Nature and Sources of Ionic Species in Precipitation across the Indo-Gangetic Plains, India

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ABSTRACT

The spatial distribution of rainwater chemistry over the densely-populated and highly polluted Indo-Gangetic Plains (IGP) was investigated using samples (total = 687) collected during three consecutive summer monsoon seasons from 2009 to 2011. The concentrations of secondary ionic species (SO\textsubscript{4}\textsuperscript{2–} and NO\textsubscript{3}–) were measured along with the other major ions (F –, Cl –, Na +, K +, Ca\textsuperscript{2+}, Mg\textsuperscript{2+} and NH\textsubscript{4}+) and pH and specific conductivity. The weighted mean pH (± std) and conductivity of rainwater were 5.73 (± 0.17) and 31.6 (± 31.0) µS cm\textsuperscript{–1}, respectively. Approximately 16% of rainwater samples were acidic (pH < 5.61) with a mean pH = 5.38 of acid rain and rest of them were more alkaline (pH > 5.61) (mean pH = 6.34 for the more basic samples). Specific conductivity was ~39% lower (20.6 µS cm\textsuperscript{–1}) for the acidic rain compared to the more basic (33.6 µS cm\textsuperscript{–1}) samples. The mean sum of all of the measured ions is 351.6 ± 130.1 µeq L\textsuperscript{–1} with the highest contributions being Ca\textsuperscript{2+} (30%) and SO\textsubscript{4}\textsuperscript{2–} (15%). Mean [SO\textsubscript{4}\textsuperscript{2–}] (52 µeq L\textsuperscript{–1}) and [NO\textsubscript{3}–] (29 µeq L\textsuperscript{–1}) were approximately five and ten times higher, respectively, compared to background hemispheric values. Secondary ions had the highest deposition fluxes (SO\textsubscript{4}\textsuperscript{2–}, 25.2 kg ha\textsuperscript{–1} y\textsuperscript{–1} and NO\textsubscript{3}–: 18.3 kg ha\textsuperscript{–1} y\textsuperscript{–1}). The mean ratio of H\textsuperscript{+}/(NO\textsubscript{3}– + SO\textsubscript{4}\textsuperscript{2–}) was 0.02 indicating ~98% of the acidity was neutralized. Ca\textsuperscript{2+}, (57%), Mg\textsuperscript{2+} (25%), NH\textsubscript{4}+ (15%) and K\textsuperscript{+} (4%) were important neutralizing species. Positive Matrix Factorization (PMF) was applied to the deposition fluxes. Five factors were identified and identified as ammonia neutralized, sea salt, soil, biomass burning, and calcium neutralized.

Keywords: Rainwater chemistry; Ion balance; Positive matrix factorization; Specific conductivity; Acid rain.

INTRODUCTION

Precipitation is an important mechanism for scavenging of atmospheric pollutants, both particles and gases (Migliavacca et al., 2005). These species affect the chemistry of rainwater and reflect the air quality in the region where the precipitation samples were collected (Al-Khashman, 2005, 2009). Precipitation is affected by local and transported particles (Tiwari et al., 2007; Chate et al., 2011; Niu et al., 2014; Akpo et al., 2015). The presence of dissolved ions provides information on both local and long-range transported pollutants and changes the precipitation’s effect on ecosystems through wet deposition (Mphepya et al., 2004; Li et al., 2007). The chemical composition of rainwater is affected by a combination of local and regional pollutants, cloud formation processes, and rainfall amounts (Zhao et al., 2008; Calvo et al., 2010). Quantitative measurement of wet deposition compositions enables the identification of the temporal and spatial variability and determining the relative contributions of the various natural and anthropogenic sources.

Acid rain, which is an outcome of precipitation scavenging, is defined as having a pH lower than 5.61, the value expected on the equilibrium of pure water and atmospheric CO\textsubscript{2} at 400 ppm (Seinfeld and Pandis, 2006). Acid precipitation is a global environmental issue (Rodhe et al., 2002) because
of its transboundary impact on the biogeochemical cycles. Increasing SO₂ and NO₃ (acidifying gases) emissions during the past few decades have increased acid deposition everywhere (Wai et al., 2008; references therein). Decreasing pH values in rainwater is the result of major inorganic acids such as sulfuric, nitric, and organic acids including carboxylic acids, carbonic acids, acetic acid, formic acid etc., resulting from complex homogeneous and heterogeneous phase reactions in the atmosphere (Rocha et al., 2003; Niu et al., 2014). The precursors of these the first three acids are emissions of oxides of sulfur and nitrogen, carboxylic compounds and hydrocarbons (Migliavacca et al., 2005). North America and Europe have also been adversely affected by acidic deposition (Rodhe et al., 2002).

In the atmosphere, gases like SO₂ and NO₂ dissolve in water and are converted into acidic forms. Baron and Denning (1993) suggested that different climate conditions also influence trace substance concentrations in the rainwater. Kulshrestha et al. (2003, 2005) suggested that the chemistry of rainwater varies largely from region to region and site to site because it is influenced by natural/anthropogenic particles and provides information on the input of anthropogenic as well as natural components to various ecosystems.

In recent years, a program was initiated under World Meteorological Organization (WMO)/Global Atmospheric Watch to provide a critical review of worldwide acidic deposition (Vet et al., 2014). Also, systematic studies have been conducted in North America, East Asia, and Europe through long term observation networks such as the National Atmospheric Deposition Program (NADP) in United States, the Acid Deposition Monitoring Network in East Asia, and the European Monitoring and Evaluation Programme (EMEP) in Europe, respectively. However, there are only limited monitoring sites across the globe particularly in India (Kulshrestha et al., 2005; references therein). In addition to this, continuous monitoring program called Background Air Pollution Monitoring Network (BAPMoN) studies of Global Atmospheric Watch (GAW) are ongoing (Mukhopadhyay et al., 1992).

