PM$_{10}$ CHARACTERISTICS OF A RECEPTOR SITE: A STUDY AT A RURAL INSTITUTIONAL AREA OF ASSAM

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by

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Dedicated to my beloved Parents and family members

Abstract

Particulate matter (PM) is the tiny particles of solid or liquid droplets suspended in the atmosphere. It can be generated by natural or anthropogenic sources in to the atmosphere. Primary PM is directly emitted from the source itself, while transformation of primary particles results in the formation of secondary particles. PM results in net cooling of the atmosphere. Aerosol particles influence the chemistry and kinetics of atmospheric processes and can act as reservoir for many pollutants [1].

Along with vehicular and industrial emission, biomass burning is also an important source of atmospheric particles. Global emission flux estimates by savanna and tropical forest biomass burning showed that biomass burning could be an important source of heavy metals and black carbon to the atmosphere [2]. Airborne particulate trace metals are considered to represent a health hazard since they can be absorbed into human lung tissues during breathing [3,4].

Studies on PM in India are sporadic and mostly concentrated in large cities [5-7]. Indian villages where most population lives are receptors of emission from the city and industrial centres. Also studies on PM_{10} are few in Northeast India. With this background we had decided to study the PM_{10} at a rural receptor site. The objectives of the present study were: 1. To investigate PM_{10} concentration at a rural site and its temporal characteristics. 2. Characterization of PM_{10} to see the major components and source signatures and derive seasonal trends of the constituents. 3. To explore impact of extraordinary emission days on PM_{10} load and characteristics. 4. To explore the dependencies of PM_{10} characteristics on rural household biomass burning. 5. To assess the major contributing sources of PM_{10} at a receptor site of the region.

The present study was conducted at Tezpur University, a rural institutional area of Assam, India. PM_{10} samples were collected using High Volume Sampler (Envirotech APM 460 BL). Whatman Glass Fibre Filter paper and Quartz Microfiber Filters were used for PM_{10} collection. Also, collection of particles emitted by household biomass burning in traditional rural kitchens and soil sampling was done to meet our objectives. We used Biomass Fuel Smoke Particles (BFSPs) to denote the particles of biomass burning. BFSPs were collected holding Whatman Glass Fibre Filter paper just above the cooking stove in the roof. It was removed after the ascertained period and samples

were collected in Aluminum foil and stored in refrigerator for further analysis. Soil samples were collected from top soil (1-3 cm) and air dried. After coning and quartering samples were stored in self shielding plastic bags for elemental analysis.

For elemental analysis, samples were acid digested with standard methods and analyzed in ICP-OES (Perkin Elmer, OPTIMA-2100 DV). HNO_3 was used for PM_{10} acid digestion [8,19]. Soil samples were digested using aqua regia [9] and HNO_3 and $HClO_4$ were used for BFSPs. Elements of some samples were also analyzed using EDX (Oxford instruments, Model 7582). For water soluble ions samples were extracted by ultrasonic agitation [10] and analyzed in Metrohm 882 Professional IC. Analytikjena TOC analyzer was used for carbon analysis. Carbon of solid samples was determined using HT1300 solid module while multi N/C 2100 TOC Analyzer was used for water soluble carbon. TC samples were directly heated in the combustion chamber while for EC analysis method given by Lin and Tai [11] was used. PM_{10} and BFSP samples were extracted in Dichloromethane (DCM) [12] and cleaned up using USEPA 3630C method following PAHs analysis in HPLC.

PM_{10} was monitored for a period of two years. The first period of sampling was carried out during 2008 – 2009 and the second during 2010 – 2011. The average PM_{10} was $147.10\pm153\mu gm^{-3}$ during 1st year which was 2.5 times higher than the annual National Ambient Air Quality Standards (NAAQS) of 60 μgm^{-3} [13]. Average PM_{10} was 47.96 ± 31 μgm^{-3} during 2nd year.

The elemental concentration of 1st year PM_{10} was higher than that of 2nd year. Most of the elements were maximum during the winter. To see the seasonal variation one way ANOVA was done which showed significant seasonal variation for Ca, Co, Cd and Pb at 95% of significance level during 1st year. Significant seasonal variation of Mn and Cu was found during 2nd year.

Among the analyzed ions SO_4^{2-} was maximum and F^- was minimum. Most of the ions were maximum during the winter and minimum during monsoon season. The annual trend of ions was $SO_4^{2-}>Cl^->Na^+>NO_3^->Ca^{2+}>K^+>NH_4^+>Mg^{2+}>F^-$. The annual mean of Anion Equivalents/Cation Equivalents was 1.16±0.86, suggesting acidic nature of aerosols.

Annual average of TC was 21.06 ± 10 μgm^{-3} contributing 44% of PM_{10}. EC was 3.68 ± 4 μgm^{-3}, whereas OC was 17.42 ± 8 μgm^{-3}. WSOC/OC was very high (0.63±0.37) in this study suggesting Cloud Condensation Nuclei (CCN) activity of aerosol and presence of aged aerosols [14,15]. We had also calculated Secondary Organic Carbon (SOC) as per Castro et al. [16] and found very high percentage of SOC in OC.

Enrichment Factors (EF) was calculated taking Fe as reference material. EF showed similar results for both the year with maximum enrichment for Cd. Correlation matrix and Principal Component Analysis-Multiple Linear Regression (PCA-MLR) was carried out to apportion the sources. It revealed biomass burning, soil, coal combustion and vehicular emission as the possible sources of PM_{10}.

For extraordinary day characterization we had chosen Diwali and *Meji* burning, two festivals that are associated with high emissions of PM. PM_{10} characterization during Diwali fireworks revealed short time incremental effect on atmospheric particles. Elements and ions of the study were slightly higher on Diwali day than mean of whole monitoring campaign. Present study elemental and ionic concentration was lower than other fireworks studies. Correlation matrix, PCA and Diwali Induced Enrichment (DIE) showed marginal impact of Diwali fireworks in Brahmaputra Valley of India. Due to its marginal impact on air quality further study was not carried out.

Meji is a structure build of bamboo, wood, leaves, straw, stubble of paddy held tier above tier giving a temple shaped structure. It is lit in every Assamese village of Brahmaputra Valley of Northeast India during mid-January as a part of the Bhogali bihu festival. *Meji* study during 2009 revealed high PM_{10} loading during the *meji* day and also high PM_{10} during later period due to prevailing thermal inversion and lower mixing height. PM_{10} was highly carbonaceous and enriched with Br and other metallic species. Probable sources of Br were biomass burning and agricultural emission by Brassicaceae family [17,18].

The interesting results found during 2009 *meji* burning inspired for detail characterization of PM_{10} during 2012 and 2013. PM_{10} samples were analyzed for elements, ions, carbon and PAHs. High WSOC emphasize on CCN activity of organic aerosols along with presence of smoldering phase during *meji* burning period. Linear relationships between different chemical species along with molecular diagnostic ratios of PAHs indicate influence of biomass burning on PM_{10} load.

Characterization of Biomass Fuel Smoke Particles (BFSPs) revealed higher concentration of elements, anions, carbon and PAHs in cow dung BFSP and least in sugar cane bagasse BFSP. PAHs were more during monsoon season than winter season probably due to incomplete combustion of biomass fuel. 4-ring PAHs were dominant in all BFSPs. Ca, K, Fe and Mg were the major elements and SO_4^{2-}, Cl^- and PO_4^{2-} were the dominant anions in all BFSPs.

Soil samples were collected from undisturbed area to see if there is any atmospheric deposition signature of PM on soil. Correlation between chemical species of PM_{10} and BFSPs revealed dependency of PM_{10} on biomass burning of this region.

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Declaration by the candidate

I hereby declare that the thesis entitled "PM_{10} characteristics of a receptor site: a study at a rural institutional area of Assam" is the record of original research works done by me under the supervision of Dr. R. R. Hoque, Department of Environmental Science, Tezpur University.

The results and related interpretations included in this thesis are based on my reading and understanding of the original works. The resources (books, research articles, websites etc.) used when writing the thesis are acknowledged at the respective place in the text.

I would also like to mention that no degree or diploma has been conferred on me by other university or institutions for the present thesis, which I am submitting to Tezpur University.

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Certificate of the Supervisor

This is to certify that the thesis entitled "PM_{10} characteristics of a receptor site: a study at a rural institutional area of Assam" submitted to the School of Sciences, Tezpur University in partial fulfillment for the award of the degree of Doctor of Philosophy in Environmental Science is a record of research work carried out by Ms Pratibha Deka under my supervision and guidance.

All help received by her from various sources have been duly acknowledged.

No part of this thesis has been submitted elsewhere for award of any other degree.

Place: Tezpur

Date: 10-3-2015

Dr R R Hoque

22/4/15

External Examiner

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Pratibha Deka

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ABBREVIATIONS

Abbreviations	**Full form**
AAQS	Ambient Air Quality Standards
ABCs	Atmospheric Brown Clouds
ACE	Acenaphthene
ACY	Acenaphthylene
AD	Aerodynamic Diameter
AE	Anion Equivalents
ANOVA	Analysis of Variance
ANT	Anthracene
AOD	Aerosol Optical Depth
ARL	Air Resource Laboratory
B[a]Peq	Benz[a]pyrene-equivalents
BaA	Benz[a]anthracene
BaP	Benz[a]pyrene
BB	Biomass burning
BbF	Benz[b]fluoranthene
BC	Black Carbon
BFSPs	Biomass Fuel Smoke Particles
BkF	Benz[k]fluoranthene
BoB	Bay of Bengal
BPER	Benz[ghi]perylene
CCN	Cloud Condensation Nuclei
CD	Cowdung Fuel Stick
CDMBF	Cowdung-Mixed Biomass Fuel
CE	Cation Equivalents
CH_3Br	Methyl Bromide
CHR	Chrysene
CMB	Chemical Mass Balance
COPD	Chronic Obstructive Pulmonary Disease
CPCB	Central Pollution Control Board
DBA	Dibenz[a,h] anthracene
DE	Diesel Engine

DIE	Diwali Induced Enrichments
EC	Elemental Carbon
EDX	Energy Dispersive X-ray Spectrometer
EF	Enrichment Factors
EPA	Environment Protection Agency
EU	European Union
FLA	Fluoranthene
FLU	Fluorene
gcm^{-3}	Gram per centimeter cube
$gmkg^{-1}$	Gram per kilogram
GoI	Government of India
HPLC	High Performance Liquid Chromatography
HYSPLIT	Hybrid Single Particle Lagrangian Integrated Trajectory
IARC	International Agency for Research on Cancer
IC	Ion Chromatograph
ICP-OES	Inductive Couple Plasma-Optical Emission Spectroscopy
IGP	Indo Gangetic Plain
IND	Indeno[1,2,3-cd]pyrene
kgh^{-1}	Kilogram per hour
kHz	Kilo hertz
MBF	Mixed Biomass Fuel
MBIE	*Meji* Buring Induced Enrichment
μgm^{-3}	Micro gram per meter cube
MDL	Method Detection Limit
$mgkg^{-1}$	Milligram per kg
mgL^{-1}	Milligram per litre
mgg^{-1}	Milligram per gram
MLR	Multiple Linear Regression
ms^{-1}	Meter per second
NAAQS	National Ambient Air Quality Standards
NAP	Naphthalene
NDIR	Non Dispersive Infrared
NE	Northeast
ngm^{-3}	Nano gram per meter cube

NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
OC	Organic Carbon
OECD	Organization for Economic Co-operation and Development
OH	Hydroxyl radicals
PAHs	Polycyclic Aromatic Hydrocarbons
PC	Principal Component
PCA-MLR	Principal Component Analysis-Multiple Linear Regression
PHE	Phenanthrene
PMF	Positive Matrix Factorization
PYR	Pyrene
RCA	Regional Co-operation Agreement
RSPM	Respirable Suspended Particulate Matter
SATW	Super Atmosphere Supporting Thin Window
SD	Standard deviation
SEM	Scanning Electron Microscopy
SGC	Sugarcane bagasse
SOA	Secondary Organic Aerosols
SOC	Secondary Organic Carbon
SPM	Suspended Particulate Matter
SPSS	Statistical Package for Social Science
SRM	Standard Reference Material
TC	Total Carbon
TEF	Toxic Equivalance Factor
TEL-A	Tetraethyl-lead A
TOC	Total Organic Carbon
TSP	Total Suspended Particulates
TSPM	Total Suspended Particulate Matter
UFP	Ultrafine Particles
UNEP	United Nations Environment Program
USEPA	United States Environment Protection Agency
UV	Ultra Violet
VE	Vehicular Emission
VORGs	Volatile Organic Reactive Gases

WHO	World Health Organization
WSIC	Water Soluble Inorganic Carbon
WSOC	Water soluble organic carbon
WSTC	Water Soluble Total Carbon

CHAPTER 1
INTRODUCTION

1.1. Particulate Matter (PM)

Particulate pollution in the atmosphere has drawn remarkable attention today for its effects on human health, ecosystems, atmospheric chemistry and the climate system. Particulate effects can also lead to a weaker hydrological cycle, which connects directly with availability and quality of fresh water [1]. Recently, International Agency for Research on Cancer (IARC) had declared outdoor air pollution as carcinogenic to humans [2]. They had also evaluated separately particulate matter, a major component of outdoor air pollution and were also classified as carcinogenic to humans. Aerosol particles influence the chemistry and kinetics of atmospheric processes and can act as reservoir for many pollutants [3].

Concentration, composition, and size distribution of atmospheric particles depend on the source strength, prevailing meteorology condition and their sink mechanisms. This results in their explicit temporal and spatial variability. Meteorological condition affects the particle release and dispersion, and as a result human exposure [4]. Major natural particulate sources include volcanic emissions, sea spray, and mineral dust emissions, while anthropogenic sources include emissions from industry and combustion processes [5].

1.1.1. Definition

Particulate matter (PM) is defined as the small solid or liquid droplets suspended in the atmosphere. Airborne PM is a mixture of many sub-classes of pollutants. Composition, formation mechanism, sources and effects on the environment vary for fine and coarse mode PM. PM is some time interchangeably used with aerosols.

PM can be again classified into Total Suspended Particulate Matter (TSPM), PM_{10}, $PM_{2.5}$, ultrafine particles, fine particles and coarse particles. TSPM denotes all size ranges of particles, PM_{10} are those having Aerodynamic Diameter (AD) less than or equal to 10 μm, $PM_{2.5}$ are those having smaller or equal to 2.5 μm AD. Ultrafine particles (UFP) have an AD of <0.1 μm, fine particles generally have an AD <1 μm and coarse particles have an

AD of 1-10 µm. Smaller size of particles can easily go into the lungs causing a serious risk to people of all age-groups. The aerodynamic diameter depends on particle density and is defined as the diameter of a spherical particle with equal settling velocity but a material density of 1 gcm^{-3}. Particles having the same physical size and shape but different densities will exhibit different aerodynamic diameter.

According to their origin PM can be classified into primary and secondary. Primary particles are generated directly by the sources, while transformation of primary particles leads to formation of secondary particles. Fine-mode PM is derived from combustion material that has volatilized and condensed back to form primary PM or from precursor gases reacting in the atmosphere to form secondary PM.

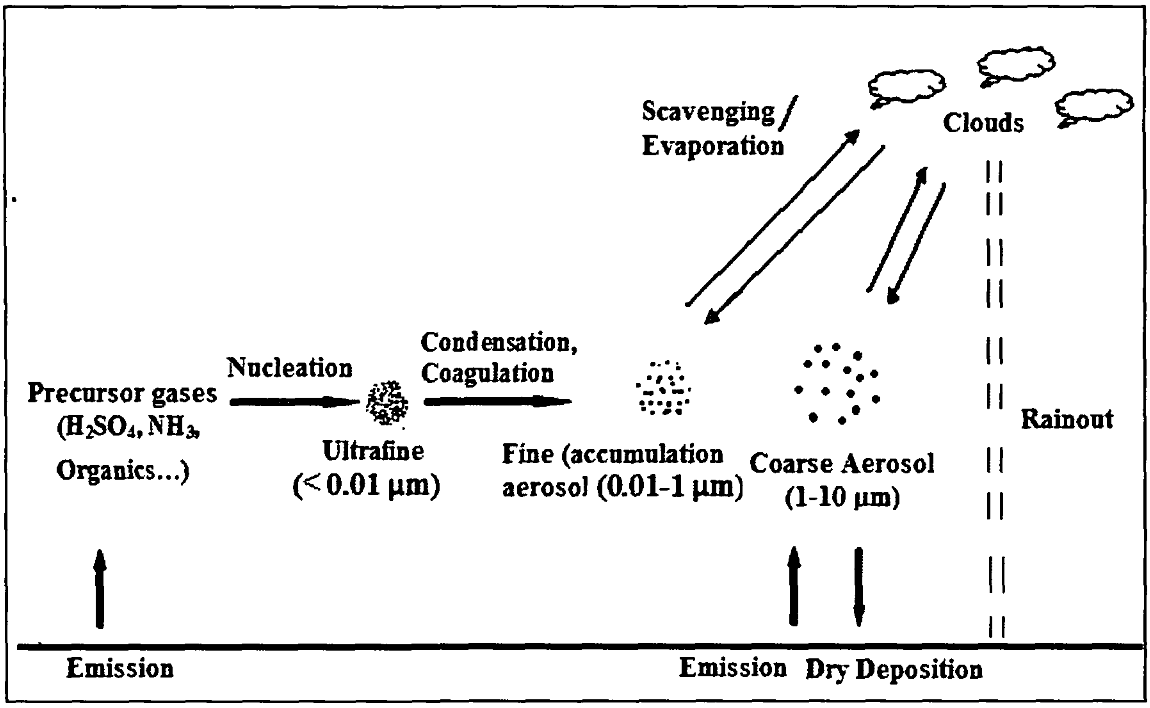

Fig. 1.1. Production, growth and removal of atmospheric aerosols (Source: Jacob [6])

By another classification, PM can be divided into nucleation, aitken, accumulation and coagulation mode particles [6]. Nucleation mode particles (<25 nm) results from gas-to-particle conversion of different chemical compounds such as sulphuric acid and ammonia. Aitken mode (25-100 nm) particles result from the condensation growth of nucleation mode particles and also directly come from traffic exhaust. Accumulation mode particles (100-2000 nm) originate from industrial combustion and re-suspension of roadbeds. Natural sources may also release a fraction of accumulation mode particles. In presence of sufficient vapor, aitken mode particle may grow into accumulation mode. Particles having diameter of 1-10 μm are mainly mechanically generated and come from dust re-suspension, industrial processes and sea spray [7].

1.1.2. Environmental Fate of PM

Atmospheric particles get deposited by dry or wet deposition processes after a certain period of time. Primary and secondary fine particles have long lifetimes in the atmosphere that is to say, they stay afloat in the atmosphere for quite sometime (days to weeks) and travel long distances (hundreds to thousands of kilometers). They tend to be uniformly distributed over urban areas and larger regions. In contrast to fine particles, coarse particles normally have shorter lifetimes (ranging from minutes to hours) and travel only short distances. Therefore, coarse particles tend to be unevenly distributed across a place and tend to have more localized effects than fine particles. However, dust storms occasionally cause long range transport of the smaller coarse-mode particles.

Coarse particles are efficiently removed by dry deposition. Dry deposition occurs by sedimentation, in-cloud diffusion, wind-driven impaction or by absorption by soil, water and biota. Small size particles up to 1μm size range are too small to sediment at a significant rate. These particles act as Cloud Condensation Nuclei (CCN) and are subsequently removed by wet deposition. Particles having 60 to 90 nm size are of particular importance for cloud droplets nucleation [8]. Wet deposition is an effective mechanism for the removal of aerosols, especially in the size range of 0.1–10 μm [9].

1.2. Sources of atmospheric PM

Sources of atmospheric particulates may be natural or anthropogenic depending upon their origin. Main natural sources include sea salt, soil, re-suspended dust, volcanoes, wild fires, lighting etc. Natural sources mainly results in formation of coarse particulates while fine particulates are generated by anthropogenic sources. Anthropogenic sources are more concentrated in urban areas which mainly results in fine particle emission. These sources include traffic, industrial activities, building and emission from household works.

Table 1.1. Main organic aerosol constituents and sources (Source: Calvo et al. [10])

	Primary					Secondary		
	Fossil fuel combustion (e.g. vehicles)	Other Anthropogenic processes (e.g. manufacturing, cooking)	Biogenic (e.g. vascular waxes) and bioparticles (e.g. spores)	Biomass burning	Soil	Gas-particle partition (adsorption and absorption)	Reactive condensation (e.g. acid catalysed reactions)	In-cloud processing
Alkanes, alkenes, alkanals, alkanoic acids, diacids	✓	✓	✓	✓		✓		?
Aromatics, PAHs	✓	✓		✓		✓	?	?
Hopanes, steranes, unresolved complex mixture (UCM)	✓							
Photochemical products (e.g. carbonyls, methyl tetrols, carboxylic acids, organosulphates)						✓	✓	✓
Sugars, polyols, polysaccharides			✓	✓	✓			
Levoglucosan				✓				
HULIS					?		?	?

Table 1.2. Inorganic marker species associated with various emission sources or processes (Source: Calvo et al. [10])

Secondary aerosols		SO_4^{2-}, NO_3^- and NH_4^+
Sea salt		Cl, Na, Na^+, Cl^-, Br, I, Mg and Mg^{2+}
Crustal or geological tracers		Elements associatedwith feldspars, quartz,micas and their weathering products (mostly clay minerals), i.e. Si, Al, K, Na, Ca, Fe and associated trace elements such as Ba, Sr, Rb, and Li. In addition, there will be accessory silicates (notably zircon, titanite and epidote), and representatives from the minority non-silicate mineral groups, namely carbonates, sulphates, oxides, hydroxides and phosphates
Technogenic tracers	Steel industry	Cr, Ni and Mo
	Copper metallurgy	Cu and As
	Ceramic industries	Ce, Zr and Pb
	Heavy industry (refinery, coal mine, power stations)	Ti, V, Cr, Co, Ni, Zn, As and Sb
	Petrochemical industry	Ni and V
	Oil burning	V, Ni, Mn, Fe, Cr, As, S and SO_4^{2-}
	Coal burning	Al, Sc, Se, Co, As, Ti, Th, S, Pb and Sb
	Iron and steel industries	Mn, Cr, Fe, Zn, W and Rb
	Non-ferrous metal industries	Zn, Cu, As, Sb, Pb and Al
	Cement industry	Ca
	Refuse incineration	K, Zn, Pb and Sb
	Biomass burning	K and Br
	Firework combustion	K, Pb, Ba, Sb and Sr
	Vehicle tailpipe	Platinum group elements, Ce, Mo and Zn
	Automobile gasoline	Ce, La, Pt, SO_4^{2-} and NO_3^-
	Automobile diesel	S, SO_4^{2-} and NO_3^-
	Mechanical abrasion of tyres	Zn
	Mechanical abrasion of brakes	Ba, Cu and Sb

Sources of different organic aerosol and elements with their possible emission sources are given in Table 1.1 and 1.2.

1.3. Effects of PM on the environment

Particulate matter has many fold adverse impact on the environment. Small size particles are more harmful to the environment. Regional air pollution problems like reduced visibility and acid deposition are apparent in the South Asian region as a result of increasing population and growing urbanization [11]. With the increase in population industrial activities, household activities, traffic emission etc. also increase rapidly.

1.3.1. Effects of PM on vegetation and ecosystems

Effects of particulate matter on vegetation may be associated with the reduction in light required for photosynthesis and an increase in leaf temperature due to changed surface optical properties [12]. Atmospheric particles are deposited onto vegetation surface by three major routes- (1) wet deposition, (2) dry deposition and (3) occult deposition, obscured from measurements that determine wet and dry deposition, by fog, cloud-water, and mist interception [12]. Dust interception and retention is influenced by leaf orientation, age, roughness and wettability of the leaf surface [13,14]. The mechanisms of action are through smothering of the leaf; physical blocking of the stomata; bio-chemical interactions; and/or indirect effects through the soil. It is to be noted that absorption of particles by vegetation helps in keeping the pollutants level in control. Pollution tolerant tree species can be used to develop green belt [15].

1.3.2. Effects of PM on materials

The deposition of particulate matter on materials can reduce their aesthetic appeal as well as increase their physical and chemical degradation. Primarily particulate matter affects the rates of corrosion and erosion, and soiling and discoloration of materials. Deposition of acidic particles accelerate the chemical degradation of susceptible material surfaces. Acid forming aerosols promote the corrosion of metals.

1.3.3. Effects of PM on visibility

Visibility can be defined as the distance at which an object can be clearly discerned. Air particulates reduce the visibility by scattering the light. Fine particles reduce visibility to a greater extent in comparison to coarse particles. In tropical and subtropical countries carbonaceous aerosols are the main visibility impairing particles in comparison to sulphate in temperate countries [16,17].

1.3.4. Effects of PM on climate

Atmospheric particles affect the climate both by direct and indirect effects. They affect the climate directly by scattering and absorbing solar and infrared radiation in the atmosphere. Particles affect the climate indirectly by changing cloud behavior and precipitation pattern. Absorption of solar radiation results in positive radiative forcing; while scattering results in negative radiative forcing. This can be evident via the total direct aerosol effect which was quantified with a best estimate of –0.5 [±0.4] Wm^{-2} in the AR4 IPCC report [18].

1.3.5. Effects of PM on human health

Levels of atmospheric particulates are positively correlated with human health. Epidemiological studies and toxicological studies have found associations between PM mass and adverse health outcomes [19,20]. It has been reported that, among the ambient air pollutants, particulate matter (PM) has shown the most consistent associations with mortality [21-23].

The aerodynamic diameter and their trace elements content are the two main characteristics of particulate matter that need to be considered to examine the health impact [24]. Particles of $\leq 10\ \mu m$ in diameter (PM_{10}) can be inhaled into the lungs where chemicals ranging from metal compounds to acid droplets lead to severe health risk [25]. After deposited in the respiratory tract the fate of the particles depends upon the body's clearance mechanism and the ability to resist it [26].

Concentrations of $PM_{2.5}$ and PM_{10} exhibit direct relation with traffic-related pollutants (both diesel and gasoline vehicles) and their health effect through respiratory and cardiac diseases [27]. PM_{10} is able to penetrate in the bronchi, $PM_{2.5}$ in the lung and nano particles are able to pass through the lungs and enter the circulatory system [28,29]. In a recent study by Park et al. [30] found a significant positive association between PM_{10} exposure and non-accidental mortality among Asian populations. They have reported percentage change or risk per 10 μgm^{-3} increase in PM_{10} as 0.33%. Again, Lippmann [31] had reported that the total daily mortality increases by approximately 1% for every 10 μgm^{-3} increase in PM_{10} concentration..

Meanwhile, metals too may have adverse effects on human health due to their biochemical activity and production of free radicals [32,33]. Metals in PM may release free radicals in lung via the Fenton reaction, and are hypothesized to cause cellular inflammation [34]. Pro-oxidative organic hydrocarbons (e.g. Polycyclic Aromatic Hydrocarbons (PAHs) and quinines) and transition metals, such as copper, vanadium, chromium, nickel, cobalt, and iron play a significant role in producing reactive oxygen species [35].

Other chemical constituents like sulfate [36,37], elemental carbon [38], and PAHs [39] are also related with health effects. An IARC evaluation showed correlation between an increasing risk of lung cancer with increasing levels of exposure to particulate matter and air pollution [40].

1.4. Chemical species of PM

1.4.1. Elements

Natural sources like dust, sea salt spray, volcanic emission etc. emit particulates in the coarse fraction while fine particulates are emitted by anthropogenic sources like vehicular or industrial emission. Anthropogenic metal emissions are up to several orders of magnitude higher than natural contents [41]. Pereira et al. [42] reported that on a global scale, re-suspended surface dusts make a large contribution to the total natural emission of trace metals to the atmosphere, accounting for >50% of Cr, Mn and V and >20% of Cu, Mo, Ni, Pb, Sb and Zn while volcanic activity probably generates up to 20% of atmospheric Cd, Hg, Cr, As, Cu, Ni, Pb and Sb. Sea salt aerosols may contribute with around 10% of total trace metal emission, while elements contained in biological aerosols are important in forested regions [42]. The source and pollution characteristic category of metallic elements are given in Table 1.3 and 1.4.

1.4.2. Ions

Fluoride, Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Mg^{2+} and Ca^{2+} associated with PM_{10} were considered in this study. Brick kilns are a potent source of F^- [45,46]. Chloride, Na^+, K^+, Mg^{2+} represent a contribution from maritime sources [47]. For Ca^{2+}, Mg^{2+}, Na^+ soil act as significant source. For K^+, the sources may be soil, vegetation burning [48], biomass burning [49,50], and emission from vegetation [51].

Table 1.3. The source and pollution characteristic category of the metallic elements around the World (Source: Wu et al. [43] and references therein)

Sources	The pollution characteristic category of the metallic elements
Sea salt	Na, Ca, Mg and K
The industry processes	Mn, Zn and K
Soils and dusts	Ca, Mg, Al, Si, Fe and Mn
The vehicle exhaust	Cr, Pb, Cu, Zn, Cd, Sb, Br, Fe and Ba
Construction site	Al, Fe, Si, Mn and Ti
Industrial oil combustion	Ni and V
Incinerator	K, Zn and Pb
Metals industry	Fe, Mn and Pb
The coal combustion	Cr

Table 1.4. Elements with their emission sources (Source: Kulshrestha et al. [44] and references therein)

Emission sources	Characteristics elements
Fossil fuel combustion	Al, Fe, Ca, Mg, K, Na, As, Pb, Cd, Sc, Hg
Wood combustion	Pb and Zn
Vehicular traffic	Cd, Cr, Cu, Ni, Pb & Zn
Electroplating	Cr
Metal alloy industries	Cd, Cr, Al, Fe, Ni, Zn, Pb, Cu etc.

Also, researchers had attributed soil as the natural sources of Ca^{2+} along with SO_4^{2-}, Cl^- and K^+ [52,53]. Ions with both crustal and pollution origin are Cl^-, K^+ and SO_4^{2-} [54]. Five major ions including K^+, NH_4^+, Cl^-, NO_3^- and SO_4^{2-} are emitted by all types of biomass burning [55]. Other researchers had also reported emission of these ions from biomass burning and smoke emitted from biomass burning [49,56-58].

Sulphate, nitrate and ammonium constitute the secondary ions associated with PM_{10}. These are mainly found as fine PM. Possible sources for sulphate include fuel combustion in vehicles and industries [59]. Atmospheric sulphate particles may also be formed primarily from sea salt. Oxidation of SO_2 is the major mechanism of sulphate formation in the atmosphere. Reactions of SO_2 to sulphate include both gaseous phase oxidation by hydroxyl radicals [60] and aqueous phase oxidation by O_2 (catalyzed by

Fe^{3+} and Mn^{2+}), O_3 and H_2O_2 [61,62]. Sulphate particles scatter sunlight and act as cloud condensation nuclei (CCN). It results in visibility degradation and acid deposition of a region.

Nitrate originates mainly from fossil fuel combustion in motor vehicles [54]. Atmospheric ammonia, the reduced form of nitrogen is emitted by plants, animals, soil microorganisms and by various industrial and agricultural processes, including direct volatilization of solid NH_4NO_3 salts and fertilizers [63,64].

Seinfeld and Pandis [65] have explained the vital role that NH_3 plays in neutralizing acidic substances such as H_2SO_4 and HNO_3, mostly as a sole neutralizer of acidic species, which leads to formation of secondary particles. It is also reported that available NH_3 will be first taken up by H_2SO_4 and then the remaining NH_3 will be available to react with HNO_3 to produce ammonium nitrate.

1.4.3. Carbonaceous PM

Carbonaceous aerosols in the atmosphere arise from the burning of fossil fuel, biomass, and other forms of hydrocarbon [66-68]. Carbonaceous PM consist of elemental carbon (EC) and organic carbon (OC). Sometimes black carbon (BC) or soot is also interchangeably used for EC. EC absorbs sunlight and OC scatters it. The extent of light absorption by carbonaceous aerosol depends on the concentration of BC particles and their arrangement in relation to the other non-absorbing constituents [69]. In global scale, the major source of primary carbonaceous aerosols is biomass burning and its widespread use as fuel for cooking and heating homes [70-72]. Parashar et al. [73] had estimated >90% OC and 80% BC emission from bio-fuels and forest biomass in India. For black carbon (BC), Venkataraman et al. [74] had estimated biofuel burning as the largest single source in India.

1.4.4. VOCs, POPs and organic acids:

Volatile organic compounds (VOCs) in the Earth's atmosphere play an important role in various photochemical processes. Among the Asian countries, India is the second largest contributor to the emission of non-methane VOCs [75,76]. Pandey and Sahu [77] recognized both deforestation and agriculture waste burning as the major contributors of VOCs in India.

Under the Stockholm Convention on Persistent Organic Pollutants (POPs), 22 groups of chemicals are regulated as POPs. Due to their persistent nature, they can be transported over long distances and can be reached to remote regions in all parts of the world. Polycyclic aromatic hydrocarbons (PAHs), a well known POP are comprised of two or more fused benzene rings. Some PAHs are well known as carcinogens, mutagens and teratogens [78]. Biomass burning is the main source of PAHs in India and China [79]. Among the United States Environmental Protection Agency (US EPA) priority 16 PAHs 7 PAHs have been regarded as probable human carcinogens [80]. Recently International Agency for Research on Cancer (IARC) has included benzo[a]pyrene (BaP) in Group 1 (carcinogenic to humans) [81].

Organic acids, another important constituents of PM, includes dicarboxylic acids, aromatic diacids and fatty acids. Organic acids can act as cloud condensation nuclei and affect the radiative balance on the earth, due to their highly hygroscopic properties [82].

1.5. Effects of meteorology on PM

Meteorological factors like temperature, relative humidity (RH), wind velocity and rainfall can influence the atmospheric levels of aerosol and its components [83]. Particles are scavenged by rainfall during rainy season which lowers particulate loading in the atmosphere. During the summer, high temperature and relative humidity results in formation of secondary aerosols. Dry condition along with low temperature, lowering atmospheric mixing heights results in build up of pollutants in the atmosphere during the winter months.

During the high humidity episodes, hygroscopic growth and condensation may result in raised levels of the coarse particles [84] and may also reduce the particles release from the surface [85]. High temperature and wind velocity together with low RH increase the particle release from the surface too [85].

1.6. Scope and objectives of the study

Studies of atmospheric PM is going on throughout the world. Studies on particulates in India, however, are sporadic and mostly concentrated in major cities. Indian villages where ~70% of the population live, are receptors of emission from the city and industrial centres yet systematic study on air quality in the villages has not begun on a major scale. With this background the present study was designed to see the PM_{10} loading at Tezpur, a rural receptor site of North east India with the following objectives-

1. To investigate PM_{10} concentration at a rural site and its temporal characteristics.

2. Chemical characterization of PM_{10} to see the major components and source signatures and derive seasonal trends of the constituents.
3. To explore impact of extraordinary emission days on PM_{10} load and characteristics.
4. To explore the dependencies of PM_{10} characteristics on rural household biomass burning.
5. To assess the major contributing sources of PM_{10} at a receptor site of the region.

This study will be mainly focused on characterization of PM_{10}. Monitoring and chemical speciation of PM_{10} had been done for two year long cycles and explored for seasonal trends and apportionment of its sources at a rural receptor site of Northeast India. We had also studied PM_{10} characterization during Diwali fireworks and *meji* burning, two festivals that are associated with extraordinary emission of PM_{10}. It is worth mentioning that biomass burning is very common for household activities of this region which could be an important source of atmospheric particulates. Therefore, particles emitted from biomass fuel burning in rural kitchens were sampled and analyzed to see the dependency of PM_{10} characteristics on rural household biomass burning of this region. Also, we had collected undisturbed soil of nearby areas of PM_{10} sampling site and studied the relationship between the elements of soil with PM_{10} and particulates emitted from biomass burning.

Back trajectory analysis and meteorological parameters were studied to better understand the PM_{10} concentration trends. To apportion the sources of PM, characteristic ratios, correlation matrix, factor analysis etc. were done. We had also compared the present study with studies from other parts of India and abroad.

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CHAPTER 2
REVIEW OF LITERATURE

2.1. Particulate matter

Focused on atmospheric particulate research is gaining importance for its tremendous implications on human health, atmospheric chemistry, climate system and hydrology.

As per a joint report of U.N. Environment Program and WHO, PM is estimated to kill more than 500,000 people each year [1]. According to recent WHO update ambient (outdoor air pollution) was estimated to cause 3.7 million premature deaths worldwide in 2012 of which 88% occurred in low- and middle-income countries, and the greatest number in the WHO Western Pacific and South-East Asia regions [2]. The Organization for Economic Co-operation and Development (OECD) in its Environmental Outlook 2050 report, warns that urban air pollution could become the biggest environmental cause of premature death by 2050 with the number of premature deaths doubling if no actions to improve air quality are implemented [3]. The majority of the additional deaths are expected to be in China and India, making urban air quality very much an Asian problem. In a recent study, Park et al. [4] found a significant positive association between PM_{10} exposure and non-accidental mortality among Asian populations.

Particulates affect the climate system both directly and indirectly. Interestingly, they are engaged in both positive and negative radiative forcing and so, particulates are of a 'newer found' interest to the climate scientists. Again, climate change impacts the particulate levels which is difficult to predict [5], emphasizing the need of continuous monitoring and research on this pollutant.

Reports on particulate concentration, today, are available from all corners of the world including many such reports from the South Asian countries. The trend in developing countries differs greatly than the trend in the developed countries. This is because the pattern of energy use and fuel type, which are so different in these two worlds. For instance biomass burning is a common source of energy in the developing nations especially the South Asian countries. So, this region has a characteristic emission.

In a program study under the Regional Co-operation Agreement (RCA), Hopke et al. [6] reported that most of the participating countries exceed the WHO guidelines

[7] and the US NAAQS standards. They reiterated that China, Pakistan, Bangladesh and Sri Lanka are a cause of concern. Increases in coal combustion, increased population, and heavy traffic in urban centres might be a major factor for high pollution in India and China. Researchers pointed out use of more motor vehicles and dense population as the chief contributors of pollution in Pakistan and Bangladesh.

It is worthy to mention here that most of the studies from the South Asian countries are from urban centres. For instance, in Bangladesh reported studies are mostly from cities. In a study, Mahmud et al. [8] attributed 15000 premature death and several million cases of illness every year in Dhaka City to be from air pollution. They reported average mass of TSP and PM_{10} of 68 μgm^{-3} and 43 μgm^{-3} respectively for the period of August and September, 2005. In another study, Begum et al. [9] reported PM_{10} concentration of 140±114 μgm^{-3} at a locality in Dhaka and considered it as PM hotspot area. Researchers attributed motor vehicle and brick kilns as the major source of PM emission in Dhaka city [10,11].

Very high loadings of PM were reported by researchers in Pakistan [12,13,14]. Colbeck et al. [15] reported that the 24-hr mean levels in cities are at least 3-5 times higher than the WHO guidelines of 50 μgm^{-3}. They concluded that higher levels of PM are generally found in the summer rather than the winter and the monsoon. Ghauri et al. [16] reported the levels of TSP and PM_{10} in the range of 292-577 μgm^{-3} and 189-251 μgm^{-3} respectively in a baseline study conducted in 33 sites of six major cities of Pakistan. However, Hopke et al [6] conducted an experiment for duration of 4 years at Nilore (Islamabad), a residential campus away from major emission sources and reported mean PM_{10} concentration of 68±50 μgm^{-3}.

There are a few reported studies from the Himalayan Republic of Nepal as well. Giri et al. [17] reported daily PM_{10} concentrations from six representative sites of Kathmandu valley in the range of 7 μgm^{-3}-633 μgm^{-3}. The lowest and highest average annual concentration during the study period was found to be 47.78 μgm^{-3} and 199.80 μgm^{-3} respectively. They had found much variation in daily PM_{10} concentration in the inner city areas and concluded that the reasons of such variation to be diverse land-use, activities and consequent sources of emission.

Vahlsing and Smith [18] had conducted a study on National Ambient Air Quality Standards (NAAQSs) for PM_{10} and SO_2 (24-h) and identified 96 countries having NAAQSs. Eighty three percent of the 96 countries have 24-h AAQSs for PM_{10} and SO_2 and slightly more countries have 24-h Ambient. Air Quality Standards

(AAQSs) for SO_2 (76 countries) then PM_{10} (69 countries). The average AAQSs for PM_{10} and SO_2 are subsequently higher than the WHO guideline values.

As per the Article 48A of the Indian constitution, the onus of protecting the environment from degradation lies with the Government. The Central Pollution Control Board (CPCB), Government of India (GoI) is engaged in routine monitoring of Suspended Partculate Matter (SPM) and Respirable Suspended Partculate Matter (RSPM) at 342 operating stations covering 127 cities and towns in 26 States and 4 Union Territories of Indian State and has also taken-up a project for setting up of Continuous Real Time Air Quality Monitoring Stations in 16 cities. Recently CPCB had also conducted a source apportionment study in six cities of India [19]. Several studies have been carried out at various urban centres spread over the whole of India [20-25]. India is a vast country where most of the population (~70%) lives in rural areas, yet systematic studies on particulate pollution in these areas have not been initiated in a major scale.

In the northeastern region of India, despite being ecologically sensitive and a biodiversity hotspot, studies on air pollution is not attaining pace. There are a few reported studies on Aerosol Optical Depth (AOD) characteristics [26-28], and on carbonaceous properties of aerosols [29,30]. Biomass burning is a common sight in the rural areas of Northeast India in the form of household burning for cooking and heating, agricultural residue burning, shifting agriculture and forest fire which are few major contributors of atmospheric PM_{10} load in the region. Festive biomass burning is an important source of particulates in the Brahmaputra valley [31,32], which could also have regional implications.

2.2. Particulate concentration and atmospheric condition

Atmospheric conditions that comprise the state of the atmosphere in terms of temperature, wind, precipitation and clouds affect the particulate loading in the atmosphere. During winters temperature inversions are more frequent leading to higher PM concentration [32,33]. Also the winter mixing layer height lowers than other seasons of the year which influences atmospheric PM concentration. Lowering of mixing layer height results in increase PM levels in the atmosphere [32,34,35]. Amodio et al. [36] reported very high PM_{10} concentrations during poor atmospheric dispersion condition in Apulia of South Italy.

However, during monsoon season, rain washout results in low pollutant concentration in the atmosphere [20,37]. Secondary particulate formations are high during the winter and the monsoon due to moderate temperature and high relative humidity [38]. During the summer increased solar insolation favours resuspension of crustal dust while wind speeds are conducive to medium- and long-range atmospheric dust transport [39,40]. The long range transport of pollutants to a particular region has been addressed by back trajectory analysis by several researchers [32,36,41-43].

2.3. Monitoring methods of PM

Simple to advanced sampling devices are used for PM monitoring. High volume samplers [20,32,38,44,45], medium volume samplers [46,47] and low volume samplers [48-50] were very common for $PM_{2.5}$ and PM_{10} measurements and were used from very early days. The most commonly used size-fractionating equipment is the cascade impactor [51-55]. This works on the same principle as the regular PM samplers, but has a series of impactors and collection surfaces which allow the classification of different sizes. One of the advanced PM sampler is the Micro-Orifice Uniform Deposition Impactors (MOUDI) sampler [56]. Beta Attenuation Monitor [35,57], is also used for continuous monitoring of $PM_{2.5}$ and PM_{10}.

