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# Chemical Characteristics and Trends of Indian Summer Monsoon Rainfall: A Review

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## ABSTRACT

The Indian summer monsoon (ISM) regulates the pace of life for billions of people in the Indian subcontinent by driving the agriculture and Gross Domestic Product of the region. The chemical composition of ISM is influenced by pollutant type, meteorology, and topography. As a result, the chemical makeup of rainwater varies greatly across places. The current review article highlights the variations and trends of the principal chemical constituents of rainwater ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$ ) across six homogeneous Indian monsoon regions: Central Northeast, Hilly, Northwest, Northeast, Peninsular and West Central region. Average rainwater pH ranged from 5.31 to 6.70 in these six regions. The incidence of acidic rain events at three separate locations in the Peninsular region suggests a significant impact of anthropogenic emissions. The chemical composition of rainwater in all these regions varied considerably and seemed to form a regional pattern. The majority of the ions in rainwater were highest in the Northwest while lowest in the Peninsular region.  $\text{Cl}^-$  had a significant correlation with  $\text{Na}^+$  and  $\text{NH}_4^+$  in the Hilly region, and with  $\text{Na}^+$  and  $\text{Mg}^{2+}$  in the West Central region suggesting it is sourced from both marine and anthropogenic sources. The soil Enrichment Factor relative to  $\text{Ca}^{2+}$  demonstrated that soil has a significant effect on rainwater composition.  $\text{Ca}^{2+}$  was determined to be the most abundant neutralizing ion in all the regions. Furthermore, the synthesis of rainwater chemistry reveals a strong relationship with dominant interannual climate variability El Niño Southern Oscillation with significantly higher concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  in rainwater during El Niño year compared to La Niña year.

**Keywords:** Rainwater, Major ions, Enrichment factor, Trend analysis, ENSO

## 1 INTRODUCTION

The Indian summer monsoon (ISM) provides more than 80% of the annual rainfall over the Indian subcontinent (e.g., Samanta *et al.*, 2020), and thereby plays an important role in India's groundwater resources. For the billions of people and flora and fauna living on the Indian subcontinent, the ISM regulates the pulse of life (Roy *et al.*, 2019) as the monsoon has a major effect on agriculture, Gross Domestic Product (Gadgil and Gadgil, 2006), and overall socio-economic infrastructure of the region. Thus, any changes in ISM rainfall amount and its properties have a far-reaching impact on the stability of the region.

The ISM is best considered as a regional ocean-atmosphere-land coupled system owing to local feedback (i.e., internal dynamics) along with remote influences of various modes of climate variability in different timescales (Samanta *et al.*, 2020). The influencing factors of ISM involve variabilities in synoptic (e.g., monsoon depression), intraseasonal, interannual (such as El Niño-Southern Oscillation (ENSO)), and decadal timescale. ENSO is the dominant mode of interannual climate variability which has a strong influence on ISM via atmospheric teleconnection and has a typical negative correlation with seasonal ISM rainfall (Pant and Parthasarathy, 1981; Rasmusson and Carpenter, 1983; Roy, 2017). While ENSO explains 40% of ISM rainfall variance

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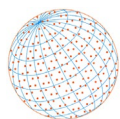
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(Webster and Yang, 1992), monsoon intraseasonal oscillations are also modulated by ENSO (Samanta *et al.*, 2020).

Most of the previous studies focused on the variability and the factors affecting the ISM (Cane, 2010; Gadgil, 2003; Roy, 2017; Samanta *et al.*, 2013, 2018, 2020; Sikka and Gadgil, 1980; Singh, 2012). The prime focus of the earlier observational and modelling studies was in the key ISM rainfall zones: the Western Ghats, central India, and the northern Bay of Bengal region. Nonetheless, ISM rainfall shows substantial spatial variability. Therefore, it is also common to see studies based on subdivisional rainfall zones over India. While factors influencing multi-scale ISM variability and their modelling remain important, this study is driven by the importance of understanding rainwater chemistry during ISM on the subdivisional scale.

Rainwater plays a vital role in atmospheric cleansing by scavenging atmospheric gases and aerosols (Andreae and Merlet, 2001) that can result in pollutant and nutrient transfer from the atmosphere to the soil and aquatic ecosystem. The major ions in rainwater could be perilous to both aquatic and terrestrial ecosystems. For example, rainwater containing  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  potentially contributes to the acidification of ecosystems (Ayers and Yeung, 1996; Cowling and Nilsson, 1995; Galloway *et al.*, 1982). Rainwater chemistry aids in determining the relative contributions of various pollutants in the atmosphere. Kulshrestha *et al.* (2005) compiled results from 100 locations such as rural, rural forest, urban, suburban, industrial, and demonstrated the variability of the major ion composition of rainwater. Large differences across close stations were noticed, probably due to complicated emission sources, making it difficult to generate large-scale concentration fields. However, a synthesis of rainwater chemistry in individual ISM regions and its connection with dominant interannual climate variabilities (such as ENSO) is lacking, yet remains important.

In this study, we have compiled rainwater pH and ionic composition data from the literature for the past three decades from different locations in India. The studied sites were divided into six homogeneous ISM regions based on regional rainfall patterns. The objectives of this review are to (1) characterize the regional rainwater chemistry of individual ISM regions and (2) investigate the influence of ENSO on the rainwater chemistry.

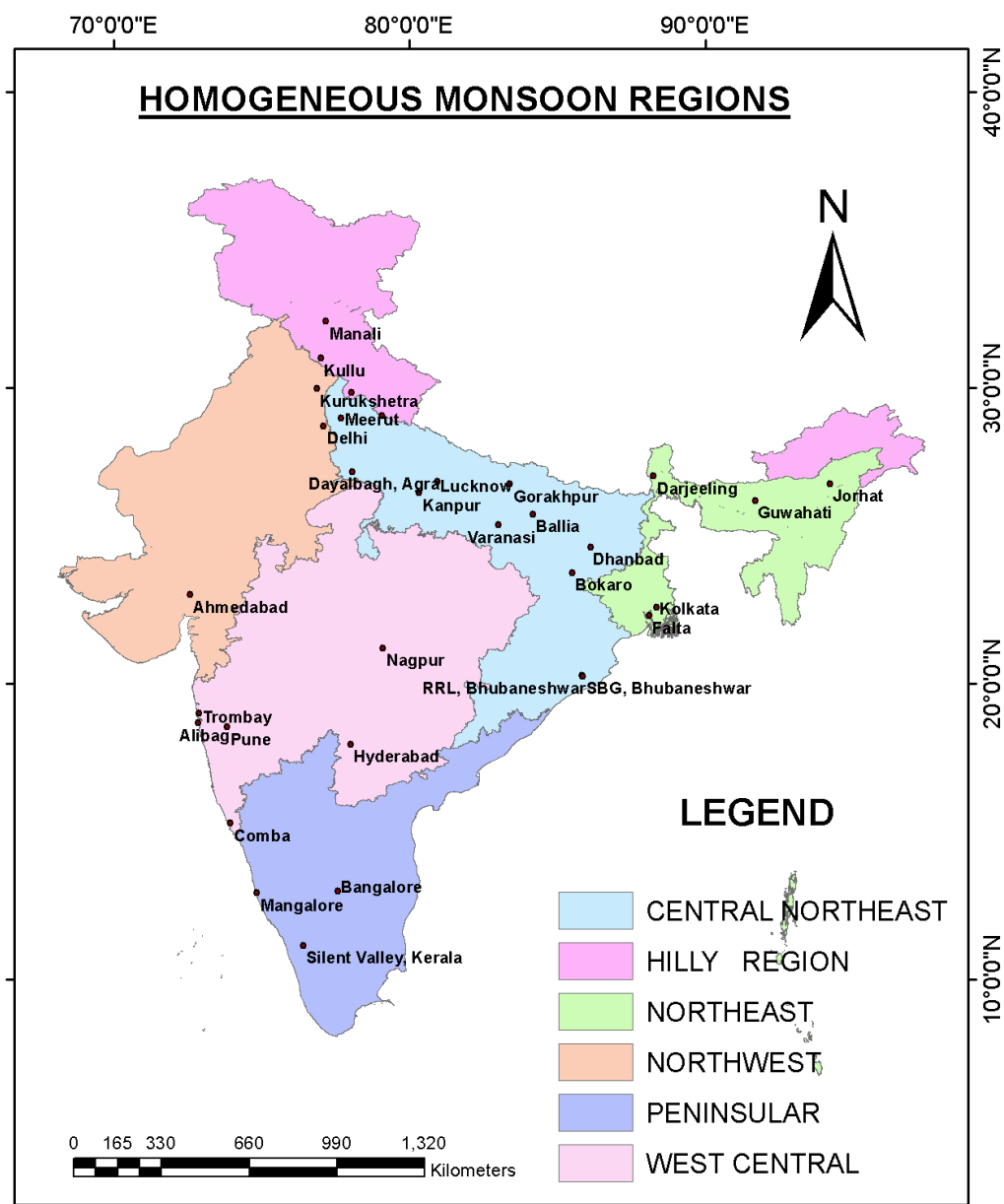
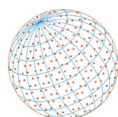
## 2 DATA AND METHODOLOGY

