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Spatial and Seasonal Variations of Water Soluble Ions in PM_{10} of Mid-Brahmaputra Plain of Assam Valley

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Abstract: A year-long study on water soluble ionic constituents of PM_{10} was conducted at mid-Brahmaputra plain during 2012-2013. Water soluble ions associated with PM_{10} viz. SO_4^{2-}, NO_3^-, Cl^-, F^-, NH_4^+, K^+, Ca^{2+}, Na^+ and Mg^{2+} were analyzed using Ion chromatograph (Metrohm 882 Compact IC Professional) for three representative sites. Marked differences were observed regarding PM_{10} loading and concentrations of major ions in three different sites, with maximum PM_{10} (71.1±56 μg/m^3) at urban site. Among anions, dominance of SO_4^{2-} and Cl^- were observed and Na^+, NH_4^+ and K^+ were found to be predominant cations. An explicit seasonal variation of ionic constituents was observed during the study period with maximum abundance of ions during winter season, and SO_4^{2-} was the most abundant ion during all the seasons. Pre-monsoon season showed influence of crustal input with high mass concentrations of Ca^{2+} and Na^+ in PM_{10}.The equivalent ion balance reveals the fact that except winter season, all other seasons experienced alkaline nature of particulates in the atmosphere. Influence of anthropogenic activities to the ionic constitutions of PM_{10} was revealed by calculating ionic ratios and enrichment factor. HYSPLIT trajectory analysis showed influence of long-range transport of pollutants to this region.

Key words: PM_{10}, major ions, seasonality, HYSPLIT air mass trajectories.

Introduction

Chemical constituents of particulate matter (PM), especially the characterisation of water soluble inorganic ions have been a major concern due to their adverse effect on climate as well as human health, and hence gained attention among the air pollution and climate researchers. There have been attempts world over to systematically understand the origin and chemical behaviour of the ions associated with the PM.

Water soluble ions play vital roles in several atmospheric processes, such as cloud formation, solar radiation, and haze formation because of their affinity with water (Cong et al., 2015; Deng et al., 2011). Ions like SO_4^{2-} act effectively as a reflector of solar radiation and as CCN (Cloud Condensation Nuclei) and thereby control the cloud microphysical properties and cloud albedo (Charlson et al., 1987). Again SO_4^{2-} and NO_3^- are major damaging ions when they get combined with water vapour by respective acids. Sea salt aerosols species such as Cl^- and Na^+ can affect the chemical and microphysical properties of other aerosol components by taking up and releasing chemically reactive compounds including sulphur and halogen compounds. Moreover, sea salt aerosol particles are hygroscopic by nature (Tang et al., 1997) and hence act as CCN (Ayash et al., 2008; Quinn et al., 2000). It has been observed that sea salts do not possess direct health affects rather has an important contribution in increasing PM. Water soluble potassium is a good tracer for biomass

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burning (Andreae, 1983). Atmospheric NH_3, one of the precursors of secondary aerosols, combines with acid gases with adverse effect on health, ecology and climate (Warneck, 1988; Sharma et al., 2012).

In India, several researchers have studied the chemistry of water soluble ionic constituents of PM and reported the alkaline nature of aerosol mainly due to the cations like Ca^{2+} and NH_4^+ (e.g. Khemani, 1994; Safai et al., 2005; Kumar et al., 2002). Yet these studies are mostly carried out in the urban areas of mainland India.

This paper is focused to understand the chemistry of ionic constitutes of PM at three representative sites for a year-long period in middle Brahmaputra plain of Assam Valley. Spatial and seasonal variations of the ions have been presented and discussed.

Methods and Methodology

Site Description

Monitoring of aerosols (aerodynamic diameter ≤ 10 μm or PM_{10}) at three stations namely Tezpur University campus, Napaam (Rural, Site 1: 26°64′N and 92°81′E), Silghat (Rural industrial site, Site 2: 26°37′N 92°56′E) and North Eastern Regional Institute of Water and Land Management (NERIWALM), Tezpur (Urban, Site 3: 26°37′N and 92°50′E), and was carried out for the period of 2012-2013 (Figure 1). Tezpur and Napaam sites are located on the north bank of Brahmaputra River and Silghat is located on the South bank. Stations are centrally located along the length of Brahmaputra River in Assam Valley.

According to the 2011 census, population of Sonitpur district is 2.0 million with a population density of 365 per square km (Census of India 2011). The State of Assam has over 1.8 million registered vehicles for transport and non-transport purposes as on 31st March 2012. The region is underdeveloped in terms of industrial growth. There are no heavy industries around the sampling station yet most tea estates have processing units of their own. The region as a whole has a few petroleum refineries, cement and paper industries and mines. Conventional biomass burning for cooking and some other household activities are prevalent in this region. Vast majority of the population in the region is dependent on solid biomass like wood, cow dung, crop residue and bamboo to deal with daily energy needs. Forest fires and agricultural biomass burning are seen during the months preceding the monsoon.

In summer the temperature of the region rises up to 38.6°C and during winters the temperatures may drop to 12°C. Pre-monsoon season starts from the month of March to May and this experience severe Nor'wester wind locally known as *Bordoichila*. The effect of *Bordoichila* is experienced by the whole

Figure 1: Map of the study area showing three different sampling sites at the mid-Brahmaputra plain. (*Courtesy:* Google maps)

Assam region. This thunderstorm is accompanied by the lightning flashes, torrential rainfall, strong wind gust, hail and occasional tornadoes developed due to intense convection. Winter is accompanied with dry, cold weather along with fog.