In addition to this, the studies of precipitation chemistry in South Asian region especially in India have been performed (Rao et al., 1992; Granat et al., 2002; Kulshrestha et al., 2003; Safai et al., 2004; Kulshrestha et al., 2005; Momin et al., 2005; Mouli et al., 2005; Tiwari et al., 2007; Rastogi and Sarin, 2007; Salve et al., 2008; Badhavant et al., 2009; Safai et al., 2010; Shakla and Sharma, 2010; Badhavant et al., 2011, Das et al., 2011; Salve et al., 2011; Tiwari et al., 2011, 2012; Badhavant et al., 2014; references therein). However, there have been no systematic, long-term measurements of rainwater chemistry have been made over Indgo Gangetic Plains (IGP) region to date (Satsangi et al., 1998a, b; Das et al., 2005; Singh et al., 2007a; Tiwari et al., 2007; Das et al., 2010; Shakla and Sharma, 2010; Das et al., 2011; Tiwari et al., 2012; Bisht et al., 2014; references therein). The IGP supports nearly 70% of India’s population and is one of the highly polluted and industrialized regions of the world. Significant heterogeneity in physical, chemical, and optical properties of atmospheric particles has been observed (Jethva et al., 2005; Srivastava et al., 2012; Tiwari et al., 2013). It is a region of interest because of its unique topography and significant variability in the ambient particulate matter given the variety of sources operating at different times (Singh et al., 2010; Srivastava et al., 2012; Srivastava and Ramachandran, 2013).

The chemistry of rainwater over IGP region needs to be measured at multiple locations to review the acidic atmospheric deposition and to evaluate the characteristics of ions over this large region. The present study describes measurements of pH, specific conductivity, and chemical constituents of rainwater collected at eight different climatic locations from west to east across the IGP region (India) during the three consecutive summer monsoon seasons of 2009 to 2011. The objectives of this study are to (i) characterize the chemical composition of rainwater collected during different rainy seasons over IGP region, (ii) investigate the spatial variability of wet deposition flux of measured ions in rainwater in this polluted region, and (iii) provide a better understanding of the sources of SO₄²⁻ and NO₃⁻ as well as other measured ions that contribute to the rainwater contents at a scale of the season and year.

EXPERIMENTAL

Sampling Collection Procedure and Site Description

Rainwater samples were collected daily basis from around 10:00 every day (24 hr sample) using a bulk collector during the southwest summer monsoon seasons of 2009 to 2011 at eight locations across the IGP region (Fig. 1). The IGP region includes North West [Himachal Pradesh (HP), Punjab, Chandigarh and Haryana], North [Uttarakhand, Delhi, and Uttar Pradesh (UP)] and East [Bihar, Jharkhand, and West Bengal (WB)]. It is one of most populous regions in the world (http://en.wikipedia.org/wiki/Indo-Gangetic_Plain). The area of IGP covers about 700000 km² from Pakistan to Bangladesh. Sampling locations were established at Ballia (BAL) eastern Uttar Pradesh (UP), Varanasi (VAR), Gorakhpur (GOR) and Kanpur (KAN) in central IGP, Meerut (MEE) in western UP, Kurukshetra (KUR) in Haryana and New Delhi (DEL), western IGP and at Manali (MAN) located in Western Himalayan region (see lat. and long. in Fig. 1), a high altitude location. Of these eight locations, two of the locations are urban with industrial background locations (DEL and KAN), three locations are semi-urban (GOR, KUR and VAR), two are rural (BAL and MEE), and one is a background location (MAN).

The collector consists of a polypropylene funnel (20 cm diameter) connected with a 2 liter bottle. It was placed on the rooftop (typically ~15 m above the ground and 1 m from the roof top). Each collector was set to be away from any specific pollutant sources and the surface soil. The collected rainwater samples were then loaded into the pre-cleaned polyethylene sample bottles after each daily collection. Thymol (< 5 mg) was added to the collection bottle immediately after collection and before transferring the samples to avoid any chemical changes in rainwater.

Chemical Analysis and Quality Control

After the collection of each daily rain sample, the samples
Fig. 1. Geographical locations of sampling sites (Ballia: 25°44'N, 84°11'E, 64 m a.s.l.; Gorakhpur: 26°45'N, 83°24'E, 78 m a.s.l.; Varanasi: 25°22'N, 83°00'E, 76 m a.s.l.; Kanpur: 26°28'N, 80°20'E, 126 m a.s.l.; Meerut: 28°59'N, 77°42'E, 219 m a.s.l.; New Delhi: 28°37'N, 77°12'E, ~250 m a.s.l.; Kurukshetra: 29°96'N, 76°83'E, 260 m a.s.l.; Manali: 13°10'N, 80°16'E, 2050.1 m a.s.l.) in IGP region.

(n = 687) were kept in a refrigerator at sampling site and transferred (once in a week) to the regional laboratory of Indian Institute of Tropical Meteorology (IITM) Pune in Delhi for analysis. The pH and specific conductivity along with rainfall volume were measured immediately. The pH and conductivity were measured by a pH (Cyber Scan 510 pH) and conductivity (Elico CM-183) meters, with reference solutions of pH 4.0 and 7.0; and KCl solution, respectively. The samples were then filtered through Whatman-41 filter paper and stored in a refrigerator at 4°C until the chemical analysis. The major anions (F−, Cl−, NO3− and SO42−) and cations (NH4+, Na+, K+, Ca2+ and Mg2+) were quantitatively analyzed by ion chromatography (Dionex -2000, USA). An IonPac-AS15 analytical column with micro-membrane suppressor ASRS ultra II 2 mm, 38 mM potassium hydroxide and the IonPac-CS17 column with micro-membrane suppressor (CSRS ultra II 2 mm), 6 mM methyl sulfonic acid as eluent and tripled distilled water as the regenerator were used for the determination of anions and cations, respectively (Tiwari et al., 2012). The detection limit of the measured ions were 3.38, 4.35, 7.29, 7.78, 0.43, 0.26, 1.00 and 0.42 µeq L−1 for Cl−, NO3−, SO42−, NH4+, Na+, K+, Ca2+ and Mg2+, respectively.

