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

Pranamika Bhuyan^{1,2}, Md. Sahbaz Ahmed¹, Philip K. Hopke^{3,4*}, Raza R. Hoque^{1,3*}

¹ Department of Environmental Science, Tezpur University, Tezpur 784028, India

² Department of Environmental Studies, Assam Women's University, Jorhat 785004, India

³ Department of Public Health Sciences, University of Rochester Medical Center, Rochester, NY 14642, USA

⁴ Center for Air Resources Engineering and Science, Clarkson University, Potsdam, NY 13699, USA

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 (SO_4^{2-} , NO_3^- , Cl^- , F^- , Br^- , Ca^{2+} , NH_4^+ , Mg^{2+} , Na^+ , K^+ , and Li^+), organic acids (HCOO^- and CH_3COO^-) 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 $\text{pH} < 5$. Ionic concentration followed the order $\text{NH}_4^+ > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} > \text{H}^+ > \text{HCO}_3^- > \text{Br}^- > \text{F}^- > \text{Li}^+$, indicating dominance of alkaline ions over acidic ions such that 94% of mineral acid was neutralized. The secondary ions, NH_4^+ , SO_4^{2-} , and NO_3^- , showed high wet deposition fluxes. The chemistry exhibits explicit seasonality. The air mass 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.

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; Likens *et al.*, 1976; Charlson and Rodhe, 1982; Galloway *et al.*, 1982; Zeng and Hopke, 1989; 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 (Rastogi and Sarin, 2005; Mimura *et al.*, 2016). 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., Tiwari *et al.*, 2007; Chate *et al.*, 2011; Niu *et al.*, 2014; Akpo *et al.*, 2015), 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; Safai *et al.*, 2004; Kulshrestha *et al.*, 2005b; Momin *et al.*, 2005; Mouli *et al.*, 2005; Rastogi and Sarin, 2007; Tiwari *et al.*, 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

* Corresponding authors.

E-mail address: phopke@clarkson.edu (P.K. Hopke);
rrh@tezu.ernet.in (R.R. Hoque)

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. Consequentially, 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 (2014a, b), 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 air mass 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 (10 m 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 (Keene *et al.*, 1983; WMO, 2004).

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; Kieber *et al.*, 2002; Campos *et al.*, 2007). 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 measurements. The conductivity meter (Systronics, 304) was periodically calibrated using 0.1 N 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

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).

Metrosep Organic Acids-100/7.8 and a standard eluent ($0.5 \text{ mmol L}^{-1} \text{ H}_2\text{SO}_4$: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 Meteorological 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 $18.2 \text{ M}\Omega\cdot\text{cm}$) 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 $\text{RSD} \leq 5\%$. In case of pH, the difference

between replicate measurements were found to be less than 0.05 while for EC, they were less than $1 \mu\text{S cm}^{-1}$.

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. 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):

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

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):

$$\text{pH}_{\text{VWM}} = -\log \left(\frac{\sum (10^{-\text{pH}_i}) \times V_i}{\sum V_i} \right) \quad (2)$$

where pH_{VWM} is the volume weighted average pH, and 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):

Fig. 2. Relationship between ΣAnion and ΣCation during the study period 2012-14.

$$\text{VWM } (\mu\text{eq L}^{-1}) = \frac{\sum_{i=1}^n C_i P_i}{\sum_{i=1}^n P_i} \quad (3)$$

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., Junto 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 ± 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 NO_3^- and SO_4^{2-} (e.g., Rastogi and Sarin, 2005). In the sample having the lowest pH (4.51), NO_3^- and SO_4^{2-} contributed 33% and 55%, respectively, of the total anion concentrations and HCO_3^- ion concentrations were negligible. NH_4^+ and Ca^{2+} contributed 38% and 18%, respectively, to the total cation concentrations. The difference

Fig. 3. Percentage frequency distribution of rainwater pH in Tezpur.

in the free acidity, i.e., H^+ between the sample having the lowest pH [$\text{H}^+ = 30.90 \mu\text{eq L}^{-1}$; pH = 4.51] and natural rainwater in equilibrium with atmospheric CO_2 [$\text{H}^+ = 2.51 \mu\text{eq L}^{-1}$; pH = 5.61] (Tiwari *et al.*, 2015) is $28.39 \mu\text{eq L}^{-1}$. 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 $16.22 \mu\text{S cm}^{-1}$ and the arithmetic mean was $29.16 \mu\text{S cm}^{-1}$. 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 ($\sum \text{Anion} / \sum \text{Cation}$) 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

Fig. 4. Temporal variation of mean pH and EC ($\mu\text{S cm}^{-1}$) along with average volume (mm) of rainwater collected during the study period.