For convention, the whole year has been divided into four distinct periods according to India Meteorological Department (IMD), i.e. Pre-monsoon (March-May), Monsoon (June- September), Post-monsoon (October-December) and winter (January-February).

Sampling

The PM_{10} samples were collected on Whatman Glass microfibre (GF/A; size 8''×10'') by Respirable Dust Sampler (NEERI designed). Samplers were placed about 10-15 m above ground at all three sites. Sample collection frequency was once per week with duration of 24 hours from May 2012 to May 2013 covering all the seasons. A total of 116 numbers of valid samples were collected from three sites (Site 1 = 52, Site 2 = 34, Site 3 = 30). Sample collections were avoided during rainy days.

Analysis

Aliquot of PM_{10} samples was extracted using ultra sonication method for 20 minutes in ultrapure water and filtered (Deka and Hoque, 2014). Sample volume was adjusted up to 10 ml. Anions, F^-, Cl^-, NO_3^- and SO_4^{2-} and cations, Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+} were analyzed by Ion Chromatography (Metrohm 882 Professional IC). Anions were analyzed using Metrosep A Supp 5 250/4.0 column and Metrosep A Supp 4/5 guard column with 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ standard eluent at a flow rate of 0.7 ml/min. The cations were measured using Metrosep C4-150/4.0 and guard column Metrosep C4 Guard/4.0 with eluents as 1.7 mmol/L HNO_3 and 0.7 mmol/L Pyridin-2, 6-dicarboxylic acid at a flow rate of 0.9 ml/min. Before injection, the samples were filtered with 0.22 μm pore size nylon filter paper (Make: Millipore).

Quality Control

Before sampling of PM_{10}, filter papers were conditioned properly to remove any artifacts. Whatman filter papers were desiccated using a desiccator (Silica gel coarse) for 24 hours before sampling and after sampling to remove any traces of moisture associated with particulate matter. After 24-hour desiccation only pre and post sampling weight of the filter was taken. For estimation of anions Multielement Ion Chromatography Anion standard solution (Fluka Analytical) was used to calibrate the IC. Adequate care was taken to minimize external contamination of sample due to handling and carrying of samples in various processes. To determine the detection efficiencies of the analytical instruments, spiking with known standard concentrations were done with the help of ultrapure water.

Meteorology and Air Mass Trajectory

Meteorological data such as temperature, relative humidity, and wind speed were obtained from Weather underground (http://www.wunderground.com) for Tezpur station (Station code: ID-42451). Table 1 presents the information regarding the meteorological conditions during the study period. It was observed that average annual relative humidity was 72±8% with

Table 1: Prevailing meteorological conditions during the study period over Tezpur region

		Annual	*Pre-monsoon*	*Monsoon*	*Post-monsoon*	*Winter*
Relative Humidity(%)	Average	72	69.5	81.1	70.3	69.0
	SD	8	10	4	4	8
	Minimum	52	52	74	64	56
	Maximum	87	83	87	78	87
Temperature (°C)	Average	23	25.7	28.5	20.6	17.7
	SD	5	2.2	1.6	2.3	3.0
	Minimum	12	21.0	26.0	16.0	12.0
	Maximum	31	30.0	31.0	25.0	23.0
Wind speed (mph)	Average	0.8	1.3	0.8	0.7	0.5
	SD	0.7	1.2	0.4	0.5	0.3
	Minimum	0.0	0.2	0.2	0.2	0.0
	Maximum	4.3	4.3	1.4	2.3	0.9

a range of 52-87%. Minimum relative humidity (52%) was observed during pre-monsoon season and highest (87%) during monsoon and winter season. With 23ºC for annual average, temperature of this region changes from 31 to 12 °C with highest during monsoon season and lowest during winter season. Wind speed was recorded highest during pre-monsoon period with 4.3 mph and nearly calm condition during winter season. Annual wind speed ranges from calm to 4.3 mph with an average of 0.8 mph.

Five days backward trajectories arriving over the region, at 500 m, 100 m and 1500 m above the ground level and time ending at 00.00 hrs, were computed using the HYSPLIT model, developed by NOAA/ARL (http://ready.arl.noaa.gov/HYSPLIT.php) (Draxler and Rolph, 2003). The global meteorological data from the National Centres for Environmental Prediction's Global Data Assimilation System (GDAS) were used for trajectory calculation.

Results and Discussions

Spatial and Seasonal Variation of PM_{10}

Table 1 includes the mean concentration of PM_{10} at three different sites, computed as the averages of all the weekly mass concentrations. The arithmetic mean concentrations and standard deviation were found to be 43.2±38, 39.5±34 and 71.1±56 μg/m^3 at Tezpur University (Site 1), Silghat (Site 2) and NERIWALM (Site 3) respectively. It has been observed that Site 3, which is an urban place as mentioned earlier, experienced the highest loading of PM_{10}. High traffic density, more exposure to emissions from small scale industries and construction and demolition might have contributed enormous amount of particulate matters to this region. Sites 1 and 2 are rurally situated places in the Brahmaputra valley, which showed comparatively lower loading of PM_{10}. If we consider overall annual average for the three sites together, the mass concentration was found to be 51.3±17, which was within the limit of National Ambient Air Quality Standards (NAAQS) for PM_{10} (annual = 60 μg/m^3) proposed by Central Pollution Control Board (CPCB), India.