There were occasional bird dropping and leaves in the funnel such that some samples had visible contamination. Those samples were discarded, the funnel washed and reinstalled for the next collection. Collected field blanks during cleaning of the funnel were kept for its further analysis as samples and their concentrations were found negligible. Thereafter, the data (chemical) was assessed by the measured ion balance that indicated the completeness of analysis. If the ratio of the sum of anions (Σ−) to the cations (Σ+) balance is unity, there is an ion balance. However, the average ratio was 0.65 ± 0.37 indicating the contribution of anions that were not measured in the present study. These ions may be organic anions such as formate (HCOO−) and oxalate (C2O42−), etc. (Al-Momani et al., 2000). The production of formic acid is dominated by in situ secondary aerosol formation, while direct emissions are dominant for acetic acid production (Chebbi and Carlier, 1996; and references therein). Dicarboxylic acids are produced by photochemically induced reactions (e.g., Kawamura and Ikushima, 1993; Khwaja, 1995; Ray and McDow, 2005). Kumar et al. (1996) reported low concentrations (µeq L−1) of acetate and formate in rainwater. In the present study, the bicarbonate (HCO3−) concentrations (Granat, 1972) and free acidity (H+) were calculated based on measured pH and included in the sum of anions and cations, respectively. After including bicarbonate, the ionic ratio in rainwater samples increased to 0.78 ± 0.35 with a linear regression [r = 0.81 (p < 0.0001; Y = 31.495 + 1.328x)]. A significant positive relationship between sums of anions and cations indicates that the near completeness of the measurement of ions in rainwater (Sanusi et al., 1996).

The sum of measured ion concentrations during the study period was ~351.6 ± 130 µeq L−1 that is in the typically observed range of 100–500 µeq L−1 (Tiwari et al., 2012). The large deviation in ion-balance indicates unmeasured species that are likely to be organic acids. Weak organic acids were not measured although they are important components of rainwater samples in clean environments (Sunder Raman et al., 2008).

RESULTS AND DISCUSSION

Variability of pH and Specific Conductivity

In part, the burning of fossil fuels like coal, oil and natural
gas has increased the CO₂ concentration in the atmosphere (~400 ppm), and thus, the threshold value of pH (5.61) for “acid rain” has changed from the original value of 5.65 (Charlson and Rodhe, 1982). The volume weighted mean (VWM) pH value across the 8 locations was 5.73 ± 0.17 varying from 5.44 (GOR) to 6.03 (BAL) (Fig. 2) indicating the generally non-acidic nature of the rainfall over IGP region. However, in some cases, the VWM pH values were lower than the threshold value for acid rainwater. During the study period, ~16% of the precipitation samples were acidic (mean pH = 5.38 of acid rain: H⁺ = 5.38 µeq L⁻¹) and rest of the samples were more basic than “acid rain.” The specific conductivity was also measured and was ~39% (20.6 µS cm⁻¹) lower specific conductivity for the acid rain samples when compared to the non-acidic rain (33.6 µS cm⁻¹) samples. Thus, higher concentrations of alkaline species produced these more basic samples (Anatolaki and Tsitouridou, 2009; Piñeiro et al., 2014).

Mean regional specific conductivity was 31.6 ± 31.1 µS cm⁻¹ varying from 3.2 µS cm⁻¹ to 288.0 µS cm⁻¹. Spatially, mean specific conductivity values were in the order of 18.4 (VAR), 23.7 (BAL), 26.1 (KAN), 29.2 (MAN), 30.0 (MEE), 34.3 (GOR), 39.3 (DEL) and 43.6 (KUR) µS cm⁻¹. The mean specific conductivity over IGP region is much higher than that reported by IMD (1982) in rainwater at 10 background locations in India (5–57 µS cm⁻¹). Prior studies (Ghude et al., 2008; Srivastava et al., 2012; Tiwari et al., 2013; Kaskaoutis et al., 2014; http://www.moef.nic.in, and references therein) of the atmospheric aerosol over the IGP region indicated high concentrations of fine particles produced by man-made and natural sources.

Of the eight locations, the pH value of rainwater was lowest (5.44) at GOR due to higher concentrations of acidic species produced locally from industrial sources and/or transported from more distance sources in Nepal (Lumbini) where many industrial operations are located (http://unesdoc.unesco.org/images/0021/002196/219621e.pdf). The highest pH at BAL (6.03) is due to high ammonia and the alkaline species in the calcareous soil of this rural environment (Kulshrestha et al., 2003). Pandey and Singh (2012) reported the pH at Varanasi (central IGP region) ranged from 6.3 to 7.9 with ~70% rains being alkaline. In two industrial locations (DEL and KAN), the mean pH values were similar (~5.81) due to local anthropogenic primary pollutant sources.

Higher monthly arithmetic mean pH values were observed in June (pH = 6.55) during the onset (less rainfall) of monsoon with decreasing pH values in July (6.36), August (6.15), and September (5.94). The lowest pH value (October: 5.86) was observed after the end of the monsoon and may have been due to increased emissions from fossil fuel combustion and biomass burning (Kaskaoutis et al., 2014; Tiwari et al., 2014, 2015). The higher pH in June may be due to a lower volume of precipitation and corresponding lower dilution since the ion concentrations were generally higher in the low precipitation events (Raynor and Hypes, 1982; Chat and Devara, 2009). The frequency distribution of pH show that highest pH were in the range of 6.0 to 6.5 at most locations (36% of the samples). Approximately 11% of the samples had pH values below 5.5 whereas 89% of them were higher.

The analysis of the year to year pH variability indicated higher pH (5.94) in 2010, and lower pH values in 2009 (5.62) followed by 2011 (5.83). However, for specific conductivity, an increasing temporal trend was observed ranging from 28.9 µS cm⁻¹ (2009) to 30.9 µS cm⁻¹ (2010) to 35.1 µS cm⁻¹ (2011). The higher specific conductivity in the rainwater samples indicated increasing ionic concentrations in the precipitation (Niu et al., 2015). The corresponding sum of the measured ions were 265.6 (2009), 394.4 (2010), and 366.0 (2011) µeq L⁻¹ indicating the direct impact of measured ions on specific conductivity during study period. Anatolaki, and Tsitouridou (2009) reported higher conductivity (44 µS cm⁻¹ varied from 7.50–439 µS cm⁻¹) and higher pH (> 7) in rainwater over an urban site "Thessaloniki" in Greece and suggested that the impact of high amounts of alkaline constituents. In a study at a suburban site in Spain, Piñeiro

![Fig. 2. Mean pH values over the IGP region.](image-url)
et al. (2014) reported that the lower pH could be due to absence of excess dust cations.

