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 (Na⁺, K⁺, Ca²⁺, Mg²⁺, NH₄⁺, NO₃⁻, SO₄²⁻, and 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. Cl⁻ had a significant correlation with Na⁺ and NH₄⁺ in the Hilly region, and with Na⁺ and Mg²⁺ in the West Central region suggesting it is sourced from both marine and anthropogenic sources. The soil Enrichment Factor relative to Ca²⁺ demonstrated that soil has a significant effect on rainwater composition. Ca²⁺ 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 Na⁺, K⁺, Ca²⁺, Cl⁻, and SO₄²⁻ 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) regulates 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
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 SO$_4^{2–}$ and 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° and 37.6°N latitude and 68.7° and 97.25°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 (Martinez-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 km × 25 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
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 Cl\(^-\), SO\(_4\)\(^{2-}\), Ca\(^{2+}\), Mg\(^{2+}\), and K\(^+\), using Na\(^+\) as the reference element, assuming entire Na\(^+\) is of marine origin (Al-Khashman, 2005; Keene et al., 1986).

\[
\text{% SSF} = 100\left(\frac{\text{Na}(X/\text{Na})_{\text{sea}}}{X}\right)
\]

where X is the component concentration of interest, and

\[
\text{% NSSF} = 100 - \text{SSF}
\]

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, Na\(^+\) is commonly used as the reference element with the assumption that all Na\(^+\) in rainwater has a marine origin (Keene et al., 1986; Kulshrestha et al., 1996, 2003). Al and Ca\(^{2+}\) are two standard lithophilic elements used to calculate EF relative to seawater ratio.

