



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

Suresh Tiwari^{1,2†}, Philip K. Hopke^{2*}, Devraj Thimmaiah², Umesh C. Dumka³, Atui K. Srivastava¹, Deewan S. Bisht¹, Pasumarti S.P. Rao⁴, Dilip M. Chate⁴, Manoj K. Srivastava⁵, Sachchida N. Tripathi⁶

¹ Indian Institute of Tropical Meteorology, New Delhi-110 060, India

² Clarkson University, Box 5708, Potsdam, NY-13699-5708, USA

³ Aryabhata Research Institute of Observational Science, Nainital-263 001, India

⁴ Indian Institute of Tropical Meteorology, Pune-411 008, India

⁵ Department of Geophysics, Banaras Hindu University, Varanasi-221 005, India

⁶ Department of Civil Engineering, Indian Institute of Technology Kanpur-208016, India

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_4^{2-} and NO_3^-) were measured along with the other major ions (F^- , Cl^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} and NH_4^+) and pH and specific conductivity. The weighted mean pH (\pm std) and conductivity of rainwater were 5.73 (\pm 0.17) and 31.6 (\pm 31.0) $\mu\text{S cm}^{-1}$, 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 $\mu\text{S cm}^{-1}$) for the acidic rain compared to the more basic (33.6 $\mu\text{S cm}^{-1}$) samples. The mean sum of all of the measured ions is $351.6 \pm 130.1 \mu\text{eq L}^{-1}$ with the highest contributions being Ca^{2+} (30%) and SO_4^{2-} (15%). Mean [SO_4^{2-}] (52 $\mu\text{eq L}^{-1}$) and [NO_3^-] (29 $\mu\text{eq L}^{-1}$) were approximately five and ten times higher, respectively, compared to background hemispheric values. Secondary ions had the highest deposition fluxes (SO_4^{2-} : 25.2 $\text{kg ha}^{-1} \text{y}^{-1}$ and NO_3^- : 18.3 $\text{kg ha}^{-1} \text{y}^{-1}$). The mean ratio of $\text{H}^+ / (\text{NO}_3^- + \text{SO}_4^{2-})$ was 0.02 indicating ~98% of the acidity was neutralized. Ca^{2+} , (57%), Mg^{2+} (25%), NH_4^+ (15%) and K^+ (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_2 at 400 ppm (Seinfeld and Pandis, 2006). Acid precipitation is a global environmental issue (Rodhe *et al.*, 2002) because

* Corresponding author.

Tel.: 001-315 268 3861

E-mail address: phopke@clarkson.edu

† Corresponding author.

Tel.: 0091-11-28743976

E-mail address: smbtiwari@tropmet.res.in

of its transboundary impact on the biogeochemical cycles. Increasing SO₂ and NO_x (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 cloud 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; Budhavant et al., 2009; Safai et al., 2010; Shukla and Sharma, 2010; Budhavant et al., 2011; Das et al., 2011; Salve et al., 2011; Tiwari et al., 2011, 2012; Budhavant et al., 2014; references therein). However, there have been no systematic, long-term measurements of rainwater chemistry have been made over Indo 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; Shukla 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

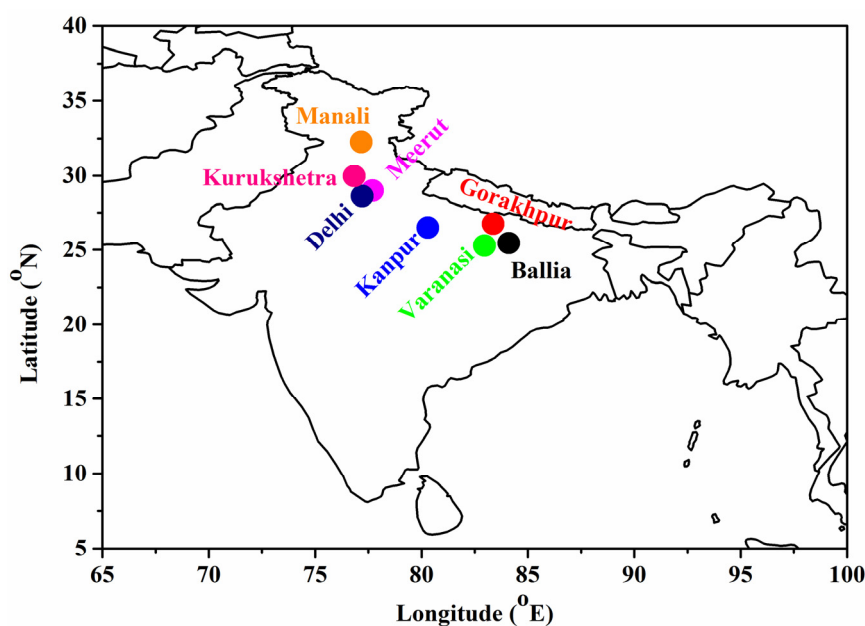


Fig. 1. Geographical locations of sampling sites (Ballia: 25°44'N, 84°11'E, 64 m a.s.l.; Gorakhpur: 26°45'N, 83°24'E, 78 m a.s.l.; Varanasi: 25°22'N, 83°00'E, 76 m a.s.l.; Kanpur: 26°28'N, 80°20'E, 126 m a.s.l.; Meerut: 28°59'N, 77°42' E, 219 m a.s.l.; New Delhi: 28°37'N, 77°12'E, ~250 m a.s.l.; Kurukshetra: 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^- , NO_3^- and SO_4^{2-}) and cations (NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+}) 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 triple 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 $\mu eq L^{-1}$ for Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+} , 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 ($C_2O_4^-$), 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 ($\mu eq L^{-1}$) of acetate and formate in rainwater. In the present study, the bicarbonate (HCO_3^-) 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 $\sim 351.6 \pm 130 \mu eq L^{-1}$ that is in the typically observed range of 100–500 $\mu eq L^{-1}$ (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 rainwater 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: $H^+ = 5.38 \mu\text{eq L}^{-1}$) and rest of the samples were more basic than “acid rain.” The specific conductivity was also measured and was ~39% ($20.6 \mu\text{S cm}^{-1}$) lower specific conductivity for the acid rain samples when compared to the non-acidic rain ($33.6 \mu\text{S cm}^{-1}$) 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 $31.6 \pm 31.1 \mu\text{S cm}^{-1}$ varying from $3.2 \mu\text{S cm}^{-1}$ to $288.0 \mu\text{S cm}^{-1}$. 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 $43.6 \mu\text{S cm}^{-1}$. The mean specific conductivity over IGP region is much higher than that reported by IMD (1982) in rainwater at 10 background locations in India ($5\text{--}57 \mu\text{S cm}^{-1}$). 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; Chate 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 $28.9 \mu\text{S cm}^{-1}$ (2009) to $30.9 \mu\text{S cm}^{-1}$ (2010) to $35.1 \mu\text{S cm}^{-1}$ (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) $\mu\text{eq L}^{-1}$ indicating the direct impact of measured ions on specific conductivity during study period. Anatolaki, and Tsitouridou (2009) reported higher conductivity ($44\mu\text{S cm}^{-1}$ varied from $7.50\text{--}439 \mu\text{S cm}^{-1}$) 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

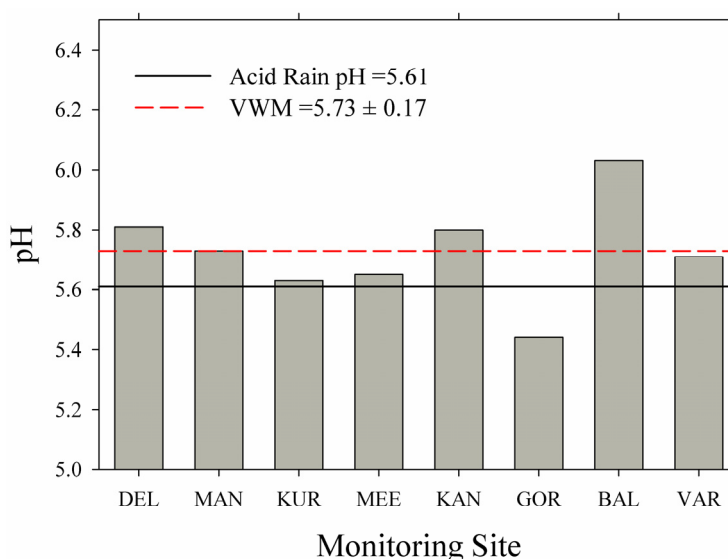


Fig. 2. Mean pH values over the IGP region.