A very popular technique of PM measurement is using an optical method of laser scattering like Aerosol Spectrometer [35,58,59]. These instruments can be operated in a mode to collect a single particle size or multiple size ranges continuously. Scanning mobility particle sizer (SMPS) [60], Differential mobility particle sizer (DMPS) [61-63] are commonly used for ultra fine particles. A Wide-range Particle Spectrometer (WPS) was used to measure aerosol size distributions in the range of 10 nm-10 μm. The instrument is a high-resolution aerosol spectrometer which combines the principles of Differential Mobility Analysis (DMA), Condensation Particle Counting (CPC) and Laser Light Scattering (LPS) [43].

2.4. Source apportionment of PM

Source apportionment (SA) describes techniques used to quantify the contribution of different sources to atmospheric PM concentrations [64]. There are mainly three groups of SA models viz., methods based on monitoring data, emission or dispersion model and receptor model. Principal component/factor analysis are commonly used for SA because of that detailed prior knowledge of the sources and source profiles is not required [65]. The fundamental principle of receptor modelling is that mass and species conservation can be assumed and a mass balance analysis can be used to identify and apportion sources of airborne PM in the atmosphere [66]. Receptor modelling was also used in epidemiological and health related studies [67,68] Researchers from different parts of the world were using different receptor models like Principal Component Analysis-Multiple Linear Regression (PCA-MLR) [24,69,70], Principal Component Analysis- Absolute Principal Component Scores (PCA-APCS) [71-73], Positive Matrix Factorization (PMF) [56,74,75], UNMIX [70,71], Chemical Mass Balance (CMB) [21,76] etc. for SA. In Indian context, source apportionment by CMB is limited and factor analysis is widely used [21].

2.5. Festivities and PM emission

Festivals emit large volume of particulates in to the atmosphere. Earlier studies [46,77,78] reported that festivals often emit huge bulk of air pollutants in the Asian cities that pose serious implications to air quality. Diwali and *meji* burning of North east India are two major emitters of air pollutants in India.

2.5.1. Diwali fireworks

Fireworks are generally associated with celebrations worldwide. Such celebrations range from smaller local events like birthday parties, wedding ceremony, and victory in a sports event to huge nationwide celebrations. In India, Diwali is one such festival marked with lighting of lamps and celebrations with major fireworks all over the country. The main fascinating characteristic of Diwali is the participation of almost every household in bursting firecrackers, leading to emission of huge volume of aerosols into the atmosphere in one single day.

There are reports of many fold rise of PM_{10} loadings and elevated levels of harmful gases and elements in the atmosphere during fireworks [79-83]. Increase in the carbonaceous materials [46,83,84], ionic components of particulates are also reported from India and elsewhere in the world during fireworks [46,81,85,86]. However, organic emission is reported to be less when compared with other chemical species from fireworks [80,81,83]. Nishanth et al. [78] reported increase in PM_{10}, O_3, NO_2, NO along with various hazardous organics in the atmosphere which are released from burning of firecrackers during traditional Vishu festival of Kerala, India. There are also studies on effects of Diwali celebrations on high ground or surface ozone concentration [87,88]. Deka and Hoque [89] had studied Diwali fireworks in rural Brahmaputra Valley and reported marginal incremental effect of Diwali as compared to the events in the 'mainland India'.

2.5.2. Festive biomass burning

Previous studies [90,91] have reported that biomass burning emits large volume of particulates and chemical oxidants into the atmosphere. Festive biomass burning, the traditional *meji* burning, is a unique feature of the Brahmaputra Valley during winter time, which releases significant volume of particulates posing regional implications [31]. Deka and Hoque [32] had found incremental effects of PM_{10} load during *meji* burning in the Brahmaputra Valley atmosphere which in turn has implications on the characteristic of PM_{10} of this region. They reported that PM_{10} of being extremely carbonaceous and enriched with Br and other metallic species.

2.6. Biomass burning in rural kitchens

Biomass burning as fuel in kitchen is a concern as large volume of air pollutants and particulates mainly in the submicron size could affect indoor air quality. It is the primary energy source in rural India [92].

Cooking practice has several adverse impacts on indoor air quality. Household solid fuels use in developing countries produces exposures to smoke components that are remarkably high by the standards set for outdoor air in developed countries [93]. It emits hazardous chemicals and gases which not only affect human health, but also contribute to regional and global air pollution and climate forcing [94-96]. Women and children pass several hours of a day inside the home, who may get exposed to this unknown types and loads of air pollutants. Indoor air pollution has caused 400000-550000 premature deaths, annually in India, of children under five and adult women [97]. Globally, 4.3 million premature deaths were attributable to household air pollution as of 2012 [2]. Women exposed to biomass smoke are 3-times as likely to suffer from chronic obstructive pulmonary disease (COPD), than women who cook with cleaner fuels such as electricity, gas etc. [98]. Mondal et al. [99] reported 3-times more PM_{10} and $PM_{2.5}$ in indoor air of biomass using households than LPG-using families. Chronic inhalation of biomass smoke elicits oxidative stress and extensive DNA damage.

It has been estimated that 39% of the global population use biomass fuels for cooking and heating, and large amounts of biomass fuels are consumed in developing countries [100]. It had been estimated that approximately 76% of all global particulate matter air pollution occurs indoors in developing world [101]. Biomass in the form of wood, crop residues and animal dung is used in more than two fifths of the world's household as the principal fuel [93]. In India, about 80% of rural households still use unprocessed solid biomass like wood, dung and agricultural refuges for cooking and heating [102]. Biomass accounts for more than 80% of domestic energy in India [103] and about 90% biomass using households of the country use wood or animal dung as their primary cooking fuel [104].

Carbon, H, N, S, Cl, and O are the elementary biomass composition. Potassium, Na, Mg, Ca, P, and some heavy metals such as As, Cd, Cr, Cu, Hg, Ni, Pb and Zn are present in a lower proportion [105]. Five major ions including K^+, NH_4^+, Cl^-, NO_3^- and SO_4^{2-} are emitted by all types of biomass burning [106]. Emission of these ions were also reported by other researchers from biomass burning [63,107-109].

At the global scale, the major source of primary carbonaceous aerosols is biomass burning and its widespread use as fuel for cooking and heating homes [110-112]. Venkataraman et al. [113] had estimated biofuel burning as the largest single source of black carbon in India. Biomass burning in kitchens also emits high concentration of PAHs. It contributed more than 90% and 60% of total PAHs emissions in India and China, respectively [114].

2.7. Soil and atmospheric PM_{10}

Soil, the upper surface of earth is a receptor site of atmospheric particulate matter and, therefore, signature of PM_{10} characteristics may be found in the topsoil. Atmospheric particles get deposited on soil by wet or dry deposition. Sampling and analysis of wet and dry atmospheric deposition can provide a clear picture of the environmental quality of an ecosystem and can lead to actions aimed at reducing pollutant emissions in the atmosphere. Atmospheric deposition is measured as a part of ecosystem studies and regional pollutant monitoring networks [115].

Most studies on heavy metal levels in urban soils have usually been carried out in large cities with dense traffic or a high degree of industrialization and few studies have addressed this issue in smaller cities [116]. There are a few studies on heavy metal and its impact on agricultural soil reported from India. Different studies suggests that if the present trend of atmospheric deposition is continued, it will lead to a destabilizing effect on the sustainable agricultural practice and will increase the dietary intake of toxic metal leading to long term health implications [117,118].

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CHAPTER 3
MATERIALS AND METHODS

3.1. Sampling site

The study was conducted at Tezpur University campus and surrounding areas of Tezpur, a rural receptor site situated in middle Brahmaputra Valley of Assam, India, which is geographically positioned around 26°37′ N and 92°50′ E, close to the foothills of Eastern Himalayas to the North. The site is situated at about 15 km on the east from Tezpur city's downtown area. The study area is shown in Fig. 3.1. The campus is sylvan, surrounded by villages and agricultural fields.

The average elevation of the area is about 48 meters above mean sea level. The climate of Tezpur is of monsoon type with muggy summer and cool winter. During monsoon the region receives moderate to high rainfall. Frequent inversion and calm conditions are observed during winter months (December to February). Tezpur is the Administrative Headquarter of Sonitpur district. According to the last Census of Government of India in 2011, Sonitpur has a population of 1.7 million, 89% of which live in villages.

3.2. Sampling

3.2.1. PM_{10} sampling

Sampling of PM_{10} was carried out by a high volume Respirable Dust Sampler (Envirotech APM 460 BL) on Whatman glass fibre filter (8"X10" size-GF/A Schleicher & Schuell). The glass fibre filters were carefully desiccated prior and after sampling to ascertain correct gravimetric estimation by an Analytical Balance (Sartorius make: CP225D). Sensitivity of the balance was 0.01 mg. The sampling height was 8 meters above the ground.

PM_{10} sampling was carried out for two full cycles of a year during December 2008 to November, 2009 and December 2010 to November 2011. 24-hr samples were collected on random days spread the whole year; 3-5 samples in every month.

Besides the routine monitoring, PM_{10} samples were also collected during Diwali fireworks and *meji* burning, two festivals that are associated with extraordinary emission days.

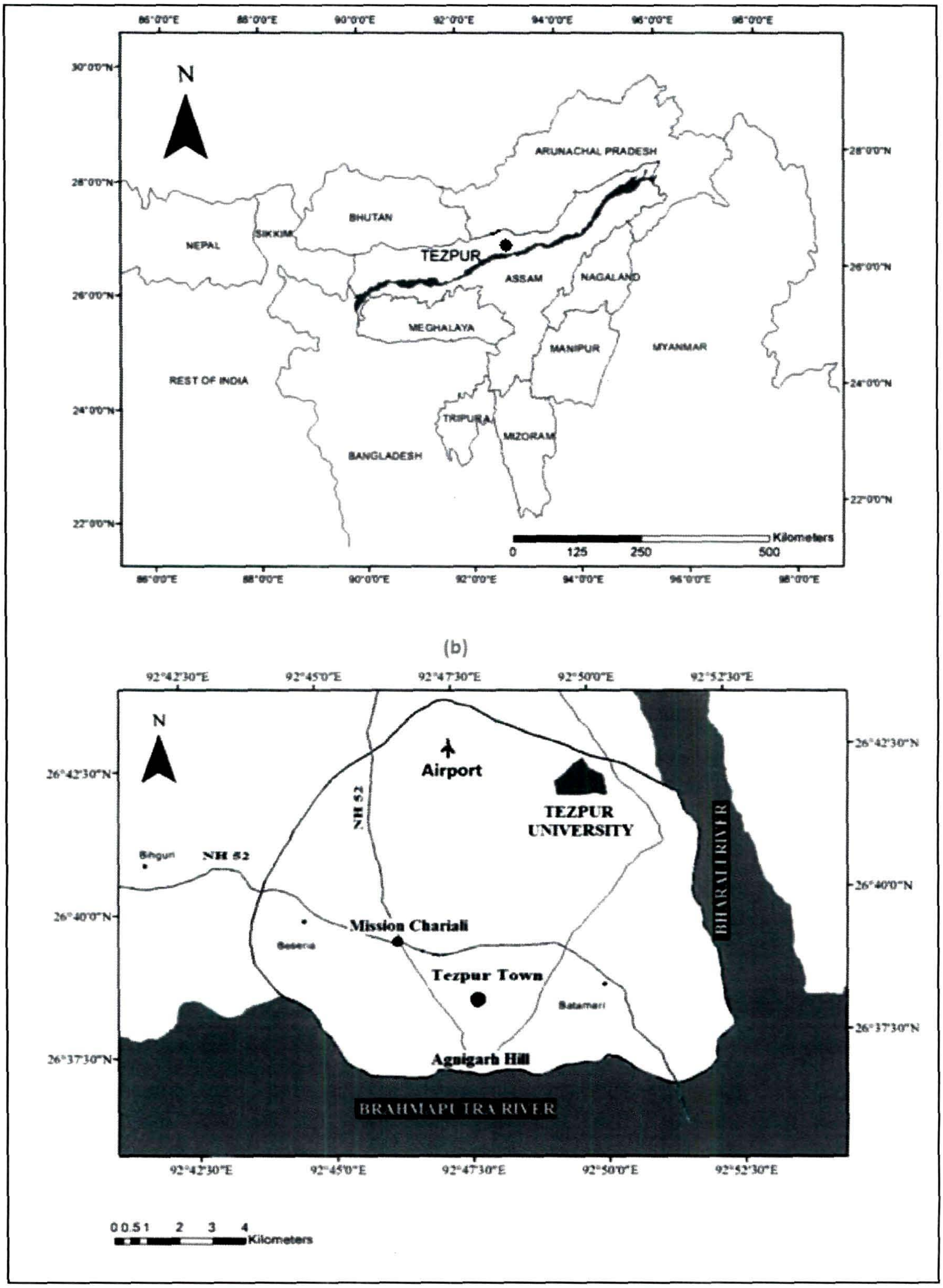

Fig 3.1. Map of study area (a) Northeast India and adjoining regions (b) Tezpur and surrounding areas-the sampling station, Tezpur University

PM_{10} was monitored during Diwali-fireworks of 2009. Diwali was celebrated on the night of October 17, 2009 and sampling protocol was started from October 11, 2009. Day and night samples (12 hourly) were collected for 13 consecutive days in a time series. A total of 26 samples of PM_{10} were collected during the monitoring campaign. For convenience samples are divided into festive days and background days. October 16 – 18, 2009 was taken as the festive days and the days prior to the event and after the festive days were taken as background days. Details of sample collecteion is given in Table 3.1.

Table 3.1. Details of the sample collection during Diwali fireworks of 2009

Sample identity	**Description**
Background Day & Background Night	Include day and night samples, starting from 11-10-2009 to 15-10-2009 and again from 19-10-2009 to 23-10-2009, respectively
Pre-Diwali Day & Pre-Diwali Night	Day and night sample of 16-10-2009, respectively
Diwali Day & Diwali Night	Day and night sample of 17-10-2009, respectively
Post-Diwali Day & Post-Diwali Night	Day and night sample of 18-10-2009, respectively

PM_{10} samples were also collected during *meji* burning period of 2009, 2012 and 2013. During 2009 *meji* burning period sampling was carried out in the cycle of 7 am - 7 pm – 7 am. Thirty-one twelve-hourly (day/night) samples were collected in a time series. The campaign had started on the evening of January 12, 2009, continued through the *meji* burning event (late night of January 13-14) and ended on the morning of January 27, 2009. On getting encouraging results the experiment was repeated during 2012 and 2013.

During 2012 and 2013 *meji* burning, sampling of PM_{10} was carried out periodically. First sample was collected two days before *meji*; the 2nd sample covers the *meji* burning episode, 3rd and 4th samples were collected on one and two days after the *meji* as celebration continue with lesser intensity for the following two days too. 5th and 6th samples were collected one and two weeks after the *meji*, respectively to see if there is any influence of long range transport on PM_{10} constituents from *meji* burning areas of Assam. Sampling was carried out in the cycle of 8 a.m. - 8 a.m. Six 24-hr samples were collected during January of 2012 and 2013 *meji* burning events. Details of sample collection is given in Table 3.2.

Days with rain were avoided for PM_{10} sampling. Whatman glass fibre filters were used for collection of PM_{10}. During *meji* burning experiment of 2012 and 2013, Whatman Quartz microfiber filters (20.3 x 25.4 cm) were used for sample collection.

Table 3.2. Details of sample collection during 2012 and 2013 *meji* burning event

Sample identity	Collection time
1st sample	Two days befor *meji* burning
2nd sample	On the *meji* burning day
3rd and 4th samples	One and two days after *meji* burning day, respectively
5th and 6th samples	One and two weeks after *meji* burning day, respectively

3.2.2. Biomass fuel smoke particle (BFSP) sampling

Pilot survey was carried out to select representative kitchens of different biomass fuel used. Data on biomass fuel use, strength of family, number of meal cooked in a day etc. were collected. Based on this, 14 households were selected for sample collection. Samples were collected during winter (December to February) and monsoon (June to September) seasons. Cooking stoves are similar and built of mud and mainly comprises two chambers for burning of biomass. Most of the kitchens are attached with the living rooms with poor ventilation. Roof of the kitchens selected for the study were mainly made up with bamboo having mud covering or tin.

Two Whatman glass fibre filters were placed above the cooking stoves for each households in each season. After the stipulated time period filter papers were removed and deposited BFSPs were scratched out on aluminium foil with a stainless still spatula and stored in refrigerator at 4°C for further chemical analysis. Different BFSPs produced as a result of different biomass fuel burning was named after the respective biomass fuel and it is summarised in Table 3.3.

Table 3.3. Brief description of different biomass fuel used in the kitchens and abbreviations used for the biomass fuel smoke particles (BFSPs)

Biomass fuel	**Abbreviations (Winter)**	**Abbreviations (Monsoon)**	**Number of households**
Cowdung fuel stick	CD-W	CD-M	4
Mixed biomass fuel	MBF-W	MBF-M	8
Cowdung and mixed biomass fuel	CDMBF-W	CDMBF-M	1
Sugarcane bagasse	SGB-W	SCB-M	1

3.2.3. Soil sampling

20 undisturbed points (Fig. 3.2) were selected taking Tezpur University as the centre. Samples were collected during February and November of 2011 to represent pre-monsoon and post- monsoon seasons, respectively. Top soil (0-3 cm) was collected after removing the surface vegetation. Collected samples were brought to the lab, air dried at room temperature and mixed thoroughly. Five sub-samples were collected and mixed to form the composite sample. After coning and quartering mixed soil samples were stored in plastic bags for further analysis.

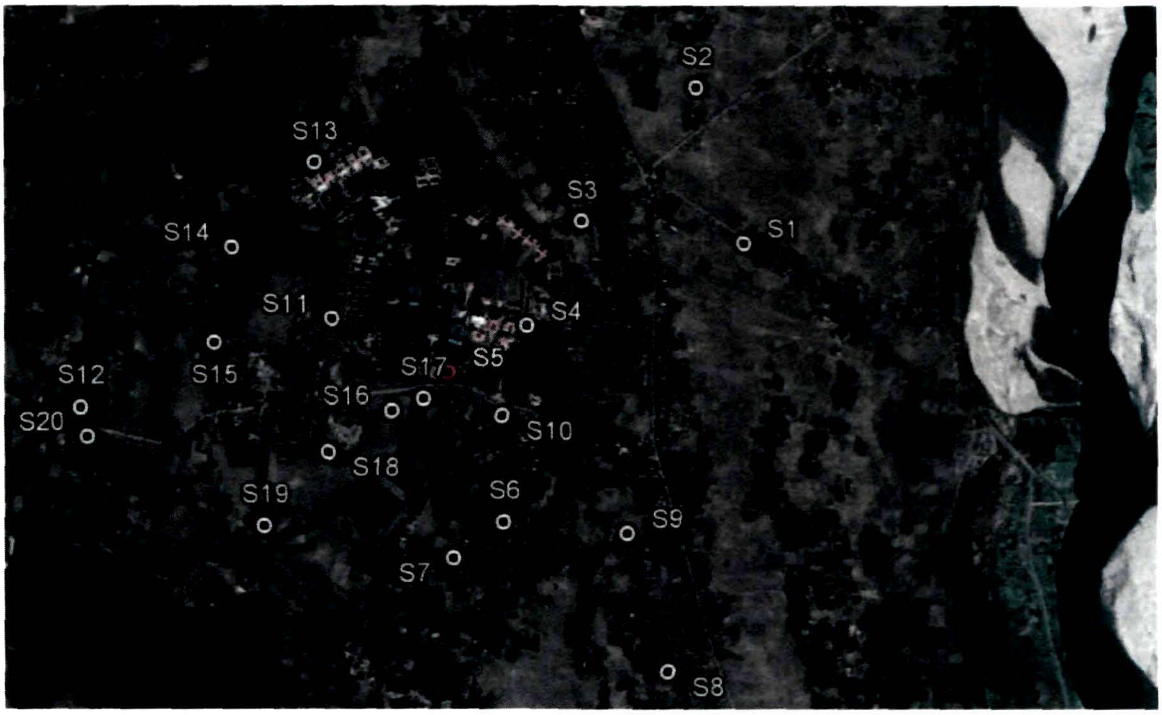

Fig 3.2. Sampling points for soil sampling

3.3. Analysis

3.3.1. Elemental analysis

3.3.1.1. Elemental analysis by SEM-EDX

For 2009 *meji* samples, elemental analysis were carried out by 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). The EDX was equipped with a Silicon (Lithium drifted)

Crystal Detector capable of having an extended acquisition rate to 50,000cps. The detector also had a Super Atmosphere Supporting Thin Window (SATW) which ensures good resolution at the low energy end of the spectrum and allows chemical analysis of elements down to Boron under suitable conditions. Quant optimization was done with high purity (99.99%) Cu and Ni for accurate quantitative measurement of elements in the sample. The minimum quantification limit of detector was 0.01 wt%. The resolution of the instrument was 137 eV at 5.9 KeV.

The analytical protocol adopted was as per method used by earlier workers [1-4]. It is assumed that there was uniform deposition of particles on the filters. Three areas were randomly chosen for EDX analysis from respective sample filters and quantification results were means of three measurements. The means with SDs within ±10% were accepted. While taking measurements, magnification was set to 120x and a detection area of 1 mm^2 of the sample filter was subjected to the x-ray excitation.

Si and O, 38.69 and 61.3 wt% respectively, were detected in the blank filters and presence of other elements was in extremely low concentrations to be detected by the equipment. ZAF correction was automatically taken care by the INCA software.

3.3.1.2. Elemental analysis by ICP-OES

Elemental analysis of remaining PM_{10} samples were done by HNO_3 acid digestion method [5,6]. Aliquot of PM_{10} sample was digested in 9 ml HNO_3 at an oven temperature of 100°C for 8-hrs. In case of BFSP samples, 0.15 gm sample was digested in 5ml HNO_3 and 2.5 ml $HClO_4$ in 2:1 ratio in at an oven temperature of 120°C for 4-hrs. Aqua regia was used for digestion of soil samples [7]. Soil samples were digested using HNO_3 and HCl in 3:1 ratio at an oven temperature of 100 °C. Teflon bomb was used for sample digestion.

After volume makeup filtered samples were kept in pre-washed polyethylene bottles maintaining a pH of ~ 2. Elements of all samples were analyzed in an ICP-OES (PerkinElmer, OPTIMA-2100 DV).

3.3.2. Ions

For water soluble ions, aliquot of sample was soaked in ultra pure water and ultrasonicated for 20 minutes and filtered [8]. The filtrate volume was adjusted to 20 ml in pre washed polyethylene bottles and kept at 4°C until analysis. Ions were analyzed in an Ion Chromatograph (Metrohm 882 Professional IC). Same procedure was followed for BFSPs with 0.1 gm of sample.

The anion analysis was done by an anion column (Metrosep A Supp 5-250/4.0) with suppressor. A solution mixture of 3.2 mM Na_2CO_3 and 1 mM $NaHCO_3$ was used as the eluent and the flow rate was kept at 0.7 mL/min. 50 mM H_2SO_4 was used as the regenerant in anion analysis.

Cations were analyzed by a cation column (Metrosep C 4-150/4.0). The eluent for cation analysis was prepared in ultrapure water with 1.7 mmol/L nitric acid and 0.7 mmol/L dipicolinic acid.. The eluent flow rate during cation analysis was kept at 0.9 mL/min.

An inbuilt loop that measures 20 μl of sample for injection was used. Before injecting the samples in to the IC system, samples were filtered through Millipore 0.22 μm PTFE filters.

3.3.3. Carbon

Carbon analysis was done using analytikjena TOC analyzer. The TOC analyzer was accompanied with HT 1300 solid module for total carbon and with multi N/C 2100 module for the water soluble carbon. 99.99% pure O_2 gas is used as carrier gas in the system. Samples were introduced in to the hot zone of the reactor tube in a ceramic boat where samples were incinerated forming CO_2, which was measured by the non dispersive infrared (NDIR) detector system. TC was determined directly by feeding the sample in to the heating furnace. To calculate EC samples were preheated in a muffle furnace to remove OC and then fed in to the heating chamber [9]. OC was obtained by subtracting EC from TC.

The liquid module was calibrated with Na_2CO_3, $NaHCO_3$ and $C_8H_5KO_4$. Water soluble organic carbon (WSOC) was determined by differential method where water soluble inorganic carbon (WSIC) is subtracted from water soluble total carbon (WSTC). Samples were dosed into the vertical combustion tube for WSTC and into the acidic TIC reactor for WSIC. Platinum catalyst aids in the pyrolysis and oxidation of sample. One part of the extract of sonication was used for water soluble carbon.

3.3.4. PAHs

Samples were extracted in Dichloromethane for PAHs analysis [10]. For PAHs analysis of PM_{10}, a circular portion (4.44 diameter) of filter paper was cut from the sampled filters and were extracted in 20 ml Dichloromethane for 20 min by ultrasonic agitation (Bandelin Sonorex) using 20 kHz frequency in a water bath. 0.1 g Biomass fuel smoke particles (BFSPs) were taken for PAHs analysis of BFSP samples. This extract was subsequently mixed and filtered and concentrated to 0.5-1 ml in a rotary evaporator (Hahnshin Scientific Co.). Silica gel column clean up (USEPA method 3630 C) was applied to the concentrated extracts to fractionate the PAHs. Again fraction containing PAHs was concentrated to 0.5-1 ml and the solvent was exchanged with acetonitrile for further chromatographic analysis. High Performance Liquid Chromatography (HPLC) system (Waters, USA), equipped with tunable absorbance UV detector and Waters PAH C18 column (Symmetry C^{18}, 4.6 x 250 mm) was used for PAHs analysis. The mobile phase was a gradient of acetonitrile and degassed water. Identification of PAHs was done by matching their retention time with a mixture of PAH standard (EPA method 610 Polynuclear aromatic hydrocarbon 16 solution in acetonitrile, procured from Supelco, USA).

We had analyzed USEPA priority 16 PAHs viz., naphthalene (NAP) acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR), benz[b]fluoranthene (BbF), benz[k]fluoranthene (BkF), benz[a]pyrene (BaP), dibenz[a,h] anthracene (DBA), benz[ghi]perylene (BPER), and indeno[1,2,3-cd]pyrene (IND). For BFSP samples BPER and IND was not considered.

3.4. Quality control

Glass fibre filters were dessicated for 24-hr before and after collection of samples. Quartz fibre filters were pre-heated for 1-hr at 600 °C and then desiccated for 24 hours prior and after the sampling to avoid traces of moisture and attain right accuracy of measurements. Samples were analyzed in duplicate and the means showed a standard deviation of ±2 %. The ICP-OES was calibrated using ICP-Multi element standard solution VIII (Merck) and 2% HNO_3 (Solution-Optima Blank-Perkin Elmer Pure Plus) was used as reagent blank. To see the recovery of elements NIST SRM for Urban Particulate Matter (1648a) was used, which showed a recovery rate of 82 to 110% for the analyzed elements. For estimation of anions Multielement Ion Chromatography Anion Standard Solution (Fluka Analytical) was used to calibrate the IC. Cation standards were prepared in the laboratory with high purity reagents. Field blanks were analyzed and incorporated in the measurements. All dilutions were made in ultrapure water (18.2 grade). Care was taken to prevent contamination of the samples. Chemicals used in TC and TOC calibration were procured from Merck (India) Ltd. The analytical error in duplicate analysis was within 10%. All the reagents used in PAHs analysis were procured from Merck (India) Ltd. and of HPLC grade. At no point sample containers were touched with bare hands to avert contamination.

As a measure of quality control method detection limits of ICP-OEC and IC was also calculated. To see the method detection limit the standard with minimum concentration was run for 7 times. MDL was calculated as the three times of half of standard deviation (Table 3.4).

3.5. Statistical analysis

SPSS software was used for statistical analysis of data.

Table 3.4. Method detection limit of elements and ions

Elements	MDL, mgL^{-1}	Ions	MDL, mgL^{-1}
Cd	0.017	Li^+	0.004
Co	0.015	Na^+	0.012
Cr	0.027	NH_4^+	0.004
Cu	0.029	K^+	0.018
Fe	0.023	Mg^{2+}	0.041
Mn	0.030	Ca^{2+}	0.074
Ni	0.013	F^-	0.001
Pb	0.011	Cl^-	0.008
Zn	0.021	**Br-**	0.068
		NO_3^-	0.006
		SO_4^{2-}	0.008
		PO_4^{3-}	0.002

3.6. References

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CHAPTER 4
RESULTS AND DISCUSSION

4.1. Characterization of PM_{10}

PM_{10} was monitored for a period of two years. The first period of sampling was carried out during 2008 – 2009 (1st year) and the second period during 2010 – 2011 (2nd year). The first year samples were analyzed for elements and more detailed analysis was done for the second year samples. The entire year was divided in to four distinct seasons prevails in this region to see the seasonal variation of PM and its associated components. The seasons were, winter (December to February); pre-monsoon (March to May); monsoon (June to September) and post-monsoon (October and November).

PM_{10} characteristics and its impact on the atmosphere during two periods of festivals viz., Diwali and *meji*, both having varied emission strengths and profiles, were taken up elaborately for the study. We had also characterized the particles emitted from biomass burning in rural kitchens of this region and see how emission from these kind of biomass burning impacts on the loading and properties of PM_{10}. Undisturbed top soil of the nearby areas were collected to see if there is any atmospheric deposition signature of PM_{10} on soil.

4.1.1. Levels of PM

The mean concentrations of different fractions of PM along with their positive standard deviation are shown in Fig. 4.1.

The average concentration of PM_{10} during 1st year was 147.10±153 μgm^{-3} (Fig. 4.1a) with a maximum and minimum of 495.14 μgm^{-3} (in July) and 15.20 μgm^{-3} (in October) respectively. The average PM_{10} was 2.5 times higher than the annual National Ambient Air Quality Standards (NAAQS) of 60 μgm^{-3} [1] and it was 7 times higher than the World Health Organization (WHO) annual mean of 20 μgm^{-3} [2]. During the study period average concentration of $PM_{>10}$ was 254.91 μgm^{-3} in the range between 9.74 μgm^{-3} and 1413.99 μgm^{-3}. An average of 402.00 μgm^{-3} was recorded for TSPM showing a range between 54.36 μgm^{-3} and 1628.57 μgm^{-3}.

However, during 2nd year average PM_{10} was found to be 47.96±31.44 μgm^{-3}, which was much lower than the first year (Fig 4.1b). PM_{10} maximum was 151.60 μgm^{-3} (in January) and PM_{10} minimum was 4.69 μgm^{-3} (in July). PM_{10} was within the annual national standard and WHO limit. Average $PM_{>10}$ was 62.94±68 μgm^{-3}. The maximum $PM_{>10}$ was observed in April (320.20 μgm^{-3}) and minimum in November (6.29 μgm^{-3}). During pre-monsoon season prevailing wind uplifts the coarse particles from the surface resulting higher concentration of $PM_{>10}$ during that period. Annual average TSPM was 110.90±86 μgm^{-3} with the range 27.93 μgm^{-3} to 373.74 μgm^{-3}.

It is noticeable that during the first year of study PM_{10} exceeded the 24-hr NAAQS value 20 number of times which is 41.67% of total data and it exceeded annual national standard 30 number of times accounting 62.5% of the total collected data. The number of data exceeding 24-hr mean of NAAQS during 2nd year was 4 contributing 7.84% of total data and it was 14 accounting 27.45% of total data for annual NAAQS.

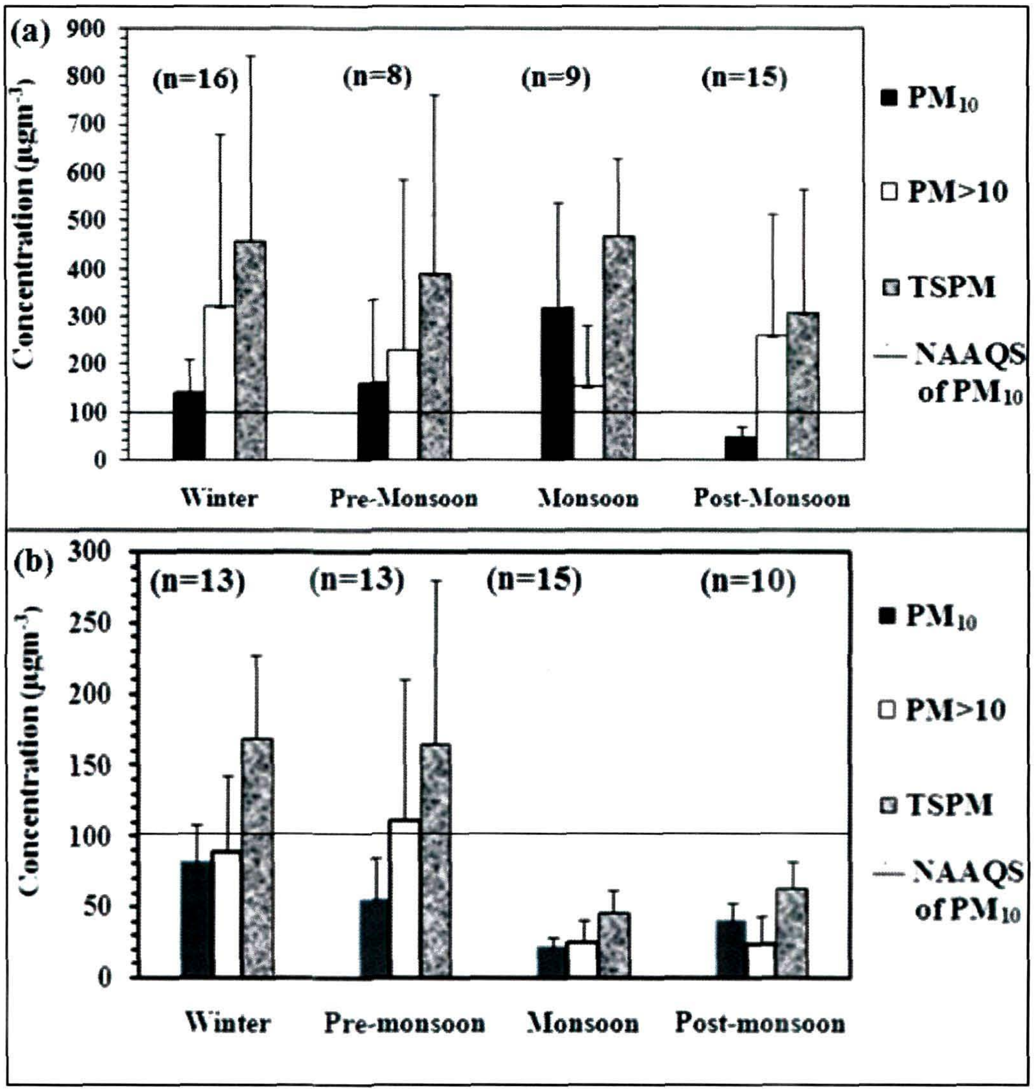


Fig. 4.1. Concentration of different fractions of particulate matter with positive standard deviation. (a) 2008-2009 (b) 2010-2011

Table 4.1. Comparative account of PM_{10} mass concentration of the present study and studies elsewhere

Study site	Year	PM_{10} (μgm^{-3})	References
Tezpur, India (rural/residential)	Dec, 2008-Nov, 2009	147 10±153	Present study
	Dec, 2010-Nov, 2011	47 96±31	Present study
Vikas Nagar, Kanpur, India (commercial)	Oct, 2002-Feb, 2003	272 70±65	Sharma and Maloo [3]
Juhi Colony, Kanpur, India (residential)	Oct, 2002-Feb, 2003	281 97±171	Sharma and Maloo [3]
Kolkata, India (urban)	Dec, 2003-Feb, 2004	288 93±124	Gupta et al [4]
Delhi, India (urban)	Jan-Dec, 2007	219±84	Tiwari et al [5]
Delhi, India (residential)	Dec 2008-Nov 2009	178 2 ± 63	Khillare and Sarkar [6]
Aliganj, Lucknow, Inida (residential)	March, 2007–Feb, 2008	163 96 (111 8–215 7)	Pandey et al [7]
Talkatora, Lucknow , India (commercial/industrial)	March, 2007-Feb, 2008	217 23 (157 8–315 6)	Pandey et al [7]
Dhanbad, India (coal mining area)	Dec, 2008-Nov, 2009	258 (170-339)	Dubey et al [8]
Dhanbad, India (non coal mining area)	Dec, 2008-Nov, 2009	134 (59-1760	Dubey et al [8]
Dayalbagh, Agra, India (residential area)	May-Sept, 2006 and 2007	68 7	Satsangi et al [9]
Agra, Inida (urban)	May, 2006-March, 2008	154 2	Kulshrestha et al [10]
Agra, India (rural)	May, 2006-March, 2008	148 4	Kulshrestha et al [10]
LinAn, China (urban)	2006-2007	328 5	Zhang et al [11]
XiAn, China (rural)	2006-2007	114 2	Zhang et al [11]
	2005	53	
Colombo, Sri Lanka	2000	65	Seneviratne et al [12]
Barcelona, North-eastern Spain (urban background station)	2005-2006	45	Perez et al [13]
Athens, Europe (Sub-urban area)	2008	30 6 ± 24	Pateraki et al [14]
Ulsan, Korea(urban/residential)	Spring and Summer, 2007	37 2	Lee and Hieu [15]
Tehran, Iran (urban)	Feb-June, 2007	90 ± 38	Leili et al [16]
Leece, Italy (urban background)	Jan, 2007-Jan, 2008	26 3±12	Contini et al [17]
Jeddah, Saudi Arabia (urban/residential)	Summer 2011 (June-Sep)	87 3±47	Khodeir et al [18]

The standard deviations of particulate means were very high in both the year which is indicative of mix sources of particulates varying from season to season and high uncertainties associated.

A comparative account of PM_{10} mass concentrations of the present study with studies elsewhere is put up in Table 4.1. Average PM_{10} concentration of 1st year of the present study was lower than other studies carried out in India except Dayalbagh [9], a residential area away from industries and heavy vehicles and non-coal mining area of Dhanbad [8], however comparable with PM_{10} levels of rural Agra [10]. The PM_{10} concentration in urban China [11] was also quite higher. However, the present study PM_{10} concentration was much higher than the studies mentioned from other parts of the world [12-18]. It was interesting that during 2nd year PM_{10} concentrations of the present study was lower than all Indian studies [3-10], China [11], urban area of Iran [16] and urban residential area of Saudi Arabia [18], Sri Lanka [12], yet the levels were higher than sub-urban area of Europe [14], urban residential area of Korea [15] and urban background station of Italy [17].

The lower levels of PM_{10} in developed nations could probably due to successful improvement of air quality in the last few decades [19] and also success in improved use of pollution reduction methods and policies [20] which are however lacking in developing countries.

4.1.2. Seasonal variation of PM

In this study, average PM_{10} during 1st year were found to be 139.05±69 μgm^{-3}, 158.98±178 μgm^{-3}, 316.54±221 μgm^{-3} and 47.68±21 μgm^{-3} in winter, pre-monsoon, monsoon and post-monsoon seasons, respectively. The PM_{10} was maximum in the monsoon and minimum in the post-monsoon with the following order: monsoon>pre-monsoon>winter>post-monsoon. The PM_{10} trend during 2nd year was different. PM_{10} trend during 2nd year was winter>pre-monsoon>post-monsoon>monsoon with 80.11±28 μgm^{-3}, 53.64±31 μgm^{-3}, 39.26±14 μgm^{-3} and 21.00±8 μgm^{-3}, respectively.

Khare et al. [21] reported 207.9±39 μgm^{-3} in summer (May to August, 2009) and 222.9±47 μgm^{-3} in winter (November to February, 2009) in a study from upper Brahmaputra Valley of Assam, India. They referred to the usage of wood for domestic heating in winter months to be the cause of high PM_{10} in winter. However, Pathak et al. [22] had reported lower concentration of PM_{10} in a study, covering 5 years compared to the present study and the levels reported by Khare et al. [21]. The 5 year average PM_{10} of 57.2±32.4 μgm^{-3}, 53.2±27.9 μgm^{-3}, 39.5±19.6 μgm^{-3} and 45±24.3 μgm^{-3} was reported by Pathak et al. [22] in winter, pre-monsoon, monsoon and post-monsoon seasons, respectively. They had also studied $PM_{2.5}$ and concluded that in terms of absolute concentrations, PM_{10} may be attributed to $PM_{2.5}$.

High concentration of PM_{10} in winter than other seasons was reported by many aerosol researchers [5,7,11,22,23]. During winter months, lower mixing height, dry weather condition, thermal inversion and stable atmospheric boundary layer and foggy condition favor the stagnation of particulates in the lower atmosphere [5,24,25] causing high PM loading in the atmosphere.

There are studies where maximum concentration of PM_{10} was recorded not in winter. Khillare and Sarkar [6] reported maximum PM_{10} concentration in summer than in winter in a study from residential areas of Delhi, and pointed out crustal resuspension and local dust storms as the causes of the high PM_{10} level. In a study from a suburban area of Athens, Pateraki et al. [14] reported maximum PM_{10} concentration in warmer period than in cold period and emphasized on secondary aerosol formation during warmer period.

In this study, maximum PM_{10} during 1st year was found in monsoon season probable reason of which may be the formation of secondary aerosols favored by high temperature and humidity. Gas to particle conversion is favored by high relative humidity [10]. Kgabi [26] reported an increase in PM_{10} with increase in temperature and wind speed.

Particles easily get scavenged by rain in wet season [27]. In 2009, India witnessed a deficit in the all-India rainfall of 54% during the summer monsoon (June-September) [28]. For NE India, the season rainfall of the year 2009 is the second lowest rainfall recorded since 1901 [29]. Again, it is interesting to note that in 2009, Assam witnessed a drought like situation or deficit rainfall [30] resulting in minimum washout of particles from the atmosphere. Bhawar and Rahul [31] had studied details about the cause of deficit rainfall during 2009 monsoon season. The Atmospheric Brown Clouds (ABCs) were observed from March to September of 2009 which slowed down the microphysical effect and enhanced the radiative effect resulting 30% reduction in the total cloud fraction that may have reduced precipitation and invigorated drought conditions during 2009. They reported 84% cumulative increase in aerosol occurrence frequency in 2009 compared to 2008 in the altitude below 6 km.