### 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.

<table>
<thead>
<tr>
<th>Region</th>
<th>Cl(^-)/Na(^+)</th>
<th>Mg(^{2+})/Na(^+)</th>
<th>K(^+)/Na(^+)</th>
<th>Ca(^{2+})/Na(^+)</th>
<th>SO(_4)(^{2-})/Na(^+)</th>
<th>NO(_3)(^-)/Na(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Seawater Ratio</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Northwest Region</strong></td>
<td>1.166</td>
<td>0.227</td>
<td>0.022</td>
<td>0.044</td>
<td>0.125</td>
<td>0.00002</td>
</tr>
<tr>
<td>Rainwater</td>
<td>1.104</td>
<td>0.466</td>
<td>0.138</td>
<td>1.455</td>
<td>1.907</td>
<td>0.227</td>
</tr>
<tr>
<td>EF (marine)</td>
<td>0.95</td>
<td>2.1</td>
<td>6.3</td>
<td>33</td>
<td>15</td>
<td>113.59</td>
</tr>
<tr>
<td>% SSF</td>
<td>106</td>
<td>49</td>
<td>16</td>
<td>3</td>
<td>6.6</td>
<td>0</td>
</tr>
<tr>
<td>% NSSF</td>
<td>51</td>
<td>84</td>
<td>97</td>
<td>93</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td><strong>Hilly Region</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rainwater</td>
<td>1.411</td>
<td>1.004</td>
<td>0.564</td>
<td>3.225</td>
<td>0.847</td>
<td>0.742</td>
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<tr>
<td>EF (marine)</td>
<td>1.2</td>
<td>4.4</td>
<td>26</td>
<td>73</td>
<td>6.8</td>
<td>370.82</td>
</tr>
<tr>
<td>%SSF</td>
<td>83</td>
<td>23</td>
<td>3.9</td>
<td>1.4</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>%NSSF</td>
<td>17</td>
<td>77</td>
<td>96</td>
<td>99</td>
<td>85</td>
<td>100</td>
</tr>
<tr>
<td><strong>Central Northeast Region</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Rainwater</td>
<td>1.108</td>
<td>1.433</td>
<td>0.207</td>
<td>1.813</td>
<td>1.631</td>
<td>0.876</td>
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<tr>
<td>EF (marine)</td>
<td>1.0</td>
<td>6.3</td>
<td>9.4</td>
<td>41</td>
<td>13</td>
<td>437.95</td>
</tr>
<tr>
<td>% SSF</td>
<td>105</td>
<td>16</td>
<td>11</td>
<td>2.4</td>
<td>7.7</td>
<td>0</td>
</tr>
<tr>
<td>%NSSF</td>
<td>84</td>
<td>89</td>
<td>98</td>
<td>92</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td><strong>Northeast Region</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rainwater</td>
<td>1.125</td>
<td>0.277</td>
<td>0.124</td>
<td>1.069</td>
<td>1.179</td>
<td>2.925</td>
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<tr>
<td>EF (marine)</td>
<td>0.96</td>
<td>1.2</td>
<td>5.6</td>
<td>24</td>
<td>9.4</td>
<td>146.259</td>
</tr>
<tr>
<td>% SSF</td>
<td>104</td>
<td>82</td>
<td>18</td>
<td>4.1</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>%NSSF</td>
<td>18</td>
<td>82</td>
<td>96</td>
<td>92</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td><strong>Peninsular Region</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rainwater</td>
<td>1.022</td>
<td>0.316</td>
<td>0.137</td>
<td>1.074</td>
<td>0.608</td>
<td>0.238</td>
</tr>
<tr>
<td>EF (marine)</td>
<td>0.88</td>
<td>1.4</td>
<td>6.2</td>
<td>24</td>
<td>4.9</td>
<td>118.89</td>
</tr>
<tr>
<td>%SSF</td>
<td>114</td>
<td>72</td>
<td>16</td>
<td>4.1</td>
<td>21</td>
<td>0.01</td>
</tr>
<tr>
<td>%NSSF</td>
<td>28</td>
<td>84</td>
<td>96</td>
<td>79</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td><strong>West Central Region</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rainwater</td>
<td>2.464</td>
<td>0.470</td>
<td>0.449</td>
<td>2.299</td>
<td>0.978</td>
<td>0.555</td>
</tr>
<tr>
<td>EF (marine)</td>
<td>2.1</td>
<td>2.1</td>
<td>20</td>
<td>52</td>
<td>7.8</td>
<td>277.47</td>
</tr>
<tr>
<td>% SSF</td>
<td>47</td>
<td>48.3</td>
<td>4.9</td>
<td>1.9</td>
<td>13</td>
<td>0</td>
</tr>
<tr>
<td>%NSSF</td>
<td>53</td>
<td>51.7</td>
<td>95</td>
<td>98</td>
<td>87</td>
<td>100</td>
</tr>
</tbody>
</table>
Table 2. Enrichment factors relative to the soil for rainwater constituents across six homogeneous monsoon regions.