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 $351.6 \pm 130.1 \mu\text{eq L}^{-1}$

indicating high atmospheric pollution concentrations over the IGP region. The annual VWM of ionic constituents over IGP region rainwater have been calculated as:

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

where C_i is the ionic concentration for each element in $\mu\text{eq L}^{-1}$, 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 ($\mu\text{eq L}^{-1}$) 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

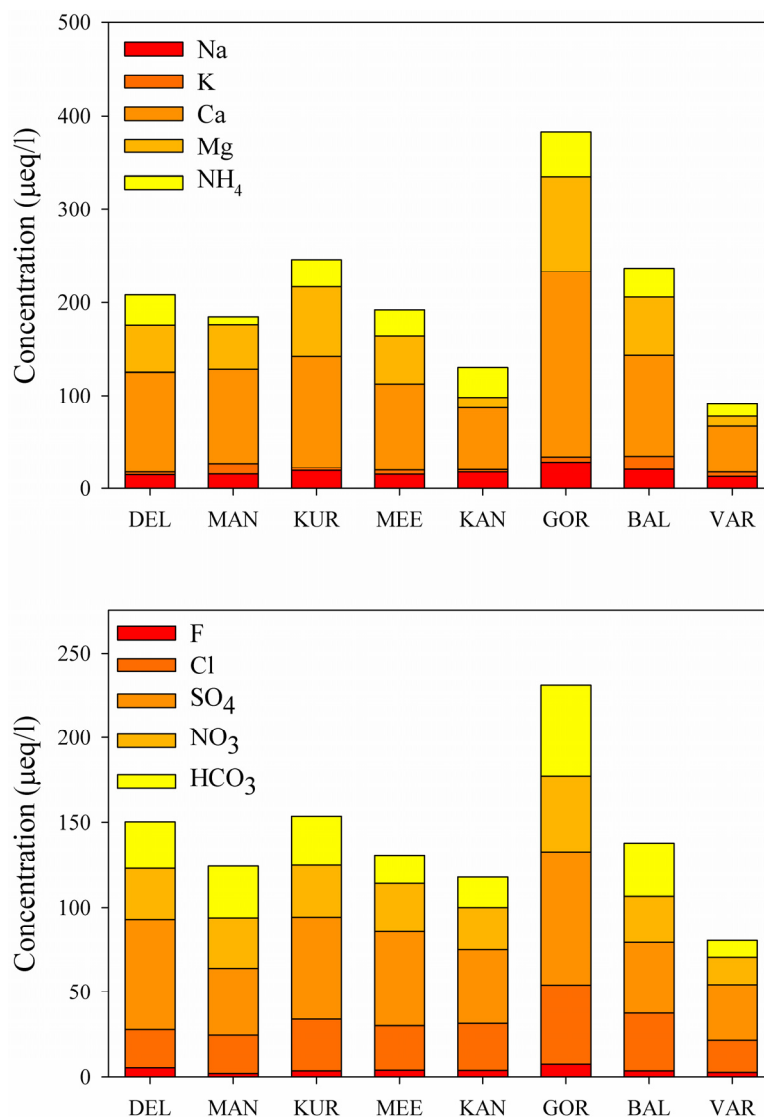


Fig. 3. Water soluble chemical species ($\mu\text{eq L}^{-1}$) in rainwater at eight monitoring locations over IGP region during the southwest summer monsoon of 2009–2011.

Table 1(a). Water soluble cations ($\mu\text{eq L}^{-1}$) in rainwater at eight monitoring locations over IGP region during southwest summer monsoons from 2009 to 2011, where N = number of samples and nss = non sea salt.

| Site | N | H ⁺ | Na ⁺ | NH ₄ ⁺ | K ⁺ | nssK ⁺ | Mg ²⁺ | nssMg ²⁺ | Ca ²⁺ | nssCa ²⁺ |
|-----------|-----|----------------|-----------------|------------------------------|----------------|-------------------|------------------|---------------------|------------------|---------------------|
| DEL (SD) | 95 | 1.5 ± 1.2 | 14.4 ± 15.2 | 32.0 ± 34.8 | 3.0 ± 10.7 | 2.7 ± 10.6 | 51.0 ± 74.7 | 47.7 ± 72.8 | 107.7 ± 148.9 | 107.1 ± 148.4 |
| MAN (SD) | 79 | 1.9 ± 1.8 | 15.1 ± 7.9 | 8.4 ± 11.7 | 11.3 ± 10.0 | 11.0 ± 9.9 | 48.3 ± 70.2 | 44.8 ± 70.0 | 101.7 ± 106.2 | 101.0 ± 106.1 |
| KUR (SD) | 73 | 2.3 ± 2.9 | 19.1 ± 18.3 | 29.3 ± 48.3 | 2.8 ± 6.0 | 2.4 ± 5.9 | 74.4 ± 100.9 | 70.0 ± 100.4 | 120.2 ± 164.2 | 119.4 ± 163.7 |
| MEE (SD) | 74 | 2.2 ± 2.3 | 15.0 ± 11.0 | 27.6 ± 40.1 | 4.5 ± 16.3 | 4.2 ± 16.3 | 52.3 ± 49.8 | 48.9 ± 49.3 | 93.0 ± 93.7 | 92.3 ± 93.4 |
| KAN (SD) | 92 | 1.6 ± 1.7 | 17.4 ± 20.1 | 32.0 ± 29.1 | 2.5 ± 5.9 | 2.1 ± 5.8 | 11.13 ± 26.3 | 7.2 ± 22.9 | 67.1 ± 145.9 | 66.3 ± 145.2 |
| GOR (SD) | 135 | 3.6 ± 2.8 | 28.1 ± 13.0 | 48.1 ± 34.0 | 5.7 ± 10.0 | 5.0 ± 9.9 | 102.3 ± 70.3 | 95.9 ± 69.7 | 198.7 ± 159.2 | 197.5 ± 158.9 |
| BAL (SD) | 68 | 0.9 ± 1.6 | 20.3 ± 13.9 | 30.8 ± 39.2 | 14.2 ± 16.0 | 13.8 ± 15.8 | 62.3 ± 42.4 | 57.7 ± 41.2 | 108.8 ± 82.9 | 107.9 ± 82.6 |
| VAR (SD) | 71 | 2.0 ± 6.1 | 13.1 ± 9.8 | 13.6 ± 24.1 | 5.1 ± 8.2 | 4.6 ± 8.2 | 11.3 ± 12.7 | 8.1 ± 11.5 | 51.6 ± 54.7 | 48.8 ± 54.3 |
| Mean (SD) | 687 | 2.0 ± 0.7 | 17.8 ± 4.8 | 28.0 ± 12.4 | 6.1 ± 4.3 | 5.7 ± 4.3 | 52.0 ± 30.4 | 47.6 ± 29.6 | 106.0 ± 43.8 | 105.1 ± 44.1 |

Table 1(b). Water soluble anions ($\mu\text{eq L}^{-1}$) in rainwater at eight monitoring locations over IGP region during southwest summer monsoons from 2009 to 2011, where N = number of samples and nss = non sea salt.