### 2.1 Study Area

India is located between  $8.4^\circ$  and  $37.6^\circ\text{N}$  latitude and  $68.7^\circ$  and  $97.25^\circ\text{E}$  longitude. Based on the frequency and distribution pattern of temperature and rainfall, India can be classified into four homogeneous climate regions, such as North-East India (NE India), Central India, North-West India (NW India), and Peninsular India (Guhathakurta and Rajeevan, 2008). Although almost all types of climates are encountered by the entire country due to its physiographic position (Martínez-Austria *et al.*, 2016), India, however, observes four seasons: winter (January–February), summer (March–May), southwest monsoon or rainy season (June–September) and northeast monsoon (October–December) (Rakhecha, 2016). India receives an average of 125 cm of annual rainfall (<https://imdpune.gov.in/>), 80% of which occurs during the months of the southwest monsoon (Bushra *et al.*, 2020). In this study, we synthesized the ionic composition of rainwater from the existing literature for the rainy season or ISM period.

### 2.2 Data Collection

Published data on rainwater major ion chemistry from peer-reviewed literature were collected for this study. However, all the previous studies do not provide information on daily rainfall. Therefore, we have retrieved rainfall data during specific rainfall events from gridded ( $25\text{ km} \times 25\text{ km}$ ) daily rainfall data available from India Meteorological Department (IMD) (<https://imdpune.gov.in/>). The nearest grid of the station was considered during the rainfall data retrieval. We assessed the ionic composition of rainfall, the average concentration of the major ionic species, along with rainwater pH collected during the summer monsoon season from a literature survey categorized across six homogeneous Indian monsoon regions (Central Northeast region, Hilly region, Northwest region, Northeast region, Peninsular region and West Central region) following classification given by the Indian Institute of Tropical Meteorology (Dhanya and Kumar, 2009; Fig. 1). This classification is based on a coherent pattern of rainfall at regional scales. The variations of

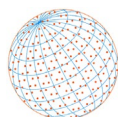


**Fig. 1.** Sampling locations from six homogeneous monsoon regions.

regional convective activity over each region are closely related to the specific rainfall aspects across each region. These homogeneous monsoon regions have also been used for analysis by previous studies (Pattanaik, 2007a, 2007b). These studies investigated rainfall variability in these parts of India with monsoon depression frequency (Pattanaik, 2007a) and variability of convective activity over the northern Indian Ocean (Pattanaik, 2007b). It's easier to understand the temporal and spatial variability of rainfall on a regional scale by looking at rainfall averaged over a homogeneous region rather than averaging rainfall at all individual stations within that region. For regional forecasts, this minimises small-scale variability and increases signal variation (Nicholson, 1986). It is also vital to define a homogeneous rainfall zone to improve the understanding of rainfall chemistry over smaller regions.

### 2.3 Statistical Analysis

Statistical analysis is used to evaluate the measure of central tendency (mean) and dispersion (range and standard deviation) for the ionic composition of rainwater along with pH data across different homogeneous monsoon regions of India given in Supplementary Tables S1–S6.



## 2.4. Marine and Non-marine Contribution

To quantify the marine and non-marine sources of the major ions in rainwater, percentage contributions of sea salt fraction (% SSF) and a non-sea salt fraction (% NSSF) are determined for  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$ , using  $\text{Na}^+$  as the reference element, assuming entire  $\text{Na}^+$  is of marine origin (Al-Khashman, 2005; Keene *et al.*, 1986).

$$\% \text{SSF} = 100(\text{Na})(\text{X}/\text{Na})_{\text{sea}}/\text{X} \quad (1)$$

where X is the component concentration of interest, and

$$\% \text{NSSF} = 100 - \text{SSF} \quad (2)$$

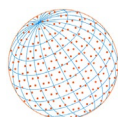
Table 1 presents the, %SSF, and %NSSF.

### 2.4.1 Enrichment factors

The marine, soil, and anthropogenic origin of ionic species in rain is inferred using Enrichment Factor (EF). To determine marine EF,  $\text{Na}^+$  is commonly used as the reference element with the assumption that all  $\text{Na}^+$  in rainwater has a marine origin (Keene *et al.*, 1986; Kulshrestha *et al.*, 1996, 2003). Al and  $\text{Ca}^{2+}$  are two standard lithophilic elements used to calculate EF relative to

**Table 1.** Marine enrichment factor (EF), percentage sea salt (SSF), and percentage non-sea salt (NSSF) fractions of ionic species in precipitation across six homogeneous monsoon regions.

	$\text{Cl}^-/\text{Na}^+$	$\text{Mg}^{2+}/\text{Na}^+$	$\text{K}^+/\text{Na}^+$	$\text{Ca}^{2+}/\text{Na}^+$	$\text{SO}_4^{2-}/\text{Na}^+$	$\text{NO}_3^-/\text{Na}^+$
<b>Seawater Ratio</b>	1.166	0.227	0.022	0.044	0.125	0.00002
<b>Northwest Region</b>						
Rainwater	1.104	0.466	0.138	1.455	1.907	0.227
EF (marine)	0.95	2.1	6.3	33	15	11359
%SSF	106	49	16	3	6.6	0
%NSSF		51	84	97	93	100
<b>Hilly Region</b>						
Rainwater	1.411	1.004	0.564	3.225	0.847	0.742
EF (marine)	1.2	4.4	26	73	6.8	37082
%SSF	83	23	3.9	1.4	15	0
%NSSF	17	77	96	99	85	100
<b>Central Northeast Region</b>						
Rainwater	1.108	1.433	0.207	1.813	1.631	0.876
EF (marine)	1.0	6.3	9.4	41	13	43795
%SSF	105	16	11	2.4	7.7	0.0
%NSSF		84	89	98	92	100
<b>Northeast Region</b>						
Rainwater	1.125	0.277	0.124	1.069	1.179	2.925
EF (marine)	0.96	1.2	5.6	24	9.4	146259
%SSF	104	82	18	4.1	11	0.0
%NSSF		18	82	96	89	100
<b>Peninsular Region</b>						
Rainwater	1.022	0.316	0.137	1.074	0.608	0.238
EF (marine)	0.88	1.4	6.2	24	4.9	11889
%SSF	114	72	16	4.1	21	0.01
%NSSF		28	84	96	79	100
<b>West Central Region</b>						
Rainwater	2.464	0.470	0.449	2.299	0.978	0.555
EF (marine)	2.1	2.1	20	52	7.8	27747
%SSF	47	48.3	4.9	1.9	13	0
%NSSF	53	51.7	95	98	87	100

**Table 2.** Enrichment factors relative to the soil for rainwater constituents across six homogeneous monsoon regions.

	$K^+/Ca^{2+}$	$Mg^{2+}/Ca^{2+}$	$SO_4^{2-}/Ca^{2+}$	$NO_3^-/Ca^{2+}$
<b>Northwest Region</b>				
Rainwater	0.095	0.32	1.31	0.156
Soil	0.504	0.561	0.0188	0.0021
<b>EF (soil)</b>	<b>0.19</b>	<b>0.57</b>	<b>70</b>	<b>74</b>
<b>Hilly Region</b>				
Rainwater	0.175	0.311	0.263	0.23
Soil	0.504	0.561	0.0188	0.0021
<b>EF (soil)</b>	<b>0.35</b>	<b>0.55</b>	<b>14</b>	<b>109</b>
<b>Central Northeast Region</b>				
Rainwater	0.114	0.79	0.9	0.483
Soil	0.504	0.561	0.0188	0.0021
<b>EF (soil)</b>	<b>0.23</b>	<b>1.4</b>	<b>48</b>	<b>230</b>
<b>Northeast Region</b>				
Rainwater	0.116	0.26	1.103	2.737
Soil	0.504	0.561	0.0188	0.0021
<b>EF (soil)</b>	<b>0.23</b>	<b>0.46</b>	<b>59</b>	<b>1303</b>
<b>Peninsular Region</b>				
Rainwater	0.128	0.294	0.566	0.221
Soil	0.504	0.561	0.0188	0.0021
<b>EF (soil)</b>	<b>0.25</b>	<b>0.52</b>	<b>30</b>	<b>105</b>
<b>West Central Region</b>				
Rainwater	0.195	0.204	0.425	0.241
Soil	0.504	0.561	0.0188	0.0021
<b>EF (soil)</b>	<b>0.39</b>	<b>0.36</b>	<b>23</b>	<b>115</b>

crustal soil (Das *et al.*, 2005; Safai *et al.*, 2004; Zhang *et al.*, 2007). In this study, soil enrichment factors were calculated using  $Ca^{2+}$  as a reference element and marine sources were determined using  $Na^+$  as a reference element:

$$EF \text{ for marine} = (X/Na^+)_{\text{rainfall}} / (X/Na^+)_{\text{sea}} \quad (3)$$

$$EF \text{ for soil} = (X/Ca^{2+})_{\text{rainfall}} / (X/Ca^{2+})_{\text{soil}} \quad (4)$$

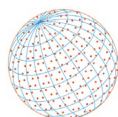
where X was the concentration of the desired ion, marine  $X/Na^+$  ratio is taken from Keene *et al.* (1986) and  $X/Ca^{2+}$  ratio of the crust is from Taylor (1964).