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 $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , CaSO_4 , and $\text{Ca}(\text{NO}_3)_2$. 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 $\text{HNO}_3/\text{H}_2\text{SO}_4$ (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 $19.8 \mu\text{eq L}^{-1}$. The ratio of acetate to formate (A/F) can signify the degree of photochemical production ($\text{A/F} < 1$) of these acids against their primary emissions ($\text{A/F} > 1$); (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., $65.5 \mu\text{eq L}^{-1}$ 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–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 $\text{kg ha}^{-1} \text{yr}^{-1}$ and was calculated by multiplying the VW mean value in mgL^{-1} by the annual average rainfall amount (P in mm).

Table 1. Concentrations of species associated with various clusters of trajectories during the monsoon and non-monsoon seasons (all ions in $\mu\text{eq L}^{-1}$). The contributions were calculated as: anthropogenic – $[\text{NO}_3^- + \text{NH}_4^+ + \text{nssSO}_4^{2-} + \text{nssK}^+]$; dust – $[\text{nssCa}^{2+} + \text{nssMg}^{2+}]$.

Season	Cluster	% age	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}	Anthropogenic	Dust
Monsoon	1	15.8	24.9	44.6	16.8	46.7	11.4	0.6	20.4	13.9	21.3	93.0	51.4
	2	20.9	24.4	56.6	18.6	54.7	13.0	1.1	26.6	26.5	37.4	135.6	61.1
	3	28.8	20.4	31.4	16.8	44.9	10.1	0.4	20.0	14.9	18.8	79.0	49.5
	4	12.4	22.2	42.2	20.7	52.5	11.3	0.5	24.6	21.6	27.1	108.4	57.8
	5	22.0	22.6	40.1	20.2	47.8	11.5	2.0	22.4	17.7	21.0	95.8	53.2
Non-monsoon	1	17.4	48.3	200.2	76.5	160.4	33.8	28.7	252.7	215.5	210.4	695.7	181.2
	2	7.3	18.4	60.4	22.5	72.4	16.2	1.7	25.1	30.7	49.1	160.1	83.7
	3	49.5	28.2	107.8	33.4	112.3	20.7	4.3	34.1	53.4	60.9	251.5	125.4
	4	16.5	34.2	64.5	32.1	88.8	19.9	1.7	37.2	38.7	39.5	170.0	99.5
	5	9.2	56.4	186.4	63.3	166.3	36.8	9.7	59.2	96.2	122.1	460.0	187.9

$$\text{WD (kg ha}^{-1} \text{ yr}^{-1}) = \text{VWM (mgL}^{-1}) \times \frac{P}{100} \quad (4)$$

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., $\text{FA} = \text{H}^+ / (\text{NO}_3^- + \text{SO}_4^{2-})$ (Balasubramanian *et al.*, 2001). A value of $\text{FA} = 1$ 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-} .

Fig. 5. Seasonal deposition flux of ions (PrM - Premonsoon, M - Monsoon, PoM - Postmonsoon, W - Winter).

The $(\text{Ca}^{2+} + \text{NH}_4^+ + \text{Mg}^{2+})/(\text{NO}_3^- + \text{SO}_4^{2-})$ 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 $\text{NO}_3^-/(\text{NO}_3^- + \text{nssSO}_4^{2-})$ (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_4NO_3 (Akpo *et al.*, 2015).

Neutralizing factors for Ca^{2+} , NH_4^+ , K^+ and Mg^{2+} have been calculated using Eq. (5):

$$\text{NF}_x = [\text{X}]/[\text{NO}_3^- + \text{SO}_4^{2-}] \quad (5)$$

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 $\text{Ca}^{2+} > \text{NH}_4^+ > \text{K}^+ > \text{Mg}^{2+}$. 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 (Parashar *et al.*, 1996; Kulshrestha *et al.*, 2003; Das *et al.*, 2005; Rastogi and Sarin, 2005; Budhavant *et al.*, 2009; Budhavant *et al.*, 2011; 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 air mass 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.*, 2013). 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_3COO^- (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_3COO^- 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^{-1} , in biomass burning smoke particles collected from rural kitchens of the Brahmaputra Valley.

Although HCOO^- and CH_3COO^- 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_3COO^- 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

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).

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_3COO^- 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_3COO^- 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 NH_4^+ , and may be attributed to agricultural emissions. Ammonia is a typical species out of agricultural emission (e.g., Kirchmann et al., 1998; Misselbrook et al., 2000; 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 CH_3Br (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 NH_4^+ 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 (CH_3Br) is the likely precursor. Wofsy et al. (1975) explained the sources of atmospheric Br^- , especially CH_3Br . 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 CH_3Br 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 CH_3Br in compliance with the Montreal Protocol. The tea sector of this region was a major user of CH_3Br in the past and that has been replaced

by alternatives over a decade ago. Over the years, the use of CH_3Br 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_3Br (Gan et al., 1998). There are reported increasing trends in the emission of CH_3Br 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., Reddy and Venkataraman, 2002; Moldanová et al., 2009; 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 SO_3 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 SO_4^{2-} 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 SO_4^{2-} and NH_4^+ 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 NO_3^- and SO_4^{2-} . 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 NO_2 or SO_2 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 Ca^{2+} and Mg^{2+} , but factor 1 has little NO_3^- or SO_4^{2-} while factor 6 does. Factor 1 explains most of the Ca^{2+} and Mg^{2+} meaning it is the main soil factor while Factor 6 has much of the NO_3^- and SO_4^{2-} with less explained variation for Ca^{2+} and Mg^{2+} . This result implies that most of the soil is not taking up acidic NO_3^- and SO_4^{2-} , but that process represents a major mechanism for getting NO_3^- and SO_4^{2-} 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 ($\text{pH} > 5.6$) 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.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <https://doi.org/10.4209/aaqr.2020.02.0072>

