄	0.84	0.10	0.03	0.18						
Κ	0.60	0.16	0.18	0.57						
Ca	0.14	-0.03	0.94	0.13						
Mg	0.12	0.00	0.96	0.03						
Cl	0.32	-0.12	0.50	0.31						
NO ₃	0.82	0.01	0.01	0.08						
SO_4	0.80	0.05	0.37	-0.21						
EC	0.81	0.07	0.10	0.09						
OC	0.63	0.08	0.02	0.09						
WSOC	0.78	0.13	0.33	-0.18						
WSIC	0.06	0.26	0.27	0.71						
Total	4.26	3.90	2.62	2.40						
% of Variance	23.68	21.66	14.56	13.31						
Cumulative %	23.68	45.34	59.90	73.21						
Sources	Combustion: Biomass burning+ vehicular+ emission and coal burning formation	Road dust	Construction dust	Soil/crustal						
Extraction Metho	d: Principal Comp	onent Analysis.								

Table 5.12.3a: Principal Component Analysis-Multiple linear regression (n=250)

Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 5 iterations.

Multiple Linear Regression (MLR) was done as per Larsen and Backer, 2003. MLR helps to give quantitative strength of the identified sources. The PCA factor scores 1–4 were taken as independent variables and z-scores of sum total chemical species of each sample (Xi) taken in the PCA as dependent variable. In order of their individual simple correlation from highest to lowest, each independent variable was added into stepwise regression. The percent contribution of each source/ group of sources was calculated from the coefficients (Table

5.12.3b). The observed and model predicted concentrations showed very good agreement with R^2 value of 0.91 (Figure 5.12.3)

Table 5.12.3b: Percent contribution of sources of aerosol over mid-Brahmaputra (Tezpur region) obtained from PCA-MLR analysis

Source (From PCA)	Percent contribution
Combustion – biomass burning, vehicular	56%
emission, coal burning	
Street dust	16%
Construction dust	13%
Suspended Soil/Crustal matter	15%



Figure 5.12.3: Linear correlation between observed and model predicted total species concentration ($R^2=0.907$).

5.12.4 Chemical Mass Balance (CMB)

To identify and appreciate the strengths of various sources of aerosol over the study area, Chemical Mass balance model (CMB 8.2) was applied. CMB is a regulatory receptor model for air pollution source apportionment. The model is freely available on the USEPA official website. The description of the model is elaborately given in the manual of CMB (http://www3.epa.gov/scram001/receptor_cmb.htm).



Figure 5.12.4: Percentage contribution of major sources during the whole study period and in different seasons by CMB model

CMB gives strength of selected sources based on source inventory. The source profile has been prepared form the standard inventory procured from Central Pollution Control Board (CPCB)(<u>http://www.cpcb.nic.in/Source_Apportionment_Studies.php</u>).The inventories are not local inventories. They are inventories from large cities of mainland India viz., Mumbai, Kanpur, Delhi and Chennai. There are no source inventories from the northeastern region of India as yet. Given the number of sources, CMB model was run till the model converges with a maximum limit of 20 runs for each sample. The source selections have been done by removing similar sources based on colinearity test. The model results were estimated for each sampling day from which seasonal and annual source contributions were calculated. Model estimates with $R^2 > 0.8$ and $\chi^2 > 1.0$ were accepted. The results are presented in Figure 5.12.4

The CMB model estimates explain that biomass burning, road dust and vehicular emissions are the major contributors of atmospheric aerosol over mid-Brahmaputra region.

Road dust (paved and unpaved) has been found to be major contributor of aerosol of the region. Actually conditions of road, road geometry, vehicular condition, etc are added attributes that influence of emission of dust from the roads. It was observed from the model output that contribution from road dust dominated all through the year including the period of high rainfall (monsoon season). In fact the region represents moderate to high rainfall areas and during the rainy days lots of debris come to the roads carried by the vehicles from village roads and carried by runoff from the hills. When the rain stops the entire load of debris is blown by moving vehicles during the dry spells. This leads to continuous input of dust into the atmosphere all through the year including the monsoon.

Biomass burning is ubiquitous all through the northeastern region and the neighbouring Southeast Asian countries. Biomass burning in households is most common, which is a daily affair in majority of households of rural areas, besides there are seasonal biomass burning periods associated with forest fire, agricultural waste burning and festive burning.

Coal burning was also identified as one of the major contributors. Coal is extensively used in the brick industries, which is an unorganized sector in the region, and in the tea processing industries. The tea processing industries are at the peak of production during the premonsoon and monsoon period, and on the other hand the brick industries operate during the post monsoon and winter season. So, the signatures of coal and its contribution were found all through the year.

Source contribution from petroleum refining was also traced; however, the contribution was low, which was seen only in a particular season.

5.13 Visibility:

Visibility is impaired due to attenuation of light in the atmosphere, which is caused by two processes – (1) light scattering(s) and light absorption (a). It is known that both particles and gases absorb and scatter light. So, the total light extinction is the sum of both, i.e. $b_{\text{ext(total)}}=b_{\text{s(particle)}}+b_{\text{a(particle)}}+b_{\text{s(gas)}}+b_{\text{a(gas)}}$; where b_{s} and b_{a} refers to coefficients of scattering and absorption.

The light scattering by gases in the atmosphere is considered as Rayleigh scattering. The contribution by gaseous absorption is negligible in nature. Thus light attenuation and,

therefore, visibility may be determined by the size distribution and chemical composition of aerosol. Therefore, taking chemical properties of aerosol the light extinction can be written as (reconstructed):

 $b_{\text{ext}} = b_{\text{ray}} + \Sigma b_i C_i$(Eq4)

where, b_i is the light extinction efficiency (m²/g) of species i and Ci is the concentration of light interacting species i (μ g/m³) – sulphate, nitrate, organic carbon, elemental carbon and other particles (i.e. $\Sigma b_i C_i$ is the sum total b_{scat} and b_{abs} of the particles). The b_{ray} , contribution from gaseous scattering, or the Rayleigh scattering can be considered as a constant (200 Mm⁻¹) (Groblichi et al 1981).

It is understood that the soluble/ hygroscopic aerosol grow in size with rise of relative humidity. So higher the humidity would result in greater scattering. So a function of RH (fRH) explained by Malm et al (1996) by an empirical exponential curve, which explains the relationship between scattering efficiencies of sulphate /nitrate and RH. The f(RH) was calculated from the polynomial equation of the curve. The coefficients- bo, b1 and b2 were computed as per below (Table 5.13.1)

Table 5.13.1: Coefficients computed from ammonium sulphate growth curve – used to compute f(RH)

Season	<i>b0</i>	<i>b1</i>	<i>b2</i>	<i>R2</i>
Spring	-0.01097	0.78095	0.08015	0.93
Summer	-0.18614	0.99211	0.09164	0.91
Autumn	-0.24812	1.01865	0.01074	0.93
Winter	0.34603	0.81984	0.09164	0.77
ANNUAL	0.33713	0.58601	0.09164	0.93

Singh et al (2008) used an equation from the IMPROVE programme of the US EPA as per below:

 $b_{\text{ext}} = b_{\text{ray}} + 3x \text{ f(RH)}[\text{SO}_4] + 3x \text{ f(RH)}[\text{NO}_3] + 4[\text{OMC}] + (1)[\text{soil}] + 0.6.[\text{coarse mass}] + b_{\text{abs}}$

where, b_{abs} may be taken as 10 times EC (Sisler and Malm, 1999) and OMC can be assumed and 1.4 times OC, then the equation becomes:

 $b_{\text{ext}} = b_{\text{ray}} + 3x \quad f(\text{RH})[\text{SO}_4] + 3xf(\text{RH}) \quad [\text{NO}_3] + 4[1.4 \quad \text{X} \quad \text{OC}] + (1)[\text{soil}] + 0.6.[\text{coarse}] + 10x[\text{EC}]....$ (Eq 5)

The eq xx was used to calculate the b_{ext} (in Mm⁻¹) over Tezpur of mid-Brahmaputra region.