Since the marine contribution of  $NO_3^-$  and  $NH_4^+$  is usually negligible, EFs for marine sources were calculated for  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $SO_4^{2-}$ , and  $Cl^-$  while EFs for soil sources were calculated for  $K^+$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $Cl^-$ ,  $SO_4^{2-}$ , and  $NO_3^-$ . Tables 1 and 2 summarize the EF values for soil and marine sources.  $EF > 1$ , is considered enriched compared to the reference source.

#### 2.4.2 Neutralization factors (NF)

The neutralization factor (NF) is a measurement of how many acidic components are neutralized by crustal components and ammonium ions. Alkaline particles have an important role in regulating the acidity of rainwater in wet deposition (Rodhe *et al.*, 2002). The two main neutralizing agents for sulfuric and nitric acids are calcium and ammonium. Soil dust is the primary source of calcium, while combustion processes are the primary source of ammonium (Kulshrestha *et al.*, 2003). By measuring the neutralization factor (NF) (Kulshrestha *et al.*, 1995; Possanzini *et al.*, 1988), the neutralizing potential of  $Ca^{2+}$ ,  $NH_4^+$ , and  $Mg^{2+}$  for neutralization has been validated as follows:

$$[NF_{Ca^{2+}}] = [Ca^{2+}] / ([NO_3^-] + [SO_4^{2-}]) \quad (5)$$

**Table 3.** Neutralization Factors for the cationic species in rainwater across six homogeneous monsoon regions.

Region	NF(Ca <sup>2+</sup> )	NF(Mg <sup>2+</sup> )	NF(NH <sub>4</sub> <sup>+</sup> )
Northwest	0.68	0.22	0.19
Hilly	2.03	0.63	0.41
Central Northeast	0.72	0.57	0.5
Northeast	0.26	0.07	0.12
Peninsular	1.27	0.37	0.51
West Central	1.5	0.31	0.48

$$[\text{NF}_{\text{Mg}^{2+}}] = [\text{Mg}^{2+}] / [\text{NO}_3^-] + [\text{SO}_4^{2-}] \quad (6)$$

$$[\text{NF}_{\text{NH}_4^+}] = [\text{NH}_4^+] / [\text{NO}_3^-] + [\text{SO}_4^{2-}] \quad (7)$$

The NFs for the cationic species for all the regions are shown in [Table 3](#).

## 2.5 Correlation Analysis

Pearson's correlation analysis was used for each species to identify the origin of major anions and cations in rainwater collected from different regions, as well as to apportion the sources and possible linkages, with a significant correlation defined as  $r > 0.70$  at a 95% confidence level. SPSS software was used to conduct the correlation study.

## 2.6 Linear Regression Analysis

Using linear regression analysis, the neutralising effect of base cations on  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , the two major anions responsible for the acidic nature of rainwater, is examined. The ionic concentrations of acidic species ( $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) were used as a dependent variable and different combinations of the major cations ( $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{NH}_4^+$ ) as independent variables in a linear regression model, with  $R^2 > 0.60$  considered significant.

## 2.7 Trend Analysis

The Mann-Kendall (MK) test is a non-parametric statistical test commonly used to identify trends in climatological variables ([Kiros \*et al.\*, 2016](#); [Tabari \*et al.\*, 2015](#)) as it has a low sensitivity to the outliers. MK examines a time series for a trend without identifying whether the trend is linear or non-linear ([Yue \*et al.\*, 2002](#)). In this study, the MK test is applied to the ionic concentrations (Cations:  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and Anions:  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) for several different locations in India. The MK data analysis was undertaken using Geological Survey of India (GSI) Mann-Kendall Toolkit for Constituent Trend Analysis software and an excel spreadsheet.

# 3 RESULT AND DISCUSSION

We assess the ionic composition of rainwater, the average concentration of the major ionic species, along with rainwater pH, collected during the summer monsoon season across six homogeneous Indian monsoon regions. Descriptive statistics of the data are given in Supplementary [Tables S1–S6](#) and plotted as box plots ([Fig. 2](#)).

## 3.1 Northwest Region

The study sites are Ahmedabad in Gujarat, Delhi, and Kurukshetra in Haryana ([Table S1](#)). The average rainwater pH in the Northwest region based on these locations was  $6.70 \pm 0.79$ , indicating the non-acidic nature of the rainwater over this region in comparison with pristine rainwater pH of 5.6 in equilibrium with the atmospheric  $\text{CO}_2$  ([Charlson and Rodhe, 1982](#)). The pH value of rainwater was lowest at Ahmedabad, during the 2008–2011 sampling (average =  $5.21 \pm 0.29$ , range 4.6–5.7) and is on the lower side of those measured in the 2000–2002 range (average =  $6.70 \pm 0.49$ , range 5.2–8.2). The MK test statistic 'S' revealed a stable trend for pH in Ahmedabad



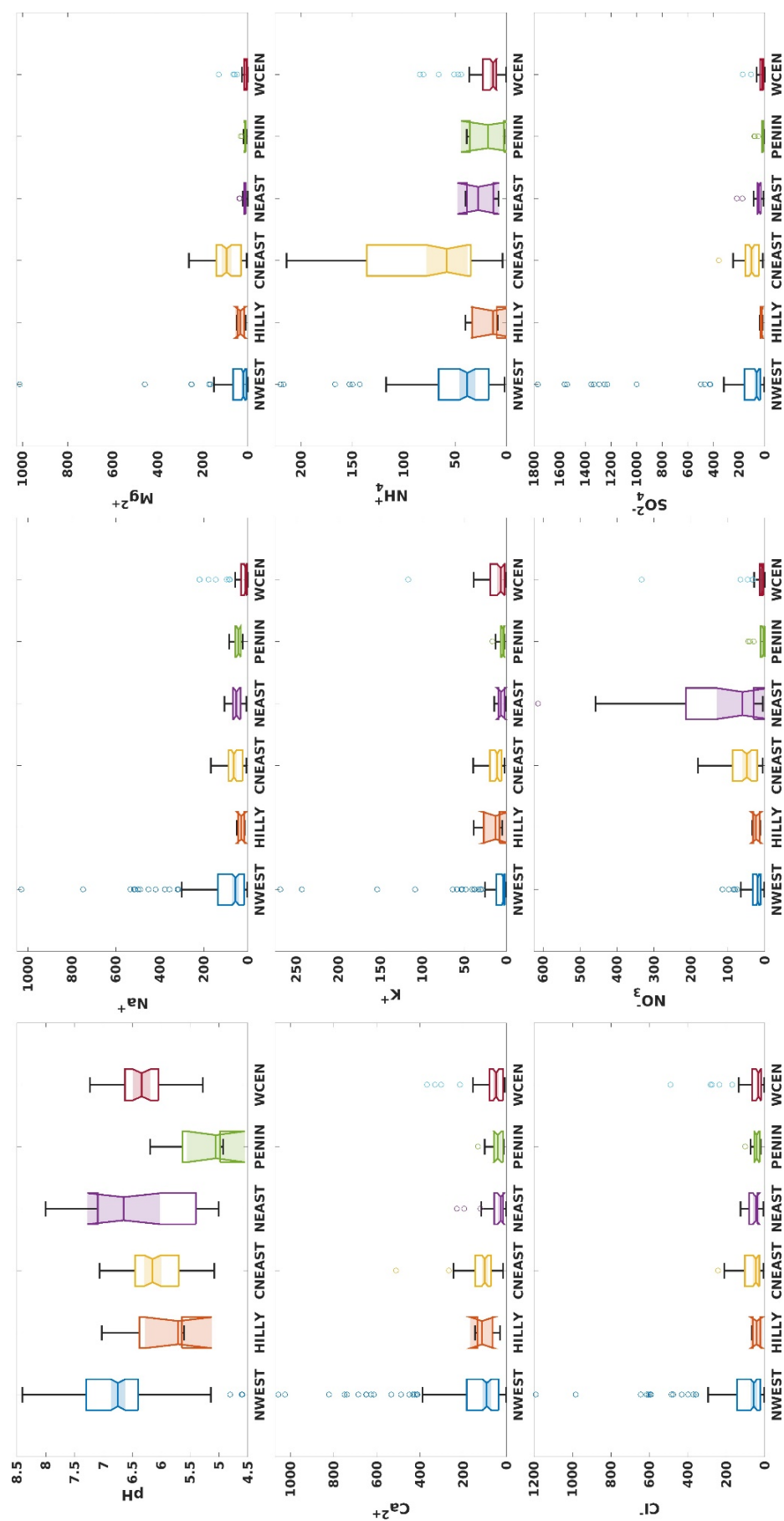
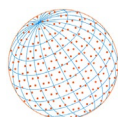
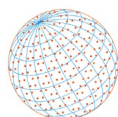


