Understanding the Chemistry and Sources of Precipitation Ions in the Mid-Brahmaputra Valley of Northeastern India

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Abstract
The chemistry of rainwater over Mid-Brahmaputra Valley was studied for three consecutive years (2012-2014; n=285). The samples were analyzed for major chemical parameters viz. pH, electrical conductivity (EC), and ions (SO4²-, NO3-, Cl-, F-, Br-, Ca²+, NH4+, Mg²+, Na+, K+, and Li+), organic acids (HCOO- and CH₃COO-) and dissolved organic carbon (DOC). The mean pH for the entire study period was found to be 5.66, which ranged from 4.51 to 7.68, and the volume weighted (VW) mean pH was found to be 5.16. Over 55% of the samples showed pH between 5 and 6, and a few samples had pH<5. Ionic concentration followed the order NH4+>Ca²+>SO4²->NO3->Cl->Na+>K+>Mg²+>H+>HCO3->Br>F>Li+, indicating dominance of alkaline ions over acidic ions such that 94% of mineral acid was neutralized. The secondary ions, NH4+, SO4²-, and NO3-, showed high wet deposition fluxes. The chemistry exhibits explicit seasonality. The airmass clusters of monsoon and non-monsoon seasons, and the associated chemistry varied, which showed influence of long-range transport. The interspecies correlations varied between the monsoon and non-monsoon time samples meaning variation in the source strengths of the contribution sources of the chemical species of the rainwater. Positive Matrix Factorization (PMF) was applied to the data which extracted six factors that explained the sources and chemistry of the rainwater constituents which are of sea, agriculture, coal burning, biomass burning, and secondary origin.

Keywords: Rainwater chemistry; Source apportionment; HYSPLIT Back trajectory; PMF

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INTRODUCTION

For many decades, rainwater chemistry has drawn significant attention because of its acidity and the associated consequences on ecosystems. Researchers from various parts of the world have extensively studied rainwater chemistry to gain understanding of this issue (Eriksson, 1952; Charlson and Rodhe, 1982; Zeng and Hopke, 1989; Galloway et al., 1982; Likens et al., 1976; Galloway, 1995; Lacaux et al., 2009; Akpo et al., 2015; Mimura et al., 2016 and references therein). The chemistry of rainwater remains important because of its ecological impacts on biogeochemical cycling of nutrients and climate.

Water-soluble gases and particles present in the atmosphere combine with rainwater through the processes of cloud condensation and/or below cloud scavenging. They are then deposited on the earth’s surface. These chemical constituents come from both natural and anthropogenic sources (Mimura et al., 2016; Rastogi and Sarin, 2005). Thus, rainwater chemistry of a region can be considered as an indicator of prevalent atmospheric conditions where the rainwater samples were collected (Al-Khasman, 2005; 2009). The presence of dissolved ions also provides information on both local and long-range transported pollutants (e.g. Akpo et al., 2015; Niu et al., 2014; Chate et al., 2011; Tiwari et al., 2007), and quantitative assessment of wet deposition enables identification of the various natural and anthropogenic source strengths, and their temporal and spatial variabilities (Tiwari et al., 2015).

In India, studies of rainwater chemistry have been performed in different ecological and physical environments (e.g. Rao et al., 1992; Granat et al., 2001; Kulshrestha et al., 2003, 2005b; Safai et al., 2004; Momin et al., 2005; Mouli et al., 2005; Tiwari et al., 2007; Rastogi and Sarin, 2007; Salve et al., 2008; Budhavant et al., 2009, 2011; Das et al., 2011; Tiwari et al., 2015; Rao et al., 2016). Many studies in India have commonly reported alkaline rainwater in multiple locations (e.g.
Handa et al., 1969; Khemani et al., 1985; Rastogi and Sarin, 2005; Kumar et al., 2002; Parashar et al., 2001) due to dominance of neutralizing compounds like calcium carbonate and ammonia in the atmosphere (Norman et al., 2001). However, there has been a lack of systematic, long-term studies of rainwater chemistry over the Brahmaputra Valley with only a couple of studies being reported (Kulshrestha et al., 2005a; 2014).

The Brahmaputra Valley is one of the most fertile valleys in the world and is rich with biodiversity. The Valley has been experiencing rapid growth in recent years like many other regions of India. Consequently, significant heterogeneity has been observed in terms of physical, chemical, and optical properties of the particulate matter across this region as reported by Deka and Hoque, (2014, 2014a), Pathak et al. (2012), and Bhuyan et al. (2016a). Therefore, there is a need to better understand the chemistry of rainwater over the Brahmaputra Valley, through systematic measurements and to assess the effects of atmospheric deposition chemistry in this ecologically fragile region. This paper provides the initial source characterization and apportionment of the rainwater constituents in this region.

**EXPERIMENTAL**

**The Site**

This work was conducted at Tezpur (26°38' N 92°48'E and 26°63'N 92°8'E), of the mid-Brahmaputra Valley of northeastern India. The airmass back-trajectory clusters, of the monsoon and non-monsoon periods, reaching the site (Tezpur) during the study period are shown in Fig. 1. The climate is sub-tropical with mild winters and hot-and-humid summers and maximum rainfall is received during the monsoon season.
Bhuyan et al. (2016) has described the population and land use type of Tezpur. The region does not have any heavy industries, however, there are some small-scale industries like tea-processing, petroleum refining, cement manufacturing, and mining of minor minerals. The region being mostly rural, the village folks majorly dependent on solid biomass fuels to meet the daily energy needs. Forest fires and agricultural biomass burning are observed during the months preceding the monsoon. Agricultural biomass burning and forest fires are seen during the pre-monsoon season.