The standard visibility range (SVR) was also calculated from the computed b_{ext} results using eq 6 given below:

$$SVR = 3912/(b_{ext} - Ray - 10)...$$
 (Eq 6)

Where, SVR in km, Ray is the Rayleigh scattering constant (200 Mm⁻¹) and 3912 is the constant derived assuming 2% contrast detection threshold. The monthly b_{ext} and SRV over Tezpur region of mid-Brahmaputra valley have been presented in table 5.13.2.

Table 5.13.2: b_{ext} and standard visibility range (SVR) over Tezpur in the mid-Brahamputra Valley during the study period

	$b_{\text{ext}} (\text{Mm}^{-1})$			SVR (Km)		
Months						
	Mean	SD	Range	Mean	SD	Range
Jan	656	223	356-1006	11	7	4.8-23
Feb	545	114	424-784	12	3	6.6-17
Mar	414	97	281-578	21	10	10.1-43
Apr	352	54	288-411	27	9	17.6-40
May	374	36	305-414	22	6	17.5-34
Jun	329	24	292-347	29	6	25-38
Jul	324	52	233-393	36	23	19-89
Aug	322	53	286-417	32	9	17-40
Sep	336	89	272-468	33	14	14-48
Oct	341	96	246-501	34	20	13-69
Dec	494	134	311-720	16	8	7.0-32

An SVR > 19 km is considered very good visibility (Gomez and Smith, 1987). Therefore, the visibility over mid-Brahmaputra valley is very good with an exception of Dec, Jan and Feb months.

REFERENCES:

- Ackerman, A. S., Toon, O. B., Stevens, D. E., Heymsfield, A. J., Ramanathan, V., and Welton,E. J., 2000. Reduction of tropical cloudiness by soot. Science 288, 1042–1047.
- Adachi, K., Buseck, P.R. 2015. Changes in shape and composition of sea salt particles upon aging in an urban atmosphere, Atmos. Environ. 100, 1-9.
- Agarwal, A., Upadhyay, V.K., Sachdeva, K. 2011. Study of aerosol behavoiur on the basis of morphological characteristics during festival events in India. Atmos. Environ. 45, 3640-3644.
- Aggarwal, S. G.; Kawamura, K., 2009. Carbonaceous and inorganic composition in longrange transported aerosols over northern Japan: Implication for aging of water-soluble organic fraction. Atmos. Environ. 43 (16), 2532–2540.
- Akimoto, H., 2003. Global air quality and pollution. Science 302, 1716–1719.
- Akoto, O., Darko, G., Nkansah, M.A., 2011. Chemical composition of rainwater over a mining area in Ghana. Int. J. Environ. Res. 5(4), 847-854.
- Andreae, M. O., 1983. Soot carbon and excess fine potassium: Longrange transport of combustion-derived aerosols. Science 220 (4602), 1148–1151.
- Aneja, V.P., Roelle, P. A., Murray, G.C., Southerland, J., Erisman, J.W., Fowler, D., Asman, W.A.H, Patni, N., 2001. Atmospheric nitrogen compounds II: emissions, transport, transformation, deposition and assessment. Atmos. Environ. 35, 1903-1911.
- Anttila, P., Salmi, T. 2006. Characterizing temporal and spatial patterns of urban PM10 using six years of Finnish monitoring data. Boreal Environ. Res. 11, 463–479.
- Attri, A.K., Kumar, U., Jain, V.K., 2001. Formation of ozone by fireworks.Nature 411, 1015.
- Azri, C., Mabrouk, C., Abida, H., Medhioub, K. 2010. Water-soluble components in PM10 aerosol over an urban and suburban site in the city of Sfax (Tunisia). Atmsofera,23 (2), 197-211.

- Badarinath, K. V. S., MadhaviLatha, K., Chand K. T. R., Gupta P. K. 2009. Impact of biomass burning on aerosol properties over tropical wet evergreen forests of Arunachal Pradesh, India. Atmos Res. 91, 87–93.
- Boreddy, S.K. R., Kawamura, K., 2015. A 12 year observation of water-soluble ions in TSP aerosols collected at a remote marine location in the western North Pacific : an outflow region of Asian dust. AtmosChem Phys. 15, 6437-6453.
- Bouwman, A.F., Lee, D.S., Asman, W.A.H., Dentener, F.J., Van Der Hoek, K.W., Olivier, J.G.J., 1997. A global high resolution emission inventory for ammonia.Global Biogeochem.Cy. 11, 561-587.
- Cadle, S.H., Vandekopple, R., Mulawa, P.A., Dasch, J.M., 1990. Ambient concentrations, scavenging ratios and sources regions of acid related compounds and trace metals during winter in Northern Michigan. Atmos Environ. 24A, 2981–2989.
- Chakraborty, A., Gupta, T., 2009. Chemical characterization of submicron aerosol in Kanpur region: a source apportionment study. Int. J. Env. Ac. Eng. 1, 19–27.
- Charlson, R.J., Rodhe, H., 1982. Factors controlling the acidity of natural rainwater.Nature 295, 683–685.
- Charlson, R.J., Schwartz. S.E., Hales. J.M., Cess. R.D., Coakley Jr., J.A., Hansen, J.E., Hofmann, D.J., 1992. Climate forcing by anthropogenic aerosols. Science 255, 423– 430.
- Chate, D.M., Rao, P.S.P., Naik, M.S., Momin, G.A., Safai, P.D., Ali, K., 2003. Scavenging of aerosols and their chemical species by rain. Atmos Environ. 37 (18), 2477-2484.
- Chelani A. B. et al., 2008. Source Apportionment of PM10 in Mumbai, India Using CMB Model. Bull Environ ContamToxicol 81,190–195
- Chen, M., Ma, L.Q. 2001.Comparison of three aqua regia digestion methods for twenty Florida soils. Soil Sci. Soc. Am J. 65, 491-499.
- Chithra, V.S., Nagendra, S.M.S. 2013. Chemical and morphological characteristics of indoor and outdoor particulate matter in an urban environment. Atmos Environ. 77, 579-587.
- Chonga, N. S., Sivaramakrishnan, K., Wells, M., Jones, K., 2002. Characterization of inhalable particulate matter in ambient air by scanning electron microscopy and energy-dispersive X-ray analysis. Elec J EnvironAgricult Food Chem. 1(3), 145–164.
- Chowdhury, Z., Zheng, M., Schauer, J. J., Sheesley, R. J., Salmon, L. G. and co-authors. 2007. Speciation of ambient fine organic carbon particles and source apportionment of

PM2.5 in Indian cities. J. Geophys. Res. 112, D15303, doi:10.1029/2007JD008386, 1-14

- Chung, S.H., Seinfeld, J.H., 2002. Global distribution and climate forcing of carbonaceous aerosols, J. Geophys.Res.107 (D19), 4407.
- CPCB. 2009. Central pollution control Board, Government of India, <u>http://www.cpcb.nic.in/National_Ambient_Air_Quality_Standards.php</u> (as on 30-09-2015).
- Cusack M., Perez N, Pey J., Alastuey A., and Querol X. (2013) Source apportionment of fine PM and sub-micron particle number concentrations at a regional background site in the western Mediterranean: a 2.5 year study. Atmos. Chem. Phys., 13, 5173–5187, 2013
- Dan, M., Zhuang, G., Li, X., Tao, H., Zhuang, Y. 2004. The characteristics of carbonaceous species and their sources in PM2.5 in Beijing. Atmos Environ. 38, 3443–3452. doi:10.1016/j.atmosenv.2004.02.052.
- Das, N., Baral., S.S., Sahoo, S.K., Mohapatra, R.K., Ramulu, T.S., Das, S.N., Roy Chaudhury,
 G. 2009. Aerosol physical characteristics at Bhubaneswar, East coast of India. Atmos
 Res. 93 (4), 897-901.
- Das, S.K., Jayaraman, A., 2011. Role of black carbon in aerosol properties and radiative forcing over western India during pre-monsoon period. Atmos Res. 102 (3), 320-334.
- Deka, P. and Hoque, R.R., 2014a, Incremental effect of festive biomass burning on wintertime PM10 in Brahmaputra valley of Northeast India. Atmos Res. 143, 380-391.
- Deka, P., Hoque R.R. 2014. Incremental effect of festive biomass burning on wintertime PM10 in Brahmaputra valley of Northeast India. Atmos Res.143, 380-391.
- Deka, P., Hoque R.R. 2015. Chemical characterization of biomass fuel smoke particles of rural kitchens of South Asia. Atmos Environ.108, 125-132.
- Deka, P., Hoque, R.R. 2014a. Diwali Fireworks: early signs of impact on PM10 properties of rural Brahmaputra valley. Aerosol Air Qual. Res. 14, 1752-1762.
- Deka, P., Hoque, R.R., 2014b. Diwali Fireworks: early signs of impact on PM10 properties of rural Brahmaputra valley. Aerosol Air Qual Res. 14, 1752-1762.
- Deka, P., Hoque, R.R., 2015. Chemical characterization of biomass fuel smoke particles of rural kitchens of South Asia. Atmos Environ. 108, 125-132.