Fig. 2. Box plots of pH and major ions in rainwater over six homogeneous regions. Box plots for (a) pH, (b) Na<sup>+</sup>, (c) Mg<sup>2+</sup>, (d) Ca<sup>2+</sup>, (e) K<sup>+</sup>, (f) NH<sub>4</sub><sup>+</sup>, (g) Cl<sup>-</sup>, (h) NO<sub>3</sub><sup>-</sup>, and (i) SO<sub>4</sub><sup>2-</sup>.

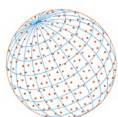


for the year 2001 and a decreasing trend in the following year. In the region, the highest average pH ( $7.47 \pm 0.28$ ) was reported in Delhi in, 1978 that decreased to 5.81 in 2009–2011. Similar acidic pH (5.62) was reported from Kurukshetra, and Haryana during the same time interval (2009–2011). The decrease of pH over time in Delhi in 30 years can be explained as a rise in  $\text{SO}_4$  and  $\text{NO}_x$  in the ambient air (Migliavacca *et al.*, 2005). The major anthropogenic emission sources of  $\text{NO}_x$  and  $\text{SO}_4$  are road traffic and coal combustion (Huang *et al.*, 2012). According to the Indian Census, Delhi had a massive influx of migrants and the population roughly doubled in a short period (Mohan *et al.*, 2011). To accommodate such a vast influx of people, the city has grown in an unplanned and unregulated manner (Rahman, 2007). The automobile traffic in Delhi has increased significantly during the time gap between the two studies (Sharma, 2017). Similarly, medium and small-scale industries are sprawling in the National Capital Region (NCR) that are major sources of atmospheric  $\text{SO}_4^{2-}$  ions. The cation budget of the rainwater is dominated by  $\text{Ca}^{2+}$  in the northwest region with  $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{NH}_4^+ > \text{K}^+$  (Figs. 2(b–f)). The aerosolized calcareous soil in the atmosphere is washed out in the rain resulting in higher  $\text{Ca}^{2+}$  content in the northwest (Srivastava *et al.*, 2014). Average relative abundances of anions are of the order  $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$  with  $\text{SO}_4^{2-}$  dominating the anion budget (Figs. 2(g–i)). The major ion concentration of all the rainwater measured in Ahmedabad from 2000–2002 (Rastogi and Sarin, 2005), shows a greater range than the study conducted in Ahmedabad from 2008–2011 (Chatterjee and Singh, 2012). The major ions measured in Delhi from 2009–2011 by Tiwari *et al.* (2016), are on the lower side of the range of the study conducted in 1978 by Subramanian and Saxena (1980). The MK test statistic 'S' showed a decreasing trend of  $\text{NO}_3^-$  in Ahmedabad in 2000 possibly due to the washout effect as rainfall negatively ( $r = -0.59$ ) correlates with  $\text{NO}_3^-$ . In Ahmedabad, for both the studies rainfall correlates negatively with most of the major ions implying the washout effect. The %SSF, %NSSF,  $\text{EF}_{\text{marine}}$ , and  $\text{EF}_{\text{soil}}$  for rainwater major ions in the northwest region are given in Tables 1 and 2.  $\text{Cl}^-$  had an  $\text{EF}_{\text{marine}}$  value of 0.94 close to that of the seawater ratio (1.2). The negative value for %NSSF  $\text{Cl}^-$  implies the absence of non-sea-salt and it was entirely of sea spray origin. The strong correlation between  $\text{Na}^+$  and  $\text{Cl}^-$  ( $r = 0.96$ ) corroborates marine origin.  $\text{Ca}^{2+}$  was of non-marine origin (NSSF of 97%) with an  $\text{EF}_{\text{marine}}$  value of 33, indicating a terrestrial source (Cao *et al.*, 2009). 16% of  $\text{K}^+$  and 49% of  $\text{Mg}^{2+}$  are sea salt derived with low  $\text{EF}_{\text{marine}}$  of 6.3 and 2.0 respectively.  $\text{K}^+$  ( $r = 0.35$ ) and  $\text{Mg}^{2+}$  ( $r = 0.37$ ) also shows a significant ( $p < 0.01$ ) moderate correlation with  $\text{Cl}^-$ . Only 6.6% of  $\text{SO}_4^{2-}$  was of marine origin and had an  $\text{EF}_{\text{marine}}$  value of 15.3 and  $\text{EF}_{\text{soil}}$  of 70, suggesting that  $\text{SO}_4^{2-}$  was primarily derived from anthropogenic sources (Cao *et al.*, 2009). Anthropogenic activities were regarded as significant nitrate sources due to high  $\text{EF}_{\text{soil}}$  (74) of  $\text{NO}_3^-$ . Neutralization is caused by the alkaline species  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  that are often derived from the natural background of soil dust. Ammonia can be released from animal waste, treatment of wastewater, and biomass burning (Kulshrestha *et al.*, 1995; Possanzini *et al.*, 1988). The NF values are in the order  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{NH}_4^+$ , implying  $\text{Ca}^{2+}$  (NF = 0.68) as the major neutralizing ion followed by  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$  (Table 3). Significant correlations among  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  ( $r = 0.77$ ),  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ( $r = 0.64$ ) and  $\text{Mg}^{2+}$  and  $\text{NO}_3^-$  ( $r = 0.66$ ) indicate the presence of alkaline dust particles that are scavenged by the rainfall droplets. These results indicate that the crustal component neutralizes the rainwater acidity over the northwest region in concurrence with other Indian studies (Budhavant *et al.*, 2011; Das *et al.*, 2005; Kulshrestha *et al.*, 2003; Rastogi and Sarin, 2005; Tiwari *et al.*, 2012).

### 3.2 Hilly Region

The sites considered for the study of rainwater chemistry in the hilly region are Kullu and Manali in Western Himalayas, Nainital in Central Himalayas, and Roorkee in Uttarakhand (Table S2). The average pH value across these four locations was  $6.01 \pm 0.68$ . The highest pH of the hilly region is in the Roorkee site (pH value of  $7.03 \pm 0.12$ ) resulting from the high loading of particulate matter in the Indian atmosphere (Khare *et al.*, 2004). In the remaining three Himalayan towns, rainwater pH was close to that of pristine natural rainwater (pH = 5.6) due to the relatively low pollution index in the hill stations. Rainwater pH in Nainital was lowest ( $5.60 \pm 0.30$ ), followed by Kullu and Manali (5.68 and 5.73 each). Cation concentrations are of the order  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{NH}_4^+ > \text{K}^+$ , while the concentrations of the anions are of the order  $\text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$  (Figs. 2(b–i)).  $\text{Ca}^{2+}$  is highest at Roorkee due to high loadings of calcareous dust particles in the atmosphere. The concentrations of most of the ionic species were found to be low at the high latitude Himalayan