It must be mentioned here that meteorological parameters of a region influence the pollutant dispersion. Therefore, to see the possible reason for very high concentration of PM_{10} during monsoon further study on meteorological condition was carried out. Presence of stable atmospheric condition along with subsidence condition and thermal inversion during most of the days was found. Wind speed and rainfall were

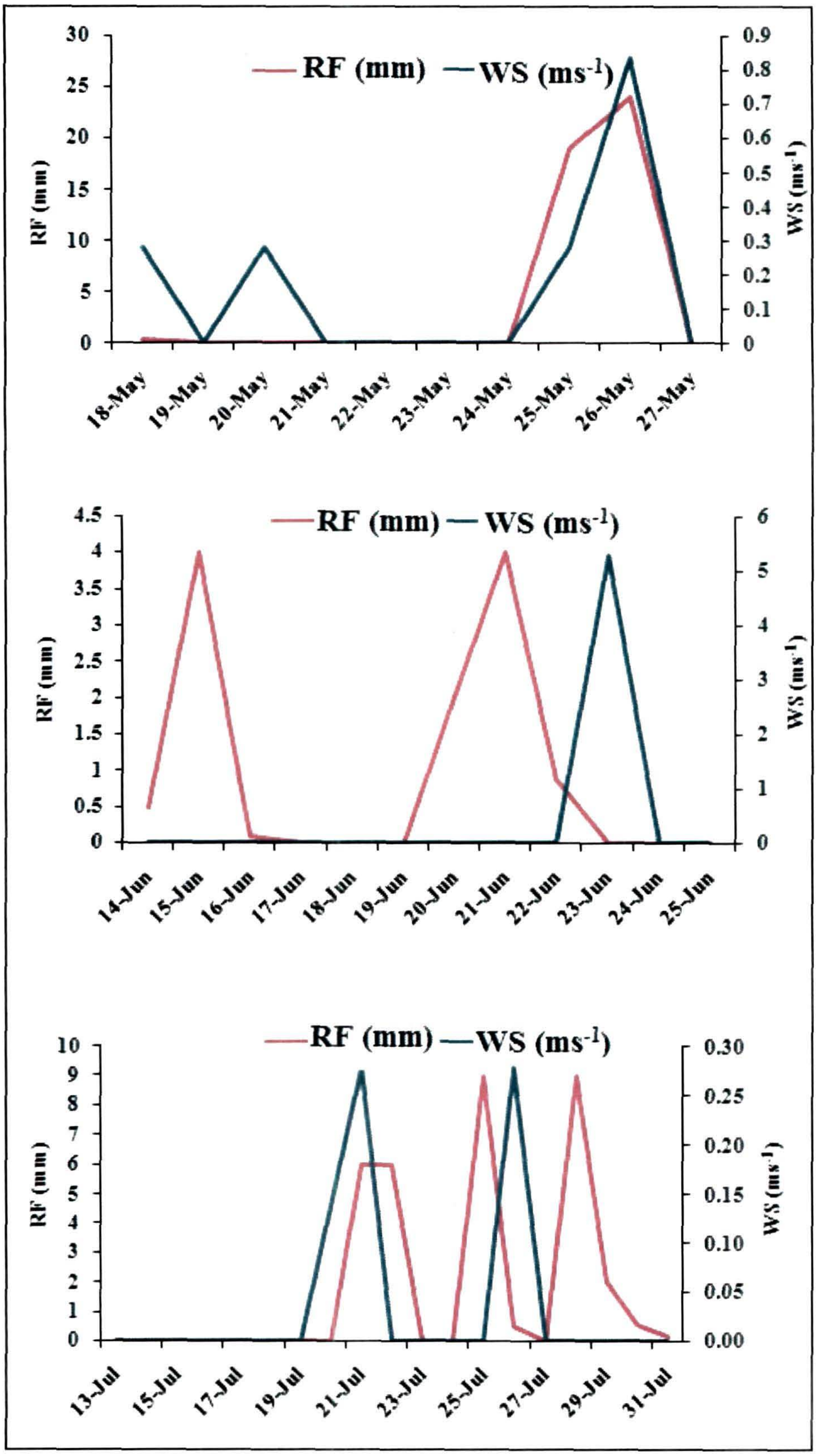
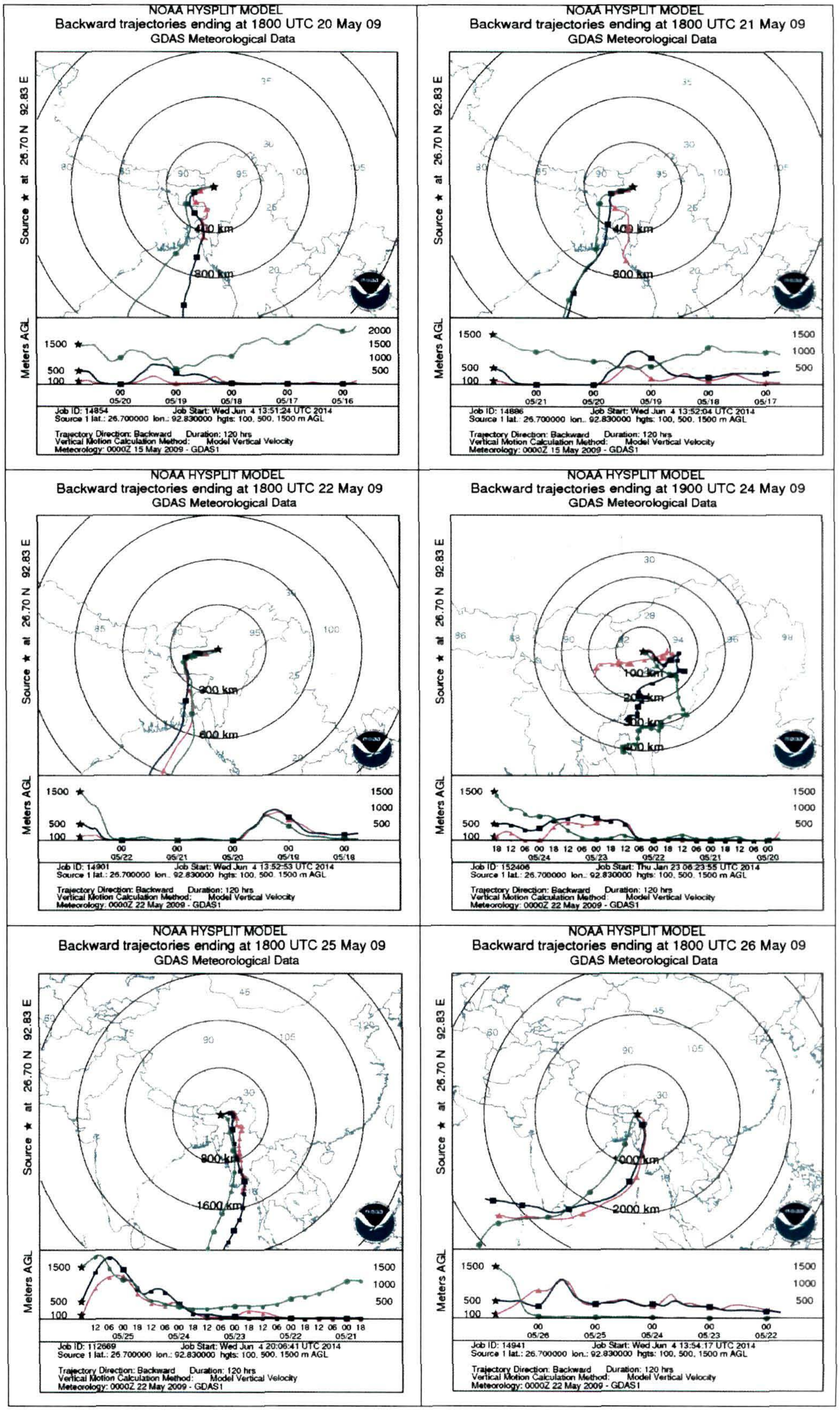


Fig. 4.2. Wind speed (ms^{-1}) and Total Rain fall (mm) of the days including sampling days of May, June and July of 2009



NOAA HYSPLIT MODEL
Backward trajectories ending at 1800 UTC 20 May 09
GDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 1800 UTC 21 May 09
GDAS Meteorological Data

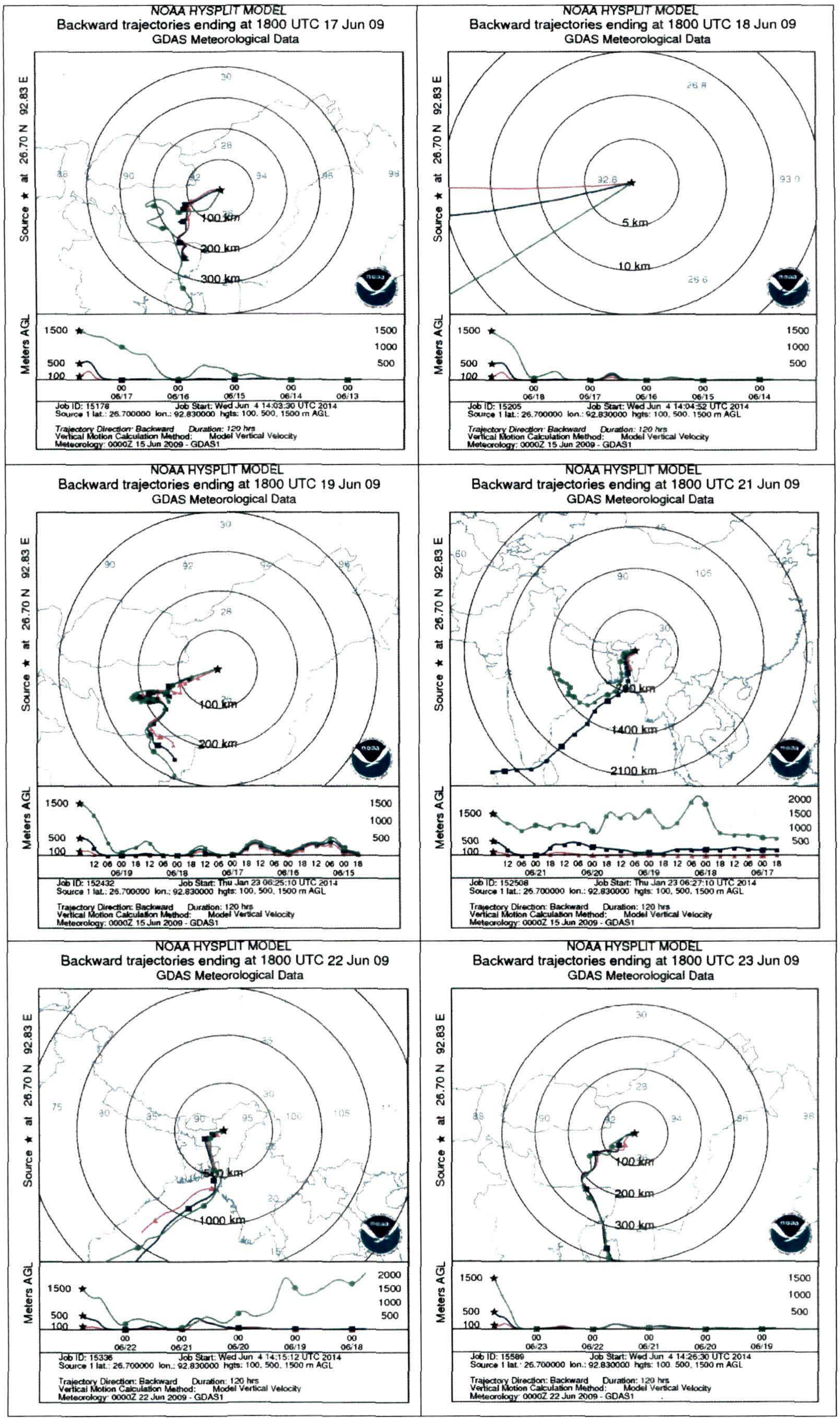
NOAA HYSPLIT MODEL
Backward trajectories ending at 1800 UTC 22 May 09
GDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 1900 UTC 24 May 09
GDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 1800 UTC 25 May 09
GDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 1800 UTC 26 May 09
GDAS Meteorological Data

Fig 4.3. Backward trajectories during May of 2009


NOAA HYSPLIT MODEL
Backward trajectories ending at 1800 UTC 17 Jun 09
GDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 1800 UTC 18 Jun 09
GDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 1800 UTC 19 Jun 09
GDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 1800 UTC 21 Jun 09
GDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 1800 UTC 22 Jun 09
GDAS Meteorological Data

NOAA HYSPLIT MODEL
Backward trajectories ending at 1800 UTC 23 Jun 09
GDAS Meteorological Data

Fig 4.4. Backward trajectories during June of 2009

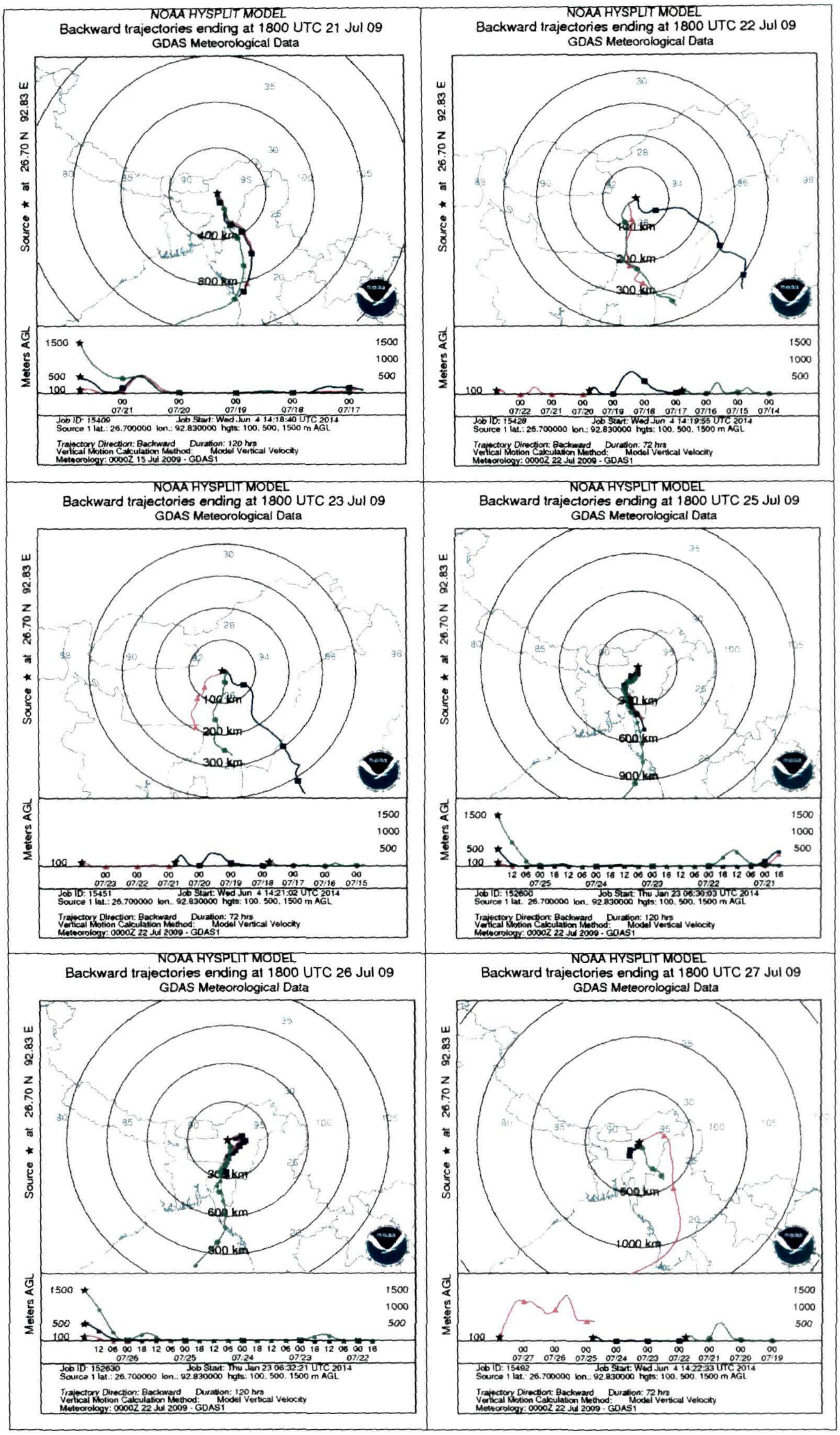


Fig. 4.5. Backward trajectories during July of 2009

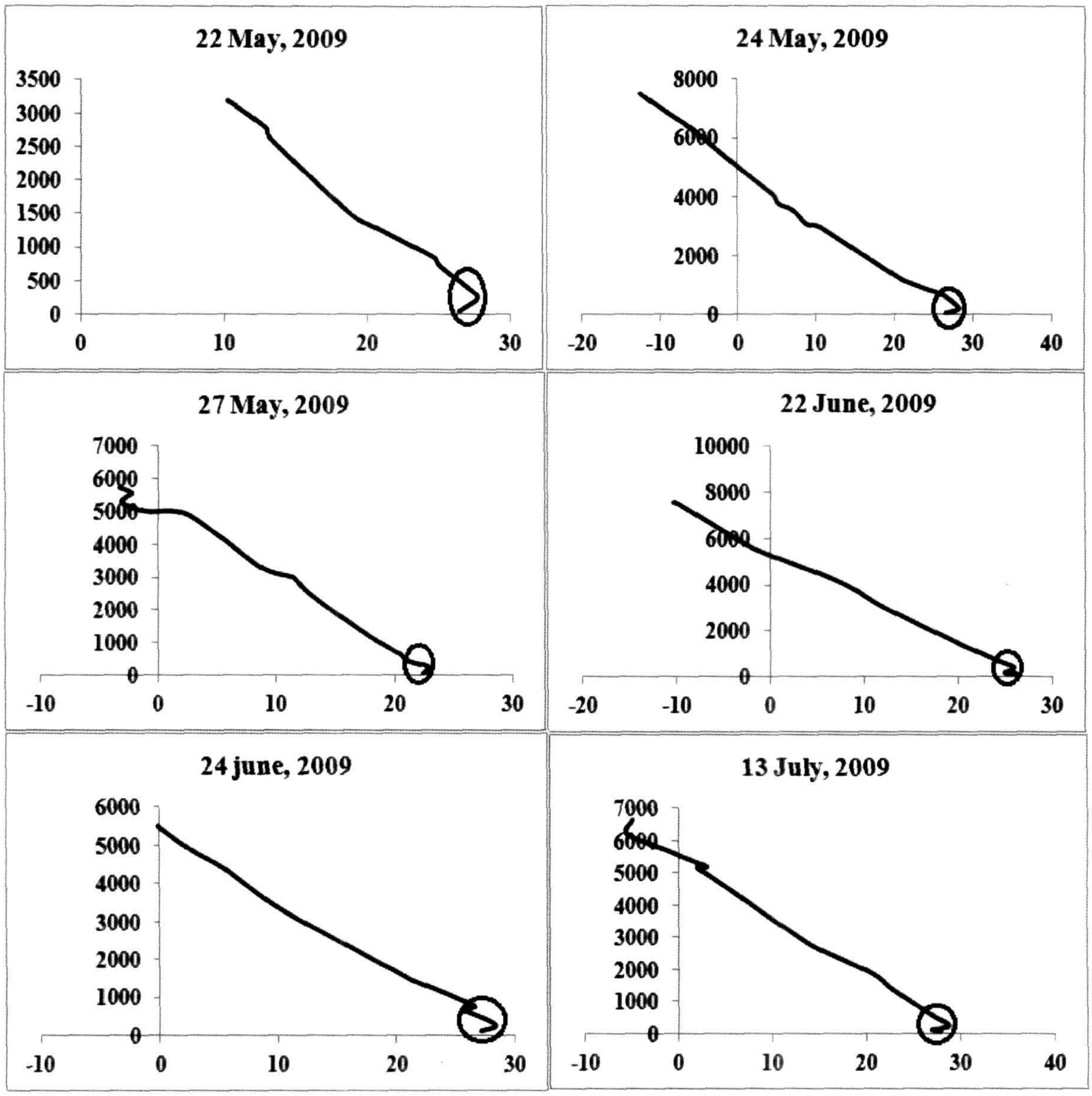


Fig. 4.6. Temperature inversion on some selective days of May, June and July of 2009. Ground level temperature inversions are encircled.

very low (Fig. 4.2). Mostly calm wind condition (wind speed <1 ms^{-1}) was prevalent during the sampling days. Especially, during July, winds were calm. The backward trajectories of May, June and July were also computed (Figs. 4.3; 4.4 & 4.5). Air mass trajectories were computed from the data archive of Global Data Assimilation System model using NOAA Air Resource Laboratory's (ARL) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) Model available at www.arl.noaa.gov/HYSPLIT.php. The trajectory study showed that winds were coming mostly from Bay of Bengal (BoB). Subsidence condition was prominent during May, June and July (Figs. 4.3,4.4 & 4.5). This subsidence condition results in temperature inversion. Vertical temperature profile of some representative days of May, June and July are shown in Fig. 4.6. Temperature inversion was prominent. All these factors, viz.

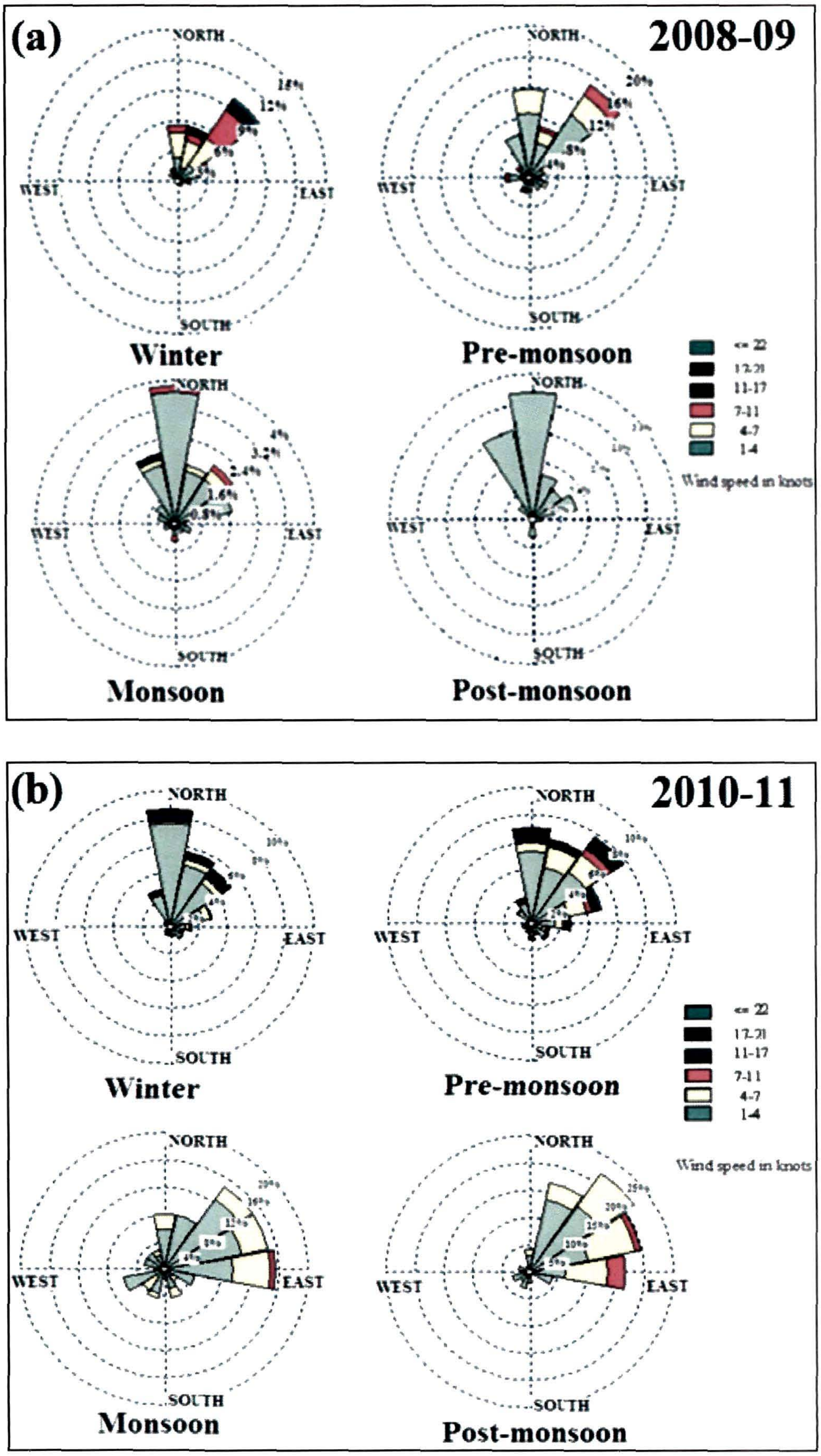


Fig. 4.7. Wind rose of the study period. (a) wind rose during 2008-09; (b) wind rose during 2010-11

low wind speed and rain fall, subsidence condition and thermal inversion hinders in pollution dispersion resulting high pollutant accumulation in the atmosphere.

Wind roses (Fig. 4.7) of different seasons were plotted for the study period. The prevailing wind was mainly from north-east, north and north-west directions during the study period of 2008-09 (1st year). However during 2010-11 (2nd year), the prevailing wind directions were north, north-east and east. River Jia-Bharali is situated in north-east direction which was the prevailing wind direction in the winter season of 1st year. Therefore, we can say that the coarse PM during this season was contributed by the sand deposits of Jia-Bharali.

4.1.3. Chemical characterization of PM_{10}

4.1.3.1. Levels of elements

PM_{10} samples were analyzed for eleven elements viz., Mg, K, Ca, Mn, Fe, Cr, Co, Ni, Cu, Cd and Pb. Elemental analysis of Mg, K and Ca were not done in the second year as they were taken for ion analysis in that year. Potassium was maximum and Cd was minimum during the 1st year. Among the analyzed elements Fe was maximum and Cd was minimum during the 2nd year.

As per the World Health Organization [32] air quality guidelines, the carcinogenic pollutants, which are of great concern from the public health point of view are V, Ni, Cd, Pb. Mean annual concentration of Ni were 15.56±13 ngm^{-3} and 18.09±17 ngm^{-3} respectively during 1st and 2nd year respectively, below the national standard of 20 ngm^{-3} [1]. Annual mean Pb concentration (12.8±9 ngm^{-3} and 8.23±7 ngm^{-3} during 1st and 2nd year, respectively) was below the national standard, 50 ngm^{-3} (CPCB, 2009). For Cd, the annual mean (0.90±0.88 ngm^{-3} and 0.92±0.47 ngm^{-3} during 1st and 2nd year respectively) was lower than the European Union target (5 ngm^{-3}, EU Directive 2004/107/CE) [33].

A comparative account of elemental constituents of the present study with studies elsewhere has been put up in Table 4.2. Elements except Mg, K, Mn and Ca of 1st year and all elements of 2nd year were lower than most of the Indian studies. However, in a study from steel city (Rourkella), Kavuri and Paul [37] had reported lower concentration of elements (except Co and Cd) than the present study. Kothai et al. [34] had reported higher concentration of Ca in their study than other study. Sudheer and Rengarajan [36] reported lower Cr, Mn, Fe and Ni concentration in their study from urban Ahmadabad. Except Pb, the elemental concentration of the present study was however, far greater than the reported elemental concentration from other parts of

Table 4.2. Comparative account of elemental concentrations (ngm ^{3}) of the present study with studies elsewhere

	Tezpur [1a]	Tezpur [1b]	Mumbai [2]	Kanpur [3]	Ahmadabad [4]	Rourkella [5]	Leece [6]	Dhaka [7]	Shinjung [8]	Megalopolis [9]	Costa Rica [10]	Zaragoza [11]
Mg	388 51±360		1386			31 08±9				422±290		367±555
K	4588 86±3771		1470			30 94±9				805±670		1010±671
Ca	2563 93±1723		4240							1 16±0 4		1060±2400
Cr	30 81±29	38 64±32	59		11	30 86±9	2 2	20 57	5 4	11 4±12	0 72±0 50	7 70±5
Mn	350 56±277	16 90±11	122	110±50	119	102 14±30	8	32 32	17 5	877±810	27±16	24 7±16
Fe	910 24±1514	784 28±641	4146	1630±67	398		306	1252	541		326±68	666±396
Co	1 31±1	0 94±1	48			17 44±5			0 6	0 93±0 5		0 128±0 331
Ni	15 56±13	18 09±17	25		9 7	0 10±0 40	3		8 4	7 91±3 6	2 22±0 89	0 833±1
Cu	30 34±50	8 05±16	68		28		12 9	15 81	14 6		15 1±6 1	22 8±11
Cd	0 90±1	0 92±0 47			2 8	1 22±0 50						
Pb	12 80±9	8 23±7	289	360±290	228		7 6	400	21 6		14±12	18 7±26

1 Rural receptor site 1a during 2008-09, 1b during 2010-11

2 India (urban residential), Kothai et al [34]

3 India (commercial area), Shukla [35]

4 India (urban), Sudheer and Rengarajan [36]

5 India (steel city), Kavuri and Paul [37]

6 Italy (urban background), Contini et al [17]

7 Bangladesh (urban background), Begum et al [38]

8 Taiwan (urban background), Gugamsetty et al [39]

9 Southern Greece (urban), Manousakas et al [40]

10 Central America (transition between traffic and residential area), Murillo et al. [41]

11 Spain (transition between traffic and residential area), Lo´pez et al [42]

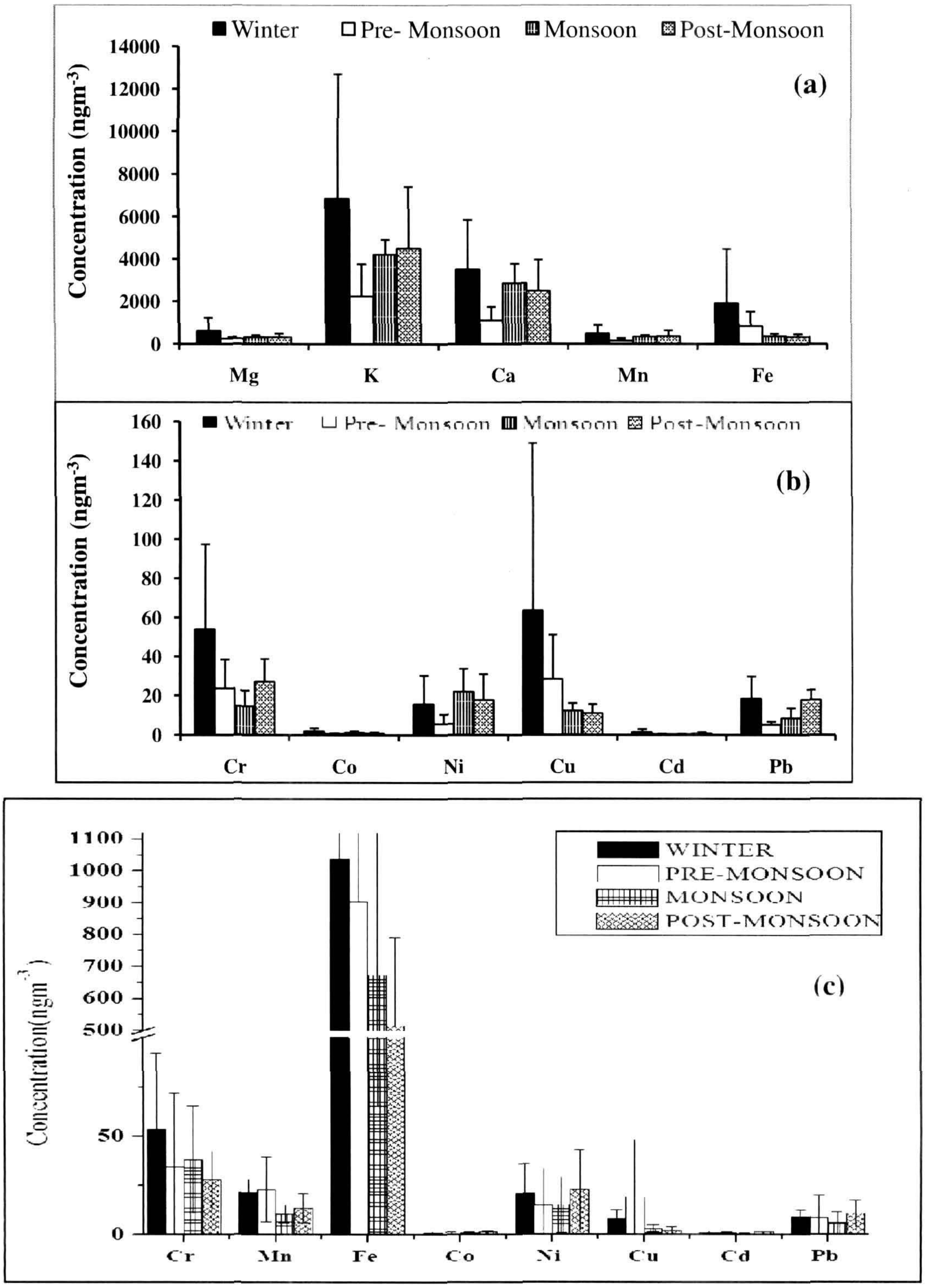


Fig. 4.8. Elemental concentrations of PM_{10}. (a) and (b) elemental concentration during 2008-09 (1st year) ; (c) elemental concentration during 2010-11 (2nd year)

Table 4.3. Seasonal variation of elements over the study period along with the ANOVA. Significance level *<0.05

(a) 2008-09	Winter	Pre-monsoon	Monsoon	Post-monsoon	Annual	F	Sig
Mg	620±604	247 15±574	316 51±468	320 57±415	388 51±360	2 24	0 104
K	6855.86±5849	2241.02±1528	4217 72±709	4520.46±2892	4588 86±3771	2 25	0 103
Ca	3525 25±2333	1110 89±2225	2855 85±1861	2486 90±1729	2563 93±1723	3 38	0 021*
Cr	53 99±43	89 95±114	14 74±126	27 12±110	30 81±29	1 10	0 365
Mn	491 04±405	157 33±371	350 02±301	368 81±280	350 56±277	2 43	0 084
Fe	1906 54±2565	846 93±2449	370 40±2051	335 50±1826	910 24±1514	2 51	0 077
Co	1 98±2	0 78±2	1 37±1	0 95±1	1 31±1	3 15	0 039*
Ni	15 73±15	5 67±13	22 08±13	17 90±13	15 56±13	2 89	0 051
Cu	63 55±86	28 23±82	12 35±68	11 18±61	30 34±50	2 52	0 076
Cd	1 58±1	0 53±1	0 47±1	0 90±1	0 9±1	3 36	0 031*
Pb	18 52±11	5 20±11	8 54±9	18 03±9	12 8±9	7 92	0*

(b) 2010-11	Winter	Pre-monsoon	Monsoon	Post-monsoon	Annual	F	Sig
Cr	53 82±38	34 44±38	38 13±28	27 73±15	38 64±32	1 47	0 24
Mn	21 51±7	23 08±17	10 35±5	13 51±8	16 90±11	5 04	**0.00***
Fe	1037 86±837	904 07±645	674 47±609	515 82±277	784 28±641	1 62	0 20
Co	0 94±0 65	0 77±1	0 84±0 36	1 29±1	0 94±0 58	2 03	0 12
Ni	21 05±15	14 66±19	15 09±14	23 01±21	18 09±17	0 76,	0 53
Cu	7 70±5	19 33±29	3 02±2	1 94±2	8 05±16	3 71	**0.02***
Cd	0 99±1	0 82±0 42	0 75±0 36	1 20±0 42	0 92±0 47	2 52	0 07
Pb	8 87±3	8 60±11	5 66±6	10 60±7	8 23±7	1 02	0 39

the world [17,38-42]]. Contini et al. [17] had reported Pb concentration lower than the present study from Leece, Italy.

During the 1st year, except Cr and Ni, all the elements were showing higher concentration during the winter (Fig. 4.8a & 4.8b). In winter months dry weather and building of inversion layer helps to accumulate pollutants in the atmosphere. Maximum concentration of Cr and Ni was found in pre-monsoon and monsoon season respectively. To see the seasonal variation of elements one way ANOVA was done which showed significant seasonal variation for Ca, Co, Cd and Pb at 95% of significance level during 1st year (Table 4.3a). Seasonal variation of elements of PM_{10} was not very distinct in the 2nd year (Fig. 4.8c). Chromium and Fe was maximum during the winter. Mn and Cu showed maximum concentration during pre-monsoon season. Co, Ni, Cd and Pb was maximum during post-monsoon season. Overall Fe was higher than other elements and Co and Cd were minimum. Mn and Cu of 2nd year PM_{10} showed significant seasonal variation at 95% of significance level (Table 4.3b).

4.1.3.2. Enrichment Factors (EF)

Researchers used EF to see the anthropogenic input to elemental concentration of PM [6,43,44]. EF values near to unity signify crust predominance. Earlier studies [45-47] suggest that an EF of more than one for an element can be attributed to anthropogenic activities. Rahn [48] suggested classification criteria of EF, according to which if EF <7, then air particulate is of crustal origin and if EF>10, then it is of the anthropogenic one. Again, other researchers had used a cut off value of 10 to see the non-crustal or anthropogenic inputs [49,50]. EF, however, is largely dependent on particle size [51-53].

EF is calculated taking Fe as reference element as per Eq. 1.

$$EF = (E/R)_{PM10}/(E/R)_{crust} \qquad \text{Eq. 1}$$

Where, E indicates the elemental concentration and R indicates the reference elements in PM_{10} and crust. Concentration of Fe was considered as the reference. The crustal data are taken from the compiled list of abundance of elements in the earth's crust presented by Lee [54].

EF of the elements of the present study is given in Fig. 4.9. EF value showed similar results for both the year. During 1st year Ca, Mg, Mn, Co and Cu were not enriched. Moderately enriched elements were K, Cr, Ni and Pb showing EF below 100. Cd was highly enriched for both the year. Cr, Ni and Pb were enriched to some extend during 2nd year.

Sharma and Srinivas [55] had reported EF values close to one for K, Ca, Mn and Fe, and the EFs were quite high in case of Zn and Pb, which indicate their emission from anthropogenic sources in a study from Chandigarh, India. Khillare and Sarkar [6] had reported Mn as non-enriched elements ; Cr, Cu, Ni and Pb as moderately enriched with EF <100 and Cu as highly enriched with EF>100 in a study from Delhi, India. Bilos et al. [56] in a study in La Plata city of Argentina had found higher enrichment for Pb, Zn, Cd and Cu, whereas for Mn, Cr, Ni, Ca and Mg EFs were lower, compatible with prevailing natural sources.

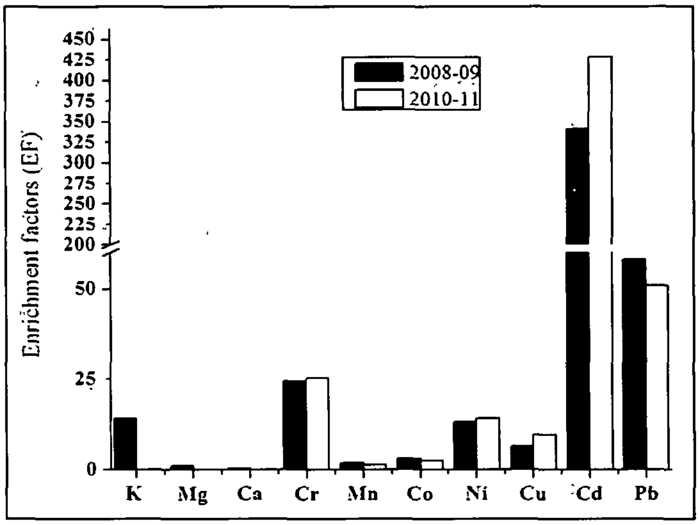


Fig. 4.9. EF of the elements during 2008-09 (1st year) and 2010-11 (2nd year)

4.1.4. Water soluble ions of PM_{10}

4.1.4.1. Levels of ions

The 2nd year samples were analyzed for water soluble ions. Relative contribution of ions was given in Fig. 4.10 for the whole year. Among the analyzed ions SO_4^{2-} was maximum and F^- was minimum. Most of the ions were maximum during the winter and minimum during the monsoon. Overall, in all seasons anions were contributing more to ionic load of PM_{10}. The annual mean trend of ions was $SO_4^{2-}>Cl^->Na^+>NO_3^- >Ca^{2+}>K^+>NH_4^+>Mg^{2+}>F^-$.

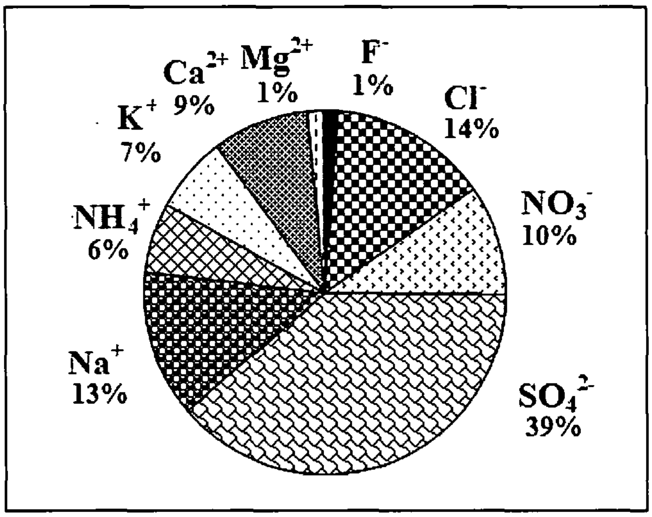


Fig. 4.10. Relative contribution of different ions during 2010-11

Table 4.4 shows the present study ionic concentration along with the reported studies from India and abroad. Most of the ions of the present study were lower than other Indian studies [57-60], Bay of Bengal [61], Highway and urban sites of China [62,63]. Urban residential area of Korea [64] was also higher as compared to the present study. However, most ions were higher than that of Mt. Moriyoshi of Japan [65] and urban site of Spain [66]. Among the studies it was interesting to see that ions were many times higher during October, 2008 to September, 2009 than that of July 2009 to June 2010 as reported by Deshmukh et al. [58,59]. Both the studies were conducted at same site of Raipur, India. This showed that within a year of time, concentration could be differed significantly probably due to the meteorological condition of a site.

Concentrations of ions in different seasons is shown in Fig. 4.11. Except F^- and Na^+, other ions were maximum during the winter. Secondary ions viz., NO_3^-, SO_4^{2-} and NH_4^+ showed maximum concentration in winter followed by pre-monsoon, post-monsoon and monsoon season. K^+ also showed similar trend as that of secondary ions. It is noticeable that Na^+, a crustal component was maximum during pre-monsoon season. Probable reason may be the uplifting of crustal dust due to prevailing high wind speed in that period. Also, K^+, Ca^{2+} and Mg^{2+} were almost same in winter and pre-monsoon season. F^- was maximum in post-monsoon season and it was in very low amount in other seasons. All except Ca^{2+} and Mg^{2+}, showed significant seasonal variation at 95% level of significance when tested by one way ANOVA (Table 4.5).