Bhuyan et al. (2018) presented the distinct seasons of this region as per India Meteorological Department (IMD), which are Winter (January-February), Pre-monsoon (March-May), Monsoon (June-September), and Post-monsoon (October-December).

**Sampling**

Rainwater samples were collected on the Tezpur University campus characterized as a remote, rural background location. The collections were done on an event basis for three consecutive years (2012, 2013, and 2014) using a high density 20.7cm diameter polypropylene funnel fitted onto a 2L high density polypropylene bottle. The rain sampler was positioned on the rooftop (10m from ground) and the collector height was maintained at 1m above the resting surface to avert contamination of samples from splashes as per Rastogi and Sarin (2005).

Measurements of pH, electrical conductivity (EC), and volume were taken immediately in the laboratory after each rain event. It was then filtered to remove any insoluble materials. Two aliquots were stored for further analyses. One was used for the determination of anions and the other was for cations. It was treated with chloroform to minimize microbial degradation of ions such as ammonium and stored at 4°C (GAW, 2004; Keene et al., 1983).
For the analysis of carbon, filtered samples were stored in brown vials at 4°C to avert degradation of organics till analysis (Willey et al., 2000; Campos et al., 2007; Kieber et al., 2002). This campaign included 285 rain events (2012 = 116, 2013 = 102, and 2014 = 67).

**Chemical Analyses**

The pH of rain samples was measured with a glass electrode pH meter (Sartorius, PT 10), which was calibrated with standard buffer solutions of pH 4 and 7 (NIST) prior to measurements. The conductivity meter (Systronics, 304) was periodically calibrated using 0.1N KCl (aqueous) solution. The ions were analyzed by an ion chromatograph (IC) (Metrohm, 882). The anion column, Metrosep A Supp 5 250/4.0 and the cation column Metrosep C4-150/4.0 were used with standard protocols for analyses of anions and cations, respectively (Bhuyan et al. 2016, 2018).

The formic and acetic acids were measured using the Metrosep Organic Acids-100/7.8 and a standard eluent (0.5 mmol L⁻¹ H₂SO₄ : Acetone :: 85:15). The DOC was measured with a TOC analyzer (Multi NC/2100, Analytikjena make, Germany) with a non-dispersive infrared (NDIR) detector as per Bhuyan et al. (2016).

**Airmass back trajectory and clustering**

Daily 120-hr trajectories at starting height of 500 m agl reaching Tezpur were calculated from Reanalysis Data downloaded from the Gridded Meteoroogical Data Archives (ready.noaa.gov/archives.php). The HYSPLIT back trajectory clusters have been computed using GIS based software - TrajStat (Wang et al. 2009).

**Data quality**
Quality assurance/quality control (QA/QC) procedures were followed for the precipitation chemistry monitoring. Samples contaminated with direct leaf fall or bird droppings were excluded. The bottles and funnels were pre-washed with ultrapure water (Ultrapure Type 1, Simplicity, Millipore, resistivity 18.2 MΩ.cm) before sampling. The collectors were deployed just before the start of rain and removed immediately after the rain stopped. Field blanks were evaluated frequently and analyzed for all the parameters by the same procedures as the rain samples. Field blanks were taken by pouring ultra-pure water into the sampler and following the procedures as previously described. The sample values were adjusted by subtracting the field blank values.

Replicate measurements were also conducted for the samples that showed RSD ≤ 5%. In case of pH, the difference between replicate measurements were found to be less than 0.05 while for EC, they were less than 1 µS/cm.

The ion balance was evaluated by linear regression analysis between sum of anions and sum of cations. The result showed a good correlation between total anions and cations (r = 0.876), which was significant at p < 0.01 (Fig. 2). The slope (m = 1.546) deviated to the higher side of ideal 1:1 relationship, which would mean that more anions were missed from the analyses, e.g. phosphate, organic acids, etc. Also, in the assessment of ion balance, bicarbonate (HCO$_3^-$) and hydrogen ion (H$^+$) concentrations were also considered by indirectly estimating their concentrations from the pH values. HCO$_3^-$ was estimated using the relationship between pH and HCO$_3^-$ (Granat, 1972) explained by Eq 1:

$$\text{[HCO}_3^-\text{]} = 10^{(-11.24 + \text{pH})}$$  \hspace{1cm} (1)

The volume weighted mean concentrations (VWM) were calculated to eliminate the influence of different rainfall intensities on the pH (Ge et al., 2011). The VWM pH was calculated as per Eq. 2:
\[ \text{pH}_{\text{VWM}} = -\log \left( \frac{\sum (10^{-\text{pH}_i} \times V_i)}{\sum V_i} \right) \]  

(2)

Where \( \text{pH}_{\text{VWM}} \) is the volume weighted average pH, and \( \text{pH}_i \) and \( V_i \) are the value of pH and volume of the sample \( i \), respectively. The volume weighted mean concentrations (VWM) of ionic constituents were calculated using Eq 3:

\[ \text{VWM (\mu eq L}^{-1}) = \frac{\sum_{i=1}^{N} C_i P_i}{\sum_{i=1}^{N} P_i} \]

(3)

Where \( C_i \) is the ionic concentration of each ion in \( \mu \text{eq L}^{-1} \), \( P_i \) is the volume of each rainy event in ml, and ‘n’ is the number of samples. VWM takes into account the effect of dilution by the rainfall amount and it is useful in comparative studies of rain events. The data were scrutinized for extreme values.