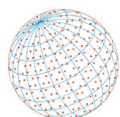




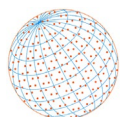
town of Kullu due to less soil erosion and hence less windblown dust coupled with higher rainfall (Tiwari *et al.*, 2012). However, Manali and Nainital rainwater had ionic compositions comparable to Roorkee. The number of tourists visiting Kullu, Manali, and Nainital is increasing every year because they are globally acclaimed tourist destinations and some of India's top hill stations (Singh, 2008). Development and population growth are thus driving the expansion of built-up areas (Vijay *et al.*, 2015). Landslides in the region are common, the bulk of which occurs near built-up areas, including roadways and agricultural land on higher degree slopes (Nandy *et al.*, 2015). The changing land use and land cover (LULC) pattern is probably increasing the concentrations of ionic species in Manali and Nainital rainwater. Marine and non-marine contributions of different ionic ratios are estimated with  $\text{Na}^+$  as the reference element with the basic assumption that all  $\text{Na}^+$  is of marine origin (Keene *et al.*, 1986; Kulshrestha *et al.*, 1996, 2003). The observed rainwater ratio of  $\text{Cl}^-/\text{Na}^+$  (1.5) is slightly higher than that of the seawater ratio (1.2), indicating that rainwater  $\text{Cl}^-$  in this region is influenced by anthropogenic sources in addition to sea-salt.  $\text{Cl}^-$  significantly correlates with  $\text{NH}_4^+$  ( $r = 0.99$ ;  $p < 0.05$ ) and  $\text{Na}^+$  ( $r = 0.98$ ) supporting anthropogenic and sea salt origin. In irrigation water, chlorine from sodium hypochlorite or dissolved  $\text{Cl}$  gas has a complex chemistry.  $\text{Cl}$  is transformed to hypochlorite ( $\text{OCl}^-$ ) and hypochlorous acid when it is introduced to water ( $\text{HOCl}$ ). When water-soluble fertilisers containing ammonium are used in conjunction with  $\text{Cl}$ , hypochlorous acid is likely to be rapidly transformed into complex  $\text{Cl}$  forms (Meador and Fisher, 2013). Ammonia may be present in the soil as a result of the decomposition of naturally occurring organic matter or through artificial sources such as livestock operations, local nitrogen fertilizer application, sewage infiltration, industrial processes, and cement mortar pipelining. Ammonium is carried into the atmosphere as  $\text{NH}_3$  (Al-Momani, 2003; Sutton *et al.*, 2008). A natural, mineralogical form of ammonium chloride called sal ammoniac ( $\text{NH}_4\text{Cl}$ ) is also commonly formed from coal burning. It is used as a fertilizer as well. The %SSF, %NSSF,  $\text{EF}_{\text{marine}}$ , and  $\text{EF}_{\text{soil}}$  for rainwater major ions in the hilly region given in Tables 1 and 2 indicate that 77 to 100 percent of  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  are of non-marine origin. The  $\text{EF}_{\text{marine}}$  of the major ions ( $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ ) were greater than 1, which suggests a significant contribution of non-sea-salt sources.  $\text{Mg}^{2+}$  had a soil source ( $\text{EF}_{\text{soil}} = 0.5$ ) whereas sulphate ( $\text{EF}_{\text{soil}} = 14$ ) and nitrate ( $\text{EF}_{\text{soil}} = 110$ ) were of anthropogenic origin (Cao *et al.*, 2009). The  $\text{NFCa}$  (2.0) was highest followed by  $\text{NFMg}$  (0.63) and  $\text{NFNH}_4$  (0.41) indicating the role of crustal components in the neutralization of anions. Furthermore, as  $\text{Cl}^-$  has an anthropogenic source besides marine origin, the rainfall acidity is possibly contributed by  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  in the hilly region.

### 3.3 Central Northeast Region

The Central northeast meteorological subdivision consists of the states of Orissa, Jharkhand, Bihar, and Uttar Pradesh. The sites considered are Dayalbagh (Agra), Regional Research Lab (RRL) and State Botanical Garden (SBG), Bhubaneswar, Lucknow (Uttar Pradesh), Ballia (Eastern UP), Varanasi (Eastern UP), Gorakhpur (UP); Kanpur (UP); Meerut (UP), Dhanbad (Jharkhand) and Bokaro (Jharkhand) (Table S3). The average pH value across these ten locations was  $6.11 \pm 0.53$ . The pH value of rainwater was lowest ( $5.08 \pm 0.70$ ) during 2005 sampling at Dhanbad, the "Coal Capital of India" which is home to some of India's largest coal mines (Dubey *et al.*, 2012). The rainwater pH in Dhanbad between 2003 and 2005 showed that the monitoring site received acidic rainfall. Acid rains are connected to site-specific practices, most notably coal mining, mine fires, and coal-based industries, all of which emit  $\text{SO}_2$  and  $\text{NO}_x$  (Singh *et al.*, 2007). In this region, the highest pH (7.07) was reported in Dayalbagh, Agra in, 1996 and fluctuated between 6.70–7.07 from 1991–1995. The pH at RRL, Bhubaneswar was less acidic (6.3) than pristine rainwater during 1995–1997. However, during 1997–1998, the pH value became slightly acidic (5.5) at SBG, Bhubaneswar. The reason could be the low  $\text{Ca}^{2+}$  concentration at SBG, Bhubaneswar ( $15 \mu\text{eq L}^{-1}$ ) compared to RRL, Bhubaneswar ( $37 \mu\text{eq L}^{-1}$ ). The low  $\text{Ca}^{2+}$  concentration in rainwater may be explained by the dense vegetation cover coupled with low calcium carbonate/bicarbonate content of the soil (hence  $\text{pH} < 5.6$ ) (Das *et al.*, 2005). Of the five locations considered at UP during 2009–2011, the pH value of rainwater was lowest (5.44) at Gorakhpur because of higher concentrations of acidic species locally emitted from industrial sources (Tiwari *et al.*, 2016). Since 1989, when Gorakhpur Industrial Development Authority (GIDA) was created, around 159 industries have sprouted up in the GIDA Project Area (Choudhary and Pandey, 2014). The highest pH at Ballia



(6.03) was due to high ammonia levels and alkaline species in this rural environment's calcareous soil (Kulshrestha *et al.*, 2003). The average pH value in Bokaro was 6.1 and varied from 5.1 to 6.9 in the collected rainwater samples. The cation budget of the rainwater is dominated by  $\text{Ca}^{2+}$  in the central north-eastern region with the sequence  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{NH}_4^+ > \text{Na}^+ > \text{K}^+$ . Average relative abundances of anions follow the sequence  $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$  with  $\text{SO}_4^{2-}$  dominating the anion budget (Figs. 2(b–i)). Dissolution of carbonates (calcite/dolomite) and gypsum are primary natural sources of major ions such as calcium, magnesium, bicarbonate, and sulphate (Frank *et al.*, 2019; Garrels and Mackenzie, 1971; Wu *et al.*, 2018). The concentration of  $\text{SO}_4$  at Dhanbad and Bokaro, Jharkhand (sites with huge deposits of fossil fuels) is high as compared to other locations in this region. No specific pattern was observed in the variation of  $\text{SO}_4^{2-}$  level from year to year in Dayalbagh, Agra. The mean value of  $\text{NO}_3^-$  in Dayalbagh was found to be  $15 \pm 7.0 \mu\text{eq L}^{-1}$  while the yearly mean values varied between 5.7 and  $28 \mu\text{eq L}^{-1}$ , the maximum being five times the minimum. Increased line sources may be responsible for the rise in  $\text{NO}_3^-$  concentration as motor vehicles are increasingly growing in Agra (Saxena *et al.*, 1991, 1996). Automobile exhaust is the primary source of  $\text{NO}_x$ , which is a precursor to  $\text{NO}_3^-$  (Kumar *et al.*, 2002). The mean value of  $\text{Ca}^{2+}$  in Dayalbagh was found to be  $82 \pm 34 \mu\text{eq L}^{-1}$  and the yearly mean value varied between 48 and  $137 \mu\text{eq L}^{-1}$ . The value of  $\text{Ca}^{2+}$  decreased over time, most likely due to rapid urbanization and a decline in barren land (Kumar *et al.*, 2002). The major ion concentrations in Bokaro, Jharkhand were considerably higher than in the other locations in the region. Anthropogenic pollution from thermal power plants, open cast mining, coal washeries, coal burning and mine fires, are often responsible for the higher ionic concentrations (Singh and Mondal, 2008). The MK test was performed to detect the trend of major ions in Bokaro. The MK test statistic 'S' revealed an increasing trend for  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{Cl}^-$ , a stable trend for  $\text{NO}_3^-$  and  $\text{Na}^+$  and a decreasing trend for  $\text{Ca}^{2+}$ . In comparison between Banaras Hindu University (BHU) and Maldahiya (MAL) at Varanasi, most of the mean ionic concentrations, specifically calcium, sulphate, and nitrate were higher at the site MAL, an urban location than at BHU. High concentrations of these ions could be due to a combination of windblown dust, different sources of pollution and pollutant transport (Pandey *et al.*, 1992). The highest concentrations of  $\text{Ca}^{2+}$  ( $199 \mu\text{eq L}^{-1}$ ) and  $\text{Mg}^{2+}$  ( $102 \mu\text{eq L}^{-1}$ ) were recorded at Gorakhpur and the lowest was measured at Varanasi ( $51$  and  $11 \mu\text{eq L}^{-1}$ , respectively). As compared to the other five locations at UP,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were also highest at Gorakhpur ( $79$  and  $45 \mu\text{eq L}^{-1}$ , respectively) and lowest at Varanasi ( $38$  and  $22 \mu\text{eq L}^{-1}$  respectively). High concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  at Gorakhpur may arise from the industrial sources nearby, such as GIDA (Tiwari *et al.*, 2016). The low ion concentrations in Varanasi may be due to the location of the sampling site adjacent to the River Ganga with a vegetation cover at Banaras Hindu University (Singh *et al.*, 2007). The measured rainwater ratio of  $\text{Cl}^-/\text{Na}^+$  (1.1) is close to that of the seawater ratio (1.2), which indicates that a major part of the  $\text{Na}^+$  and  $\text{Cl}^-$  originated from sea salt. The ratios  $\text{SO}_4^{2-}/\text{Na}^+$ ,  $\text{Ca}^{2+}/\text{Na}^+$ ,  $\text{K}^+/\text{Na}^+$ , and  $\text{Mg}^{2+}/\text{Na}^+$  in rainwater of the central northeast region were found to be greater than the seawater ratios. These higher values indicated contribution from non-marine sources (Khemani, 2000; Kulshrestha *et al.*, 1996). This observation is also supported by %SSF and %NSSF values. Approximately 92% of  $\text{SO}_4^{2-}$ , 98% of  $\text{Ca}^{2+}$ , 89% of  $\text{K}^+$ , and 84% of  $\text{Mg}^{2+}$  in rainwater samples had a non-marine origin. The EF values for soil and marine sources are listed in Tables 1 and 2. An EF value much less than or much higher than 1 is considered to be diluted or enriched relative to the reference source (Cao *et al.*, 2009).  $\text{Cl}^-$  had  $\text{EF}_{\text{marine}}$  value of 0.95, clearly indicating that  $\text{Cl}^-$  had been enriched relative to seawater. The average  $\text{EF}_{\text{marine}}$  value of  $\text{Ca}^{2+}$  was 41, suggesting its origin from a terrestrial source.  $\text{Mg}^{2+}$  was mostly from the marine source but showed moderate soil enrichment as well.  $\text{NO}_3^-$  had  $\text{EF}_{\text{soil}}$  value of 230, showing high enrichment relative to soil source. These high EF values of  $\text{NO}_3^-$  indicated that  $\text{NO}_3^-$  mainly originated from anthropogenic sources.  $\text{SO}_4^{2-}$  had  $\text{EF}_{\text{marine}}$  value of 13 and  $\text{EF}_{\text{soil}}$  value of 48. Thus, anthropogenic activities were also considered the major sources of sulphate. The trend in the strength of NF in rainwater samples in this region ( $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{NH}_4^+$ ) remains nearly similar to the northwest region and the hilly region. But the NF values of individual cationic species are slightly higher in the hilly region as compared with the rainwater samples of this region. Linear regression ( $p < 0.01$ ) indicated that the acidity ( $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) in this region is neutralized by magnesium and ammonium ( $R^2 = 0.64$ ). Also, significant correlations among  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ( $r = 0.70$ ) and  $\text{Mg}^{2+}$  and  $\text{NO}_3^-$  ( $r = 0.55$ ) indicate the scavenging of alkaline dust particles by the rainwater droplets.