- Deshmukh, D.K., Deb, M.K., Tsai, Y.I., Mkoma, S.L., 2011. Water soluble ions in PM2.5 and PM1 aerosols in Durg City, Chhattisgarh, India. Aerosol Air Qual Res. 11, 696–708.
- Draxler, R. R. and Rolph, G. D.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model, access via NOAA ARL READY Website, available at: <u>http://www.arl.noaa.gov/</u>ready/hysplit4.html (last access: July 2013), NOAA Air Resources Laboratory, Silver Spring, 10 MD, 2003.
- Durga, M., Bharathi, S., Balakrishnamurthy, P., Devasena, T., 2015.Characterization and phytotoxicity studies of suspended particulate matter (SPM) in Chennai urban area. J Environ Biology. 36, 583-589.
- Encinas, D., Casado, H., 1999. Rain-aerosol coupling in a rural area in the Basque Country (Spain): Scavenging ratios. Aerosol Sci Technol. 30, 411-419.
- Encinas, D., Casado, H., 1999.Rain-aerosol coupling in a rural area in Basque country (Spain).Scavenging Ratios. Aerosol Sci. Technol. 30, 411–419
- Fu, P. Q., Kawamura, K., Pavuluri, C. M. and Swaminathan, T., 2009. Molecular characterization of urban organic aerosol in tropical India: contributions of biomass/biofuel burning, plastic burning, and fossil fuel combustion. AtmosChem Phys Disc. 9, 21669–21716.
- Fu, P. Q., Kawamura, K., Pavuluri, C. M., Swaminathan, T. and Chen, J. 2010. Molecular characterization of urban organic aerosol in tropical India: contributions of primary emissions and secondary photooxidation. Atmos. Chem. Phys. 10, 2663–2689.
- Galloway, J.N., Savoie, D.L., Keene, W.C., Prospero, J.M., 1993. The temporal and spatial variability of scavenging ratios for nsssulface, nitrate, methanesulfonate, and sodium in the atmosphere over the North Atlantic Ocean. Atmos Environ. 27, 235–250.
- Ganguly, D., Gadhavi, H., Jayaraman, A., Rajesh, T.A., Misra, A., 2005. Single scattering albedo of aerosols over the central India: implications for regional aerosol radiative forcing, Geophys Res Letters, 32, L18803.
- Ganguly, D., Jayaraman, A., Rajesh, T.A., Gadhavi, H., 2006. Wintertime aerosol properties during foggy and nonfoggy days over urban center Delhi and their implications for shortwave radiative forcing. J Geophys Res. 111, D15217.

- Goldberg, E.D., Broecker, W.S., Gross, M.G., Turekian, K.K., 1971. Marine chemistry.Radioactivity in the Marine Environment. National Academy of Sciences, Washington, DC, 137–146.
- Gomez, B., & Smith, C. G. (1987). Visibility at Oxford 1926–1985. Weather, 42,98–106.
- Gomiscek, B., Hauck, H., Stopper, S., Preining, O., 2004. Spatial and temporal variations of PM1, PM2.5, PM10 and particle number concentration during the AUPHEP—project. Atmos Environ. 38, 3917–3934. doi:10.1016/j.atmosenv.2004.03.056.
- Gong, S.L., Barrie, L.A., Lazare, M., 2002. Canadian aerosol module (CAM): A size segregated simulation of atmospheric aerosol processes for climate and air quality models 2. Global sea salt aerosol and its budgets.J Geophys Res. 107 (D24), 4779.
- Gorsuch, R. L. 1983. Factor analysis (2nd ed.). Hillsdale, NJ: Erlbaum.
- Grantz, D.A., Garner, J.H.B., Johnson, D.E., 2003. Ecological effects of particulate matter. Environ. Int. 29, 213–239.
- Grimm, H., Eatough, D.J., 2009. Aerosol measurement: the use of optical light scattering for the determination of particulate size distribution, and particulate mass including the semi volatile fraction. J Air & waste manage Assoc. 59, 101-107.
- Groblicki, P. J., George, T. W., & Countess, 1981.Visibilityreducingspecies in the Denver "Brown Cloud."I.Relationship between extinction and chemical composition.Atmospheric Environment, 15(12), 2473–2484.
- Guazzotti, S. A., Suess, D. T., Coffee, K. R., Quinn, P. K., Bates, T. and co-authors. 2003. Characterization of carbonaceous aerosols outflow from India and Arabia: biomass/biofuel burning and fossil fuel combustion. J. Geophys Res Atmos 108, 4485–4499.
- Gupta, T., Mandariya, A. 2013.Sources of Submicron Aerosol during Fog-Dominated Wintertime at Kanpur. Environ. Sci. Pollut. Res. 20, 5615–5629.
- Han, J. S., Moon, K. J., Lee, S. J., Kim, Y. J., Ryu, S. Y., Cli, S. S., and co authors, 2005. Size-resolved source apportionment of ambient particles by positive matrix factorization. AtmosChem Phys Disc. 5, 5223–5252.
- Han. G., Wu. Q., Tang Y., 2011. Acid rain and alkalization in southwestern China: chemical and strontium isotope evidence in rainwater from Guiyang. J Atmos Chem. 68, 139-155.

- Harrison, R. M., Pio, A. P. 1983. Size Differentiated Composition of Inorganic Atmospheric Aerosols of Both Marine and Polluted Continental Origin, Atmos. Environ. 17,1733– 1738.
- Harrison, R. M., Pio, A. P., 1983. Size Differentiated Composition of Inorganic Atmospheric Aerosols of Both Marine and Polluted Continental Origin. Atmos Environ. 17:1733– 1738.
- Harrison, R.M., Allen, D.G., 1991. Scavenging ratios and deposition of sulphur, nitrogen and chlorine species ineastern England. Atmos Environ. 25A, 1719–1723
- He, J. and Balasubramanian, R. 2008. Rain-aerosol coupling in the tropical atmosphere of Southeast Asia: distribution and scavenging ratios of major ionic species. J Atmos Chem. 60, 205-220.
- Jaffrezo, J.L., Colin, J.L., 1988. Rain-aerosol coupling in urban area: Scavenging ratios measurements and identification of some transfer processes. Atmos Environ. 22, 929–935. doi:10.1016/0004-6981(88)90270-3
- Jayaraman, A., Gadhavi, H., Misra, A., Ramachandran, S., Rajesh, T.A. 2006. Spatial variations in aerosol characteristics and regional radiative forcing over India: Measurements and modeling of 2004 road campaign experiment. Atmos Environ. 40 (34), 6504-6515.
- Johnson, K. S., de Foy, B., Zuberi, B., Molina, L. T., Molina, M. J., Xie, Y., and co authors 2006. Aerosol composition and source apportionment in the Mexico city metropolitan area with PIXE/PESA/STIM and multivariate analysis. AtmosChem Phys. 6, 4591– 4600.
- Jung, C.H., Kim, Y.P. 2006, Numerical estimation of the effects of condensation and coagulation on visibility using the moment method. J. Aerosol Sci. 37, 143–161.
- Karar, K., Gupta, A.K., Kumar, A., Biswas, A.K. 2006. Characterization and identification of the sources of chromium, zinc, lead, cadmium, nickel, manganese and iron in PM10 particulates at the two sites of Kolkata, India. EnvrionMonit Assess. 120 (1-3), 347-360.
- Khare, P. and Baruah, B. P. 2008.Partitioning of sulphur, nitrogen and carbon compounds in PM10 and PM2.5 at a Tropical Indian site. In: Proceedings of AGU Fall Meeting, San Francisco, CA, 15–19.