**Positive Matrix Factorization (PMF)**

PMF is widely applied for source apportionment studies of environmental pollutants present in various matrices. Previous work has successfully applied PMF for the apportionment of rainwater chemical constituents (e.g. Juntto and Paatero, 1994; Anttila et al., 1995; Rao et al 2016). From the rainwater constituent concentrations in micro-equivalents per liter, total deposition per event values were calculated as concentration (\( \mu \text{eq L}^{-1} \)) of species in a given event times the total volume (L) collected during that event. These values were used in the PMF model (EPA PMF 5.014). The model requires uncertainties for each data point, which were calculated as per Anttila et al. (1995), and an additional model uncertainty of 5% was added. The agreement of the number of factors was reached on getting symmetrical residuals, within \( \pm 3.0 \) for each chemical parameter, and the
solution with interpretable factors was accepted. The identification of the factors was decided considering species with minimum displacements (DISP) of concentrations.

The errors, which were estimated by displacement (DISP) and bootstrap (BS) methods, were acceptable for the solution. The DISP analysis did not have any swaps and there were no unmapped factors found in the BS analysis.

RESULTS AND DISCUSSION

Chemistry of rainwater

pH

The arithmetic and volume weighted (VW) mean pH and EC of rainwater observed during the study period are given in Supplementary Table S1. The mean pH for the entire study period was found to be 5.66 and ranged from 4.51 to 7.68. The VW mean pH was 5.16. The yearly means of pH were found to decrease in the order of 2012 (5.87), 2013(5.63), and 2014 (5.35). The difference of means was found to be significant (F=13.802; p=0.000). The frequency distribution of pH has been illustrated in Fig.3 showing that most rain events were in the pH range of 5.5 to 6.0, which pointed at near the alkaline nature of the rainwater.

Rain events characterized by low pH (< 5.6) often have significant contributions from NO₃⁻ and SO₄²⁻ (e.g. Rastogi and Sarin, 2005). In the sample having the lowest pH (4.51), NO₃⁻ and SO₄²⁻ contributed 33% and 55%, respectively, of the total anion concentrations and HCO₃⁻ ion concentrations were negligible. NH₄⁺ and Ca²⁺ contributed 38% and 18%, respectively, to the total cation concentrations. The difference in the free acidity, i.e. H⁺ between the sample having the lowest pH [H⁺=30.90 µeq L⁻¹; pH=4.51] and natural rainwater in equilibrium with atmospheric CO₂ [H⁺=2.51 µeq L⁻¹; pH=5.61] (Tiwari et al., 2015) is 28.39 µeq L⁻¹. This difference would
suggest the influence of strong acidic components like NO$_3^-$, SO$_4^{2-}$, and Cl$^-$ derived from anthropogenic activities, and it also indicates minimum neutralization of these acids by alkaline ions in the atmosphere. A year-long study of water-soluble ions in airborne PM (sampled during 2012-13) across the Tezpur region also revealed high loading of SO$_4^{2-}$ and Cl$^-$ (Bhuyan et al., 2016b) that might have been scavenged by rainfall. The sample with the highest pH (7.68) had high contributions from Ca$^{2+}$ (64%) and NH$_4^+$ (16%) to the total cation concentration, with HCO$_3^-$ representing 63% of the total anions and NO$_3^-$ and SO$_4^{2-}$ contributing 11% and 18%, respectively, to the total anions. The monthly variations in pH against volume rainwater are shown in Fig. 4. The months that experienced very low rainfall volume and/or rain events that came after a long spell of dry days were found to have higher pH values suggesting that crustal dust raised the rainwater pH during the dry periods. March to September experience high rainfall and showed uniform pH values. After long and continuous rainy periods, the pH decreased in the subsequent samples due to lack of enough alkaline ions in the atmosphere.

**EC**

The VW-mean EC was 16.22 $\mu$S cm$^{-1}$ and the arithmetic mean was 29.16 $\mu$S cm$^{-1}$. The monthly variation of EC against volume of rainwater is shown in Fig. 4. The EC of the rain events decreased with the increasing rainfall volume. Thus, after continuous, heavy rainfall, the particles and gases contributing to the EC of rainwater decreased because of ‘washing and cleaning’ the atmosphere.