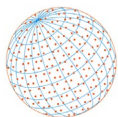


### 3.4 Northeast Region

The Northeast meteorological subdivision consists of the states of West Bengal, Assam, Nagaland, Meghalaya, Manipur, Mizoram, Tripura, and Sikkim. Previous study sites were Kolkata, Falta, and Darjeeling in West Bengal, Jorhat, and Guwahati in Assam (Table S4). The average rainwater pH in the Northeast region based on these locations was  $6.43 \pm 0.92$ , indicating the non-acidic nature of the rainwater over this region as compared to pristine rainwater pH of 5.6 (Charlson and Rodhe, 1982). The pH value of rainwater was lowest at Darjeeling (average =  $5.00 \pm 0.80$ , range 4.2–6.1) followed by Guwahati, Falta, and Jorhat. Such acid rain events indicate a high level of  $\text{SO}_2$  and  $\text{NO}_x$  emissions as well as a lack of soil buffering ability (Kulshrestha *et al.*, 2014). Furthermore, heavy rainfall over the densely vegetated Northeast India makes soil-borne components less susceptible to resuspension to the atmosphere, resulting in acid rain events (Bhaskar and Rao, 2016). As a result, this area's soil's ability to neutralize acidity is limited. Rainwater pH,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{NH}_4^+$  at Jorhat was the highest among the northeastern hill stations reported in this study. Poor land management due to deforestation, jhum farming, soil erosion, low-quality soil-and-water conservation measures, and unplanned infrastructural development are among the key Land Use Land Cover (LULC) changes that possibly contributed to higher ionic concentrations of the above-mentioned species (Ritse *et al.*, 2020). The highest average pH was reported from Kolkata in, 2019 (average =  $6.80 \pm 0.74$ , range 5.4–8.0) which was similar to those reported in 2013–2014 (average =  $6.10 \pm 1.40$ , range 4.4–6.9).  $\text{Ca}^{2+}$  dominates the cation budget of the rainwater of the northeast region with the sequence  $\text{Ca}^{2+} > \text{Na}^+ > \text{NH}_4^+ > \text{Mg}^{2+} > \text{K}^+$  (Figs. 2(b–f)). Some of the highest  $\text{Ca}^{2+}$  concentrations are reported from the megacity Kolkata, possibly due to calcareous soil and cement dust from endless urban constructions (Majumdar *et al.*, 2020a). Additionally, the road dust of Kolkata primarily contains minerals such as quartz, plagioclase, K-feldspars, calcite, dolomite and mica (Nath *et al.*, 2007), which gets aerosolized into the atmosphere followed by a washout in the rain (Srivastava *et al.*, 2014). Average relative abundances of anions are of the order  $\text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$  with  $\text{NO}_3^-$  dominating the anion budget (Figs. 2(g–i)). The concentration of  $\text{NO}_3^-$  was higher in Kolkata (2019) than those reported from other sites in this region. Anthropogenic sources of  $\text{NO}_3^-$  include vehicle emissions, coal combustions, soil emissions driven by fertilizer use, and biomass burning (Li *et al.*, 2019). It is noteworthy that  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  were also the most abundant species over Kolkata during 2013–2014. The largest source of air pollutant emissions in Kolkata is vehicular movement, specifically non-exhaust vehicular emissions such as brake, clutch, and tyre wear, corrosion of vehicle components, and road surface wear followed by resuspension of road dust (Majumdar *et al.*, 2020b). The MK test statistic 'S' showed a decreasing trend of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$  in Kolkata in 2019 due to the washout effect (Majumdar *et al.*, 2020a). The %SSF, %NSSF,  $\text{EF}_{\text{marine}}$ , and  $\text{EF}_{\text{soil}}$  for rainwater major ions in the northeast region are given in Tables 1 and 2.  $\text{Cl}^-$  had an  $\text{EF}_{\text{marine}}$  value of 0.96 close to that of the seawater ratio (1.2). The strong correlation between  $\text{Na}^+$  and  $\text{Cl}^-$  ( $r = 0.92$ ) corroborates marine origin. High marine contribution of  $\text{Mg}^{2+}$  (82%) in rainwater samples was found in this region.  $\text{Mg}^{2+}$  also shows a significant ( $p < 0.01$ ) moderate correlation with  $\text{Cl}^-$  ( $r = 0.65$ ).  $\text{Ca}^{2+}$  was of non-marine origin (NSSF of 96%) with an  $\text{EF}_{\text{marine}}$  value of 24, indicating a terrestrial source (Cao *et al.*, 2009). 17.73% of  $\text{K}^+$  is sea salt derived with a low  $\text{EF}_{\text{marine}}$  of 5.6. Only 11% of  $\text{SO}_4^{2-}$  was of marine origin and had an  $\text{EF}_{\text{marine}}$  value of 9.4 and  $\text{EF}_{\text{soil}}$  of 59, suggesting that  $\text{SO}_4^{2-}$  was primarily derived from anthropogenic sources (Cao *et al.*, 2009). Anthropogenic activities were regarded as significant nitrate sources due to very high  $\text{EF}_{\text{soil}}$  (~1303) of  $\text{NO}_3^-$ . The NF values are in the order  $\text{Ca}^{2+} > \text{NH}_4^+ > \text{Mg}^{2+}$ , indicating major neutralization is caused by  $\text{Ca}^{2+}$  (NF = 0.26) followed by  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$ . Also, significant correlations among  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ( $r = 0.68$ ),  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ( $r = 0.90$ ), and  $\text{K}^+$  and  $\text{SO}_4^{2-}$  ( $r = 0.97$ ) imply alkaline dust particles are scavenged by the rainwater droplets. These findings suggest that the crustal element neutralizes the acidity of rainwater in the northeast region.