<table>
<thead>
<tr>
<th>Region</th>
<th>K⁺/Ca²⁺</th>
<th>Mg²⁺/Ca²⁺</th>
<th>SO₄²⁻/Ca²⁺</th>
<th>NO₃⁻/Ca²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Northwest Region</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rainwater</td>
<td>0.095</td>
<td>0.32</td>
<td>1.31</td>
<td>0.156</td>
</tr>
<tr>
<td>Soil</td>
<td>0.504</td>
<td>0.561</td>
<td>0.0188</td>
<td>0.0021</td>
</tr>
<tr>
<td>EF (soil)</td>
<td>0.19</td>
<td>0.57</td>
<td>70</td>
<td>74</td>
</tr>
<tr>
<td><strong>Hilly Region</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rainwater</td>
<td>0.175</td>
<td>0.311</td>
<td>0.263</td>
<td>0.23</td>
</tr>
<tr>
<td>Soil</td>
<td>0.504</td>
<td>0.561</td>
<td>0.0188</td>
<td>0.0021</td>
</tr>
<tr>
<td>EF (soil)</td>
<td>0.35</td>
<td>0.55</td>
<td>14</td>
<td>109</td>
</tr>
<tr>
<td><strong>Central Northeast Region</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rainwater</td>
<td>0.114</td>
<td>0.79</td>
<td>0.9</td>
<td>0.483</td>
</tr>
<tr>
<td>Soil</td>
<td>0.504</td>
<td>0.561</td>
<td>0.0188</td>
<td>0.0021</td>
</tr>
<tr>
<td>EF (soil)</td>
<td>0.23</td>
<td>1.4</td>
<td>48</td>
<td>230</td>
</tr>
<tr>
<td><strong>Northeast Region</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rainwater</td>
<td>0.116</td>
<td>0.26</td>
<td>1.103</td>
<td>2.737</td>
</tr>
<tr>
<td>Soil</td>
<td>0.504</td>
<td>0.561</td>
<td>0.0188</td>
<td>0.0021</td>
</tr>
<tr>
<td>EF (soil)</td>
<td>0.23</td>
<td>0.46</td>
<td>59</td>
<td>1303</td>
</tr>
<tr>
<td><strong>Peninsular Region</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rainwater</td>
<td>0.128</td>
<td>0.294</td>
<td>0.566</td>
<td>0.221</td>
</tr>
<tr>
<td>Soil</td>
<td>0.504</td>
<td>0.561</td>
<td>0.0188</td>
<td>0.0021</td>
</tr>
<tr>
<td>EF (soil)</td>
<td>0.25</td>
<td>0.52</td>
<td>30</td>
<td>105</td>
</tr>
<tr>
<td><strong>West Central Region</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rainwater</td>
<td>0.195</td>
<td>0.204</td>
<td>0.425</td>
<td>0.241</td>
</tr>
<tr>
<td>Soil</td>
<td>0.504</td>
<td>0.561</td>
<td>0.0188</td>
<td>0.0021</td>
</tr>
<tr>
<td>EF (soil)</td>
<td>0.39</td>
<td>0.36</td>
<td>23</td>
<td>115</td>
</tr>
</tbody>
</table>

crustal soil (Das et al., 2005; Safai et al., 2004; Zhang et al., 2007). In this study, soil enrichment factors were calculated using Ca²⁺ as a reference element and marine sources were determined using Na⁺ as a reference element:

EF for marine = (X/Na⁺)_{rainfall} / (X/Na⁺)_{sea}  (3)

EF for soil = (X/Ca²⁺)_{rainfall} / (X/Ca²⁺)_{soil}  (4)

where X was the concentration of the desired ion, marine X/Na⁺ ratio is taken from Keene et al. (1986) and X/Ca²⁺ ratio of the crust is from Taylor (1964).

Since the marine contribution of NO₃⁻ and NH₄⁺ is usually negligible, EFs for marine sources were calculated for Ca²⁺, Mg²⁺, K⁺, SO₄²⁻, and Cl⁻ while EFs for soil sources were calculated for K⁺, Na⁺, Mg²⁺, Cl⁻, SO₄²⁻, and NO₃⁻. 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 Ca²⁺, NH₄⁺, and Mg²⁺ for neutralization has been validated as follows:

\[ \text{[NF}_{\text{Ca}^{2+}}] = \text{[Ca}^{2+}] / \text{[NO}_3^{-}] + \text{[SO}_4^{2-}] \]  (5)
Table 3. Neutralization Factors for the cationic species in rainwater across six homogeneous monsoon regions.

<table>
<thead>
<tr>
<th>Region</th>
<th>NF(Ca²⁺)</th>
<th>NF(Mg²⁺)</th>
<th>NF(NH₄⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northwest</td>
<td>0.68</td>
<td>0.22</td>
<td>0.19</td>
</tr>
<tr>
<td>Hilly</td>
<td>2.03</td>
<td>0.63</td>
<td>0.41</td>
</tr>
<tr>
<td>Central Northeast</td>
<td>0.72</td>
<td>0.57</td>
<td>0.5</td>
</tr>
<tr>
<td>Northeast</td>
<td>0.26</td>
<td>0.07</td>
<td>0.12</td>
</tr>
<tr>
<td>Peninsular</td>
<td>1.27</td>
<td>0.37</td>
<td>0.51</td>
</tr>
<tr>
<td>West Central</td>
<td>1.5</td>
<td>0.31</td>
<td>0.48</td>
</tr>
</tbody>
</table>