- Khare, P., Baruah, B. P., 2009. Aliphatic and polyaromatic hydrocarbons in PM2.5 released from coal-based industries. In: Proceedings on International Symposium on Environmental Pollution, Ecology and Human Health, SVU, Tirupati, India. 25–27.
- Khare, P., Baruah, B.P., Rao, P.G., 2011. Water soluble organic compounds (WSOCs) in PM2.5 and PM10 at a subtropical site of India.Tellus 63B, 990-1000.
- Kharol, S.K., Badarinath, K.V.S., 2006. Impact of biomass burning on aerosol properties over tropical urban region of Hyderabad, India, Geophys Res. Letters. 33, L20801, doi:10.1029/2006GL026759
- Khillare, P.S., Balachandran, S., Meena, B.R., 2004. Spatial and temporal variation of heavy metas in atmospheric aerosol of Delhi. Environ Monit Assess. 90, 1-21.
- Kiehl, j.T., Rodhe, H., 1995.Modeling geographical and seasonal forcing due to aerosols in Aerosol Forcing of Climate, R.J. Charlson and J. Heintzenberg. Eds., Wiley, New York, 281-296.
- Kiss, G., Varga, B., Galambos, I., Ganszky, I., 2002. Characterization of water-soluble organic matter isolated from atmospheric fine aerosol. J. Geophys. Res. 107, 8339– 8348, doi:10.1029/2001JD000603.
- Kleeman, M.J., Schauer, J.J., Cass, G.R. 1999. Size and composition distribution of fine particulate matter emitted from wood burning, meat charboiling, and cigarettes. Environmental Sci. Technol. 33, 3516-3523.
- Kline, P. 1979. Psychometrics and psychology. London: Acaderric Press.
- Kothai, P., Saradi, F. V., Prathibha, P., Hopke, P. K., Pandit, G. G. and co-authors. 2008. Source apportionment of coarse and fine particulate matter at Navi Mumbai, India. Aerosol Air Qual Res. 8, 423–436.
- Kulshrestha, A., Bisht, D.S., Masih, J., Massey, D., Tiwari, S., Taneja, A., 2009.Chemical characterization of water-soluble aerosols in different residential environments of semi arid region of India. J Atmos Chem. 62,121–138
- Kulshrestha, M.J., Singh, R., Duarah, R., Rao, P.G., 2014. Influence of crustal aerosols on wet deposition at a rural site of North-east India. Int. J. Environ. Stud. 71(4), 510-525.
- 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 (7), 968-972.

- Kulshrestha, U.C., Raman, R.S., Kulshrestha, M.J., Rao, T.N., Hazarika, P.J. 2009. Secondary aerosol formation and identification of regional source locations by PSCF analysis in the Indo-Gangetic region of India.J Atmos. Chem. 63,33-47.
- Kumar, A. V., Patila R. S. and Nambi, K. S. V. 2001. Source apportionment of suspended particulate matter at two traffic junctions in Mumbai, India. Atmos Environ. 35, 4245– 4251.
- Kyotani, T., Iwatsuki, M. 2002.Characterization of soluble and insoluble components in PM2.5 and PM10 fractions of airborne particulate matter in Kofu city, Japan.Atmos Environ. 36, 639–649. doi:10.1016/S1352-2310(01)00494-0.
- Larsen, R.K., Baker, J.E., 2003. Source apportionment of polycyclic aromatichydrocarbons in the urban atmosphere: a comparison of three methods. Environ Sci technol. 37, 1873-1881.
- Lawley, D. N., Maxwell, A. E. 1971. Factor analysis as a statistical method. London: Butterworth and Co.
- Lee B.K., Hieu, N.T., 2011. Seasonal variation and sources of heavy metals in atmospheric aerosols in a residential area of Ulsan, Korea. Aerosol Air Qual Res. 11, 679-688.
- Li, J., Anderson, J.R., Buseck, P.R., 2003. TEM study of aerosol particles from clean and polluted marine boundary layers over the North Atlantic.J Geophy Res. 108 (D6), 4189.
- Li, W., Shao, L., 2009.Transmission electron microscopy study of aerosol particles from the brown hazes in northern China. J Geophys Res. 114, D09302.
- Li, Y., Schwab, J.J., Demerjian K.L. 2006. Measurement of ambient ammonia using a tunable diode laser absorption spectrometer: characteristics of ambient ammonia emissions in an urban area of New York City. J. Geophys Res. 111,(D10). doi:10.1029/2005 JD006275
- Liao, H., Adams, P.J., Seinfeld, J.H., Mickley, L.J., Jacob, D.J., 2003. Interactions between tropospheric chemistry and aerosols in a unified general circulation model. J. Geophys. Res., 108 (D1) 4001.

- Liao, H., Seinfeld, J.H., Adams, P.J., Mickley, L.J., 2004. Global radiative forcing of coupled tropospheric ozone and aerosols in a unified general circulation model.J Geophys.Res.109, D16207.
- Lin, J.J., Tai, H.S., 2001. Concentrations and distributions of carbonaceous species in ambient particles in Kaohsiung City, Taiwan. Atmos. Environ. 35, 2627-2636.
- Liousse, C., Penner, J.E., Chuang, C., Walton, J.J., Eddleman, H., Cachier, H., 1996. A global three dimensional model study of carbonaceous aerosols. J. Geophys. Res., 101, 19411-19432.
- Loh, N.D., Hampton, C.Y., Martin, A.V., Starodub, D., Sierra, R.G., Barty, A., Aquila, A., Schutz, J., Lomb, L., Steinbrener, J., Shoeman, R.L., and co authors, 2012. Fractal morphology, imaging and mass spectrometry of single aerosol particles in flight. Nature, 486, 513-517.
- Mader, B. T., Yu, J. Z., Xu, J. H., Li, Q. F., Wu, W. S. and co-authors. 2004. Molecular composition of the water soluble fraction of atmospheric carbonaceous aerosols collected during ACE-Asia. J. Geophys.Res. 109, D06206, doi:10.1029/2003JD004105.
- Malm, W. C., Molenar, J. V., Eldred, R. A., &Sisler, J. F.(1996). Examining the relationship among atmosphericaerosols and light scattering and extinction in the GrandCanyon area. Journal of Geophysical Research, 101(D14)(19), 251–265.
- Mamane, Y., Gottlieb, J. 1992. Nitrate Formation on Sea-Salt and Mineral Particles—A Single Particle Approach. Atmos Environ. 26A,1763–1769.
- Mamane, Y., Gottlieb, J. 1992. Nitrate Formation on Sea-Salt and Mineral Particles—A Single Particle Approach, Atmos. Environ. 26A,1763–1769.
- Maria, S., Russel, L.M., 2005.Organic and inorganic aerosol below cloud scavenging by suburban New Jersey Precipitation.EnvrionSci Technol. 39, 4793-4800.
- Massey, D., Kulshrestha, A., Masih, J., Taneja, A., 2012. Seasonal trends of PM10, PM5.0, PM2.5&PM10 in indoor and outdoor environments of residential homes located in North-Central India. Build Environ. 47, 223-231.
- McFiggans, G., Artaxo, P., Baltensperger, U., Coe, H., Facchini, M. C., Feingold, G., Fuzzi, S., Gysel, M., Laaksonen, A., Lohmann, U., Mentel, T. F., Murphy, D. M., O'Dowd,

C. D., Snider, J. R., Weingartner, E. 2006. The effect of physical and chemical aerosol properties on warm cloud droplet activation. Atmos. Chem. Phys. 6, 2593-2649.