### 3.5 Peninsular Region

The peninsular region consists of the southern states of Andhra Pradesh, Tamil Nadu, Karnataka, and Kerala. Previous studies quantified the major ion composition of rainwater from Silent valley, Kerala (Prakasa Rao *et al.*, 1995), Bangalore (Prasad *et al.*, 2008), and Mangalore (Gurumurthy *et al.*, 2012) in Karnataka (See Table S5). The average pH value across these three locations was 5.31



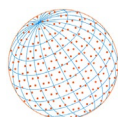
$\pm 0.59$ , indicating the slightly acidic nature of the rainwater over this region as compared to pristine rainwater pH. The lowest average pH was observed in Bangalore (5.07 in the year 2005–2006; 4.93 in the year 2006–2007). This could be due to the highest concentration of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  at this site as compared to the other sites in this region since sulphuric and nitric acids are the primary sources of acidity in the rainwater (Prakasa Rao *et al.*, 1995). The highest rainwater pH of 6.19 in the region was reported from Silent valley during the monsoon season of 1989 which decreased to 5.04 in the following year's monsoon. As  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations were similar to background levels, the decrease in pH was attributed to the release of formic and acetic acid from the forest canopy (Khare *et al.*, 1999).

The general pattern of regional average concentration of cations is  $\text{Ca}^{2+} > \text{Na}^+ > \text{NH}_4^+ > \text{Mg}^{2+} > \text{K}^+$ , while those of the anions is  $\text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$  (Figs. 2(b–i)).  $\text{Ca}^{2+}$  is the dominant dissolved cation (range 38 to 101  $\mu\text{eq L}^{-1}$ ) and  $\text{Cl}^-$  is the dominant dissolved anion (range 35 to 48  $\mu\text{eq L}^{-1}$ ).  $\text{Ca}^{2+}$  was the most abundant cation in Bangalore due to the high resuspension of calcareous dust particles in the atmosphere and subsequent washout in the rain (Srivastava *et al.*, 2014). The LULC shift due to anthropogenic activity has the potential to influence rainfall chemistry. In this region, forest cover is reducing and the proportion of fallow, plantation, and built-up land is increasing (Ramachandran *et al.*, 2018) which increases the proportion of soil dust resuspension in the atmosphere. Silent Valley in Kerala and Mangalore in Karnataka is bordered by the Arabian Sea in the west and they are located close to the south and central stretch of the Malabar Coast respectively. This corroborates the high concentration of  $\text{Cl}^-$  and  $\text{Na}^+$  in Silent valley and Mangalore rainwater in comparison to Bangalore. The MK test statistic 'S' revealed a decreasing trend for  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  in Mangalore for the years 2009–2010. No particular trend for rainfall was observed in Mangalore during this period hence the decrease in  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  cannot be attributed to the washout effect. No other specific pattern was observed in the variation of ionic composition of rainwater in this region. The %SSF, %NSSF,  $\text{EF}_{\text{marine}}$ , and  $\text{EF}_{\text{soil}}$  for rainwater major ions in the peninsular region are given in Tables 1 and 2. The observed rainwater ratio of  $\text{Cl}^-/\text{Na}^+$  (1.0) is close to the seawater ratio (1.2), indicating that the  $\text{Cl}^-$  in rainwater in this region is sourced from sea-salt.  $\text{Cl}^-$  significantly correlates with  $\text{Na}^+$  ( $r = 0.96$ ) supporting sea salt origin.  $\text{Ca}^{2+}$  was of non-marine origin (NSSF of 96%) with an  $\text{EF}_{\text{marine}}$  value of 24, indicating a terrestrial source (Cao *et al.*, 2009). 84% of  $\text{K}^+$  and 28% of  $\text{Mg}^{2+}$  are sea salt derived with low  $\text{EF}_{\text{marine}}$  of 6.2 and 1.4 respectively.  $\text{K}^+$  ( $r = 0.54$ ) and  $\text{Mg}^{2+}$  ( $r = 0.93$ ) also shows a significant ( $p < 0.01$ ) correlation with  $\text{Cl}^-$ . Only 21% of  $\text{SO}_4^{2-}$  was of marine origin and had an  $\text{EF}_{\text{marine}}$  value of 4.9 and  $\text{EF}_{\text{soil}}$  of 30, suggesting that  $\text{SO}_4^{2-}$  was primarily derived from anthropogenic sources (Cao *et al.*, 2009). Anthropogenic activities were regarded as significant nitrate sources due to high  $\text{EF}_{\text{soil}}$  (~105) of  $\text{NO}_3^-$ . The neutralization factor followed the order  $\text{NF}_{\text{Ca}}$  (1.3)  $>$   $\text{NF}_{\text{NH}_4}$  (0.51)  $>$   $\text{NF}_{\text{Mg}}$  (0.37). Furthermore, linear regression indicated that the acidity ( $\text{SO}_4^{2-} + \text{NO}_3^-$ ) in this region is neutralized by calcium and ammonium ( $R^2 = 0.76$ ).

### 3.6 West Central Region

West central region consists of the states of Maharashtra, Madhya Pradesh, Chhattisgarh, north interior Karnataka, Konkan & Goa, and Telangana. Previous studies quantified the major ion composition of rainwater from Pune, Kalyan, Colaba, Alibag, Trombay, and Nagpur in Maharashtra; Hyderabad (Kulshrestha *et al.*, 2003) in Telangana; and Comba in Goa (Table S6). The average rainwater pH in the West central region based on these locations was  $6.3 \pm 0.42$ , indicative of the non-acidic nature of the rainwater over this region as compared to pristine rainwater pH of 5.6 (Charlson and Rodhe, 1982). The pH value of rainwater was lowest at Kalyan in Mumbai, (average = 5.28, range 4.0–7.5) followed by Trombay (average = 5.7, range 4.8–6.4).  $\text{SO}_4$  (110  $\mu\text{eq L}^{-1}$ ) and  $\text{NO}_3$  (66  $\mu\text{eq L}^{-1}$ ), control the pH of Kalyan rainwater (Naik *et al.*, 2002). A refinery, petrochemical complex, thermal power plant, and other major industrial establishments are located upwind of Kalyan. As a result, anthropogenic emissions are likely to have affected the rainwater samples of Kalyan, making them acidic. However, the average pH value at the other sites such as Alibag (average = 6.74, range 6.0–8.0) and Colaba (average = 6.38, range 5.46–7.50) in Mumbai, Pune (average =  $6.42 \pm 0.38$ , range 5.71–6.60), Goa (average =  $6.25 \pm 0.28$ , range 5.36–6.91) had higher pH, similar to the regional average. Similar pH was reported Nagpur (average =  $6.30 \pm 0.30$ , range 6.0–7.3), and Hyderabad (average = 6.4, range 5.5–7.2). The cation budget of rainwater of the



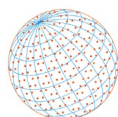


northwest region is dominated by  $\text{Ca}^{2+}$  with the sequence  $\text{Ca}^{2+} > \text{Na}^+ > \text{NH}_4^+ > \text{Mg}^{2+} > \text{K}^+$  (Figs. 2(b–f)). Average relative abundances of anions are of the order  $\text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$  with  $\text{Cl}^-$  dominating the anion budget (Figs. 2(g–i)). The major ion concentration of most of the samples measured at Trombay shows a range much greater than the other sites in the region. The proximity of Trombay to the marine environment and the presence of numerous industries around 432 sq. km area possibly contribute to the large variability. Sulphate in rainwater is a product of the region's coal-fired thermal power plants. The major ions measured in Pune from 1988–1989 (Naik *et al.*, 1994), are in the same range as that of the study conducted during 1992–1999 (Pillai *et al.*, 2001). At Pune, the MK test statistic 'S' showed an increasing trend of  $\text{NO}_3^-$  from 1988 to 1998. The major source of  $\text{NO}_3^-$  is road traffic. Like all other metro cities in India, road traffic in Pune probably doubled in 10 years. We could not find data for the studied period, however, data from Transport Research Wing, Ministry of Road Transport and Highways, Government of India shows more than 100 percent (568 K–1163 K) increase in the registered motor vehicle in Pune between 1999 and 2009 (Singh, 2012). The MK test statistic 'S' showed an increasing  $\text{Mg}^{2+}$  trend and a decreasing  $\text{NO}_3^-$  trend in Hyderabad during 1999–2001. The increase in  $\text{Mg}^{2+}$  is attributed to the enhanced soil-derived particles and re-suspended road dust in the air due to the influence of increased road traffic. Additionally, building construction peaked during 2000–2001 in Hyderabad which contributed to an increase in  $\text{Mg}^{2+}$ . As expected for the washout effect, rainfall negatively correlates with all the species in Hyderabad except  $\text{NO}_3^-$  ( $r = 0.43$ ). Vehicle traffic and biomass combustion are major sources of  $\text{NO}_x$  (Merico *et al.*, 2020). The authors postulated longer rains oxidize precursors of  $\text{NO}_3^-$  like  $\text{NO}_x$  to  $\text{NO}_3^-$ , as shown by higher  $\text{NO}_3^-$  concentrations with increased rainfall.