**Ions**
The equivalence ratio, sum of the anions to sum of the cations (∑Anion/∑Cation) and the indicator of the completeness of measured major constituents (Wang and Han, 2011), was found to be 0.78, suggesting that most of the major anions and cations were measured. It was observed that the arithmetic means were greater than the VW mean concentrations, which might mean that higher concentrations are usually associated with lower volume of precipitation as reported by (Xiao, 2016). On average, the ionic representation of rain samples followed the order of

$$\text{NH}_4^+ > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} > \text{H}^+ > \text{HCO}_3^- > \text{Br}^- > \text{F}^- > \text{Li}^+.$$

A comparison of the concentrations with the reported studies from elsewhere in India has been put up in Table S1. It was observed that the VWM concentration of acid buffering ions (i.e. Ca$^{2+}$, Mg$^{2+}$, and HCO$_3^-$) in rainwater showed much higher values in the rainwater of the arid regions of India such as Ahmedabad (Rastogi and Sarin, 2005), Pune (Rao et al. 2016), and the Indo-Gangetic Plain (IGP) (Tiwari et al., 2015). A similar pattern was observed for the acidic ions, SO$_4^{2-}$ and NO$_3^-$, from Pune and the IGP when compared to our study. Higher acidic ions (SO$_4^{2-}$ and NO$_3^-$) were reported from the upper Brahmaputra (Jorhat) area of Assam (Kulshrestha et al., 2014), compared to the current results. The present study found that alkaline ions (Ca$^{2+}$, NH$_4^+$) were dominant during the entire study period. Ca$^{2+}$ and NH$_4^+$ contributed 18% and 17%, respectively, while SO$_4^{2-}$ and NO$_3^-$ provided 12% and 11%, respectively, to the total ion budget (Fig. 2). So, SO$_4^{2-}$ acted as a dominant acidic ion in the study region followed by NO$_3^-$. This result would suggest that most of the associations between these alkaline and acidic species might be in the form of neutral salts such as (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$, CaSO$_4$, and Ca(NO$_3$)$_2$. The presence of Ca$^{2+}$ could be soil derived from construction activities, and/or might be due to the long-range transport from more arid regions. Cl$^-$ and Na$^+$, markers of sea salt, also contributed averages of 18% and 8%, respectively, to the total ion balance of rainwater during the entire study period.
To appreciate the influence of season in rainwater composition, the relationship between measured Na\(^+\) and Cl\(^-\) ions of each event with reference to seawater Cl\(^-\)/Na\(^+\) have been plotted in supplemental Fig. S1. It was observed that the relationship was poor, except for the year 2014. During 2012 and 2013, scattered distributions were observed with an excess of Cl\(^-\) in 2013, and an excess of Na\(^+\) in 2012. The excess of Cl\(^-\) could have come from additional source contributions like biomass burning and open waste burning, and/or as a reflection of Cl\(^-\) displacement from sea-salts (NaCl) by anthropogenic HNO\(_3/\)H\(_2\)SO\(_4\) (Sarin et al., 2010). K\(^+\), the signature ion of biomass burning, contributed 6\%, 9\%, and 8\% to the total ionic budget during 2012, 2013, and 2014, respectively. These results indicate the prevalence of biomass burning and its impact on regional atmospheric chemistry.

Among the two organic acids, formic acid showed the higher average concentration during the study period with a value 19.8 \(\mu\)eq L\(^{-1}\). The ratio of acetate to formate (A/F) can signify the degree of photochemical production (A/F<1) of these acids against their primary emissions (A/F>1); (Sunder Raman et al., 2008 and references therein). The samples of the pre-monsoon seasons were observed to have ratios >1, and rains during all other seasons were observed to have ratios <1. The pre-monsoon season is the time when the brick kilns are at their peak of production, which means that the combustion of coal is at its maximum and adding significant organic acid primary emissions. Increased Dissolved Organic Carbon (DOC) concentrations were seen during 2013 (8.43 mgC L\(^{-1}\)). The presence of organic carbon constituents could be attributed to various source contributors. Organic carbon particles emitted from biomass burning, intensive coal combustion, or formation in the atmosphere during long-range transport could account for their presence (Deka and Hoque, 2014b).
Seasonal variability

Seasonal variations in the ionic composition were observed (Fig. S2). Concentrations of ions except Cl\(^-\) followed the order: Pre-monsoon>Winter>Post-monsoon>Monsoon. This trend shows that pre-monsoon and winter are the two seasons that experienced maximum concentrations of most ions. Winter season receives substantially less rainfall (2013, n=2; 2014, n=2) compared to the monsoon season. However, most of the industrial activities (brick kilns, tea industries, stone quarries, construction, etc.) peak during winter and are sustained until the region receives monsoonal showers. Therefore, the pre-monsoon season behaves like winter until Nor’wester showers begin. The rainfall received during these seasons is more concentrated with pollutants that have been emitted from local sources. Monsoon receives the highest rainfall. As the monsoon proceeds, the atmosphere becomes cleaner due to efficient scavenging of particles. Therefore, there are decreased concentrations of all the ions during the monsoon and post-monsoon seasons.

It was observed that Cl\(^-\) showed maximum concentration i.e. 65.5 µeq L\(^-1\) during the pre-monsoon period. Among other ions concentrations, SO\(_4^{2-}\) reached its during winter.

The seasonal variability in the composition of rainwater may also be related to long-range transport. There is an explicit shift of directions from where the air mass trajectories that reached Tezpur originate in different seasons. Trajectory clusters reaching Tezpur of Brahmaputra Valley at 500m height above ground level for monsoon and non-monsoon period illustrated in Fig. 1 and the associated concentrations (Table 1) show that air masses travelled over long distances and from different directions. During monsoons (June to September), the trajectories come mainly from the Bay of Bengal and the Arabian Sea. During this period, trajectories crossed the landmass the deccan plateau of India and Bangladesh. The concentrations of the species were higher in the non-
monsoon period and those rains were associated with the clusters that originated from and/or crossed the polluted regions like the IGP.