Seasonal variations of PM_{10} in the mid-Brahmaputra plain have been evaluated by taking the composite data set of the representative sites. Table 2 presents the mean mass concentrations of PM_{10} during the four seasons viz. pre-monsoon, monsoon, post-monsoon and winter. The average concentration was observed to be highest during the winter season, 94.47±48 μg/m^3 and lowest during the monsoon season, 19.75±12 μg/m^3. Highest loading of PM_{10} during winter season could be associated with the long dry period without rain, comparatively more calm atmospheric condition and long residence time for the particles and to form more secondary particles. During monsoon time, southwest monsoon brings ample amount of rain to this region. Scavenging of particles by rain occurs during this period; thereby keeping the atmosphere comparatively cleaner. Pre-monsoon period has been associated with strong wind gust, sometimes heavy rain and starts immediately after winter. The PM_{10} concentration during this season was found to be 45.61±42 μg/m^3 followed by post-monsoon period with concentration 42.91±25 μg/m^3.

Water Soluble Ions

Spatial Variation

The average concentrations of water soluble ions (WSI) at Site 1, Site 2 and Site 3 are shown in Table 2. The concentrations of WSI at Site 1 were found to be in the order SO_4^{2-}> Na^+>NH_4^+>NO_3^->K^+>Ca^{2+}>Cl^->Mg^{2+}>F^-; at Site 2 trend was SO_4^{2-}> Na^+> NO_3^-> K^+> NH_4^+> Cl^-> Ca^{2+}> Mg^{2+}>F^- and at Site 3 concentrations followed the order Na^+> Cl^-> K^+> SO_4^{2-}> NO_3^-> NH_4^+> Ca^{2+}> Mg^{2+}>F^-. It shows that at all the three sites cations with maximum concentrations were sodium, potassium and ammonium while predominant anions were sulphate, nitrate and chloride.

Table 2: Annual mean mass concentration of PM_{10} (μg/m^3) and concentrations of other water soluble ions (μg/m^3) at various sites

Sites	*PM_{10}*	*F^-*	*Cl^-*	*NO_3^-*	*SO_4^{2-}*	*Na^+*	*NH_4^+*	*K^+*	*Ca^{2+}*	*Mg^{2+}*
Site 1*	43.2±38.2	0.02±0.05	0.24±0.44	0.79±0.98	2.33±2.79	1.14±0.55	1.05±1.49	0.75±0.72	0.45±0.30	0.06±0.05
Site2**	39.5±34.5	0.03±0.01	0.98±0.64	1.11±1.39	1.64±1.58	1.37±0.46	1.02±1.12	1.04±0.84	0.46±0.37	0.05±0.04
Site 3***	71.1±56.0	0.06±0.14	2.54±1.56	1.49±1.53	2.20±1.74	2.65±1.41	1.33±1.34	2.29±1.61	0.67±0.43	0.09±0.05
All sites	51.3±17	0.03±0.02	1.3±1.2	1.1±0.4	2.1±0.4	1.7±0.8	1.1±0.2	1.4±0.8	0.5±0.1	0.1±0.02

*Tezpur University (*n* = 52); **Silghat (*n* = 34); ***NERIWALM (*n* = 30).

This reveals that though all the three sites are geographically apart from each other still possess similar chemical nature of PM_{10} during the study period. Figure 2 shows the linear regression analysis of sum of anions vs. sum of cations for the three study sites. A strong relation between the measured anions and cations has been observed with R^2 value of 0.851, 0.921 and 0.951 for site 1, site 2 and site 3 respectively. This indicates the completeness of measurements of major ions of PM_{10} from all the three sites.

Seas onal Variations

During pre-monsoon season concentrations of water soluble ions followed the order $SO_4^{2-}>Na^+>K^+>NH_4^+>Cl^->NO_3^->Ca^{2+}>Mg^{2+}>F^-$. Among anions SO_4^{2-} was found to be dominant and Na^+ among cations. Pre-monsoon season has been associated with high wind gust, comparatively drier weather and falls just after the winter period. Comparatively higher concentrations of Na^+ (1.91±1.28 µg/m^3) and Ca^{2+} (0.69±0.46 µg/m^3) in this season can be attributed to the re-suspension of soil dust or crustal input from the exposed surface soil. Again, long-range transport could also carry Na and mineral dusts containing Ca^{2+} salts from continental mass. Backward trajectory analysis (Figure 3i) showed the route of air mass travelled to this region. Table 1 reveals that pre-monsoon period experiences highest wind speed of 4.3 mph with an average of 1.3 mph and this strong wind speed can carry mineral particles.

Monsoon season is the rainiest season and southwesterly winds carry moisture from Bay of Bengal. Among the measured ions Na^+ showed maximum concentration (1.31±0.43 µg/m^3) followed by SO_4^{2-} (1.08±0.55 µg/m^3). Na^+ being the predominant ion reveals that long-range transport of sea salts is an important phenomenon during this period. Table 3 shows the details of concentrations of ions. It was observed that during monsoon period all the ions were found to be minimum in concentrations. This could be due to the scavenging of particles by rain. Among anion SO_4^{2-} was found to be predominant which could be due to the exchange of sulphur containing gases by Cl^- ion while travelling through long distances, commonly known as Cl^- depletion phenomenon (Harrison and Pio, 1983; Wall et al., 1988; Mamane and Gottlieb, 1992; Sarin et al., 2010; Adachi and Buseck, 2015). Moreover high humidity (87%) can enhance the formation of secondary ions such as SO_4^{2-}. Kulshrestha et al. (2009) reported that high relative humidity levels favour the conversion and partitioning of gaseous SO_2, NOx and NH_3 to their aerosol phase. Figure 3 reveals