REFERENCES

- Akpo, A., Lacaux, C.G., Laoualli, D., Delon, C., Liousse, C., Adon, M., Gardrat, E., Mariscal, A. and Darakpa, C. (2015). Precipitation chemistry and wet deposition in a remote wet savanna site in west Africa: Djougou (Benin). *Atmos. Environ.* 115: 110–123. <https://doi.org/10.1016/j.atmosenv.2015.04.064>
- Al-Khashman, O.A. (2005). Ionic Composition of Wet Precipitation in the Petra Region, Jordan. *Atmos. Res.* 78: 1–12. <https://doi.org/10.1016/j.atmosres.2005.02.003>
- Al-Khashman, O.A. (2009). Chemical characteristics of rainwater collected at a western site of Jordan. *Atmos. Res.* 91: 53–61. <https://doi.org/10.1016/j.atmosres.2008.05.007>
- Ando, M., Tadano, M., Asanuma, S., Tamura, K., Matsushima, S., Watanabe, T., Kondo, T., Sakurai, S., Ji, R., Liang, C. and Cao, S. (1998). Health effects of indoor fluoride pollution from coal burning in China. *Environ. Health Perspect.* 106: 239–244. <https://doi.org/10.1289/ehp.98106239>
- Ando, M., Tadano, M., Yamamoto, S., Tamura, K., Asanuma, S., Watanabe, T., Kondo, T., Sakurai, S., Ji, R., Liang, C., Chen, X., Hong, Z. and Cao, S. (2001). Health effects of fluoride pollution caused by coal burning. *Sci. Total Environ.* 271: 107–116. [https://doi.org/10.1016/s0048-9697\(00\)00836-6](https://doi.org/10.1016/s0048-9697(00)00836-6)
- Anttila, P., Paatero, P., Tapper, U. and Jarvinen, O. (1995). Application of positive matrix factorization to source apportionment: results of a study of bulk deposition chemistry in Finland. *Atmos. Environ.* 29: 1705–1718.
- Balasubramanian, R., Victor, T. and Chun, N. (2001). Chemical and statistical analysis of precipitation in Singapore. *Water Air Soil Pollut.* 130: 451–456. <https://doi.org/10.1023/A:1013801805621>
- Bhuyan, P., Barman, N., Begum, S., Gogoi, D., Borah, S., Kumar, M., Sarma, K.P. and Hoque, R.R. (2016). Spatial and seasonal variations of water soluble ions in PM_{10} of mid-Brahmaputra plain of Assam valley. *Asian J. Water Environ. Pollut.* 13: 69–81. <https://doi.org/10.3233/ajw-160018>
- Bhuyan, P., Barman, N., Bora, J., Daimari, R., Deka, P. and Hoque, R.R. (2016a). Attribution of aerosol bound water soluble ions and carbon, and their relationship with AOD over the Brahmaputra valley. *Atmos. Environ.* 142: 194–209. <https://doi.org/10.1016/j.atmosenv.2016.07.045>
- Bhuyan, P., Deka, P., Prakash A., Balachandran S. and Hoque, R.R. (2018). Chemical characterization and source