The %SSF, %NSSF,  $\text{EF}_{\text{marine}}$ , and  $\text{EF}_{\text{soil}}$  for rainwater major ions in the west central region are given in Tables 2 and 3.  $\text{Cl}^-$  had an  $\text{EF}_{\text{marine}}$  value of 2.1, higher than that of the seawater ratio (1.2). The higher value for %NSSF  $\text{Cl}^-$  (53) implies that there was some non-sea-salt source and it wasn't entirely of sea spray origin.  $\text{Cl}^-$  significantly correlates with  $\text{SO}_4^{2-}$  ( $r = 0.43$ ;  $p < 0.01$ ) and  $\text{Na}^+$  ( $r = 0.47$ ) supporting anthropogenic and sea salt origin.  $\text{Ca}^{2+}$  was of non-marine origin (NSSF of 99%) with an  $\text{EF}_{\text{marine}}$  value of 52, indicating a terrestrial source (Cao *et al.*, 2009). 95% of  $\text{K}^+$  is non-sea salt derived with  $\text{EF}_{\text{marine}}$  of 20. The %SS contribution of  $\text{Mg}^{2+}$  was 48% indicating the remaining major contribution was from the non-sea spray.  $\text{Mg}^{2+}$  ( $r = 0.41$ ) also shows a significant ( $p < 0.01$ ) moderate correlation with  $\text{Cl}^-$ . Only 13% of  $\text{SO}_4^{2-}$  was of marine origin and had an  $\text{EF}_{\text{marine}}$  value of 7.8 and  $\text{EF}_{\text{soil}}$  of 23, suggesting that  $\text{SO}_4^{2-}$  was primarily derived from anthropogenic sources (Cao *et al.*, 2009). Anthropogenic activities were considered significant nitrate sources due to high  $\text{EF}_{\text{soil}}$  (~115) of  $\text{NO}_3^-$ . The NF values are in the order  $\text{Ca}^{2+} > \text{NH}_4^+ > \text{Mg}^{2+}$ , indicating  $\text{Ca}^{2+}$  (NF = 1.50) as the major neutralizing ion followed by  $\text{NH}_4^+$  and  $\text{Mg}^{2+}$ . Significant correlation between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ( $r = 0.76$ ) suggested similar sources. Also, significant correlations among  $\text{Ca}^{2+}$ – $\text{SO}_4^{2-}$  ( $r = 0.60$ ) and  $\text{Mg}^{2+}$ – $\text{SO}_4^{2-}$  ( $r = 0.75$ ) indicate the presence of alkaline dust particles that the rainwater droplets are scavenging. These findings suggest that the crustal component in the west central region neutralizes the acidity of rainwater.

### 3.7 Characteristics of Major Ions during ENSO

ISM rainfall has an inverse relationship with ENSO, causing summer monsoon drought conditions in India during El Niño (positive phase). Despite the changing ENSO-ISM rainfall relationships in recent decades (e.g., Samanta *et al.*, 2020), ENSO is still used as one of the estimators for seasonal ISM rainfall predictions (Rajeevan *et al.*, 2007). Furthermore, measurements often display a distinct rise in solute concentration as rainfall amount decreases (Stout, 2019). Washout effect occurrences influence the decrease in solute concentration during rainfall (Dey and Tripathi, 2007; Ram *et al.*, 2010). Smaller rainfall episodes (weakened due to El Niño effects) often have a considerably higher concentration of dissolved mineral content than longer rain events (Handa, 1969; Mordy, 1953; Woodcock, 1952). Consequently, a higher washout effect occurs owing to reduced rainfall events, giving rise to increased major ion concentrations. The reverse conditions are observed during a La Niña phase. This was corroborated by studying the major ion concentrations as well as pH during the El Niño and La Niña years. The chemical composition of rainfall was sourced from previous studies, conducted across various locations of India viz., Pune (1988), Ahmedabad (2000, 2002, 2008–2011), Hyderabad (2003), Bokaro (2012), Jharkhand (2012), and Mangalore (2006). Data from other locations were not available. We observed that during the El Niño years, due to

**Table 4.** Concentrations of major ions during the El Niño and La Niña years.

Major ions	El Niño	La Niña	p-value
Na <sup>+</sup>	87	41	0.04
K <sup>+</sup>	8.9	8.5	0.04
Ca <sup>2+</sup>	156	82	0.03
Mg <sup>2+</sup>	26	19	0.27
NH <sub>4</sub> <sup>+</sup>	46	48	0.25
Cl <sup>-</sup>	61	45	0.01
SO <sub>4</sub> <sup>2-</sup>	138	135	0.06
NO <sub>3</sub> <sup>-</sup>	21	24	0.95

lesser rainfall amount (mean rainfall amount = 14.41 cm) as compared to the La Niña years (mean rainfall amount = 17.66 cm), the major ion concentrations were significantly higher. We further used a paired t-test on the major ion concentrations during the El Niño and La Niña years to examine whether there was a statistically significant difference between them (Table 4). A statistically significant difference between concentrations of major ions during the El Niño and La Niña years (i.e., the corresponding two-tailed p-value is less than 0.05) was observed in the case of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>.

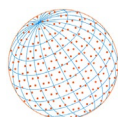
### 3.8 Significance of the Study

Studies of the chemical characteristics of ISM on regional scales are vital for a variety of agricultural and water management applications in India. So far, our understanding in India on this matter is limited to scattered localised information from earlier published literatures. However, a comprehensive review over the entire India on a regional scale is much essential. To fill that gap here we present the chemical composition of the major ions in rainwater across six homogenous monsoon regions. Additionally, we lack a comprehensive understanding of the relationship between chemical characteristics of ISM rainfall and dominant mode of interannual climate variabilities such as ENSO. Despite diminishing fingerprint of ENSO on the ISM (Kumar *et al.*, 2011; Samanta *et al.*, 2020), it remain important to understand the variations of chemical characteristics (such as major ions) in contrasting phases of ENSO.

## 4 CONCLUSIONS

The present study summarizes the chemical characteristics of rainfall during the summer monsoon season in different regions of India in terms of the long-term change in chemical composition over 28 years. The pH of rainwater across the six homogeneous Indian monsoon regions varied from 5.31 to 6.70. The occurrence of rain events at three different sites in the Peninsular region indicated that the region is under the significant influence of anthropogenic emissions. Most of the water-soluble chemical species in rainwater over the Northwest region were higher compared to the other five regions while in the Peninsular region, they were observed to be the lowest. Percent sea salt species were higher over Northeast and Peninsular (due to long coastline) regions, whereas the percent non-sea salt species over the Hilly region were higher than the other stations. Ionic ratios along with %SSF and %NSSF indicated the non-marine origin of most of the species except Cl<sup>-</sup>. However, Cl<sup>-</sup> at the Hilly region had 17% NSSF and has been observed to be well correlated with Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup>. Similarly, in the West Central region 53% Cl<sup>-</sup> is NSSF and correlates well with Na<sup>+</sup> and Mg<sup>2+</sup>. Association of Cl<sup>-</sup> with Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and Mg<sup>2+</sup> suggest its origin from marine as well as crustal and anthropogenic sources in the two regions. The EF with respect to Ca<sup>2+</sup> indicated that soil plays a major role in regulating rainwater composition. Soil EF indicated Mg<sup>2+</sup> in all the regions were soil-derived except for Central Northeast region where EF of Mg was slightly greater than one indicating some anthropogenic sources. NO<sub>3</sub><sup>+</sup> and SO<sub>4</sub><sup>-</sup> had high soil EF (> 10) indicating anthropogenic sources. Ca<sup>2+</sup> due to its abundance in suspended soil was found to be the most potent and abundant neutralizing species in all the regions. Furthermore, it was found that rainwater chemistry has an association with ENSO with significantly higher ionic (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>-</sup>) composition during El Niño compared to La Niña years.





## ACKNOWLEDGEMENTS

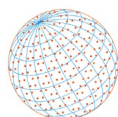
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## SUPPLEMENTARY MATERIAL

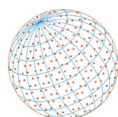
Supplementary material for this article can be found in the online version at <https://doi.org/10.4209/aaqr.220019>

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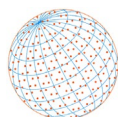
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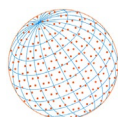


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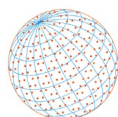


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