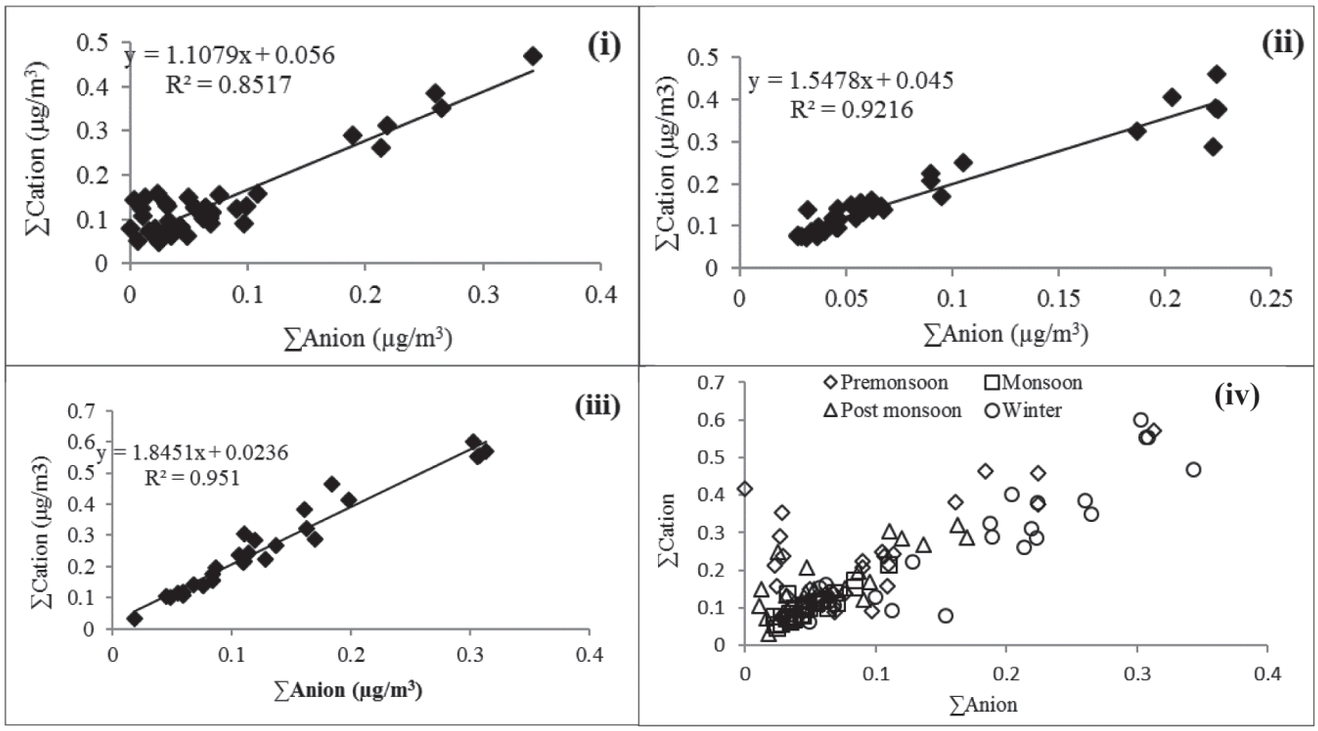

Figure 2: Spatial characteristics of ion balance between the measured anions (∑Anion) and cations (∑Cation)—(i) Tezpur University, (ii) Silghat, (iii) NERIWALM and (iv) seasonal variation for the study period.

Table 3: Seasonal variations of mass concentrations of PM_{10} and water soluble ions (μgm^{-3})

	Pre-monsoon (n = 32)		*Monsoon (n = 28)*		*Post-monsoon (n = 26)*		*Winter (n = 23)*	
PM_{10}	45.61	± 42.08	19.75	± 11.92	42.91	±25.22	94.47	±48.10
F^-	0.02	± 0.03	0.01	±0.01	0.07	±0.16	0.02	±0.02
Cl^-	0.99	± 1.25	0.65	±0.65	1.13	±1.13	1.29	±1.63
NO_3^-	0.97	± 0.9	0.34	±0.17	0.63	±0.40	2.43	±1.78
SO_4^{2-}	2.02	± 1.49	1.08	±0.55	0.94	±0.61	4.77	±3.24
Na^+	1.91	± 1.28	1.31	±0.43	1.56	±0.78	1.27	±0.92
NH_4^+	1.11	± 0.98	0.34	±0.19	0.66	±0.38	2.53	±2.02
K^+	1.32	±0.98	0.49	±0.39	1.10	±0.89	1.93	±1.65
Ca^{2+}	0.69	± 0.46	0.22	±0.13	0.51	±0.26	0.54	±0.30
Mg^{2+}	0.09	±0.06	0.03	±0.02	0.06	±0.03	0.07	±0.03

the fact about the influence of air masses travelling from Bay of Bengal and crossing various geopolitical boundaries during monsoon season, which brings ample amount of sea salts bearing ions and other cloud bearing particles as CCN.

Post-monsoon period starts from October to December months of the year. This season starts immediately after the rainy season and gradually leads to the drier, lesser humid with scanty rainfall conditions. The concentrations of ions showed the order like $Na^+ > Cl^- > K^+ > SO_4^{2-} > NO_3^- > NH_4^+ > Ca^{2+} > F^- > Mg^{2+}$. This season is immediately followed by winter season, comparatively more drier and cold. After the rainy season ends comes the non-rainy, dry and cold season when most of the activities associated with combustion (brick kilns, tea industries, wood burning, waste burning, natural biomass burning at forest areas) starts immediately. As winter approaches these activities reaches its peak thereby releasing ample amount of particulates to the atmosphere. It has been observed that except Na^+ and Ca^{2+}, all other ions viz. Cl^-, NO_3^-, SO_4^{2-}, NH_4^+ and K^+ showed higher concentrations during winter season as compared with other seasons (details in Table 3).