- Menon, S., Hansen, J., Nazarenko, L., Luo, Y., 2002, Climate effects of black carbon aerosols in China and India.Science 297, 2250–2253.
- Mitra A.P., Sharma C., 2002. Indian aerosols: present status. Chemosphere 49.
- Mohan, M., Payra, S., 2009. Influence of aerosol spectrum and air pollutants on fog formation in urban environment of megacity Delhi, India. Environ Monit Assess 151, 265-277.
- Mönkkönen, P., Uma, R., Srinivasan, D., Koponen, I. K., Lehtinen, K. E. J., Hämeri, K., Suresh, R., Sharma, V. P., Kulmala, M., 2004. Relationship and variations of aerosol number and PM10 mass concentrations in a highly polluted urban environment—New Delhi, India. Atmos Environ. 38, 425–433
- Mouli, P.C., Mohan, S.V., Reddy, S.J., 2005. Rainwater chemistry at a regional representative urban site: influence of terrestrial sources on ionic composition. Atmos. Environ. 39, 999-1008.
- Mumford, J.L., He, X.Z., Chapman, R.S., Cao, S.R., Harris, D.B., Li, X.M., Xian, Y.L., Jiang, W.Z., Xu, C.W., Chuang, J.C., Wilson, W.E., Cooke, M., 1987. Lung-cancer and Indoor Air-pollution in Xuan-wei, China. Science 235, 217–220.
- Muranszky, G., _Ov_ari, M., Vir_ag, I., Csiba, P., Dobai, R., Z_aray, G., 2011.Chemical characterization of PM10 fractions of urban aerosol.Microchem. J. 98, 1-10.
- Nair, P.R., George, S.K., Kumar, S.V., Parameswaran, K., Jocab, S., Abraham, A., 2006. Chemical composition of aerosols over peninsular India during winter, Atmos Environ. 40, 6477–6493
- Nel, A. 2005. Air Pollution-related Illness: Effects of Particles. Science 308, 804-806.
- Paglione, M., Saarikoski, S., Carbone, S., Hillamo, R., Facchini, M.C., Finessi, E., Giulianelli, L., Carbone, C., Fuzzi, S., Moretti, F., Tagliavini, E., Swietlicki, E., Stenstr€om, K.E., Pr_ev^ot, A.S.H., Massoli, P., Canaragatna, M., Worsnop, D., Decesari, S., 2014.
 Primary and secondary biomass burning aerosols determined by proton nuclear magnetic resonance (1H-NMR) spectroscopy during the 2008 EUCAARI campaign in the Po valley (Italy). Atmos. Chem. Phys. 14, 5089-5110.
- Pant, P.,Hegde, P., Dumka, U.C., Saha, A., Srivastava, M.K., Sagar, R., 2006. Aerosol characteristics at a high altitude location during ISRO-GBP Land campaign-II.Curr.Sci.91 (8), 1053-1061.

- Park, K., Dam, H.D., 2010. Characterization of metal aerosols in PM10 from urban, industrial and Asian dust sources. Environ Monit Assess. 160, 289-300.
- Patil, R.S., Kumar, R., Menon, R., Shah, M.K., Sethi, V. 2013. Development of particulate matter speciation profiles for major sources in six cities in India. Atmos. Res. 132-133, 1-11.
- Pavuluri, C. M., Kawamura, K. and Swaminathan, T., 2010.Water soluble organic carbon, dicarboxylic acids, ketoacids, and α- dicarbonyls in the tropical Indian aerosols. J. Geophys. Res. 115, D11302, doi: 10.1029/2009JD012661.
- Pavuluri, C.M., Kawamura, K., Aggrawal, S.G., and Swaminathan, T., 2011.Characteristics, seasonality and sources of carbonaceous and ionic components in the tropical aerosols from Indian region.AtmosChem Phys. 11, 8215-8230.
- Pineiro, J.M., Rodriguez, E. A., Perez, C.M., Heras, G.B., Carou, I.T., Mahla, P.L., Lorenzo, S. M., Rodriguez, D.P., 2014. Influence of marine, terrestrial and anthropogenic sources on ionic and metallic composition of rainwater at a suburban site (northwest coast of Spain). Atmos. Environ. 88, 30-38.
- Pipal, A.S., Kulshrestha, A., Taneja, A., 2011. Characterization and morphological analyisi of airborne PM2.5 and PM10 in Agra located in north central India. Atmos Environ. 45, 3621-3630.
- Posfai, M., Xu, Huifang, X., Anderson, J.R., Buseck, P.R., 1998. Wet and dry sizes of atmospheric aerosol particles: An AFM-TEM study. Geophys Res Letters 25 (11), 1907-1910.
- Ram, K., Sarin, M.M., 2011. Day-night variability of EC, OC, WSOC and inorganic ions in urban environment of Indo-Gangetic plain: implications to secondary aerosol formation. Atmos Envrion. 460-468.
- Ram, K., Sarin, M.M., Sudheer, A.K., Rengarajan, R., 2012a. Carbonaceous and secondary inorganic aerosols during wintertime fog ad haze over urban sites in the Indo Gangetic plain. Aerosol Air Qual Res. 12, 359-370.
- Ram, K., Sarin, M.M., Tripathi, S.N. 2010. A 1 year record of carbonaceous aerosols from an urban site in the Indo-Gangetic Plain: Characterization, sources, and temporal variability. J Geophys Res.115, D24313, doi:10.1029/2010JD014188.

- Ram, K., Sarin, M.M., Tripathi, S.N. 2012. Temporal trends in atmospheric PM2.5, PM10, elemental carbon, organic carbon, water soluble organic carbon and optical properties: impact of biomass burning emissions in the Indo-Gangetic plain, Environ. Sci.Technol. 46, 686-695.
- Ram, K., Sarin, M.M., Tripathi, S.N., 2012b. Temporal trends in atmospheric PM2.5, PM10, Elemental carbon, organic carbon, water soluble organic carbon and Optical properties: Impact of biomass burning emissions in the Indo Gangetic plain. Environ Sci. Technol. 46, 686-695.
- Ram, K.; Sarin, M. M., 2010.Spatio-temporal variability in atmospheric abundances of EC, OC and WSOC over northern India. J. Aerosol Sci. 41 (1), 88–98.
- Ram, K.; Sarin, M. M., 2011. Day-night variability of EC, OC, WSOC and inorganic ions in urban environment of Indo-Gangetic Plain: Implications to secondary aerosol formation. Atmos Environ. 45, 460–468.
- Ramanathan V. Crutzen P. J., Mitra A. P., Sikka D., 2002. The Indian Ocean Experiment and the Asian Brown Cloud.Curr Sci. 83
- Ramanathan V., Feng Y., 2009. Air pollution, greenhouse gases and climate change: Global and regional perspectives. Atmos Environ. 43, 37–50
- Ramanathan, V., Crutzen, P. J., Kiehl, J. T., Rosenfeld, D., 2001, Aerosols, Climate, and the hydrological cycle.Science 294, 2119–2124.
- Rastogi, N., Sarin, M. M., 2009. Quantitative chemical composition and characteristics of aerosols over western India: one-year record of temporal variability. Atmos Environ. 43, 3481–3488.
- Rastogi, N., Sarin, M.M., 2005. Chemical characteristics of individual rain events from a semi-arid region in India: three year study. Atmos Envrion. 39, 3313-3323.
- Rastogi, N., Singh, A., Sarin, M.M., Singh, D., 2015. Temporal variability of primary and secondary aerosols over northern India: Impact of biomass burning emissions. Atmos Environ. <u>http://dx.doi.org/10.1016/j.atmosenv.2015.06.010</u>
- Reisinger, P., Wonaschütz, A., Hitzenberger, R., Petzold, A., Bauer, H., Jankowski, N., Puxbaum, H., Chi, X., Maenhaut, W., 2008. Intercomparison of measurement techniques for black or elemental carbon under urban background conditions in wintertime : influence of biomass combustion. Environ. Sci. Technol. 42, 884-889.