\[ [\text{NF}_{\text{Mg}^{2+}}] = \frac{[\text{Mg}^{2+}]}{[\text{NO}_3^-] + [\text{SO}_4^{2-}]} \]  \hspace{1cm} (6)

\[ [\text{NF}_{\text{NH}_4^+}] = \frac{[\text{NH}_4^+]}{[\text{NO}_3^-] + [\text{SO}_4^{2-}]} \]  \hspace{1cm} (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 asportion 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 ± 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 CO₂ (Charlson and Rodhe, 1982). The pH value of rainwater was lowest at Ahmedabad, during the 2008–2011 sampling (average = 5.21 ± 0.29, range 4.6–5.7) and is on the lower side of those measured in the 2000–2002 range (average = 6.70 ± 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\(^+\), (c) Mg\(^2+\), (d) Ca\(^2+\), (e) K\(^+\), (f) NH\(_4\)\(^+\), (g) Cl\(^-\), (h) NO\(_3\)\(^-\), and (i) SO\(_4\)\(^2-\).
for the year 2001 and a decreasing trend in the following year. In the region, the highest average pH (7.47 ± 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 SO₄ and NOₓ in the ambient air (Migliavacca et al., 2005). The major anthropogenic emission sources of NOₓ and SO₄ 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 SO₄²⁻ ions. The cation budget of the rainwater is dominated by Ca²⁺ in the northwest region with Ca²⁺ > Na⁺ > Mg²⁺ > NH₄⁺ > K⁺ (Figs. 2(b–f)). The aerosolized calcareous soil in the atmosphere is washed out in the rain resulting in higher Ca²⁺ content in the northwest (Srivastava et al., 2014). Average relative abundances of anions are of the order SO₄²⁻ > Cl⁻ > NO₃⁻ with SO₄²⁻ 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 NO₃⁻ in Ahmedabad in 2000 possibly due to the washout effect as rainfall negatively (r = –0.59) correlates with NO₃⁻. In Ahmedabad, for both the studies rainfall correlates negatively with most of the major ions implying the washout effect. The %SSF, %NSSF, EFmarine, and EFsoil for rainwater major ions in the northwest region are given in Tables 1 and 2. Cl⁻ had an EFmarine value of 0.94 close to that of the seawater ratio (1.2). The negative value for %NSSF Cl⁻ implies the absence of non-sea-salt and it was entirely of sea spray origin. The strong correlation between Na⁺ and Cl⁻ (r = 0.96) corroborates marine origin. Ca²⁺ was of non-marine origin (NSSF of 97%) with an EFmarine value of 33, indicating a terrestrial source (Cao et al., 2009). 16% of K⁺ and 49% of Mg²⁺ are sea salt derived with low EFmarine of 6.3 and 2.0 respectively. K⁺ (r = 0.35) and Mg²⁺ (r = 0.37) also shows a significant (p < 0.01) moderate correlation with Cl⁻. Only 6.6% of SO₄²⁻ was of marine origin and had an EFmarine value of 15.3 and EFsoil of 70, suggesting that SO₄²⁻ was primarily derived from anthropogenic sources (Cao et al., 2009). Anthropogenic activities were regarded as significant nitrate sources due to high EFsoil (74) of NO₃⁻. Neutralization is caused by the alkaline species Ca²⁺ and Mg²⁺ 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 Ca²⁺ > Mg²⁺ > NH₄⁺, implying Ca²⁺ (NF = 0.68) as the major neutralizing ion followed by Mg²⁺ and NH₄⁺ (Table 3). Significant correlations among Ca²⁺ and NO₃⁻ (r = 0.77), Mg²⁺ and SO₄²⁻ (r = 0.64) and Mg²⁺ and NO₃⁻ (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 ± 0.68. The highest pH of the hilly region is in the Roorkee site (pH value of 7.03 ± 0.68) with an EFmarine value of 33, indicating a terrestrial source (Cao et al., 2012). The average pH value across these four locations was 6.01 ± 0.68. The highest pH of the hilly region is in the Roorkee site (pH value of 7.03 ± 0.68) with an EFmarine value of 33, indicating a terrestrial source (Cao et al., 2012). The highest pH value of the hilly region is in the Roorkee site (pH value of 7.03 ± 0.68) with an EFmarine value of 33, indicating a terrestrial source (Cao et al., 2012).
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., 2012). 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 Na⁺ as the reference element with the basic assumption that all Na⁺ is of marine origin (Keene et al., 1986; Kulshrestha et al., 1996, 2003). The observed rainwater ratio of Cl⁻/Na⁺ (1.5) is slightly higher than that of the seawater ratio (1.2), indicating that rainwater Cl⁻ in this region is influenced by anthropogenic sources in addition to sea-salt. Cl⁻ significantly correlates with NH₄⁺ (r = 0.99; p < 0.05) and Na⁺ (r = 0.98) supporting anthropogenic and sea salt origin. In irrigation water, chlorine from sodium hypochlorite or dissolved Cl gas has a complex chemistry. Cl⁻ is transformed to hypochlorite (OCl⁻) and hypochlorous acid when it is introduced to water (HOCl). When water-soluble fertilisers containing ammonium are used in conjunction with Cl⁻, hypochlorous acid is likely to be rapidly transformed into complex 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 NH₃ (Al-Momani, 2003; Sutton et al., 2008). A natural, mineralogical form of ammonium chloride called sal ammoniac (NH₄Cl) is also commonly formed from coal burning. It is used as a fertilizer as well. The %SSF, %NSSF, EFmarine, and EFsoil for rainwater major ions in the hilly region given in Tables 1 and 2 indicate that 77 to 100 percent of Ca²⁺, K⁺, Mg²⁺, NO₃⁻, and SO₄²⁻ are of non-marine origin. The EFmarine of the major ions (Mg²⁺, K⁺, Ca²⁺, NO₃⁻, and SO₄²⁻) were greater than 1, which suggests a significant contribution of non-sea-salt sources. Mg²⁺ had a soil source (EFsoil = 0.5) whereas sulphate (EFsoil = 14) and nitrate (EFsoil = 110) were of anthropogenic origin (Cao et al., 2009). The NFCa (2.0) was highest followed by NF_Mg (0.63) and NF_NH4 (0.41) indicating the role of crustal components in the neutralization of anions. Furthermore, as Cl⁻ has an anthropogenic source besides marine origin, the rainfall acidity is possibly contributed by Cl⁻, NO₃⁻, and SO₄²⁻ 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), Bhubaneshwar, 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 ± 0.53. The pH value of rainwater was lowest (5.08 ± 0.53) 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 SO₂ and NOₓ (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, Bhubaneshwar 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, Bhubaneshwar. The reason could be the low Ca²⁺ concentration at SBG; Bhubaneshwar (15 µeq L⁻¹) compared to RRL, Bhubaneshwar (37 µeq L⁻¹). The low Ca²⁺ concentration in rainwater may be explained by the dense vegetation cover coupled with low calcium carbonate/bicarbonate content of the soil (hence 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