Abundance of K^+ in PM_{10} is directly associated with the biomass burning as reported by many researchers (Kleeman et al., 1999; Simoneit et al., 2004; Watson et al., 2008). It has contributed 14, 11, 16 and 13% (Figure 4) to the PM_{10} mass concentration during pre-monsoon, monsoon, post-monsoon and winter season respectively. Presence of K^+ in PM_{10} during all the seasons can be attributed to the prevalent conventional and/or non-conventional biomass burning throughout the year. Similarly Cl^- and NO_3^- or their precursors HCl and NOx have been reported to be emitted during wood combustion (Patil et al., 2013). SO_4^{2-} showed maximum concentration during winter season, which might be due to the emissions of precursors from coal-fed brick kilns, biomass burning and/or secondary formation (Seinfeld and Pandis, 1998; Deka and Hoque, 2015; Kuniyal et al., 2015).

We have calculated total secondary formation considering SO_4^{2-}, NO_3^- and NH_4^+ during all the seasons and found that average concentration of secondary ions was highest during winter season with total average concentration of 9.7±6 $\mu g/m^3$. These secondary ions all together contributed 65% to the PM_{10} mass concentration during winter period. NH_4^+ can be formed from the precursors like NH_3 emitted to the atmosphere by plants, animals, soil microorganisms and by various agricultural processes which include direct volatilization of solid NH_4NO_3 salts and fertilizers (Sutton et al., 200; Li et al., 2006; Sharma et al., 2010). Adams et al. (1999) reported that the temperature >25°C prevents formation of significant amount of particulate NH_4NO_3. Since temperature during winter season comes down below 25°C, this may induce formation of more particulate ammonium salts like NH_4NO_3 or $(NH_4)_2SO_4$.

Presence of SO_4^{2-} indicates the direct emissions from the sources, photochemical production and/or gas to particle conversion of precursor gases like SOx released from the combustion sources. Coal burning in various industries like brick kilns, tea industries and many other day to day activities, wood combustion are major emitters of sulphur-containing gases in the study sites (Deka and Hoque, 2015). Moreover long-range transport air masses might be an important carrier of pollutants from other polluted regions. Figure 3 (iii-iv) represents the backward trajectories during post-monsoon and winter seasons. Trajectory analysis reveals that air parcel travelling through continental masses e.g. Indo-