During the past three decades, studies of pH of rainwater have been performed in India, but they were mostly in urban locations with a few cases in rural and high altitude indicating large variability in pH depending upon sampling sites (Khemani, 1989; Mahadevan et al., 1989; Kumar et al., 1993; Kulshrestha et al., 1996; Kulshrestha et al., 2003; Ali et al., 2004; Safai et al., 2004; Kulshrestha et al., 2005; Momin et al., 2005; Tiwari et al., 2007; Budhavant et al., 2009; Satyanarayana et al., 2010; Salve et al.; 2011; Tiwari et al., 2012; Budhavant et al., 2014; references therein).

**Ionic Composition of Rainwater**

Rainwater chemistry is a function of the proportions of acidic and alkaline constituents in it. During the study period, it was found that the sum of VWM of ionic constituents across the eight locations was 351.6 ± 130.1 µeq L⁻¹ indicating high atmospheric pollution concentrations over the IGP region. The annual VWM of ionic constituents over IGP region rainwater have been calculated as:

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

where \(C_i\) is the ionic concentration for each element in µeq L⁻¹, \(P_i\) is the rainfall amount for each rainy event (mm), and \(N\) is the total number of precipitation event (Akpo et al., 2015). The VWM values of water soluble chemical species (µeq L⁻¹) in the rainwater samples collected at the eight monitoring locations are shown in Fig. 3. The overall weighted mean values, the numbers of rain events, the non-sea salt contributions of ions, hydrogen ions and rainfall at each location were also presented in Tables 1(a) and 1(b). Non-sea salt values are calculated from the measured concentrations of the species of interest using as
<table>
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<th>Site</th>
<th>$N$</th>
<th>$\text{H}^+$</th>
<th>$\text{Na}^+$</th>
<th>$\text{NH}_4^+$</th>
<th>$\text{K}^+$</th>
<th>$\text{NSSK}^+$</th>
<th>$\text{Mg}^{2+}$</th>
<th>$\text{NSSMg}^{2+}$</th>
<th>$\text{Ca}^{2+}$</th>
<th>$\text{NSSCa}^{2+}$</th>
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<td>DEL (SD)</td>
<td>95</td>
<td>1.5 ± 1.2</td>
<td>14.4 ± 15.2</td>
<td>32.0 ± 34.8</td>
<td>3.0 ± 10.7</td>
<td>2.7 ± 10.6</td>
<td>51.0 ± 74.7</td>
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<td>15.0 ± 11.0</td>
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<td>BAL (SD)</td>
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</tr>
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<td>VAR (SD)</td>
<td>71</td>
<td>20.6 ± 13.2</td>
<td>21.5 ± 23.5</td>
<td>2.8 ± 2.1</td>
<td>38.3 ± 41.0</td>
<td>30.9 ± 40.5</td>
<td>10.3 ± 15.3</td>
</tr>
<tr>
<td>Mean (SD)</td>
<td>687</td>
<td>29.0 ± 8.4</td>
<td>29.6 ± 6.9</td>
<td>4.04 ± 1.7</td>
<td>53.0 ± 14.5</td>
<td>49.8 ± 15.1</td>
<td>27.0 ± 13.1</td>
</tr>
</tbody>
</table>
sodium ion as the reference element (Singh et al., 2007a) and assuming that all of the sodium is derived from sea salt (Keene et al., 1986), the equation for the non-sea salt contribution can be written as

\[
[NSS-X] = [X_i] - [Na^+] \left( \frac{[X]_{sea salt}}{[Na^+]} \right)
\]

(2)

where \([NNS-X]\) is the concentration of non-sea salt concentration of species \(X\) in sample i, \([X_i]\) is the total concentration of species \(X\) in sample i, \([Na^+]\) is the concentration of Na\(^+\) in sample i, and \([X]/[Na^+]_{sea salt}\) is ratio of these species as measured in seawater (Goldberg, 1963).

The dominant ionic species were \(Ca^{2+}\) (106 µeq L\(^{-1}\)) followed by \(SO_{4}^{2-}\) (52 µeq L\(^{-1}\)), \(Mg^{2+}\) (51 µeq L\(^{-1}\)), and \(NO_3^-\) (29 µeq L\(^{-1}\)). The ionic concentrations followed the sequence \(Ca^{2+} > SO_{4}^{2-} > Mg^{2+} > NO_3^- > Cl^- > NH_4^+ > HCO_3^- > Na^+ > K^+\) and \(F^-\). These values are similar to other environments where the chemical species concentrations are high (Kulshrestha et al., 2003, 2005; Mouli et al., 2005; Tiwari et al., 2007, 2012; Bisht et al., 2015; references therein). The overall contributions of cations and anions to the ionic strength were 60% and 40%, respectively, indicated therein. The overall contributions of cations and anions to the ionic strength were 60% and 40%, respectively, indicated therein. The overall contributions of cations and anions to the ionic strength were 60% and 40%, respectively, indicated therein. The overall contributions of cations and anions to the ionic strength were 60% and 40%, respectively, indicated therein.

After China and USA, India is the third-largest global producer of coal. The contribution of coal in power generation in India is ~66% which produces huge emissions of \(SO_2\) in the regional environment (https://www.coalindia.in/en-us/company/aboutus.aspx). Also, coal is burned extensively to produce bricks in India. In Sec 3.1, it was found that only ~16% events of rain were acidic, it may be due to the impact of burning of coal in this regional environment which is used for man-made activities. The measured chemical species were also separated between acidic and non-acidic rain events. The sums of ions for acidic and non-acidic samples during the study period were 246.1 and 431.0 µeq L\(^{-1}\), respectively, which indicate that high loading particles during non-acidic rainy period. During the acidic events, the anions (55%) dominated the cations (45%) in terms of the fraction of ions present in the samples. In the case of the non-acidic events, 38% of the ions were anions while 62% were cations. Sulfate was around 19% higher in acidic events compared to the basic rain events. However, there were no large differences in the nitrate concentrations in both cases. This result indicated the impact of sulfur on precipitation. \(SO_{4}^{2-}\) and \(NO_3^-\) were highest at DEL. It may be caused by local industrial emissions. The \(NO_3^-\) concentrations were observed higher after a temporal break between the rain events (dry period).