84% of Mg$^{2+}$ in rainwater samples had a non-marine origin. The EF values for soil and marine considered to be diluted or enriched relative to the reference source (Cao et al., 2019; Garrels and Mackenzie, 1971; Wu et al., 2018). The concentration of SO$_4^{2–}$ 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 SO$_4^{2–}$ level from year to year in Dayalbagh, Agra. The mean value of NO$_3$– in Dayalbagh was found to be 15 ± 7.0 µeq L$^{-1}$ while the yearly mean values varied between 5.7 and 28 µeq L$^{-1}$, the maximum being five times the minimum. Increased line sources may be responsible for the rise in NO$_3$– concentration as motor vehicles are increasingly growing in Agra (Saxena et al., 1991, 1996). Automobile exhaust is the primary source of NO$_x$, which is a precursor to NO$_3$– (Kumar et al., 2002). The mean value of Ca$^{2+}$ in Dayalbagh was found to be 82 ± 34 µeq L$^{-1}$ and the yearly mean value varied between 48 and 137 µeq L$^{-1}$. The value of 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 Mg$^{2+}$, NH$_4^+$, and Cl$^–$, a stable trend for NO$_3$– and Na$^+$ and a decreasing trend for Ca$^{2+}$. In comparison between Banaras Hindu University (BHU) and Mal da hiya (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 Ca$^{2+}$ (199 µeq L$^{-1}$) and Mg$^{2+}$ (102 µeq L$^{-1}$) were recorded at Gorakhpur and the lowest was measured at Varanasi (51 and 11 µeq L$^{-1}$, respectively). As compared to the other five locations at UP, SO$_4^{2–}$ and NO$_3$– were also highest at Gorakhpur (79 and 45 µeq L$^{-1}$, respectively) and lowest at Varanasi (38 and 22 µeq L$^{-1}$ respectively). High concentrations of Ca$^{2+}$, Mg$^{2+}$, SO$_4^{2–}$, and 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 Cl$^–$/Na$^+$ (1.1) is close to that of the seawater ratio (1.2), which indicates that a major part of the Na$^+$ and Cl$^–$ originated from sea salt. The ratios SO$_4^{2–}$/Na$^+$, Ca$^{2+}$/Na$^+$, K$^+$/Na$^+$, and Mg$^{2+}$/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; Kulshreshtha et al., 1996). This observation is also supported by %SSF and %NSSF values. Approximately 92% of SO$_4^{2–}$, 98% of Ca$^{2+}$, 89% of K$^+$, and 84% of 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). Cl$^–$ had EF$_{marine}$ value of 0.95, clearly indicating that Cl$^–$ had been enriched relative to seawater. The average EF$_{marine}$ value of Ca$^{2+}$ was 41, suggesting its origin from a terrestrial source. Mg$^{2+}$ was mostly from the marine source but showed moderate soil enrichment as well. NO$_3$– had EF$_{soil}$ value of 230, showing high enrichment relative to soil source. These high EF values of NO$_3$– indicated that NO$_3$– mainly originated from anthropogenic sources. SO$_4^{2–}$ had EF$_{marine}$ value of 13 and EF$_{soil}$ 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 (Ca$^{2+} >$ Mg$^{2+} >$ Na$^+$) remains nearly similar to the northwestern 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 (NO$_3$– and SO$_4^{2–}$) in this region is neutralized by magnesium and ammonium (R$^2$ = 0.64). Also, significant correlations among Mg$^{2+}$ and SO$_4^{2–}$ (r = 0.70) and Mg$^{2+}$ and 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 ± 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 ± 0.80, range 4.2–6.1) followed by Guwahati, Falta, and Jorhat. Such acid rain events indicate a high level of SO$_2$ and 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, Ca$^{2+}$, Mg$^{2+}$, and 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 higherionic concentrations of the above-mentioned species (Rišt et al., 2020). The highest average pH was reported from Kolkata in, 2019 (average = 6.80 ± 0.74, range 5.4–8.0) which was similar to those reported in 2013–2014 (average = 6.10 ± 1.40, range 4.4–6.9). Ca$^{2+}$ dominates the cation budget of the rainwater of the northeast region with the sequence Ca$^{2+}$ > Na$^+$ > NH$_4^+$ > Mg$^{2+}$ > K$^+$ (Figs. 2(b–f)). Some of the highest 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 NO$_3^-$ > SO$_4^{2-}$ > Cl$^-$ with NO$_3^-$ dominating the anion budget (Figs. 2(g–i)). The concentration of NO$_3^-$ was higher in Kolkata (2019) than those reported from other sites in this region. Anthropogenic sources of NO$_3^-$ include vehicle emissions, coal combustions, soil emissions driven by fertilizer use, and biomass burning (Li et al., 2019). It is noteworthy that Ca$^{2+}$ and SO$_4^{2-}$ were 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 Na$^+$, Mg$^{2+}$, SO$_4^{2-}$, and Cl$^-$ in Kolkata in, 2019 (average = 6.80 ± 0.74, range 5.4–8.0) compared to the year 2013–2014 (average = 6.10 ± 1.40, range 4.4–6.9). Ca$^{2+}$ dominates the cation budget of the rainwater of the northeast region with the sequence Ca$^{2+}$ > Na$^+$ > NH$_4^+$ > Mg$^{2+}$ > K$^+$ (Figs. 2(b–f)). The highest average pH was reported from Kolkata in, 2019 (average = 6.80 ± 0.74, range 5.4–8.0) which was similar to those reported in 2013–2014 (average = 6.10 ± 1.40, range 4.4–6.9). Ca$^{2+}$ dominates the cation budget of the rainwater of the northeast region with the sequence Ca$^{2+}$ > Na$^+$ > NH$_4^+$ > Mg$^{2+}$ > K$^+$ (Figs. 2(b–f)). Some of the highest 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).