- apportionment of aerosol over mid Brahmaputra Valley, India. *Environ. Pollut.* 234: 997–1010. <https://doi.org/10.1016/j.envpol.2017.12.009>
- Bouwman, A.F., Lee, D.S., Asman, W. a. H., Dentener, F.J., Hoek, K.W.V.D. and Olivier, J.G.J. (1997). A global high-resolution emission inventory for ammonia. *Global Biogeochem. Cycles* 11:561–587. <https://doi.org/10.1029/97GB02266>
- Budhavant, K.B., Rao, P.S.P., Safai, P.D. and Ali, K. (2009). Chemistry of monsoon and postmonsoon rains at a high altitude Location, Sinhadgad, India. *Aerosol Air Qual. Res.* 9: 65–79. <https://doi.org/10.4209/aaqr.2008.07.0033>
- Budhavant, K.B., Rao, P.S.P., Safai, P.D. and Ali, K. (2011). Influence of local sources on rainwater chemistry over Pune region, India. *Atmos. Res.* 100: 121–131. <https://doi.org/10.1016/j.atmosres.2011.01.004>
- Campos, M.L.A.M., Nogueira, R.F.P., Dametto, P.R., Francisco, J.G. and Coelho, C.H. (2007). Dissolved organic carbon in rainwater: glassware decontamination and sample preservation and volatile organic carbon. *Atmos. Environ.* 39: 8924–8931. <https://doi.org/10.1016/j.atmosenv.2007.08.017>
- Cao, Yu Z., Wang, S., Zhang, G., Luo, J. and Lu, S. (2009). Chemical characteristics of wet precipitation at an urban site of Guangzhou, South China. *Atmos. Res.* 94: 462–469. <https://doi.org/10.1016/j.atmosres.2009.07.004>
- Chaliyakunnel, S., Millet, D.B., Wells, K.C., Cady-Pereira, K.E. and Shephard, M.W. (2016). A large underestimate of formic acid from tropical fires: Constraints from space-borne measurements. *Environ. Sci. Technol.* 50: 5631–5640. <https://doi.org/10.1021/acs.est.5b06385>
- Charlson, R.J. and Rodhe, H. (1982). Factors controlling the acidity of natural rainwater. *Nature* 295: 683–685. <https://doi.org/10.1038/295683a0>
- Chate, D.M., Murugavel, P., Ali, K., Tiwari, S. and Beig, G. (2011). Below-cloud rain scavenging of atmospheric aerosols for aerosol deposition models. *Atmos. Res.* 99: 528–536. <https://doi.org/10.1016/j.atmosres.2010.12.010>
- Churkina, G., Kuik, F., Bonn, B., Lauer, A., Grote, R., Karolina Tomiak, K. and Butler, T.M. (2017). Effect of VOC emissions from vegetation on air quality in Berlin during a heatwave. *Environ. Sci. Technol.* 51: 6120–6130. <https://doi.org/10.1021/acs.est.6b06514>
- Crutzen, P.J. and Andreae, M.O. (1990). Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles. *Science* 250: 1669–1678. <https://doi.org/10.1126/science.250.4988.1669>
- Das, R., Das, S.N. and Misra, V.N. (2005). Chemical composition of rainwater and dustfall at Bhubaneswar in the east coast of India. *Atmos. Environ.* 39: 5908–5916. <https://doi.org/10.1016/j.atmosenv.2005.06.030>
- Das, R., Granat, L., Leck, C., Praveen, P.S. and Rodhe, H. (2011). Chemical composition of rainwater at maldives climate observatory at hanimaadhoo (MCOH). *Atmos. Chem. Phys.* 11: 3743–3755. <https://doi.org/10.5194/acp-11-3743-2011>
- Deka, P. and Hoque, R.R. (2014a). Incremental effect of festive biomass burning on wintertime PM₁₀ in Brahmaputra valley of Northeast India. *Atmos. Res.* 143: 380–391. <https://doi.org/10.1016/j.atmosres.2014.03.003>
- Deka, P. and Hoque, R.R. (2014b). Diwali Fireworks: early signs of impact on PM₁₀ properties of rural Brahmaputra valley. *Aerosol Air Qual. Res.* 14: 1752–1762. <https://doi.org/10.4209/aaqr.2013.09.0287>
- Deka P. and Hoque, R.R. (2015). Chemical characterization of biomass fuel smoke particles of rural kitchens of South Asia. *Atmos. Environ.* 108: 125–132. <https://doi.org/10.1016/j.atmosenv.2015.02.076>
- Dordas, C. (2009). Foliar application of calcium and magnesium improves growth, yield, and essential oil yield of oregano (*Origanum vulgare* ssp. *hirtum*). *Ind. Crops Prod.* 29: 599–608. <https://doi.org/10.1016/j.indcrop.2008.11.004>
- Eriksson, E. (1952). Composition of atmospheric precipitation. *Tellus* 4: 280–303. <https://doi.org/10.1111/j.2153-3490.1952.tb01014.x>
- Galloway, J.N. (1995). Acid deposition: perspectives in time and space. *Water Air Soil Pollut.* 85: 15–24. <https://doi.org/10.1007/BF00483685>
- Galloway, J.N., Thornton, J.D., Norton, S.A., Volchok, H.L. and McLean, R.A.N. (1982). Trace metals in atmospheric deposition: A review and assessment. *Atmos. Environ.* 16: 1677–1700. [https://doi.org/10.1016/0004-6981\(82\)90262-1](https://doi.org/10.1016/0004-6981(82)90262-1)
- Gan, J., Yates, S.R., Ohr, H.D. and Sims, J.J. (1998). Production of methyl bromide by terrestrial higher plants. *Geophys. Res. Lett.* 25: 3595–3598. <https://doi.org/10.1029/98gl52697>
- Ge, B.Z., Wang, Z. F., Xu, X.B., Tang, J., He, Y.J., Uno, I. and Ohara, T. (2011). Impact of the East Asian summer monsoon on long-term variations in the acidity of summer precipitation in Central China. *Atmos. Chem. Phys.* 11: 1671–1684. <https://doi.org/10.5194/acp-11-1671-2011>
- Granat, L. (1972). On the relation between pH and the chemical composition of atmospheric precipitation. *Tellus* 24: 550–560. <https://doi.org/10.1111/j.2153-3490.1972.tb01581.x>
- Granat, L., Das, S.N., Tharkur, R.S. and Rodhe, H. (2001). Atmospheric deposition in a area in India-net and potential acidity. *Water Air Soil Pollut.* 130: 469–474. <https://doi.org/10.1023/A:1013810007438>
- Guttikunda, S.K., Begum, B.A. and Wadud, Z. (2013). Particulate pollution from brick kiln clusters in the Greater Dhaka region, Bangladesh. *Air Qual. Atmos. Health* 6: 357–365. <https://doi.org/10.1007/s11869-012-0187-2>
- Handa, B.K. (1969). Chemical composition of monsoon rains over Calcutta. Part I. *Tellus* 21: 95–100. <https://doi.org/10.1111/j.2153-3490.1969.tb00421.x>
- Hopke, P.K., Zhou, L. and Poirot, R. (2005). Reconciling trajectory ensemble receptor model results with emissions. *Environ. Sci. Technol.* 39: 7980–7983. <https://doi.org/10.1021/es049816g>
- Jala, S. and Goyal, D. (2006). Fly ash as a soil ameliorant for improving crop production – A review. *Bioresour. Technol.* 97: 1136–1147. <https://doi.org/10.1016/j.biortech.2004.09.004>
- Juntto, S. and Paatero, P. (1994). Analysis of daily precipitation data by positive matrix factorization.