- Rozwadowska, A., Zieli'nski, T., Petelski, T., Sobolewski, P., 2010. Cluster analysis of the impact of air back-trajectories on aerosol optical properties at Hornsund, Spitsbergen. AtmosChem Phys. 10, 877–893, doi:10.5194/acp-10-877-2010.
- Saitoh, K., Sera, K., Shirai, T., 2008.Characterization of atmospheric aerosol particles in a mountainous region in northern Japan. Atmos. Res. 89, 324–329.
- Samburova, V., Zenobi, R., Kalberer, M., 2005. Characterization of high molecular weight compounds in urban atmospheric particles. AtmosChem Phys. 5, 2163–2170.
- Sannigrahi, P., Sullivan, A.P., Weber, R.J., Ingall, E.D., 2006. Characterization of water soluble organic carbon in urban atmospheric aerosols using solid state ¹³C NMR Spectroscopy. Environ Sci Technol. 40, 666-672.
- Sarin, M., Kumar, A., Srinivas, B., Sudheer, A.K., Rastogi, N. 2010. Anthropogenic sulphate aerosols and large Cl-deficit in marine atmospheric boundary layer of tropical Bay of Bengal. J. Atmos. Chem. 66, 1-10.
- Sarin, M., Kumar, A., Srinivas, B., Sudheer, A.K., Rastogi, N., 2010. Anthropogenic sulphate aerosols and large Cl-deficit in marine atmospheric boundary layer of tropical Bay of Bengal. J. Atmos. Chem. 66, 1-10.
- Sarkar, S., Khillare, P.S., Jyethi, D.S., Hasan, A., Parween, M., 2010.Chemical speciation of respirable suspended particulate matter during a major firework festival in India.J Hazard Mater. 184, 321-330.
- Saxena, P., Hildemann, L. M., McMurry, P. H., Seinfeld, J. H., 1995. Organics alter hygroscopic behavior of atmospheric particles. J. Geophys. Res. 100 (18), 18755-18770.
- Shah, M.H., Shaheen, N., Jaffar, M., Khalique, A., Tariq, S.R., Manzoor, S., 2006. Spatial variations in selected metal contents and particle size distribution in an urban and rural atmosphere of Islamabad, Pakistan, J. Environ. Manage. 78 (2), 128-137.
- Shandilya, K.K., Kumar, A., 2010. Morphology of single inhalable particle inside public transit biodiesel fueled bus. J Environ Sci. 22 (2), 263-270.
- Sharma, M., and Maloo, S. 2005. Assessment of ambient air PM10 and PM2.5 and characterization of PM10 in the city of Kanpur, India. Atmos Environ. 39, 6015–6026.

- Sharma, M., Kishore, S., Tripathi, S. N., Behara, S. N., 2007. Role of atmospheric ammonia in the formation of inorganic secondary particulate matter: a study at Kanpur, India. J Atmos Chem. 58, 1–17.
- Sharma, R.K., Agarwal, M., Marshall, F.M., 2008. Heavy metal (Cu, Zn, Cd and Pb) contamination of vegetables in urban India: A case study in Varanasi. Environ Pollut. 154, 254-263.
- Sharma, S.K., Datta, A., Saud, T., Mandal, T.K., Ahammed, Y.N., Arya, B.C., Tiwari, M.K. 2010. Study on concentration of ambient NH3 and interactions with some other ambient trace gases. Environ Monit Assess.162, 225–235.
- Shi, Z., Shao, L., Jones, T. P., Whittaker, A. G., Lu, S., Berube, K. A., and co authors. 2000. Characterization of airborne individual particles collected in an urban area, a satellite city and a clean air area in Beijing, 2001. Atmos Environ. 37, 4097– 4108.doi:10.1016/S1352-2310(03)00531-4.
- Simoneit, B.R.T., Elias, V.O., Kobayashi, M., Kawamura, M., Rushdi, A.I., Medeiros, P.M., Rogge, W.F., Didyk, B.M., 2004.Sugars- dominant water-soluble organic compounds in soils and characterisation as tracers in atmospheric particulate matter. Environ Sci. Technol. 38,5939-5949.
- Singh T, Khillare PS, Shridhar V, Agarwal T., 2008. Visibility impairing aerosol in urban atmosphere of Delhi.Environ Monit Assess (2008) 141:67–77
- Singh, A., Rastogi, N., Sharma, D., Singh, D., 2015. Inter and Intra-Annual variability in aerosol characteristics over Northwestern Indo-Gangetic Plain. Aerosol Air Qual Res. 15, 376-386.
- Singh, R., Sharma, B.S., Chalka, S.N., 2010. Seasonal air quality profile of inorganic ionic composition of PM10 near Taj Mahal in Agra, India. Environ Monit Assess. 168, 195-203.
- Sisler, J., &Malm, W. (1999). Interpretation of trends of PM2.5and reconstructed visibility from the improve network.Journal of the Air and Waste Management Association, 50(5), 775–785.
- Slowik, J.G., Stainken, K., Davidovits, P., Williams, L.R., Jayne, J.T., Kolb, C.E., Worsnop, D.R., Rudich, Y., DeCarlo, P.F., Jimenez, J.L., 2004. Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part

2: Application to combustion-Generated soot aerosols as a function of fuel equivalence ratio, Aerosol Sci Technol. 38, 1206-1222.

- Souza, D.Z., Vasconcellos, P.C., Lee, H., Aurela, M., Saarnio, K., Teinila, K., Hillamo, R. 2014. Composition of PM2.5 and PM10 collected at urban sites in Brazil, Aerosol Air Qual Res. 14, 168-176.
- Sumari, S.M., Darus, F.M., Kantasamy, N., Taib, N.I., Sinyaw, S.U., Othman, I.R., 2009. Compositions of rainwater and aerosols at global atmospheric watch in Danum Valley, Sabah.The Malaysian Journal of Analytical Sciences, 13 (1), 107-119.
- Sutton, M.A., Dragostis, U., Tang, Y.S., Flower, D. 2000. Ammonia emissions from nonagricultural sources in the UK. Atmos Environ.34, 855–869.
- Tang, A., Zhuang, G., Wang, Y., Yuan, H., Sun, Y., 2005. The chemistry of precipitation and its relation to aersol in Beijing. Atmos Environ. 39, 3397-3406.
- Taylor, S.R., 1964, Abundance of chemical elements in the continental crust: a new table. Geochim.Cosmochim.Acta. 28, 1273-1285.
- Taylor, S.R., McLennan, S.M., 1995. The geochemical evolution of the continental crust, Rev Geophys. 33, 241-265.
- TERI 2001. Review of past and on-going work on urban air quality in India. A report submitted to the World Bank, Tata Energy Research Institute. TERI Project Report No. 2001EE41, 49–58 <u>www.teriin.org</u>.
- Tiwari, S., Bisht, D.S., Srivastava, A.K., Pipal, A.S., Taneja, A., Srivastava, M.K., Attri, S.D., 2014. Variability in atmospheric particulates and meteorological effects on their mass concentrations over Delhi, India. Atmos Res. 145-146, 45-56.
- Tiwari, S., Pipal, A.S., Hopke, P.K., Bisht, D.S., Srivastava, A.K., Tiwari, S., Saxena, P.N., Khan, A.H., Pervez, S., 2015. Study of the carbonaceous aerosol and morphological analysis of fine particles along with their mixing state in Delhi, India: a case study, Environ SciPollut Res. DOI 10.1007/s11356-015-4272-6
- Tiwari, S., Srivastava, A.K., Bisht, D.S., Bano, T., Singh, S., Behura, S., Srivastava, M.K., Chate, D.M., Padmanabhamurty, B., 2009.Black carbon and chemical characteristics of PM10 and PM2.5 at an urban site of North India. J. Atmos. Chem. 62 (3), 193–209.