| Site | N | Cl ⁻ | NO ₃ ⁻ | F ⁻ | SO ₄ ²⁻ | nssSO ₄ ²⁻ | HCO ₃ ⁻ |
|-----------|-----|-----------------|------------------------------|----------------|-------------------------------|----------------------------------|-------------------------------|
| DEL (SD) | 95 | 22.8 ± 27.0 | 29.8 ± 32.2 | 5.4 ± 6.4 | 64.9 ± 58.4 | 63.1 ± 57.3 | 27.4 ± 49.6 |
| MAN (SD) | 79 | 22.9 ± 11.6 | 30 ± 24.1 | 2.0 ± 1.2 | 39.2 ± 38.0 | 37.3 ± 37.9 | 30.1 ± 51.9 |
| KUR (SD) | 73 | 30.5 ± 30.7 | 30.2 ± 41.0 | 3.6 ± 2.7 | 60.3 ± 70.8 | 57.9 ± 69.6 | 29.0 ± 79.2 |
| MEE (SD) | 74 | 26.3 ± 17.8 | 28.3 ± 23.9 | 3.9 ± 2.4 | 55.5 ± 38.2 | 53.6 ± 37.5 | 16.6 ± 26.0 |
| KAN (SD) | 92 | 27.7 ± 32.3 | 25.0 ± 56.1 | 3.8 ± 2.5 | 43.5 ± 84.3 | 41.3 ± 82.4 | 17.7 ± 32.5 |
| GOR (SD) | 135 | 46.6 ± 20.9 | 45.0 ± 28.8 | 7.4 ± 6.2 | 78.5 ± 49.4 | 75.0 ± 48.2 | 53.4 ± 39.8 |
| BAL (SD) | 68 | 34.1 ± 20.6 | 27.2 ± 20.0 | 3.5 ± 2.0 | 41.8 ± 26.2 | 39.2 ± 25.3 | 31.6 ± 26.6 |
| VAR (SD) | 71 | 20.6 ± 13.2 | 21.5 ± 23.5 | 2.8 ± 2.1 | 38.3 ± 41.0 | 30.9 ± 40.5 | 10.3 ± 15.3 |
| Mean (SD) | | 29.0 ± 8.4 | 29.6 ± 6.9 | 4.04 ± 1.7 | 53.0 ± 14.5 | 49.8 ± 15.1 | 27.0 ± 13.1 |

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

$$[\text{NSS} - X]_i = [X_i] - [\text{Na}^+]_i \left[\frac{[X]}{[\text{Na}^+]} \right]_{\text{sea salt}} \quad (2)$$

where $[\text{NSS} - X]_i$ 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, $[\text{Na}^+]_i$ is the concentration of Na^+ in sample i, and $\left\{ \frac{[X]}{[\text{Na}^+]} \right\}_{\text{sea salt}}$ is ratio of these species as measured in seawater (Goldberg, 1963).

The dominant ionic species were Ca^{2+} ($106 \mu\text{eq L}^{-1}$) followed by SO_4^{2-} ($52 \mu\text{eq L}^{-1}$), Mg^{2+} ($51 \mu\text{eq L}^{-1}$), and NO_3^- ($29 \mu\text{eq L}^{-1}$). The ionic concentrations followed the sequence $\text{Ca}^{2+} > \text{SO}_4^{2-} > \text{Mg}^{2+} > \text{NO}_3^- > \text{Cl}^- > \text{NH}_4^+ > \text{HCO}_3^- > \text{Na}^+ > \text{K}^+$ 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 the dominance of alkaline components in rainwater especially Ca^{2+} , Mg^{2+} and NH_4^+ ions. The mean value of SO_4^{2-} is $52 \mu\text{eq L}^{-1}$ and of NO_3^- is $29 \mu\text{eq L}^{-1}$ that were approximately five and ten times higher than the proposed background hemispheric values (10 and $2.8 \mu\text{eq L}^{-1}$) at remote sites, respectively (Galloway *et al.*, 1982; Casimiro *et al.*, 1991).

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 $431.0 \mu\text{eq L}^{-1}$, 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-acid samples. The acidic species were 22% higher during acid 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+} ($199 \mu\text{eq L}^{-1}$) and Mg^{2+} ($102 \mu\text{eq L}^{-1}$) were recorded at GOR and the lowest were measured at VAR (55 and $11 \mu\text{eq L}^{-1}$, respectively). SO_4^{2-} and NO_3^- were also highest at GOR (79 and $45 \mu\text{eq L}^{-1}$, respectively) and lowest at VAR (38 and $22 \mu\text{eq L}^{-1}$, 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 ($120.2 \mu\text{eq L}^{-1}$) 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+} ($106 \mu\text{eq L}^{-1}$), and SO_4^{2-} ($52 \mu\text{eq L}^{-1}$) were lower at Tirupati (157 and $135 \mu\text{eq L}^{-1}$) (Mouli *et al.*, 2005) and Gopalpura, U.P. (134 and $15 \mu\text{eq L}^{-1}$) (Satsangi *et al.*, 1998) and higher at Panipat, Haryana (75 and $95 \mu\text{eq L}^{-1}$) (Tiwari *et al.*, 2007), Dhanbad: (70 and $63 \mu\text{eq L}^{-1}$) (Singh *et al.*, 2007), Ahmedabad (78 and $50 \mu\text{eq L}^{-1}$) (Rastogi and Sarin, 2000), Varanasi, U.P. (67.1 and $37.0 \mu\text{eq L}^{-1}$) (Bisht *et al.*, 2015), Ballia, U.P. (41 and $33 \mu\text{eq L}^{-1}$) (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 $41.6 \mu\text{eq L}^{-1}$ and SO_4^{2-} from 4.7 to $25.2 \mu\text{eq L}^{-1}$. Kulshrestha *et al.* (2005) reported high concentrations (30 – $70 \mu\text{eq L}^{-1}$) of ammonium over the entire IGP region as well as higher SO_4^{2-} ($\sim 70 \mu\text{eq L}^{-1}$) and NO_3^- ($\sim 35 \mu\text{eq L}^{-1}$) 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-} ($104.2 \mu\text{eq L}^{-1}$) and Ca^{2+} ($264.4 \mu\text{eq L}^{-1}$) 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 ($\text{kg}^{-1} \text{ha}^{-1} \text{y}$) in rainwater during southwest summer monsoon of 2009, 2010 and 2011 over IGP.

| Species | 2009 | 2010 | 2011 |
|-------------------------------|------|------|------|
| F ⁻ | 00.5 | 01.1 | 00.9 |
| Cl ⁻ | 06.4 | 14.9 | 12.5 |
| SO ₄ ²⁻ | 15.3 | 37.2 | 29.0 |
| NO ₃ ⁻ | 10.6 | 27.1 | 20.4 |
| HCO ₃ ⁻ | 00.2 | 00.1 | 00.1 |
| Na ⁺ | 02.7 | 06.1 | 04.8 |
| K ⁺ | 02.2 | 02.7 | 02.5 |
| Ca ²⁺ | 17.4 | 24.4 | 26.8 |
| Mg ²⁺ | 03.5 | 06.5 | 10.1 |
| NH ₄ ⁺ | 01.9 | 06.4 | 09.2 |
| Rainfall (mm) | 975 | 1426 | 1292 |

$$WD (\text{kg ha}^{-1} \text{yr}^{-1}) = VWM (\text{mg L}^{-1}) \times \frac{RF}{100} \quad (3)$$

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 $\text{kg ha}^{-1} \text{y}^{-1}$ 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

$\text{kg ha}^{-1} \text{y}^{-1}$) and nitrate (18.3 $\text{kg ha}^{-1} \text{y}^{-1}$) (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 $\text{kg ha}^{-1} \text{y}^{-1}$ and nitrate: 30.2 $\text{kg ha}^{-1} \text{y}^{-1}$) and the second largest were at KUR (sulfate; 28.4 $\text{kg ha}^{-1} \text{y}^{-1}$ and nitrate: 18.7 $\text{kg ha}^{-1} \text{y}^{-1}$). 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 $\text{kg ha}^{-1} \text{y}^{-1}$ with the sulfate having the highest deposition flux (25.2 $\text{kg ha}^{-1} \text{y}^{-1}$) with the lowest being fluoride (0.8 $\text{kg ha}^{-1} \text{y}^{-1}$).