- Environmetrics* 5: 127–144. <https://doi.org/10.1002/env.3170050204>
- Keene, W.C., Galloway, J.N. and Holden, J.D., Jr. (1983). Measurement of weak organic acidity in precipitation from remote areas of the world. *J. Geophys. Res.* 88: 5122–5130. <https://doi.org/10.1029/jc088ic09p05122>
- Khemani, L.T., Momin, G.A., Naik, M.S., Prakash Rao, P.S., Kumar, R. and Ramanamurthy, Bh.V. (1985). Impact of alkaline particulates on pH of rainwater in India. *Water Air Soil Pollut.* 24: 365–376. <https://doi.org/10.1007/BF00283789>
- Kieber, R.J., Peake, B., Willey, J.D. and Avery, G.B. (2002). Dissolved organic carbon and organic acids in coastal New Zealand rainwater. *Atmos. Environ.* 36: 3557–3563. [https://doi.org/10.1016/s1352-2310\(02\)00273-x](https://doi.org/10.1016/s1352-2310(02)00273-x)
- Kirchmann, H., Esala, M., Morken, J., Ferm, M., Bussink, W., Gustavsson, J. and Jakobsson, C. (1998). Ammonia emissions from agriculture. *Nutr. Cycling Agroecosyst.* 51: 1–3. <https://doi.org/10.1023/A:1009738825468>
- Kotnala, G., Sharma, S.K. and Mandal, T.K. (2020). Influence of vehicular emissions (NO, NO₂, CO and NMHCs) on the mixing ratio of atmospheric ammonia (NH₃) in Delhi, India. *Arch. Environ. Contam. Toxicol.* 78: 79–85. <https://doi.org/10.1007/s00244-019-00689-8>
- Kulshrestha, M.J., Singh, R., Duarah, R. and Rao, P.G. (2014). Influence of crustal aerosols on wet deposition at a rural site of North-East India. *Int. J. Environ. Stud.* 71: 510–525. <https://doi.org/10.1080/00207233.2014.942151>
- Kulshrestha, M.J., Sekar, R., Krishna, D., Hazarika, A.K., Dey, N.C. and Rao, P.G. (2005a). Deposition fluxes of chemical components of fog water at a rural site in north east India. *Tellus B* 57: 436–439. <https://doi.org/10.3402/tellusb.v57i5.16566>
- Kulshrestha, U.C., Kulshrestha, M.J., Sekar, R., Sastry, G.S.R. and Vairamani, M. (2003). Chemical characteristics of rainwater at an urban site of south Central India. *Atmos. Environ.* 37: 3019–3026. [https://doi.org/10.1016/s1352-2310\(03\)00266-8](https://doi.org/10.1016/s1352-2310(03)00266-8)
- Kulshrestha, U.C., Granat, L., Engardt, M. and Rodhe, H. (2005b). Review of precipitation monitoring studies in India—a search for regional patterns. *Atmos. Environ.* 39: 7403–7419. <https://doi.org/10.1016/j.atmosenv.2005.08.035>
- Kumar, R., Rani, A., Singh, S.P., Kumari, K.M. and Srivastava, S.S. (2002). A long term study on chemical composition of rainwater at Dayalbagh, a suburban site of semiarid region. *J. Atmos. Chem.* 41: 265–279. <https://doi.org/10.1023/A:1014955715633>
- Kumar, P.P., Broekhuizen, K. and Abbatt, J.P.D. (2003). Organic acids as cloud condensation nuclei: Laboratory studies of highly soluble and insoluble species. *Atmos. Chem. Phys.* 3: 509–520. <https://doi.org/10.5194/acp-3-509-2003>
- Lacaux, C.G., Laouali, D., Descroix, L., Gobron, N. and Liousse, C. (2009). Long term precipitation chemistry and wet deposition in a remote dry savanna site in Africa (Niger). *Atmos. Chem. Phys.* 9: 1579–1595. <https://doi.org/10.5194/acp-9-1579-2009>