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±...
NO₃⁻ (66 µeq L⁻¹) and SO₄²⁻ (110 µeq L⁻¹) were the most abundant anions in the rainwater of the West central region. Similar patterns were observed in the West central region consisting 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 ± 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). SO₄²⁻ (110 µeq L⁻¹) and NO₃⁻ (66 µeq 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 ± 0.38, range 5.71–6.60), Goa (average = 6.25 ± 0.28, range 5.36–6.91) had higher pH, similar to the regional average. Similar pH was reported Nagpur (average = 6.30 ± 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 Ca\(^{2+}\) with the sequence Ca\(^{2+}\) > Na\(^{+}\) > NH\(_4\)\(^{+}\) > Mg\(^{2+}\) > K\(^{+}\) (Figs. 2(b–f)). Average relative abundances of anions are of the order Cl\(^{-}\) > SO\(_4^{2-}\) > NO\(_3^{-}\) with 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 NO\(_3^{-}\) from 1988 to 1998. The major source of 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 Mg\(^{2+}\) trend and a decreasing NO\(_3^{-}\) trend in Hyderabad during 1999–2001. The increase in 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 Mg\(^{2+}\). As expected for the washout effect, rainfall negatively correlates with all the species in Hyderabad except NO\(_3^{-}\) (r = 0.43). Vehicle traffic and biomass combustion are major sources of NO\(_x\) (Merico et al., 2020). The authors postulated longer rains oxidize precursors of NO\(_x\) like NO to NO\(_3^{-}\), as shown by higher NO\(_3^{-}\) concentrations with increased rainfall.