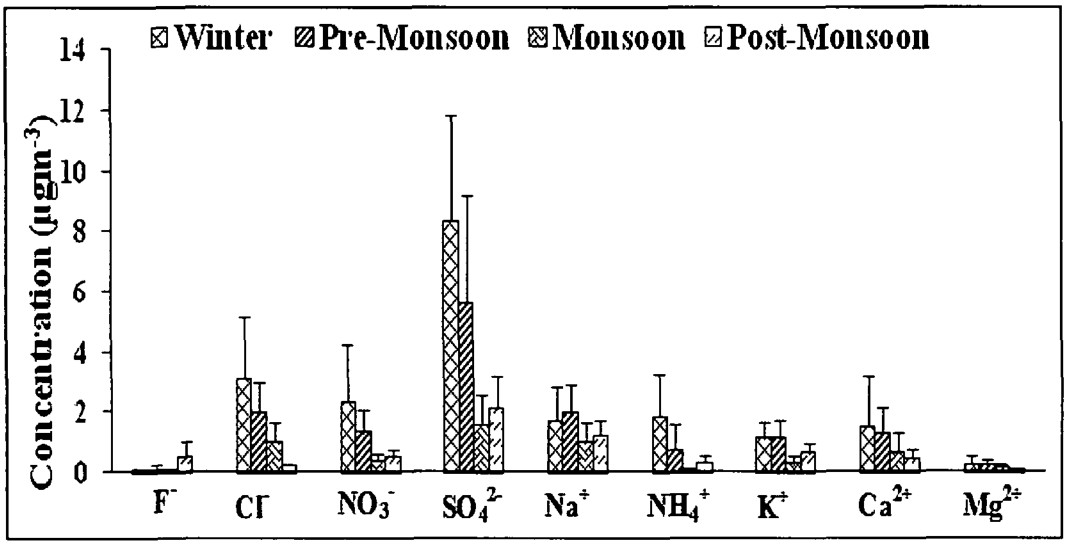


Fig. 4.11. Concentration trends of ions in different seasons of 2010-11

Table 4.4. Comparative account of ions of PM_{10} of the present study with studies elsewhere

Site	Time	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Present study	Dec, 2008-Nov, 2009	0.14±0.32	1.57±1.52	1.09±1.26	4.30±3.71	1.46±0.91	0.69±1.05	0.76±0.58	0.17±0.19	0.96±1.05
Kanpur[2]	19-30 Oct, 2008 (Day sample)	-	0.14±0.09	5.4±2.5	16.8±9.4	0.5±0.2	5.4±1.8	2.6±1.9	0.3±0.1	3.1±1
Kanpur[3]	19-30 Oct, 2008 (Night sample)	-	1.8±2.1	12.9±4.8	15.7±6.2	0.6±0.2	5.5±1.9	3±0.9	0.3±0.1	3±0.9
Raipur[4]	Oct ,2008-Sept, 2009	-	18.95	35.07	54.64	9.49	19.59	13.02	4.89	59.44
Raipur[5]	July, 2009-June, 2010	-	3.4±2.9	5.5±4.4	9.9±4.4	1.7±1.4	2.9±2	0.7±0.5	0.8±0.7	3±1.1
Agra[6]	Jan-Dec, 2007	1.10±1.39	5.36±5.73	4.69±3.66	6.93±7.93	3.73±3.95	4.66±5.13	4.42±5.58	0.64±0.82	2.71±2.75
Bay of Bengal[7]	Dec 2008-Jan, 2009	0.15±0.07	2.48±0.78	1.92±1.75	8.68±3.75	4.85±0.96	1.96±1.66	1.51±0.92	0.28±0.10	1.18±0.49
Taiwan[8]	March 4-april 2, 2006	-	2.97±1.51	17.28±5.68	15.59±4.79	1.24±0.68	9.45±3.18	0.61±0.35	0.34±.19	1.38±1
Shanghai[9]	2009	-	3.53	32.93	28.71	0.6	19.31	3	0.23	2.97
Ulsan[10]	April, 2008-Jan, 2009	-	1.1	4.4	11	2.9	3.2	0.5	0.4	0.5
Mt. Moriyoshi[11]	Summer, 2004	0.074	0.197	1.122	5.174	0.148	1.666	0.029	0.019	0.039
Elche[12]	Oct , 2008-Oct, 2009	-	0.71	3.06	3.11	1	0.52	0.29	0.16	1.68

[1] Rural receptor site

[2] India (Urban); Ram and Sarin [57]

[3] India (urban); Ram and Sarin [57]

[4] India (urban, industrial); Deshmukh et al. [58]

[5] India (urban, industrial); Deshmukh et al. [59]

[6] India(urban); Singh et al. [60]

[7] Bay of Bengal (Coastal); Sharma et al. [61]

[8] China (highway); Fang et al. [62]

[9] China (urban); Du et al. [63]

[10] Korea (urban, residential); Lee and Hieu [64]

[11] Japan (mountain area), Saitoh et al. [65]

[12] Spain (urban); Galindo et al. [66]

Table 4.5. Seasonal variation of ions over the study period along with the ANOVA. Significance level *<0.05

	Winter	**Pre-Monsoon**	**Monsoon**	**Post-Monsoon**	**Whole year**	**F value**	**Sig**
F^-	0.03±0.03	0.08±0.16	0.02±0.03	0.47±1	0.14±0.32	7.62	**0.00**
Cl^-	3.08±2	1.94±1	1.02±1	0.24±0.003	1.57±2	13.28	**0.00**
NO_3^-	2.35±2	1.31±1	0.36±0.26	0.47±0.24	1.09±1	10.37	**0.00**
SO_4^{2-}	8.31±3.	5.62±4	1.56±1	2.11±1	4.30±4	19.28	**0.00**
Na^+	1.70±1	1.96±1	1.01±1	1.23±0.49	1.46±1	3.53	**0.02**
NH_4^+	1.82±1	0.73±1	0.05±0.04	0.29±0.21	0.69±1	11.40	**0.00**
K^+	1.11±1	1.10±1	0.27±0.24	0.62±0.31	0.76±1	10.63	**0.00**
Mg^{2+}	0.25±2	0.22±0.03	0.12±0.11	0.07±0.06	0.17±0.19	2.89	0.07
Ca^{2+}	1.47±2	1.28±1	0.66±1	0.45±0.31	0.96±1	2.52	0.05

4.1.4.2. Ion balance

The ion balance is a good and significant indicator to study the acidity of aerosol [67,68]. Ion balance is determined by both anion equivalents (AE) and cation equivalents (CE) calculated with the following equations:

$$AE= [F^-]/19 + [Cl^-]/35.5 + [NO_3^-]/62 + [SO_4^{2-}]/48 \qquad \text{Eq. 2}$$

$$CE= [Na^+]/23 + [NH_4^+]/18 + [K^+]/39 + [Mg^{2+}]/12 + [Ca^{2+}]/20 \qquad \text{Eq. 3}$$

Here the respective mass of the ions were divided by their equivalent mass.

The AE/CE ratio of 1 reflects that all the significant ions have been quantified. According to the electro neutrality of solutions, AE must be equal to CE [69]. AE/CE values were higher than 1 in winter (1.43±1.08), pre-monsoon (1.16±0.89) and monsoon (1.13±0.86) seasons. It was found to be less than 1 in the post-monsoon (0.86±0.49). The annual mean of AE/CE was 1.16±0.86 which suggest the acidic nature of aerosols. The cation deficient condition was also proved by linear relationship between cation equivalents and anion equivalents which give a R^2 value of 0.81 (Fig. 4.12). Xu et al. [68] had said that H^+ which was not calculated was the probable reason for high AE/CE ratios in their study.

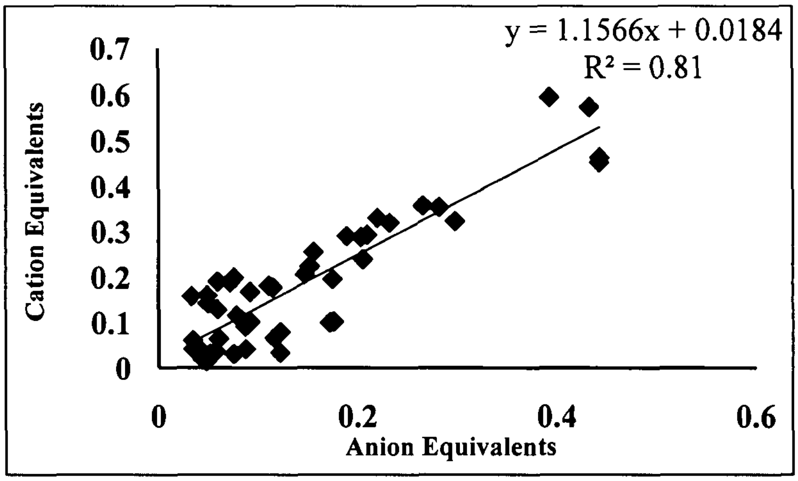


Fig. 4.12. Correlation between cation equivalents and anion equivalents during 2010-11

4.1.5. Carbon in PM_{10}

PM_{10} samples of the 2nd year were also analyzed for different carbon fractions viz., TC, EC, OC and WSOC.

4.1.5.1. Levels of carbon

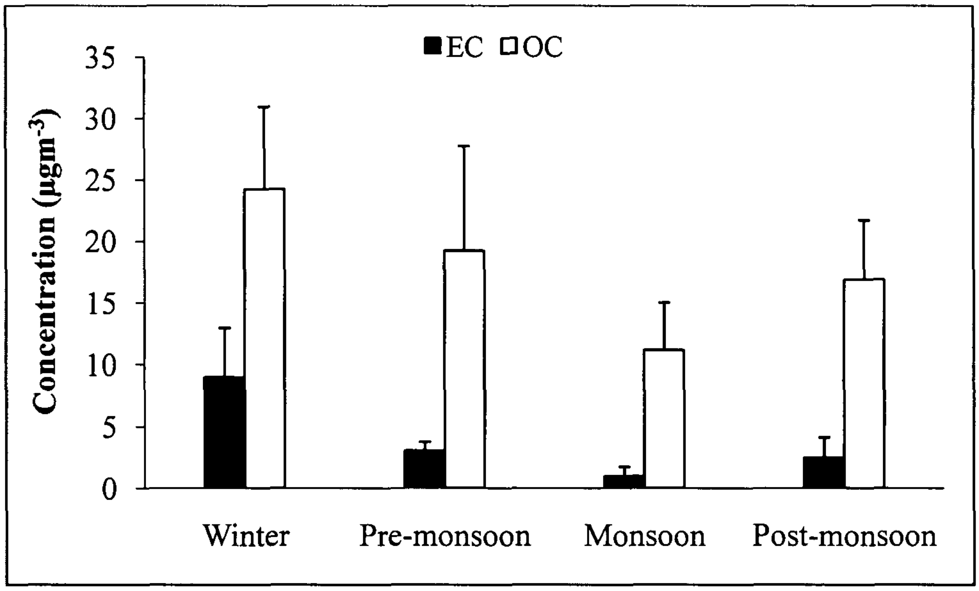


Fig. 4.13. EC and OC in different seasons during 2010-11

Carbon was maximum during the winter and minimum during the monsoon. Carbon had contributed 43.91% of PM_{10} mass. EC and OC were given in Fig. 4.13. TC concentration varied between 2.52 μgm^{-3} and 51.05 μgm^{-3} with the annual mean of

21.06±10 μgm^{-3}. EC concentration varied between 0.04 μgm^{-3} and 15.40 μgm^{-3} (avg: 3.68±4 μgm^{-3}; 7.67% of PM_{10} mass), whereas OC concentration varied between 2.48 and 39.08 (avg: 17.42±8 μgm^{-3}; 36.32% of PM_{10} mass). TC, EC and OC followed same trend with maximum concentration in the winter followed by pre-monsoon, post-monsoon and monsoon seasons (Table 4.6). During winter months biomass burning is a very common practice in this region. Also, people of this region use biomass for household cooking.

4.1.5.2. Secondary organic carbon (SOC)

SOC is a part of Secondary Organic Aerosols (SOA). Volatile organic reactive gases (VORGs) and oxidizing agents; and the photochemical activity are the two main factors affecting SOA formation [70]. The oxidizing agents can be ozone (O_3), hydroxyl radicals (OH) or oxides of nitrogen (mainly free radicals) while source of photochemical activity is mainly the solar radiation (particularly UV region). Chang and Lee [71] had reported that SOA formation shows a diurnal pattern, increases with O_3 concentration and photochemical activity, and reaches to the maximum when O_3 concentration exceeds 120 ppbv. SOA formation also shows a seasonal pattern with higher SOA during summer and lower during winter months.

Table 4.6. Carbon fractions (μgm^{-3}) of PM_{10} during different seasons of 2010-11

	Winter	**Pre-monsoon**	**Monsoon**	**Post-monsoon**	**Annual**
TC	33.20±8	22.28±9	12.11±4	19.20±6	21.06±10
EC	8.98±4	3.05±1	0.96±1	2.51±2	3.68±4
OC	24.22±7	19.23±9	11.15±4	16.92±5	17.42±8
WSOC	19.29±10	11.45±5	5.17±2	9.71±3	10.98±8
SOC	16.27±7	16.53±9	10.30±4	14.70±5	14.15±7
WSOC/OC	0.84±1	0.69±0.47	0.46±0.15	0.57±0.07	0.63±0.37
SOC/OC(%)	64.71±23	82.35±13	92.68±5	86.18±10	81.23±17

SOC was calculated for the collected samples. SOC was calculated according to the EC tracer method after Častro et al. [72]. Considering the primary OC/EC ratio to be relatively constant in all samples SOC can be calculated using the following equation-

$$OC_{sec} = (OC)_{total} - (OC/EC)_{min} \times EC \qquad \text{Eq. 4}$$

The minimum value of OC/EC ratios can be used to estimate the amount of SOC in the atmospheric aerosol for a specific region of interest [72]. $(OC/EC)_{min}$ was 0.89, 1.47, 4.61 and 2.67 during winter, pre-monsoon, monsoon and post-monsoon season respectively. Calculated SOC was found to be 16.27±7 μgm^{-3}, 16.53±9 μgm^{-3}, 10.30±4 μgm^{-3} and 14.70±5 μgm^{-3}, respectively during winter, pre-monsoon, monsoon and post-monsoon season respectively. The annual mean was 14.15±7 with 81.23±17% contribution to OC. The percent seasonal contribution of SOC to OC were 64.71±23, 82.35±13, 92.68±5 and 86.18±10 during winter, pre-monsoon, monsoon and post-monsoon season, respectively. Satsangi et al. [73] had reported SOC to be 49% to 55% of OC at Dayalbagh, India. They found high seasonal averaged values of SOC during summer and post monsoon which were greater than the annual average.

4.1.5.3. Water soluble organic carbon (WSOC)

Atmospheric particles can act as Cloud Condensation Nuclei (CCN). WSOC enhances the CCN activity of a particle [74-76]. WSOC concentration varied between 1.28 and 40.88 μgm^{-3} with annual mean of 10.98±8 μgm^{-3}. Seasonal concentration trend was winter>pre-monsoon>post-monsoon>monsoon (Table 4.6).

Annual WSOC/OC ratio was 0.63±0.37. It indicates that a significant portion of OC was water soluble. Timonen et al. [77] had reported a value of 0.54 for WSOC/OC of PM1 in Helsinki, Finland. They had reported slightly higher contribution of WSOC to OC during biomass burning episode as compared with other times. Rajput et al. [78] had also reported WSOC/OC ratio more than 0.5 in NE-Himalaya, a high altitude site where they had attributed biomass burning as the sources of carbonaceous aerosol. The high value of WSOC/OC in this study suggest CCN activity of atmospheric particles along with biomass burning as the dominant sources of PM_{10} in this region. Higher WSOC to OC contribution suggest presence of aged aerosols [70,79].

4.1.6. Characteristics ratios of PM_{10} constituents

4.1.6.1. Sea water ratio

Sea is an important source of some water soluble ions viz., Na^+, K^+, Mg^{2+}, Ca^{2+} and SO_4^{2-}. In order to find contribution of sea salt, ratios of these ions in respect to Na^+ were calculated and compared with sea water ratio [80]. These ratios (Table 4.7) did not agree with sea water ratios nullifying the contribution from the sea. Annual mean of Cl^- $/Na^+$, K^+/Na^+, Ca^{2+}/Na^+ and SO_4^{2-}/Na^+ were higher than sea water ratio. Higher ratios indicate influence of other stronger sources rather than sea salt. However, Mg^{2+}/Na^+ was lower than sea water ratio.

4.1.6.2. NO_3^-/ SO_4^{2-} ratio

NO_3^-/ SO_4^{2-} was used to have idea about the dominance of stationary vs. mobile sources [81]. Lower value of this ratio suggests dominance of stationary sources over mobile sources. We have found the ratio to be 0.29±0.16, 0.28±0.16, 0.23±0.10 and 0.28±0.15 during winter, pre-monsoon, monsoon and post-monsoon season respectively (Table 4.7). The annual mean was 0.27±0.14 for NO_3^-/SO_4^{2-} ratio. This indicates contribution of stationary sources to NO_3^- and SO_4^{2-} of the present study.

Table 4.7. Ionic ratios of PM_{10}

	Winter	Pre-Monsoon	Monsoon	Post-Monsoon	Annual	Sea water ratio [80]
Cl^-/Na^+	3.89±5.89	1.42±1.61	1.55±1.67	0.30±0.31	1.82±3.26	1.16
K^+/Na^+	0.74±0.26	0.53±0.23	0.25±0.14	0.57±0.11	0.50±0.27	0.0218
Mg^{2+}/Na^+	0.19±0.31	0.11±0.08	0.10±0.05	0.08±0.07	0.12±0.16	0.227
Ca^{2+}/Na^+	1.04±1.39	0.63±0.39	0.50±0 30	0.46±0.39	0.65±0.75	0.0439
SO_4^{2-}/Na^+	8.82±13.24	2.98±1.21	1.88±1.02	2.05±1.21	3.83±6.89	0.121
NO^{3-}/SO_4^{2-}	0.29±0.16	0.28±0.16	0.23±0.10	0.28±0.15	0.27±0.14	

4.1.6.3. Some more vital ratios

Researchers had used EC/TC, OC/EC, K^+/OC and K^+/EC ratios to characterize the emission sources, biomass burning vis-a-vis fossil fuel. Potassium is a tracer of biomass burning and OC and EC are released by biomass burning along with fossil fuel and vehicular emission.

Relatively high K^+/EC ratios had been reported as an indicator of biomass burning (range: 0.21-0.46) and low ratios for fossil-fuel combustion emissions (range: 0.025-0.09). We had found 0.45±0.71, 0.04±0.03, 0.14±0.08 and 7.58±4.91 for K^+/EC, K^+/OC, EC/TC and OC/EC ratios respectively in this study. The ratios of the present study agree with other studies (Table 4.8) which reported biomass burning as the dominant source of carbon. OC/EC ratio was also used to know about secondary aerosol formation. OC/EC ratio greater than 2 suggests secondary organic aerosol formation in addition to primary emission sources [73,87,88]. The present study. OC/EC ratio was always greater than 2 indicating presence of secondary organic formation which was quite obvious from the SOC concentration in different seasons of the year.

Table 4.8. Comparative account of the ratios of the present study with studies elsewhere

Sampling site	References	K^+/EC	K^+/OC	EC/TC	OC/EC	Emission sources
Tezpur		0.45±0.71	0.04±0.03	0.14±0.08	7.58±4.91	
Kanpur, India	Ram and Sarin [57]	0.28±0.10	0.06±0.02		6.0±1.3	Biomass Burning
Kanpur, India	Ram and Sarin [70]	0.42±0.18	0.04±0.01		6.2±3.7	Biomass Burning
Allahabad, India	Ram and Sarin [70]	0.44±0.11	0.05±0.01		8.1±1.7	Biomass Burning
Hisar, India	Rengarajan et al. [82]	0.64±0.19	0.08±0.02		8.5±2.2	Biomass Burning
Agra, India	Satsangi et al. [73]	0.39±0.25	0.08±0.02		8.7±6.5	Biomass Burning
	Echaler et al. [83]		0.08-0.10			Savanna Burning
Cerrado fire, Brazil	Yamasoe et al. [84]	0.22				Cerrado fire
Tropical forest fire	Yamasoe et al. [84]	0.11				Tropical forest fire
Brazil	Ferek et al. [85]	0.52±0.11		0.10±0.03		Biomass Burning
Ivory coast, Africa	Cachier [86]			0.12±0.07		Biomass burning

4.1.7. Source characterization

Source identification of two years was done separately. The first year's elemental data was examined and conventionally tried to trace the sources by looking at the correlations between the elements. A more elaborate source apportionment was done with the second year's data. It was possible because more analytical attributes were available- elements, ions and carbon. As evident that two sampling years had different meteorological conditions as well as aerosol characteristics, it was decided to treat the two periods separately.

4.1.7.1. Source identification during 1st year

Pearson's correlation was carried out on analyzed elements during 2008-09 (1st year) to have an idea about the contributing sources and similarity in their chemical behavior (Table 4.9). Good correlation was observed between elemental pair Mg and Fe ($r=0.85$; $p<0.01$), Mg and Co ($r=0.83$; $p<0.01$), Ca and Mn ($r=0.85$; $p<0.01$), Fe and Co ($r=0.80$; $p<0.01$) indicating their probable crustal origin.

Good correlation between K and Ca ($r=0.86$; $p<0.01$) and K and Mn ($r=0.98$; $p<0.01$) suggests biomass and soil as the soures of potassium. K is an important products of biomass burning [84,89], vegetation burning [90], and emission from vegetation [91] along with soil [92,93]. The sampling site was located in a rural area where use of biomass as a fuel in the kitchens is a common practice.

Fe and Cu showed perfect correlation ($r=1$; $p<0.01$). Good correlation between elemental pair K and Ni ($r=0.65$; $p<0.01$), K and Cr ($r=0.52$; $p<0.01$), Mg and Cu ($r=0.85$;

$p<0.01$), Ca and Ni ($r=0.85$; $p<0.01$), Co and Cu ($r=0.80$; $p<0.01$) and Mn and Ni ($r=0.66$; $p<0.01$) were also observed. These correlations indicate resuspended dust as one of the contributing sources of these elements.

Pb was moderately correlated with Mg ($r=0.47$; $p<0.01$), Cr ($r=0.55$; $p<0.01$) and Co ($r=0.45$; $p<0.05$) which indicates its contribution both from resuspended soil and vehicular emission. Vehicular Pb has been phased out in India over a decade ago.

Table 4.9. Pearson's correlations of elemental concentration of PM_{10} during 2008-09

	Mg	K	Ca	Cr	Mn	Fe	Co	Ni	Cu	Cd	Pb
Mg	1										
K	0.15	1									
Ca	0.41*	0.86**	1								
Cr	0.07	0.52**	0.38*	1							
Mn	0.18	0.98**	0.85**	0.48**	1						
Fe	0.85**	-0.09	0.14	0.07	-0.12	1					
Co	0.83**	0.06	0.40*	0.19	0.05	0.80**	1				
Ni	0.07	0.65**	0.85**	0.20	0.66**	-0.22	0.19	1			
Cu	0.85**	-0.09	0.14	0.07	-0.12	1.00**	0.80**	-0.22	1		
Cd	0.16	0.45**	0.41*	0.30	0.42*	0.01	0.09	0.25	0.01	1	
Pb	0.47**	0.32	0.32	0.55**	0.32	0.35*	0.45**	0.12	0.35*	0.40*	1

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

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

4.1.7.2. Source identification during 2nd year

4.1.7.2.1. Correlation matrix

Pearson's correlation was established between different chemical species of 2010-11 (Table 4.10). Good correlation was found between Cr and Fe ($r=0.78$), Cr and Ni ($r=0.69$), Fe and Ni ($r=0.61$), Co and Ni ($r=0.65$), Co and Cd ($r=0.73$), Cu and Pb ($r=0.61$), Mn and Ni ($r=0.58$) at a significant level of $p<0.01$. These correlations indicate vehicular emission as the possible sources of these elements.

Mn was showing good correlation with Fe ($r=0.66$), which are crustal elements. Good correlations were found between Cl^- with Ca^{2+} ($r=0.59$) and Mg^{2+} ($r=0.56$), Na^+ with K^+ ($r=0.74$), Ca^{2+} ($r=0.81$) and Mg^{2+} ($r=0.75$) and Ca^{2+} with Mg^{2+} ($r=0.97$) at a significant level of $p<0.01$. Researchers had attributed soil as the natural sources of Ca^{2+}

Table 4.10. Pearson's correlations of different chemical species of PM_{10} during 2010-11

	Cr	Mn	Fe	Co	Ni	Cu	Cd	Pb	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	TC	EC	OC	WSOC
Cr	1 00																				
Mn	48**	1 00																			
Fe	78**	66**	1 00																		
Co	46**	36**	29*	1 00																	
Ni	69**	58**	61**	65**	1 00																
Cu	0 13	34*	0 26	-0 15	0 03	1 00															
Cd	0 21	0 23	-0 06	73**	33*	-0 05	1 00														
Pb	0 10	0 26	0 08	0 22	0 14	61**	0 22	1 00													
F^-	0 01	0 01	-0 04	0 24	0 17	-0 08	0 08	0 04	1 00												
Cl^-	0 20	326*	0 12	0 00	0 12	0 02	0 10	-0 03	- 283*	1 00											
NO_3^-	0 08	41**	0 20	-0 14	-0 05	0 21	-0 03	0 02	-0 06	0 19	1 00										
SO_4^{2-}	0 26	60**	32*	-0 01	0 07	0 27	0 11	0 13	-0 07	49**	772**	1 00									
Na^+	0 11	39**	0 18	-0 01	-0 07	0 14	0 05	0 06	-0 06	42**	0 27	63**	1 00								
NH_4^+	0 16	43**	0 21	-0 07	0 02	0 09	0 03	-0 03	-0 05	0 26	92**	82**	36**	1 00							
K^+	0 11	51**	0 27	-0 04	-0 06	31*	0 03	0 13	-0 03	0 25	68**	80**	74**	73**	1 00						
Ca^{2+}	0 11	0 21	0 11	0 08	-0 08	-0 04	0 21	-0 03	-0 17	59**	0 08	50**	81**	0 18	44**	1 00					
Mg^{2+}	0 17	0 18	0 11	0 17	-0 05	-0 05	28*	-0 02	-0 18	56**	0 04	45**	75**	0 14	39**	97**	1 00				
TC	0 09	43**	0 13	-0 06	0 01	0 27	0 11	29*	0 06	36**	77**	81**	29*	77**	64**	0 16	0 12	1 00			
EC	0 14	0 25	0 08	0 04	-0 01	0 05	0 17	0 06	-0 04	49**	68**	75**	31*	71**	51**	35*	37**	77**	1 00		
OC	0 05	45**	0 13	-0 09	0 01	32*	0 07	36**	0 10	0 24	69**	71**	0 24	68**	60**	0 05	-0 02	95**	55**	1 00	
WSOC	0 20	34*	0 16	0 03	0 00	0 21	0 16	0 14	0 06	36**	78**	86**	55**	79**	72**	45**	42**	78**	74**	68**	1 00

** Correlation is significant at the 0 01 level (2-tailed)

* Correlation is significant at the 0 05 level (2-tailed)

along with SO_4^{2-}, Cl^-, Na^+ and K^+ [92,93]. This indicates soil as the sources of these chemical species.

NO_3^- was well correlated with SO_4^{2-} (r=0.77), which tell about their similar chemistry and sources. NO_3^- also showed good correlation with NH_4^+ (r=0.92) and K^+ (r=0.68) at a significant level of $p<0.01$. This suggests the role of NH_4^+ and K^+ in neutralizing NO_3^- in the atmosphere. SO_4^{2-} was showing good correlation with Na^+ (r = 0.63), NH_4^+ (r=0.82), K^+ (r=0.80) and Ca^{2+} (r=0.50) at a significant level of $p< 0.01$, which indicates neutralization of SO_4^{2-} by these cations and also contribution of soil to sulphate loading.

Strong correlation between NH_4^+ and K^+ (r=0.73), NH_4^+ with all carbon fractions and K^+ with all carbon fractions indicate their sources as biomass burning. K^+ is a well known tracers of biomass burning [84,89].

Strong correlation was found between different fractions of carbon. This indicates cogenetic sources of different fractions of carbon and as reflected by earlier discussion of carbon, the source is biomass burning. Again, OC is well correlated with WSOC (r = 0.68) at a significant level of $p<0.01$ which also suggests biomass burning as the sources of carbon.

4.1.7.2.2. Principal Component Analysis-Multiple Linear Regression

Principal component analysis-Mutiple Linear Regression was done on normalized data to see the contributing sources for the monitoring period. By extracting the eigenvalues and eigenvectors from the correlation matrix, principal factors with eigenvalues >1 were chosen for Varimax rotation with Keiser Normalization. The initial eigenvalues extracted were 'cleaned up' by means of Varimax rotation. Multiple linear regressions was done according to Larsen and Backer [94]. PC scores were obtained by running PCA on normalized data which were then regressed against the total chemical species. The coefficient obtained by this was then used to convert the PC scores into total source contribution for the entire monitoring period and for each sampling day.

PCA revealed 5 component explaining 79% of variance (Table 4.11). PC1 explained 29.5% of variance and was loaded with secondary particulates viz., NO_3^-, SO_4^{2-} and NH_4^+ and with K^+, TC, EC, OC and WSOC. This indicates biomass burning as the principal source of particulates. PC2 explained 16.2% of variance and was loaded with Na^+, Mg^{2+} and Ca^{2+} and moderately with Cl^-, SO_4^{2-} and K^+ indicating soil as the possible source of this chemical species. High loading of Cr, Mn, Fe, Ni and moderate loading of Co was found in PC3 explaining 14.7% of variance. This indicates coal burning as the possible source. 9.8% of variance was explained by PC4 which was loaded with Co, Cd and Ni and PC5 was loaded with Cu and Pb explaining 8.9% of variance. Factors 4 and 5 were indicative of vehicular emission.

Table 4.11. Principal Component Analysis (PCA) of chemical species of PM_{10} during 2010-11

	PC1	**PC2**	**PC3**	**PC4**	**PC5**
Cr	0.06	0.06	**0.86**	0.17	-0.02
Mn	0.38	0.19	**0.70**	0.10	0.28
Fe	0.10	0.09	**0.92**	-0.15	0.09
Co	-0.10	0.06	**0.44**	**0.80**	-0.02
Ni	-0.04	-0.14	**0.82**	**0.40**	0.00
Cu	0.15	0.01	0.16	-0.21	**0.86**
Cd	0.06	0.13	0.06	**0.89**	0.07
Pb	0.08	-0.03	0.03	0.28	**0.88**
F^-	0.05	-0.08	0.01	0.22	-0.06
Cl^-	0.29	**0.44**	0.12	0.15	-0.07
NO_3^-	**0.92**	-0.01	0.09	-0.16	-0.01
SO_4^{2-}	**0.84**	**0.41**	0.21	-0.02	0.11
Na^+	0.28	**0.90**	0.09	-0.12	0.10
NH_4^+	**0.92**	0.09	0.14	-0.09	-0.11
K^+	**0.69**	**0.50**	0.14	-0.19	0.19
Mg^{2+}	0.08	**0.92**	0.02	0.21	-0.08
Ca^{2+}	0.12	**0.94**	0.01	0.12	-0.06
TC	**0.93**	0.02	0.00	0.09	0.22
EC	**0.80**	0.18	-0.02	0.21	-0.11
OC	**0.85**	-0.06	0.01	0.03	0.34
WSOC	**0.84**	0.36	0.05	0.08	0.05
Total	6.20	3.41	3.09	2.05	1.86
% of Variance	29.52	16.25	14.71	9.78	8.87
Cumulative %	29.52	45.76	60.47	70.26	79.13
Possible sources*	BB	Soil	Coal	VE	VE

* BB-biomass burning; VE-vehicular emission

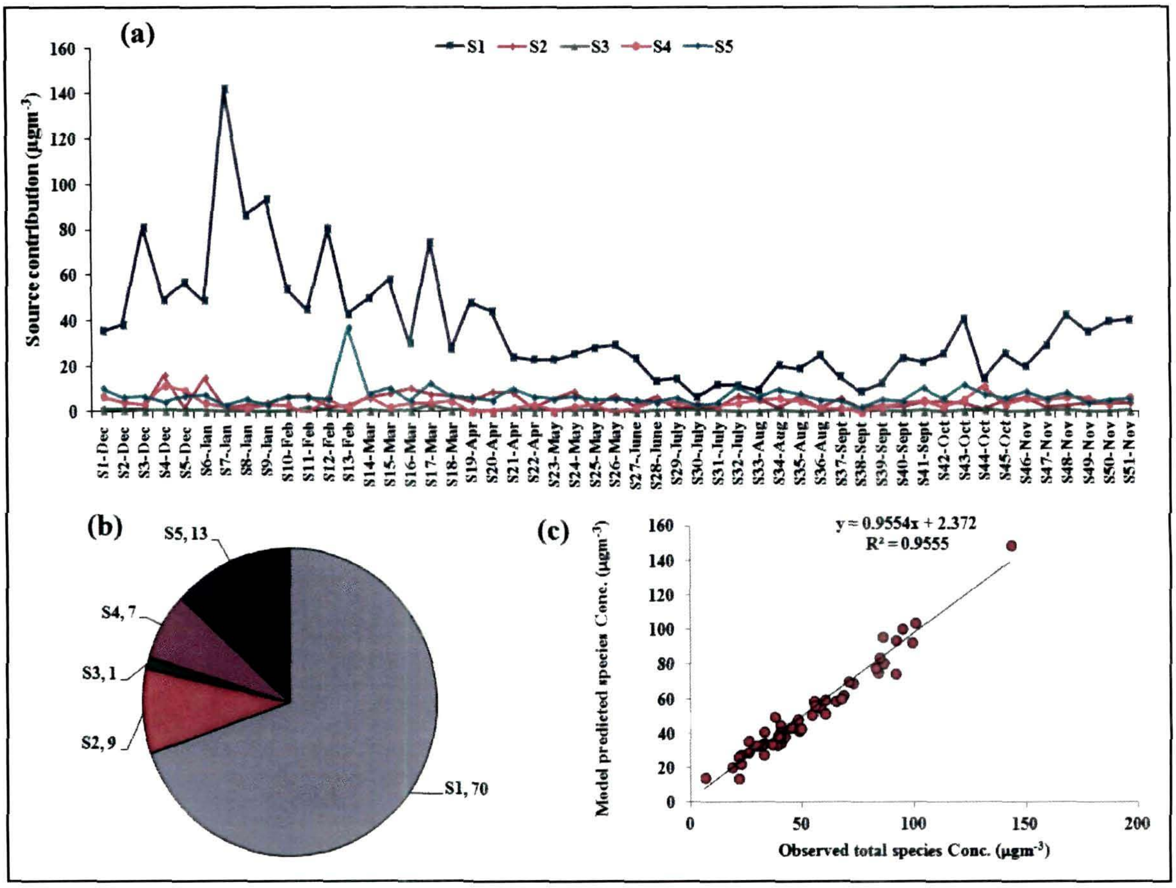


Fig. 4.14. PCA-MLR results. (a) time evolved source contribution to different samples (ngm^{-3}) (b) mean annual percent contribution by different sources (c) linear correlation between observed and model predicted total species concentration. Here, S1, S2, S3, S4 and S5 are indicating to Source 1 (biomass burning), Source 2 (soil), Source 3 (coal), Source 4 (vehicular emission) and Soutrce 5(vehicular emission), respectively.

PCA-MLR results are put up in Fig 4.14. The contribution of sources to the chemical species of different samples was shown in Fig. 4.14a. Source 1 was very strong during the winter months. The influence of other sources during different period of the year was almost similar. The annual contribution of the sources (Fig. 4.14b) shows that Source 1 was dominant with 70% contribution to the analyzed species followed by source 5, 2, 4 and 3 respectively. The observed and model predicted concentration showed very good agreement with R^2 value of 0.96 (Fig. 4.14c).

This study revealed that PM_{10} was higher during the 1st year than that of 2nd year. First year average PM_{10} was 2.5 times higher than the annual national standard. During the 1*st* year, PM_{10} was maximum in the monsoon; possible reasons of which could be dry conditions, stable atmospheric condition with subsidence condition and thermal inversion. Winter time PM_{10} was maximum followed by pre-monsoon, post-monsoon and monsoon concentration during the 2nd year. In normal condition, during winter months dry weather condition along with low mixing height, thermal inversion, low temperature etc. results in high pollutant loading in the atmosphere. PM_{10} of 2nd year was within the annual national standard. Most of the chemical species were showing maximum concentration during the winter. Cation deficit condition was found indicating possibility of acid rain in this region. We had found very high percentage of SOC in OC and very high ratio of WSOC/OC in the present study. Source apportionment of PM_{10} showed biomass burning as the major sources of particulates of this region. Other sources include soil resuspension, vehicular emission and coal burning.

4.2. PM_{10} emission from festival celebrations

Celebrations during festivals are often accompanied with specific activities like burning of firecrackers, wood burning etc. These activities emit high volume of particulates in to the atmosphere which suggest importance for detail characterization of atmospheric PM during different festivals. Therefore, we had chosen to characterize PM_{10} during Diwali and *meji* burning, two festivals that are associated with high emissions of PM.

4.2.1. Diwali

Fireworks are very common scene ranging from birthday celebrations to worldwide victory. Diwali is a festival of India marked with lighting of lamps and burning firecrackers in large amount. Materials used in firecrackers contain chemicals and toxic substances, burning of which release toxic gases and particulate matter of fine size to the atmosphere leading to severe health and environmental hazards [95,96]. All studies reported so far on Diwali fireworks are from urban centres. The effect of Diwali celebrations on rural air quality has not gained much attention despite these areas being receptors of pollutants that are emitted from city centres.

Diwali is, essentially, a festival of the 'mainland India', which has slowly spread over whole of the country in the past few decades. For over a century there have been internal migrations from 'mainland India' to the northeastern states for trade and governance carrying the festival to the region. Keeping note of this and being inspired by the findings of studies from India and other countries the present study was designed to see the impact of Diwali fireworks on air quality of a rural receptor site of the Brahmaputra Valley.

In this work, PM_{10} samples of an extended festive period were chemically characterized for elements and ions. Relationships between various species were built from Pearson's correlations and multivariate analysis – Principal Component Analysis (PCA) to trace the effect of Diwali. The enrichments of elements in PM_{10} due to Diwali festivities, which we coined as Diwali Induced Enrichments (DIE), were estimated to understand the extent of the effect.

4.2.1.1. PM_{10}

Concentration and variability of aerosols in the atmosphere depends on the source strength and prevailing meteorological condition. So, wind rose for the Diwali period was plotted (Fig. 4.15). Prevailing wind was found to be from the north with high percentage of calm (90.35%) condition.

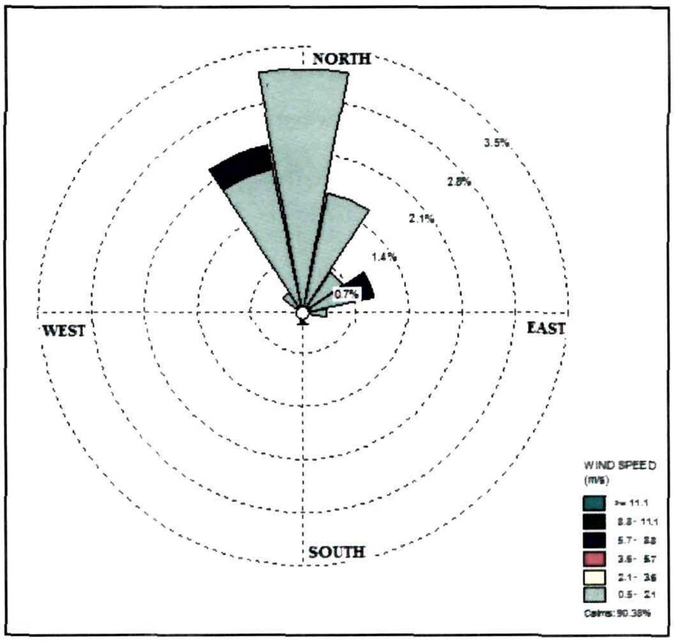


Fig. 4.15. Windrose of the study period

The 12 hourly mean PM_{10} was found to be 40.88±19 μgm^{-3} during the monitoring period (Table 4.12a). Concentration trends of PM_{10} of the study have been illustrated in Fig. 4.16a. Daytime PM_{10} was found to be the maximum on Diwali day (Fig. 4.16b), which was much on the lower side of other fireworks studies; but was comparable with the study conducted during FIFA world cup victory [97]. Nighttime PM_{10} maximum was observed on Pre-Diwali night (Fig. 4.16b), which could be due to thermal inversion at ~200m above ground (Fig. 4.16c).

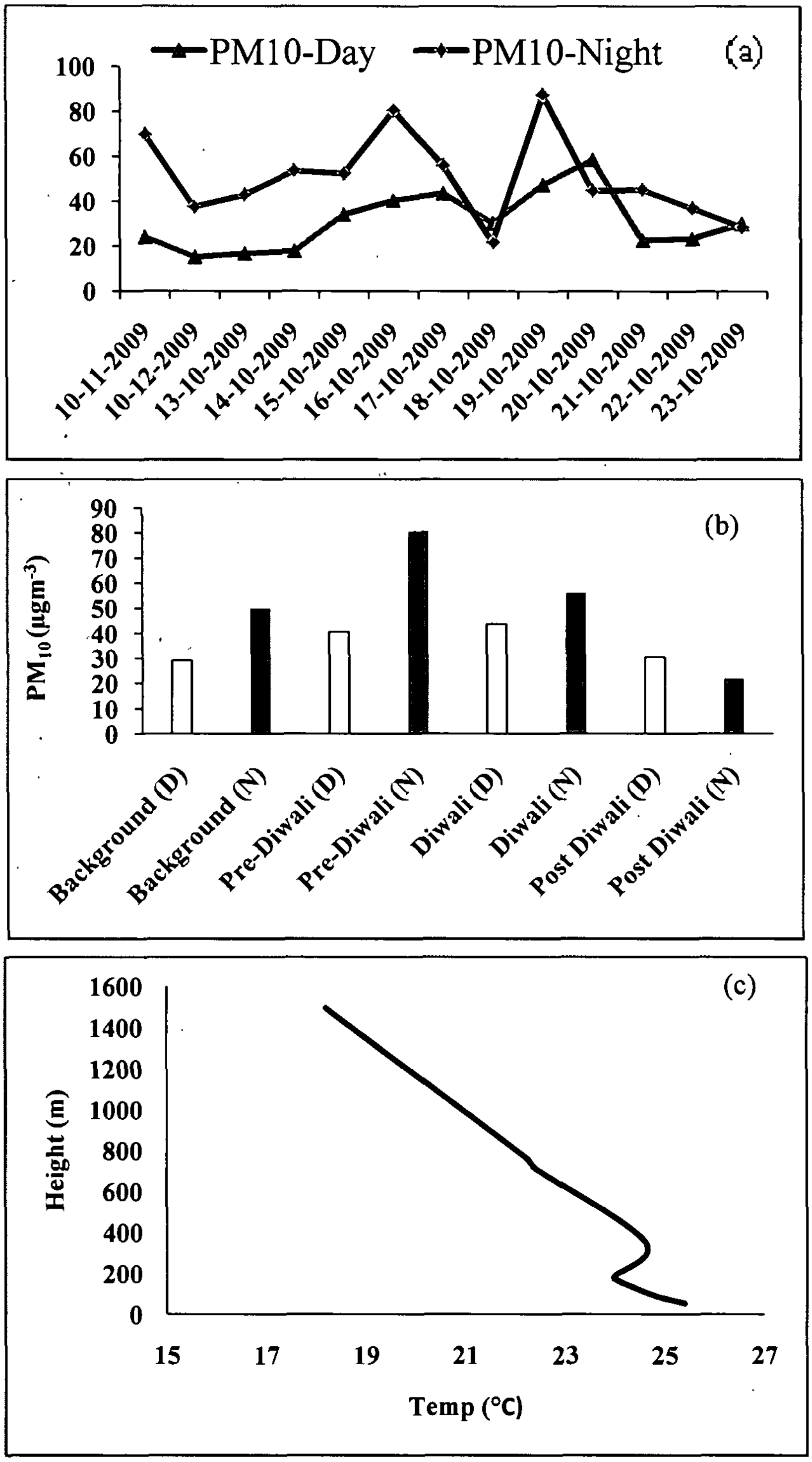


Fig. 4.16. PM_{10} trends and atmospheric condition. (a) Concentration of PM_{10} during the monitoring period (b) Diurnal variation of PM_{10} during the festive days [D~ Day and N~Night] (c) Thermal inversion prevalent on Pre-Diwali day (16-10-2009)

4.2.1.2. Elements and ions

Fireworks carry specific elemental signatures. Firecrackers contain large amount of nitrates and sulphates of lead, cadmium, potassium, ammonium and magnesium [96]. Wang et al. [98] had used K and Cl as the elements for fireworks indicators. Sarkar et al.