The calculated anthropogenic contribution of the chemistry was found to be much higher during the non-monsoon period. The clusters 1 and 5 represent airmasses arriving from the polluted IGP region and, therefore, the associated anthropogenic contributions were found to be maximum. It is also evident that the contribution of dust was higher during the non-monsoon period. So, the chemistry suggests that both local and trans-boundary movement of pollutants with the rain bearing airmasses did influence the rainwater chemistry of the study area.

Differences in the chemical properties of pollutants influenced the rainwater chemistry. It was found that alkaline ions (Ca\(^{2+}\), NH\(_4^+\), K\(^+\)) were mostly locally driven, and maintained the alkaline nature of rainwater during most of the year even with substantial sources of acidic compounds. During non-monsoon seasons, rainwater composition was dominated by Ca\(^{2+}\), NH\(_4^+\), K\(^+\), SO\(_4^{2-}\) and NO\(_3^-\) that originated locally from the sources like soil suspended from roads and agricultural fields, biomass burning, automobiles, and local industries like brick kilns. However, the monsoonal rain chemistry differs from the rest of the period. This period receives much greater amounts of rainfall originating from sea and crossing the land. Air masses reaching the study site during other periods have been found to have originated from distant places like Northern India as well as South Asia (Fig.1).

**Deposition flux of ions**

The annual wet deposition (WD) was calculated using the approach of Akpo et al., 2015. The WD was expressed in kg ha\(^{-1}\) yr\(^{-1}\) and was calculated by multiplying the VW mean value in mg L\(^{-1}\) by the annual average rainfall amount (P in mm).
The annual wet deposition along with the standard deviations and annual total rainfall collected during the study period over the mid-Brahmaputra valley are given in Table S2. It has been observed that SO$_4^{2-}$ and NO$_3^-$ among the anions, and Ca$^{2+}$ and NH$_4^+$ among the cations were important ionic constituents in terms of wet deposition. The study year 2014 showed comparatively higher deposition of most ions except for Cl$^-$, Br$^-$, and F$^-$. Deposition of Na$^+$ ion was almost equal in all the three years. Among the measured ions, K$^+$, NH$_4^+$, F$^-$, Cl$^-$, NO$_3^-$, and SO$_4^{2-}$ showed significant difference (one-way ANOVA) in terms of wet deposition at 0.05 significant levels having p values 0.03, 0.00, 0.00, 0.00, 0.00, 0.01 respectively. The ions showed highest deposition flux during pre-monsoon seasons followed by winter (Fig.5). The global assessment of precipitation chemistry and deposition under the World Meteorological Organization (WHO) Global Atmosphere Watch (GAW) reported that Northeast India has been prone to nitrogen and sulfur deposition compared to industrial sites like western Europe, northeastern United States, and East Asia (Vet et al., 2014). Deposition of high sulfur and nitrogen compounds in this region could be associated with the high precipitation depths reported by the WHO-GAW.

**Acidity and Neutralization**

The acidity of rainwater is strongly dependent on the concentrations of (i) acid-forming ions like SO$_4^{2-}$, NO$_3^-$, Cl$^-$, and organic acids, and (ii) alkaline species such as NH$_4^+$, Ca$^{2+}$, and Mg$^{2+}$ responsible for neutralization of the acidity. The capacity of acid neutralization is calculated as fractional acidity (FA), i.e. FA=$H^+/\left(NO_3^-+SO_4^{2-}\right)$ (Balasubramanian et al., 2001). A value of FA=1 indicates rainwater acidity generated by SO$_4^{2-}$ and NO$_3^-$ has not been neutralized at all by other ions. The FA value for the entire study period was 0.06. This value indicates that about 94% of the
Acidity caused by mineral acids was neutralized by alkaline species. There is a 6% gap in terms of species that caused the rainwater acidification that could be due to the species other than NO$_3^-$ and SO$_4^{2-}$.

The (Ca$^{2+}$+NH$_4^+$+Mg$^{2+}$)/(NO$_3^-$+SO$_4^{2-}$) ratio was greater than one (=1.76) during the entire study period indicating that there were sufficient alkaline species present to neutralize the acidity. The relative contribution of NO$_3^-$ to the acidity was calculated by $\frac{NO_3^-}{NO_3^- + nssSO_4^{2-}}$ (Cao et al., 2009). The result was found that 42% of rainwater acidity was caused by NO$_3^-$ and 58% was due to SO$_4^{2-}$. Thus, NO$_3^-$ also played a major role in the acidification of rainwater. NO$_3^-$ in rainwater could be due to the homogeneous and heterogeneous gas-phase transformations of NO$_x$ to HNO$_3$, followed by reactions with basic ions such as NH$_3$ to form NH$_4$NO$_3$ (Akpo et al., 2015).