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

<table>
<thead>
<tr>
<th>Major ions</th>
<th>El Niño</th>
<th>La Niña</th>
<th>p-value</th>
</tr>
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<td>Na⁺</td>
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</tr>
<tr>
<td>K⁺</td>
<td>8.9</td>
<td>8.5</td>
<td>0.04</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>156</td>
<td>82</td>
<td>0.03</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>26</td>
<td>19</td>
<td>0.27</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>46</td>
<td>48</td>
<td>0.25</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>61</td>
<td>45</td>
<td>0.01</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>138</td>
<td>135</td>
<td>0.06</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>21</td>
<td>24</td>
<td>0.95</td>
</tr>
</tbody>
</table>

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⁺, K⁺, Ca²⁺, Cl⁻, and SO₄²⁻.

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⁻. However, Cl⁻ at the Hilly region had 17% NSSF and has been observed to be well correlated with Na⁺ and NH₄⁺. Similarly, in the West Central region 53% Cl⁻ is NSSF and correlates well with Na⁺ and Mg²⁺. Association of Cl⁻ with Na⁺, NH₄⁺, and Mg²⁺ suggest its origin from marine as well as crustal and anthropogenic sources in the two regions. The EF with respect to Ca²⁺ indicated that soil plays a major role in regulating rainwater composition. Soil EF indicated Mg²⁺ 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. NO₃⁻ and SO₄²⁻ had high soil EF (> 10) indicating anthropogenic sources. Ca²⁺ 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⁺, K⁺, Ca²⁺, Cl⁻, and SO₄²⁻) composition during El Niño compared to La Niña years.
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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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