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 the any component in the rain water 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)):

$$\begin{aligned} [NF_{Ca^{2+}}] &= \frac{[nssCa^{2+}]}{[NO_3^-] + [nssSO_4^{2-}]} \\ [NF_{Mg^{2+}}] &= \frac{[nssMg^{2+}]}{[NO_3^-] + [nssSO_4^{2-}]} \\ [NF_{NH_4^+}] &= \frac{[NH_4^+]}{[NO_3^-] + [nssSO_4^{2-}]} \\ [NF_{K^+}] &= \frac{[nssK^+]}{[NO_3^-] + [nssSO_4^{2-}]} \end{aligned} \quad (4)$$

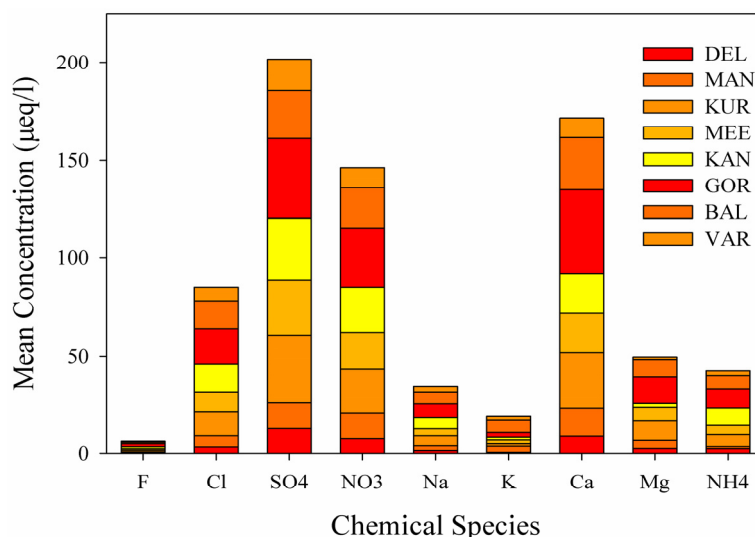


Fig. 4. Distribution of mean wet deposition flux of measured ions at eight different locations in IGP region during the study period.

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 Ca²⁺ (99%) > SO₄²⁻ (96%) > K⁺ (94%) > Mg²⁺ (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%) > Mg²⁺ (8%) > K⁺ (6%) > SO₄²⁻ (4%) and Ca²⁺ (< 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 Ca²⁺, Mg²⁺, NH₄⁺, 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 (NO₃⁻ and SO₄²⁻) concentrations at all of the sites. In addition, significant correlations among Ca²⁺ and SO₄²⁻ (r = 0.63), and NO₃⁻ (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 CaCO₃ (Al-Momani et al., 1995, 2003; Al-Khashman, 2009).

The NF values were estimated for each location (Table 4). It was found that Ca²⁺ was the dominant neutralizing ion at all locations. Mg²⁺ was the second largest except at two locations, Kanpur and Varanasi, whereas ammonia was the second largest with NF being 30% and 18%, respectively. These results indicate that the crustal component especially Ca²⁺ and Mg²⁺ neutralize the rainwater acidity (82%) over IGP region. The contribution of NH₄⁺ 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 (Ca²⁺ > Mg²⁺ > NH₄⁺ > K⁺) is in agreement with the report of Budhavant et al. (2011) for Pune, India. Most of the Indian studies reported that Ca²⁺, Mg²⁺ and NH₄⁺ 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⁺/(NO₃⁻ + SO₄²⁻), (NO₃⁻ + Cl⁻)/(SO₄²⁻), (Ca²⁺ + NH₄⁺)/(NO₃⁻ + SO₄²⁻), NO₃⁻/SO₄²⁻, NH₄⁺/NO₃⁻ and NH₄⁺/SO₄²⁻) were calculated (Table 3). The average H⁺/(NO₃⁻ + SO₄²⁻) 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 [(NO₃⁻ + Cl⁻)] and (SO₄²⁻) 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 SO₂ or sulfuric acid (Singh et al., 2007) from local industrial emissions. The ratios (Ca²⁺ + Mg²⁺ + NH₄⁺)/(NO₃⁻ + SO₄²⁻) > 1.0 (mean: 2.21) along with significant correlation (0.66) in between them indicate that Ca²⁺, Mg²⁺ and NH₄⁺ 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 (Ca²⁺ + NH₄⁺)/(NO₃⁻ + SO₄²⁻) with values ranging from 0.42 to 5.13 at Dhanbad, a coal producing city. The mean ratio of SO₄²⁻/NO₃⁻ 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 ⁺ /(NO ₃ ⁻ +SO ₄ ²⁻) | 0.02 | 0.03 | 0.03 | 0.03 | 0.02 | 0.03 | 0.01 | 0.04 | 0.02 |
| SO ₄ ²⁻ /NO ₃ ⁻ | 2.18 | 1.31 | 1.99 | 1.96 | 1.74 | 1.74 | 1.53 | 2.02 | 1.81 |
| NH ₄ ⁺ /NO ₃ ⁻ | 1.07 | 0.28 | 0.97 | 0.97 | 1.28 | 1.07 | 1.13 | 0.83 | 0.95 |
| NH ₄ ⁺ /SO ₄ ²⁻ | 0.49 | 0.22 | 0.49 | 0.50 | 0.74 | 0.61 | 0.74 | 0.41 | 0.52 |
| (Ca ²⁺ + Mg ²⁺ + NH ₄ ⁺)/(NO ₃ ⁻ + SO ₄ ²⁻) | 2.01 | 2.29 | 2.47 | 2.06 | 1.61 | 2.83 | 2.93 | 1.52 | 2.21 |
| (NO ₃ ⁻ + Cl ⁻)/SO ₄ ²⁻ | 0.81 | 1.35 | 1.01 | 0.98 | 1.21 | 1.17 | 1.47 | 1.09 | 1.14 |
| (NO ₃ ⁻ + SO ₄ ²⁻)/(Ca ²⁺ + 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 Ca²⁺, Mg²⁺, NH₄⁺, and K⁺ in rainwater over the IGP.

| | DEL | MAN | KUR | MEE | KAN | GOR | BAL | VAR | Mean |
|--------------------------------|------|------|------|------|------|------|------|------|------|
| NFCa ²⁺ | 56.5 | 61.1 | 54.0 | 53.4 | 61.6 | 57.0 | 51.3 | 65.2 | 56.8 |
| NFNH ₄ ⁺ | 16.9 | 5.1 | 13.2 | 15.9 | 29.8 | 13.9 | 14.6 | 17.8 | 15.1 |
| NFMg ²⁺ | 25.2 | 27.1 | 31.7 | 28.3 | 6.7 | 27.7 | 27.5 | 10.8 | 24.6 |
| NFK ⁺ | 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 NO_x . The relative contributions of the ions to the acidity of rainwater were variable for event to event and location to location. Earlier studies reported the contributions of H_2SO_4 and HNO_3 in rainwater were between 60–70% and 30–40%, respectively (Al-Khashman, 2009; Tiwari et al., 2012). The ratios $\text{NH}_4^+/\text{NO}_3^-$ and $\text{NH}_4^+/\text{SO}_4^{2-}$ 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 ensamples 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), Junnto 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, σ_{ij} , as follows.

$$\sigma_{ij} = \sqrt{e_j^2 + (d_j x_{ij})^2} \quad (5)$$

where x_{ij} is the concentration of species j in sample i , e_j 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 SO_4^{2-} ($3 \times 10^3 \mu\text{eq cm}^{-2}$), NO_3^- ($1 \times 10^3 \mu\text{eq cm}^{-2}$), NH_4^+ ($9 \times 10^2 \mu\text{eq cm}^{-2}$) and F^- ($1 \times 10^2 \mu\text{eq cm}^{-2}$) were observed. This factor explained most of the NH_4^+ 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 SO_2 and NO_x . 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 Mg^{2+} and Ca^{2+} . 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 (7×10^2 to $3 \times 10^3 \mu\text{eq cm}^{-2}$). 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 SO_4^{2-} and Ca^{2+} with some NO_3^- . The major sources of SO_4^{2-} and NO_3^- are oxidation of SO_2 and NO_x from combustion sources. This factor represents the additional heterogeneous oxidation of SO_2 and NO_2 that can occur in droplets containing neutralizing components like Ca^+ . 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 NO_2 over IGP region was from thermal power plants and coal-burning industries that would also be sources of SO_2 . 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 $5.73 \pm$