Neutralizing factors for Ca$^{2+}$, NH$_4^+$, K$^+$ and Mg$^{2+}$ have been calculated using Eq. 5:

$$NF_x = \frac{[X]}{[NO_3^- + SO_4^{2-}]}$$ (5)

Where X stands for component of interest (Das et al., 2005). Fig.S3 illustrates the annual and seasonal variations in the neutralization factors for the major alkaline ions. The ions followed the order Ca$^{2+}$>NH$_4^+$>K$^+$>Mg$^{2+}$. Ca$^{2+}$ was found to be the most neutralizing alkaline ion present in the rainwater followed by NH$_4^+$. This order of neutralization agrees with most studies reporting from different geographical locations of India (Budhavant et al., 2011; Parashar et al., 1996; Kulshrestha et al., 2003; Das et al., 2005; Rastogi and Sarin, 2005; Budhavant et al., 2009; Tiwari et al., 2015). Fig.S3 shows the neutralization factors of major cations during different seasons of the study period.

Source apportionment of the rainwater constituents
PMF was employed to investigate the sources and the chemistry of the composition of rain. A solution with six factors was obtained, which was the best fit in terms of the distributions of scaled residuals and had reasonable physical interpretation (Fig. 6). The displacement approach (DISP) was used to explore the rotational ambiguity in the solution (Paatero et al., 2014). Individual values in the profiles were pulled away from the best fit values until the objective function value, Q, rose beyond a specified limit. Also pulling on a value should not cause the factors to change identities (“factor swapping”). The mean DISP value is indicated in Fig. 6 by the open circles and the minimum and maximum values are denoted by the error bars.

Factor 1: This factor has contributions from Na\(^+\) and Cl\(^-\), with high explained variation (EV), that is typically attributed to sea-salt (Rao et al., 2016). This result suggests the mixing of sea salt with crustal dust while being transported from the sea to the study area. The monsoon season airmass back trajectories (Fig. 1) show that they originated from the Bay of Bengal, and the Arabian Sea, travelling over Bangladesh and India’s mainland before reaching the study area. In the process, the air was well mixed and included local dust inputs. Also, during the monsoon, a large volume of crustal debris, which is carried by the runoff water from the hills, settled on the roads. Following the rainy days, the sunny, dry days allow the dust to dry and moving vehicles then suspend the dry debris into the air (Bhuyan et al., 2018). This process is more pronounced in the case of unpaved village roads where the rain loosens the surface of the road leading to greater release of crustal matter from such roads on dry days.

Factor 2: The principal contributors to this factor were F\(^-\), Ca\(^{2+}\), Mg\(^{2+}\), and NH\(_4^+\), and organic acids. The spread of DISP values for these species are very small demonstrating that they are important species in this profile. This factor makes large contributions (EV) to these species including 100% of the F. F\(^-\) has been reported as a marker species for coal burning (e.g. Ando et al, 1998; 2001),
and F$^-$ appears only in this factor. Thus, this factor can be attributed to emission from coal combustion. Ca and Mg are important components of fly ash in Indian coal. Jala and Goyal, (2006) reported that the fly ash collected by an electrostatic precipitator had a Ca content of 3.4% and a Mg concentration of 0.14%. Some ammonia is also emitted from coal burning (e.g. Bouwman et al., 1997). However, most of the ammonia comes from agricultural sources. The major users of coal are the brick kilns and the tea processing units, where coal is used to generate heat for drying. Brick kilns in this region operate mostly during post monsoon and winter periods and reduce their activity with the coming of pre-monsoon showers. Alternatively, tea processing intensifies during the pre-monsoon and monsoon periods since this time of the year is the main growing period for tea plants and this is the period of the year when the region receives maximum rainfall. Also, brick industries operating in neighboring Bangladesh (~1000 units just around Dhaka city alone) by burning Indian coal and agricultural wastes (Guttikunda et al., 3013). Back trajectory analysis (Fig. 1) suggests that trajectories that originate and/or pass over Bangladesh could bring emissions to the region. The presence of HCOO$^-$ and CH$_3$COO$^-$ (with high EV) may be attributed to the start-up and burn-out phases of the coal burning cycle where secondary-like species are emitted (Li et al., 2019). The analysis of the ratios of the acids (F/A) provides signs of primary emission, which appears to be coal burning.

Factor 3: This factor has representation of K$^+$, Cl$^-$, HCOO$^-$ and CH$_3$COO$^-$ and DOC. K$^+$ is a marker species of biomass burning emissions (Wang et al., 2011; Masiol et al., 2017). It has also been reported that K$^+$ associated with Cl$^-$ could be typical of biomass burning emission. Sillapapiromsuk et al., (2013) reported extremely high emission factors for K$^+$ and Cl$^-$ compared to other ions from crop residue burning experiments. Deka and Hoque (2015) had found K$^+$ and Cl$^-$ to be the most
abundant species, several, hundred mg/kg, in biomass burning smoke particles collected from rural kitchens of the Brahmaputra Valley.

Although HCOO$^-$ and CH$_3$COO$^-$ are the oxidized by-products of atmospheric VOC degradation, much of which are biogenic (e.g. Chaliyakunnel et al., 2016 and references therein), there are also reports of primary emission of them from biomass burning (Talbot et al., 1988). They hypothesized that the seasonality of HCOO$^-$ and CH$_3$COO$^-$ could be an outcome of differential contributions of biogenic burning versus anthropogenic emissions. Emission of very large volumes of organic species is very typical of biomass burning as is evident in the association of DOC with the markers of biomass burning. Crutzen and Andreae (1990) reported that biomass burning is responsible for emission of a huge volume of trace gases into the atmosphere, especially CO, methane, and non-methane hydrocarbons. These hydrocarbons undergo photochemical oxidation initiated by hydroxyl radical attack and as a result several oxidized forms of organics are formed in the atmosphere. The oxidized organics tend to be water soluble, and it is expected that they are readily scavenged by the water droplets. Additionally, carboxylic acids tend to enhance CCN activities (Kumar et al., 2003).