[99] proposed Ba, K and Sr as tracers of Diwali fireworks. Various elements like Na and K as metal oxidizers, Al, Mg, Cu and Sr as color and sparkle emitters are used in firecrackers [100]. Ba gives green color, Ca deepens the colors and Fe helps to produce spark in fireworks [101]. Calcium chlorides and sulphates give rise to orange flames [33]. Firecrackers lead to an increased level of these elements and ions in atmospheric particulate during fireworks.

A comparative account of elemental concentrations of PM_{10} of the present study along with fireworks studies from India and elsewhere has been put up in Table 4.12(a). Elemental concentrations during Diwali day were found to be above mean concentrations of the elements during the monitoring campaign, which are otherwise of much lower concentrations as compared to other reported studies on fireworks. However, Cr concentration of the Diwali day was extraordinarily high as compared to other elements, which was also much on the higher side than studies elsewhere except one reported by Sarkar et al. [99] and attributed to vehicular and industrial activities. Enhanced vehicular movement on the Diwali day is an add characteristic of the roads on Diwali, which adds up to the normal levels of metals in the PM_{10}. Reports on Diwali from Delhi often have higher levels of particulate matter and heavy metals. Rajarathnam et al. [104] reported PM_{10} concentrations of as high as 1200 μgm^{-3} in Delhi during Diwali celebrations. When compared to such studies, increased level of elements in the present study from fireworks was found to be marginal.

Anion concentrations of PM_{10} were showing a decreasing order of $SO_4^{2-}>Cl^->NO_3^->F^-$ and cations in the order of $Mg^{2+}>Na^+>Ca^{2+}>NH_4^+>K^+$ during the study period (Table 4.12b). There are not many studies on ionic composition of PM_{10} during fireworks as compared to studies focusing on elements, though a few researchers had reported many fold increase in the levels of ions during fireworks events in comparison to normal day samples. In a study during Yanshui Lantern Festival Chang et al. [106] reported 143, 69, 38, 6, 4 and 3.8 times increase for K^+, Cl^-, Mg^{2+}, Na^+, Ca^{2+} and SO_4^{2-}, respectively. However, they had not noticed any increase in the concentrations of NO_3^- and NH_4^+. Again, Chatterjee et al. [107] conducted an experiment during Diwali in Kolkata and reported many fold increase in metal and ionic concentrations than normal days. They had found 1.6 - 6 times higher concentration of ionic species on Diwali night with remarkable increase for K^+, Ca^{2+}, Mg^{2+} and SO_4^{2-} in PM_{10}. In the present study, except for K^+ and NO_3^-, higher concentrations of ionic species were recorded on the Post-Diwali night (Fig. 4.17c and 4.17d). Nitrate is the main constituent of firecrackers. There are studies where researchers did not notice any remarkable increase in NO_3^- and NH_4^+

Table 4.12. (a) PM_{10} (μgm^{-3}), elemental concentrations (ngm^{-3}) and a comparison with studies elsewhere; (b) inorganic ionic concentration (μgm^{-3}) and a comparison with studies elsewhere (NA- data not available and nd-not detectable; NM-not mentioned

(a)

Event, year	Diwali, 2009 [1a]	Diwali, 2009[1b]	Diwali, 2009[2]	Diwali, 2005[3]	Diwali, 2009[4]	Lantern festival, 2006[5]	FIFA world cup, 2006[6]	Yanshui, 2008[7]
Location	Present study	Present study	Delhi, india	Lucknow, India	Delhi, India	Beijing, China	Milan, Italy	Tainan, Taiwan
PM_{10}	40 88±19	49.83	507.2	NA	620	466.2	63.9	NA
Cr	176.18±151(8.51-660.60)	216.26	290	42.1	100	NA	11	10
Mn	106.68±87 (6.70-344.94)	77.42	930	83.9	170	400	30	80
Fe	2462.08±1530 (142.58-5424.98)	2353.65	6300	747.23	3900	5000	1731	410
Co	6.62±8 (0.21-26.07)	4.44		78.69		NA		NA
Ni	143.57±108 (6.32-439.76)	150.94	70	41.47	13	NA	5	NA
Cu	19.93±15 (0.26-59.74)	30.84	550	454.03	100	600	105	50
Pb	17.70±5 (0.52-83.55)	12.55	360	307.54	940	1100	57	100

[1a] Present study; 12-h average of whole monitoring campaign

[1b] Present study; 24-h average on Diwali day

[2] Sarkar et al. [99]; 24-h average of three sites on Diwali day

[3] Barman et al. [102]; 24-h mean of four sites on Diwali day

[4] Perrino et al. [95]; 24-h average on Diwali day

[5] Wang et al. [98]; 12-h night time sample, Values are approximate (ascertained from graphs)

[6] Vecchi et al. [97]; 4-h sampling duration, 12 am-4 am, 10-07-2006

[7] Do et al. [103]; 11-h sampling duration, 8 am–7 pm, 22-02-2008

(b)

Event, year	Diwali, 2009 [1a]	Diwali, 2009 [1b]	Diwali, (NM) [2]	Diwali, 2009 [3]	New Year, 2005 [4]
Location	Assam, India	Assam, India	Nagpur, India	Delhi, India	Mainz, Germany
F^-	0.05±0.02 (0.02-0.11)	0.063	NA		NA
Cl^-	6.28±4.20 (1.36-21.78)	5.81	NA	16	5.13
NO_3^-	0.84±0.70 (0.05-2.58)	1.23	16	11	6.48
SO_4^{2-}	8.05±2.68 (2.68-13.72)	8.05	19.9	44	36.17
Na^+	4.43±2.19 (0.97-11.27)	4.47	NA	1.6	NA
NH_4^+	1.13±1.23 (0.01-0.92)	0.14	16.8	0.64	2.39
K^+	0.15±0.20 (0.10-6.22)	1.15	26	Nd	33.15
Mg^{2+}	5.10±1.55 (1.55-7.83)	5.85	29.6	5.1	NA
Ca^{2+}	1.26±0.42 (0.42-2.53)	1.28	NA	6.2	NA

[1a] Present study; 12-h average of whole monitoring campaign

[1b] Present study; 24-h average on Diwali day

[2] Rao et al. [96]; 24-h average on Diwali day

[3] Perrino et al. [95]; 24-h average on Diwali day

[4] Drewnick et al. [105]; sampling time covers 23.45 of 31-12-04 until 8.00 0f 01-01-05

concentrations during fireworks [105,106]. Apparently all nitrates in fireworks quantitatively get converted into NO_x, concentration of which is often seen to rise during fireworks [108,109]. Contrary to this, however, many fold raise in the concentrations of SO_4^{2-}, K^+ and Cl^- during fireworks had been reported.

Comparison of the levels of ions found in the present study was made with a few studies elsewhere (Table 4.12b). Drewnick et al. [105] reported much higher levels of SO_4^{2-} , NO_3^- and NH_4^+ during New Year celebrations in Mainz, Germany. Rao et al. [96] also reported ionic constituents of PM_{10} collected during Diwali celebrations. They reported much higher levels of SO_4^{2-} , NO_3^- and Mg^{2+} than the levels of the present study. However, Na^+ concentration of the present study was found to be higher. As such, ionic enhancement of PM_{10} due to Diwali in the rural Brahmaputra Valley was found to be marginally above the mean concentration levels during the monitoring campaign, which was also much on the lower side compared to other studies.

4.2.1.3. Diurnal variability during Diwali period

Diurnal variation of PM_{10} concentrations has been illustrated in Fig. 16a. Nighttime PM_{10} concentrations were found to be higher than the daytime concentrations during the study period. The probable reason behind this could be the shrinkage of boundary layer towards the evening which is not conducive for particulates dispersion and dilution. During daytime, in the presence of sunlight, pollutants get more space to disperse due to elevation of boundary layer height. Also, fireworks activity is more intense during night.

Diurnal variations of elements and ions are put up in Fig. 4.17. All the elements manifest an increase on the Diwali night, which was, again, not seen in the case of Mn (Fig. 4.17a and 4.17b). The maximum concentration of Cl^- and SO_4^{2-} were recorded on the post-Diwali night (Fig. 4.17c). As Cl^- and SO_4^{2-} are constituents of firecracker emission, post-event maximum would mean that aged particulates laden with secondary ions were reaching the site. This observation has been further stressed upon in the later section while appreciating enrichments.

On the other hand maximum concentration of NO_3^- was found on the pre-Diwali night (Fig. 4.17c). NO_3^- being secondary product of NOx emission from vehicles, enhanced vehicular traffic during the period could have brought about this change. F^- levels in the PM_{10} were quite low and consistent yet a marginal rise was observed on the Diwali day. F^- is often considered to be a constituent of emission from coal combustion.

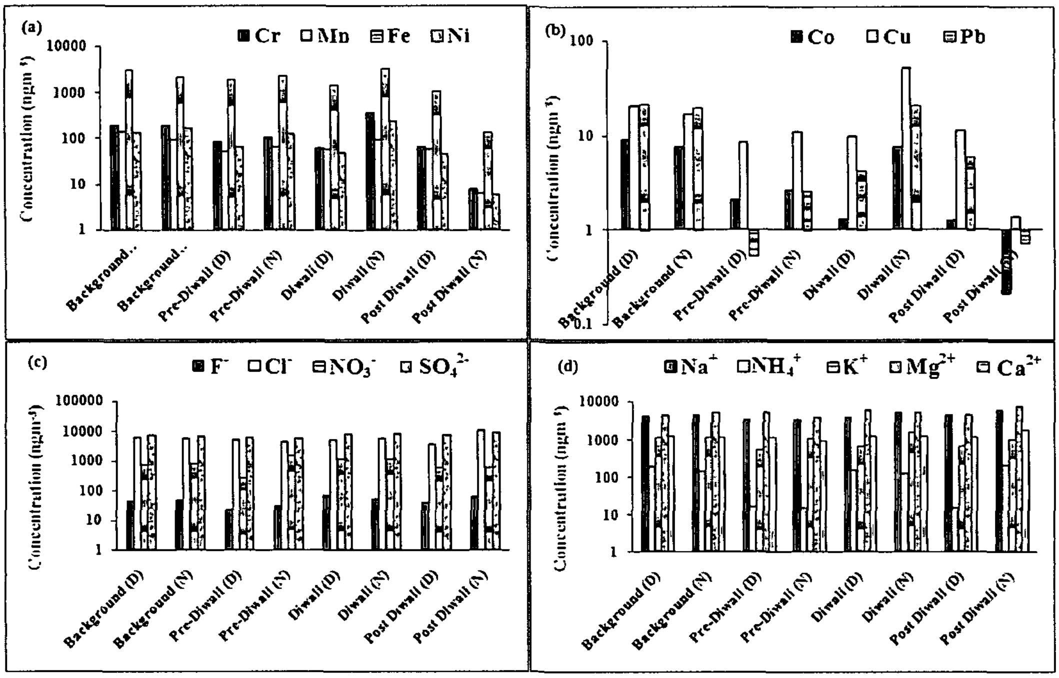


Fig. 4.17. Diurnal variations during the study period: (a) and (b) – elements; (c) anions and (d) cations (D~Day and N~Night)

Brick kilns which are coal fed in nearby localities could be the likely source of F^- [110,111].

Among cations, maximum concentrations were recorded on the Post-Diwali night for Na^+, NH_4^+, Ca^{2+} and Mg^{2+}(Fig.4.17d). On the Diwali night, K^+, an important tracer of firework, was found to be maximum. When concentrations of the ions for the entire monitoring campaign and the concentrations during festive days were compared, it was found that there was only marginal increase of ions. Marginal increase of elemental and ionic concentrations indicated the beginning of the effect of Diwali on PM_{10} in the Brahmaputra Valley.

4.2.1.4. Probable sources and effects of Diwali

4.2.1.4.1. Ionic ratios

The calculated ratio of $\sum$anions to $\sum$cations for the study period was found to be 1.26, which was indicative of a cation deficient condition. This would mean that either all the contributing cations were not estimated in the study or, on the other hand, the atmosphere was cation deficient indicating probability of acid rain in this region. A strong correlation (R^2=0.89) between anionic and cationic components of PM_{10} was, of course, found (Fig. 4.18), but the slope was less than unity indicating for cation deficiency in PM_{10} samples.

Sulphur and nitrogen in the atmosphere originate from both stationary like and mobile sources. Arimoto et al. [81] used the mass ratio of $[NO_3^-]/[SO_4^{2-}]$ as an indicator of relative importance of stationary versus mobile sources of sulphur and nitrogen in the atmosphere. High $[NO_3^-]/[SO_4^{2-}]$ mass ratios indicate the predominance of mobile source over stationary source of pollutants. In the present study, this ratio was found to be 0.10 indicating of stationary sources to be dominant for nitrate and sulphate. Diwali and coal fed brick kilns are two main stationary sources what would have impact on the PM_{10} properties, like the concentrations of NO_3^- and SO_4^{2-} during the study period.

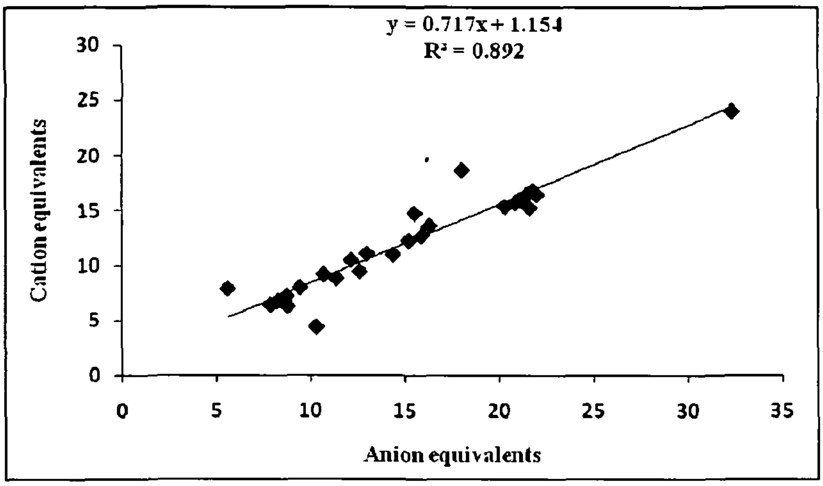


Fig. 4.18. Correlation between anion and cation equivalents of PM_{10}

4.2.1.4.2. Inter species correlations

Pearson's correlations were built to find associations between chemical species (Table 4.13a). In principle, the chemical species pairs having good significant correlations are assumed to have come from similar sources, or having similar chemical behaviour. Good significant correlations were obtained between element pairs Cr and Fe (r=0.52), Cr and Ni (r=0.60), Cr and Pb (r=0.58), Co and Pb (r=0.73), Mn and Pb (r=0.66) and Fe and Pb (r=0.65) at a significant level of $p<0.01$.

Elements of crustal origin, Mn and Fe showed a good correlation with Pb which could mean that the source of Pb could be from resuspended soil/dust. Vehicular Pb has been phased out in India over a decade ago. It is interesting to note that good correlations

Table 4.13. Pearson's correlations of elemental and inorganic ionic species of PM_{10}. (a) entire monitoring period (n=26); (b) festive days (n=6)

(a)

	Cr	Mn	Fe	Co	Ni	Cu	Pb	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	NH_4^+	Mg^{2+}	Ca^{2+}
Cr	1.00															
Mn	0.16	1.00														
Fe	0.52**	0.86**	1.00													
Co	0.25	0.92**	0.88**	1.00												
Ni	0.60**	0.30	0.52**	0.46*	1.00											
Cu	0.41*	-0.22	0.09	-0.23	0.29	1.00										
Pb	0.58**	0.66**	0.65**	0.73**	0.40*	-0.25	1.00									
F^-	-0.05	-0.17	-0.28	-0.14	-0.11	-0.04	0.08	1.00								
Cl^-	-0.11	-0.32	-0.39	-0.29	-0.22	-0.08	-0.05	0.66**	1.00							
NO_3^-	-0.12	-0.30	-0.28	-0.35	-0.15	0.35	-0.36	0.03	-0.03	1.00						
SO_4^{2-}	-0.18	-0.41*	-0.48*	-0.43	-0.33	0.23	-0.25	0.35	0.46*	0.65**	1.00					
Na^+	-0.30	-0.42*	-0.55*	-0.42	-0.30	0.05	-0.25	0.67**	0.88**	0.29	0.72**	1.00				
K^+	-0.25	-0.35	-0.44*	-0.40	-0.33	0.04	-0.31	0.52**	0.75**	0.32	0.55**	0.83**	1.00			
NH_4^+	-0.23	-0.33	-0.40	-0.36	-0.24	0.03	-0.28	0.60**	0.83**	0.12	0.41*	0.87**	0.92**	1.00		
Mg^{2+}	-0.15	-0.46*	-0.53**	-0.41	-0.19	0.18	-0.19	0.48*	0.34	0.43*	0.65**	0.49*	0.16	0.08	1.00	
Ca^{2+}	-0.27	-0.44*	-0.55*	-0.41	-0.33	0.01	-0.19	0.65**	0.92**	0.15	0.67**	0.94**	0.74**	0.76**	0.57**	1.00

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

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

(b)

	Cr	Mn	Fe	Co	Ni	Cu	Pb	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	NH_4^+	Mg^{2+}	Ca^{2+}
Cr	1.00															
Mn	0.80	1.00														
Fe	0.86*	0.91*	1.00													
Co	0.97**	0.84*	0.93**	1.00												
Ni	0.99**	0.81	0.89*	0.98**	1.00											
Cu	0.99**	0.79	0.80	0.93**	0.98**	1.00										
Pb	0.95**	0.74	0.68	0.86*	0.92*	0.98**	1.00									
F^-	-0.04	-0.22	-0.36	-0.16	-0.09	0.06	0.20	1.00								
Cl^-	-0.22	-0.74	-0.54	-0.30	-0.23	-0.20	-0.16	0.47	1.00							
NO_3^-	0.33	0.46	0.43	0.49	0.35	0.31	0.31	0.24	-0.20	1.00						
SO_4^{2-}	0.07	-0.28	-0.43	-0.13	0.00	0.19	0.35	0.82*	0.58	-0.12	1.00					
Na^+	0.11	-0.38	-0.41	-0.06	0.05	0.19	0.32	0.58	0.74	-0.19	0.90*	1.00				
K^+	-0.02	-0.43	-0.38	-0.15	-0.06	0.05	0.13	0.89*	0.80	0.09	0.79	0.71	1.00			
NH_4^+	0.77	0.38	0.51	0.78	0.77	0.76	0.76	0.16	0.28	0.50	0.28	0.46	0.31	1.00		
Mg_2^+	-0.27	-0.70	-0.61	-0.43	-0.31	-0.22	-0.15	0.72	0.88*	-0.29	0.72	0.68	0.91*	0.03	1.00	
Ca_2^+	-0.22	-0.73	-0.61	-0.38	-0.25	-0.17	-0.10	0.55	0.95**	-0.41	0.73	0.82*	0.81	0.16	0.94**	1.00

existed between Mn and Co ($r=0.92$; $p<0.01$) and Fe and Co ($r=0.88$; $p<0.01$) indicating probable source of Co to be crustal.

F^- was showing good correlations with Cl^- ($r=0.66$), Na^+ ($r=0.67$), K^+ ($r=0.52$), NH_4^+ ($r=0.60$) and Ca^{2+} ($r=0.65$) and Cl^- with all cations except Mg^{2+}. These relationships could indicate vegetation/biomass burning and, as such, use of biomass as fuel in the kitchens is a common practice in the rural areas of this region [112,113].

Good correlation between SO_4^{2-} and NO_3^- ($r= 0.65$; $p<0.01$) was also found, which could indicate their similar chemistry of formation as both of them originate as secondary product in the atmosphere. Na^+ was well correlated with Mg^{2+} and Ca^{2+}. Mg^{2+} and Ca^{2+} are known constituents of mineral dust and, interestingly, SO_4^{2-} was showing better correlation with Na^+ ($r=0.72$), Mg^{2+} ($r=0.65$) and Ca^{2+} ($r=0.67$) at a significant level of $p<0.01$ than with NH_4^+ (0.41; $p<0.05$). This could explain that in neutralization of SO_2 crustal materials played a greater role than NH_4^+. Similarly, NO_3^- was correlated with Mg^{2+} ($r=0.43$; $p<0.05$) indicating neutralization by cations of mineral dust.

A varied relationship was found when Pearson's correlations were calculated for the festive days only viz. Pre-Diwali, Diwali and Post-Diwali days (Table 4.13b). All the elements were showing good inter element correlations. Similarly, most of the ionic species especially, Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} were well correlated with each other. These chemical species are important constituents of fireworks [33,98-101]. This could explain that the effect of Diwali could be traced; however, for a very short duration.

4.2.1.4.3. Principal Component Analysis (PCA)

PCA was executed on normalized data to find factors that could identify contributing sources of particulates for the entire monitoring campaign and for the festive days separately.

PCA for the entire monitoring period (Table 4.14) did exhibit 5 components explaining 88.24% of variance. PC1 accounted for 31% of total variance and was loaded with F^-, Cl^-, SO_4^{2-}, Na^+, K^+, NH_4^+ and Ca^{2+} indicating a mix source (soil, biomass burning, livestock and agricultural activities, fireworks). Mn, Fe, Co and Pb were placed in PC2, explaining 21.69% of variance. Higher loadings of Co, Mn, Fe and Pb explain that resuspension of soil as mineral dust from agricultural land and loosely bound sediment of riverine areas could have sufficient influence on the PM_{10} loading.

PC3 has high loadings of Cr, Ni and Cu, explaining 13.42% of variance, which could be attributed to fuel combustion [114,115]. PC4 was loaded with Cu, NO_3^- and SO_4^{2-} explaining 11.92% of variance and PC5 with F^-, SO_4^{2-} and Mg^{2+} explaining 10.13%

of variance. As discussed, NO_3^- and SO_4^{2-} could be mainly from stationary sources. This indicates brick kilns and soil as the possible sources of these chemical species. F^- may be attributed to coal fed brick kilns and Mg from soil [110,111]. Some NO_3^- and SO_4^{2-} could also have come as contributions from soil [92,93].

Thus, PCA did not show the influence of Diwali explicitly as did for other sources.

Table 4.14. Principal Component Analysis of PM_{10} attributes during the monitoring period (n=26)

	PC1	PC2	PC3	PC4	PC5
Cr	-0.10	0.22	**0.88**	-0.13	0.03
Mn	-0.20	**0.93**	-0.03	-0.06	-0.21
Fe	-0.28	**0.80**	0.37	-0.05	-0.30
Co	-0.20	**0.93**	0.08	-0.15	-0.11
Ni	-0.16	0.31	**0.72**	-0.15	-0.07
Cu	0.00	-0.15	**0.75**	**0.45**	0.00
Pb	-0.03	**0.78**	0.30	-0.31	0.23
F^-	**0.71**	0.04	0.02	-0.09	**0.46**
Cl^-	**0.93**	-0.11	-0.03	-0.11	0.19
NO_3^-	0.03	-0.19	0.00	**0.91**	0.11
SO_4^{2-}	**0.45**	-0.18	-0.09	**0.67**	**0.42**
Na^+	**0.89**	-0.20	-0.13	0.24	0.23
K^+	**0.87**	-0.20	-0.14	0.28	-0.18
NH_4^+	**0.94**	-0.20	-0.07	0.07	-0.20
Mg^{2+}	0.19	-0.27	-0.02	0.32	**0.86**
Ca^{2+}	**0.85**	-0.21	-0.12	0.10	0.36
Eigenvalues	4.97	3.47	2.15	1.91	1.62
% of variance	31.08	21.69	13.42	11.92	10.13
Cumulative %	31.08	52.77	66.19	78.11	88.24
Possible sources	Mix source	Soil	Fossil fuel combustion	Brick kilns & soil	Brick kilns & soil

4.2.1.4.4. Diwali Induced Enrichment (DIE)

For better understanding of incremental effect of Diwali, Diwali Induced Enrichments (DIEs) were calculated (Table 4.15). DIE for each chemical species was calculated as $[X_{ij} \,/\, \overline{X}_i]$, where X_{ij} is the mass concentration for i^{th} species (i = 1 - 16) in j^{th} sample (j = 1 – 6; only festive days) and $\overline{X}_i$ is the mean mass concentration. We had not incorporated the data beyond Post-Diwali days for the DIE as Agrawal et al. [116] proved that the atmospheric residence time of fireworks particulates is just 1.5 days. Also, Pearson's correlations and PCA did not reveal any effect of Diwali for a longer period. To avoid bias $\overline{X}\,i$ was calculated separately for day and night samples. $\overline{X}_i$ was calculated for an element present in first two and last two day/night samples of the time series assuming effects of firework to be least in these samples. DIE>1 was assumed to the indication of Diwali impact.

Table 4.15. Diwali Induced Enrichment (DIE) - DIE>1 are in bold; D ~Day and N ~Night

	Cr	Mn	Fe	Co	Ni	Cu	Pb	F^-	Cl	NO_3	SO_4^{2}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Pre-Diwali (D)	0.52	0.59	0.93	0.31	0.40	0.50	0.04	0.53	0.98	0.31	0.86	0.77	0.11	0.47	**1.03**	**1.07**
Pre-Diwali (N)	0.55	0.71	**1.04**	0.35	0.73	0.66	0.13	0.62	0.78	**1.91**	0.80	0.73	0.11	0.96	0.75	0.80
Diwali (D)	0.39	0.67	0.68	0.20	0.30	0.58	0.32	**1.60**	0.99	**1.41**	**1.12**	0.89	0.98	0.55	**1.23**	**1.07**
Diwali (N)	**1.91**	0.99	**1.45**	0.99	**1.39**	**3.07**	**1.06**	**1.08**	**1.03**	**1.41**	**1.14**	**1.11**	0.84	**1.41**	**1.03**	**1.08**
Post-Diwali (D)	0.42	0.68	0.52	0.19	0.28	0.67	0.45	0.92	0.71	0.72	**1.11**	**1.05**	0.10	0.58	0.90	1.00
Post- Diwali (N)	0.04	0.07	0.06	0.03	0.04	0.08	0.04	**1.29**	**1.90**	0.80	**1.23**	**1.28**	**1.40**	0.91	**1.48**	**1.52**

DIE are put up in Table 4.15. DIE>1 was observed for Cr, Fe, Ni, Cu and Pb on the Diwali night. For ions, NO_3^- had a DIE value of 1.91 on Pre-Diwali night and 1.41 on Diwali Day. K^+ had maximum DIE on Diwali night (1.41). However, Cl^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+} and Ca^{2+} had DIE of 1.90, 1.23, 1.28, 1.4, 1.48 and 1.52, respectively on Post-Diwali night. Tandon et al. [117] had also calculated Enrichment Factor (EFi) for different chemical species during Diwali study in Delhi. They had reported 1-58 times enrichment of various elements. In the present context, the enrichments were just marginally greater than 1 indicating that effect of Diwali in the rural areas of Brahmaputra Valley was weak and short-lived.

The study revealed that the impact of Diwali fireworks on PM_{10} characteristics in the rural Brahmaputra Valley could be traced; however, the impact could be noticed for a very short period with very marginal increase of the associated chemical species - elements and ions. The incremental effect of Diwali was also very marginal as compared to the 'mainland India'. The study also revealed that PM_{10} in the atmosphere of rural Brahmaputra Valley could be cation deficient which could also mean acidic nature of the particulates. As mentioned by Ocskay et al. [118], water soluble fraction of particulate matter determines their bioavailability, their effect on human health, and their role in the radiative forcing it is imminent to have more studies on ionic constituents of aerosol together with precipitation chemistry of the region to have better understanding of these effects.

We did not carry out Diwali fireworks study further due to its marginal incremental effect on PM_{10}.

4.2.2. Festive biomass burning-*meji* burning in the Brahmaputra Valley

The *meji* is a structure built of bamboo, wood, leaves, straw and stubble of paddy held tier above tier with bamboo poles giving it a lofty temple shaped structure. It is lit in every Assamese village after community gathering and feasting on the *Bhogali Bihu* festival each year during mid-January. Biomass burning is a ubiquitous phenomenon in the northeastern states of India. Shifting agriculture, forest fire and household burning for cooking and heating and agricultural residue burning are few major contributors of atmospheric PM_{10} load in the region.

We had designed to study PM_{10} along with its chemical species to see if *meji* burning have any incremental impact on the PM_{10} load and its constituents. The limited study on the effect of *meji* burning was done in January, 2009. On getting some directions from the 2009 study two more *meji* events of 2012 and 2013 were covered for detailed study.

4.2.2.1. PM_{10} characterization during *meji* burning of 2009

4.2.2.1.1. PM_{10}

The PM_{10} mass concentration showed a 12 hourly average of 148.79±45 μgm^{-3} (n =31) during the experimental period. The maximum and minimum concentrations of PM_{10} were found to be 292.59 μgm^{-3} and 93.04 μgm^{-3} respectively. It is important to note that the maximum level of PM_{10} was observed on the day of *meji* burning (Fig. 4.19).

The 24-hour average Indian National Air Quality Standard of PM_{10} is 100 μgm^{-3} [1]. The observed levels of PM_{10} in the present study mostly exceed this limit, which may be considered quite alarming for a rural receptor site that apparently looks clean and far from the hustle and bustle of traffic and polluting industries. Interestingly, explicit diurnal variation of PM_{10} was not seen during the monitoring campaign. Also, after the first peak

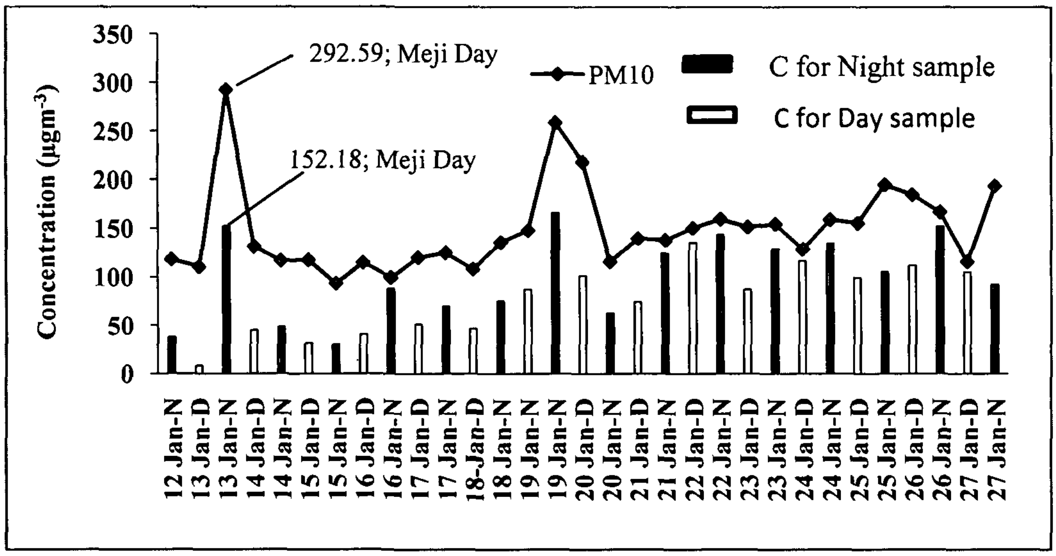


Fig 4.19. Trend of PM_{10} and Carbon during the study period. Similar trend of PM_{10} and C and dominance of C in the nighttime sample was observed. The concentration of the days prior to *meji* day may be taken as background concentration of air quality attributes as the *meji* burning day and time is very strictly followed by the people as per traditional belief and customs. Burning of the *meji* also customarily starts with special prayers

of PM_{10} on the *meji* day a sharp rise of PM_{10} concentration was seen on around January 19 and then the build up remained more or less steady for the later period (Fig. 4.19).

Backward trajectory analysis (Fig. 4.20b) shows that air mass of height 1500m traveling through the Indo Gangetic Plain (IGP), started subsiding as it moved nearer to this region and reached the surface within a few hundred km of the sampling station and mixed with local and lower trajectories. The IGP has been considered as a region of high carbonaceous aerosols due to high incidence of biomass burning in the form of household and post-harvest agricultural waste burning [119,120]. The trajectories, therefore, explain how large volumes of carbonaceous aerosols have been carried to this region from IGP leading to higher levels of PM_{10}. Also, trajectories of heights 100 and 500 meters originated from nearby areas remained confined in the lower surface layer (Fig. 4.20b) due to prevailing thermal inversion together with calm conditions (Fig. 4.20a). The forward trajectory of 7 days (Fig. 4.20c) and backward trajectories of every 72 hours (Fig. 4.20d) also indicated inversion condition. The heights of thermal inversions on January 17, 19 and 22 were within 200 m above the ground (Fig. 4.21a, b, c), which could have added to build up of pollutants during later period of the monitoring campaign.

To understand the PM_{10} concentration trends better, daily maximum mixing heights of the study period have been computed (Fig. 4.21d) and it was found that the maximum mixing height dipped to as low as 424m on January 19 and remained low during the later period of the campaign. This would probably lend support to the conjecture that the first concentration peak of PM_{10} could be due to *meji* burning while the second peak on January 19 and concentration built up during the later period of the campaign because of lowering of mixing heights and thermal inversion.

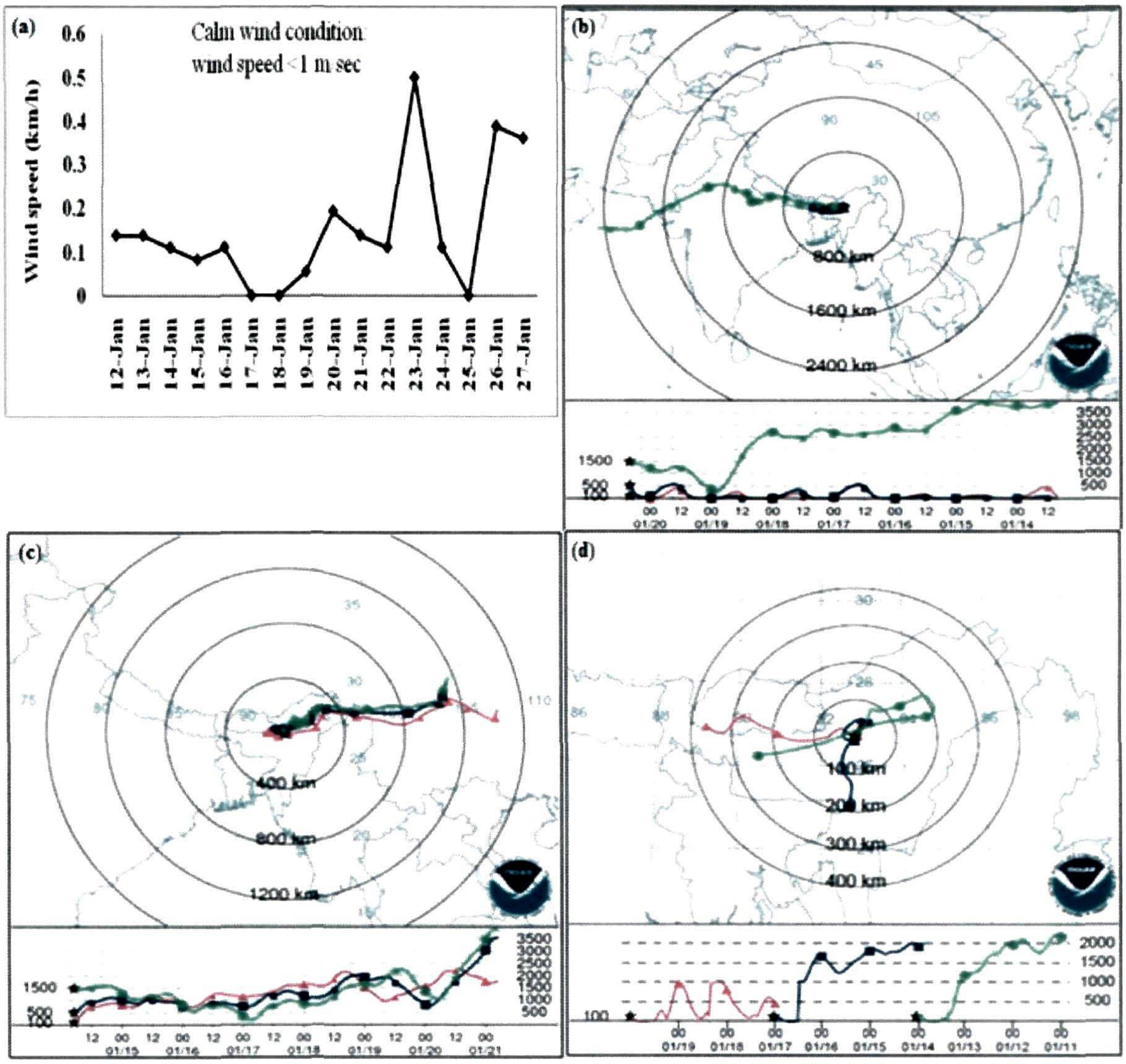


Fig. 4.20. Meteorology and trajectories: (a) Wind speed over the study period, (b) 7 day backward trajectories arriving at Tezpur (c) 7 day forward trajectories leaving from Tezpur (d) 7 day backward trajectories where a new trajectory had started after every 72 hours

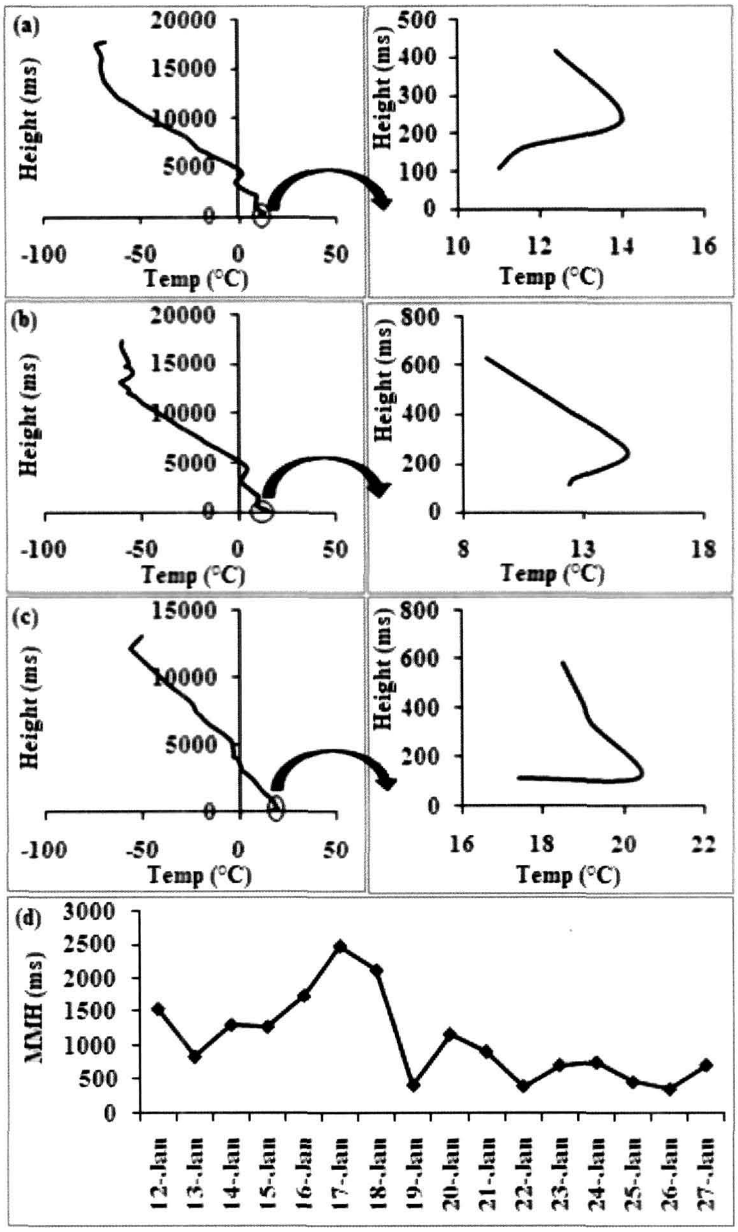


Fig. 4.21. Temperature profile and mixing layer height: Thermal inversion prevalent on (a) 17th January, (b) 19th January and (c) 22nd January of 2009 (d) Maximum mixing height (MMH) during the sampling dates

4.2.2.1.2. Elemental composition of PM_{10}

The elemental concentrations during the study period have been put up in Table 4.16. The concentration of V (0.03±0.04 μgm^{-3}) and Mn (0.06±0.04 μgm^{-3}) in the present study were found to be much lower than the WHO limit though Cd (0.52±0.28) and Pb (1.05±0.8 μgm^{-3}) were on the higher side. Government of India has notified Pb and Ni as criteria air pollutants in year 2009 and prescribed their standards for the ambient air quality [1]. As per WHO [32] air quality guidelines, limit values for individual substances based on effects other than cancer or odour/annoyance are - V (1 μgm^{-3}, 24 hr average), Mn (0.15 μgm^{-3}, annual average), Cd (5.0 ngm^{-3}, annual average) and Pb (0.5 μgm^{-3}, annual average). Ni concentration of the present study was higher than annual Indian standard (20 ng m^{-3}) and Pb concentration of a few samples of the monitoring campaign exceeded 24-hour Indian standard though the mean Pb concentration was found to be within the standard (1.0 $\mu g\ m^{-3}$) notified by Government of India [1]. Lead has been phased out as an antiknocking additive of gasoline in India more than a decade back yet vehicular contribution continues to be the major source of atmospheric Pb emissions [121] because of the exponential rise in the growth of vehicles.

A comparative account of elemental constituents of PM_{10}, of the present study and studies elsewhere has also been shown in Table 4.16. Elemental concentrations in the present study were found to be lower than one conducted by Kulshrestha et al. [10] in a rural locality in Agra, India. However, Tyagi et al. [122] had reported much lower elemental concentrations than the present study. Elemental concentrations reported from a remote location of Japan's Mt. Moriyoshi during winter month [65] were also much lower than our values.

Our results are comparable with other Indian studies [49,117,123,124]; though, Ti, V, Cd and Pb levels were on the higher side. Concentrations of the present study were also higher than the levels reported by Dongarra et al. [43] from a large urban area of Italy. However, the concentrations of Fe, S, Cl, Ca, and K reported by Chow et al. [125] from a residential area of Netzahualcoyotl (Mexico) were higher than our values.

4.2.2.1.3. Carbonaceous nature of PM_{10}

Percent carbon (C%) by weight of PM_{10} was found to be dominating in the present study. It is worth mentioning here that most of the PM_{10} samples had over 50% of the weight by carbon and in several samples the levels of carbon were close to 90%. The average C% in the present study was found to be 58.72±23% (Table 4.16).