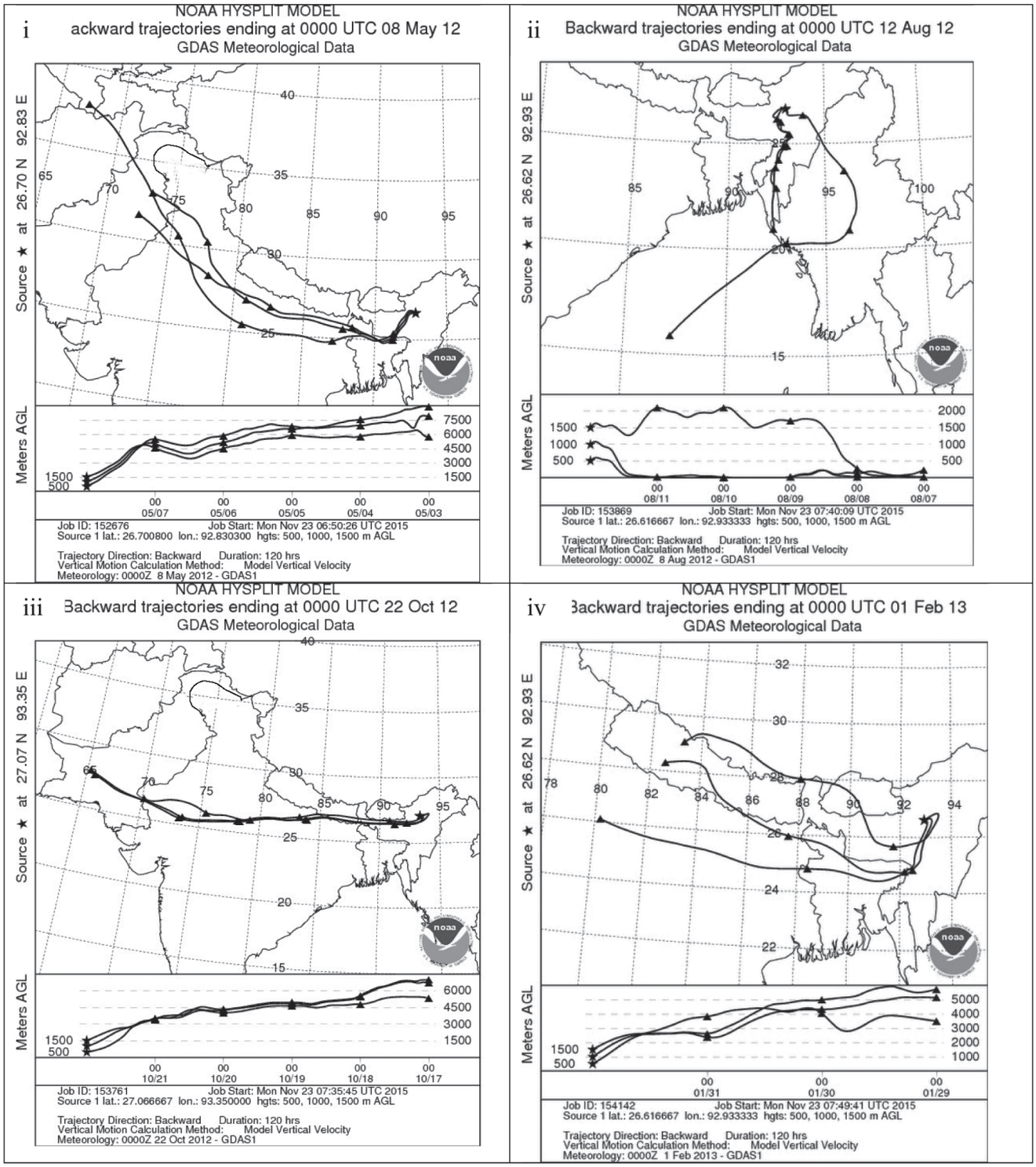

Figure 3: Seasonal variations of 5-days backward trajectory analysis using HYSPLIT model at 500 m, 1000 m and 1500 m above ground level considering each sampling site separately, representing (i) pre-monsoon, (ii) monsoon, (iii) post-monsoon and (iv) winter.

Gangetic plain, may carry pollutants such as SO_4^{2-} and K^+ to this region. Various studies have reported that extended Indo-Gangetic plain region of mainland India is a hotspot for combustion of biomass, fossil fuel for different purposes (Ram et al., 2012, 2010; Rastogi and Sarin, 2005).

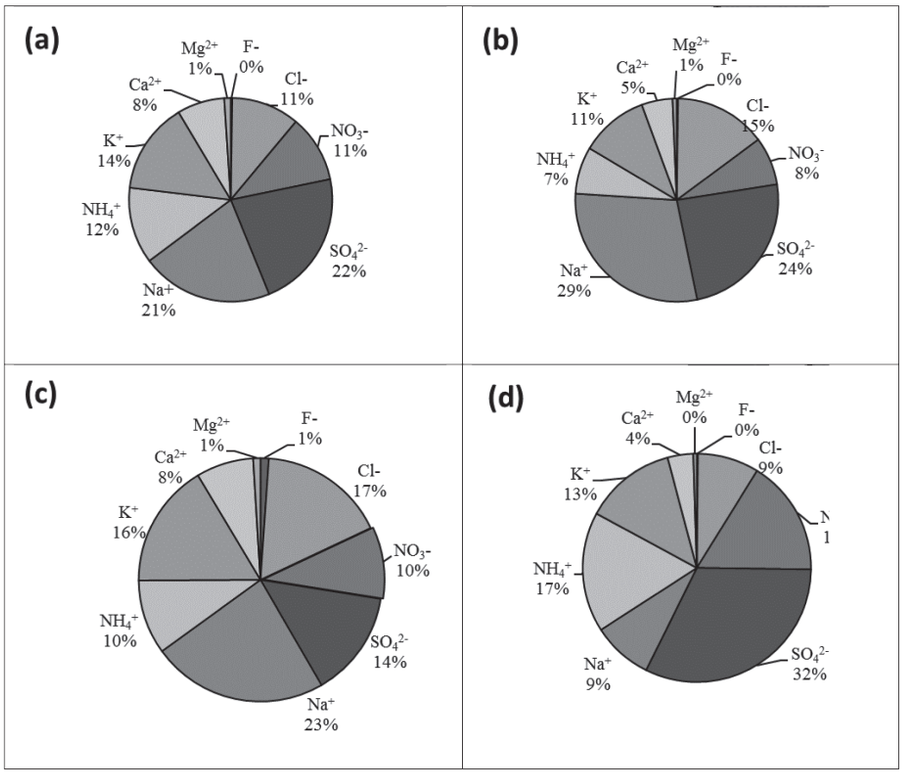

Figure 4: Percentage contribution of ionic constituents in (a) Pre-monsoon, (b) Monsoon, (c) Post-monsoon and (d) Winter.

Ion Charge Balance and Neutralizing Factor

The ratios of equivalent concentrations of cations ($\sum^{+}$) to anions ($\sum^{-}$) were calculated spatially and seasonally. The average and standard deviation of $\sum^{-}/\sum^{+}$ ratio for the sampling sites were found to be 0.47±0.35, 0.44±0.09 and 0.49±0.05 for Tezpur University, Silghat and NERIWALM respectively. This lower value for equivalent ionic ratio indicates the predominance of base cations and alkaline nature of aerosols although significant level of acidic ions like SO_4^{2-}, NO_3^{-} and Cl^{-} are present in PM_{10} samples. Similarly ion balance ratio also showed seasonal variation and followed the order post-monsoon (average 0.40)< pre-monsoon (average 0.42)< monsoon (average 0.46)< winter (average 0.68). This indicates that towards the winter period there occurs more abundance of anions in the particulate matter and hence the slightly higher value for the $\sum^{-}/\sum^{+}$ ratio. Figure 2(iv) also indicates the alignment of more anions towards X-axis during winter period compared to other seasons.

Neutralizing factors were evaluated for major ions i.e. NH_4^{+}, Ca^{2+}, Mg^{2+} and K^{+} as per Equation (1):

$$\%\text{Neutralizing factor} = \frac{[X]}{[SO_4^{2-}]+[NO_3^{-}]} \times 100 \qquad (1)$$

where [*X*] is the desired ion for which neutralization factor is to be evaluated.