- Li, X., Yang, K., Han, J., Ying, Q. and Hopke, P.K. (2019). Sources of humic-like substances (HULIS) in PM_{2.5} in Beijing: Receptor modeling approach. *Sci. Total Environ.* 671: 765–775. <https://doi.org/10.1016/j.scitotenv.2019.03.333>
- Liken, G.N., Johnson, N.M., Galloway, J.N., Bormann, F.H., Murphy, T.J., Schaugh, J., Semb, A., Huebert, B.J., Wright, R.F., Henriksen, A., Frohlinger, J.O. and Kane, R. (1976). Acid precipitation: Strong and weak acids. *Science* 194: 643–647. <https://doi.org/10.1126/science.194.4265.646-b>
- Manö, S. and Andreae, M.O. (1994). Emission of methyl bromide from biomass burning. *Science* 263: 1255–1257. <https://doi.org/10.1126/science.263.5151.1255>
- Masiol, M., Hopke, P.K., Felton, H.D., Frank, B.P., Rattigan, O.V., Wurth, M.J. and LaDuke, G.H. (2017). Source apportionment of PM_{2.5} chemically speciated mass and particle number concentrations in New York City. *Atmos. Environ.* 148: 215–229. <https://doi.org/10.1016/j.atmosenv.2016.10.044>
- Mead, M.I., White, I.R., Nickless, G., Wang, K. and Shallcross, D.E. (2008). An estimation of the global emission of methyl bromide from rapeseed (*Brassica napus*) from 1961 to 2003. *Atmos. Environ.* 42: 337–345. <https://doi.org/10.1016/j.atmosenv.2007.09.020>
- Mimura, A.M.S., Almeida, J.M., Vaz, M.A.L., de, Ferreira, C.C.M. and Silva, J.C.J. (2016). Chemical composition monitoring of tropical rainwater during an atypical dry year. *Atmos. Res.* 169: 391–399. <https://doi.org/10.1016/j.atmosres.2015.11.001>
- Misselbrook, T.H., Van Der Weerden, T.J., Pain, B.F., Jarvis, S.C., Chambers, B.J., Smith, K.A., Phillips, V.R., and Demmers, T.G.M. (2000). Ammonia emission factors for UK agriculture. *Atmos. Environ.* 34: 871–880. [https://doi.org/10.1016/S1352-2310\(99\)00350-7](https://doi.org/10.1016/S1352-2310(99)00350-7)
- Moldanová, J., Fridell, E., Popovicheva, O., Demirdjian, B., Tishkova, V., Faccinetto, A. and Focsa, C. (2009). Characterisation of particulate matter and gaseous emissions from a large ship diesel engine. *Atmos. Environ.* 43: 2632–2641. <https://doi.org/10.1016/j.atmosenv.2009.02.008>
- Momin, G.A., Ali, K., Rao, P.S.P., Safai, P.D., Chate, D.M., Praveen, P.S., Rodhe, H. and Granat, L. (2005). Study of chemical composition of rainwater at an urban (Pune) and a rural (Sinhadgad) location in India. *J. Geophys. Res.* 110: D08302. <https://doi.org/10.1029/2004jd004789>
- Mouli, P.C., Venkata, M.S. and Jayarama, R.S. (2005). Rainwater chemistry at a regional representative urban site: Influence of terrestrial sources on ionic composition. *Atmos. Environ.* 39: 999–1008. <https://doi.org/10.1016/j.atmosenv.2004.10.036>
- Niu, H., He, Y., Lu, X.X., Shen, J., Du, J., Zhang, T., Pu, T., Xin, H. and Chang, L. (2014). Chemical Composition of Chemical composition of rainwater in the Yulong Snow Mountain region, Southwestern China. *Atmos. Res.* 144: 195–206. <https://doi.org/10.1016/j.atmosres.2014.03.010>
- Norman, M., Das, A.N., Pillai, A.G., Granat, L. and Rodhe, H. (2001). Influence of air mass trajectories on the chemical composition of precipitation in India. *Atmos. Environ.* 35: 4223–4235. [https://doi.org/10.1016/s1352-2310\(01\)00251-5](https://doi.org/10.1016/s1352-2310(01)00251-5)