Stone et al. [126] emphasised biomass burning and fossil fuel combustion to be the significant factors for carbonaceous aerosol at a receptor site in the Himalayas. Aldabe et al. [127] had reported TC 21% of PM_{10} at rural Bertiz of North of Spain. Maximum portion of $PM_{2.5}$ mass (33%) was contributed by biomass burning in urban Chengdu, China during springtime [128]. Khare et al. [21] found 56% total carbon content in PM_{10} in their study in the upper Brahmaputra valley. In another Indian study, Ram and Sarin [70] reported 25% of carbon in Total Suspended Particulates (TSP) samples from rural

Table 4.16. Mean elemental concentrations (μgm^{-3}) with range and Enrichment Factors (EF) observed in the present study with a comparative account with studies elsewhere

Elements	Present work[1]	Agra[2]	Molna[3]	Mt Moriyoshi[4]	Delhi[5]	Navi Mumbai[6]	Cossipore[7]	Kasba[8]	Goregaon[9]	Palermo[10]	Netzahualcoyotl[11]	EF (Present study)
C[#]	58 72±23 (7 52 – 91 27)					-						6 2 E4
Mg	0 06±0 07 (nd-0 24)			0 082	0 210	0 9	-	-	0 009			0 95
S	0 66±0 95 (0 12-5 25)			0 943	-	2 493	-	-			1 470	5 8 E2
Cl	0 30±0 31 (0 07-1 58)			0 167	-	2 56	1 210	0 710	1 95		1 060	8 8 E2
K	1 30±0 69 (0 01-3 28)			0 067	3 580	0 71	-	-	1 183		1 330	29
Ca	0 77±0 30 (0 36-1 53)			0 119	1 040	2 71	-	-	0 469		4 500	0 66
Ti	0 87±0 31 (0 01-1 47)			0 006	-	0 193	-	-			0 260	59
V	0 03±0 04 (nd-0 19)			0 001	-	0 016	-	-	0 087	0 010	0 020	1 E2
Mn	0 06±0 04 (nd-0 20)	0 900	3 1E-04	0 005	0 020	0 05	0 002	0 002	0 023	0 007	0 050	25
Fe	0 15±0 15 (0 03-0 68)	3 200	9 29E-03	0 076	0 340	2 21	0 120	0 087	0 706	0 298	2 830	
Co	0 03±0 02 (nd-0 07)				-	-	-	-	0 003	0 000	0 000	4 5 E2
Ni	0 03±0 03 (nd-0 15)	1 700	8E-05	0 001	-	0 009	0 010	0 010	0 015	0 005	0 000	1 5 E2
Cu	0 12±0 08 (0 03-0 35)	0 300	1 1E-04	0 001	0 020	0 025	-	-	0 016	0 010	0 040	7 6 E2
Zn	0 75±0 24 (0 41-1 46)	1 600	4 19E-03	0 011	0 590	0 148	0 540	0 490	1 638	0 017	0 150	4 1 E3
As	0 21±0 13 (nd-0 44)			0 002	-	0 013	-	-		0 002	0 000	4 0 E4
Br	3 27±1 32 (1 32-6 59)			0 006	-	0 023	-	-			0 020	5 0 E5
Cd	0 52±0 28 (0 11-1 40)		1E-05		0 002	-	0 010	0 002	0 001		0 000	1 0 E6
Pb	1 05±0 80 (0 26-3 43)	2 200		0 006	0 130	0 06	0 120	0 040	0 051	0 010	0 100	3 0 E4

[#] %wt of PM_{10}

[1] Rural receptor site , range in the parenthesis (nd ~ not detected)

[2] Agra, India (rural) (Kulshrestha et al [10])

[3] Molna, India (rural, residential) (Tyagi et al [122])

[4] Japan (Saitoh et al [65])

[5] India (Large city) (Tandon et al [117])

[6] Mumbai , India (Residential area) (Kothai et al [49])

[7] Kolkata, India (Industrial area) (Gupta et al [123])

[8] Kolkata, India (Residential area) (Gupta et al [123])

[9] Mumbai, India (residential, moderate traffic) (Chelani et al [124]

[10] Italy (largest urban area) (Dongarra et al [43])

[11] Mexico (low income commercial, residential area) (Chow et al [125]

Jaduguda during December, 2004. Badarinath et al. [129] reported increase of BC during agricultural clearing and burning day than normal day in a study from Arunachal Pradesh. They had found fraction of BC to total aerosol mass concentration to be ~5% during normal days and ~14% during burning day. Guazzotti et al. [130] did back trajectory analysis and found high contribution of biomass/biofuel burning to carbonaceous aerosols (accounting for approximately 75% of the carbon containing particles), even in areas located far remote from sources, showing the possibility of long-range transport. The incidence of C% to an extent of 90% in some of our samples is extraordinary and we would like to attribute this large contribution to biomass burning in this region

Concentrations trends of C and PM_{10} have been illustrated in Fig. 4.19. Similar trends of C and PM_{10} were found, which were consistent during the monitoring campaign. Another important observation was the diurnal characteristic of C i.e. higher concentrations were observed during night time. This diurnal characteristic could be indicative of the fact that the region's rural population primarily depends on biomass burning as the domestic source of energy. In the winter months, biomass burning is intense during nights for general heating due to cold weather. Lighting a fire in the open and sitting around it by the village folks, in the winter nights, is a common sight during the festive season in this part of the world. An increase of three fold for primary organic carbon concentration during cold front periods in Hong Kong, China had been reported by Li et al. [131].

Akimoto and Narita [132] had attributed fuel combustion and industrial activity as the main contributor to CO_2, NO_x and SO_2 emission in Asia. An airport within a distance of 10 km from the monitoring station apparently looks to have contributed sufficiently to the atmospheric load of carbon and other species as airports are areas where there is greater fuel burning activity. Tezpur airport is not operating as of today and there are no flight services to Tezpur except for government supply flights occasionally, which may not have sufficient effect on PM loading. As such, biomass is the principal fuel for about 89% of population of the region, represented in the present study that lives in rural areas. Therefore, the contribution from biomass burning could have greater share to loading of PM_{10} and constituents like carbon. The PM_{10} and C relationship has been further qualified by the Pearson's correlation between them ($r=0.69$, $p<0.01$) (Table 4.18). This further supports greater influence of biomass burning on PM_{10} loading.

Morphology of a few select samples was investigated by Scanning Electron Microscope (SEM) (Fig. 4.22). Particles of diameter of ≈ 1- 2 μm, which have greater implications to human health, were found to be mostly spherical or globular in shape indicative of more carbon as earlier works (e.g. McElroy et al. [133] suggest that cubic and spherical particles are rich in silicon and organic carbon respectively.

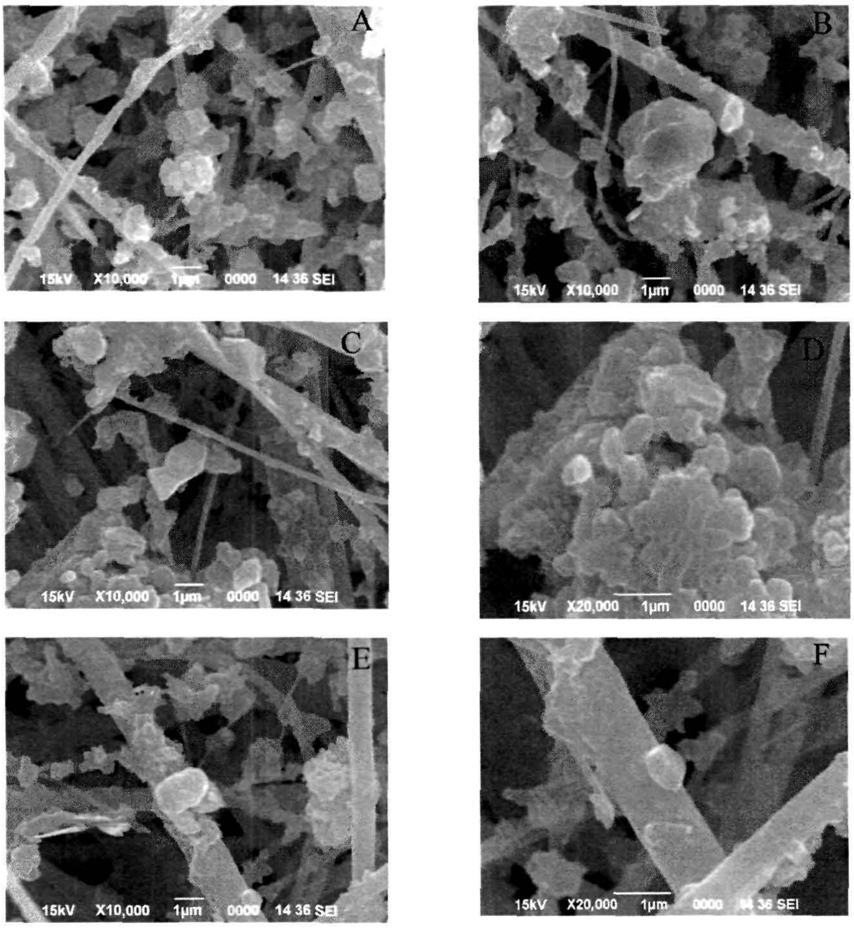


Fig. 4.22. Scanning Electron Microscope (SEM) images of PM_{10}

4.2.2.1.4. Bromine

The high concentration of bromine (3.27±1.32 μgm^{-3}) in the present study is quite extraordinary (Table 4.17). Earlier studies recommend that sea-salt particles are a significant source of particulate bromine in the troposphere and there have been a number of laboratory investigations into bromine production from aqueous bromide-containing aerosols acting as mimics for sea salt [134-136]. Table 4.17 shows the ratio of elements along with their sea-salt ratio counterparts [80]. The ratios suggest that there is least influence of the sea in the present study. Also, Tezpur is continentally located and marine contribution comes and goes with the monsoon that prevails between June and September. Our study was conducted in the month of January when there was no monsoon wind at all.

Seven day back trajectory analysis revealed that the trajectories (Fig.4.20b) originated in the Arabian Sea, however, the signatures did not carry to the site. Previous studies reiterated for a residence time of atmospheric particulates to be 5 days [137,138] and, therefore, sea salt load of the air mass probably got deposited on the way before reaching the monitoring site.

Table 4.17. Elemental ratios for source characteristics

Ratio	Elemental ratio	Reference elemental ratio
Cl/Na	0.09±.19	1.16[a]
K/Na	0.39±.44	0.02[a]
Mg/Na	0.02±.05	0.23[a]
Ca/Na	0.23±.19	0.04[a]
Br/Pb	3.12±2	0.38[b]

[a] Sea water ratio (Wilson [80])

[b] Leaded gasoline fuel vehicular exhaust (Owen and Coley [139])

Tetraethyl-lead A (TEL-A), which is frequently used as antiknock additive in leaded gasoline, results in a Br/Pb ratio of 0.38 in fresh vehicle exhaust emissions [139]. The Br/Pb ratio in the present study was found to be 3.12±2 (Table 4.17). This means that the Br presence is comparatively too large when compared with Pb, which indicates that there could be additional stronger source of Br than vehicular emission. As methyl bromide (CH_3Br) is considered as the main reservoir of atmospheric bromine, we would like to attribute this high particulate bromine level to photochemical degradation of CH_3Br.

Methyl bromide has been historically used as a soil fumigant in most part of the northern countries. However, soil fumigation is not practiced in this part of world. We must take into account that agriculture is slightly 'underdeveloped' in this part of the world. There are, however, reports that plants belonging to Brassicaceae family take up bromide from soil and subsequently release CH_3Br to the atmosphere deriving a significant volume (~7 Gg yr^{-1}) [140]. Mead et al. [141] reported the emission of CH_3Br by rapeseed (*Brassica napus*), mustard (*Brassica rapa*) and cabbage (*Brassica oleracea*) and concluded that there is an increasing trend of emission. They presented that there is an increase of CH_3Br emission from 0.51Gg (in 1961) to 5.12 Gg (in 2003). It is to be noted that during our monitoring campaign, agricultural fields around the sampling station were covered with rapeseed, mustard and cabbage cultivation. It is, therefore, suspected that high background bromine was already present thanks due to CH_3Br emission from these crops.

Biomass burning also emits large volume of CH_3Br. Manö and Andreae [142] conducted laboratory biomass combustion experiment and found that CH_3Br was emitted by various types of fuels they tested. They also found CH_3Br in the smoke plumes of wildfires in savanna, chaparral and boreal forest and estimated that globally 10 to 50 Ggs of CH_3Br is released from biomass burning. This is also supported by good correlations of Br found with K ($r=0.77$; $p<0.01$) and Cl ($r=0.48$; $p<0.01$). K and Cl (Table 4.18) are known constituent of biomass burning plume and in some earlier studies [84,89] used K as an indicators of biomass burning. The prevalence of potassium and chloride in biomass burning has made them to be favoured smoke tracer species for receptor modelling [143-145]. Again, bromine has also been found to correlate well with biomass burning particles [144].

We, therefore, would like to stress upon that there is substantial incremental effect of *meji* burning in the overall concentration of CH_3Br, which could have photochemically degraded and contributed to higher levels of particulate bromine. However, a significant correlation between Br and C was not found. This could be because there has been enough background bromine form the agricultural sector during the monitoring campaign.

Correlations of Br (Table 4.18) with some of the metal species (Pb, Ni, K, Fe, Zn and Cd) point at Br of having chemical affinity with these metals. These high correlations could indicate similar sink mechanism of bromine and metals through formation of metal bromides such as lead (II) bromide, nickel (II) bromide, potassium bromide, iron (III) bromide, zinc bromide and cadmium bromide, which would probably help scavenging of both metals and bromine from the atmosphere.

4.2.2.1.5. Enrichment factors (EF)

EFs of the elements of PM_{10} were calculated using Eq. 1. as discussed in section 4.1.3.2. EFs are put up in Table 4.18. Ca and Mg had an EF lower than unity being crustal in origin. K and Mn were enriched and the values were below 30. The EF values of S, Cl, Ti, V, Co, Ni and Cu were within 1000. Enormously enriched elements in our samples were Cd (10^6), Br (10^5), C (10^4), As (10^4), Pb (10^4) and Zn (10^3) which is indicative of strong influence of anthropogenic sources.

Particles having smaller size have long residence time and can be transported long distance; in the process the coarser crustal fraction gets deposited and the finer fraction gets enriched. This would mean that particulates carried to the site through long range transport from IGP let to higher level of enrichment. Kothai et al. [49] found higher EFs in the fine fraction than the coarse fraction of aerosols samples. Except Zn the EF values in their study was within 100 for the analyzed elements in coarse fraction. As, Br, Pb and Zn showed EFs to the level of several hundreds to thousands. They also found EF values of about 10^5 for As, Cr, Cu, Mn, Pb, Ni, V, Fe and Ti when considering the marine EF in reference to Na element. Petaloti et al. [146] found S, Cl, Cu, As, Se, Br, Cd and Pb as most enriched elements (EF>100) in the TSP samples suggesting that their atmospheric concentrations are primarily due to anthropogenic emissions released directly into the atmosphere.

4.2.2.1.6. Inter-element relationship

The correlation matrix of the data set was built to find associations between variables (Table 4.18). Elements showing significant strong correlations can be explained in terms of common source or chemical similarity.

Good correlations were also observed for element pairs like Cd and Br ($r = 0.70$), Pb and Ni ($r = 0.53$), Pb and Fe ($r = 0.60$), Pb and Br ($r = 0.84$), Pb and Cd ($r = 0.90$), Pb and Zn ($r = 0.73$) and Cd and Ni($r = 0.55$), which are significant at a confidence level of $p<0.01$.

It is noticeable that Br, Cd, Pb and Zn were showing good correlations with most of the analyzed elements at a significant level of $p<0.01$. Also, Ca and Mg (0.73 at $p<0.01$), K and Cl ($r=0.58$ at $p<0.01$) and K and Ca ($r=0.82$ at $p<0.01$) were showing significant relationship. Strong correlations were seen for K and Mn ($r=0.60$), K and Cu ($r=0.68$), Ca and Ti ($r=0.74$), Ca and Fe ($r=0.74$), Ca and Cu ($r=0.67$), Mg and Ti ($r= 0.52$), Mg and Mn ($r=0.59$), Mg and Fe ($r=0.55$), K and Fe ($r=0.54$), K and Ni ($r=0.54$) at a significant level of $p<0.01$. Significant correlations of Ca, Mg, K and Mn with Fe indicate crustal origin, which is also evident from the low EF values.

4.2.2.1.7. Incremental effect of *meji*

The incremental effect of *meji* burning was quantified as *Meji* Buring Induced Enrichment (MBIE), calculated as $[X_{ij} / \overline{X}_i]$, where X_{ij} is the mass concentration in μgm^{-3} of the i^{th} element ($i = 1-18$) in the j^{th} sample ($j = 1 - 31$) and $\overline{X}_i$ is the mean mass

Table 4.18. Pearson's correlations of elemental concentration and PM_{10} (n=31)

	PM_{10}	C	Mg	S	Cl	K	Ca	Ti	V	Mn	Fe	Co	Ni	Cu	Zn	As	Br	Cd	Pb
PM_{10}	1.00																		
C	0.69**	1.00																	
Mg	0.04	-0.46**	1.00																
S	0.09	-0.10	0.10	1.00															
Cl	0.68**	0.37*	0.02	0.22	1.00														
K	0.61**	0.06	0.54**	0.27	0.58**	1.00													
Ca	0.33	-0.29	0.73**	0.25	0.44*	0.82**	1.00												
Ti	0.14	-0.35	0.52**	0.13	0.41*	0.55**	0.74**	1.00											
V	-0.09	-0.21	0.39*	-0.03	-0.06	-0.07	0.12	0.37*	1.00										
Mn	0.39*	-0.05	0.59**	0.15	0.06	0.60**	0.49**	0.14	0.07	1.00									
Fe	-0.02	-0.44	0.55**	0.39*	0.21	0.54**	0.74**	0.41*	0.00	0.41*	1.00								
Co	0.11	0.00	0.23	-0.10	-0.04	0.13	0.23	0.33	0.40*	0.22	0.07	1.00							
Ni	0.39*	0.09	0.46**	-0.06	0.11	0.54**	0.35	0.18	0.05	0.46**	-0.04	0.15	1.00						
Cu	0.37*	-0.04	0.53**	0.08	0.13	0.68**	0.67**	0.42*	-0.02	0.50**	0.30	0.18	0.49**	1.00					
Zn	0.41*	-0.20	0.69**	0.01	0.23	0.71**	0.75**	0.59**	0.24	0.58**	0.34	0.44*	0.65**	0.77**	1.00				
As	0.45*	0.25	-0.28	0.03	0.42*	0.21	0.18	-0.04	-0.35	-0.03	0.18	-0.14	-0.02	0.10	0.07	1.00			
Br	0.37*	-0.30	0.61**	0.21	0.48**	0.77**	0.85**	0.61**	0.11	0.47**	0.71**	0.15	0.44*	0.54**	0.73**	0.33	1.00		
Cd	0.58**	0.04	0.66**	0.22	0.59**	0.90**	0.79**	0.46**	0.03	0.61**	0.48**	0.15	0.55**	0.63**	0.72**	0.12	0.70**	1.00	
Pb	0.61**	-0.01	0.69**	0.32	0.56**	0.87**	0.84**	0.49**	0.10	0.64**	0.60**	0.13	0.53**	0.62**	0.73**	0.21	0.84**	0.90**	1.00

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

*Correlation is significant at the 0.05 level (2-tailed) concentration in μgm^{-3}. The term $\overline{X}_i$ is calculated for an element present in first two and last two samples of the time series assuming effects of *meji* burning to be least in these samples as earlier computed by Tandon et al. [117] for enhancement factors of Diwali. MBIE of 3rd, 4th and 5th samples are put up in Fig. 4.23. The 3rd sample covers the *meji* burning episode. Celebration continues with lesser intensity for the following two days too, so 4th and 5th samples were also considered. It was observed that in the 3rd sample, elements like C, Mg, Cl, K, Ca, Mn, Ni, Cu, Zn, As, Br, Cd and Pb did show MBIE> 1 and further C, K, Mn, Ni, Cu, Cd and Pb showed MBIE values of 2.5, 3.51, 3.98, 5.32, 3.22, 2.32 and 2.83, respectively. K, Ca, Ti, Fe, Cu, Zn, Br and Pb were showing MBIE>1 in the 4th sample.

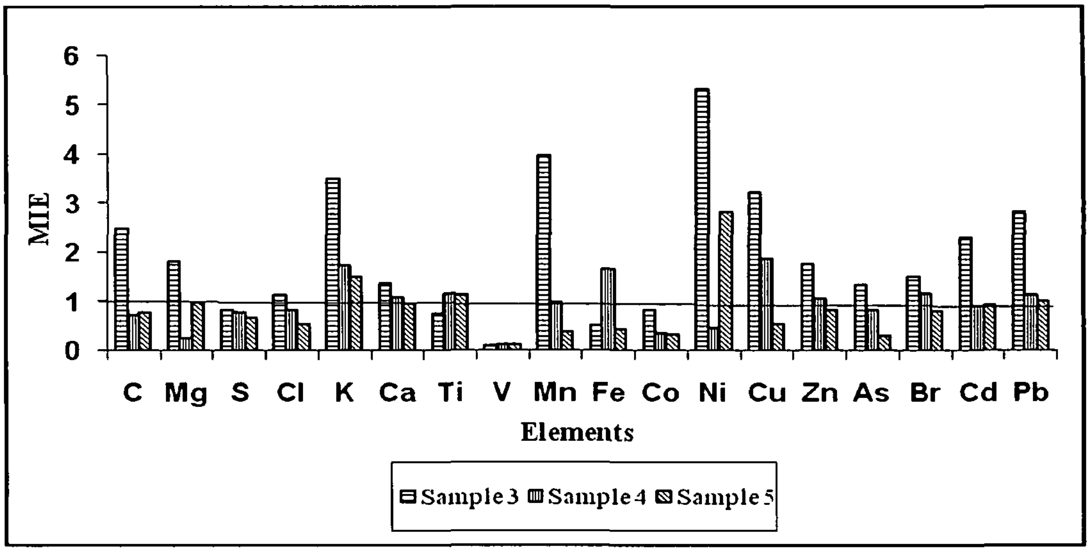


Fig 4.23. *Meji* Burning Induced Enrichment (MBIE) of elemental constituents in PM_{10} (The solid line, MIE=1, is level of no impact of *meji* burning)

It is assumed that MBIE>1 could be an indicator of incremental effect of *meji* burning. As such, there is no study as yet on the *meji* induced incremental effects and, therefore, our findings could be taken as the first report. This is also the reason why we have not been able to compare these values with other similar studies elsewhere.

Festive biomass burning like the traditional *meji* burning of the northeastern states of India is a source of huge volume of particulate matter. PM_{10} load during *meji* burning in the Brahmaputra Valley atmosphere showed incremental effects of *meji* burning which in turn has implications on the characteristic of PM_{10} of this region. PM_{10} was found to be extremely carbonaceous and enriched with Br and other metallic species. The carbon content of the PM_{10} was more pronounced in the samples taken during night-time. Temperature inversion and lowering of mixing height have lead to higher concentration of

PM_{10} during later days of the campaign. Back trajectory analysis revealed that long range transport of carbonaceous aerosol to the region. High level of particulate Br, which is a product of degradation of CH_3Br of agriculture and biomass burning origin, could be a special feature of this region. Therefore, future works on Br could be designed on accounts of findings of present study. It is a challenge to address emissions attributes of biomass burning together with long range transport of particulate in the regional scale to appreciate effects on regional climate, biota and human health. Therefore, there is a need to build a large database to model the behaviour and effects of particulates on regional climate, ecosystems, economy and health.

4.2.2.2. *Meji* burning effects-detail study during 2012 and 2013

The fascinating results found from the study conducted duirng 2009 *meji* burning inspired us to carry out detailed characterization of PM_{10} during 2012 and 2013 *meji* burning events. During 2012 and 2013 *meji* burning, collected samples were analyzed for elements, ions, carbon and PAHs.

4.2.2.2.1. PM_{10} loading

The maximum 24-hr PM_{10} was found on *meji* day (2nd sample) during 2012 *meji* burning event with 24-hr mean of 160±39 μgm^{-3}. PM_{10} was 2.18 times higher on the *meji* than the national 24-hr average of 100 μgm^{-3} [1] (Fig. 4.24). There was a fall of PM_{10} concentration on the day after *meji* burning event. The probable reason of this fall can be pegged on the occurrence of rain on 14th January, 2012. There after PM_{10} had started to build up again.

PM_{10} was maximum on the *meji* day (2nd sample) during 2013 *meji* burning event (Fig. 4.24) which was 1.65 times higher than the national 24-hr average of 100 μgm^{-3} [1] (Fig. 4.24). The 24-h mean was 113.62±32 μgm^{-3}. A decreasing trend was observed during 2013 *meji* burning event with slight increase in the 6th sample than the 5th sample.

Most of the samples were higher than the 24-hr national standard during both years. Low temperature, low wind speed, absence of rain and presence of inversion layer helped to build up pollutants during the monitoring period.

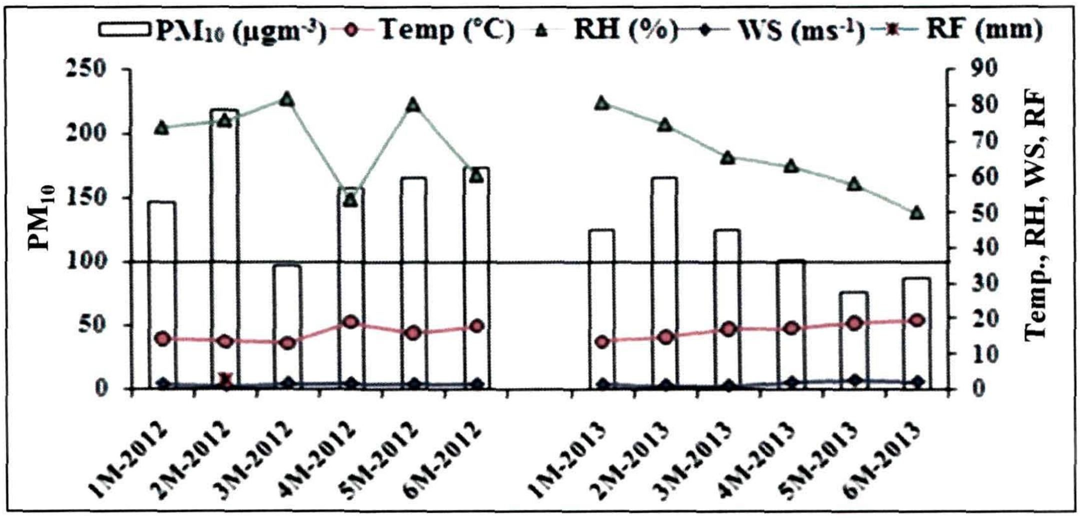


Fig. 4.24. PM_{10} concentrations and meteorological parameters over the study period. 2M is the sample of *meji* burning. The solid line indicates 24-hr national standard of PM_{10} (100 μgm^{-3})

4.2.2.2.2. Elemental concentrations

PM_{10} samples were analyzed for 11 elements. Definite trends of elements were not found during the study (Fig. 4.25). All elements were on the higher side during 2012 than that of 2013 *meji* burning event showing Cr 6 times, Mn 14 times, Fe 2 times, Cu 4 times, Zn 64 times, Co 21 times, Ni 17 times, Cd 43 times and Pb 130 times more concentration. Fe was maximum and minimum concentration was recorded for Co during 2012 and 2013 *meji* burning events (Fig. 4.25a and 4.25b). Pb and Ni have been notified as criteria air pollutant by Government of India in 2009 [1]. The National Standard of 1 μgm^{-3} (24-hr average) for Pb and 20 ngm^{-3} (annual average concentration) for Ni had been set up by Government of India [1[. Pb concentration was below the National Standard in both the years; however, Ni was 2 times higher (43.70±75.27ngm^{-3}) than the National Standard in 2012 *meji* burning event.

4.2.2.2.3. Enrichment factors (EF)

Enrichment factors (EF) of the elements of PM_{10} were calculated as per Eq. 1 as discussed in section 4.1.3.2.

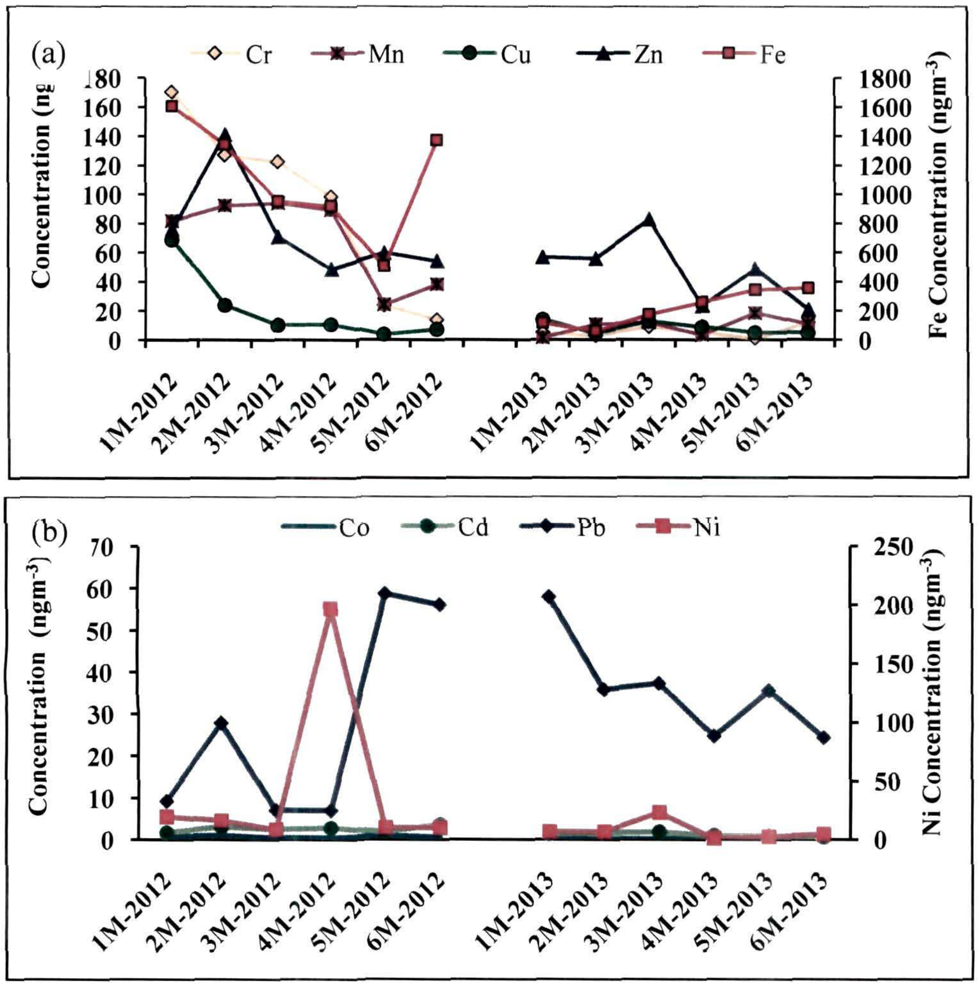


Fig. 4.25. Elemental concentrations over the study period. (2M is the sample of *meji* burning day)

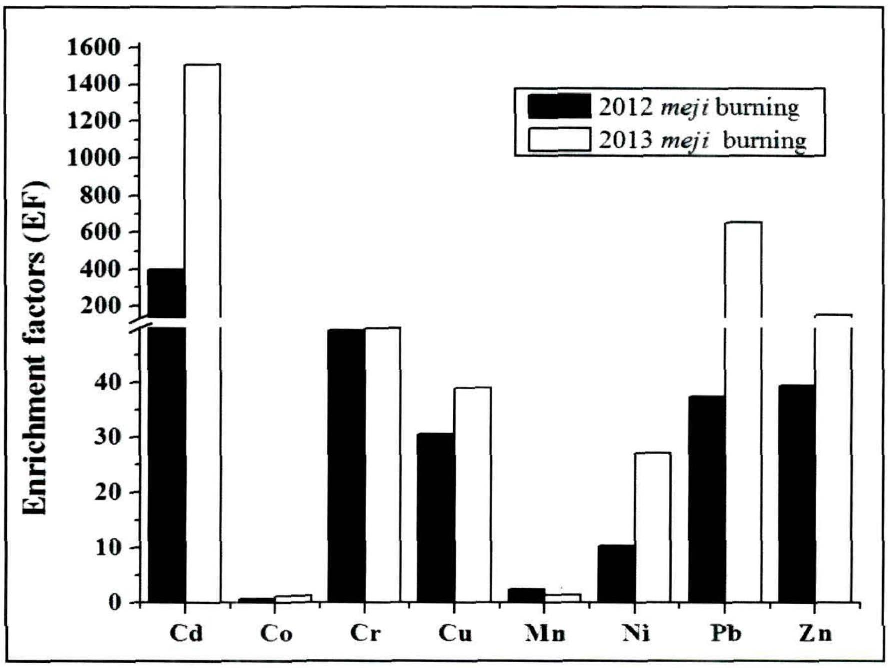


Fig. 4.26. EF of elements during 2012 and 2013 *meji* burning events

Comparatively elements were more enriched during 2013 *meji* burning period than that of 2012 (Fig. 4.26). Cd was showing maximum enrichment viz., 401 and 1505, respectively during 2012 and 2013 *meji* burning events. Low enrichment of Co and Mn showed their crustal origin. In 2012, other elements were showing EF less than 50. However, in 2013, EF of Zn and Pb were 145 and 656, respectively. The sources of Cr, Cu, Ni, Cd and Pb may be from vehicular or other industrial activities. Zn may come from biomass burning [84].

4.2.2.2.4. Water soluble ionic species

Collected samples were analyzed for 12 major cations and anions. Li$^+$ and F$^-$ were below detection limit. $\sum$Anions/$\sum$Cations ratio were 1.85 and 1.70, respectively during 2012 and 2013 *meji* burning events. This indicates deficiency in cation.

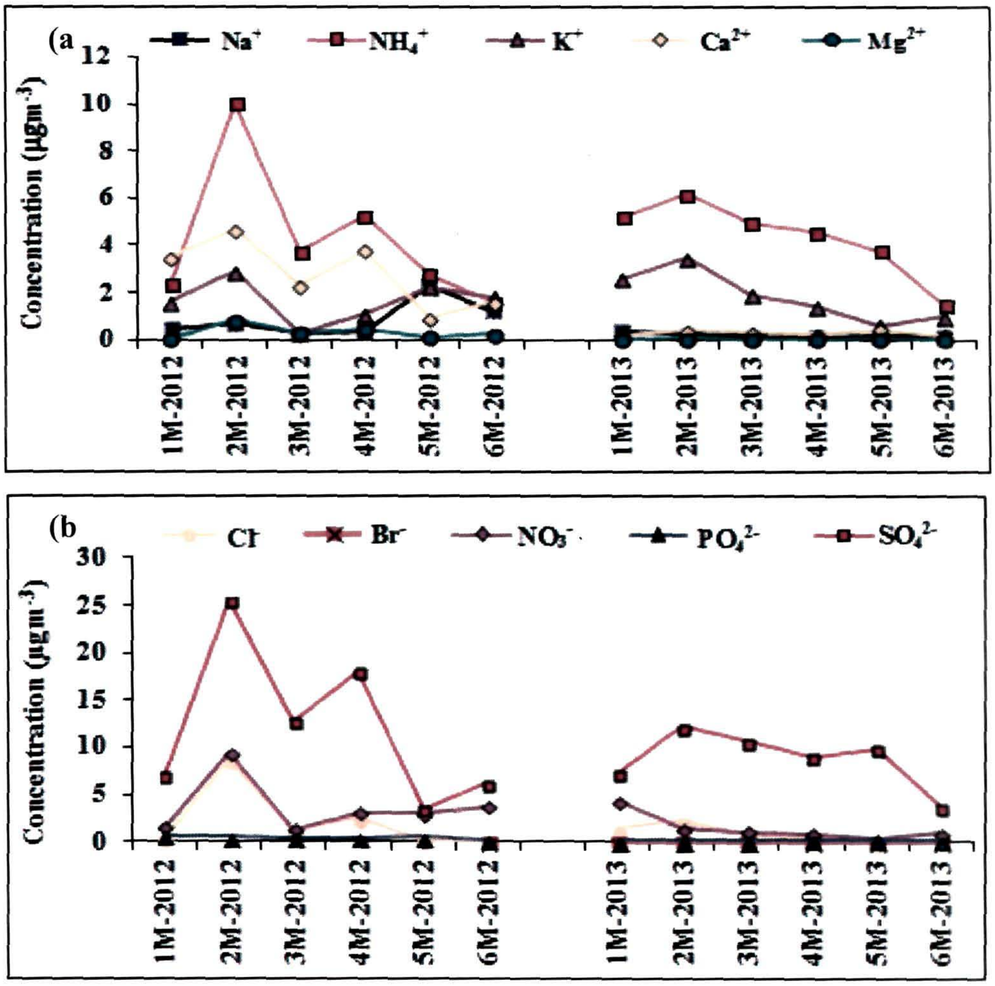


Fig. 4.27. Concentration of ions during the study period. (2M is the sample of *meji* burning day)

Most of the measured ions were on the higher side during 2012 *meji* burning event than that of 2013 (Fig 4.27a and 4.27b). Among the ions, NH$_4^+$, K$^+$, Ca^{2+}, Cl$^-$ and SO$_4^{2-}$ were found to be maximum on the *meji* day sample (i.e. 2nd sample). In 2012, Mg^{2+} and

NO_3^- were also found to be maximum on the *meji* burning day. Sulphate contributed maximum followed by NH_4^+ to the analyzed ions over the experimental period. Five major ions including K^+, NH_4^+, Cl^-, NO_3^- and SO_4^{2-} are emitted by all types of biomass burning [112]. Other researchers had also reported emission of these ions from biomass burning and smoke emitted from biomass burning [84, 147-149].

4.2.2.2.5. Carbonaceous nature of PM_{10}

4.2.2.2.5.1. TC, EC and OC

TC, EC, OC and water soluble fraction of carbon were measured for the collected samples. Maximum TC and EC were observed on the *meji* burning day (2nd sample) in both the events (Fig. 4.28). In 2013 *meji* burning event, OC was also maximum on the *meji* burning day. Carbon had contributed 38.63% and 31.45% of PM_{10} respectively during 2012 and 2013 *meji* burning events.

Khare et al. [21] had reported 56% of PM_{10} contributed by carbon at a site in the upper Brahmaputra Valley. They had attributed coal and wood burning as the sources of carbon. Again in a study from Dibrugarh of upper Brahmaputra Valley, Pathak et al. [22] had suggested stronger presence of absorbing aerosols originating from biomass burning than those originating from fossil fuel burning. Guazzotti et al. [130] had found predominance of submicron, chemically mixed particles containing abundant carbon and potassium, implying a biomass burning origin of aerosols in India. They did a back trajectory analysis and found high contribution of biomass/biofuel burning to carbonaceous aerosols (accounting for approximately 75% of the carbon containing particles), even in areas far from sources, showing the possibility of long-range transport. Venkataraman et al. [119] had estimated the relative contributions of fossil fuel combustion, open biomass burning and biofuel combustion to BC in India to be 25 %, 33 %, and 42 %, respectively, whereas those to OC to be 13 %, 43 %, and 44 %, respectively. Gustafsson et al. [150] found a much larger contribution (46 and 68%) of different fractions of black carbon from biomass burning in South Asia based on radiocarbon analyses. Stone et al. [126] had also estimated a higher contribution from biomass burning (21%) than fossil fuel (4%) to OC in the Himalayas. Ancelet et al. [151] had found that carbonaceous species made up to 47% of PM_{10} in a study conducted in Masterton, New Zealand, a wood burning rural community.

Concentrations of TC, EC and OC along with mass concentration ratio of OC/EC and EC/TC are given in Table 4.19 together with other studies elsewhere. It is noticeable that the TC and EC concentrations of *meji* period PM_{10} were higher than other studies.

However, OC concentration of 2013 *meji* burning event was lower than that reported in Kanpur [120], Beijing [154] and Hangzhou [155].

4.2.2.2.5.2. Water soluble carbon in PM_{10}

Water soluble carbon had contributed a significant percentage to TC which were 32.63±12% and 42.40±12% during 2012 and 2013 *meji* burning events respectively. Again, a higher percentage of OC was water soluble. In 2012 and 2013 *meji* burning events, WSOC/OC percent ratio was 58.44±25% and 69.64±14, respectively. Mkoma et al. [156] had reported 31% WSOC/OC percent ratio of PM_{10} in a wet season campaign in Morogoro, a rural site of Tanzania. They had also concluded that the particulate OC was originated from biofuel and charcoal burning. In another study, Mayol-Bracero et al. [157] had found 23±14 μgm^{-3} WSOC which accounted 56% of TC.

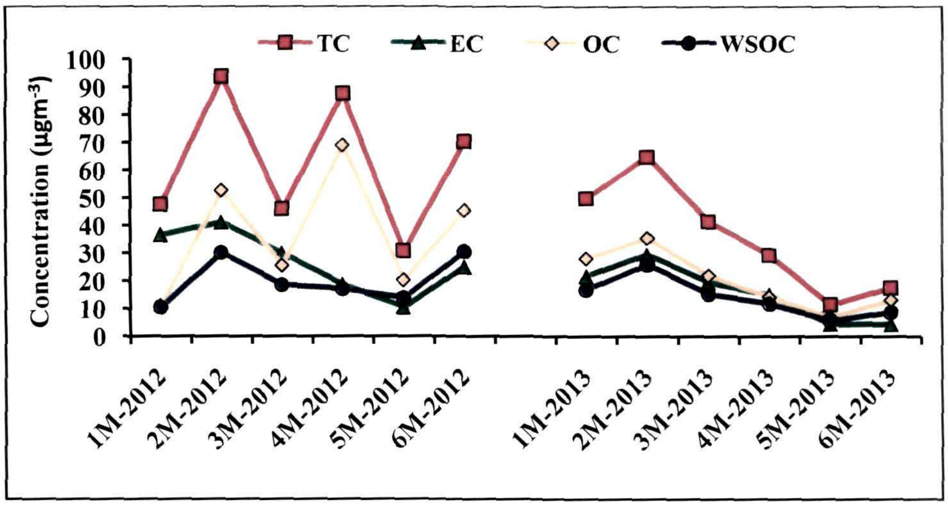


Fig. 4.28. Carbonaceous species in PM_{10} over the study period. (2M is the sample of *meji* burning day)

They had also found that the dominant fraction of the carbonaceous aerosol derived from biomass burning (smoldering) is organic, and a significant fraction of it is water soluble and can, therefore, contribute to the Cloud Condensation Nuclei (CCN) activity of biomass smoke particles. The high water-soluble fraction suggests an aerosol produced mainly by smoldering processes [158,159]. Novakov and Corrigan [159] provided strong evidence that water-soluble organic species in smoke particles from smoldering combustion could be responsible for their CCN activity.