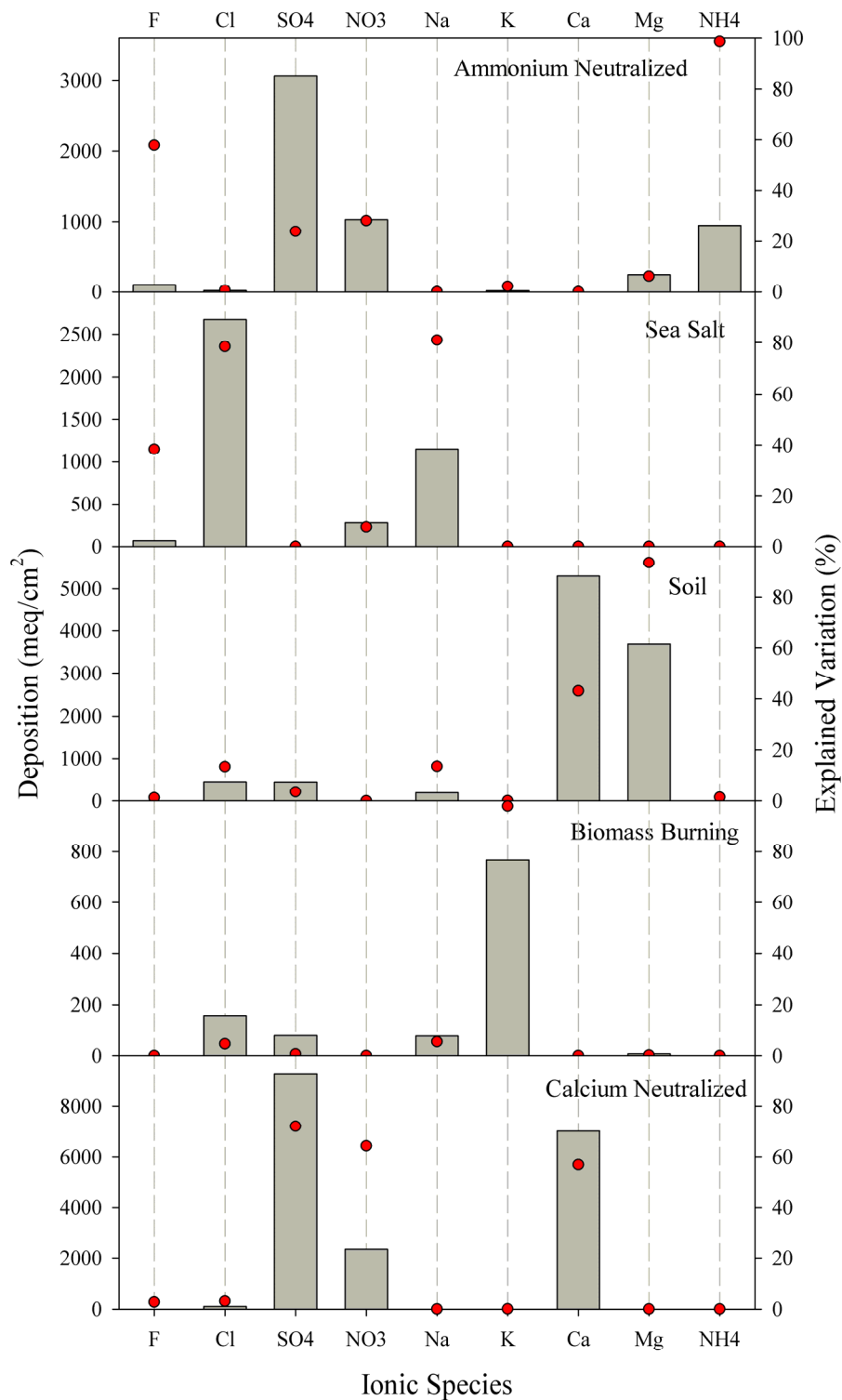


Fig. 5. PMF extracted source profile of chemical constituents in rainwater collected over IGP region during the southwest summer monsoon of 2009–2011.

0.17 and $31.6 \pm 31.0 \mu\text{S cm}^{-1}$, respectively with 16% samples were observed acidic (mean pH = 5.38 of acidic rain: $\text{H}^+ = 5.38 \mu\text{eq L}^{-1}$). The contribution of SO_4^{2-} and NO_3^- to the acidic rain samples were 69 and 31% respectively. The specific conductivity was ~39% lower ($20.6 \mu\text{S cm}^{-1}$) in acidic rain as compared to the alkaline ($33.6 \mu\text{S cm}^{-1}$) rain,

due to the higher concentration of acidic species. The sums of ions for acidic and non-acidic samples were 246.1 and $431.0 \mu\text{eq L}^{-1}$, respectively, with mean ($351.6 \pm 130.1 \mu\text{eq L}^{-1}$) indicates that high loading alkaline particles during non acidic rain. The mean value of SO_4^{2-} and NO_3^- are 52 and 29 $\mu\text{eq L}^{-1}$ 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.

| Species | Factor - 1 | Factor - 2 | Factor - 3 | Factor - 4 | Factor - 5 |
|-------------------------------|---|---------------------|------------|-----------------|---|
| F ⁻ | 57.8 | 38.3 | 1.2 | 0.0 | 2.7 |
| Cl ⁻ | 0.6 | 78.4 | 13.4 | 4.6 | 3.0 |
| SO ₄ ²⁻ | 23.8 | 0.0 | 3.5 | 0.6 | 72.0 |
| NO ₃ ⁻ | 28.1 | 7.6 | 0.0 | 0.0 | 64.3 |
| Na ⁺ | 0.0 | 81.0 | 13.6 | 5.4 | 0.0 |
| K ⁺ | 2.2 | 0.0 | 0.0 | 97.8 | 0.0 |
| Ca ²⁺ | 0.0 | 0.0 | 43.0 | 0.0 | 57.0 |
| Mg ²⁺ | 6.2 | 0.0 | 93.6 | 0.2 | 0.0 |
| NH ₄ ⁺ | 98.6 | 0.0 | 1.4 | 0.0 | 0.0 |
| Possible sources | Burning of coal & Urine excretion & Fertilizers use | Marine contribution | Soil dust | Biomass burning | Fossil fuels & re-suspension of soil dust |

ten times higher than the proposed background hemispheric values (10 and 2.8 $\mu\text{eq L}^{-1}$) at remote sites, respectively. SO₄²⁻ was higher (19%) in acidic rain as compared non-acidic rain; however, there were no large differences in the case of nitrate. Secondary particles were found to have the highest deposition fluxes (SO₄²⁻; 25.2 kg ha⁻¹ y⁻¹ and NO₃⁻: 18.3 kg ha⁻¹ y⁻¹) over the study region. The mean ratio of H⁺/(NO₃⁻ + SO₄²⁻) was 0.02 indicates that most of the acidity in rainwater was neutralized. The ratios (Ca²⁺ + Mg²⁺ + NH₄⁺)/(NO₃⁻ + SO₄²⁻) > 1.0 (mean: 2.21) along with significant correlation (0.66) in between them indicate that Ca²⁺, Mg²⁺, and NH₄⁺ ions play a crucial role in neutralizing the acidity. The Ca²⁺ (57%), Mg²⁺ (25%), NH₄⁺ (15%), and K⁺ (4%) species are the primary neutralizing species. Positive Matrix Factorization (PMF) was applied to the deposition fluxes. Five factors were identified as ammonia neutralized, sea salt, soil, biomass burning, and calcium neutralized.

ACKNOWLEDGEMENTS

Indian Institute of Tropical Meteorology, Pune is supported by the Ministry of Earth Sciences (MoES), Government of India, New Delhi. Authors sincerely acknowledge the whole hearted support of Dr. M. Rajeevan, Director IITM Pune. Authors appreciate the efforts of entire team involved in the chemical analysis of rainwater samples at IITM, Delhi.

REFERENCES

Akpo, A.B. Galy-Lacaux, C., Laouali, D., Delon, C., Liousse, C., Adon, M., Gardrat, E., Mariscal, A. and Darakpa, C. (2015). Precipitation Chemistry and Wet Deposition in a Remote Wet Savanna Site in West Africa: Djougou (Benin). *Atmos. Environ.* 115: 110–123.