- Obatolu, C.R. (1999). Correction of magnesium deficiency in tea plants through foliar applications. *Commun. Soil Sci. Plant Anal.* 30: 1649–1655. <https://doi.org/10.1080/0103629909370317>
- Paatero, P., Eberly, S., Brown, S.G. and Norris, G.A. (2014). Methods for estimating uncertainty in factor analytic solutions. *Atmos. Meas. Tech.* 7: 781–797. <https://doi.org/10.5194/amt-7-781-2014>
- Parashar, D.C., Granat, L., Kulshreshta, U.C., Pillai, A.G., Naik, M.S., Momin, G.A., Rao, P.S.P., Safai, P.D., Khemani, L.T., Naqvi, S.W.A., Narvekar, P.V., Thapa, K.B. and Rodhe, H. (1996). *Chemical composition of precipitation in India and Nepal: a preliminary report on an Indo-Swedish project on atmospheric chemistry*. Department of Meteorology; Stockholm University, Stockholm, Sweden.
- Parashar, D.C., Kulshrestha, U.C. and Jain, M. (2001). Precipitation and aerosol studies in India. *Environ. Monit. Assess.* 66: 47–61. <https://doi.org/10.1023/A:1026424013890>
- Pathak, B., Bhuyan, P.D., Gogoi, M. and Bhuyan, K. (2012). Seasonal heterogeneity in aerosol types over Dibrugarh-North-Eastern India. *Atmos. Environ.* 47: 307–315. <https://doi.org/10.1016/j.atmosenv.2011.10.061>
- Ram, R.A. and Bose, T.K. (2000). Effect of foliar application of magnesium and micro-nutrients on growth, yield and fruit quality of mandarin orange (*Citrus reticulata* Blanco). *Indian J. Hort.* 57: 215–220.
- Rao, P.S.P., Khemani, L.T., Momin, G.A., Safai, P.D. and Pillai, A.G. (1992). Measurements of wet and dry deposition at urban location in India. *Atmos. Environ.* 26: 73–78. [https://doi.org/10.1016/0957-1272\(92\)90038-t](https://doi.org/10.1016/0957-1272(92)90038-t)
- Rao, P.S.P., Tiwari, S., Matwale, J.L., Pervez, S., Tunved, P., Safai, P.D., Srivastava, A.K., Bisht, D.S., Singh, S. and Hopke, P.K. (2016). Sources of chemical species in rainwater during monsoon and nonmonsoonal periods over two mega cities in India and dominant source region of secondary aerosols. *Atmos. Environ.* 146: 90–99. <https://doi.org/10.1016/j.atmosenv.2016.06.069>
- Rastogi, N. and Sarin, M.M. (2005). Chemical characteristics of individual rain events from a semi arid region in India: Three year study. *Atmos. Environ.* 39: 3313–3323. <https://doi.org/10.1016/j.atmosenv.2005.01.053>
- Rastogi, N. and Sarin, M.M. (2007). Chemistry of precipitation Events and inter-relationship with ambient aerosols over a semi-arid region in western India. *J. Atmos. Chem.* 56: 149–163. <https://doi.org/10.1007/s10874-006-9047-5>
- Reddy, M.S. and Venkataraman, C. (2002). Inventory of aerosol and sulphur dioxide emissions from India: I—Fossil fuel combustion. *Atmos. Environ.* 36: 677–697. [https://doi.org/10.1016/s1352-2310\(01\)00463-0](https://doi.org/10.1016/s1352-2310(01)00463-0)
- Safai, P.D., Rao, P.S.P., Momin, G.A., Ali, K., Chate, D.M. and Praveen, P.S. (2004). Chemical composition of precipitation during 1984–2002 at Pune, India. *Atmos. Environ.* 38: 1705–1714. <https://doi.org/10.1016/j.atmosenv.2003.12.016>
- Salve, P.R., Gobre, T., Lohkare, H., Krupadam, R.J., Bansiwala, A., Ramteke, D.S. and Wate, S.R. (2011). Source identification and variation in the chemical composition of rainwater at coastal and industrial areas of India. *J. Atmos. Chem.* 68: 183–198. <https://doi.org/10.1007/s10874-012-9217-6>
- Salve, P.R., Maurya, A., Wate, S.R. and Devotta, S. (2008). Chemical Composition of Major Ions in Rainwater. *Environ. Contam. Toxicol.* 80: 242–246. <https://doi.org/10.1007/s00128-007-9353-x>
- Santoso, M., Lestiani, D. D., Mukhtar, R., Hamonangan, E., Syafrul, H., Markwitz, A. and Hopke, P.K. (2011). Preliminary study of the sources of ambient air pollution in Serpong, Indonesia. *Atmos. Pollut. Res.* 2: 190–196. <https://doi.org/10.5094/apr.2011.024>
- Sarin, M., Kumar, A., Srinivas, B., Sudheer, A.K. and Rastogi, N. (2010). Anthropogenic sulphate aerosols and large Cl-deficit in marine atmospheric boundary layer of tropical Bay of Bengal. *J. Atmos. Chem.* 66: 1–10. <https://doi.org/10.1007/s10874-011-9188-z>
- Sillapapiromsuk, S., Chantara, S., Tengjaroenkul, U., Prasitwattanaseree, S. and Prapamontal, T. (2013). Determination of PM₁₀ and its ion composition emitted from BB in the chamber for estimation of open burning emissions. *Chemosphere* 93: 1912–1919. <https://doi.org/10.1016/j.chemosphere.2013.06.071>
- Sunder Raman, R., Hopke, P.K. and Holsen, T.M. (2008). Carbonaceous aerosol at two rural locations in New York State: Characterization and behavior. *J. Geophys. Res.* 113: D12202. <https://doi.org/10.1029/2007jd009281>
- Talbot, R., Beecher, K., Harris, R. and Cofer, W. (1988). Atmospheric geochemistry of formic and acetic acids at a mid-latitude temperate site. *J. Geophys. Res.* 93: 1638–1652. <https://doi.org/10.1029/jd093id02p01638>
- Tiwari, S., Kulshrestha, U.C. and Padmanabhamurthy, B. (2007). Monsoon rain chemistry and source apportionment using receptor modeling in and around National Capital Region (NCR) of Delhi, India. *Atmos. Environ.* 41: 5595–5604. <https://doi.org/10.1016/j.atmosenv.2007.03.003>
- Tiwari, S., Hopke, P.K., Thimmaiah, D., Dumka, U.C., Srivastava, A.K., Bisht, D.S., Rao, P.S.P., Chate, D.M. and Srivastava, M.K. (2015). Nature and sources of ionic species in precipitation across the Indo-Gangetic plains, India. *Aerosol Air Qual. Res.* 16: 943–957. <https://doi.org/10.4209/aaqr.2015.06.0423>
- Vet, R., Artz, R.S. and Carou, S. (2014). A global assessment of precipitation chemistry and deposition of sulphur, nitrogen, sea-salt, base cations, organic acids, acidity and pH and phosphorus. *Atmos. Environ.* 93: 1–2. <https://doi.org/10.1016/j.atmosenv.2013.11.013>
- Wang, H. and Han, G.L. (2011). Chemical composition of rainwater and anthropogenic influences in Chengdu, Southwest China. *Atmos. Res.* 99: 190–196. <https://doi.org/10.1016/j.atmosres.2010.10.004>
- Wang, Y.Q., Zhang, X.Y. and Draxler, R.R. (2009). TrajStat: GIS-based software that uses various trajectory statistical analysis methods to identify potential sources from long-term air pollution measurement data. *Environ. Modell. Software* 24: 938–939. <https://doi.org/10.1016/j.envsoft.2009.01.004>
- Wang, Y., Hopke, P.K., Rattigan, O.V., Xia, X., Chalupa,