Average WSOC/OC ratio of PM_{10} were 0.50±0.25 and 0.70±0.14, respectively during 2012 and 2013 *meji* burning events. Yang et al. [160] had reported this ratio to be

0.45 at a high altitude site (Purple Mountain Observatory) in China. Again, Ram and Sarin [70] had reported a value of ~0.5 at a high altitude site (Manora peak) which emphasizes the significance of secondary organic aerosols. Pathak et al. [22] had found dominance of secondary organic aerosols in OC concentrations in upper Brahmaputra Valley of Assam, which besides from biomass burning and anthropogenic sources may also result from the large biogenic volatile organic carbon emissions from the tea gardens and vegetation surrounding the study location.

WSIC contributed very small portion to WSTC having mass concentration of $1.41\pm1\mu gm^{-3}$ and $0.67\pm0.13\mu gm^{-3}$, respectively during 2012 and 2013 *meji* burning events. Generally, the main constituents of WSIC are carbonate and hydrogen carbonate, which are formed by crustal species and emission of industries [161].

4.2.2.2.6. PAHs

USEPA 16 priority PAHs were also analyzed for PM_{10} samples. PAHs had contributed 0.11% (182.74 ± 86 ngm^{-3}) and 0.27% (311.55 ± 127 ngm^{-3}) of PM_{10} during 2012 and 2013 *meji* burning events respectively. Ancelet et al. [151] had found that the average PAHs (16 USEPA priority PAHs and retene) was 38.9 ± 26 ngm^{-3}, accounting for 0.3% of the $PM_{2.5}$ in a study conducted in Masterton, New Zealand, a wood burning rural community. They had reported FLA and PYR as the most abundant particle–phase PAHs, with concentrations ranging from 13.5–0.6 ngm^{-3} and 12.6–0.5 ngm^{-3}, respectively.

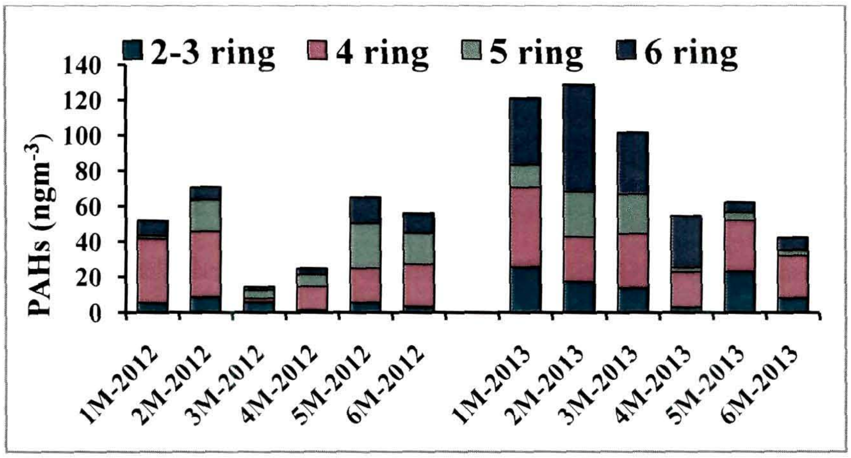


Fig. 4.29. Ring wise distribution (different colored area) and $\sum_{16}PAH$ concentration (column heights). (2M is the sample of *meji* burning day)

PAHs was maximum on *meji* burning day in both the year (Fig. 4.29). In our study, CHR was maximum with a mean of 54.53±44 ngm^{-3} and 68.57±28 ngm^{-3}, respectively during 2012 and 2013 *meji* burning events. Out of the 16 USEPA priority PAHs 7 are considered as probable human carcinogens by USEPA [162] . These carcinogenic PAHs include BaA, CHR, BbF, BkF, BaP, DBA and IND. Carcinogenic PAHs was contributing 68.24±16 % and 56.17±13% of $\sum_{16}$PAHs during 2012 and 2013 *meji* burning events. Strong correlations were observed between $\sum_{7}$PAHs and $\sum_{16}$PAHs (R^2=0.98 & 0.80, respectively). This suggests that $\sum_{16}$PAHs distribution was heavily influenced by $\sum_{7}$PAHs. Ring wise distribution of PAHs showed 4 ring>5 ring> 6 ring> 2-3 ring in 2012 and 6 ring ~ 4 ring> 2-3 ring> 5 ring during 2013 *meji* burning event (Fig. 4.29).

USEPA had mentioned BaP as the most carcinogenic PAHs. It was 11.62±11 ngm^{-3} during 2012 *meji* burning event which was 11.5 times higher than the annual mean of 1 ngm^{-3} [1]. However, BaP concentration was 0.73±0.50 ngm^{-3} during 2013 *meji* burning event. For better parameterization of carcinogenicity Benz[a]pyrene-equivalents ($B[a]P_{eq}$) was calculated as-

$$\text{Total } B[a]P_{eq}=\sum i \,(C_i \text{ x } TEF_i) \qquad \text{Eq. 5}$$

The C_i is the concentration of an individual PAHs and TEFi is the corresponding Toxic Equivalance Factor. TEF was taken from Nisbet and LaGoy [163]. The Total $B[a]P_{eq}$ was 29.51 ngm^{-3} and 59.85 ngm^{-3}, respectively for 2012 and 2013 *meji* burning events. The reason for very high value of Total $B[a]P_{eq}$ during 2013 *meji* burning event was the high TEF value of DBA and its high concentration during that period.

4.2.2.2.7. Source assessment

4.2.2.2.7.1. Mass concentration ratio of EC/TC and OC/EC

The EC/TC ratio gives clues on the sources of the carbonaceous aerosol. Low EC/TC ratios may indicate that the carbonaceous aerosol originates mainly from biogenic aerosols and/or biomass burning [164]. Biogenic matter contains no EC, whereas the TC from wood and other biomass burning has typically only around 10% or less EC [165].

In this study the EC/TC ratio was 0.40±0.11 and 0.43±0.10, during 2012 and 2013 *meji* burning events respectively (Table 4.19). Ferek et al. [85] had reported BC/TC ratio of 0.10±0.03 in a biomass burning episode from Brazil. Again, this ratio was reported as 0.12±0.07 by Cachier [86] in Ivory coast during a biomass burning episode.

Table 4.19. Concentration of different fractions of particulate carbon of PM_{10} along with their ratios and a comparative account with studies elsewhere

Location	Sampling period	Concentration			Ratio		Emission sources	References
		TC	EC	OC	OC/EC	EC/TC		
Tezpur, India	*Meji*, 2012	68 90±25	27 33±12	41 57±22	1 59±1	0 40±0 11		Present study
Tezpur, India	*Meji*, 2013	35 73±20	16 19±10	19 54±11	1 51±1	0 43±0 10		Present study
Chennai, India	Jan-Feb,2007		6 5±3	9 1±4	1 5±0 47	0 42±0 08	B B *	Pavuluri et al [152]
Kanpur, India	Jan, 2007-March, 2008		3 8±2	25 8±16	7 4±4	NA	B B *	Ram et al [120]
Uji, Japan	Nov-Dec, 1998	18	5 2	12 8	2 5	NA	V E &L R T *	Holler et al [153]
Beijing, China	Sept, 8-Nov, 30	30 1	8 9	21 2	2 4		V E &C B *	Zhang et al [154]
Hangzhou, China	Sept, 2001-Aug, 2002	25 47	4 06	21 41	5 27		C B *	Cao et al [155]
Morogoro, Tanzania	13 March-11 April, 2006	5	0 52	4 5	8 65		B B *	Mkoma et al [156]

* B.B-biomass burning; V.E.-vehicular emission; L.R.T.-long range transport; C.B.-coal burning

Table 4.20. Comparative account of the molecular diagnostic ratios of the present study with different biomass burning studies

	2012 *meji*	2013 *meji*	Paddy residue-ambient	Paddy residue-chamber	Crop residue/stove	Crop residue/stove	Crop residue/open fire	Wood /stove
	Present study	Present study	Rajput et al [173]	Rajput et al [173]	Shen et al [174]	Shen et al [174] and references there in	Shen et al [174] and references there in	Shen et al [174] and references there in
Phe/Ant	7 47±4 64	2 57±4 86						
ANT/(ANT+PHE)	0 08±0 05	0 28±0 30	0 15±0 03	0 17±0 01	0 12±0 01	0 2	0 17-0 25	0 10-0 30
FLA/PYR	1 88±1 81	1 17±1 06	0 84±0 04	0 97±0 21				
FLA/(FLA+PYR)	0 06±0 03	0 47±0 18	0 46±0 01	0 49±0 05	0 53±0 03	0 51-0 80	0 34-0 53	0 43-0 74
IND/(IND+BPER)	0 58±0 29	0 84±0 08	0 49±0 03		0 54±0 02	0 31-0 50	0 39-0 94	0 16-0 69
Bap/BaP+BPER	0 70±0 16	0 12±0 09			0 60±0 05	0 23-0 67	0 43-0 98	0 38-0 78
BbF/BbF+BkF	0 63±0 45	0 61±0 39			0 55 ± 0 03	0 50-0 65	0 35-0 80	0 35-0 51
BaA/BaA+CHR	0 43±0 16	**0.26±0.21**			0 48 ± 0 02	0 46	0 39-0 50	0 39-0 56

However, the EC/TC ratio obtained in this study is similar to that of Pavuluri et al. [152] (Table 4.19) who had found biomass burning as a major source of atmospheric aerosols in South and Southeast Asia.

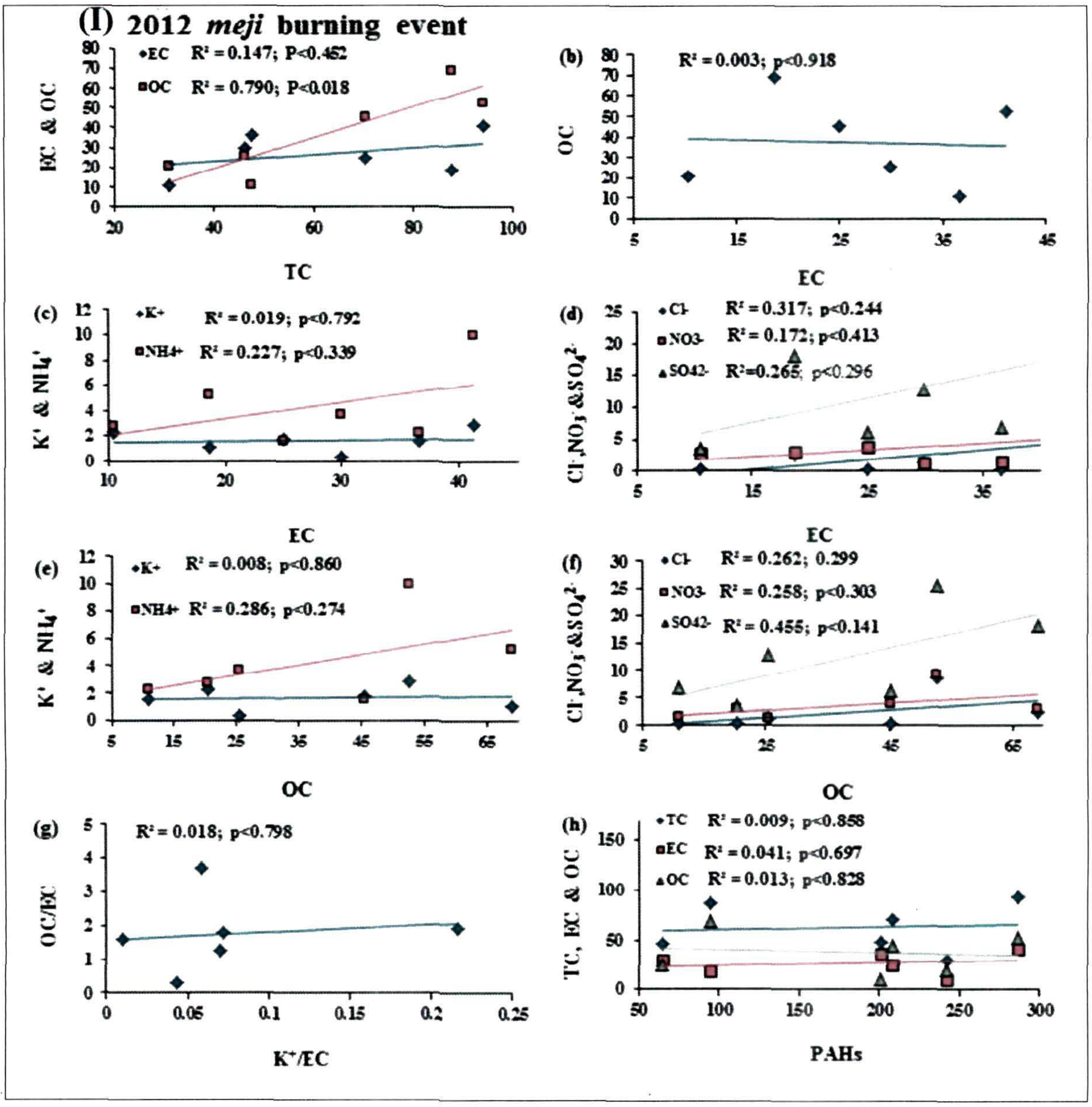
The ratio of particulate OC/EC is an important index that reflects source type and source strength [166]. Other researchers had also used the ratio of OC to EC for source assessment [120,152]. Consistent patterns of OC/EC ratio can be more easily found partly because the ratio of two chemicals tends to be less sensitive to atmospheric processing [167,168]. Long-range transport of fire emitted OC and EC, for example, do not have a large impact on the absolute levels of OC due to dilution but can significantly alter the OC/EC ratio in remote regions. OC/EC ratio in this study viz., 1.59±1 and 1.51±1, respectively were less than reported studies (Table 4.19) except that of Pavuluri et al. [152]. Saarikoski et al. [169] had estimated OC/EC ratio of 6.6 for biomass burning, 12 for long range transport, 3.3 for secondary OC and 0.71 for traffic emission.

The EC/TC and OC/EC ratio of the present study suggest the high concentration of EC compared to typical biomass burning study. EC emission from biomass burning depends on burn rate (kg h^{-1}) and type of biomass [126,170]. Stone et al. [126] reported different EC/OC ratio at high and low burn rate. For mango wood, this ratio was 1.6 for the low rate compared to 0.2 for the high rate, whereas acacia wood at low and high rates were 0.3–0.4. Researchers had concluded that EC/OC ratios alone cannot be used to differentiate between combustion sources [119,170].

4.2.2.2.7.2. Linear relations between EC and OC with other biomass burning marker species

Further to see whether there is any impact of biomass burning linear correlations was established between different carbonaceous components and marker species of biomass burning (Figs. 4.30I and II). Pavuluri et al. [152] had concluded biofuel/biomass burning as a major source of atmospheric aerosols in South and Southeast Asia on the basis of mass concentration ratios of selected components and relations of EC and OC to marker species.

Positive correlations were observed between OC and EC, OC and TC, EC and TC, OC/EC with K^+/EC suggesting cogenic emission. Different ionic ratios were compared with sea water ratio which was not significant. Therefore, nss fractions of individual ion was not calculated to see the linear relations between ions and carbon. Ions emitted from biomass burning were showing positive relations with EC and OC. These ions, especially NH_4^+, K^+ and Cl^- were showing good correlations with OC and EC showing their same source, probably emitting from biomass burning. Correlations between OC, EC and NO_3^- and SO_4^{2-} were weaker than other ions. This indicates that there were some other sources contributing to NO_3^- and SO_4^{2-} loading of PM_{10}. Arimoto et al. [81] had used mass ratio of NO_3^-/SO_4^{2-} to identify contribution from stationary vs mobile sources to these ions. A lower ratio indicates the predominant contribution from stationary sources. In this study this ratio was 0.38 and 0.20, respectively during 2012 and 2013 *meji* burning events indicating contribution of stationary sources to NO_3^- and SO_4^{2-} over the study period. Near the sampling site, many brick kilns were situated which could have influence on these two ions concentration.



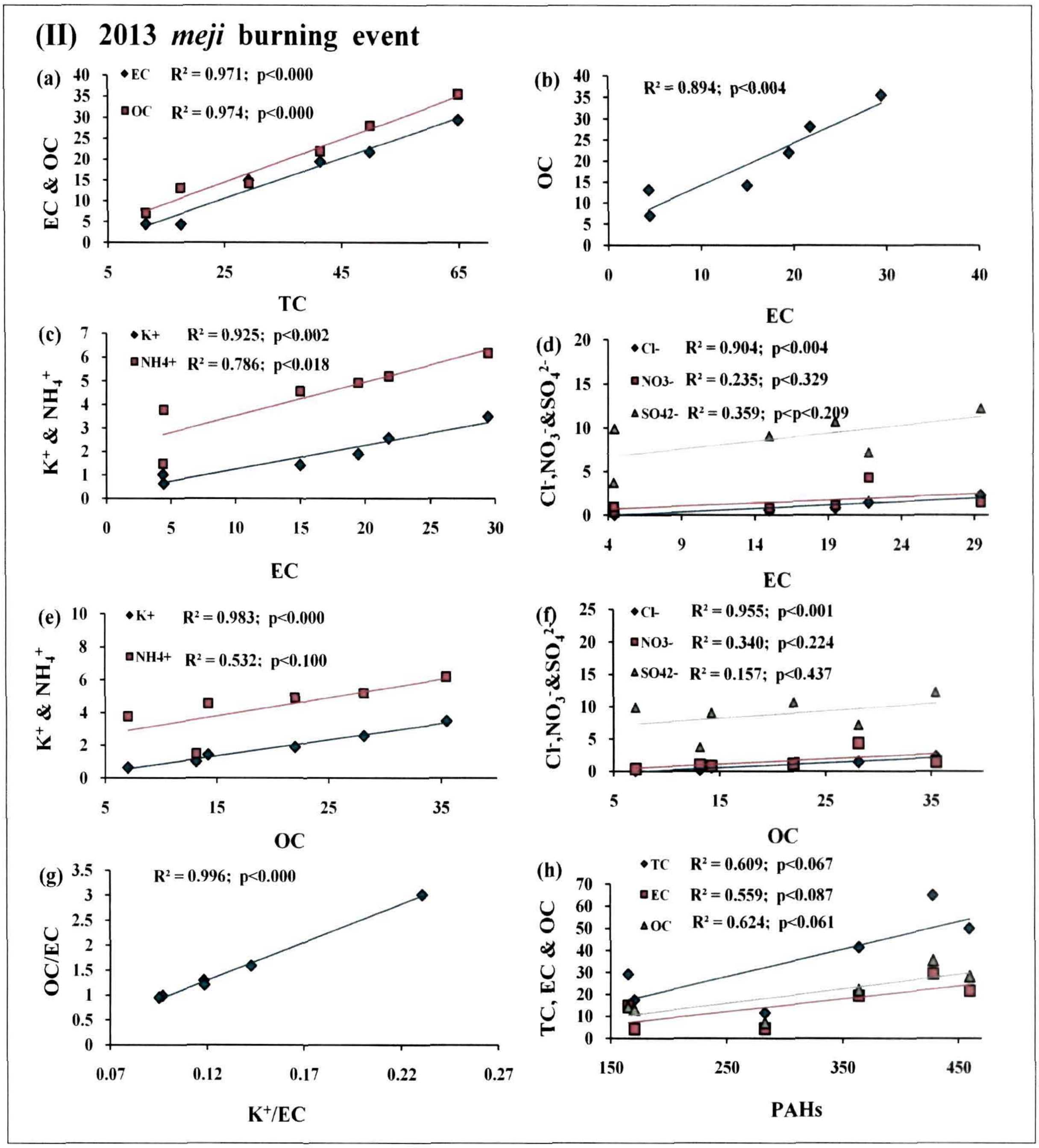


Fig 4.30. Linear relationships between different chemical species

Most of the combustion-derived PAHs are associated with particles such as BC (here EC) and soot [171]. ∑16PAHs was showing positive correlation with carbon over the study period indicating predominance of combustion derived PAHs (Fig. 4.30-I (h) & Fig. 4.30-II (h). However, the relation was not significant during 2012 *meji* burning event.

It is interesting to note that the correlation of these species were positive but relatively weaker in 2012 than that of 2013 *meji* burning event. Most of the studied correlations were very good during 2013 *meji* burning event. Occurrence of rain on 14th January 2012, which results in washout of submicron particles from the atmosphere, was the most probable reason for weaker correlation in 2012 *meji* burning event.

4.2.2.2.7.3. Molecular diagnostic ratio of PAHs

Molecular diagnostic ratios are used by the researchers to apportion the sources of atmospheric PAHs. The accurate use of diagnostic ratios depends primarily on the uniqueness of the fingerprint of the sources [171]. Molecular markers are organic species present in the ambient atmosphere that come from specific aerosol source categories, are stable in the atmosphere, and can be used quantitatively in source apportionment [172]. Some diagnostic ratios were calculated and compared with studies elsewhere on different types of biomass burning (Table 4.20). PHE/ANT ratio was <10 indicating pyrogenic origin of PAHs over the study period [175,176]. The calculated ratios were almost similar to other biomass burning studies with some exceptions. This difference may be due to the difference in measuring methods i.e. the present study sampling was done in ambient condition; however studies taken for comparison were done in chamber or near the vicinity of biomass burning.

The two year study on PM_{10} during *meji*, a festive biomass burning of the Northeastern region showed incremental effect on the regional aerosol. Except PAHs, elements, ions and carbon were higher during 2012 than 2013 *meji* burning event. Effect of *meji* burning is minimal on elements. Most of the water soluble ions and carbon were maximum on *meji* day. High WSOC emphasize on CCN activity of organic aerosols along with the presence of smoldering phase during *meji* burning period. WSOC/OC ratio revealed dominance of secondary organic aerosols. Linear relationship between EC, OC and other chemical species along with molecular diagnostic ratios of selected PAHs indicates strong influence of biomass burning on PM_{10} load.

4.3. Characterization of biomass fuel smoke particles (BFSPs)

Particles emitted from biomass burning in rural kitchens of the nearby areas of PM_{10} sampling site i.e. Tezpur University, Assam (India) were also collected and analyzed for elements, anions, carbon and PAHs. The basic idea behind this study was to understand the true nature of particles emitted from biomass burning and if any relationship existed between biomass burning particles and PM_{10} in the atmosphere.

The samples were collected during winter and monsoon seasons. The one – chambered and two-chambered cooking stoves, characteristic of this region are shown in Fig. 4.31a&b. In Fig. 4.31c, collected particles in Aluminium foil is shown.

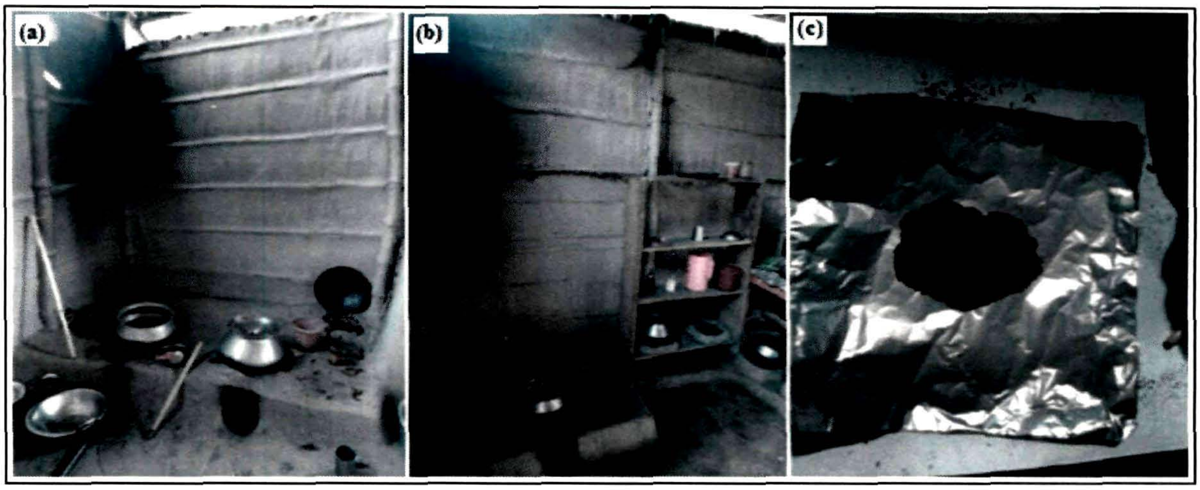


Fig. 4.31. (a) Two chambered and (b) one chambered rural kitchen. Collected BFSP is shown in (c)

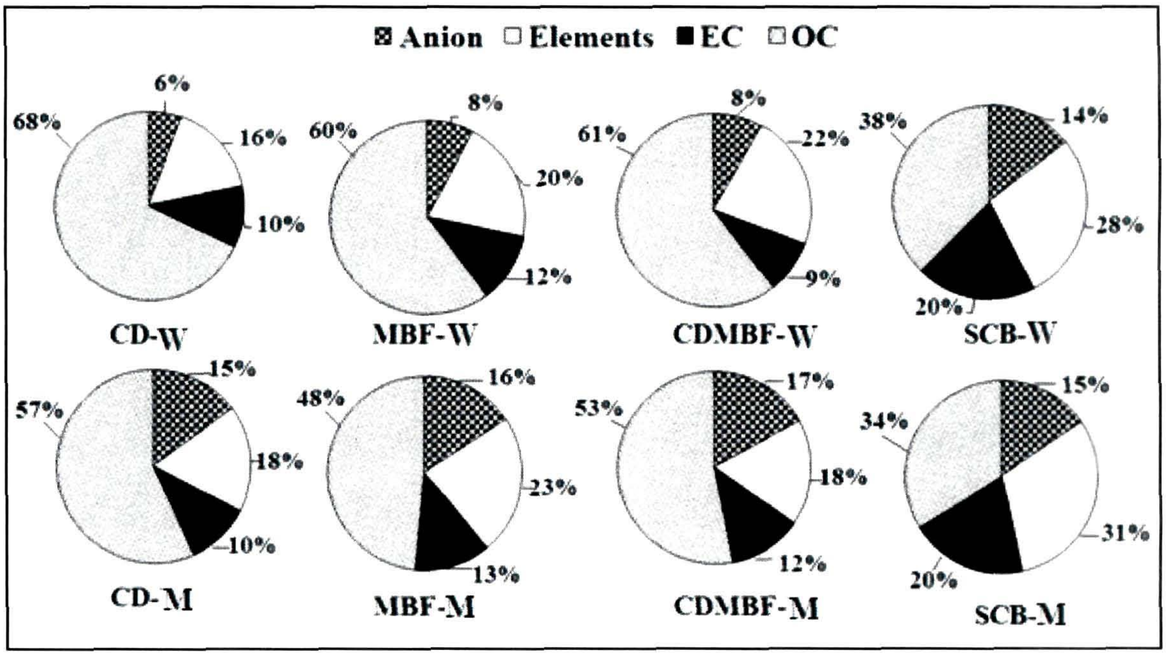


Fig. 4.32. Relative contribution of analyzed species to collected BFSPs. Relative contribution of OC was maximum followed by elements in both seasons in all BFSPs. However, except SCB, anions were more than EC in monsoon. Relative contribution is less variable in case of SCB-W and SCB-M. Contribution of carbon was maximum in CD in comparison to other BFSPs.

4.3.1. Elements

Collected BFSP samples were analyzed for 13 elements. Seasonal variation was not significant for most of the elements (Fig. 4.33a and 4.33b). Most of the elements were

Table 4.21. Elemental and ionic species in BFSPs. (Concentrations in mg kg^{-1}. DE-diesel engine & bdl-below detection limit)

	CD [1]	MBF [1]	CDMBF [1]	SCB [1]	Bamboo [2]	Rice husk coil [2]	Avg. of different biomass [2]	Rice husk [3]	Mixed biomass [3]	Cerrado fire [4]	Tropical forest fire [4]	DE-Idle [5]	DE-70% load [5]	DE-100% load [5]
Na	1271 90±340	625 14±292	463 20±44 69	454 00±52						230	140			
K	12016 30±2710	9495 68±3307	15794 30±7223 80	15180 30±4412	38169 00	15772 00	19627 00	17 10	21 50	21500 00	6000 00			
Mg	4909 87±887	4483 45±1196	4673 20±127 28	4155 20±62				443 1	534 2	335	700	2500	930	640
Ca	18579 10±8084	15596 35±4876	9124 10±3862 22	10478 10±6224	4189 00	5008 00	6418 00	1635 00	1648 00	950 00	700 00	18720	8040	5980
Fe	8663 33±1664	14702 13±13489	9423±4136 57	12187 00±1882	2624 00	3898 00	3256 00	11520 00	12360 00	610 00	395 00	5160	1910	1270
Cr	45 38±42	29 93±19	26 45±18 24	33 65±9						180 00	70 00	1180	340	230
Mn	391 03±100	313 90±118	318 60±2 26	304 20±27	72 60	108 00	98 00			75 00	40 00			
Co	4 03±1	4 39±1	4±1 56	5±1	24 40	30 90	31 00							
Ni	19 13±7	19 43±9	15 10±4 38	26 60±16						40 00		840	310	180
Cu	19 80±3	21 18±7	21 40±10 04	22 80±6	9 94	17 80	39 00			45 00	35 00			
Zn	164 23±38	313 50±588	98 10±51 19	108 40±7	77 20	172 00	126 00			150 00	50 00	1710	710	500
Pb	Bdl	bdl	bdl	bdl	50 80	50 60	262 00	95 6	125 2			700	240	130
Cd	Bdl	Bdl	bdl	Bdl				8 33	12					
F^-	238 85±171	172 33±176	224 35±210 22	213 50±130										
Cl	5806 28±3836	8486 16±9342	8428 75±6771 04	4033 75±284						16000	2500			
Br	135 92±145	114 91±81	121 35±12 23	114 30±15										
NO_3	520 32±578	353 34±327	223 15±113 35	706 65±692	bdl	0 33	0 73			4750	1200			
SO_4^{2}	15647 96±12854	13574 38±10127	13925 50±5949 17	13974 40±5095	40 30	136 30	38 00			5350 00	6450 00			
PO_4^{3}	1759 44±1513	1306 29±1440	2070 90±1019 65	2662 20±2940	0 99	0 25	0 60							

[1] Present study

[2] Salam et al [178]

[3] Hasan et al [179]

[4] Yamasoe et al [84] 4a and 4b are average of flaming and smoldering phase, air particulates were sampled directly over freshly emitted biomass burning plumes

[5] Sharma et al [182]

in higher side for CD than other BFSPs. In CD and MBF Ca was maximum (18579.10±8084 mg kg^{-1} and 15596.35±4876 mg kg^{-1}, respectively). CDMBF and SCB contained maximum K (15794.30±7224 and 15180.30±4412 mg kg^{-1}, respectively) in comparison to other elements. Calcium, K, Fe and Mg were the major contributing elements found in all BFSPs. Na, Mn and Zn were in the range of hundreds mg kg^{-1}. Concentrations of Cr, Co, Ni and Cu were less and did not vary much for different BFSPs. Cu and Ni are present in plant tissue in very low concentration [177]. Among the analyzed elements Co was minimum in all BFSPs.

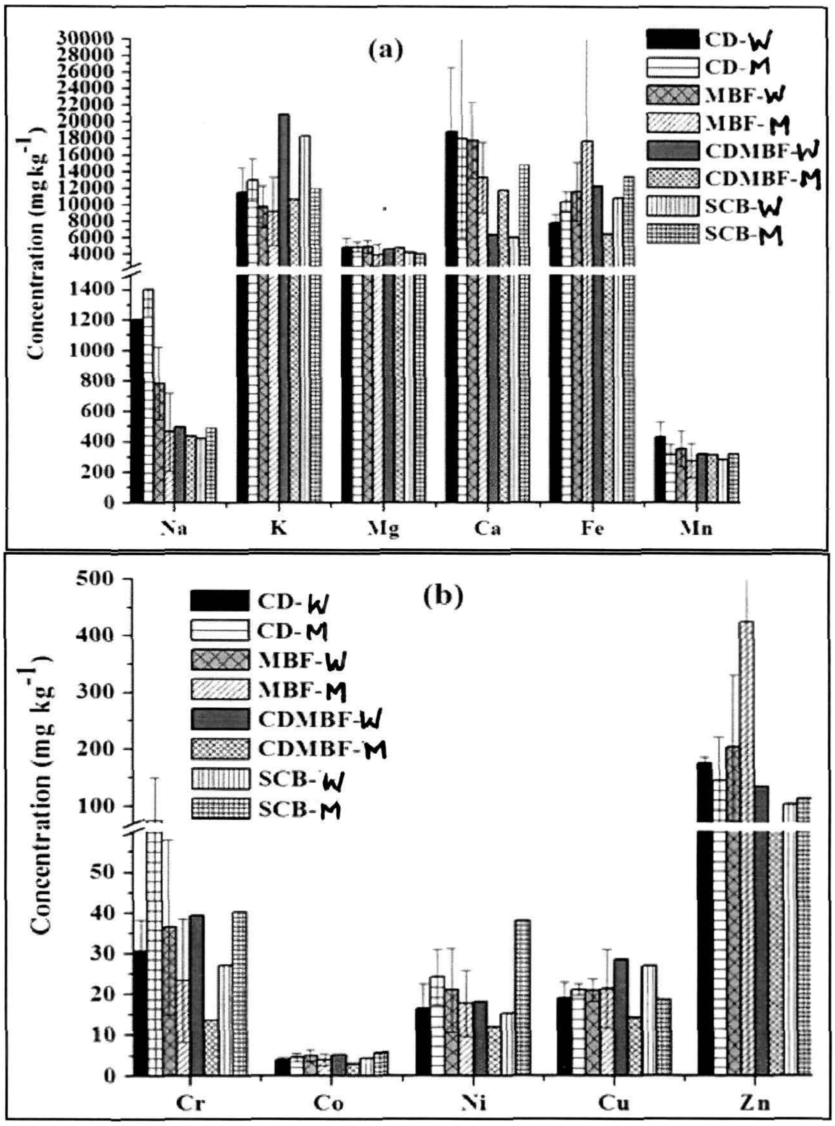


Fig. 4.33. Elemental concentration of different BFSPs in winter and monsoon season

A comparative account of elements and ions of the present study with other studies is given in Table 4.21. Salam et al. [178] and Hasan et al. [179] had done similar study in Bangladesh. Salam et al. [178] had reported maximum K in comparison to other elements and they reported more Co than the present study. In another study, however, Hasan et al. [179] had reported maximum concentration of Fe followed by Ca among all analyzed elements. We had also compared our results with the study by Yamasoe et al. [84]. They reported very high concentration of K in comparison to other analyzed elements. The reported K and Ni in Cerrado fire and Cr and Cu from both Cerrado fire and tropical forest fire were more than the present study. Zn is an important elements emitted from biomass burning [84,180] and wood combustion [181]. Except MBF, Zn was comparable with other studies. Cadmium and Pb were not detected in this study. However, researchers had reported Pb and Cd from biomass burning smoke deposits in Bangladesh [178,179]. Salam et al. [178] had also found higher Pb in Bangladesh soil which was suspected to be the reason of high level of Pb in biomass fuel. Cd and Pb were not present in plant biomass. Some elements under study viz., Cr, Cu, Ni, Zn, Pb, Cd are characteristics of fossil fuel emission. To have an idea our data is compared with the Diesel Engine Particulates' metal concentration as reported by Sharma et al. [182]. They reported much higher values of Cr, Ni, Zn and Pb than the present study. Concentration of Mg, Ca and Fe which are important plant nutrients were much lower than the present study.

4.3.2. Anions

All BFSP samples were analyzed for 6 anions viz., F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-} and PO_4^{3-}. For all BFSPs the trend of ions was $SO_4^{2-} > Cl^- > PO_4^{3-} > NO_3^- > F^- > Br^-$. Seasonal concentration of different BHSPs is given in Fig. 4.34. Bromide and SO_4^{2-} were higher in monsoon samples in all BFSPs. F^- and PO_4^{3-} were higher in monsoon period samples in CD and MBF. CDMBF and SCB contain higher F^- and PO_4^{3-} in winter. Cl^- was higher in winter for MBF and SCB and in monsoon CD and CDMBF contained more Cl^- than winter. Except SCB, other biomass fuel smoke particles contain higher NO_3^- in winter. Yamasoe et al. [84] had reported Cl^- and SO_4^{2-} as the dominant anion from biomass burning in Cerrado and tropical forest fire. Cl^- and $SO_4^{\ 2-}$ were the major anions from Savanna fire in Southern Africa [183]. Saud et al. [184] had reported anion trend of $Cl^- > NO_3^- > SO_4^{2-} > PO_4^{3-} > F^-$ for wood and dung cake in a study characterizing different biomass fuel in India.

Bromine is an important chemical species in the atmosphere. Deka and Hoque [185] had reported high concentration of Br during festive biomass burning in northeastern Indian states. Yamasoe et al. [84] also reported emission of Br from vegetation fire in the Amazon basin.

Average concentration of anions is put up in Table 4.21. CD contained maximum SO_4^{2-} (15647.96±12854 mg kg^{-1}), F^- (238.85±171 mg kg^{-1}) and Br^-(135.92±145 mg kg^{-1}). Cl^- was maximum in MBF (8486.16±9341.94 mg kg^{-1}). Maximum PO_4^{3-} (2662.20±2940 mg kg^{-1}) and NO_3^-(706.65±692 mg kg^{-1}) were found in SCB.

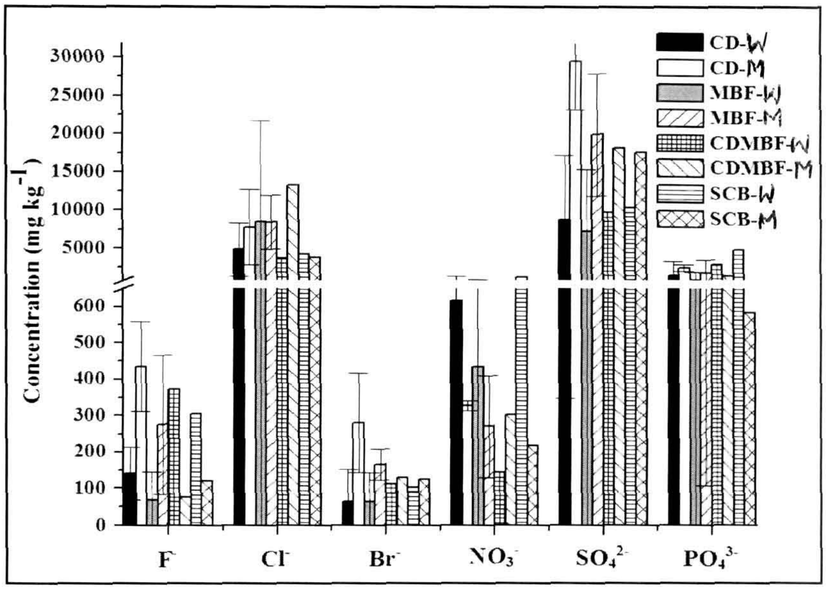


Fig 4.34. Anion concentration of different BFSPs in winter and monsoon season

Anion concentrations were compared with other studies (Table 4.21). The concentrations of NO_3^-, PO_4^{3-} and SO_4^{2-} of the present study were higher than a similar study by Salam et al. [178]. However, Yamasoe et al. [84] had found high Cl^- in Cerrado fire and NO_3^- in both Cerreado fire and tropical forest fire than the present study. Attributes like soil quality, weather, ground water quality etc. can affect the chemical species composition of different biomass fuel used of a region [184] and, therefore, there could be geographical bias in the context of emissions too.

4.3.3. Carbon content

Carbon content of different BFSPs along with typical biomass burning ratios are given in Table 4.22. Carbon was maximum in CD and minimum in SCB. Seasonal variation of carbon was distinct for all biomass fuels except SCB. TC and OC was higher in winter than monsoon samples. EC did not vary much in concentration for different BFSPs and in different seasons. Yamasoe et al. [84] had reported EC as a main component of biomass burning and reported higher value than the present study. OC and EC reported in other studies were much lower than the present study [186,184]. Concentration of EC of

Table 4.22. Carbon (g kg^{1}) and some characteristic ratios in BFSPs and other studies

Type of biomass	References	TC	FC	OC	WSTC	WSOC	EC/TC	OC/EC	WSOC/OC	Cl /EC	SO$_4^{2}$ /EC
CD W [1]	Present study	217 55±28 14	28 64±3 16	188 91±25 82	27 64±9 04	26 68±8 76	0 13±0 01	6 6±0 63	0 11±0 03	0 17±0 13	0 31±0 29
CD M [1]	Present study	183 45±44 48	28 72±1 77	154 74±42 70	7 91±2 91	7 50±2 88	0 16±0 03	5 35±1 16	0 05±0 03	0 28±0 19	1 02±0 16
MBF W [1]	Present study	160 35±40 35	25 95±3 23	134 40±37 93	15 51±4 14	14 49±4 07	0 17±0 03	5 13±1 03	0 11±0 04	0 32±0 46	0 27±0 28
MBF M [1]	Present study	119 21±26 67	24 44±2 85	94 76±27 22	11 48±5 88	10 56±5 47	0 21±0 06	3 94±1 26	0 13±0 11	0 34±0 14	0 85±0 45
CDMBF-W [1]	Present study	140 00	17 88	122 12	6 744	6 404	0 13	6 83	0 05	0 20	0 54
CDMBF M [1]	Present study	127 00	23 70	103 30	10 71	10 36	0 19	4 36	0 10	0 56	0 77
SCB W [1]	Present study	82 99	28 75	54 24	7 108	6 721	0 35	1 89	0 12	0 15	0 36
SCB M [1]	Present study	78 00	28 68	49 32	7 186	6 92	0 37	1 72	0 14	0 13	0 61
Cerrado fire [2a]	Yamasoe et al [84]		95 5±7 2							0 16	0 06
Tropical forest fire [2b]	Yamasoe et al [84]		56±3 7							0 05	0 11
Crop waste of PM$_{2 5}$, China [3a]	Li et al [186]		0 43±0 32	2 93±1							
Wood fuel of PM$_{2 5}$, China [3b]	Li et al [186]		1 49±0 69	1 13±0 40							
Dung cake, India [4a]	Saud et al [184]		0 53	3 93				16 20±1 65		1 40±0 16	0 24±0 02
Agricultural residue India [4b]	Saud et al [184]		0 35	1 02				3 77±0 89		1 72±0 15	0 24±0 03
Fuel wood, India [4c]	Saud et al [184]		0 36	0 91				2 82±0 21		1 14±0 12	0 24±0 05

1 Present study

[2] Air particulates were sampled directly over freshly emitted biomass burning plumes, EC is the average of flaming and smoldering phase

[3] PM$_{2 5}$ were collected from household during biomass burning in cooking stoves Fuel size and feeding were consistent with the local cooking practice during the measurements

[4] Particulate matter were collected burning same amount of each sample for twenty times

EC and OC in Saud et al , 2013 are calculated from given average of respective biomass type of different states

CD and SCB was almost similar and concentration of OC was maximum in CD. Maximum OC and EC concentration had been reported from dung cake burning in a study from India by Saud et al. [184].

We had also analyzed WSTC and WSOC of BFSPs. WSTC and WSOC were maximum in CD and MBF during winter. However, these two parameters were maximum in CDMBF during monsoon. SCB contained almost similar concentration in both seasons. These two parameters could not be compared with other studies due to unavailability of literature.