For the more basic rain events, the concentrations of \(Ca^{2+}\) and \(Mg^{2+}\) concentrations were approximately three times higher and \(NH_4^+\) about two times higher than in the acidic events. High variability was observed for the bicarbonate ion that was ~15 times higher for the more basic rain events. Also, large differences were seen in the sum of anions and cations for the acidic and non-acidic samples. The acidic species were 22% higher during acidic events whereas cations were 39% higher in non-acid rain.

The elevated \(Ca^{2+}\) over IGP region can be attributed to the calcareous soil aerosolized into the atmosphere and washed out into the rain. Some of the dust is transported from the Thar Desert located in western India (Srivastava et al., 2014). The highest concentrations of \(Ca^{2+}\) (199 µeq L\(^{-1}\)) and \(Mg^{2+}\) (102 µeq L\(^{-1}\)) were recorded at GOR and the lowest were measured at VAR (55 and 11 µeq L\(^{-1}\), respectively). \(SO_{4}^{2-}\) and \(NO_3^-\) were also highest at GOR (79 and 45 µeq L\(^{-1}\), respectively) and lowest at VAR (38 and 22 µeq L\(^{-1}\), respectively). Higher concentrations of \(Ca^{2+}\), \(Mg^{2+}\), \(SO_4^{2-}\), and \(NO_3^-\) at GOR may arise from major sources in the Gorakhpur Industrial Development Area (GIDA) and from the large cement industries located at Lumbini, Nepal around 100 km north of the Gorakhpur. The low concentrations of ions at VAR may be the result of the sampling site which is located at Banaras Hindu University adjacent to the Ganga River surrounded by vegetation (Singh et al., 2007a). The second largest \(Ca^{2+}\) concentration (120.2 µeq L\(^{-1}\)) was observed at KUR, located near the Thar Desert. Northern India is regularly affected by windblown dust from this desert. High concentrations of \(Ca^{2+}\) have been found in the rainwater collected in the initial stages of an event suggesting rapid below-cloud scavenging of coarse calcium-containing particles (Chate et al., 2011). \(Ca^{2+}\) concentrations could also be associated with suspended road dust and cement production (Sanusi et al., 1996).

The mean concentrations of \(Ca^{2+}\) and \(SO_{4}^{2-}\) were compared with other inland studies reported in India. It was found that \(Ca^{2+}\) (106 µeq L\(^{-1}\)) and \(SO_{4}^{2-}\) (52 µeq L\(^{-1}\)) were lower at Tirupati (157 and 135 µeq L\(^{-1}\)) (Mouli et al., 2005) and Gopalpur, U.P. (134 and 15 µeq L\(^{-1}\)) (Satsangi et al., 1998) and higher at Panipat, Haryana (75 and 95 µeq L\(^{-1}\)) (Tiwari et al., 2007), Dhanbad: (70 and 63 µeq L\(^{-1}\)) (Singh et al., 2007), Ahmadabad (78 and 50 µeq L\(^{-1}\)) (Rastogi and Sarin, 2000), Varanasi, U.P. (67.1 and 37.0 µeq L\(^{-1}\)) (Bisht et al., 2015), Ballia, U.P. (41 and 33 µeq L\(^{-1}\)) (Tiwari et al., 2006). In another study, Pandey and Singh (2012) reported that the concentrations of major ions (VWM) over Varanasi were much lower than reported here with \(Ca^{2+}\) ranging from 11.6 to 41.6 µeq L\(^{-1}\) and \(SO_{4}^{2-}\) from 4.7 to 25.2 µeq L\(^{-1}\). Kulshreshtha et al. (2005) reported high concentrations (30–70 µeq L\(^{-1}\)) of ammonium over the entire IGP region as well as higher \(SO_{4}^{2-}\) (~70 µeq L\(^{-1}\)) and \(NO_3^-\) (~35 µeq L\(^{-1}\)) in the western part of the IGP. In a study over Lucknow (Singh et al., 2007) in the central IGP region, high concentrations of \(SO_{4}^{2-}\) (104.2 µeq L\(^{-1}\)) and \(Ca^{2+}\) (264.4 µeq L\(^{-1}\)) were observed.

**Inter-Annual Variability of Wet Deposition Flux**

The annual wet deposition (WD) flux is calculated by multiplying the value if mean (VWM) concentrations (mg L\(^{-1}\)) by the annual mean rainfall (RF) amounts in mm according to the following expression.
Table 2. Water soluble annual ionic depositions (kg·ha⁻¹·y⁻¹) in rainwater during southwest summer monsoon of 2009, 2010 and 2011 over IGP.

<table>
<thead>
<tr>
<th>Species</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>F⁻</td>
<td>0.5</td>
<td>0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.6</td>
<td>1.4</td>
<td>1.2</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>1.5</td>
<td>3.7</td>
<td>2.9</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.6</td>
<td>2.7</td>
<td>2.0</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Na⁺</td>
<td>2.7</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>K⁺</td>
<td>2.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>1.7</td>
<td>2.4</td>
<td>2.6</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.3</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.1</td>
<td>0.6</td>
<td>0.9</td>
</tr>
<tr>
<td>Rainfall (mm)</td>
<td>975</td>
<td>1426</td>
<td>1292</td>
</tr>
</tbody>
</table>

The estimated annual wet deposition (WD) fluxes for ionic species from 2009 to 2011 are presented in Table 2 and varied from year to year due to the different precipitation amounts in each year. Generally, the WD fluxes were higher for acidic species such as sulfate and nitrate when the precipitation amount increased. However, the opposite occurred when the precipitation amount decreased, and the alkaline species WD fluxes increased. The year-to-year variation in the annual WD fluxes of total measured ions were in the order of 125.5, 116.4 and 60.7 kg·ha⁻¹·y⁻¹ and their corresponding averaged annual rainfall amounts were 1426, 1292 and 975 mm for 2010, 2011, and 2009, respectively. Large differences in the annual deposition fluxes of anions to cations were obtained. There were 19%, 74%, and 18% higher anions than cations during 2009, 2010, and 2011, respectively.