- D.C. and Utell, M.J. (2011). Characterization of residential wood combustion particles using the two-wavelength aethalometer. *Enviro. Sci. Technol.* 45: 7387–7393. <https://doi.org/10.1021/es2013984>
- Willey, J.D., Kieber, R.J., Eyman, M.S. and Avery, G.B. (2000). Rainwater dissolved organic carbon: concentrations and global flux. *Global Biogeochem. Cycles* 14: 139–148. <https://doi.org/10.1029/1999gb900036>
- Wofsy, S.C., McElroy, M.B. and Yung, Y.L. (1975). The chemistry of atmospheric bromine. *Geophys. Res. Lett.* 2: 215–218. <https://doi.org/10.1029/GL002i006p00215>
- Wolff, G.T. (1984). On the nature of nitrate in coarse continental aerosols. *Atmos. Environ.* 18: 977–981. [https://doi.org/10.1016/0004-6981\(84\)90073-8](https://doi.org/10.1016/0004-6981(84)90073-8)
- World Meteorological Organization (WMO) (2004). *Manual for the GAW precipitation chemistry programme - Guidelines, data quality objectives and standard operating procedures* (GAW Report No. 160; WMO TD No. 1251), 186 pp., World Meteorological Organization, Geneva, Switzerland.
- Xiao, J. (2016). Chemical composition and source identification of rainwater constituents at an urban site in Xi'an. *Environ. Earth Sci.* 75: 209. <https://doi.org/10.1007/s12665-015-4997-z>
- Yildirim, E., Karlidag, H. and Turan, M. (2009). Mitigation of salt stress in strawberry by foliar K, Ca and Mg nutrient supply. *Plant Soil Environ.* 55: 213–221. <https://doi.org/10.17221/383-PSE>
- Zeng, Y. and Hopke, P.K. (1989). A study of the sources of acid precipitation in Ontario, Canada. *Atmos. Environ.* 23: 1499–1509. [https://doi.org/10.1016/0004-6981\(89\)90409-5](https://doi.org/10.1016/0004-6981(89)90409-5)
- Zhao, D., Song, X., Zhu, T., Zhang, Z., Liu, Y. and Shang, J. (2018). Multiphase oxidation of SO₂ by NO₂ on CaCO₃ particles. *Atmos. Chem. Phys.* 18: 2481–2493. <https://doi.org/10.5194/acp-18-2481-2018>
- Zhou, C., Zhou, H., Holsen, T.M., Hopke, P.K., Edgerton, E.S. and Schwab, J.J. (2019). Ambient ammonia concentrations across New York State. *J. Geophys. Res.* 124: 8287–8302. <https://doi.org/10.1029/2019JD030380>

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