- Tiwari, S., Srivastava, A.K., Bisht, D.S., Bano, T., Singh, S., Behura, S., Srivastava, M.K., Chate, D.M., Padmanabhamurty, B. 2009. Black carbon and chemical characteristics of PM10 and PM2.5 at a urban site of North India, J. Atmos.Chem., 62, 193-209.
- Tripathee, L., Kang, S., Huang, J., Sillanpaa, M., Sharma, C.M., Luthi, Z.L., Guo, J., Paudyal, R., 2013. Ionic composition of wet precipitation over southern slope of central Himalayas, Nepal. Environ. Sci. Pollut. Res. 21 (4), 2677-2687. DOI 10.1007/s11356-013-2197-5
- Tsai, W.T., Altwicker, E.R., Asman, W.A.H., 1990. Numerical simulation of wet scavenging of air pollutants-II.Modeling of rain composition at the ground, Atmos Environ.PartA, 24 (9), 2485-2498.
- Tsapakis, M., Lagoudaki, E., Stephanou, E., Kavouras, G., Koutrakis, O. and co-authors. 2002. The composition and sources of PM2.5 organic aerosol in two urban areas of Chile. Atmos Environ. 36, 3851–3863.
- Vet, R., Artz, R.S., Carou, S., Shaw, M., Ro, C., Aas, W., Baker, A., Bowersox, V.C., Dentener, F., and co authors. 2014. A global assessment of precipitation chemistry and deposition of sulphur, nitrogen, sea-salt, base cations, organic acids, acidity and pH and phosphorus. Atmos Env. 93, 3-100.
- Viana, M., López, J.M., Querol, X., Alastuey, A., Garcıía-Gacio, D., Blanco-Heras, G., López-Mahía, P., Piñeiro-Iglesias, M., Sanz, M.J., Sanz, F., Chi, X., Maenhaut, W., 2008. Tracers and impact of open burning of rice straw residues on PM in Eastern Spain. Atmos. Environ. 42, 1941-1957.
- Voisin, D., Legrand, M., Chaumerliac, N., 2000. Scavenging of acidic gases (HCOOH, CH3COOH,HNO3,HCl and SO2) and ammonia in mixed liquid-solid water clouds at the Puy de Dome Mountain (France). J. Geophys. Res. Atmos. 105(D5), 6817– 6835.doi:10.1029/1999JD900983
- Wall, S. M., John, W., Ondo, J. L. 1988. Measurement of Aerosol Size Distributions for Nitrate and Major Ionic Species, Atmos. Environ. 22(8), 1649–1656.
- Wall, S. M., John, W., Ondo, J. L., 1988. Measurement of Aerosol Size Distributions for Nitrate and Major Ionic Species. Atmos Environ. 22(8),1649–1656.
- Wang, X., Bi, X., Sheng, G., Fu, J., 2006.Chemical composition and sources of PM10 and PM2.5 aerosols in Guangzhou, China. Environ Monit Assess. 119, 425-439.
- Ward, T.J., Lincoln, E., 2006. Concentrations of PM2.5-associated OC, EC, and PCDD/Fs measured during the 2003 wildfire season in Missoula, Montana. Environ. Monit. Assess. 115, 39–50.

- Watson, J.G., Chen, L.-W.A., Chow, J.C., Doraiswamy, P., Lowenthal, D.H. 2008. Source apportionment: findings from the U.S. Supersites Program. J. Air & Waste Manag.Assoc. 58, 265-288.
- WHO. 2000. Air quality guidelines for Europe (2nd ed.).Copenhagen: WHO.
- Wilson, T.R.S., 1975. Salinity and the major elements of sea water. In: Riley, J.P., Skirrow, G. (Eds.), Chemical Oceanography. Academic, Orlando, FL, 365–413.
- World Bank ,2001. A report on urban air pollution. ESMAP, South Asia Urban Air Quality Management Briefing, Note No. 4. <u>http://www.worldbank.org/sarurbanair</u>.
- Xu, J., Bergin, M.H., Yu, X., Liu, G., Zhao, J., Carrico, C.M., Baumann, K., 2002.Measurement of aerosol chemical, physical and radiative properties in the Yangtze delta region of China.Atmos Environ. 36, 161-173.
- Yadav, R., Sahu, L.K., Jaaffrey, S.N., Beig, G., 2014. Temporal variation of particulate matter (PM) and potential sources at an urban site of Udaipur in Western India. Aerosol Air Qual Res.14, 1613-1629.
- Zender,C.S., Bian, H., and Newman,D., 2003. Mineral dust entrainment and deposition (DEAD) model: Description and 1990s dust climatology. J Geophys.Res.107 (D24), 4416.
- Zeng, F., Wang, W., Yang, Zh., Pan, Zh., Yin, L., 2001. Study and analysis of acidifying buffer capacity of aerosols. Environmental Monitoring in China 17 (4), 13–17 (in Chinese).
- Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., Worsnop, D. R., 2007. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes.Geophys. Res. Lett. 34, L13801 DOI: 10.1029/2007GL029979.

- Zhang, R., Khallzov, A.F., Pagels, J., Zhang, D., Xue, H., McMurry, P.H., 2008. Variability in morphology, hygroscopicity and optical properties of soot aerosols during atmospheric processing. PNAS 105 (30), 10291-10296.
- Zhang, R., Wang, G., Guo, S., Zamora, M.L., Ying, Q., Lin, Y., Wang, W., Hu, M., Wang, Y., 2015.Formation of urban fine particulate matter.Chem Rev. 115, 3803-3855, DOI: 10.1021/acs.chemrev.5b00067
- Zielinski, T., Weslawski, M., Kulinski, K., 2014.Impact of Climate Changes on Marine Environments. Springer International publishing, Switzerland, doi:10.1007/978-3-319-14283-8.

6. Achievements and how the deliverables have contributed in the overall programmes of the Ministry-

Laboratory set up for aerosol characterization at a remote location (Tezpur) which will cater the local needs in the future and a large dataset obtained for the region, which is untouched so far, from the facility created. An overall regional scenario of aerosol sources and rainwater chemistry has been understood under the objectives of the project.

Capacity building: the project has been able to train manpower on aerosol monitoring and analysis, and modeling of aerosol for source apportionment studies.

The deliverables of the project will add to the national repository of atmospheric data and knowledge, which the Ministry is putting efforts to develop.

7. Scope for future-

With the present set up of laboratory created under the project source apportionment studies of aerosol of neighboring regions (upper- Brahmaputra and Lower-Brahmaputra plains) and other hilly regions of northeast India though joint / collaborative approach research is an immediate future scope.

8. Publication of results/presentation of papers (to be clearly mentioned that MoES is not responsible for any result interpretations expressed in the report)

- Two papers have been published from the project from the objectives of the project
- Five M.Sc. students have submitted their course credited dissertation working under this project and availing the facilities procured from this project.
- Two papers have been presented in the International and National conferences within India.

9. Capacity Building –

- Laboratory set up for aerosol characterization at a remote location (Tezpur) which will cater the local needs in the future.
- Ph.D. -two candidates working on the broad objectives of the project (expected to submit thesis in Aug 2016 and Aug 2017)
- M.Sc.- 5 M.Sc students have submitted dissertation working under this project
- Two batches of M.Sc. students (30 Nos each) are given exposure to aerosol and rainwater sampling, and chemical analysis – with complete exposure on IC and TOC analyzer

10. Number of Workshops conducted if any, related to the project along with date & name of the workshop- Nil

11.Abstract in 300 words for possible publication on MoES Newsletter/Website.-

The project is an attempt to understand the aerosol characteristics of Tezpur region of mid-Brahmaputra plain with a special focus to apportion the major contributing sources of aerosol of the region. As aerosol has bearing on the precipitation chemistry, rainwater chemistry was also studied. Aerosol as PM10 and rainwater was characterised for a long period to create chemical database of aerosol which is used for the source apportionment modelling. Size distribution and number densities of aerosol were also monitored.