Formate and some CH$_3$COO$^-$ are major products of methane combustion in CNG vehicles, which are in use in the major cities in mainland India and not around the study area of India’s northeastern states. The nearest areas with CNG use are in Bangladesh and Kolkata in India’s mainland. HCOO$^-$ and CH$_3$COO$^-$ are reactive organic species, and so long-range transport of them to the study area would end up forming further oxidized forms like CO.

Biomass burning is prevalent in the Brahmaputra Valley region where this study has been undertaken. Agricultural residue burning, forest fire and burning for cooking are many forms of biomass burning have been identified by researchers (e.g. Bhuyan et al. 2018), which intensifies
during the winter and pre-monsoon seasons. A unique episodic festive biomass burning takes place each year during mid-January and is characteristic of the Brahmaputra Valley (Deka and Hoque, 2014a).

Factor 4: This factor has contributions from Br⁻, DOC and NH₄⁺, and may be attributed to agricultural emissions. Ammonia is a typical species out of agricultural emission (e.g. Misselbrook et al., 2000; Kirchmann et al., 1998; Zhou et al., 2019). Some Br⁻ is also present in the sea salt fraction of the aerosol. However, Br⁻ did not associate strongly with Na⁺ or Cl⁻. Biomass burning also has been reported to emit CH₃Br (Manö and Andreae, 1994). However, there is no association of Br⁻ with K⁺. Instead, Br⁻ associated with DOC and ammonia. Agriculture is ascribed to be the major contributor of ammonia into the atmosphere. Br⁻ correlating with NH₄⁺ would suggest that this group of species represent agricultural emissions. Br⁻ was not present in detectable amounts in all samples and during all seasons, and therefore, the source of Br⁻ has to do with some seasonal activity like agriculture. This region is known for its tea cultivation. Tea is plantation agriculture. Pruning and plucking of tender leaves is a usual activity in the tea gardens that are spread over thousands of acres. It is known that foliage damage enhances organic emission (Churkina et al. 2017 and references therein). Thus, it is envisaged that large volumes of organics are emitted by plantations and forests.

Br⁻ is suspected to be of agricultural origin and methyl bromide (CH₃Br) is the likely precursor. Wofsy et al., (1975) explained the sources of atmospheric Br⁻, especially CH₃Br. They described the reactivity of atmospheric Br⁻ and its removal from the atmosphere by wet scavenging. Methyl bromide is a major reservoir of bromine in the atmosphere. Although historically CH₃Br was used in agriculture as soil fumigant, it is no longer in use in this form in India. There is a strict restriction on the use of CH₃Br in compliance with the Montreal Protocol. The tea sector of this region was a
major user of CH$_3$Br in the past and that has been replaced by alternatives over a decade ago. Over
the years, the use of CH$_3$Br became limited under strict surveillance of the Indian government.
Neighboring Sri Lanka also banned this chemical in 2015. However, crops belonging to
Brassicaceae family take up bromine from soil as bromide that is then emitted into the atmosphere
as CH$_3$Br (Gan et al., 1998). There are reported increasing trends in the emission of CH$_3$Br from
rapeseed (Brassica napus), mustard (Brassica rapa), and cabbage (Brassica oleracea) (Mead et
al. 2008). There is a considerable land area covered with these crops in the region and in India’s
mainland. This factor also includes contributions of Mg$^{2+}$ and Ca$^{2+}$. Mg and Ca are essential
nutrients for plant growth, which are used in the foliar application, especially in fruits and
vegetable orchards (e.g. Ram et al., 2000; Yildirim et al., 2009). Foliar application of Ca and Mg
improves growth, yield (Dordas, 2009). Foliar application of Mg in tea plants is an old practice
(e.g. Obatolu, 1999). Large area of the region under tea plantation which resort to application of
Mg in a large volume. The process of foliar application could have released much of particulate
Ca and Mg that have shown association with other indicator species of agricultural emission.
Factor 5: This factor has contributions from SO$_4^{2-}$, NH$_4^{+}$, and DOC, which are attributed to
secondary sulfate. The precursor of SO$_4^{2-}$, SO$_2$, is emitted by diesel engine burning high sulfur
fuels (e.g. Moldanová et al., 2009; Reddy and Venkataraman, 2002) as well as from coal
combustion including coal-fired power plants and brick kilns (e.g. Hopke et al., 2005). As reported
by the Indian Ministry of Road Transport and Highways, India currently has two fuel quality
standards: one that applies to places that meet Bharat Stage IV (BS IV) such as in major cities, and
the other follows BS III. Nearly half of the country now requires 50 ppm sulfur diesel and gasoline.
The rest of the country, including the region represented in this study, allows up to 150 ppm sulfur
in gasoline and 350 ppm sulfur in diesel fuel. Diesel fuel is also used in varieties of other activities
like locomotives, captive power generation, and in agricultural irrigation machines. Internal combustion engines will emit a significant amount of the sulfur as SO₃ due to adiabatic cooling in the expansion stroke. Thus, these fuels can contribute sulfur in both the S(IV) and S(VI) forms (Santoso et al., 2008). Therefore, there are multiple sources of sulfur both local and distant. Ammonia is the common neutralizer of SO₄²⁻ as observed in this factor.