Ali, K., Momin, G.A., Tiwari, S., Safai, P.D., Chate, D.M. and Rao, P.S.P. (2004) Fog and Precipitation Chemistry at Delhi, North India. *Atmos. Environ.* 38: 4215–4222.

Al-Khashman, O.A. (2005). Ionic Composition of Wet Precipitation in the Petra Region, Jordan. *Atmos. Res.* 78: 1–12.

Al-Khashman, O.A. (2009). Chemical Characteristics of

Rainwater Collected at a Western Site of Jordan. *Atmos. Res.* 91: 53–61.

Al-Momani, I.F., Ataman, O.Y., Anwari, M.A., Tuncel, S., Köse, C. and Tuncel, G. (1995). Chemical Composition of Precipitation near an Industrial Area at Izmir, Turkey. *Atmos. Environ.* 29: 1131–1143.

Al-Momani, I.F., Momani, K.A. and Jaradat, Q.A. (2000). Chemical Composition of Wet Precipitation in Irbid, Jordan. *J. Atmos. Chem.* 35: 47–57.

Anatolaki, C. and Tsitouridou, R. (2009). Relationship between Acidity and Ionic Composition of Wet Precipitation: A Two Years Study at an Urban Site, Thessaloniki, Greece. *Atmos. Res.* 92: 100–113.

Anttila, P., Paatero, P., Tapper, U. and Järvinen, O. (1995). Source Identification of Bulk Wet Deposition in Finland by Positive Matrix Factorization. *Atmos. Environ.* 14: 1705–1718.

Avila, A., Queralt-Mitjans, I. and Alarcon, M. (1997). Mineralogical Composition of African Dust Delivered by Red Rains over Northeastern Spain. *J. Geophys. Res.* 102: 21977–21996.

Awasthi, A., Agarwal, R., Mittal, S.K., Singh, N., Singh, K. and Gupta, P.K. (2011). Study of Size and Mass Distribution of Particulate Matter due to Crop Residue Burning with Seasonal Variation in Rural Area of Punjab, India. *J. Environ. Monit.* 13: 1073–1081.

Balasubramanian, R., Victor, T. and Chun, N. (2001). Chemical and Statistical Analysis of Precipitation in Singapore. *Water Air Soil Pollut.* 130: 451–456.

Baron, J. and Denning, A.S. (1993). The Influence of Mountain Meteorology on Precipitation Chemistry at Low and High Elevations of the Colorado Front Range, USA. *Atmos. Environ.* 27: 2337–2349.

Bayraktar, H. and Turalioglu, F.S. (2005). Composition of Wet and Bulk deposition in Erzurum, Turkey. *Chemosphere* 59: 1537–1546.

Beiderwieden, E., Wrzesinsky, T. and Klemm, O. (2005). Chemical Characterization of Fog and Rain Water Collected at the Eastern Andes Cordillera. *Hydrol. Earth Syst. Sci.* 9: 185–191.

Bisht, D.S., Tiwari, S., Srivastava, A.K., Singh, J.V., Singh, B.P. and Srivastava, M.K. (2015). High Concentration of

- Acidic Species in Rainwater at Varanasi in the Indo-Gangetic Plains, India. *Nat. Hazards* 75: 2985–3003.
- Budhavant, K.B., Rao, P.S.P., Safai, P.D. and Ali, K. (2009). Chemistry of Monsoon and Post-Monsoon Rains at a High Altitude Location, Sinhgad, India. *Aerosol Air Qual. Res.* 9: 65–79.
- Budhavant, K.B., Rao, P.S.P., Safai, P.D. and Ali, K. (2011). Influence of Local Sources on Rainwater Chemistry over Pune Region, India. *Atmos. Res.* 100: 121–131.
- Budhavant, K.B., Rao, P.S.P., Safai, P.D., Granat, L. and Rodhe, H. (2014). Chemical Composition of the Inorganic Fraction of Cloud-water at a High Altitude Station in West India. *Atmos. Environ.* 88: 59–65.
- Calvo, A.I., Olmo, F.J., Lyaman i, H., Alados-Arboledas, L., Castro, A., Fernandez-Raga, M. and Fraile, R. (2010). Chemical Composition of Wet Precipitation at the Background EMEP Station in Viznar (Granada, Spain) (2002–2006). *Atmos. Res.* 96: 408–420.
- Casimiro, A.P., Salgueiro, M.L. and Nunes, V.T. (1991). Seasonal and Air-Mass Trajectory Effects on Rainwater Quality at the South-Western European Border. *Atmos. Environ.* 25: 2259–2266.
- Charlson, R.J. and Rodhe, H. (1982). Factors Controlling the Acidity of Natural Rainwater. *Nature* 295: 683–885.
- Chate, D.M. and Devara, P.C.S. (2009). Acidity of Raindrop by Uptake of Gases and Aerosol Pollutants. *Atmos. Environ.* 43: 1571–1577.
- Chate, D.M., Murugavel, P., Ali, K., Tiwari, S. and Beig, G. (2011). Below-thunderstorm Rain Scavenging of Atmospheric Aerosols for Aerosol Deposition Models. *Atmos. Res.* 99: 528–536.
- Chebbi, A. and Carlier, P. (1996). Carboxylic Acids in the Troposphere, Occurrence, Sources and Sinks: A Review. *Atmos. Environ.* 30: 4233–4249.
- Das, R., Das, S. and Misra, V. (2005). Chemical Composition of Rainwater and Dust Fall at Bhubaneswar in the East Coast of India. *Atmos. Environ.* 39: 5908–5916.
- Das, R., Granat, L., Leck, C., Praveen, P.S. and Rodhe, H. (2011). Chemical Composition of Rainwater at Maldives Climate Observatory at Hanimaadhoo (MCOH). *Atmos. Chem. Phys.* 11, 3743–3755.
- Galloway, J.N., Likens, G.E., Keene, W.C. and Miller, J.M. (1982). The Composition of Precipitation in Remote Areas of the World. *J. Geophys. Res.* 87: 8771–8776.
- Galy-Lacaux, C., Carmichael, G.R., Song, C.H., Lacaux, J.P. and Modi, I. (2001). Heterogeneous Processes Involving Nitrogenous Compounds and Saharan Dust Inferred from Measurements and Model Calculations Region. *J. Geophys. Res.* 106: 12559–12578.
- Ghude, S., Fadnavis, S., Beig, G., Polade, S.D. and Vander, A.R.J. (2008). Detection of Surface Emission Hot Spots, Trends and Seasonal Cycle from Satellite-retrieved NO₂ over India. *J. Geophys. Res.* 113: D20305, doi: 10.1029/2007JD009615.
- Goldberg, E.D. (1963). The Oceans as a Chemical System, In *The Sea*, Vol. II, Hill, M.H. (Ed.), Interscience, London, pp. 3–26.
- Granat, L. (1972). On the Relation between pH and the Chemical Composition in Atmospheric Precipitation. *Tellus* 24: 550–560.
- Han, G. and Liu, C.Q. (2006). Strontium Isotope and Major Ion Chemistry of the Rainwater from Guiyang, Guizhou Province, China. *Sci. Total Environ.* 364: 165–174.
- Hu, G.P., Balasubramanian, R., and Wu, C.D. (2003). Chemical Characterization of Rainwater at Singapore. *Chemosphere* 51: 747–755.
- IMD (India Meteorological Department) (1982). Atmospheric Turbidity and Precipitation Chemistry Data from Background Air Pollution Monitoring Network Location in India (1973-1980), II-10 -12.
- Jain, M., Kulshrestha, U.C., Sarkar, A.K. and Parashar, D.C. (2000). Influence of Aerosols on Wet Deposition at Urban and Rural Sites in India. *Atmos. Environ.* 34: 5129–5137
- Jethva, H., Satheesh, S.K. and Srinivasan, J. (2007). Assessment of Second-generation MODIS Aerosol Retrieval (Collection 005) at Kanpur, India. *Geophys. Res. Lett.* 34: L19802, doi: 10.1029/2007GL029647.
- Junto, S. and Paatero, P. (1994). Analysis of Daily Precipitation Data by Positive Matrix Factorization. *Environmetrics* 5: 127–144.
- Kandlikar, M. (2007). Air Pollution at a Hotspot Location in Delhi: Detecting Trends, Seasonal Cycles and Oscillations. *Atmos. Environ.* 41: 5934–5947.
- Kaskaoutis, D.G., Kumar, S., Sharma, D., Singh, R.P., Kharol, S.K., Sharma, M., Singh, A.K., Singh, S., Singh, A. and Singh, D. (2014). Effects of Crop Residue Burning on Aerosol Properties, Plume Characteristics and Long-range Transport over Northern India, *J. Geophys. Res.* 119: 5424–5444.
- Kawamura, K. and K. Ikushima (1993), Seasonal Changes in the Distribution of Dicarboxylic Acids in the Urban Atmosphere. *Environ. Sci. Technol.* 27: 2227–2235.
- Keene, W.C., Pszenny, A.P., Galloway, J.N. and Hawley, M.E. (1986). Sea Salt Corrections and Interpretations of Constituent Ratios in Marine Precipitation. *J. Geophys. Res.* 91: 6647–6658.
- Khemani, L.T., Momin, G.A., Rao, P.S.P., Safai, P.D., Singh, G., Chatterjee, R.N. and Prakash, P. (1989). Long Term Effects of Pollutants on pH of Rainwater in North India. *Atmos. Environ.* 23: 753–756.
- Khwaja, H.A. and Husain, L. (1990). Chemical Characterization of Acid Precipitation in Albany, New York. *Atmos. Environ.* 24: 1869–1882.
- Khwaja, H.A. (1995), Atmospheric Concentrations of Carboxylic Acids and Related Compounds at a Semiurban Site. *Atmos. Environ.* 29: 127–139
- Kulshrestha, U.C., Kulshrestha, M.J., Sekar, R., Sastry, G.S.R. and Vairamani, M. (2003). Chemical Characteristics of Rainwater at an Urban Site of South-central India. *Atmos. Environ.* 37: 3019–3026.
- Kulshrestha, U.C., Granat, L., Engardt, M. and Rodhe, H. (2005). Review of Precipitation Chemistry Studies in India —A Search for Regional Patterns. *Atmos. Environ.* 39: 7403–7419.
- Kumar, N., Kulshrestha, U.C., Saxena, A., Kumari, K.M. and Srivastava, S.S. (1993). Effect of Anthropogenic