It was observed that at Tezpur University neutralization factor of major ions followed the order $NH_4^{+}>K^{+}>Ca^{2+}>Mg^{2+}$. At Silghat and NERIWALM, ions followed the order of NF viz. $K^{+}>NH_4^{+}>Ca^{2+}>Mg^{2+}$ (Figure 5). Overall, K^{+} showed maximum neutralizing capacity at study region during the monitoring period and Mg^{2+} showed least.

Ionic Ratios

Table 4 presents the ratios of major ions for Tezpur University, Silghat, NERIWALM and for different seasons along with standard ratios sea water and crust taken from the literature (Mason, 1966; Keene et al., 1986). NO_3^{-}/SO_4^{2-} mass ratios can be used to evaluate the influences of mobile versus stationary pollution sources (Hu et al., 2002; Wang et al., 2005; Yao et al., 2002). We have calculated NO_3^{-}/SO_4^{2-} ratios for three sampling sites and for different seasons. It was observed that the ratios showed relatively lower value for the sampling sites and for different seasons (Table 4). Huebert et al. (1988) reported that in China, lower ratios (0.3-0.5) have usually been found because of the wide use of sulphur-rich coal. Relatively lower range

Table 4: Spatial and seasonal variations of ionic ratios of major ions during the study period

	TU	*Silghat*	*NERIWALM*	*Pre-monsoon*	*Monsoon*	*Post-monsoon*	*Winter*	*Amsterdam Island* [a]	*Earth crust* [b]
NO_3^-/SO_4^{2-}	0.34	0.68	0.68	0.45	0.35	0.75	0.64		
Cl^-/Na^+	0.58	0.71	0.95	0.45	0.44	0.65	1.59	1.2	0.003
K^+/Na^+	1.46	0.70	0.81	0.69	0.34	0.66	3.10	0.0219	0.45

[a]Keene et al., 1986
[b] Mason, 1966

of ratios indicates the influence of fossil fuel burning in this region.

Ooki et al. (2002) reported that ratio between Na^+ and K^+ can be considered as a good indicator to find out anthropogenic source of Na. In our study K^+/Na^+ ratios were found to be 1.46, 0.70 and 0.81 for Tezpur University, Silghat and NERIWALM respectively which are much higher than the sea ratio and crustal ratio (Table 4). This indicates the influence of anthropogenic sources for Na. Anthropogenic sources of Na mainly include refused burning in open areas, resuspended dust from river bed, crust etc. Similar trend of K^+/Na^+ ratio was observed in all the four seasons.

The Cl^-/Na^+ ratio in PM_{10} is also a good indicator to determine the anthropogenic input of these ions. In our study, winter season showed comparatively higher value for Cl^-/Na^+ (1.59) than the sea salt ratio. The relative abundance of Cl^- compared with Na^+ can be explained by emissions from abundant biomass burning prevalent in this region during winter period.

Enrichment Factor

For further identification of sea sprays and other crustal and anthropogenic contributions to the ionic composition of particulate matter, enrichment factors were calculated considering Na as marine origin. Calculation was done applying the following formula (Equation 2)

$$EF\ (marine) = (X/Na)_{PM_{10}}/(X/Na)_{sea} \quad (2)$$

where X is the desired ion for which EF is to be calculated.

Standard ratios for these ions with respect to sea were taken from the literature reported by Keene et al. (1986). According to Azri et al. (2010), EF less than 10 can be considered slightly enriched condition, EF > 1000 meaning highly enriched and in conditions of 10<EF<1000 would mean enriched.

In our study we have calculated EF for three sites (Figure 6). It was observed that except Cl^- and Mg^{2+}, all other ions showed enrichment at all three sites, and Tezpur University showed higher enrichment for SO_4^{2-} and K^+. This could be due to the influence of anthropogenic emissions such as biomass burning and/or fossil fuel burning like coal.

Calculations of enrichment factor for different seasons with respect to sea showed marked difference among the season. Winter season showed comparatively higher enrichment factor for all the major ions such as Cl^- (1.3), K^+ (141), Ca^{2+} (15) and SO_4^{2-} (117). This might be associated with the prominent increase in the anthropogenic activities related to fuel combustion, construction activities, etc.

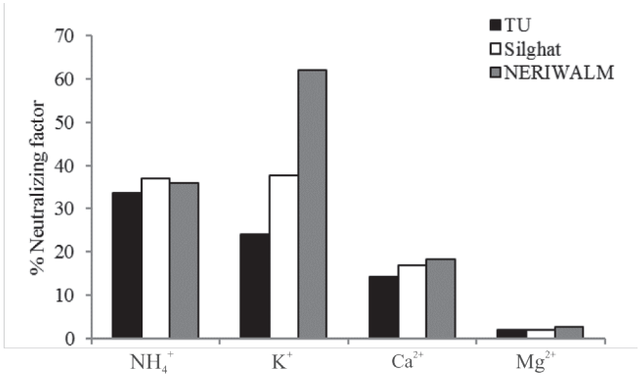

Figure 5: Percentage neutralizing factor for three different sites.

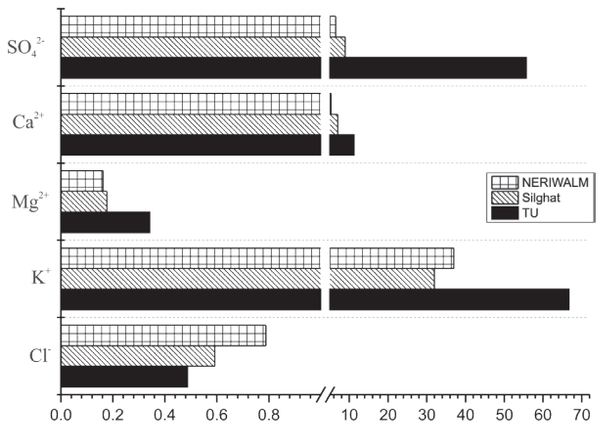

Figure 6: Spatial variations of enrichment ratios of major ions with respect to marine.