Again, VOCs undergo hydroxyl radical initiated oxidation leading to the formation of oxidized secondary organics in the atmosphere. Also, Kotnala et al. (2020) reported secondary formation of ammonia from the primary constituents of traffic emissions. Thus, DOC along with SO₄²⁻ and NH₄⁺ represent secondary aerosol formation in the atmosphere. Given the longer reaction times for the formation of secondary sulfate and secondary organic carbon (SOA), this factor likely represents particles transported into the region.

Factor 6: In this factor, crustal elements are present along with NO₃⁻ and SO₄²⁻. Nitrate forms rapidly in the atmosphere and the nitric acid can then interact with the alkaline components of the soil to deposit nitrate into the coarse mode aerosol (Wolff, 1984). There can also be reactions between NO₂ or SO₂ and these alkaline crustal components (Zhao et al., 2018). The resulting ions would be released into the droplet when these particles are washed out of the air as the droplet falls to the ground.

Both factors 1 and 6 have high Ca²⁺ and Mg²⁺, but factor 1 has little NO₃⁻ or SO₄²⁻ while factor 6 does. Factor 1 explains most of the Ca²⁺ and Mg²⁺ meaning it is the main soil factor while Factor 6 has much of the NO₃⁻ and SO₄²⁻ with less explained variation for Ca²⁺ and Mg²⁺. This result implies that most of the soil is not taking up acidic NO₃⁻ and SO₄²⁻, but that process represents a major mechanism for getting NO₃⁻ and SO₄²⁻ into the precipitation.
CONCLUSIONS

Rainwater chemistry of Mid-Brahmaputra Valley showed seasonal characteristics and the influence of the sea is explicit during the monsoon. Though the region is not fully industrialized yet compared to other regions of India, the levels of constituents in the rainwater show anthropogenic influence, which might indicate that long-range transport of constituents has implications on the rainwater chemistry of the region. As the region receives airmass back trajectories originating from different regions depending on the seasons, the chemistry of the rainfall varies considerably throughout the year. Nearly 60% of the rain events were found to be alkaline (pH>5.6) and 28% rains showed pH between 5.0 and 5.5, while 14% of the rains showed pH between 4.5 and 5.0. This shows that crustal dust present in the local atmosphere was not efficiently neutralizing the acidic ions, which could be a sign of depleted levels of basic cations in the soils of the region. The decrease in the level of pH was observed in the subsequent rainfalls, which made it clear that the early rains scavenged the below-cloud neutralizing cations (Ca$^{2+}$ and Mg$^{2+}$) of crustal origin, leading to poorly neutralized (acidic) rains. The region being ecologically fragile and a biodiversity hotspot, acidic deposition might have impacts on the land and water quality of the region, which could subsequently impact the flora and fauna. This could have implications on the flora and fauna of the unique ecosystems of the region. The PMF model application provided a reasonable solution to identify the sources (viz. Sea-salt, industrial coal burning, biomass burning, agricultural emission, secondary ions, and crustal dust) of the ions associated with the rains and to apportion their strengths. The sources of the ions were both natural and anthropogenic, and a long-term study may appreciate the dynamic nature of rainwater chemistry of the region vis a vis industrial development and climate change.
ACKNOWLEDGEMENTS

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REFERENCES


Table 1: Concentrations of species associated with various clusters of trajectories during the monsoon and non-monsoon seasons (all ions in µeq L⁻¹). The contributions were calculated as: anthropogenic – [NO₃⁻+NH₄⁺+nssSO₄²⁻+nssK⁺]; dust – [nssCa²⁺+nssMg²⁺].

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Fig. 1: Back trajectory clusters reaching the sampling station (Tezpur) of Brahmaputra Valley: (A) Monsoon and (B) Non monsoon (the color scales (blue-magenta) represent trajectories 1-5).
Fig. 2: Relationship between $\sum$ Anion and $\sum$ Cation during the study period 2012-14

$y = 1.546x + 54.11$
$r = 0.876$
$p = 0.000$
Fig. 3: Percentage frequency distribution of rainwater pH in Tezpur
Fig. 4: Temporal variation of mean pH and EC (µScm⁻¹) along with average volume (mm) of rainwater collected during the study period.
Fig. 5: Seasonal deposition flux of ions (PrM - Premonsoon, M - Monsoon, PoM - Postmonsoon, W - Winter)
Fig. 6: Factors extracted by EPA PMF 5.0: The bars are the base case values. The displacement (DISP) results as open circles with error bars showing max and min values. Solid points are the explained variations. The variables with maximum explained variations and small DISP intervals of concentrations are considered for identifying the sources associated with factors. (Factor 1- Sea Salt, Factor 2- Coal burning (industries), Factor 3- Biomass burning, Factor 4- Agricultural emission, Factor 5- secondary ions, Factor 6- Crustal dust)