- Activity on Formate and Acetate Levels in Precipitation at Four Sites in Agra, India. *Atmos. Environ.* 27: 87–91.
- Laouali, D., Galy-Lacaux, C., Diop, B., Delon, C., Orange, D., Lacaux, J.P., Akpo, A., Lavenu, F., Gardrat, E. and Castera, P. (2012). Long Term Monitoring of Precipitation Chemical Composition and Wet Deposition over Three Sahelian Savannas. *Atmos. Environ.* 50: 314–327.
- Li, C.L., Kang, S.C., Zhang, Q.G. and Kaspari, S. (2007). Major Ionic Composition of Precipitation in the Nam Co Region, Central Tibetan Plateau. *Atmos. Res.* 85: 351–360.
- Li, Y., Tang, J., Yu, X., Xu, X., Cheng, H. and Wang, S. (2012). Characteristics of Precipitation Chemistry at Lushan Mountain, East China: 1992–2009. *Environ. Sci. Pollut. Res.* 19: 2329–2343.
- Mahadevan, T.N., Negi, B.S. and Meenakshy, V. (1989). Measurements of Elemental Composition of Aerosol Matter and Precipitation from a Remote Continental Site in India. *Atmos. Environ.* 23: 869–874.
- Migliavacca, D., Teixeira, E.C., Wiegand, F., Machado, A. and Sanchez, J. (2005). Atmospheric Precipitation and Chemical Composition of an Urban Site, Guaiba Hydrographic Basin, Brazil. *Atmos. Environ.* 39: 1829–1844.
- Momin, G.A., Ali, K., Rao, P.S.P., Safai, P.D., Chate, D.M., Praveen, P.S., Rodhe, H. and Granat, L. (2005). Study of Chemical Composition of Rain- Water at an Urban (Pune) and a Rural (Sinhagad) Location in India. *J. Geophys. Res.* 110: D08302, doi: 10.1029/2004JD004789.
- Mouli, P.C., Venkata, M.S. and Jayarama, R.S. (2005). Rainwater Chemistry at A Regional Representative Urban Site: Influence of Terrestrial sources on Ionic Composition. *Atmos. Environ.* 39: 999–1008.
- Mphepya, J.N., Pienaar, J.J., Galy-Lacaux, C., Held, G. and Turner, C.R. (2004). Precipitation Chemistry in Semi-Arid Areas of Southern Africa: A Case Study of a Rural and an Industrial Site. *J. Atmos. Chem.* 47: 1–24.
- Mukhopadhyay, B., Datar, S.V. and Srivastava, H.N. (1992). Precipitation Chemistry over the Indian Region. *Mausam* 43: 249–258.
- Niu, H., He, Y., Lu, X.X., Shen J., Du J., Zhang, T., Pu, T., Xin, H. and Chang, L. (2014). Chemical Composition of Rainwater in the Yulong Snow Mountain Region, Southwestern China. *Atmos. Res.* 144: 195–206.
- Niu, H., He, Y., Luc, X.X., Shen, J., Du, J., Zhang, T., Pu, T., Xin, H. and Chang, L. (2014). Chemical Composition of Rainwater in the Yulong Snow Mountain Region, Southwestern China. *Atmos. Res.* 144: 195–206.
- Niu, Y.W., He, L.Y. and Hu, M. (2008). Chemical Characteristics of Atmospheric Precipitation in Shenzhen. *Environ. Sci.* 29: 1014–1019.
- Paatero, P. (1997). Least Squares Formulation of Robust Non-negative Factor Analysis. *Chemom. Intell. Lab. Syst.* 37: 23–35.
- Paatero, P., Hopke, P.K., Song, X.H. and Ramadan, Z. (2002). Understanding and Controlling Rotations in Factor Analytic Models. *Chemom. Intell. Lab. Syst.* 60: 253–264.
- Pandey, J. and Singh, A. (2012). Chemical Characterization of Rain Water in a Seasonally Dry Tropical Region (Varanasi), India. *J. Environ. Biol.* 33: 629–634.
- Piñeiro, J.M., Rodríguez, E.L., Pérez C.M., Heras G.B., Carou, I.T., Mahía P.L., Lorenzo S.M. and Rodríguez D.P. (2014). Influence of Marine, Terrestrial and Anthropogenic Sources on Ionic and Metallic Composition of Rainwater at a Suburban Site (Northwest Coast of Spain). *Atmos. Environ.* 88: 30–38
- Rao, P.S.P., Khemani, L.T., Momin, G.A., Safai, P.D. and Pillai, A.G. (1992). Measurements of Wet and Dry Deposition at Urban Location in India. *Atmos. Environ.* 26: 73–75.
- Rastogi, N. and Sarin M.M. (2005). Chemical Characteristics of Individual Rain Events from a Semi-arid Region in India: Three-year Study. *Atmos. Environ.* 39: 3313–3323
- Rastogi, N. and Sarin, M.M. (2007). Chemistry of Precipitation Events and Inter-relationship with Ambient Aerosols over a Semi-arid Region in Western India. *J. Atmos. Chem.* 56: 149–163.
- Ray, J. and McDow, S.R. (2005). Dicarboxylic acid Concentration Trends and Sampling Artifacts. *Atmos. Environ.* 39: 7906–7919.
- Rocha, F.R., Silva, J.A.F., Lago, C.L., Fornaro, A. and Gutz, I.G.R. (2003). Wet Deposition and Related Atmospheric Chemistry in the Sao Paulo Metropolis, Brazil: Part 1. Major Inorganic Ions in Rainwater as Evaluated by Capillary Electrophoresis with contactless Conductivity Detection. *Atmos. Environ.* 37: 105–115.
- Rodhe, H., Dentener, F. and Schulz, M. (2002). The Global Distribution of Acidifying Wet Deposition. *Environ. Sci. Technol.* 36: 4382–4388.
- Safai, P.D., Rao, P.S.P., Momin, G.A., Ali, K., Chate, D.M. and Praveen, P.S. (2004). Chemical Composition of Precipitation during 1984–2002 at Pune, India. *Atmos. Environ.* 38: 1705–1714.
- Safai, P.D., Budhavant, K.B., Rao, P.S.P., Ali, K. and Sinha, A. (2010). Source Characterization for Aerosol Constituents and Changing Roles of Calcium and Ammonium Aerosols in the Neutralization of aerosol Acidity at a Semi-urban Site in SW India. *Atmos. Res.* 98: 78–88.
- Salve, P.R., Maurya, A., Wate, S.R. and Devotta, S. (2008). Chemical Composition of Major Ions in Rainwater. *Environ. Contam. Toxicol.* 80: 242–246.
- Salve, P.R., Gobre, T., Lohkare, H., Krupadam, R.J., Bansiwala, A., Ramteke, D.S. and Wate, S.R. (2011). Source Identification and Variation in the Chemical Composition of Rainwater at Coastal and Industrial Areas of India. *J. Atmos. Chem.* 68: 183–198.
- Sanusi, A., Wortham, H., Millet, M. and Mirabel, P. (1996). Chemical Composition of Rainwater in Eastern France. *Atmos. Environ.* 30: 59–71.
- Satsangi, G.S., Taneja, A., Khare, P., Singh, S.P., Lakhani, A., Kumari, K.M. and Srivastava, S.S. (1998a). Deriving Critical Loads for the Agra Region in India. *Sci. Total Environ.* 222: 119–122.
- Satsangi, G.S., Lakhani, A., Khare, P., Singh, S.P., Kumari, K.M., Srivastava, S.S. (1998b). Composition of Rainwater at Semi-arid Rural Site in India. *Atmos. Environ.* 32:

- 3783–3793.
- Satyanarayana, J., Reddy, L.A.K., Kulshrestha, M.J., Rao, R.N. and Kulshrestha, U.C. (2011). Chemical Composition of Rain Water and Influence of Airmass Trajectories at a Rural Site in an Ecological Sensitive Area of Western Ghats (India). *J. Atmos. Chem.* 66: 101–116.
- Seinfeld, J.H. and Pandis, S.N. (2006) *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, Second Ed., J. Wiley & Sons, New York.
- Shukla, S.P. and Sharma, M. (2010). Neutralization of Rainwater Acidity at Kanpur, India. *Tellus Ser. B* 62: 172–180.
- Singh, A.K., Mondal, G.C., Suresh, K., Singh, K.K., Kamal, K.P. and Sinha, A. (2007b). Precipitation Chemistry and Occurrence of Acid Rain over Dhanbad, Coal City of India. *Environ. Monit. Assess.* 125: 99–110.
- Singh, K.P., Singh, V.K., Malik, A., Sharma, N., Murthy, R.C. and Kumar, R. (2007a). Hydrochemistry of Wet Atmospheric Precipitation over an Urban Area in Northern Indo-Gangetic Plains. *Environ Monit. Assess.* 131: 237–254.
- Singh, S., Nath, S., Kohli, R. and Singh, R. (2005). Aerosols over Delhi during Pre-monsoon Months: Characteristics and effects on Surface Radiation Forcing. *Geophys. Res. Lett.* 32: L13808, doi: 10.1029/2005GL023062.
- Srinivas, B., Kumar, M.R. and Rao, K.S.P. (1999). A Study on the Chemistry of Rain Water in and Around Hyderabad and Secunderabad. *Indian J. Environ. Prot.* 21: 210–213.
- Srivastava, A.K., Singh, S., Tiwari, S., Kanawade, V.P. and Bisht, D.S. (2012). Variation between Near-surface and Columnar Aerosol Characteristics during the Winter and Summer at Delhi in the Indo-Gangetic Basin. *J. Atmos. Sol. Terr. Phys.* 77: 57–66.
- Srivastava, A.K., Bisht, D.S., Tiwari, Suresh, Singh, S and Soni, B.K. (2014). An Early South Asian Dust Storm during March 2012 and its Impacts on Indian Himalayan Foothills: A Case Study. *Sci. Total Environ.* 493: 526–534.
- Sunder Raman, R., Hopke, P.K. and Holsen, T.M. (2008), Carbonaceous Aerosol at Two Rural Locations in New York State: Characterization and Behavior. *J. Geophys. Res.* 113: D12202.
- Tiwari, S., Ranade, A. and Singh, D. (2006). Study of Chemical Species in Rain Water at Ballia, a Rural Environment in Eastern Uttar Pradesh, India. *Indian J. Radio Space Phys.* 35: 35–41.
- Tiwari, S., Kulshrestha, U.C. and Padmanabhamurty, B. (2007). Monsoon Rain Chemistry and Source Apportionment Using Receptor Modeling in and Around National Capital Region (NCR) of Delhi, India. *Atmos. Environ.* 41: 5595–5604
- Tiwari, S., Chate, D.M., Bisht, D.S., Srivastava, M.K. and Padmanabhamurty, B. (2012). Rainwater Chemistry in the North Western Himalayan Region of India. *Atmos. Res.* 104: 128–138.
- Tiwari, S., Srivastava, A.K. and Singh, A.K. (2013). Heterogeneity in Pre-monsoon Aerosol Characteristics over the Indo-Gangetic Basin. *Atmos. Environ.* 77: 738–747.
- Tiwari S., Srivastava A. K., Chate D. M., Safai P. D., Bisht D. S., Srivastava M.K. and Beig G. (2014). Impacts of the High Loadings of Primary and Secondary Aerosols on Light Extinction at Delhi during Wintertime. *Atmos. Environ.* 92: 60–68.
- Tiwari, S., Pipal, A.S., Hopke, P.K., Bisht, D.S., Srivastava, A.K., Tiwari, S., Saxena, P.N., Khan, A. H. and Pervez, S. (2015). Study of the Carbonaceous Aerosol and Morphological Analysis of Fine Particles along with their Mixing State in Delhi, India: A Case Study. *Environ. Sci. Pollut. Res.* 22: 10744–10757, doi: 10.1007/s11356-015-4272-6.
- Tuncer, B., Bayar, B., Yeşilyurt, C. and Tuncel, G. (2001). Ionic Composition of Precipitation at the Central Anatolia (Turkey). *Atmos. Environ.* 35: 5989–6002.
- Vet, R., Artz, R.S., Carou, S., Shaw, M., Ro, C., Aas, W., Baker, A., Bowersox, V., Dentener, Wai, K.M., Tanner, P.A. and Tam, C.W.F. (2005). 2-Year Study of Chemical Composition of Bulk Deposition in a South China Coastal City: Comparison with East Asian Cities. *Environ. Sci. Technol.* 39: 6542–6547
- Wai, K.M., Lin, N.H., Wang, S.H. and Dokiya, Y. (2008). Rainwater Chemistry at a High-altitude Station, Mt. Lulin, Taiwan: Comparison with a Background Station, Mt. Fuji, *J. Geophys. Res.* 113, D06305, doi: 10.1029/2006JD008248.
- Wu, Q.X., Han, G.L., Tao, F.X. and Tang, Y. (2011). Chemical Characterization of Rainwater in a Karst Rural Site: A Case Study of Puding, China. *Huan Jing Ke Xue.* 32: 26–32.
- Xu, H., Bi, X.H., Feng, Y.C., Lin F.M., Jiao, L., Hong, S.M., Liu, W.G. and Zhang, X.Y. (2011). Chemical Composition of Precipitation and its Sources in Hangzhou, China. *Environ. Monit. Assess.* 183: 581–592.
- Zeng, Y. and Hopke, P.K. (1989). A Study of the Sources of Acid Precipitation in Ontario, Canada. *Atmos. Environ.* 23: 1499–1509.
- Zhao, Z., Tian, L., Fischer, E., Li, Z. and Jiao, K. (2008). Study of Chemical Composition of Precipitation at an Alpine Site and a Rural Site in the Urumqi River Valley, Eastern Tien Shan, China. *Atmos. Environ.* 42: 8934–8942.

Received for review, June 26, 2015

Revised, September 6, 2015

Accepted, September 22, 2015