The highest deposition fluxes were for sulfate (25.2 kg·ha⁻¹·y⁻¹) and nitrate (18.3 kg·ha⁻¹·y⁻¹) (Fig. 4). Kulshrestha et al. (2003) reported that the annual wet deposition fluxes were highest for Ca²⁺ at an urban site of south-central India and very similar values were observed in other parts of India (Jain et al., 2000). The largest WD fluxes were at GOR (sulfate; 40.8 kg·ha⁻¹·y⁻¹ and nitrate: 30.2 kg·ha⁻¹·y⁻¹) and the second largest were at KUR (sulfate: 28.4 kg·ha⁻¹·y⁻¹ and nitrate: 18.7 kg·ha⁻¹·y⁻¹). In both locations, anthropogenic emission sources such as power plants, sugar mills, refineries, and stone crushing units etc. are affecting the WD fluxes. Over the entire IGP region, the mean annual WD ion mass flux during the study period was 94.6 kg·ha⁻¹·y⁻¹ with the sulfate having the highest deposition flux (25.2 kg·ha⁻¹·y⁻¹) with the lowest being fluoride (0.8 kg·ha⁻¹·y⁻¹).

Neutralizing Factors

Neutralization is due to the alkaline species including Ca²⁺, Mg²⁺, NH₄⁺, and K⁺ that mostly derive from natural sources as soil dust, ammonia release from animal wastes and wastewater treatment, and biomass burning, respectively. The neutralizing potential of any component in the rainwater can be expressed as the neutralization factor (NF) (Possanzini et al., 1988; Kulshrestha et al., 1995). The NF values are calculated as follows (Eq. (4)):

\[
\begin{align*}
[\text{NF}_{Ca^{2+}}] &= \frac{[\text{nssCa}^{2+}]}{[\text{NO}_3^-]+[\text{nssSO}_4^{2-}]} \\
[\text{NF}_{Mg^{2+}}] &= \frac{[\text{nssMg}^{2+}]}{[\text{NO}_3^-]+[\text{nssSO}_4^{2-}]} \\
[\text{NF}_{NH_4^+}] &= \frac{[\text{NH}_4^+]}{[\text{NO}_3^-]+[\text{nssSO}_4^{2-}]} \\
[\text{NF}_{K^+}] &= \frac{[\text{nssK}^+]}{[\text{NO}_3^-]+[\text{nssSO}_4^{2-}]} 
\end{align*}
\]
The non-sea-salt fractions (F_{nss}) of any particular component were estimated using Eq. (2). The values are presented as a function of location in Tables 1(a) and 1(b). The F_{nss} was in order of Ca^{2+} (99%) > SO_4^{2–} (96%) > K^+ (94%) > Mg^{2+} (92%) and Cl^– (28%) appear to be of non-marine origin during the study period, however, the rest of the fraction may be sea salt fraction (F_{ss}) and was in the order of Cl^– (72%) > Mg^{2+} (8%) > K^+ (6%) > SO_4^{2–} (4%) and Ca^{2+} (< 1%). Earlier studies in Indian subcontinent reported the high non-marine contributions (Rastogi and Sarin, 2005; Tiwari et al., 2007; Das et al., 2010; Gobre et al., 2010; Tiwari et al., 2012).

During the study period, the NF values for Ca^{2+}, Mg^{2+}, NH_4^+, and K^+ over IGP region were calculated to be 57, 25, 15, and 4% of the contribution to the neutralization process, respectively, indicating that these species play vital role in neutralizing the acidity in rainwater (Table 4). Given these high concentrations of alkaline constituents an insignificant correlation was found between the H^+ ion and acidic species (NO_3^– and SO_4^{2–}) concentrations at all of the sites. In addition, significant correlations among Ca^{2+} and SO_4^{2–} (r = 0.63), and NO_3^– (r = 0.60) indicate the presence of alkaline dust particles being scavenged by the precipitation droplets. Galy-Lacaux et al. (2001) argued that this capture could be complete and could explain the neutralization of the rain’s potential acidity. There have been a number of observations of alkaline soil influencing rain chemistry (e.g., Avila, 1998; Hu et al., 2003, Kulshrestha et al., 2003). Neutralization of acidity in rainwater can be due to gaseous ammonia or particulate CaCO_3 (Al-Momani et al., 1995, 2003; Al-Khashman, 2009).

The NF values were estimated for each location (Table 4). It was found that Ca^{2+} was the dominant neutralizing ion at all locations. Mg^{2+} was the second largest except at two locations, Kanpur and Varanasi, whereas ammonia was the second largest with values ranging from 0.81 (MAN) to 1.47 (BAL). These results indicate that the crustal component especially Ca^{2+} and Mg^{2+} neutralize the rainwater acidity (82%) over IGP region. The contribution of NH_4^+ in neutralizing the rain was ~15%, similar to those reported previously in India (Kulshrestha et al., 2005; Tiwari et al., 2012). The neutralization contribution of K^+ was generally low (4%) but higher (7%) at the high altitude (MAN) and rural (BAL) locations.

This order of neutralization (Ca^{2+} > Mg^{2+} > NH_4^+ > K^+) is in agreement with the report of Budhavant et al. (2011) for Pune, India. Most of the Indian studies reported that Ca^{2+}, Mg^{2+} and NH_4^+ are the major neutralizing components (Saxena et al., 1991; Parashar et al., 1996; Kulshrestha et al., 2003; Das et al., 2005; Rastogi and Sarin, 2005; Budhavant et al., 2009; Tiwari et al., 2012).

To understand the relative contributions of sulfuric and nitric acid to total acidity (Chate and Devara, 2009), the ratios (H^+/\text{NO}_3^– + \text{SO}_4^{2–}), (\text{NO}_3^– + \text{Cl}^–)/(\text{SO}_4^{2–}), (\text{Ca}^{2+} + \text{NH}_4^+)/\text{NO}_3^– + \text{SO}_4^{2–}, \text{NO}_3^–/\text{SO}_4^{2–}, \text{NH}_4^+/\text{NO}_3^– and \text{NH}_4^+/\text{SO}_4^{2–} \text{ were calculated} (Table 3). The average H^+/\text{NO}_3^– + \text{SO}_4^{2–} ratio was 0.02 varying from 0.01 (BALL) to 0.04 (VAR) indicating that on average, ~98% of the inorganic acidity in rainwater was neutralized. Tiwari, et al. (2012) reported that 96% of the acidity in rainwater was neutralized over the western Himalayan region.