The PM10 concentration of the study area for the study period was found to be 53.7±46 $\mu g/m^3$ which is within the annual national ambient air quality standard (NAAQS) of PM10. Explicit spatial and seasonal variations of aerosol mass concentrations were observed. The carbonaceous fraction contributes maximum to PM10 mass concentration of the region. Two models were applied for source apportionment viz., Principal Component Analysis (PCA) followed by Multiple Linear Regression (MLR) and Chemical Mass Balance (CMB). The PCA-MLR apportioned four major sources of PM10 viz. fuel combustion - both biomass and fossil fuel (56%), street dust (16%), soil/crustal dust (13%) and construction dust (15%). The CMB model estimates give more detailed apportionment of sources - biomass burning (22%), road dust (25%) and vehicular emissions (20%), construction dust (9%) and soil/crustal emissions (10%) as major sources. Model outcome showed that the visibility over mid-Brahmaputra valley is good throughout the year. There were, of course, events of lower visibility during months of Dec, Jan and Feb as per model estimates. The project helped capacity building in the areas of aerosol and rainwater chemistry in the region; 5 MSc dissertations have been successfully completed and two PhD theses are nearing completion. Also, the facility created under the project continues to offer long term support to this region, particularly Tezpur University, in the future.

Key words: Aerosol, characterization, source apportionment, PCA-MLR, CMB, Visibility

Name and signature with date

R.R. Hoque

(Principal Investigator)

KP Sarma

(Co-PI)

UTILISATION CERTIFICATE (for the financial year:2014-15) (Amount in Rs. in Lakhs)

1. Title of the Project/Scheme: Physicochemical Characterization of Aerosol and Source Apportionment in Mid-Brahmaputra plain in Assam: A Modeling Approach.

- 2. Name of the Organization: Tezpur University, Naapam, Assam- 784028
- 3. Principal Investigator: Dr R.R. Hoque, Associate Professor, Department of Environmental Science
- 4. Ministry of Earth Sciences (MoES) letter No. and date of sanction of the Project/Scheme

: Dy. No. 787/AS&FA/2011 dated 07/03/2011

: NIL

: NIL

- Amount brought forward from the previous financial year quoting MoES's letter No. & date of sanction order showing the amount paid
 Rs -30692/-
- 6. Amount received from MoES during the financial year (Please give No. & date of sanction orders showing the amount paid)
- 7. Other receipts/interest earned, if any on the MoES grants : NIL
- 8. Total amount that was available for expenditure incurred during the financial year (S.No. 5,6 and 7) : Rs -30692/-
- 9. Actual expenditure (excluding commitments) incurring during the financial year (Statement of expenditure is enclosed)
- 10. Unspent balance refunded, if any (Please give details of Cheque No. etc.) : NIL

11. Balance amount available at the end of the financial year : Rs -30692/-

12. Amount allowed to be carried forward to the next financial year vide letter No. & date : NA

PTO

Statement of Expenditure referred to in para-9 of the Utilization Certificate

Expenditure Incurred during the period 1st April 2014 to 31st March 2015

Items	1 st year head wise allocation 2011-12	2 nd year head wise allocation 2012-13	3 rd year head wise allocation 2013-14	Unspent balance carried forward from previous year (2013- 14)	Grants received from MoES during the year (2014-15)	Other receipts/ interest earned, if any, on the MoES grant	Total	Expenditure (excluding commitments) incurred during the year	Balance
1	2	3	4	5	6	7	8	9	10
A. NON-RECU	RRING								
Permanent equipment	52,49,000	NIL	NIL	-16587	NIL	NIL	-16587	NIL	-16587
B.RECURRIN	G				2			*	
Salary (manpower)	2,14,800	2,14,800	2,40,600	-62596	NIL	NIL	-62596	NIL	-62596
Consumables	3,10,000	2,10,000	40,000	-7673	NIL	NIL	-7673	NIL	-7673
Travel (within India)	60,000	80,000	50,000	2712	NIL	NIL	2712	NIL	2712
Contingency	70,000	30,000	40,000	14397	NIL	NIL	14397	NIL	14397
Institutional overhead	65,500	53,500	37,100	39055	NIL	NIL	39055	NIL	39055
Total	59,69,300	5,88,300	4,07,700	-30692	NIL	NIL	-30692	NIL	-30692

Fund received= NIL Expenditure=NIL Balance receivable= Rs 30,692/-

Signature of project

Investigator

BRIRADA R.H. Hoques Assoc. Professor Tezpur University PI, Aerosol Project (MOES) (MOES/16/16/10-RDEAS)

23/9/15

Signature of Finance Officer Finance Officer Date zpur University Signature of Head of the Institute Registrar Date zpur University

For SURAJIT CHAKRABORTY & CO. CHARTERED ACCOUNTANTS 01.10.15 CA, SURAJIT CHAKRABORTY (Proprietor) Membership No.- 305054

- 2. Certified that rules under GFR have been followed for procuring the equipments under the project.
- 3. Certified that I have satisfied myself that the condition on which the grants in aid was sanctioned have been duly fulfilled /are being fulfilled and for procuring the equipments under the project, rules under GFR are followed and that I have exercised the following checks to see that money was actually utilized for the purpose for which it was sanctioned.

Kinds of checked exercised:

- 1. Payments have been released under direct supervision of the Finance officer.
- 2. A/Cs is audited by the C &AG, GOI

3. Prices of the equipments and other consumables are approved by the Tender & Purchase Committee.

DParaza RDA oque 15 Assoc. Professor Tezpur University PI, Aerosol Project (MoES) (MoES/16/16/10-RDEAS)

19/15

Signature of Finance Officer

Date^Einance Officer Tezpur University

Signature of Head of Institute Registrar Date gue Conversity

For SURAJIT CHAKRABORTY & CO. CHARTERED ACCOUNTANTS 01.10.20 CA. SURAJIT CHAKRABORTY (Proprietor) Membership No.- 305054

(To be counter signed by MoES officer in charge)

Summary Statement of Expenditure during the period 2011-2015 (Project No:MoES/16/16/10-RDEAS)

Items	Total Allocation 2011-14	Fund received during 2011-12	Fund received during 2012-13	Fund received during 2013-14	Fund received during 2014-15	Total fund	Expenditure during 2011-	Expenditure during 2012-	Expenditure during 2013-	Expenditure during	Total expenditure	Τ
1	2	3	4	5	6	7	12	13	14	2014-15	2011-15	Balance
A NON DECIM	1						8	9	10	11	12	13
A. NUN-RECURRI	NG				and the second second							(7.12)
equipments	5249000	5249000	NII									(1-12)
B. RECURRING				NIL	NIL	5249000	420984	4844603	NII			
Salary (Research	(2000)				-					NIL	5265587	-16587
Consult	670200	214800	NIL	240600	NIL.	455400	04000					
Consumables	560000	310000	85293	40000	NIT	435400	94093	201000	222903	NIL.	517004	(0.50 4
Travel (within India)	190000	60000	50138	50000		435293	272295	115776	54895	NII	517990	-62596
Contingency	140000	70000	NIL		NIL	160138	21048	105416	30962	NIL	442966	-7673
Institutional	1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 -	70000	INIL	40000	NIL	110000	55155	14848	05502	NIL	157426	2712
overhead	156100	65500	NIL	37100				14048	25600	NIL	95603	14397
Tetal	6965300	5969300	135.121	57100	NIL	102600	59640	3905	0	N//		
Total pr	oject cost=	Rs 60 65	200/	407700	NIL	6512431	923215	5285548	124200	NIL	63545	39055
Total Fu	nd receive	d= D= (5	2 121					0200040	334360	NIL	6543123	-30692

Total Fund received= Rs 65,12,431/-Balance receivable= Rs 30692/-

Signature of PI

Dr. PRaza & Hoge 2015 Assoc. Professer **Tezpur University** PI, Aerosol Project (MoES) (MoES/16/16/10-RDEAS)

23/9/15 Signature of Finance officer

Finance Officer

Date Tezpur University

For SURAJIT CHAKRABORTY & CO. CHARTERED ACCOUNTANTS Jo

Signature of Head of Institute Registrar Date Tezpur University

81-10-2015 CA. SURALT CHAKRABORTY (Proprietor) Membershin No - 305054