Correlations

Inter-species correlations were seen to investigate the possible sources and chemical behaviour of water soluble ionic constituents of PM_{10} for different seasons. It is worth mentioning that though geographical locations of these sites are different, all the activities prevalent are of similar kind. Therefore, we have considered the seasons to evaluate the possible relations between the ions.

Table 5 includes the correlation matrix for different seasons. During pre-monsoon and monsoon seasons except NH_4^+ all other ions showed significant correlation with PM_{10} (Table 5a-b), which indicates the predominance of particles having these ions as main constituents. Cl^- showed a good correlation with Na^+, NO_3^-, K^+ and SO_4^{2-}. Correlation with K^+, marker of biomass burning, reveals that the some amount of Cl^- could be released from the prevailing biomass burning during the study period. Again secondary ions such as SO_4^{2-} and NO_3^- showed significant correlation with each other along with K^+, Na^+ and Ca^{2+}. Strong correlation between SO_4^{2-} and NO_3^- suggests their contribution

Table 5: Inter-species correlations (a) Pre-monsoon, *n* = 32; (b) Monsoon, *n* = 28; (c) Post-monsoon, *n* = 26; and (d) Winter, *n* = 23

(a)	PM_{10}	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
PM_{10}	1								
Cl^-	.355*	1							
NO_3^-	.632**	.492**	1						
SO_4^{2-}	.684**	.393*	.804**	1					
Na^+	.351*	.838**	.424*	.504**	1				
NH_4^+	0.265	0.103	.441*	0.233	0.23	1			
K^+	.622**	.590**	.685**	.553**	.699**	.722**	1		
Ca^{2+}	.700**	.401*	.479**	.364*	.531**	.501**	.771**	1	
Mg^{2+}	.458**	0.324	0.163	0.085	.483**	.390*	.602**	.879**	1
(b)	PM_{10}	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
PM_{10}	1								
Cl^-	.449*	1							
NO_3^-	.905**	.494**	1						
SO_4^{2-}	.458*	-0.286	.531**	1					
Na^+	.710**	.812**	.776**	0.214	1				
NH_4^+	-0.105	0.119	-0.101	-0.102	-0.05	1			
K^+	.635**	.957**	.676**	-0.08	.914**	0.036	1		
Ca^{2+}	.471*	.861**	.539**	-0.143	.808**	0.167	.860**	1	
Mg^{2+}	.501**	.756**	.539**	0.09	.719**	0.175	.755**	.851**	1
(c)	PM_{10}	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
PM_{10}	1								
Cl^-	.495*	1							
NO_3^-	.782**	.407*	1						
SO_4^{2-}	.729**	0.356	.644**	1					
Na^+	.486*	.754**	0.281	0.329	1				
NH_4^+	.428*	.828**	0.334	0.286	.731**	1			
K^+	.456*	.860**	0.366	0.243	.854**	.766**	1		
Ca^{2+}	0.359	-0.031	0.218	0.367	.473*	-0.008	0.152	1	
Mg^{2+}	.461*	.537**	0.192	0.295	.875**	.529**	.667**	.661**	1

(*Contd.*)

(*Contd.* **Table: 5**)

(d)	PM_{10}	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
PM_{10}	1								
Cl^-	.603**	1							
NO_3^-	.650**	0.381	1						
SO_4^{2-}	.619**	0.057	0.125	1					
Na^+	0.373	.700**	.565**	-0.345	1				
NH_4^+	.770**	.418*	0.408	.836**	-0.002	1			
K^+	.813**	.847**	.616**	0.307	.657**	.674**	1		
Ca^{2+}	0.41	.553**	.501*	-0.107	.835**	0.158	.678**	1	
Mg^{2+}	.420*	.445*	.513*	0.012	.716**	0.231	.592**	.859**	1

*Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 level (2-tailed).

by the oxidation processes ($SO_2 \rightarrow SO_4^{2-}$; $NO_2 \rightarrow NO_3^-$) (Kulshrestha et al., 2009). Ions such as Ca^{2+} and Mg^{2+} showed good relation with Na^+, NH_4^+ and K^+. During monsoon season also similar pattern of correlation was observed for the ions.

During post-monsoon and winter seasons, except Ca^{2+} all other ions showed significant correlation with PM_{10} mass concentration (Table 5c-d). A strong significant correlation has been observed between SO_4^{2-} and NH_4^+ during winter season indicating neutralisation. Association of Mg^{2+} with K^+ has been observed during all the seasons, which is indicative of prevailing biomass burning throughout the year.

Conclusions

Spatial variation of PM_{10} was observed and the urban site, NERIWALM showed maximum loading of PM_{10} during the study period. Water soluble ions constituted major portion of PM_{10} among which SO_4^{2-} was found to be dominant in PM_{10} of all the sites. Seasonal variation was prominent with maximum loading of PM_{10} and ionic abundance during winter season. Predominance of ions viz. SO_4^{2-}, NO_3^- and NH_4^+ indicates the influence of secondary formation. Crustal input of ions was higher during pre-monsoon season with maximum concentration of Ca^{2+} and Na^+. Relatively higher enrichment factor for ions such as K^+, SO_4^{2-} and Cl^- reveals the influence of anthropogenic activities releasing tremendous amount of pollutant to the atmosphere.

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