The ratios between ([\text{NO}_3^– + \text{Cl}^–]) and (\text{SO}_4^{2–}) was 1.14 varied from 0.81 (DEL) to 1.47 (BAL). Higher ratios were found at MAN (1.35) and BAL (1.47) indicating that nitric and hydrochloric acid contributed substantially to the rainfall acidity. Alternatively, at KUR, GOR, MEE, and KAN, this ratio was approximately unity. At DEL, the value was much lower (0.81) than any other sampling locations indicating the influence of SO_3 and sulfuric acid (Singh et al., 2007) from local industrial emissions. The ratios (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{NH}_4^+)/\text{NO}_3^– + \text{SO}_4^{2–} < 1.0 (mean: 2.21) along with significant correlation (0.66) in between indicate that Ca^{2+}, Mg^{2+} and NH_4^+ ions played the major role in neutralizing the acidity (Chate et al., 2004; Tiwari et al., 2012). However, Singh et al. (2007) reported a ratio < 1.0 for \text{K}^{+}/\text{NO}_3^– + \text{SO}_4^{2–} with values ranging from 0.42 to 5.13 at Dhanbad, a coal producing city. The mean ratio of SO_4^{2–}/\text{NO}_3^– value over the sites was 1.81 varying between 1.31 (MAN) to 2.18 (DEL) suggesting that the contribution to the acidity in rainwater was about 57% due

| Table 3. Ionic ratios among measured ions over IGP region. |
|-----------------|---|---|---|---|---|---|---|---|
| Ratios                  | DEL | MAN | KUR | MEE | KAN | GOR | BAL | VAR | Mean |
| H^+/\text{NO}_3^– + \text{SO}_4^{2–} | 0.02 | 0.03 | 0.03 | 0.03 | 0.02 | 0.03 | 0.01 | 0.04 | 0.02 |
| \text{SO}_4^{2–}/\text{NO}_3^– | 2.18 | 1.31 | 1.99 | 1.96 | 1.74 | 1.74 | 1.53 | 2.02 | 1.81 |
| \text{NH}_4^+/\text{NO}_3^– | 1.07 | 0.28 | 0.97 | 0.97 | 1.28 | 1.07 | 1.13 | 0.83 | 0.95 |
| \text{NH}_4^+/\text{SO}_4^{2–} | 0.49 | 0.22 | 0.49 | 0.50 | 0.74 | 0.61 | 0.74 | 0.41 | 0.52 |
| (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{NH}_4^+)/\text{NO}_3^– + \text{SO}_4^{2–} | 2.01 | 2.29 | 2.47 | 2.06 | 1.61 | 2.83 | 2.93 | 1.52 | 2.21 |
| (\text{NO}_3^– + \text{Cl}^–)/\text{SO}_4^{2–} | 0.81 | 1.35 | 1.01 | 0.98 | 1.21 | 1.17 | 1.47 | 1.09 | 1.14 |
| (\text{NO}_3^– + \text{SO}_4^{2–})/(\text{Ca}^{2+} + \text{Mg}^{2+}) | 0.60 | 0.46 | 0.47 | 0.58 | 0.88 | 0.41 | 0.40 | 0.81 | 0.57 |

| Table 4. Location wise neutralization factor (NF in %) of Ca^{2+}, Mg^{2+}, NH_4^+, and K^+ in rainwater over the IGP. |
|-----------------|---|---|---|---|---|---|---|---|---|
| NF Ca^{2+}      | 56.5 | 61.1 | 54.0 | 53.4 | 61.6 | 57.0 | 51.3 | 65.2 | 56.8 |
| NF NH_4^+       | 16.9 | 5.1  | 13.2 | 15.9 | 29.8 | 13.9 | 14.6 | 17.8 | 15.1 |
| NF Mg^{2+}      | 25.2 | 27.1 | 31.7 | 28.3 | 6.7  | 27.7 | 27.5 | 10.8 | 24.6 |
| NF K^+          | 1.4  | 6.7  | 1.1  | 2.4  | 1.9  | 1.5  | 6.6  | 6.2  | 3.5  |
to sulfuric acid and 43% from nitric acid. The high influence of sulfur at DEL was due to urban industrial activities and vehicular emission. MAN is a tourist location with mostly vehicular emission of NOx. The relative contributions of the ions to the acidiity of rainwater were variable for event to event and location to location. Earlier studies reported the contributions of H2SO4 and HNO3 in rainwater were between 60–70% and 30–40%, respectively (Al-Khashman, 2009; Tiwari et al., 2012). The ratios NH4+/NO3− and NH4+/SO42− were 0.95 and varied from 0.28 (MAN) to 1.28 (KAN) and 0.52 varied 0.22 (MAN) to 0.74 (BAL), respectively.

**Identification of Possible Sources of Measured Ionic Constituents**

Receptor models are generally used to quantify source contributions that affect the any mass concentration of particle which present into the atmosphere by using selective particles’ macro ensembles properties. Positive Matrix Factorization (PMF) is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices: factor contributions and profiles (Paatero, 1997; Paatero et al., 2002; Kandlikar, 2007). Factor analysis has been applied to wet deposition composition data by Zeng and Hopke (1989), Junto and Paatero (2004) and Anttila et al. (2005). The analyzed chemical species (mean) in rainwater from different locations over IGP region during 2009 to 2011 were presented in Fig. 3 and their event data were used for the PMF study using Positive Matrix Factorization (EPA PMF V 5.0.14). Anttila et al. (1995) suggested an approach and values to estimate the uncertainty values, σij, as follows.

\[
\sigma_{ij} = \sqrt{e_i^2 + (d_j x_j)^2}
\]  

(5)

where \(x_j\) is the concentration of species j in sample i, \(e_i\) is the detection limit for the species j and \(d_j\) is a proportional measurement error using the values in Anttila et al. (1995).