Higher ratios of OC/EC indicate the origin of particulates from biomass burning [120,169]. Our data yielded OC/EC ratio 1.89 to 7.41 during winter and 1.72 to 6.19 during monsoon season. OC/EC ratio had been compared with the study by Saud et al. [184] (Table 4.22). They had reported OC/EC ratio between 1.45 and 6.71 for agricultural residue and wood. However, OC/EC ratio from dung cake was much higher than our results. We had also calculated WSOC/OC (Table 4.22) for different BFSPs. This ratio varied between 0.05 and 0.2 during winter and 0.3 to 0.38 during monsoon season. Mayol-Bracero et al. [157] had reported WSOC fraction accounting for 45 to 75% of the OC in biomass burning aerosols over Amazonia. They said that this high WSOC fraction suggests an aerosol derived mainly from smoldering combustion. Therefore we can say that our higher values of WSOC/OC during monsoon suggests comparatively higher smoldering phase in monsoon biomass fuel burning in kitchens. Ratio of Cl^-/EC and SO_4^{2-}/EC are also used as a signature of biomass burning. The values of the present study do not agree with the reported values by different researchers. Cl^-/EC ratio of the present study was lower than the values reported by Saud et al. [184], but higher than that of Yamasoe et al. [84]. We had found higher SO_4^{2-}/EC ratio than other studies. Again, there were differences among the reported biomass burning studies by various groups of researchers. These differences are probably due to different burning conditions, weather, types of biomass burning etc.

4.3.4. Polycyclic Aromatic Hydrocarbons (PAHs)

Average individual concentrations of 14 PAHs are given in Table 4.23. Maximum PAHs was recorded for CD. Flouranthene was maximum in CD, CDMBF and SCB. In MBF, BaA was maximum. Flouranthene, BaA, PHE and CHR were the dominant PAHs in all BFSPs. Venkataraman et al. [187] also reported higher PAHs concentrations for dung cake and briquette fuel than wood burning. Overall, low molecular weight PAHs dominate over high molecular weight PAHs in the present study. Other studies also

Table 4.23. PAHs of the present study and other studies. Concentrations in mg kg^{-1}

	Present study*				**Rajput et al. [173]**		**Khillare et al. [191]**		**Khillare et al. [192]**	
	CD	**MBF**	**CDMBF**	**SCB**	**Paddy residue**	**Wheat residue**	**Buses**	**Trucks**	**Cars**	**Auto rickshaw**
NAP	93.95±146	50.32±45	117.21±157	20.76±20	4±3	8±6				
ACY	32.81±37	43.99±32	23.83±20	28.17±40	1±0	1±1				
ACE	1.45±1	1.70±3			1±2	0±0				
FLU	6.93±5	7.96±5	6.52±5	5.37±7	1±0	0±0				
PHE	50.39±73	72.82±93	127.50±177	40.53±48	4±3	14±10	14160	15350	15080	15620
ANT	86.26±85	38.87±36	86.79±94	31.95±44	1±1	4±10	2990.00	3350	380	460
FLA	240.17±106	113.86±86	190.23±175	162.45±180	11±6	23±16	9898.00	10100	3330	2920
PYR	93.74±47	27.64±23	50.74±56	44.47±28	13±7	24±16	10510.00	13560	4850	3980
BaA	123.45±86	155.27±110	84.08±54	75.46±94	15±7	6±9	3600.00	4270	490	660
CHR	91.70±27	44.41±46	128.68±24	65.00±87			3400.00	4850	1170	1060
BbF	15.28±13	19.45±13	14.41±16	23.90±9			2840 (BFs) $^{\#}$	2480 (BFs) $^{\#}$	272.7 (BFs) $^{\#}$	600 (BFs) $^{\#}$
BkF	4.95±3	3.61±5	30.08±7	10.56±15						
BaP	2.55±1	2.58±3	9.07±3	5.38±2	52±24	29±28	760.00	750	300	570
DBA	8.35±3	2.55±2	20.26±11	13.77±3	11±5	5±7	710.00	690	140	230

*Average of winter and monsoon samples

Average of BbF and BkF

reported predominance of lower molecular weight PAHs [187,174]. Venkataraman et al. [187] had reported predominance of low molecular weight PAHs viz., FLA, PYR and B(a)A from different biofuels in a study from India. In a crop residue burning study, Shen et al. [174] found PHE, FLA, FLU and PYR as the dominant PAHs in the particulate phase.

Seasonal variation of PAHs content of different BFSP samples was distinct with maximum concentration in monsoon season (Fig. 4.35). Probable reason of high PAHs content of monsoon BFSP samples was the incomplete combustion of biomass fuel due to high moisture content during monsoon season which results in more PAHs emission. However, seasonal variation of PAHs was not distinct in case of SCB. Maximum concentration of PAHs was recorded for CD in both the seasons. It is noticeable that comparatively PAHs with even number of rings were higher than odd numbered PAHs. Overall 4-ring PAHs were dominant followed by 2-ring, 3-ring and 5-ring PAHs (Fig. 4.36).

Due to lack of similar study PAHs concentration of present study could not be compared with other such studies. There were simulated studies on PAHs emission from different biofuel used in kitchens which had reported emission factor of PAHs [187-189]. It was reported that particle Emission Factors in actual cooking activities were over three times higher than those from a simulated experiment in the laboratory [190]. PAHs concentrations of the present study were much higher than the PAHs concentrations of paddy and wheat residue burning period reported by Rajput et al. [173] (Table 4.23). However, PAHs concentrations of the present study was found to be much lower when compared with the emission factor of PAHs from diesel fueled (buses and trucks) and gasoline fueled vehicles (cars and auto rickshaws) reported by Khillare et al. [191,192] in India (Table 4.23).

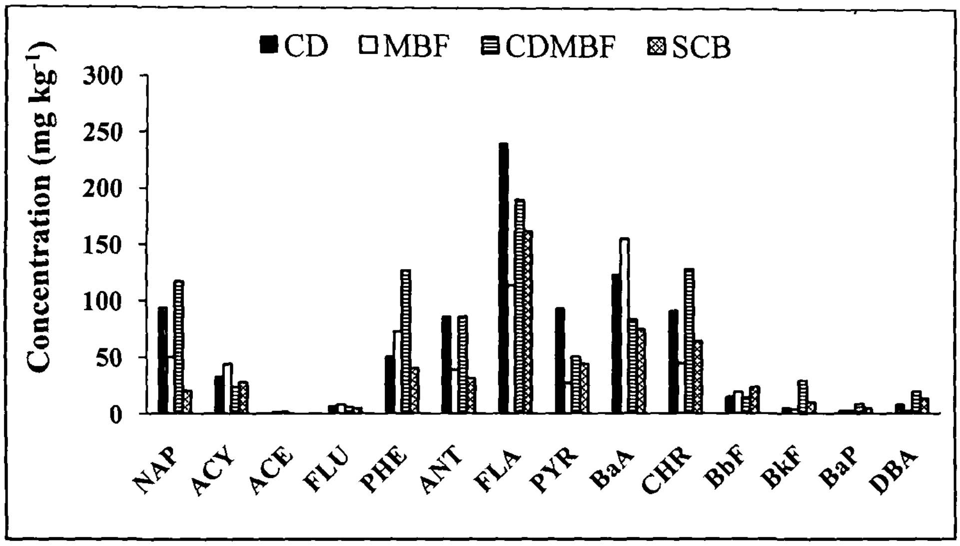


Fig. 4.35. Average PAH concentrations of different BFSPs

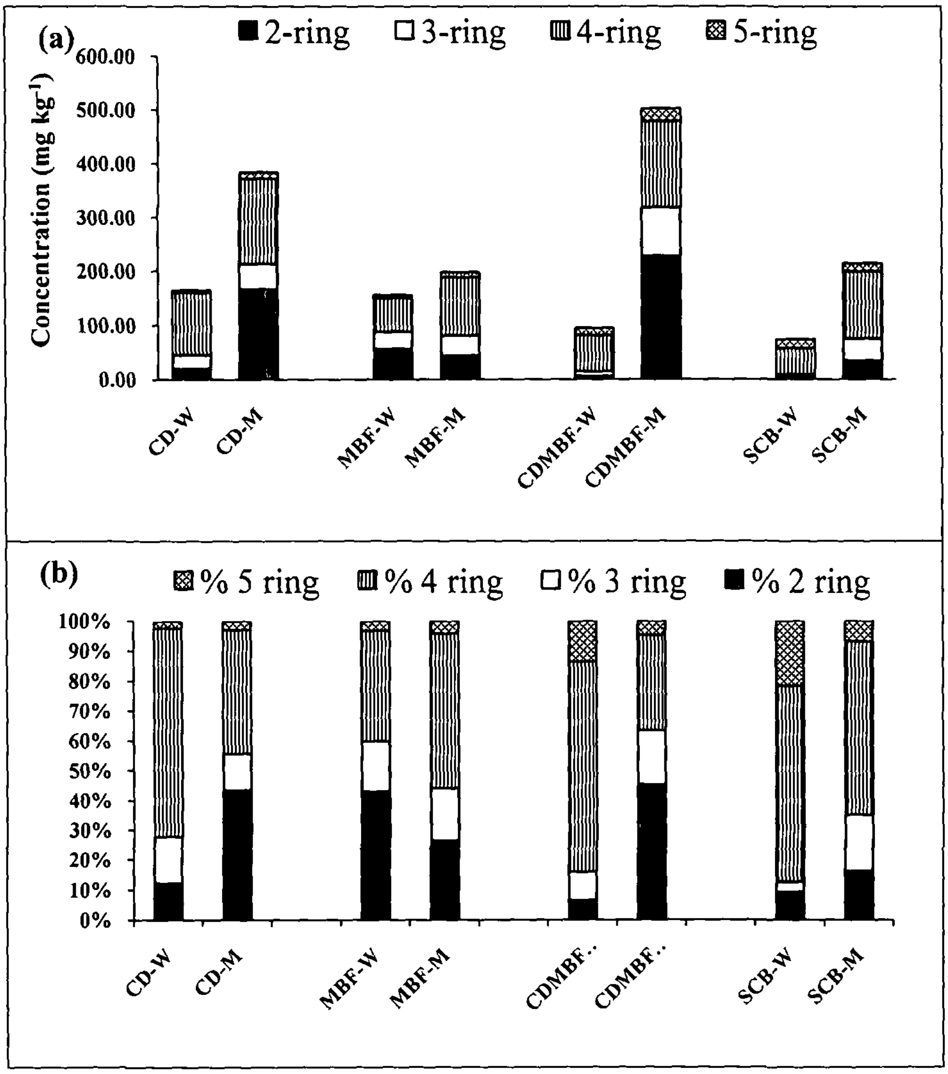


Fig . 4.36. (a) Ring wise distribution of PAHs of different BFSPs (Total column height is the $\sum_{14}$PAHs) (b) Percent contribution by different ringed PAHs

Researchers had reported characteristic diagnostic ratios of PAHs of different biomass fuels. These ratios of the present study with ratios of reported studies are given in Table 4.24. The diagnostic ratios of the present study were not similar with other studies. This may be due to the difference in burning condition and different biomass fuel used. Also, the present study is conducted in the natural biomass fuel burning in traditional rural kitchens while the reported studies were conducted in simulated conditions.

Table 4.24. Comparative account of the molecular diagnostic ratios of the present study with different biomass burning studies

		ANT/(ANT+PHE)	FLA/PYR	FLA/(FLA+PYR)	BbF/BbF+BkF	BaA/BaA+CHR
CD	This study	0 63±0 38	2 66±0 94	0 71±0 06	0 75± 25	0 51±0 29
MBF	This study	0 42±0 24	5 62±5 05	0 78±0 14	0 84±0 17	0 68±0 25
CDMBF	This study	0 63±0 36	4 64±1 63	0 81±0 05	0 27±0 21	0 38±0 20
SCB	This study	0 29±0 23	2 96±2 18	0 70±0 16	0 73±0 38	0 52±0 64
Paddy residue/ambient	Rajput et al [173]	0 15±0 03	0 84±0 04	0 46±0 01		
Paddy residue/chamber	Rajput et al [173]	0 17±0 01	0 97±0 21	0 49±0 05		
Crop residue/stove	Shen et al [174]	0 12±0 01		0 53±0 03	0 55 ± 0 03	0 48 ± 0 02
Crop residue/open fire	Shen et al [174] and references therein	0 17-0 25		0 34-0 53	0 35-0 80	0 39-0 50
Wood /stove	Shen et al [174] and references therein	0 10-0 30		0 43-0 74	0 35-0 51	0 39-0 56

4.3.5. Dependency of PM_{10} on biomass burning

As discussed earlier biomass burning is an important source of particulate matter in India. Linear relationships were established between chemical species viz., elements, carbon and anions of PM_{10} and BFSPs to see dependency of PM_{10} on biomass burning. X/X_T was calculated for each chemical species of PM_{10} and BFSPs. Here, X is the mean chemical species concentration in PM_{10} and BFSP samples and X_T is the sum of all chemical species concentration in PM_{10} and BFSPs.

A strong correlations ($R^2=0.87$) was found between chemical species of PM_{10} and BFSPs (Fig. 4.37). This suggests strong dependency of PM_{10} on biomass burning of this region.

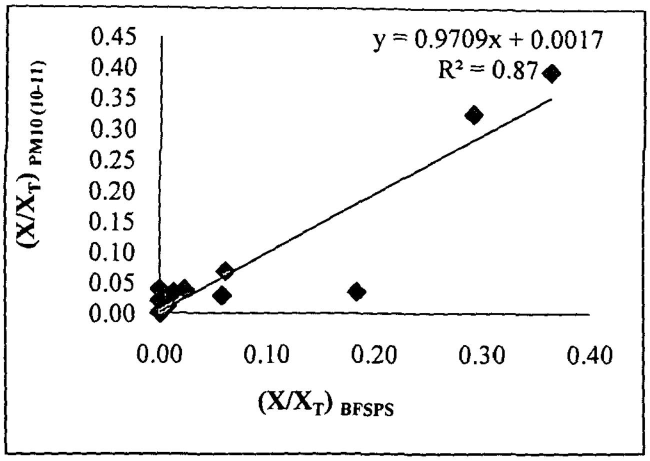


Fig 4.37. Correlation between chemical species of PM_{10} and BFSPs

Biomass burning is a significant source of atmospheric PAHs. Different types of biomass are used to build the *meji* and so the PM_{10} of the *meji* period could have been significance of biomass burning. Therefore, we examined the relationship of $PAH_i/\sum_{14}PAHs_{\text{-PM10}}$ and $PAH_i/\sum_{14}PAHs_{\text{-BFSP}}$ (Fig. 4.38). The analysis showed a positive linear relationship indicating influence of biomass burning on PM_{10} load during the *meji* burning event of 2012 (Fig. 4.38a) and 2013 (Fig. 4.38b).

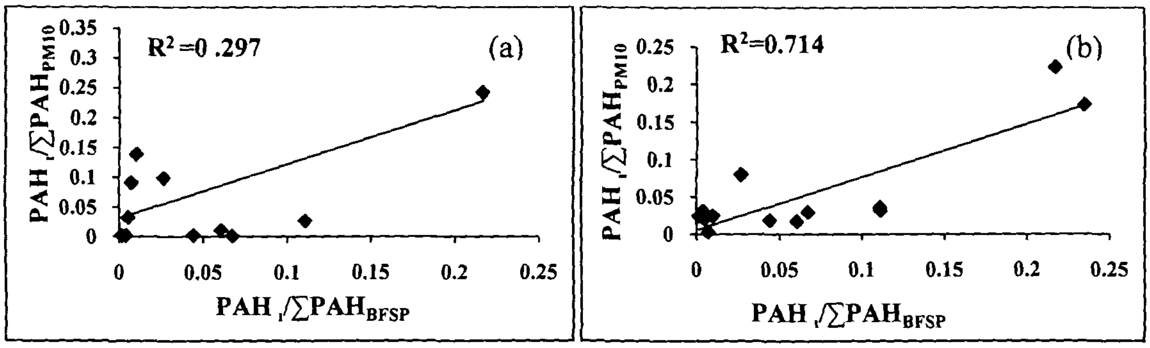


Fig 4.38. Correlation between PAHs of PM_{10} and BFSPs.

Characterizations of BFSPs collected from rural kitchens revealed that CD is the most polluting and SCB is the least polluting biomass fuels in comparison to other biomass fuels studied. Calcium, K, Fe and Mg were the major elements found in all biomass fuels. Sulphate, Cl^- and PO_4^{3-} were dominant anions present in all BFSPs. Seasonal variation was distinctive only for carbon and PAHs. Carbon was more in winter and PAHs was more in monsoon. 4-ring PAHs was contributing more to total PAHs concentration. FLA, BaA and CHR were the dominant PAHs. We had also found strong correlations between chemical species of PM_{10} and BFSP suggesting contribution of biomass burning to atmospheric loading of particulate matter of this region. The reported concentration and ratios used in this study could be used as baseline data for future works.

4.4. Exploring atmospheric deposition signatures

To see if soil elemental composition depends on atmospheric particulates linear relationships were examined between elements of soil with PM_{10} and BFSP samples. X/X_T was calculated for each elements of soil, PM_{10} and BFSPs. Here, X is the mean elemental concentration and X_T is the sum of all elements in soil, PM_{10} and BFSP samples. Elements considered for this study were Mg, K, Ca, Cr, Mn, Fe, Ni, Cd and Pb for soil and PM_{10}. Na, Mg, K, Ca, Cr, Mn, Fe, Ni and Zn were considered for soil and BFSPs. Co and Cu were below detection limit in soil.

The concentration of elements of soil samples were given in Table 4.25 for both pre-monsoon and post-monsoon season. The linear correlations between soil elements and PM_{10} indicate that soil composition does not rely much on deposition of atmospheric particulates (Fig. 4.39a).

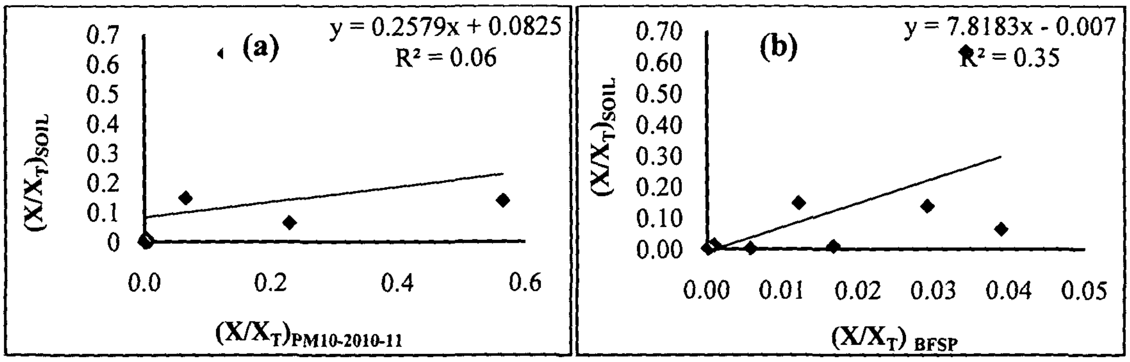


Fig. 4.39. Correlation between elements of - (a) soil and PM_{10} (b) soil and BFSP

Linear correlations were also examined between elements of soil and elements of BFSPs. It gives a R^2 value of 0.35 (Fig. 4.39b). In this region, biomass burning is very common mainly for household cooking and heating during winter months.

Table 4.25. Concentration of elements of soil (mg g^{-1}). Here, PrM- pre-monsoon & PoM- post-monsoon

	Na		Mg		K		Ca		Cr		Mn		Fe		Ni		Zn		Cd		Pb	
	PrM	PoM	PrM	PoM	PrM	PoM	PrM	PoM	PrM	PoM	PrM	PoM	PrM	PoM	PrM	PoM	PrM	PoM	PrM	PoM	PrM	PoM
Site 1	3.1E-01	4.1E-01	4.07	3.65	4.92	2.68	1.77	1.51	5.8E-02	2.6E-02	0.41	0.37	18.89	17.37	2.3E-02	1.5E-02	4.9E-02	2.2E-01	1.2E-03	8.0E-04	1.5E-03	5.2E-03
Site 2	2.9E-01	3.1E-01	5.29	4.89	3.90	6.02	1.40	1.45	6.0E-02	*5.9E-02*	0.35	0.33	23.65	21.34	3.4E-02	1.2E-01	6.4E-02	9.1E-02	1.1E-03	1.2E-03	8.8E-03	3.2E-03
Site 3	3.5E-01	5.0E-01	3.85	3.59	3.46	3.15	1.77	1.58	3.3E-02	2.8E-02	0.44	0.43	16.85	*16.31*	1.7E-02	1.6E-02	6.7E-02	9.2E-02	1.2E-03	6.8E-04	8.2E-03	6.4E-03
Site 4	2.5E-01	4.4E-01	4.64	3.89	3.94	2.94	3.14	1.83	3.9E-02	2.7E-02	0.39	0.39	18.65	16.92	1.8E-02	1.6E-02	6.2E-02	9.1E-02	9.2E-04	6.8E-04	4.2E-03	4.2E-03
Site 5	3.2E-01	2.2E-01	5.05	3.34	6.09	3.05	2.46	1.46	7.6E-02	2.5E-02	0.44	0.32	21.16	14.49	3.0E-02	1.3E-02	6.5E-02	5.5E-02	1.2E-03	5.6E-04	2.3E-03	1.8E-03
Site 6	3.2E-01	3.2E-01	5.21	2.76	5.10	2.44	2.55	1.96	4.2E-02	2.3E-02	0.45	0.36	22.47	14.77	2.1E-02	1.3E-02	7.1E-02	*7.3E-02*	1.1E-03	5.2E-04	3.7E-03	3.7E-03
Site 7	3.1E-01	3.5E-01	3.37	3.23	3.16	2.79	1.4	1.93	3.1E-02	3.8E-02	0.31	0.37	15.41	*18.18*	1.6E-02	2.1E-02	4.4E-02	7.6E-02	8.8E-04	5.6E-04	2.6E-03	4.1E-03
Site 8	3.7E-01	2.7E-01	4.18	2.61	5.28	2.11	1.67	1.34	3.2E-02	2.6E-02	0.47	0.35	18.20	14.51	1.6E-02	1.6E-02	5.8E-02	6.4E-02	9.6E-04	4.8E-04	3.8E-03	3.1E-03
Site 9	2.1E-01	3.7E-01	4.28	3.86	5.14	2.89	1.77	1.41	3.2E-02	2.8E-02	0.47	0.47	18.74	17.54	1.4E-02	1.6E-02	5.6E-02	9.4E-02	6.9E-04	9.2E-04	2.0E-03	6.0E-03
Site 10	2.7E-01	4.4E-01	3.7	3.28	3.33	2.9	1.75	1.6	4.2E-02	2.6E-02	0.41	0.39	15.91	14.27	1.8E-02	1.5E-02	6.5E-02	8.6E-02	1.0E-03	8.0E-04	5.6E-03	4.5E-03
Site 11	2.4E-01	5.0E-01	4.89	4.74	3.53	3.35	2.00	2.61	3.9E-02	3.5E-02	0.35	0.42	21.02	20.19	2.2E-02	1.9E-02	6.0E-02	9.3E-02	1.4E-03	9.6E-04	6.2E-03	5.5E-03
Site 12	3.4E-01	3.0E-01	6.08	5.54	6.24	5.6	2.04	1.73	5.1E-02	4.1E-02	0.48	0.41	24.93	23.07	2.7E-02	2.4E-02	6.9E-02	8.7E-02	1.2E-03	*1.1E-03*	7.0E-03	*6.0E-03*
Site 13	5.2E-01	4.6E-01	5.21	5.42	4.21	6.16	2.49	2.65	1.3E-01	4.4E-02	0.46	0.42	19.98	21.64	7.6E-02	2.4E-02	8.3E-02	1.3E-01	1.2E-03	1.0E-03	5.4E-03	4.1E-03
Site 14	2.7E-01	2.4E-01	5.8	4.04	4.33	3.37	2.32	1.57	4.2E-02	5.8E-02	0.53	0.37	24.37	17.51	2.6E-02	4.7E-02	7.8E-02	6.8E-02	1.1E-03	6.0E-04	6.8E-03	3.6E-03
Site 15	3.1E-01	4.4E-01	6.5	5.80	7.20	5.78	2.82	3.51	6.3E-02	4.0E-02	0.56	0.50	28.83	22.86	2.5E-02	2.3E-02	6.7E-02	8.1E-02	9.6E-04	8.0E-04	3.7E-03	5.1E-03
Site 16	3.9E-01	2.7E-01	5.58	4.78	5.66	3.64	1.55	1.83	5.3E-02	3.9E-02	0.54	0.48	24.33	21.70	*3.1E-02*	2.2E-02	7.0E-02	*1.0E-01*	1.0E-03	1.0E-03	*5.6E-03*	7.1E-03
Site 17	2.5E-01	3.6E-01	5.15	3.21	3.88	3.21	2.23	1.65	6.1E-02	2.5E-02	0.43	0.32	21.98	13.56	3.6E-02	1.3E-02	5.2E-02	*5.4E-02*	1.1E-03	6.8E-04	5.7E-03	2.6E-03
Site 18	2.9E-01	2.7E-01	4.58	4.16	4.84	3.89	2.24	1.95	2.9E-02	*3.1E-02*	0.44	0.40	11.12	19.23	2.1E-02	1.7E-02	5.9E-02	9.1E-02	6.4E-04	8.0E-04	8.0E-04	3.0E-03
Site 19	3.9E-01	3.6E-01	5.44	4.24	5.98	4.06	2.46	2.01	4.4E-02	3.5E-02	0.53	0.42	19.73	18.40	2.7E-02	1.8E-02	6.4E-02	7.5E-02	1.0E-03	1.2E-03	3.4E-03	4.4E-03
Site 20	3.5E-01	3.2E-01	6.36	5.49	4.80	5.61	1.90	1.58	1.1E-01	4.3E-02	0.39	0.34	27.46	21.97	7.1E-02	2.3E-02	7.9E-02	8.8E-02	1.2E-03	8.8E-04	1.3E-02	*6.0E-03*

4.5. References

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CHAPTER 5
CONCLUSIONS AND FUTURE SCOPE

The main objectives of this study were to characterize PM_{10} at Tezpur, a rural receptor site of Northeast India, to see the impact of extraordinary emission day on PM_{10} and to characterize the particles emitted from biomass burning in rural kitchens and to see the dependency of PM_{10} on rural household biomass burning.

The PM_{10} study for two whole years showed higher concentration of PM_{10} during 2008-09 than that of 2010-11. PM_{10} was maximum during monsoon season of 1st year. The probable reasons were low rainfall, subsidence condition of atmosphere and temperature inversion prevailed during that period. However, PM_{10} was maximum during the winter and minimum during the monsoon in the 2nd year. During winter months dry condition, low mixing height, temperature inversions leads to higher PM loading and during the monsoon rain washout removes the particulates from the atmosphere. Average annual PM_{10} was 2.5 times higher than the annual national standard during 1st year and it was within the national standard during 2nd year.

Elemental constituents of PM_{10} was higher during 1st year than that of 2nd year. Cadmium showed maximum enrichment in comparison to other elements. Comparative account of elemental concentration revealed that most of the elements were lower than other Indian studies and higher than studies from abroad. The analysis of PM_{10} for ions and carbon showed that except F^- and Na^+ other ions and all carbon fractions were maximum during the winter. Cation deficient condition was found which indicates possibility of acid rain of the region. Among the ions SO_4^{2-} was the dominant. TC accounts 44% of PM_{10}. Very high percentage of SOC in OC and high ratio of WSOC to OC indicates dominance of secondary aerosols along with CCN activity of aerosols of this region. Characteristic ratios and source apportionment of PM_{10} revealed biomass burning as the major source of PM_{10}. Other sources were contribution from soil, vehicular emission and coal burning. PCA-MLR revealed 70% source contribution from biomass burning.

PM_{10} characterization during Diwali fireworks of 2009 revealed minimum and short term impact on air quality in the rural Brahmaputra Valley. Marginal increase of associated elements and ions was found. The incremental effect of Diwali was very marginal as compared to the events in the 'mainland India'. Cation deficient condition was found during the study. DIE showed marginal increase of elements and ions during the festive days.

Study on atmospheric PM_{10} during *meji* burning period of 2009 showed incremental effects of *meji* burning in the Brahmaputra Valley of Northeast India. PM_{10} was 1.5 times higher than the 24-hr national standard with maximum concentration on the *meji* burning day. During the study period PM_{10} was found to be extremely carbonaceous. PM_{10} was enriched with Br and other elements. PM_{10} and carbon showed nighttime maximum. Studies on back trajectory analysis revealed long range transport of aerosols from the IGP region of India. Atmospheric condition was favorable for low dispersion of pollutants during the later part of the study resulted in the build up of PM_{10}.

Detail study on atmospheric PM_{10} during *meji* burning in the following years was done. Maximum PM_{10} was found on the *meji* burning day. Except elements, most of the chemical species were maximum on the *meji* burning day. High concentration of WSOC indicates the CCN activity of aerosols and the presence of smoldering phase during *meji* burning period. The PAHs diagnostic ratios were similar with other reported biomass burning studies.

Characterizations of BFSPs collected from rural kitchens revealed that CD is the most polluting and SCB is the least polluting biomass fuels in comparison to other biomass fuels studied. Among the measured elements Ca and K were the most dominant in all BFSPs. We found high emission of SO_4^{2-}, Cl^- and PO_4^{3-} from all biomass fuels. Carbon and PAHs showed significant seasonal variation. Carbon content of BFSPs was maximum in the winter. High PAHs content during monsoon samples was probably due to incomplete combustion of biomass fuel due its high moisture content. FLA and BaA were the most dominant PAHs of all BFSP samples with higher contribution of 4-ring PAHs. The strong positive relationships between elements and chemical species of PM_{10} with BFSPs showed biomass burning as a major source of PM_{10} of this region. This was further explained by good linear relationship between PAHs of PM_{10} of *meji* burning period with PAHs of BFSP samples.

To the best of our knowledge characterization of PM_{10} during Diwali and *meji* were the first study of its kind from Northeast India. We would also like to mention that there was study from South Asia on particulates emitted from rural households biomass burning, yet the method of sample collection employed by us is first of its kind till date.

The present study will work as baseline study especially for the entire Northeastern part of India and could be used for future work.

Future scope

Continuous study of atmospheric PM_{10} will enable to know the PM_{10} trends of this region. Detail study on morphology, carbonaceous nature, radiative behavior of aerosols along with meteorological data will assist to know nature and sources of PM.

Characterization of PM_{10} was done during Diwali fireworks of 2009 and did not carry the study further due to its marginal impact on the atmosphere. However, with increase in population celebrations of festivals were also growing. So further study should be planned which may revealed some more interesting findings on emission characteristics during Diwali fireworks. We are continuing with PM_{10} characterization during *meji* burning.

In depth study of indoor air monitoring of rural households and further characterization of BFSPs can be an important task. It will help to understand emission characteristics of biomass fuel. This type of pioneering work will aid in policy formulation regarding health and sanitation by the Government.

List of publications

1. Hoque, R.R. & Deka, P. Aerosol and CO emissions during *meji* burning, *Curr. Sci.* **98** (10), 1270, 2010.
2. Deka, P. & Hoque, R.R. Incremental effect of festive biomass burning on wintertime PM_{10} in Brahmaputra Valley of Northeast India, *Atmos. Res.* **143**, 380--391, 2014.
3. Deka, P. & Hoque, R.R. Diwali Fireworks: Early Signs of Impact on PM_{10} Properties of Rural Brahmaputra Valley, *Aerosol Air Qual. Res.* **14**, 1752--1762, 2014.
4. Deka, P. & Hoque, R.R. Chemical characterization of biomass fuel smoke particles of rural kitchens of South Asia, *Atmos. Environ.* **108**, 125--132, 2015.

List of papers presented in seminar(s)/conferences

National

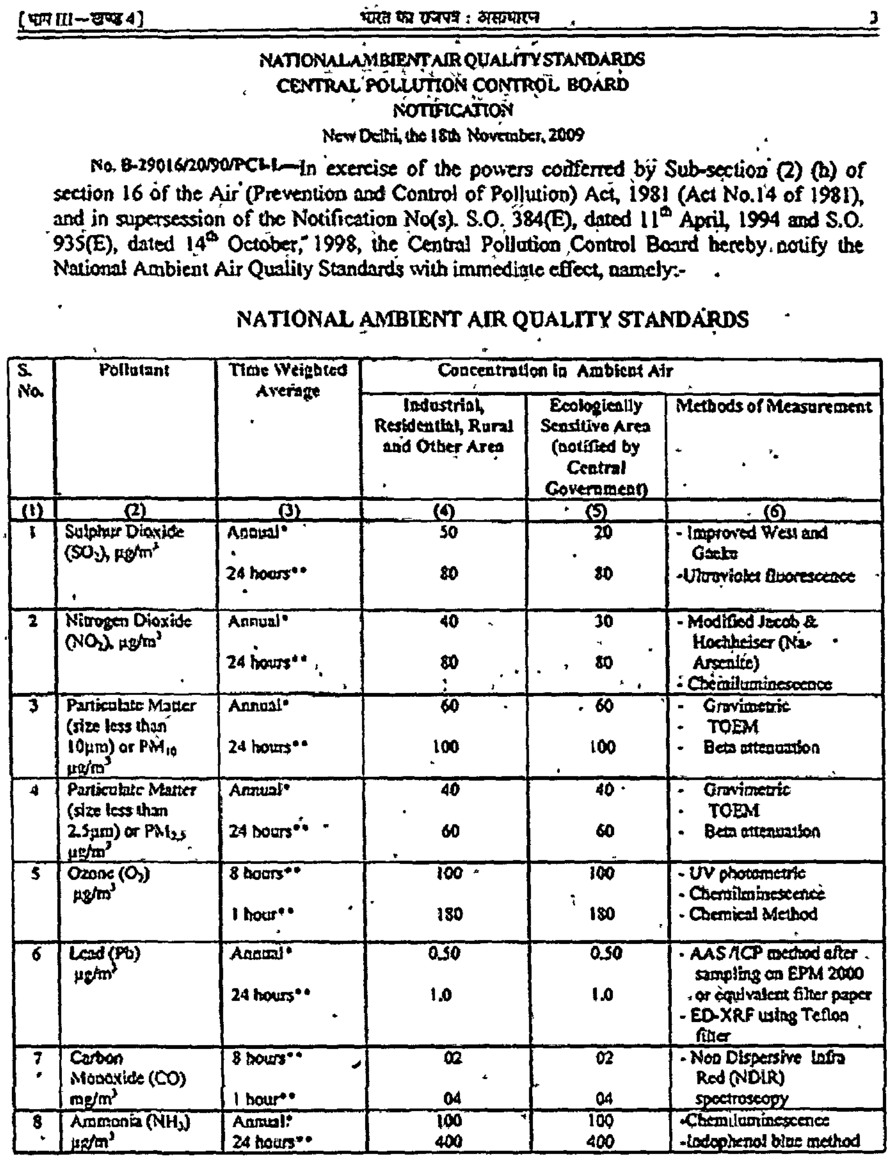
1. Radiative forcing aerosols and an overview of Indian studies. National Seminar on Climate Change and Sustainable Development with reference to India. Tezpur University, Tezpur, Assam-India, April 1- 3, 2010.
2. Bidiversity Vs people of North East India. Pre XXX IV Indian Social Science Congress Symposium. Tezpur University, Tezpur, Assam-India, October 5, 2010.

Interntional

1. $PM_{2.5}$/PM_{10} characters during *Meji* Burning in the Brahmaputra Valley (India). The Sixth International Conference on Environmental Science and Technology. Houston, Texas, USA, 25-29 June, 2012.
2. Characterization of black solid material (BSM) from rural kitchen in Assam, India. International Conference on Harnessing natural Resources for Sustainable Development- Global Trend. Cotton College, Guwahati, Assam, India, 29-31 January, 2014.

ANNEXURE

National Ambient Air Quality Standards



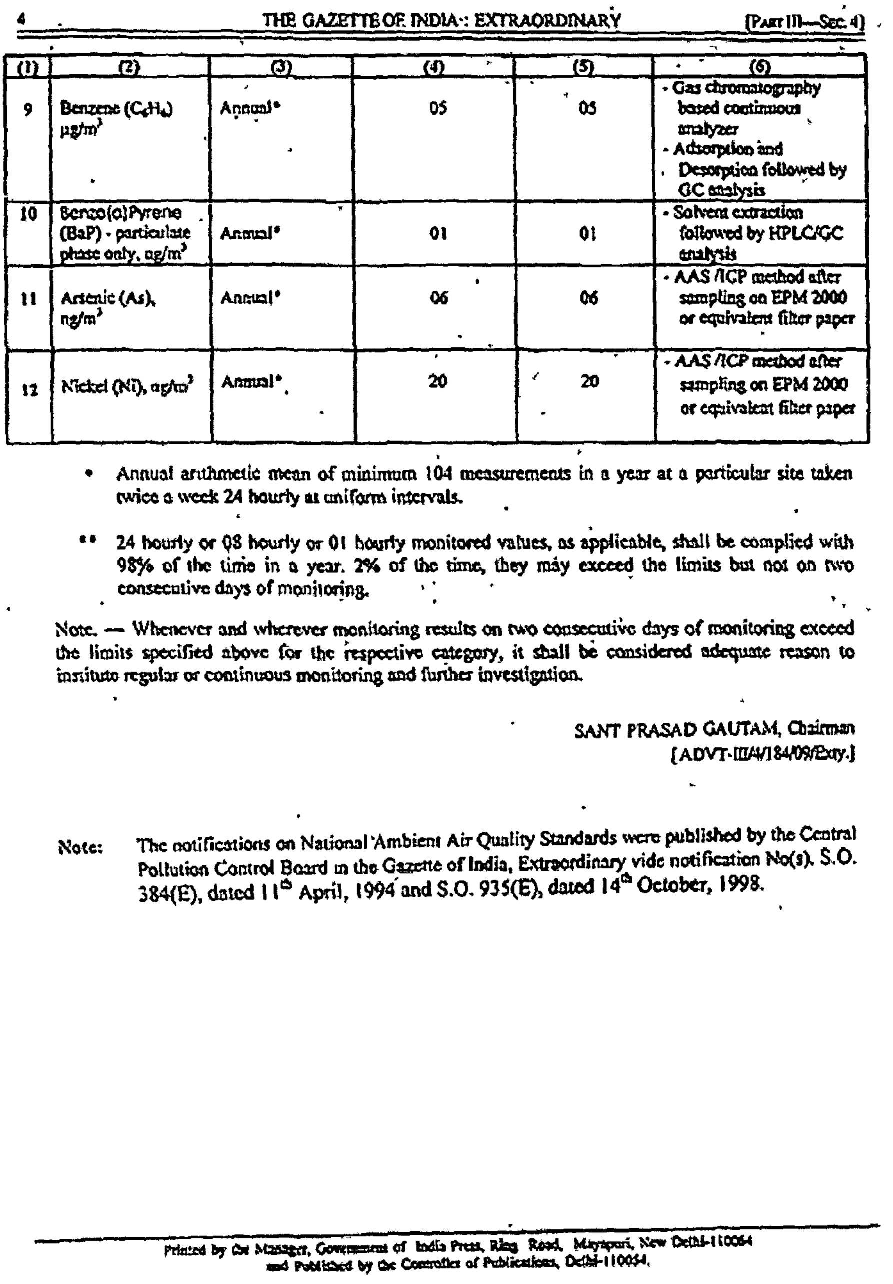
[भाग III—खण्ड 4] भारत का राजपत्र : असाधारण 3

NATIONAL AMBIENT AIR QUALITY STANDARDS
CENTRAL POLLUTION CONTROL BOARD
NOTIFICATION
New Delhi, the 18th November, 2009

No. B-29016/20/90/PCI-I—In exercise of the powers conferred by Sub-section (2) (h) of section 16 of the Air (Prevention and Control of Pollution) Act, 1981 (Act No.14 of 1981), and in supersession of the Notification No(s). S.O. 384(E), dated 11th April, 1994 and S.O. 935(E), dated 14th October, 1998, the Central Pollution Control Board hereby notify the National Ambient Air Quality Standards with immediate effect, namely:-

NATIONAL AMBIENT AIR QUALITY STANDARDS

S. No.	Pollutant	Time Weighted Average	Concentration in Ambient Air		
			Industrial, Residential, Rural and Other Area	Ecologically Sensitive Area (notified by Central Government)	Methods of Measurement
(1)	(2)	(3)	(4)	(5)	(6)
1	Sulphur Dioxide (SO_2), µg/m³	Annual* 24 hours**	50 80	20 80	- Improved West and Gaeke -Ultraviolet fluorescence
2	Nitrogen Dioxide (NO_2), µg/m³	Annual* 24 hours**	40 80	30 80	- Modified Jacob & Hochheiser (Na-Arsenite) - Chemiluminescence
3	Particulate Matter (size less than 10µm) or PM_{10} µg/m³	Annual* 24 hours**	60 100	60 100	- Gravimetric - TOEM - Beta attenuation
4	Particulate Matter (size less than 2.5µm) or $PM_{2.5}$ µg/m³	Annual* 24 hours**	40 60	40 60	- Gravimetric - TOEM - Beta attenuation
5	Ozone (O_3) µg/m³	8 hours** 1 hour**	100 180	100 180	- UV photometric - Chemiluminescence - Chemical Method
6	Lead (Pb) µg/m³	Annual* 24 hours**	0.50 1.0	0.50 1.0	- AAS /ICP method after sampling on EPM 2000 or equivalent filter paper - ED-XRF using Teflon filter
7	Carbon Monoxide (CO) mg/m³	8 hours** 1 hour**	02 04	02 04	- Non Dispersive Infra Red (NDIR) spectroscopy
8	Ammonia (NH_3) µg/m³	Annual* 24 hours**	100 400	100 400	-Chemiluminescence -Indophenol blue method



(1)	(2)	(3)	(4)	(5)	(6)
9	Benzene (C_6H_6) $\mu g/m^3$	Annual*	05	05	- Gas chromatography based continuous analyzer - Adsorption and Desorption followed by GC analysis
10	Benzo(a)Pyrene (BaP) - particulate phase only, ng/m^3	Annual*	01	01	- Solvent extraction followed by HPLC/GC analysis
11	Arsenic (As), ng/m^3	Annual*	06	06	- AAS /ICP method after sampling on EPM 2000 or equivalent filter paper
12	Nickel (Ni), ng/m^3	Annual*	20	20	- AAS /ICP method after sampling on EPM 2000 or equivalent filter paper

* Annual arithmetic mean of minimum 104 measurements in a year at a particular site taken twice a week 24 hourly at uniform intervals.

** 24 hourly or 08 hourly or 01 hourly monitored values, as applicable, shall be complied with 98% of the time in a year. 2% of the time, they may exceed the limits but not on two consecutive days of monitoring.

Note. — Whenever and wherever monitoring results on two consecutive days of monitoring exceed the limits specified above for the respective category, it shall be considered adequate reason to institute regular or continuous monitoring and further investigation.

SANT PRASAD GAUTAM, Chairman
[ADVT-III/4/184/09/Exty.]

Note: The notifications on National Ambient Air Quality Standards were published by the Central Pollution Control Board in the Gazette of India, Extraordinary vide notification No(s). S.O. 384(E), dated 11th April, 1994 and S.O. 935(E), dated 14th October, 1998.

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