EPA PMF 5.0 was run on the data from all of the sites without increasing the uncertainty values and all of the variables had high enough signal to noise ratios to be assigned as strong variables. Although the sites cover a wide geographical space, it is anticipated that similar source types will contribute to the species observed in the precipitation samples across the monitored domain. The variability in the strengths of these source types in the different locations should assist the PMF analysis in resolving the major source types. The PMF analysis was run for 4 to 7 factors. Five factors provided good fits to the data based on the scaled residuals and physically interpretable source profiles. Because there is no obvious total variable in these analyses, the profiles could not be normalized such as it is typically done using PM mass concentrations. The unnormalized profiles are provided in Fig. 5.

Factor 1 has the high concentrations of species of SO4²⁻ (3 × 10³ µeq cm⁻²), NO3⁻ (1 × 10³ µeq cm⁻²), NH4⁺ (9 × 10² µeq cm⁻²) and F⁻ (1 × 10² µeq cm⁻²) were observed. This factor explained most of the NH4⁺ variation (98.6%) and a substantial part of the F⁻ (57.8%) (Table 5). The major sources of ammonium in this region are anaerobic digestion of animal and human wastes that are spread on open fields as well as fertilizer applications (Galy-lacaux and Modi, 1998; Laouali et al., 2012). In rural environments, farmers generally used diesel pumps and tractors to farm paddy crops (rice) during the monsoon that would be sources of SO2 and NOx. Diesel fuels in India have high sulfur concentrations (350 ppm) under Bharat Stage III regulations. In the same factor, higher contribution of F⁻ is likely due to the burning of coal which is used for making bricks and coal-based thermal power plants.

In factor 2, both contributions (81% and 78%) and concentrations of Na⁺ and Cl⁻ in the rainwater were high clearly represents sea salt. Sea salt over this region arrived from the Arabian Sea. It can serve as effective cloud condensation nuclei and thus, appears in the precipitation. The ratio between Cl⁻ and Na⁺ was 1.15 which is 9% lower than the ratio of sea water (Goldberg, 1963). This result indicates displacement of chlorine from the sea salt particles primarily by nitrate.

Factor 3 has high concentrations of Mg²⁺ and Ca²⁺. Its presence in rain was due to the scavenging of local calcareous soil and particles release from limestone mines and cement manufacturing facilities across the region. Both of these cations contribute significantly to the observed neutralization (Migliavacca et al., 2005; Tiwari et al., 2012).

Factor 4 has K⁺ as the highest concentration species (7 × 10² 3 × 10³ µeq cm⁻²). This factor explains ~98% of the K⁺ indicating its major source is biomass burning. During the onset of monsoon, the farmers burn crops residue in the field (Awasti et al., 2011; Kaskaoutis et al., 2014) and agricultural burning is the major source of potassium over this region (Srivastava et al., 2012). Kulshrestha et al. (2003) reported high loadings of potassium in rainwater due to emission from vehicular emission and agricultural tillage practices.

Factor 5 has high concentrations of SO4²⁻ and Ca²⁺ with some NO3⁻. The major sources of SO4²⁻ and NO3⁻ are oxidation of SO2 and NO2 from combustion sources. This factor represents the additional heterogeneous oxidation of SO2 and NO2 that can occur in droplets containing neutralizing components like Ca²⁺. The higher pH of these droplets permits more oxidation by ozone (Seinfeld and Pandis, 2006) as well as permitting more dissolution of the gaseous species into the droplet. Ghude et al. (2008) reported a significant increase in emission of surface NO2 over IGP region was from thermal power plants and coal-burning industries that would also be sources of SO2. In addition to this, the NO emissions from motor vehicles particularly diesel powered will be substantial in urban areas and from diesel powered tractors and pumps in rural areas.

**SUMMARY**

The present study summarizes the results of systematic monitoring of individual precipitation events during the monsoon of 2009 to 2011 over IGP regions. The weighted mean pH and specific conductivity of rainwater were 5.73 ±
Fig. 5. PMF extracted source profile of chemical constituents in rainwater collected over IGP region during the southwest summer monsoon of 2009–2011.

0.17 and 31.6 ± 31.0 µS cm−1, respectively with 16% samples were observed acidic (mean pH = 5.38 of acidic rain: H+ = 5.38 µeq L−1). The contribution of SO42− and NO3− to the acidic rain samples were 69 and 31% respectively. The specific conductivity was ~39% lower (20.6 µS cm−1) in acidic rain as compared to the alkaline (33.6 µS cm−1) rain, due to the higher concentration of acidic species. The sums of ions for acidic and non-acidic samples were 246.1 and 431.0 µeq L−1, respectively, with mean (351.6 ± 130.1 µeq L−1) indicates that high loading alkaline particles during non acidic rain. The mean value of SO42− and NO3− are 52 and 29 µeq L−1 respectively which are approximately five and
Table 5. Factor Profiles (% of species sum) of source species measured in rainwater obtained from output from EPA PMF V5.0.

<table>
<thead>
<tr>
<th>Species Factor</th>
<th>Factor - 1</th>
<th>Factor - 2</th>
<th>Factor - 3</th>
<th>Factor - 4</th>
<th>Factor - 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>57.8</td>
<td>38.3</td>
<td>1.2</td>
<td>0.0</td>
<td>2.7</td>
</tr>
<tr>
<td>Cl–</td>
<td>0.6</td>
<td>78.4</td>
<td>13.4</td>
<td>4.6</td>
<td>3.0</td>
</tr>
<tr>
<td>SO4$_2$–</td>
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<td>3.5</td>
<td>0.6</td>
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<td>Na+</td>
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<td>13.6</td>
<td>5.4</td>
<td>0.0</td>
</tr>
<tr>
<td>K+</td>
<td>2.2</td>
<td>0.0</td>
<td>0.0</td>
<td>97.8</td>
<td>0.0</td>
</tr>
<tr>
<td>Ca2+</td>
<td>0.0</td>
<td>0.0</td>
<td>43.0</td>
<td>0.0</td>
<td>57.0</td>
</tr>
<tr>
<td>Mg2+</td>
<td>6.2</td>
<td>0.0</td>
<td>93.6</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>NH4+</td>
<td>98.6</td>
<td>0.0</td>
<td>1.4</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Possible sources: Burning of coal & Urine excretion & Fertilizers use, Marine contribution, Soil dust, Biomass burning, Fossil fuels & re-suspension of soil dust.

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